10/3-3-95 950861

SANDIA REPORT

SAND95-8206 • UC-411

Unlimited Release

Printed January 1995

Passive Micromechanical Tags

An Investigation into Writing Information at Nanometer Resolution on Micrometer Size Objects

R. W. Schmieder, R. J. Bastasz

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94551
for the United States Department of Energy
under Contract DE-AC04-94AL85000

Approved for public release; distribution is unlimited.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of the contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof or any of their contractors or subcontractors.

This report has been reproduced from the best available copy.

Available to DOE and DOE contractors from:

Office of Scientific and Technical Information
P. O. Box 62
Oak Ridge, TN 37831

Prices available from (615) 576-8401, FTS 626-8401

Available to the public from:

National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.
Springfield, VA 22161

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Passive Micromechanical Tags

An Investigation into Writing Information at Nanometer Resolution on Micrometer Size Objects

Robert W. Schmieder
Materials & Combustion Technology Department
and
R. J. Bastasz
Advanced Materials Research Department
Sandia National Laboratories/California

in collaboration with:

Dan Parks, Kansas State University
Martin Stockli, Kansas State University
Edward Parilis, California Institute of Technology
Ronald K. Skinner, Contractor

Project Manager: Leonard Hiles
Electronic & Mechanical Engineering Center
Sandia National Laboratories/California

ABSTRACT

We have completed a 3-year study of the technology related to the development of micron-sized passive micromechanical tags. The project was motivated by the discovery in 1990 by the present authors that low energy, high charge state ions (e.g., Xe^{+44}) can produce nanometer-size damage sites on solid surfaces, and the realization that a pattern of these sites represents information. It was envisioned that extremely small, chemically inert, mechanical tags carrying a large label could be fabricated for a variety of applications, including tracking of controlled substances, document verification, process control, research, and engineering. Potential applications exist in the data storage, chemical, food, security, and other industries.

The goals of this project were fully accomplished, and they are fully documented here. The work was both experimental and developmental. Most of the experimental effort was a search for appropriate tag materials. Several good materials were found, and the upper limits of information density were determined (ca. 10^{12} bit/cm²). Most of the developmental work involved inventing systems and strategies for using these tags, and compiling available technologies for implementing them.

The technology provided herein is application-specific: first, the application must be specified, then the tag can be developed for it. The project was not intended to develop a single tag for a single application or for all possible applications. Rather, it was meant to provide the enabling technology for fabricating tags for a range of applications. The results of this project provide sufficient information to proceed directly with such development.

MASTER

TABLE OF CONTENTS

EXECUTIVE SUMMARY	9
Overview of the Project	9
Accomplishments	10
Perspective for the Future	11
Project Bibliography	12
1. INTRODUCTION	13
1.1. Tags and Tagging	13
1.2. Writing High Density Information	14
1.3. The LDRD Proposal	15
1.4. Summary of the Project and Results	16
1.4.1. Nanobits	16
1.4.2. Other Results	23
1.5. Summary of this Report	23
2. EXPERIMENTAL RESULTS	25
2.1. Tag Fabrication	25
2.1.1. Lithographic micromachining	25
2.1.2. Laser micromachining of mica	25
2.2. Tag Labeling With High Charge State Ions	26
2.3. Materials Study	28
2.3.1. CR-39 Plastic	29
2.3.1.1. General results	29
2.3.1.2. The smallest bit size	35
2.3.1.3. Volume of the nanobits	35
2.3.1.4. Damage at the surface	36
2.3.2. Rodyne	37
2.3.3. Cronar	38
2.3.4. Mica	39
2.3.4.1. Experimental procedure	39
2.3.4.2. Clean mica scan	39
2.3.4.3. Damage sites	39
2.3.4.4. Blisters	43
2.3.4.5. Craters	47
2.3.4.6. Ion kinetic energy dependence of damage features	49
2.3.4.7. Charge state dependence of damage features	51
2.3.4.8. Erasure	53
2.3.4.9. Corrugation effect	54
2.3.4.10 Lateral force effects	55
2.3.4.11. Other work on mica	55
2.3.4.12. Conclusions regarding mica	55
2.3.5. Glass	57
2.3.6. CVD diamond	57
2.3.7. Cleaved diamond	57
2.3.8. Diamond microcrystals	57
2.3.9. UDAC (Ultra Densified Amorphous Carbon)	59
2.3.10. HOPG (Highly Oriented Pyrolytic Graphite)	60
2.3.11. Si 111 (Silicon)	62
2.3.12. SiC (Silicon Carbide)	64
2.3.13. Si ₃ N ₄ (Silicon Nitride)	66
2.3.14. Langmuir-Blodgett films	68
2.3.15. Self-assembled monolayer (SAM) films	74
2.3.16. Platinum	80
2.3.17. Polycarbonate	80

2.3.18. HOPBN	80
2.3.19. Tetracene	80
2.3.20. Alkali halides	80
2.3.21. Calcite	80
2.3.22. Metal dichalcogenides	81
2.3.23. I on Pt	81
2.3.24. MoO ₃ /MoS ₂	81
2.3.25. Polymers	81
2.4. Automatic Bit Reading	82
2.5. System Demonstrations	84
2.5.1. Micro-diamond tags	84
2.5.2. Mica tags	85
3. PHYSICAL MODELS	87
3.1. General Physical Model	87
3.2. Coulomb Energy	88
3.3. Lattice Damage	89
3.4. Ion Range in Solids	90
3.5. Cratering	92
3.5.1. Scaling law	92
3.5.2. Coulomb explosion sputtering	92
3.6. Blistering	94
3.6.1. Electrostatic delamination blistering	94
3.6.1.1. Introduction	95
3.6.1.2. Summary of experimental results	95
3.6.1.3. The basic model for the damage sites	96
3.6.1.4. Charge dependence of the damage sites	98
3.6.1.5. Conclusion	98
3.6.1.6. References	98
3.6.2. Plasma vapor-driven blistering	99
3.6.2.1. Erasure as evidence for a void	99
3.6.2.2. Formation of the blister	99
3.6.2.3. Semiquantitative model of blisters	100
3.6.2.4. Molecular granularity and metastability	101
4. NANOTAG TECHNOLOGY	103
4.1. Tag Fabrication	103
4.1.1. Ions	103
4.1.2. Materials	104
4.1.2.1. Uses of materials	104
4.1.2.2. Types of materials	104
4.1.2.3. Material properties	104
4.1.2.4. Summary of materials for use as tags	110
4.1.3. Replication	111
4.1.3.1. Overview	111
4.1.3.2. Multiplication	111
4.1.3.3. Lithographic printing:	111
4.1.3.4. Deposition	115
4.1.3.5. Mechanical pressing	115
4.1.3.6. Etching	115
4.1.3.7. Template patterning	119
4.1.3.8. Epitaxy	119
4.1.3.9. Molecular imprint polymerization:	119
4.1.3.10. Chemical pattern stamping	119
4.1.3.11. Summary of replication materials	123
4.1.4. Tag machining	124
4.1.4.1. Lithographic micromachining	124

4.1.4.2. Grid definition on lithographic bit pattern mask	124
4.1.4.3. Lithographic grid definition prior to printing	124
4.1.4.4. Lithographic grid definition after printing	124
4.1.4.5. Grid definition during chemical replication	124
4.1.4.6. Wafer bonding	124
4.1.4.7. Polysilicon films	125
4.1.4.8. Stochastic chip separation	125
4.2. Information Storage Schemes	126
4.2.1. Geometrical coding schemes	126
4.2.1.1. Random coding	128
4.2.1.2. Density coding	130
4.2.2. Whole-tag coding	130
4.2.3. Bit characteristic coding	131
4.2.4. Chemical coding schemes	132
4.2.5. Coding schemes and tag capacity	132
4.3. Tagging Operations	132
4.3.1. Matrix	133
4.3.2. Deployment	133
4.3.3. Processing	134
4.3.4. Location, concentration, recovery, identification	135
4.4. Handling The Tag	136
4.5. Pre-Read Processing Of The Tag	136
4.6. Reading The Tag	137
4.6.1. Image processing	137
4.6.2. Latent images	139
4.6.3. Nanochemistry	140
4.6.4. Covert tags	141
4.6.5. Erasure	141
4.6.6. Unstable tag	141
4.6.7. Environment sensing tags	141
5. EVALUATION OF THE TECHNOLOGY	143
5.1. Advantages and Disadvantages	143
5.2. The Technology is Composite	143
5.2.1. Precision steering of the ions is not necessary	144
5.2.2. An atomically smooth surface is not necessary	146
5.2.3. An atomic force microscope is not necessary	148
5.2.4. Writing predefined data is not necessary	148
5.3. Limits Of The Technology	149
5.3.1. Bit size and bit density	149
5.3.2. Ion steering and bit density	150
5.3.3. Writing rates	150
5.4. Turning Apparent Limitations Into Advantages	151
5.5. Relation To Other Techniques	151
5.6. Candidate Applications	152
5.6.1. Categories of applications	152
5.6.2. Material distribution	152
5.6.3. Information distribution	153
5.6.4. Natural science, esp. ecology	153
6. EXTENSIONS OF THE TECHNOLOGY	155
6.1. Nanofabricaton	155
6.1.1. Characteristics	156
6.1.2. Areas of Application	158
6.2. Active Circuit Devices	159
6.2.1. Junction diode	160
6.2.2. Metal-insulator-semiconductor devices	161

6.2.3. Anisotropic conductors	163
6.3. Biosensors	163
7. SUMMARY	165
7.1. Project Accomplishments	165
7.2. Future Directions	165
8. ANNOTATED BIBLIOGRAPHY	167
8.1. General	167
8.1.1. Nanotechnology	167
8.1.2. Atomic force microscopy	167
8.1.3. Micromechanical tags	168
8.1.4. High charge state ion surface damage	168
8.1.5. Ion tracks	169
8.1.6. Books	169
8.2. Materials	170
8.2.1. Mica (muskovite)	170
8.2.2. Highly oriented pyrolytic graphite (HOPG)	170
8.2.3. Highly oriented pyrolytic boron nitride (HOPBN)	171
8.2.4. Metal films	
(Au, Au-Cr, Ti, Ta, Pt, Pt/C, Pt/Ir, Pt/C/Ir, Va, Cr, Ni, Ag, Zr, Nb)	171
8.2.5. Polymers	
(Teflon, CR-39, PMMA, Epoxy, Poly-Carbonate, Poly-Styrene)	171
8.2.6. Minerals (calcite, albite, hematite, lizardite)	173
8.2.7. MoO_3 / MoS_2 (MoO_3 , MoS_2)	173
8.2.8. Metal Oxide films (TiO_2 , VO_2 , TiO_2/VO_2 , Cr_2O_3 , NiO , Al_2O_3)	174
8.2.9. Alkali Halide crystals (NaCl , KBr , LiF)	174
8.2.10. Silicon	175
8.2.11. Quartz	175
8.2.12. Organic molecular crystals (tetracene)	175
8.2.13. Misc. Materials	
($\text{Pb}_2\text{P}_2\text{O}_7$, Ge, Clinoptilolite, C_{60} , Pt, 1T-TaS ₂ , 1T-TaSe ₂)	175
8.2.14. Material Properties	176
8.3. Nanolithography	176
8.3.1. Nanolithography	176
8.3.2. Electron-beam nanolithography	176
8.3.3. Projection electron lithography	177
8.3.4. X-ray nanolithography	178
8.3.5. Ion beam nanolithography	178
8.3.6. Micromachining	179
8.3.7. Quantum structures	179
8.3.8. Epitaxy	180
8.3.9. Reactive ion etching	180
8.4. Nanochemistry	181
8.4.1. Nanochemistry	181
8.4.2. Ultrathin organic films	181
8.4.3. Langmuir-blodgett films	182
8.4.4. Self-assembled monolayers	183
8.4.5. Molecular imprinting	184
8.4.6. Sol-gel matrices	185
8.4.7. Impurity gettering	186
8.5. Miscellaneous	186
8.5.1. Replication	186
8.5.2. Conducting polymer lateral growth	186
8.5.3. Metrology	186

EXECUTIVE SUMMARY

OVERVIEW OF THE PROJECT

The origin of this project was a series of preliminary experiments carried out by the Principal Authors during 1989-90. It was predicted by one of us (RWS) that individual low energy, high charge state ions such as Xe^{+44} would cause permanent local damage on solid surfaces, and that this damage would be very shallow and confined to dimensions of nanometers. The second author (RJB) realized that such sites could represent single logical bits, and therefore that an array of such sites could represent information. Further collaborative work finally resulted in the observation of the damage and provided tentative explanations for it.

With the ability to write nanometer bits at great density, the concept of a very small object carrying a large label quickly developed. We envisioned that a "tag" of micron dimensions could carry up to a megabit of information. Because of the small size of the tag, it would find applications for tracking substances, small objects (including small animals), and covertly transmitting information. The wide range of possible applications seemed to indicate that implementing a technology of such "micromechanical tags" would be worthwhile, and that was the motivation for this project.

Even as the project was being implemented, it became clear that the applications were so disparate in their requirements that no single tag and tagging system would be appropriate for all. Additionally, there were major uncertainties about the limits of the technology: How dense could we write the information? What materials would be useful? How could we make replicates of the tags? How would we read the label? What strategy would we use for covert tags?

These and many similar questions formed the drivers for this project. Most of the questions that arose in the formulation of the project have been answered. Furthermore, ways have been found to circumvent certain limitations and shortcomings of the technology. For instance, we have found that steering the ions to within nanometer precision is not always required; there are applications that can make good use of random bit patterns. As another example, we have found that atomically smooth surfaces are not always required; a rough surface that is chemically activated by the ion (e.g., a polymer) still retains a latent image that is readable after chemical etching.

Most of the experimental work involved a search for appropriate materials. The technique was to identify a candidate material, examine it for atomic flatness with the atomic force microscope (AFM), irradiate it with low energy, high charge state ions, and examine it for ion-induced defects, sometimes after chemical treatment. We found that reading nanometer-sized features with the AFM was more difficult than we expected. The images often were ambiguous, and sometimes were not repeatable. Eventually we found ourselves at the state of the art in such microscopy, and extending it. In retrospect, we probably underestimated the difficulty of AFM imaging the nanobits, but we did succeed in consistently observing and characterizing them. It should also be noted that the AFM is not an essential part of the tags and tagging; it is merely a temporary means for analyzing the processes of fabricating the tags. Once the processes are well-characterized, the limitations of the AFM can be circumvented.

The other part of the project, namely the elaboration of techniques, strategies, and systems for various classes of applications, was completely successful. We invented, discovered, and assembled a wide range of ideas for making and using micromechanical tags. These include microfabrication techniques, coding schemes, replication procedures, mechanisms of latent image formation and development, automatic reading, and extensions of the technology (e.g., to fabricate active circuit devices). While we certainly did not exhaust all the possible ideas, we just as certainly provided a sufficiently rich survey and sufficiently specific guide to enable a motivated person to design and build a tag and tagging system for a specific application.

ACCOMPLISHMENTS

We list here some of the more significant specific results of this project. Some of these were alluded to in previous paragraphs, and are collected here for reference under “what’s new.” Each of these, and others not mentioned here, are elaborated in the body of this document.

- The predicted damage of solid surfaces by low energy, high charge state ions was observed for the first time.
- A new physical mechanism of damage of layered media such as mica, “electrostatic delamination,” was observed for the first time. This phenomenon makes mica a good candidate material for tags.
- A new process that can account for single-ion induced blistering in nonlayered media, “plasma vapor driven blistering,” was proposed. Molecular dynamics calculations in the literature support this prediction.
- A survey identified a list of 10 to 20 candidate materials for tags, based on their atomic flatness, chemical, and/or physical properties.
- Several candidate tag materials, including CR-39 plastic, mica, and highly oriented pyrolytic graphite (HOPG), were studied in detail with the AFM.
- The limiting bit density for several materials was determined. Typical results were mica (10^{12} bit/cm²) and plastics (10^{10-12} bit/cm². after etching).
- A path to pattern transfer and replication was identified: Self-assembled monolayer organic films (SAM) can act as masks. Evidence indicates nanometer resolution is possible.
- A class of latent image materials, namely etchable plastics, was identified. AFM scans show no evidence of ion damage, but chemical processing amplifies the sites to be easily readable with ordinary microscopy.
- Actual tags were fabricated from Si₃N₄. The tags were squares 100 x 100 microns, about 10 micron thick.
- A demonstration tag deployment, recovery, and identification was carried out, using diamond microcrystals as tags.
- A large number of coding strategies was invented, providing flexibility between using single nanobits and patterns of nanobits.
- Software was used to automatically analyze an AFM image of nanobits, and generate location, size, and shape data.
- Applications that can use random bit patterns were proposed as a path to use bit patterns at densities greater than present abilities to steer the ions.
- We identified ion-induced chemical activation and subsequent chemical processing as a strategy for use materials that do not have atomically flat surfaces.

- The concept of a composite tag, utilizing a high-resolution but fragile material protected by a low-resolution but strong cover, was developed to extend the utility of available materials.
- Various tags for covert applications were proposed, such as a tag that is read-once, a tag that becomes unreadable a short time after activating for a read operation, a tag that requires a code for reading, and a tag that will spontaneously change its label in time or due to an environmental trigger or process (such as high temperature).
- Alternative means (other than AFM) for reading the tags were identified, including operating the tag as an active circuit element and using a scanning electron beam.
- Applications to population biology were envisioned, in which individual insects or other small organisms are given a unique tag, released, and monitored or collected later. The tags could provide a powerful new tool for understanding the behavior of these important species and tracking them in specific systems such as agricultural ecosystems.

PERSPECTIVE FOR THE FUTURE

While this project achieved all of its goals, the nature of the results is more directive than definitive. We did not produce a do-all tag that would be all things to all applications. Rather, we defined the technological landscape and provided a roadmap. The opportunity is now available for affirmatively responding to an applicant's inquiry: given a problem that provides sufficiently specific definition of a tag, we (probably) know how to make it, deploy it, recover it, and read it. This is not to claim that we know everything now we would need to know. But it is probably fair to say that we could decide in advance what we would need to learn, and how much effort it would be to do the job. And it is not unreasonable to claim that the availability of the tags as a producible (as differentiated from "produced") product would itself generate need: given the possibility that we could track individual insects by name will almost surely stimulate an eager entomologist or population biologist to order up a batch of tags.

There are several areas of this project that we would have liked to have understood and explored in more detail: the response of SAM films to highly charged ions, strategies for chemical transformations that will decorate latent images and could provide functionality useful for covert tags, the detailed physical processes involved in the violent event of impact of high charge state ions on solid surfaces, the use of thin organic films in pattern transfer and replication, the electronic behavior of damage sites, time-dependent spontaneous chemical transformations of the tag and/or its message, and of course, a further exploration of candidate materials and their response to highly charged ions.

Beyond the boundaries of the goals of this project, our research over the past 3 years has solidified our earlier vision of a second major area of application for highly charged ions: active circuit elements. While the tags use the ions for information *storage*, active circuits would use the ions for information *processing*. The role of the ions in both cases is to define the geometry on a nanometer scale: they provide definition at the smallest size that falls short of atomic resolution, and therefore can still be called an "object." This represents a resolution limit that probably will be at the technological frontier for another decade. Whether this extension of the present project can be realized remains to be seen. It is clear, however, that many of the same concepts and techniques developed during the present project would be applicable and useful to that one.

PROJECT BIBLIOGRAPHY

Publications

- R. W. Schmieder and R. J. Bastasz, Surface Damage Caused by Single, Low-Energy, High-Charge-State Ions, *Proc. VIth Intl. Conf. Physics Highly Charged Ions, AIP Conf. Proc.* 274, 690 (1992).
- R. W. Schmieder and R. J. Bastasz, Potential Technological Applications of Low Energy, High Charge State Ions, *Proc. VIth Intl. Conf. Physics Highly Charged Ions, AIP Conf. Proc.* 274, 675 (1992).
- D. C. Parks, R. Bastasz, R. W. Schmieder, and M. Stockli, Nanometer-Size Surface Features Produced by Single Low-Energy, Highly Charged Ions, *J. Vac. Sci. Tech.*, in press
- D. C. Parks, R. Bastasz, R. W. Schmieder, and M. Stockli, AFM Imaging of single ion impacts on mica, *Proc. AFM/STM Conference, Natick*, in press.

Presentations

- D. C. Parks, R. Bastasz, R. W. Schmieder, and M. Stockli, Modification of surfaces by slow, highly charged ions, 40th National Symposium of the American Vacuum Society, Orlando, FL (1993).
- D. C. Parks, R. Bastasz, R. W. Schmieder, and M. Stockli, AFM characterization of nanometer-size surface features produced by single, low energy, highly charged ions, Army AFM/STM Symposium, Natick, (1994).
- D. C. Parks, M. Stockli, R. W. Schmieder, and R. Bastasz, Nanometer-size features produced by highly charged ions, 41st National Symposium of the American Vacuum Society, (1994).
- M. P. Stockli, (in collab. w/D. Parks, R. W. Schmieder, R. Bastasz), Nanometer-size surface modification produced by single, low energy, highly charged ions, 13th Intl. Conf. Applic. Accel. Res.& Ind., APS, Denton, TX, Nov. 7-10, 1994

1. INTRODUCTION

1.1. TAGS AND TAGGING

There is a continuing and growing need in our society for techniques that track controlled, dangerous, or sensitive materials and objects such as drugs, explosives, documents, and raw chemicals. Increased awareness of atmospheric dispersion of particulates, for instance resulting from waste incineration or fires, and of oceanic dispersion from intentional or unintentional disposal of toxics, increase the urgency for developing a variety of tracking techniques. Bioscience, including population ecology and population shifts associated with global climate change, need tools for monitoring the movement of materials and organisms. Many fields of pure and applied research and engineering, such as fluid mechanics, routinely make use of tag tracking, and would benefit from any new technique that offers a new range of applications or features.

Tags are potentially useful for the following tasks:

- Connect two end points of a process (tracking)
- Enable sorting into groups of kind
- Convey a previously unknown message in readily understood form
- Convey a previously unknown message in coded form
- Identify one item on a list of predefined messages
- Provide a key for deciphering a separately sent message
- Provide validation or verification

It should be clear that the nature of the tag, and its operational scheme, will strongly depend on the use to which it will be put.

The following properties of a tag are among the most important:

- Small size (for small objects and covert use)
- Nonperturbative (to the process being tracked)
- Nontoxic (to avoid health risks)
- Nonvolatile (mechanical and chemical stability)
- Noncounterfeitable
- Large number of tag names
- Large number of tags
- Low cost per tag
- Ease of deployment
- Ease of recapture
- Ease of reading

For any given application, some of these will stand out as being crucial, while others can be ignored or considered unimportant. In the context of this proposal, we want to concentrate on applications for which the first nine in the list above are most important, namely a tag that is physically small, nonperturbative, nontoxic, nonvolatile, and that offers the possibility of millions of tags with unique names. We reject chemical and physical (e.g., radioisotope and fluorescent chemical) tags on the basis of toxicity and volatility, and the very limited number of names available. We will intentionally subordinate the requirements of ease of recapture and reading to the other requirements. Other applications may require a different emphasis. Thus, we are led to consider mechanical tags: bits of inert material sufficiently small to be incorporated within the substance or object, but capable of carrying a complex name and withstanding physical abuse and long residence times. Furthermore, we are interested in passive tags: the tags have no internal power source or complex functioning. They simply carry a message that will be read at some later time. This combination of characteristics defines a range of tags and tagging procedures which we will refer to as *Passive Micromechanical Tags*.

1.2. WRITING HIGH DENSITY INFORMATION

Besides tracking, passive micromechanical tags could also be used for the transport of covert information. The information storage capacity of the tags allows a large amount of information to be contained on a single, microscopic tag. In addition, techniques for writing latent image bit patterns exist which allow the bit pattern to be recovered only after a sequence of specific development processes. This latent image microscopic bit pattern offers a high degree of security for transport of sensitive information.

There are several general tools for creating very small local marks on surfaces that constitute information storage. Among the best developed are various lithographic processes utilizing beams of electrons, x-rays, and ions. These techniques are limited by the resolution of the optical system used to focus the beam, and by the relatively low energy density attainable with minimally ionizing projectiles. At relatively high energies, focused beams can achieve resolutions in the nanometer range, sufficient for very high densities of information. However, the stopping power of such high energy projectiles is low; they penetrate deeply into the solid, leaving behind an elongated track of relatively low specific damage.

Damage of surfaces due to ion impact has been studied for many years, principally in the context of fusion reactor first walls. Characteristic of these processes is sputtering, blister formation, and exfoliation. Often a threshold fluence for these effects is observed, associated with formation of gas bubbles of sufficient volume and pressure to exceed the yield strength of the material. The tracks of individual singly charged ions of high energy are known to have transverse dimension of nanometers, but their length is very great. Lowering the energy of such ions shortens the track but also broadens it due to increased transverse scattering [O. Auciello and R. Kelly, 1984]. In the limit of low kinetic energy, these effects become negligible, and the surface is not damaged.

An entirely new process can occur if the incident ion has high charge state. If the coulomb potential energy of the ion is comparable to, or exceeds the ion's kinetic energy, the response of the surface is predominantly via the electronic interaction, rather than nuclear collisions and gas-dynamic processes. Expected processes include large secondary electron and ion yields, local plasma formation, and evaporation of neutral atoms (Parilis, et al., 1993). Experimental observations include the total yield and energy distributions of electrons, total yield and charge state distributions of scattered projectiles, and emission of x-rays (for reviews, see Varga, 1989; Winter, 1991; Andra, 1992). It was generally expected that a *single* ion, which can carry several hundred keV of coulomb energy, could create permanent structural damage on or near the surface. Presumably the damage is driven by the neutralization process as the ion approaches the solid, which results in massive disruption of the local electronic structure. In the low kinetic energy limit, the ion would act like a "bomb:" internally stored energy would be released upon impact. In contrast, at high kinetic energy, the ion would like a "bullet," depositing its energy as it penetrates deeply into the solid. Thus, the damage from an "ion bomb" is almost exclusively confined to the near surface, while an "ion bullet" damages along an extended path.

In 1989-90, one of the present authors (RWS) undertook to observe permanent damage to solid surfaces by low energy, high charge state ions. Damage of solid surfaces by single high charge-state ions was first observed by the present authors in 1990 [Schmieder and Bastasz, 1992]. In that work, individual Xe^{+44} ions of kinetic energy 0.1-7 keV/Q produced damage on a CR-39 plastic surface. The sites were made visible to a scanning electron microscope (SEM) by mild etching, which enlarged the sites into pits 200-300 nm in diameter. It was obvious from the energetic that the original damage site must have been no more than a few nm in diameter.

Some related work may be mentioned: AFM observations of single ion damage in solids has been reported for high energy Au ions impacting on MoS_2 (CERN, 1993) and for 11.4 MeV/u Pb^{+28} ions on mica (GSI, 1993). AFM observations of keV/u ion damage sites in mica after etching has been reported (Snowden-Ifft, et. al, 1993).

1.3. THE LDRD PROPOSAL

With the demonstration of the ion-induced surface damage, a new physical mechanism was available for fabricating nanobits on solid surfaces. If we associate each damage site with a single bit of information, it is immediately apparent that we have a mechanism for writing information at very high densities. For bits spaced 10 nm apart, the density is $10^{12} / \text{cm}^2$, about 10,000 times the bit density of a laser CD. The enormous potential for information storage and its technological and economic implications is obvious.

With the availability of such high bit densities, one could imagine a very small tag carrying a reasonably large label. With the ultimate density quoted above, a 1 micron square tag (area 10^{-8} cm^2) could carry a label of 10^4 bits. Even allowing for reduction by an order of magnitude for less-than-ultimate bit densities, one could reasonably expect a micron-size tag to carry a kilobyte of data. This is sufficient to provide unique names for an effectively unlimited number of tags (more than 10^{1000} different possible names).

It was therefore proposed to develop passive micromechanical tags from chemically inert materials such as minerals, oxides, ceramics, and plastics. The tags themselves would be fabricated with one of several available micromachining techniques such as lithography. The tag label would be written on the surface by bombarding it with low energy, high charge state ions. The tags would be either manufactured with a desired name, or made with random names and then read and recorded before deployment.

The general concept of this tag is shown in Figure 1.1.

Physically a collection of these tags would look like extremely fine powder: it could be incorporated into the substance during a process, sprinkled on a sensitive material to detect intrusion, etc. Being chemically inert, the tags would have essentially unlimited shelf lives, even under adverse conditions such as heat or cold, explosion or combustion, hydration and desiccation, ingestion, chemical attack, etc. After the residence time, transport, processing, or dispersal, some of the carrier substance or objects would be collected, and the tags would be extracted and read. Extraction could benefit from secondary tagging, e.g., by a general fluorescent chemical flag, if desired. Other means could include filtering, magnetic separation, centrifugation, chemical extraction, optical pattern recognition, etc. Reading of the tag would be done with a scanning atomic force microscope (AFM). This device had the necessary spatial resolution to register individual nanometer bits, and is a reasonable instrument for relatively widespread use.

The specific goals for the project were to fabricate real tags with bit density up to $1 \text{ MB} / \mu\text{m}^2$, and to elaborate various systems, strategies, and technologies for implementing tagging in a range of (as yet unspecified) applications.

Figure 1.1 - The image of a micromechanical tag

1.4. SUMMARY OF THE PROJECT AND RESULTS

The project was funded for FY92, 93, and 94. The preliminary experiments made use of the Electron Beam Ion Source (EBIS) that one of the authors (RWS) had developed at Sandia California. Later, experiments were done using the Electron Beam Ion Trap (EBIT) at Lawrence Livermore Laboratory (LLNL) as the source of ions. When the Sandia EBIS was decommissioned, and the SuperEBIS under development was canceled, arrangements were made to use the EBIS at Kansas State University (KSU) in Manhattan, Kansas. A scanning atomic force microscope (AFM) was acquired for analyzing the samples. However, it proved impossible to irradiate the samples at KSU and transport them to California for analysis, principally because we observed relatively rapid deterioration of some samples and because cleanliness was clearly an important concern. Therefore, the AFM was moved to Kansas and a postdoctoral researcher with special background in AFM work was hired to carry out the experiments. Concurrently with the experimental work, we developed the other aspects of tagging: coding schemes, deployment and recovery schemes, methods for replication and pattern transfer, composite tags, various applications, and extensions of the technology.

1.4.1. Nanobits

Some typical experimental results showing damage sites due to impact of individual ions are shown in Figures 1.2-8. We will sometimes refer to these sites as "nanobits."

Figure 1.2 shows a field of etched damage sites in a plastic, CR-39. The incident ions were Xe^{+44} , of energy about 1 keV/Q. The etching has enlarged the sites into pits, each about 200-300 nm in diameter. The etching was done in order to make the sites visible in an ordinary scanning electron microscope (SEM). If particular interest in these results is that the sites are nearly identical, that etching proceeds on each site independently (even when several sites overlap), and that each pit is produced by the impact of a single ion.

This last point is emphasized: we are not dealing here with a focused beam of ion, but single ions. The implication is that the original damage represented by these etch pits was very small; energetics suggested about 1 nm.

Figure 1.3 shows a field of these etch pits imaged with the AFM, showing that the AFM successfully imaged this material.

Figure 1.4 shows an AFM image of a single pit that was etched for a shorter period. This pit has diameter near 50 nm. The smallest etch pits we observed were about 30 nm, but we believe that any size pit down to a presumed initial damage region could be produced by careful etching.

Figure 1.5 shows a crater produced on a mica surface by a single Xe^{+44} ion of energy 100 eV/Q. This site was not enlarged by etching, or enhanced in any other way—it is observed as a primary damaged region without modification. The crater is about 10 nm in diameter. The smallest damage sites we observed with this material and this ion was near 7-8 nm.

Figure 1.6 shows a field containing four primary damage sites on mica, obtained under the same conditions as the previous figure. Clearly craters spaced 10 nm apart are completely resolved. This implies that the maximum density at which distinct craters can be observed is on the order of 10^{12} cm^{-2} . It should also be noted that the contrast in these images is very high—it is easy to identify the site against the unmodified substrate.

Figure 1.7 shows a field on a Xe^{+44} irradiated mica surface containing blisters. Convex features were sometimes observed due to an instrumental effect which we now understand. But the features shown here are really convex—blisters about 10 nm in diameter and about 0.2 nm high. The appearance of these blisters was a surprise, but we have verified their reality and believe we understand their origin.

Figure 1.8 shows an actual tag machined from silicon nitride. It measures $60 \mu\text{m} \times 60 \mu\text{m} \times 0.8 \mu\text{m}$. Although this material was too rough to use for nanobit registration, a tag of this size fabricated from mica has an ultimate capacity of 3 megabits.

Figure 1.2 - Field of etched damage sites on CR-39 plastic. Each crater resulted from impact of a single ion.

Figure 1.3 - A field of etch pits in CR-39 imaged with the AFM.

Figure 1.4 - A single etch pit in CR-39 imaged with the AFM.

Figure 1.5 - A crater produced on a mica surface by a single Xe^{+44} ion of energy 100 eV/Q, imaged with the AFM.

Figure 1.6 - A field containing four damage sites on mica, obtained under the same conditions as Fig. 1.5.

Figure 1.7 - A field of blisters on a mica surface produced by Xe^{+44} ions of energy 1.14 keV/Q.

Figure 1.8 - A prototype tag micromachined from silicon nitride.

1.4.2. Other results

We did not succeed in making a 1 megabyte 1 micron tag, as hoped in the original proposal. What we found was that the intrinsic bit size on the best material we examined (mica) was about 10 nm, not 1 nm as hoped. This limits the tag to about 10^4 bits, or about 3 kB/ μm^2 rather than 1 MB/ μm^2 . In spite of this, we feel that the capacity for storing information at greater densities than available through lithographic techniques has been demonstrated.

We also did not develop single tags for a particular application. Rather, we explored the entire range of tags that can be produced by nanotechnology in general, and those using high charge state ion impact in particular, and elaborated various strategies to respond to various classes of applications.

Besides the experimental results, a large amount of information was collected or invented in relation to materials, processes, schemes, strategies, and applications. Some of the more significant results were listed in the Executive Summary.

Among the potentially most significant developments was the identification of ultrathin organic films (Langmuir-Blodgett LB, and Self-assembled Monolayer SAM) as a path to replication and pattern transfer. These films have the potential to function as ultrahigh resolution resists. The ions produce the pattern by damage of the film, and various chemical processes (e.g., etching) transfer the pattern to a substrate.

Other results include elaborating coding schemes, development of coding schemes, identification of applications that can use random patterns, development of ideas for covert use of the tags, and relaxation of the technological requirements for specific categories of applications.

The central result of this project, aside from the technical data, is the understanding of what is needed to design a nanotag for a specific application. No single tag or tagging scheme is appropriate for the wide range of envisioned applications; the requirements of each application are very specific and the tag and tagging procedure must be carefully tailored for that application. What we have accomplished in this project is a critical technical investigation into the feasibility of producing micromechanical tags in general and the utilization of high charge state ions as a particular means for producing them. The results show that the technology works, and that there are many applications that could use the tags for tasks that currently cannot be done without them.

1.5. SUMMARY OF THIS REPORT

The remainder of this report is a systematic record of the various results of the project. It is organized as follows:

1. Introduction
2. Experimental results
3. Physical models
4. Nanotag technology
5. Evaluation of the technology
6. Extensions of the technology
7. Conclusions

This material should be considered as a resource for commencing the development of a tag for a specific application. Given the application, a tour through this document will provide guidance for selecting materials for the tags, their fabrication and structure, deployment, recovery, and reading of their labels. We have also included (Sec. 6) some ideas for carrying these results into new areas of technology.

- R. W. Schmieder and R. J. Bastasz, Surface Damage Caused by Single, Low-Energy, High-Charge-State Ions, Proc. VIth Intl. Conf. Physics Highly Charged Ions, *AIP Conf. Proc.* 274, 690 (1992).
- S. Parilis, L. M. Kishinevsky, N. Yu. Turaev, B. E. Baklitzky, F. F. Umarov, V. Kh. Verleger, S. L. Nizhnaya, and I. S. Bitensky, *Atomic Collisions on Solid Surfaces*, North Holland, Amsterdam (1993).
- Snowden-Ifft, P. B. Price, L. A. Nagahara, and A. Fujishima, *Phys. Rev. Lett.* 70, 2348 (1993).
- CERN Courier, 33 (cover), (1993).
- GSI-Nachrichten, March, 1993, pp. 7-10.
- Auciello and R. Kelly, Eds., *Ion Bombardment Modification of Surfaces*, Elsevier (Amsterdam, 1984)]

2. EXPERIMENTAL RESULTS

2.1. TAG FABRICATION

We have used two techniques to fabricate actual tags, lithography and laser micromachining. This work was done in collaboration with Department 1333, Advanced Packaging. These were demonstrations only, since we did not have a specific application for which we needed to manufacture specific tags.

Although current demonstrations of tag fabrication have focused on tags having square dimensions, other tag shapes could aid in tag recovery by providing easily recognizable shapes. Depending on the application, the shape of the tag could be varied so that it is easy to find optically, difficult to find optically (covert), has desired transport properties (e.g., settling or dispersion rates in liquids and gases), or carries additional information in the shape of the tag itself.

2.1.1. Lithographic micromachining

Silicon nitride tags having dimensions of 60 mm x 60 mm x 0.8 mm were manufactured using standard lithographic micromachining techniques. A thin film of Si_3N_4 was deposited on a sacrificial oxide layer on substrate silicon. Tags were defined using photolithographic patterning and plasma etching. A final wet HF etch released individual tags from the sacrificial oxide layer. Tags were captured on filter paper and examined with scanning electron microscopy (cf., Fig. 1.8). These tags have an information storage capacity of approximately 3 Megabits.

2.1.2. Laser micromachining of mica

We demonstrated laser micromachining of muscovite mica using a Q-switched Nd:YAG laser operating frequency doubled to 532 nm or quadrupled to 266 nm with an irradiance of 1.77×10^9 watts/cm² and a pulse rate of 4 kHz. These parameters were sufficient for cutting tags to depths of 100 μm . Figure 2.1 shows a photomicrograph of individual damage sites.

Figure 2.1 - Photomicrographs of laser damage sites on mica. (a) 532 nm laser. Crater is about 50 μm diameter; (b) 266 nm laser. Array of defects; (c) 266 nm laser. Central hole is about 5 μm diameter.

2.2. TAG LABELING WITH HIGH CHARGE STATE IONS

Tag labeling involves irradiating the tag (or tag material) with high charge state ions. We had no facility for scanning the ions, hence we were unable to create an ordered array of nanobits representing a predefined message. The purpose of this project, however, was not to create a specific tag, but to develop the technology for making tags for a specific application.

Our initial experiments were carried out using the Electron Beam Ion Trap (EBIT) facility at the Lawrence Livermore National Laboratory (LLNL) as a source of Xe^{+44} ions. The ions were produced in an electrostatic trap biased about 7 keV above ground, where they were subjected to repeated ionizing impacts by an intense electron beam. After extraction, the ions were transported at 7 keV/Q through several ion optical elements to a target chamber, where a symmetric decelerating lens was used to reduce their kinetic energy. Ions were used with energies ranging from the full 7 keV/Q ($\text{KE}=308$ keV) to a minimum of 0.1 keV/Q ($\text{KE}=4.4$ keV). Since the total Coulomb energy of a Xe^{+44} ion is about 70 keV, between 22% and 95% of an ion's total energy was potential. Thus, this work included ions carrying mostly kinetic energy as well as ions carrying mainly potential energy.

The target was positioned, using a vacuum manipulator, at the center of the decelerating lens. When the target was withdrawn, the ion flux passing through the lens could be measured using a back-mounted channel electron multiplier. Simulation of the system with a charged-particle ray tracing program code, showed that the presence of the target did not significantly alter the ion trajectories, even at the lowest kinetic energies used. The vacuum in the target chamber was kept below 10^{-8} Torr.

The samples were exposed to typical ion fluxes of 10^5 ions/cm²-s within a 1 mm diameter aperture, in pulses of about 10^3 ions/pulse at 1 pulse/s. With total exposure times of several hours, the total dose was usually 10^9 to 10^{10} ions/cm². The exposures were interrupted periodically to measure the ion flux; generally it was found to vary little during the runs.

Most of the irradiations were also made using the Kansas State University (KSU) CRYEBIS (Stöckli, et al., 1992). Figure 2.2 shows a layout diagram of the facility. Typically, the source supplied 5 pA of Xe^{+44} ions extracted at 3-5 kV. The ions passed through a series of collimators, were momentum-analyzed at 90°, and were decelerated by a 3-element symmetrical lens. Bias on the center lens element, where the sample could be inserted, reduced the beam energy to any desired value between 0.1 and 5 keV/Q. Generally more than 90% of the ions were passed through an aperture 3 mm diameter. The mica samples were placed immediately behind the aperture. A rack-and-pinion allowed insertion of the samples into the vacuum system. A multichannel-electron multiplier detector placed behind the sample in the axis of the beam provided (with the sample removed) a measure of the ion current to the target. The flux was found to be approximately 10^7 ions/cm²-s, assuming an irradiation area of 7 mm². Typical exposures provided a fluence of $1\text{-}4 \times 10^{10}$ ions/cm² over the course of about 1 hour. All irradiations were done at normal incidence.

After exposure, the CR-39 was etched in 5 N NaOH at 50°C for 5 min, with constant stirring, followed by a thorough rinse in distilled water. The sole purpose of etching was to enlarge any damage sites to a size that could be seen with the available microscopes.

After coating with Au/Pd, the samples were examined with a scanning electron microscope (SEM). Samples prepared at KSU were imaged with the AFM after etching but without overcoating.

M. Stockli, et al., in E. D. Donets and A. I. Pikin, Eds., *Proc. Vth Intl Symp. Electron Beam Ion Sources and their Applic.*, JINR, Dubna, (1992).

Figure 2.2 - Layout of the laboratory at Kansas State University.

2.3. MATERIALS STUDY

A large amount of effort in this project was invested in searching for materials that would make good tags. Initially, we searched for materials that had atomically flat surfaces, but as the project developed, it became clear that flatness was not essential for every application, and other properties, such as hardness, chemical reactivity, and stability would be more useful.

Table 2.1 lists most of the candidate materials we identified in this search. While it does not exhaust all possible materials, the list does provide several materials that would work for certain applications, and indicates the range of materials that might be explored in the future. Details of our study of some of these materials follow.

Table 2.1 - Results of tag materials AFM survey

Class	Material	Lateral scale (nm)	Vertical relief (nm)	Comments
Plastics	CR-39	≈20	≤2	values for unetched plastic
	Cronar	≈100	≈20	rough surface
	Rodyne	≈50	1	smooth; easier to image than CR-39
Oxides	Mica	atomic	≤1	very smooth; layered
	Glass			fairly smooth; can use HF etch
Diamond	CVD	30-1000	<10	microcrystalline, faceted layer
	Cleaved IIA	≥100	≤1-500	rough, with small smooth terraces
	Microcrystals	≥100	≤1-500	similar to cleaved diamond
Carbon	UDAC	≥100	≤20	rough; shows polishing scratches
	HOPG	atomic	≤1	very smooth, steps visible
Silicon	Si(111)			erupted surface due to atmos. water
	SiC	≈70	≤20-≈50	rough; polishing scratches
	Si ₃ N ₄ on Si	≤70	<2	smooth over large distances
	Si ₃ N ₄ platelets			rough surface
organic films	LB: Cr/PMMA SAM			easily damaged by AFM
Others candidate materials:				
	Pt			
	polycarbonate			
	HOPBN			
	Tetracene			
	calcite			
	metal dichalcogenides			
	I on Pt			
	MoO ₃ /MoS ₂			
	polymers			

2.3.1. CR-39 Plastic

This plastic has long been known as one of the most sensitive for imaging nuclear tracks [Cartwright, Shirk, and Price, 1978]. It is stable, has high spatial resolution, and its sensitivity (specific ionization) for high energy particles is known. Until this work, it had not been used to record damage of low energy ions. This material is a polymer of allyl diglycol carbonate and has been extensively used to detect nuclear particles from their damage tracks. The plastic was obtained in sheets 1 mm thick, which were cut into strips about 1x5 cm for mounting in the target holder.

2.3.1.1. General results

Figure 2.3 shows typical results obtained from the early LLNL experiments, imaged with a light microscope. The area within the 1 mm aperture appears crazed at low resolution, but at higher resolution, it is clear that the pattern is composed of individual dots.

Figures 2.4 shows a scanning electron microscope (SEM) image of Fig. 2.3 at much higher resolution. The observed pit diameters (about 200-300 nm) do not represent the original damage site size. In fact that size must have been considerably smaller. Further, all pits are essentially identical, their distribution is locally random, and they appear only within the 1 mm aperture zone. Finally, the density of features corresponds to the measured ion fluence. Taken together, these data prove without doubt that every etch pit represents the impact of a single ion, and that every incident ion produced a pit.

Figures 2.5 shows an SEM image of a field of etch pits at very high density. These images suggest that the pits are shallow and rounded, and that the dark center is seen in Fig. 2.4 is an artifact.

Figure 2.6 shown an SEM image of an individual etch pit. The cracked appearance apparently was due to the metal overcoating. The diameter of this pit is about 250 nm.

Figure 2.7 shows atomic force microscope (AFM) images of a clean CR-39 surface (before irradiation) and a single etch pit produced by Xe^{+44} . The etch was not carried as long in this case as for the LLNL experiments, hence the etch pit is smaller, about 100 nm

B. G. Cartwright, E. K. Shirk, and P. B. Price, A Nuclear track recording polymer of unique sensitivity and resolution, *Nucl. Inst. Meth.* 153, 457 (1978).

Figure 2.3 - Light microscope images of ion-damaged CR-39 plastic. (a) 25X; (b) 100X; (c) 400X. The crazed appearance is found to be due to individual damage sites. The gross structure in the image is due to the uneven flux of ions through the 1-mm diameter aperture.

Figure 2.4 - SEM image of ion damage sites on CR-39 plastic. The rectangular area near the center was damaged by the electron beam at high current.

Figure 2.5 - Scanning Electron Microscope (SEM) images of region of CR-39 damaged by individual ions. (a) 10,000X. The image shows many overlapping sites, indicating independence of the individual events. (b) 36,000X. The sites appear shallow and rounded.

Figure 2.6 - SEM images of damage sites on CR-39.
(a) 50,000X. The cracked appearance is due to the gold overlay.
(b) 20,000X. One of the etch pits is much shallower than the other two.

Figure 2.7 - Atomic force microscope (AFM) images of CR-39. (a) Original surface; (b) Surface after impact of a single Xe^{+44} ion and subsequent etching.

2.3.1.2. The smallest bit size

A systematic study was made of etch pit size following Xe^{+44} irradiation. Using 6 N NaOH solution at 63°C , etch times were varied from 1 to 10 minutes. Etch times of 2.5 minutes gave the best results, yielding pits that were about 30 nm wide (FW at half depth), and about 5 nm deep. The pits were of uniform size and shape. The etch pits were observed for all ion kinetic energies, down to 0.1 keV/Q, although at the lowest energies the optical quality of the lens degrades so the site density is lower. The pits appear to be essentially the same at all energies, although there is a weak indication that the pits have a larger size at higher ion KE.

Figure 2.8 shows the smallest etch pit we observed, measuring 30 nm in diameter.

Current ion optics are sufficient to focus to within the 30 nm observed diameter of these pits. Therefore, we can envision using a beam to create a regular array of these pits with spacing about 50 nm. This would have a bit density of 4×10^{10} bits/cm².

2.3.1.3. Volume of the nanobits

Figure 2.9 shows the volume of the etch pits versus kinetic energy of the incident Xe^{+44} ions. Apparently, the pit volume does not vanish towards zero kinetic energy. The result is consistent with the idea that each pit reflects weakly the larger damage due to the higher incident (kinetic) energy, but has constant size at low energy due to the constant potential energy. This suggests that some surface damage can be attributed to the ion charge alone, consistent with the coulomb explosion model of Parilis.

Figure 2.8 - Atomic force microscope (AFM) images of one of the smallest nanobit observed during this study. It measures about 30 nm in diameter.

2.3.1.4. Damage at the surface

That the damage in CR-39 occurs at the surface can be deduced from the projected range of the ions. A projected range (R_p) calculation for Xe (no charge state specified), using the TRIM code, is shown in Sect. 3.4. From that plot, it is seen that even at the highest incident energy used in this study, the ions penetrated less than 300 nm. The effect of the ion charge on the projected range was also estimated, using the screening range as parameter to simulate the charge state. A factor of two reduction in screening is predicted to result in about a factor of three reduction in the projected range.

Figure 2.9 - Volume of the CR-39 nanobits as a function of incident ion kinetic energy.

2.3.2. Rodyne

Rodyne is a commercially available plastic, similar to CR-39. Irradiation experiments with Xe^{+44} ions similar to those for CR-39 were carried out at KSU.

Figure 2.10 shows two AFM images of unmodified Rodyne.

The long parallel striations originate in the manufacturing process. The material appears to have topography of ± 5 nm over distances of about 100 nm. Thus, it is really quite smooth, although the afm images magnify the topography.

Rodyne is very soft. It easily shows previously scanned regions.

This material would be suitable for tags, but probably only if the damage sites were etched to about 100 nm diameter, for which the 5% roughness would not be a problem. Thus, we might choose it for latent imaging at a density of $10^{10}/\text{cm}^2$. A tag of size 100x100 micron would be able to carry a label of about 1 MB. Note that available technology would allow us to steer the ions to within about 0.1 micron. Hence we could actually write a pre-determined pattern on these tags.

Figure 2.10 - AFM images of unmodified Rodyne. (a) low magnification; (b) high magnification.

2.3.3. Cronar

Cronar is another commercially available plastic sometimes used for nuclear track imaging. Similar experiments were carried out with Cronar at KSU.

Figures 2.11 shows two AFM images of unmodified Cronar.

Cronar is much harder than rodyne, and it appears less sticky in the AFM. Unlike Rodyne, however, Cronar appears to be very rough on every scale. While it could be used for tags, it probably would be necessary to etch the damage sites to greater than 1 micron. Thus, the advantages of nanoscale imaging are lost. However, as a medium for recording a latent image, Cronar might also be useful. One could envision much larger tags, say 1 x1 mm, containing a latent image of a 1 MB label. As with Rodyne, the pattern is sufficiently coarse that available ion steering can be used to write a predetermined pattern.

Figure 2.11 - AFM images of unmodified Cronar. (a) high magnification; (b) high magnification.

2.3.4. Mica

Much of the effort during this project was spent studying the response of mica to high charge state ions. The attraction to mica was its ability to produce atomically flat cleavage surfaces, its chemical stability, the fact that it is an insulator, and the fact that it is readily available and inexpensive.

2.3.4.1. Experimental procedure

The material used for these experiments was Muscovite mica ($\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), which was obtained as clear 2.5×2.5 cm sheets 0.15 mm in thickness from Goodfellow Metals Ltd. This material is a layered compound of potassium aluminosilicate that provides insulating surfaces (resistivity up to 2×10^{17} W-cm) of atomic flatness. Fresh surfaces were prepared by peeling away thin layers of the material.

After irradiation, the mica samples were examined with the AFM. Scans were made in the irradiated and in the unirradiated regions as a check for features that were not associated with the ion damage. The unirradiated regions were uniform and featureless, except at scan sizes less than 50×50 nm, when the atomic scale structure became evident. Typical scans of ion-irradiated regions were 1×1 μm at 400×400 pixels. Data acquisition rates varied from 1 to 8 lines per second, with no noticeable dynamic effects in the observed features. At smaller scan sizes, the scanned area was damaged, possibly due to the increased scan line density. For the contact mode images, Si_3N_4 cantilevers were used as supplied. The shorter (100 micrometer long) triangular cantilevers were chosen because of their higher torsional rigidity and thus lower sensitivity to lateral forces. A few samples were examined by lateral force microscopy and "tapping mode" microscopy.

2.3.4.2. Clean mica scan

Figure 2.12 shows an AFM images of a freshly prepared mica surface. The hexagonal structure of the exposed layer is evident. While it is not possible to directly identify the atomic species in the images, it is very likely that it is the O_3 clusters that are being imaged. This is based on the symmetry of the image and the relatively high mobility of the K ions.

After prolonged exposure to the atmosphere, the ability to obtain atomic resolution is lost, perhaps as the result of water vapor adsorption. Since the irradiation process involves a considerable amount of sample handling in the air, during the transfer in and out of the exposure chamber, atomic resolution was not obtained on the exposed samples. Nevertheless, features less than 1 nm can be observed, which is sufficient resolution for the present experiments.

2.3.4.3. Damage sites

Figures 2.13 and 2.14 show damage sites produced by Xe^{+44} ion impact on mica.

The following points are notable:

- The features have high contrast against the background surface, hence would be easily identified by automatic scanning devices.
- The patterns are, within the statistics, random. There is no obvious clustering or repulsion that would bias close-spaced bit fabrication.
- All the sites are essentially identical, within the resolution of the instrument.
- The sites produced by ions of different energies (1.14 keV/Q and 5.2 keV/Q are identical, within the instrumental resolution.

Figure 2.12 - AFM image of unmodified Mica (atomic resolution).

Figure 2.13 - AFM image of unmodified Mica. Ion kinetic energy 1.14 keV/Q.

Figure 2.14 - AFM image of unmodified Mica. Ion kinetic energy 5.2 keV/Q.

2.3.4.4. Blisters

Figures 2.15-2.18 show several AFM images of mica surfaces irradiated at normal incidence with Xe^{44+} ions of kinetic energy 5.2 keV/Q. A random pattern of surface features is visible. The features are of nearly identical size and shape, being approximately circular with a diameter of about 15-20 nm. Cross sections show roughly conical features with heights 0.2-0.3 nm. The features only appear after irradiation and only within regions of the surface that were exposed to the ion beam. The areal density of the features is consistent with the estimated total ion fluence to the sample. Taken together, these observations demonstrate that each individual surface feature must be the result of a single ion impact on the mica surface. The operation of the AFM leaves no doubt that they are, indeed, convex features, i.e., blisters.

Once formed, the blisters persist under examination at low scanning force in the AFM. A slight enlargement in the feature size is observed in some cases, but the general characteristics of the features are not substantially affected.

The features are also stable when stored in the laboratory for more than 3 months.

Figure 2.15 - AFM image of ion-produced blisters on mica. Ion kinetic energy 5.2 keV/Q.

Figure 2.16 - AFM image of ion-produced blisters on mica. Ion kinetic energy 5.2 keV/Q.

Figure 2.17 - AFM image of ion-produced blisters on mica. Ion kinetic energy 5.2 keV/Q.

Figure 2.18 - AFM image of ion-produced blisters on mica. Ion kinetic energy 5.2 keV/Q.

2.3.4.5. Craters

Close examination of the features when scanned at higher force sometimes shows them to be shallow craters.

Figure 2.19 shows a images of craters with diameter about 15 nm and depth of 0.3 nm.

Figure 2.20 shows a line scan across two craters, demonstrating their similarity and giving their dimensions. From such scans, it is possible to estimate the volume of the crater and the number of atoms that were removed to form it. Each crater has a volume of about 40 nm^3 . From the molecular weight (398 g/mol) and density (2.8 g/cm^3) of mica, we find it has approximately 4 atoms/nm^3 . Thus, it appears that 100-200 atoms of material were removed to form each crater. The heat of vaporization of this amount of material is much less than the potential energy available from the ion.

The apparent shallowness of the craters may in part reflect the inability of the relatively large scanning tip to sample the crater bottom. However, since the vertical extent of the convex features is about the same as that for the concave features shown here, this seems unlikely.

Crater structures typically were stable for extended periods of time, even when imaged at high force. In one test, more than 500 consecutive scans were made of the same region. The only change was a slight broadening of the features.

Although the features appear clearly as blisters or craters in most AFM images, initially there was some ambiguity and uncertainty about their true nature. There were indications that the images could be either blisters or craters, depending on the force and direction of scan. We resolved these ambiguities by taking some samples to Digital Instruments where their staff used a Nanoscope III with "tapping mode" to obtain more detailed and reliable images of these features. For samples irradiated with 5 keV/Q Xe^{+44} ions, the tapping mode images were unambiguous: the features were indeed blisters, the same diameter and height as those observed by contact mode microscopy (our normal mode). The sample irradiated with 1 keV/Q Xe^{+44} ions exhibits both crater and blisters type structures. The craters are slightly smaller in diameter and depth than those observed in contact mode.

Figure 2.19 - AFM image of ion-produced craters on mica. Ion kinetic energy 0.6 keV/Q.

(a)

(b)

Figure 2.20 - Damage sites on mica. (a) AFM image of damage sites on mica. (b) Linear scan across two craters. The markers appear in pairs:

Horizontal distance [nm]	10.51	10.51
Vertical distance [nm]	0.54	0.63

2.3.4.6. Ion kinetic energy dependence of damage features

In principle, the damage features should be weakly dependent on the kinetic energy of the ion. This is due to the fact that the ion penetrates more deeply at higher energy, therefore spreads the damage over a longer path.

Figure 2.23 shows the measured heights of the blisters and depths of the craters vs kinetic energy of ions, obtained from all four scan directions. Each point is the mean obtained by measuring from 10 to 20 separate damage sites from a single sample. Error bars are the standard deviation of the measured individual event height for one sample. A 300×300 nm square was selected from the 1×1 micron image that contained a representative sample of the features in that image. The heights of single events then were measured by taking a cut in a direction parallel to the scanning direction through the highest part of the feature and measuring the peak height relative to the local background level. Noise in the background and determining the proper baseline makes individual measurements uncertain by ± 0.05 nm, with a tendency to underestimate the height. Craters are plotted as negative heights. Features smaller in height than 0.1 nm could not be distinguished from the noise, consequently the averages may be skewed towards larger values, especially on samples having a greater fraction of smaller features.

Figure 2.21 - Blister height and crater depth (negative height) as a function of kinetic energy of the incident ion.

Figure 2.22 shows the measured heights of the blisters and depths of the craters vs kinetic energy of ions, obtained from the same data as Fig. 2.21. Craters are not differentiated in these plots. The very low aspect ratios of the features indicate that a systematic difference in the measured size of pits vs blisters due to finite probe radius is not a significant concern. These data show that the heights and diameters of the features to be essentially independent of the ion kinetic energy.

2.3.4.7. Charge state dependence of damage features

The damage phenomenon is potentially very sensitive to the charge state of the incident ion. The is because the surface damage is predicted to depend strongly on available coulomb energy, and rather weakly on kinetic energy. Furthermore, vacancies in the inner atomic shells should produce far greater damage than ions with only outer shell vacancies. Thus, it is a matter of great importance to measure the charge state dependence of the damage.

Figure 2.23 shows a series of AFM images of blisters on mica produced by Xe^{+Q} ions, with $Q=30, 33, 37, 40, 42$, and 44 . Clearly there is a major systematic effect of the charge state on the damage sites produced.

Figure 2.22 - Blister and crater diameter as a function of kinetic energy of the incident ion. (Data same as Fig. 2.21).

Figure 2.23 - Damage on mica as a function of incident charge state.
 (a) Xe^{+30} ; (b) Xe^{+33} ; (c) Xe^{+37} ; (d) Xe^{+40} ; (e) Xe^{+42} ; (f) Xe^{+44} .

Figure 2.24 shows the measured diameters, heights, and volumes of the blisters as a function of ion charge Q . These data show that the blister sizes do indeed increase significantly with increasing incident ion charge.

The theory developed by Parilis (cf. Sect. 3.6) predicts that the crater volume should be proportional to the coulomb energy W_Q . The data of Fig. 2.24 are roughly in agreement with this prediction.

Figure 2.24 - Blister geometry as a function of charge state Q of the incident Xe^{+Q} ion.
(a) diameter; (b) height; (c) volume.

2.3.4.8. Erasure

The blisters observed in mica are susceptible to modification by the AFM tip, even at the lowest stable scanning forces obtainable. Repeated scanning causes the features to become less distinct, eventually leading to their disappearance. Increasing the tip force hastens the erasure.

Figure 2.25 shows a sample with very high density of ion impacts sites, overlapping in some instances. First, a region 1×1 micron was scanned at the bottom center. Next, a similar area at 45° was scanned near the center. Clearly, these regions show the effects of these scans. Note that there is no ejecta or debris buildup at the edges of the previously scanned regions. This suggests that the features are being flattened out rather than scraped away.

Figure 2.25 - Erasure of blisters by repeated scanning of the AFM.

2.3.4.9. Corrugation effect

During the course of our AFM studies of mica, a peculiar effect was observed: cooperative corrugation.

Figure 2.26 shows a typical image, in which the larger surface of mica was irradiated with 10 keV/Q Xe⁴⁴⁺ and a small rectangular area in the middle was scanned at high tip force.

Apparently, the AFM has caused the surface to corrugate. This observation suggests that de-lamination of the layered mica structure is occurring. We emphasize that this phenomenon is a cooperative one: neither the ions alone nor the AFM scans alone produces the corrugations.

This phenomenon was elusive: it was not observed consistently or in all samples. It was, however, apparently a real effect, and we reproduce it here for reference. The delamination effectively obscured any individual ion damage features. This effect obviously would present limitations on layered media as candidates for micromechanical tags.

Figure 2.26 - Apparent delamination of mica surface by AFM scanning.

2.3.4.10 Lateral force effects

The quantitative and sometimes qualitative interpretation of the AFM images is not always straightforward. When regions on the same sample were scanned with very low normal forces in differing directions relative to the cantilever, the results were sometimes markedly different.

Figures 2.27-28 shows data taken for leftward and rightward traveling scans in constant tip deflection mode for the same region.

The apparent topographic inversion is due to lateral forces on the tip. Lateral forces contribute an additional bending torque on the lever that deflects the reflected laser beam, effectively mimicking topography. Images are then some combination of real topography and lateral forces. Using lateral force microscopy, the reversal of apparent topography upon reversal of scan direction is apparent. Single ion features image as bumps on one scan and upon reversal of scan direction as pits in the same pattern and locations as the previously observed bumps.

To minimize the effects of lateral forces, samples were imaged with the minimum stable forces that were attainable in air. This corresponds to the point near zero force, neglecting attractive interactions between the tip and sample surface. This minimum is constrained by the adhesion effects of adsorbed water from the atmosphere, and is independent of cantilever stiffness. Scans were obtained for the tip traveling in four different directions: 0° , 90° , 180° , and 270° , with 0° corresponding to motion toward the free end of the cantilever. Approximately 25% of the scans taken in the 0° and 90° directions show pit type features. Scans taken in the 180° and 270° directions never exhibited pit features. If the tip and cantilever contain left-right mirror symmetry and are perpendicular to the monitoring laser beam and the scanning direction, one would expect to see differences between the 90° and 270° scans. Misalignment of the cantilever mount, microscopic asymmetries of the probe tip, or tilt of the microscope head relative to the sample may have broken this symmetry. Pits usually were observed on samples irradiated by low kinetic energy ions (typically 0.6 keV/Q or less, but rarely pits were seen on the 5 keV/Q samples. Increasing the applied normal force on the tip caused the 0° scan to show pits more frequently.

Effects similar to those we saw on mica were observed also on graphite [Baselt and Baldschweiler, 1992].

2.3.4.11. Other work on mica

Thibaudau and coworkers (1991) observed latent tracks in mica produced by fast Kr ions. The ions had energies 7.6-34.5 MeV/AMU. At these high energies, the ions penetrate deeply in the solid, and the damage is in the form of an amorphous cylinder 1-5 nm in diameter. This high-energy regime has been studied for many years. The present work differs from that in that here the damage is confined to the near surface.

2.3.4.12. Conclusions regarding mica

Quantitative measures of the vertical components of single ion damage sites is not easily done. Some problems we encountered include: effects of lateral forces, thermal drift in the piezo ceramic scanners, changing relative humidity, wear of the contact point of the tip, torsional rigidity of the cantilever, precise tip-sample orientation, and contamination. The apparent heights obtained by scans in opposite directions should give lower limits for the true topographic dimensions. Averaging scans in two directions should give an estimate of the true height. For features that are altered by the scan itself, e.g., blisters, opposite scans have to be made over different paths, and the assumption made that the features on the two paths are essentially the same. This is a good assumption in the present experiments.

The preponderance of evidence obtained in this study when scan forces were minimized indicate that the damage sites produced by low energy ions on mica are convexities, i.e., blisters, and not craters. At higher energies and high scan forces, the features either appear as, or are, concavities, i.e., craters.

D. R. Baselt and J. D. Baldschweiler, Lateral forces during atomic force microscopy of graphite in air, *J. Vac. Soc.* B10, 2316 (1992).

F. Thibaudau, J. Cousty, E. Balanzat, and S. Bouffard, Atomic Force Microscopy Observations of tracks induced by swift Kr ions in mica, *Phys. Rev. Lett.* 67, 1582 (1991).

Figure 2.27 - AFM image of mica taken scanning left-to-right.

Figure 2.28 - Image of same sample as Fig. 2.27 taken scanning right-to-left.

2.3.5. Glass

We used the AFM to examine a microscope slide. The surface was fairly smooth. Glass can be readily etched by HF, and a great deal is known about that process. We believe glass is a good candidate for many tag applications.

2.3.6. CVD diamond

AFM images of a CVD-diamond showed vertical relief of less than 10 nm over distances of about 1000 nm. Thus, it has potential for recording features significantly larger than 10 nm, it probably would not be the material of choice for a tag.

2.3.7. Cleaved diamond

AFM images of cleaved diamond showed that it was rather rough, having numerous large-scale (0.1 micron) features that reflect extensive microfracturing. It is possible to find small flat terraces of good smoothness. Atomic-scale resolution may be possible, but it has not yet been definitely shown. The irradiated sample was found to be covered with much small-scale dust or debris, probably the result of contamination during handling. The irradiated sample surface was examined for evidence of ion damage but none was immediately evident.

Three diamond samples (two cleaved and one microcrystals immobilized on an epoxy base) were cleaned in spectroanalyzed acetone, in an ultrasonic cleaner 3 times for 15 minutes. These AFM imaged surfaces are much cleaner. We were able to resolve flat regions and terraces of micron scales. The cleaning, however, does appear to leave 0.1-0.5 micron adsorbates on the surfaces which get brushed out after some tens of minutes of scanning the same region. Larger scale scan show the cleaned region bordered by the debris. Not all regions are contaminated equally; in fact, some are quite clean. We were not able to observe atomic structure on the crystals.

2.3.8. Diamond microcrystals

Naturally grown diamond was examined with the AFM. The material is supplied [Beta Diamond] as a powder of individual crystals, in mean sizes of 1-100 microns, in dispersions of about 10% FWHM.

Figure 2.29 shows an SEM photo of a mixture of two sizes of these diamonds.

Figure 2.29 - SEM of diamond powder, containing a mixture of two crystal sizes.

Figure 2.30 shows AFM images of the surface of 100 micron diamonds, one that is contaminated and one that is clean. The contaminated diamonds obviously have limited usefulness for writing complex messages. Assuming the contaminants can be removed, the diamond surface itself is relatively smooth, and could form a good writing surface.

We have not observed single ion damage of the diamond surface, primarily because of the contamination problem. We predict, however, that the damage should occur readily, and that the surface will be extremely stable.

Diamond is very attractive as a passive mechanical tag because of its hardness. Although our results with these diamonds are not particularly encouraging for immediate application, the technology of diamond synthesis is evolving rapidly, and it is likely that better quality material will be available in the future that could make diamond tags feasible.

Beta Diamond Products, Inc., 20503 Yorba Linda Blvd., Yorba Linda, CA 92686, Tel. (714) 777-7144.

Figure 2.30 - AFM of diamond microcrystal surfaces. (a) contaminated; (b) clean.

2.3.9. UDAC (Ultra Densified Amorphous Carbon)

Figure 2.31 shows AFM images of Ultra-Densified Amorphous Carbon (UDAC). They show structures very similar to Si_3N_4 . The material is very rough on all scales. See remarks for SiC for usefulness as a tag.

Figure 2.31 - AFM of UDAC. (a) low magnification; (b) high magnification.

2.3.10. HOPG (Highly oriented pyrolytic graphite)

Figure 2.32 shows AFM images of HOPG on several scales. We found HOPG to be among the smoothest materials we examined.

The roughness appears to be less than 0.1 nm over many 100's of nm. We observed single layer steps between large atomically flat layers, folded back flaps, layer ruptures, ridges and grooves, and possibly sample flexure.

We did not directly observe ion impacts on HOPG, and we were unable to assemble the necessary chemical processing facilities to implement etching during this project. However, we have found considerable evidence from various sources that HOPG will record ion impacts and that the damage sites can be enlarged or decorated. For instance, Chang and Bard [1990] have observed pits in HOPG produced by gasification reactions at elevated temperatures in air. These pits are 20-30 nm in diameter, and appear after heating the material to 650°C in air for 5 minutes. The features are about 0.3 nm deep, and have raised lips. This depth is exactly the spacing between the graphite layers. The diameter of the pits was proportional to etch time.

Nucleation of these sites was associated with impurity particles. Evidence for this was that pits were induced by deliberately added NaCl, CrO₃, and H₂PtCl₆ impurities. This provides a very convenient etch method for HOPG: simple heating in air.

Villeneuve, et al., observed topographic modification of HOPG surface using 50 keV Ar⁺ ions. In this energy regime, the ions penetrate more deeply into the solid (42 nm). The raised bumps have diameters 5 nm and heights 0.24 nm, slightly smaller than we observed on mica. The blisters are attributed to residual defect-induced stresses from the collision cascade.

HOPG is one of two materials (the other being mica) that has large atomically flat surfaces. It is, however, soft and easily damaged. Therefore, it would be useful as a tag surface only if it could be used in a composite structure. One good possibility is to protect it inside a silicon nitride case (cf. Fig. 2.37).

H. Chang and A. Bard, *J. Amer. Chem. Soc.* **112**, 4598 (1990).

C. H. Villeneuve, M. Phaner, L. Porte, N. Monocoffre, P. Pertosa, and J. Tousset, Topographic Modifications on the graphite surface induced by high energy single ion impact, *Vacuum* **41**, 1686 (1990).

Figure 2.32 - AFM of HOPG. (a) low magnification;

Figure 2.32 (con't) - AFM of HOPG. (b) intermediate magnification; (c) high magnification.

2.3.11. Si 111 (Silicon)

Silicon has obvious technological importance. The potential for fabricating nanometer structures on silicon presents the possibility of combining tagging functions with active circuit devices. While this goes beyond the original goal of developing "passive" tags, it was sufficiently interesting that we decided to examine the pure silicon surface.

Single crystal silicon, oriented with the (111) face, was obtained from Brookhaven National Laboratory. The following procedure was used to prepare the surface:

1. First etch:

HF (48-51%) [1 part] + H₂O [7 parts]. 5 minute dip at room temperature.

Teflon container, not glass. There should be no visible effect. Rinse:

deionized water ($\rho > 12$ MH) 3 times several minutes.

2. Oxidation:

H₂O₂ (30%) [1 part] + HCl (38%) [1 part] + H₂O [5 parts]. 10 minute dip at

80°C. Bubbles, agitates. Rinse: same as First etch.

3. Second etch:

NH₄F (40% in H₂O). 5 minute dip at room temperature. Teflon container, not glass. Rinse: same as First etch. Do not save chemicals from previous etch.

Figures 2.33 shows AFM images of the samples prepared in this way.

The surface appears rough on a 1 nm scale, but this roughness is even over dimensions of 20 nm. Thus, this material might be useful for recording nanobits, but not at the nm level.

We expected to be able to obtain atomic resolution on this surface, but we did not. The AFM behaved in a rather strange manner. Apparently the attraction between the tip and the surface is so strong it is impossible to obtain the externally applied force. This is not a problem if there are no significant lateral forces. However, if there are lateral forces, they may overwhelm all other signals. All the apparent topography in the above images may be stick-slip phenomena.

Because of the uncertainties in interpreting the AFM images, we elected not to attempt to image ion-induced defects. Upgrading the AFM to a Nanoscope III with tapping mode would provide unambiguous images of this surface.

Figure 2.33 - AFM of Si(111). (a) Low magnification; (b) High magnification.

2.3.12. SiC (Silicon Carbide)

Silicon carbide is attractive because of its great strength and hardness.

Figures 2.34 show AFM images of commercially available SiC.

Clearly, this material shows large scratches due to polishing. Furthermore, it is bumpy on a scale of 100 nm. Therefore, this material would not be useful for recording nm damage sties.

In spite of this, rough materials such as polished SiC might be useful for making tags for certain applications, namely applications that depend on the specific chemical, thermal, or mechanical properties of the material itself rather than the message that is written on the tag. That is, the label on the tag is an intrinsic part of the tag as manufactured, rather than being applied after manufacture. We might say that the tag label is applied during manufacture of the material, and is characteristic of that manufacture, rather than being added to a blank material after manufacture.

In the case of polished materials like SiC, we could apply different polishing sequences, which would produce different scratch patterns that could be easily recognized by the AFM. One would not search for an exact image or location on the tag; rather, one would analyze the surface features (presumably by image-processing software), and generate a low-dimensional representation of the surface, such as the distribution of scratch groove angles, or the mean groove width. The material therefore has a "fingerprint" that provides the label on the tag. Figure 2.35 shows two easily distinguishable patterns that could be deliberately impressed on the material by polishing. These are easily machine-readable.

The same function, of course, could be done using a high-quality flat surface damaged by the ions in a random pattern. The ion beam could be modulated to impress a desired statistical pattern on the damage sites (such as mean density, distribution of blister shapes resulting from oblique incidence, etc.). This is an example of "statistical coding" discussed elsewhere in this report.

We emphasize that for this kind of tag there is no externally written message. Because of this, no independently specified information can be conveyed by the tag. It would be useful only for tracking.

Figure 2.35 - Tag labeling by linear feature contrast. The two patterns represent two specific specimens that have different manufacture marks.

Figure 2.34 - AFM of SiC. (a) Low magnification; (b) High magnification.

2.3.13. Si_3N_4 (Silicon Nitride)

Silicon nitride was obtained from Sandia New Mexico, where it is used as raw material for micromechanical devices.

Figure 2.36 show two AFM images of this material as received.

This material is clearly very rough on all scales. It is, however, extremely strong and hard, and can be fabricated into tag-like shapes with readily available technology (mostly lithographic techniques). We therefore suggest that Si_3N_4 would be a useful for fabricating composite tags. Bonding a high-resolution material like mica to a high-strength material like Si_3N_4 would produce a tag that combines good properties of both materials, much as layered composite coins do.

Figure 2.37 shows a proposed composite tag structure. This tag would have very high capacity and very high strength. Reading it would involve opening the composite and scanning the mica surface.

Figure 2.37- Proposed design for a protected tag.

Figure 2.36 - AFM of Si_3N_4 . (a) Low magnification; (b) High magnification.

2.3.14. Langmuir Blodgett films

LB films are one of a class of organic materials that can be made with essentially single crystalline structures over large areas.

Figure 2.38 shows an AFM image of an LB film (Schwartz, et al., 1992), showing an almost perfect hexagonal close-packed array over an area of many nanometers. This is typical of a class of surface films (see [139] for review).

The procedure for fabricating the films is shown in Figure 2.39.

Our interest in organic films was stimulated by a publication from Stanford reporting that ultra-thin (monolayer) LB films of Poly(methyl methacrylate) (PMMA) had been fabricated and used as a mask for pattern transfer. While the features that were transferred were much larger than nm (because of the lithographic method of feature definition), the fact that the *monolayer* film had functioned as a mask was extremely exciting: it implied that the film could maintain integrity within dimensions of one monolayer, i.e., in the nanometer range. It therefore implied that such films might work as masks for pattern transfer of nanometer size images. We envisioned using the high charge state ions to create individual damage sites on the LB film, and then etching a substrate on that pattern. The relatively fragile film would be stripped away, leaving a negative image on a durable substrate.

Figure 2.38 - AFM image of LB film.

spread film after solvent evaporation

compressed film

1st layer deposition
upstroke

Figure 2.39 - Procedure for fabricating LB films.

Poly(methylmethacrylate) (PMMA) is a material capable of forming high quality LB films, and is well-known as a high resolution electron beam resist. Thus, the possibility of using such an ultra thin LB film in microlithography has been extensively studied. Typically, the substrate is a Si wafer on which 100 nm of SiO₂ has been thermally grown, and 50 nm of Cr evaporated on top of that. The structure is similar to the standard Cr photomasks used in the microelectronics industry, where Cr is deposited on a quartz wafer.

After several discussions with the Stanford Group, we carried out an experimental investigation of PMMA LB films. A set of PMMA LB films was prepared by Marina Despotopoulou, Stanford University Chemistry Department. The following three paragraphs on materials and procedure were provided by her in reference to this work:

The PMMA LB films were deposited in a Joyce-Loeble Langmuir trough equipped with a microbalance for measurement of the surface pressure by the Wilhemly plate method. The substrate wafer was first immersed in the water in the trough, and then about 100 microliter of a dilute 0.5 mg/ml solution of PMMA in chloroform was spread on the air-water interface. Then a 20-30 minute period is allowed for the solvent to evaporate. On account of the modest hydrophylic C=O groups/water interaction, the PMMA chains are expected to lie approximately parallel to the water surface. The barriers are then moved toward each other and the film is slowly compressed to a surface pressure of 15 dyn/cm. After an equilibration waiting period of 20 minutes, the first monolayer of the PMMA film formed on the air-water interface is transferred onto the wafer by withdrawing the wafer from the water. The film is then baked at 170°C for 20 minutes and the deposition of subsequent monolayers of PMMA follows in the LB trough. The film is transferred on both upstrokes and downstrokes with a deposition ratio of 1.0 during the former and 0.8 during the latter. The deposition ratio is a measure of the transfer efficiency, and is defined by the area of the water that is covered with it. In total, 17 layers of PMMA were transferred with an average thickness of 0.9 nm per layer. Finally, the film was baked at 100°C for 8 hours.

PMMA prepared in this way behaves as a positive resist for electron beam doses up to 1000 μ Coulombs/cm². The films are developed in a 3:7 cellosolve solution to strip the exposed material, postbaked at 90°C for 30 minutes, and immersed in Cr etch solution for pattern transfer in the Cr layer. The rest of the PMMA layer is then dissolved and the structures are examined under the SEM or an optical microscope. The thin layer of the SiO₂ initially deposited on the silicon wafer provides a good contrast layer for this step. The pinhole densities of films prepared in this way has been found to be dramatically lower than the spin-cast films.

The Stanford group produced LB films of 1, 5, and 9 monolayers, and we examined them with the AFM. Figure 2.40 shows our AFM images of these films.

The 1 monolayer film was relatively smooth and nonsticky in the AFM. The 5 monolayer film was quite soft, and the surface was perturbed by scanning. The 9 monolayer film was sticky, but tougher than the 5 layer film. These observations probably should not be generalized; the exact processing of these films was not known, and we were unable to repeat the measurements. The results do, however, give an indication of the range of structures expected from LB films, and emphasize that they are fragile and susceptible to damage by the AFM.

The films have considerable structure on the 100 nm scale, and featureless regions on scale smaller than this. We did not see any molecular size features.

There was some scan-induced damage after scanning the same region for 10-20 minutes, but this could be reduced by lowering the contact force of the tip.

Based on the publications that appeared to indicate that these films were capable of nanometer resolution, we expected to see much greater uniformity in their structure. The results were disappointing. However, this difficulty may not be important in an application. We observed that these films were very easily damaged by the AFM, but the AFM is only being used in this work as a diagnostic. It is entirely possible that high quality ultra-thin LB films can be made, damaged by ions, and used for pattern transfer to a material that is durable.

D. K. Schwartz, J. Garnaes, R. Viswanathan, and J. Zasadzinski, *Scanning* 14, 2-3 (1992).

Figure 2.40 - AFM image of the LB films at low magnification.
 (a) 1 monolayer; (b) 5 monolayers; (c) 9 monolayers.

Figure 2.40 (con't) - AFM image of the LB films at medium magnification.
 (a) 1 monolayer; (b) 5 monolayers; (c) 9 monolayers.

Figure 2.40 (cont) - AFM image of the LB films at high magnification.
(a) 1 monolayer; (b) 5 monolayers; (c) 9 monolayers.

2.3.15. Self-assembled monolayer (SAM) films

Another class of ultrathin organic films is self-assembled monolayers (SAM). These organic films form spontaneously on a variety of substrates and consist of a head group which covalently bonds to the substrate, an alkyl chain, and a surface functional group which can be engineered to provide specific characteristics. Figure 2.41 shows a monomer, and a monolayer film that spontaneously assembles from a solution of these monomers. Typical SAM films are on the order of several nanometers thick, are highly insulating, and are resistant to most acids and organic solvents.

SAM films have several advantages over LB films: They are easier to fabricate (simply dip the substrate in the solution and wait). They are stronger (covalent bonding instead of Van der Waals). They are extremely thin. And they can be chemically processed to replace the functional group with a wide variety of other functional groups, providing a range of chemical specificity.

For these reasons, we believe that SAM films have great potential for nanometer lithographic processes, including pattern transfer. We able to carry out some preliminary observations of these films, which we describe here. Because of their great potential, we also review some of the major techniques for using SAM films in nanometer patterning technology.

Figure 2.42 shows a proposed procedure for pattern transfer using a SAM film. The fact that they are so thin enables nanometer resolution of the pattern.

Figure 2.43 shows a proposed procedure for fabricating nanometer knobs on top of an SAM film.

Figure 2.41 - A monomer and a SAM film that self-assembles from a solution of monomers.

A set of SAM films was prepared by staff at Penn State University (courtesy David Allara) and shipped to KSU. The samples were a single monolayer of octadecyltrichlorosilane (OTS) on SiO_2 . The silane end binds to the SiO_2 and forms a SiO polymer with no Cl remaining. The binding sites are thought to be such that the alkyl chains close pack. The chain director has been measured to be less than 15° from the surface normal. There is an alternative polymerization scheme that packs the chains much less efficiently. The chains are then tilted about 35° . Figures 2.44-47 show AFM images of these films.

Figure 2.42 - A proposed method for pattern transfer using a SAM film.

Figure 2.43 - A proposed method for nanobit construction using a SAM film.

Figure 2.44 show 3x3 micron consecutive scans over the same area. The impurity (dust) particle near the center serves as a fiducial. There is a fairly consistent modulation of ~ 0.5 nm. Figure 2.42(a) (taken on the initial scan) shows several dark features 50-100 nm in diameter, especially noticeable in the upper left. These features are mostly absent from Fig. 2.42(b) (taken after extensive scanning), while the background appears about the same.

Figure 2.44 - AFM image of the Penn State University SAM film.
(a) Initial scan; (b) after extensive scanning.

Figures 2.45 show consecutive 5x5 micron scans centered at the same location as the previous two figures. The small dark regions appear only outside the previously scanned 3x3 micron region (Fig. 2.43(a)) and are absent in the repeat scan (Fig. 2.43(b)). This erasure of the small darks features is common in this kind of AFM work; the dark features are present on the first imaging and rapidly disappear. This is almost certainly due to sweep-cleaning of the surface by the tip.

Figure 2.45 - AFM image of the Penn State University SAM film.
(a) Initial scan; (b) after extensive scanning.

Figures 2.46 show first scans of different regions using the softest cantilever available. The dark regions are shown with more resolution. Again, the background undulations appear to be unmodified by the scanning. Note that although some of the dark spots are removed, not all are. One possibility is that the soft cantilever is only partially cleaning the surface, but the images also are consistent with the idea that the spots are not topographic features at all, but rather spots that strongly attract the tip (sticky), appearing in the images as false topography.

Figure 2.46 - AFM image of the Penn State University SAM film.
(a) Initial scan; (b) after extensive scanning.

Figures 2.47 show a first scan and second scan of the same area in the reverse direction, again using the soft cantilever. Many of the dark spots in the first scan appear as bright spots in the reverse scan, consistent with the idea that they represent sticky spots on the film.

To date we have been unable to conclusively demonstrate single ion damage of the SAM films. However, all our experience indicates that the damage occurs; it is the limitations of AFM imaging that have prevented our observation of the damage. There are evolving techniques that can image these films, and we fully expect that eventually ion damage can be seen using scanning microscopy.

Figure 2.47 - AFM image of the Penn State University SAM film. (a) Initial scan; (b) Second scan of the same film as Fig. 2.47(a) taken in reverse direction.

We include here additional information about surfaces that are potential candidates for tags. Most of these have very flat surfaces.

2.3.16. Platinum

Teichert, et al., [1994] have observed defects created in Pt(111) surfaces by single Xe^{+1} ions using a scanning tunneling microscope (STM). The surface appears to be extremely smooth.

C. Teichert, M. Hohage, T. Michely, and G. Comsa, Nuclei of the Pt(111) network reconstruction created by single ion impacts, *Phys. Rev. Lett.* **72**, 1682 (1994).

2.3.17. Polycarbonate

Ackermann, et al., [1993] have used AFM to observe single ion impact defects in polycarbonate, polyimide, and glass.

J. Ackermann, S. Grafstrom, M. Neitzert, R. Neumann, C. and, J. Vetter, and N. Angert, Scanning force microscopy of heavy-ion tracks, *Rad. Effects and Defects in Solids* **126**, 213 (1993).

2.3.18. HOPBN

Albrecht and Quate [1987,1988] have used AFM to obtain atomic resolution images of various insulators, including graphite, molybdenum disulphide, and Highly Oriented Pyrolytic Boron Nitride (HOPBN).

T. R. Albrecht and C. F. Quate, Atomic resolution imaging of a nonconductor by atomic force microscopy, *J. Appl. Phys.* **62**, 2599 (1987).

T. R. Albrecht and C. F. Quate, Atomic resolution with the atomic force microscope on conductors and nonconductors, *J. Vac. Sci. Tech.* **A6**, 271 (1988).

2.3.19. Tetracene

Overney et al., [1991] have used AFM to image the surface of tetracene.

R. M. Overney, L. Howard, J. Frommer, E. Meyer, and H.-J. Guntherodt, Molecular surface structure of tetracene mapped by the atomic force microscope, *J. Chem. Phys.* **94**, 8441 (1991).

2.3.20. Alkali halides

We examined a sample of sodium fluoride (NaF) with the AFM. It was very smooth and gave near-atomic resolution. However, its surface was unstable in air. On time scales of hours, circular pits of depth 1 nm appeared and grew until the whole surface was removed. The resulting new surface was just as smooth as the previous one was. The problem may be due to etching by water vapor. If so, the problem is common to all alkali halides. This material therefore probably is not a good choice for tags, due to its instability. The problem may originate in reactions with atmospheric water-vapor. If so, all the alkali halides will exhibit similar instabilities.

2.3.21. Calcite

Local forces from the end of the tip may displace surface atoms until the forces are made very small. Adsorbed liquid films can make these forces very large. However, using the tip completely submerged in a saturated CaCO_3 /water solution may reduce these forces.

2.3.22. Metal dichalcogenides

Meyer et al., [1990] have studied various metal dichalcogenides using AFM and STM.

E. Meyer, R. Weisendanger, D. Anselmetti, H. R. Hidber, H.-J. Guntherodt, F. Levy, and H. Berger, Different response of atomic force microscopy and scanning tunneling microscopy to charge density waves, *J. Vac. Sci. Tech.* A8, 495 (1990).

2.3.23. I on Pt

Schardt et al., [1989] have observed very regular lattice surfaces of I adsorbed on Pt(111) using STM.

B. C. Schardt, S-L. Yau, and F. Rinaldi, Atomic resolution imaging of adsorbates on metal surfaces in air: Iodine adsorption on Pt(111), *Science* 243, 1050 (1989).

2.3.24. MoO₃/MoS₂

Xiaowei, et al., [1992] have single ion impact damage on MoS₂ surfaces using STM.

T. Xiaowei, Y. Junen, and Z. Pengji, A nuclear detector with super-high spatial resolution, *Nucl. Inst. Meth.* A320, 396 (1992).

2.3.25. Polymers

Hansma, et al., [1992] have used AFM to image the surface of Teflon.

H. Hansma, F. Motamedi, P. Smith, P. Hansma, and J. C. Wittman, Molecular resolution of thin, highly oriented poly(tetrafluoroethylene) films with the atomic force microscope, *Polymer* 33, 647 (1992).

2.4. AUTOMATIC BIT READING

Automatic recognition of features would presumably be an important part of any tagging system. In the absence of a particular application, it was inappropriate to invest much resources within this project in developing pattern recognition. We feel that for any given application, the tag must be designed and the method of labeling determined. Given these, the appropriate tools could be assembled from existing sources.

We did, however, exercise some available software to demonstrate the automatic identification of damage features. Several representative AFM images of a Xe^{+44} irradiated mica sample was analyzed using the NIH software package *Image*. By adjusting the threshold value of the image intensity to be near the midpoint elevation (or depression) value of the damage features, the *Image* software could easily trace the edges of each damage feature, count them, measure the characteristics of each feature (size, axes of best fitting ellipse, etc.), and catalog these features with their positional coordinates. This provided a route to go from an AFM image to a filtered digital representation of the HCI produced bit pattern.

Using *Image*'s "density slice" feature, which highlights pixels within a selected range of z values, the pits were highlighted. Next, an edge-tracing routine was used to locate and trace the outline of each feature. A built-in particle analysis routine then evaluated the area, mean, and mode values, positions, perimeter lengths, and the best fit ellipse enclosing the feature.

Figure 2.48 shows an AFM image of damage sites in mica.

The scan data for this image is given in Table 2.2 (The entries in this table are not calibrated).

Clearly, the software easily analyzed the four sites in this image, and produced reasonably accurate measures of their positions, size, and shapes.

A more difficult task was to identify features in larger scale images (smaller feature size in the image). Figure 2.49 shows a larger scale image of the same sample just described, and the sites located by the software.

The software identified 7 candidate features, including the 4 in the previous image (features 4,5,6,7). Of the 3 additional features, visual inspection showed that feature 2 was possibly a scan artifact. Statistical analysis of the numerical data (Table 2.3) indicates that it is an outlier. Clearly, the numerical data can be used to discriminate true ion-impact features from scanning artifacts.

This exercise, although modest, clearly demonstrates that automatic feature recognition and analysis in AFM images is straightforward.

NIH Image reference: NIH Image, Version 1.52 (1993), by Wayne Rasband, National Institutes of Health, USA. The software is in the public domain.

Table 2.2 - Data for the image in Fig. 2.48

	area	mean	S. D.	X	Y	Mode	Length	Major	Minor
1	0.22	77.26	12.85	3.90	6.60	91	3.39	0.82	0.36
2	0.19	77.70	12.93	7.62	4.82	86	3.08	0.64	0.40
3	0.21	80.48	11.18	7.56	4.04	91	3.25	0.66	0.42
4	0.23	80.64	11.03	3.80	1.90	96	3.18	0.65	0.45

Table 2.3 - Data for the image in Fig. 2.49

	area	mean	S. D.	X	Y	Mode	Length	Major	Minor
1	0.03	93.66	7.94	5.16	6.66	103	0.78	0.25	0.16
2	0.02	100.89	3.03	6.44	6.16	103	0.94	0.35	0.06
3	0.01	98.31	4.82	3.66	5.30	103	0.57	0.22	0.07
4	0.03	92.77	9.33	5.88	4.30	100	0.73	0.21	0.16
5	0.03	89.39	10.36	7.10	3.70	93	0.74	0.24	0.16
6	0.02	98.22	4.18	7.12	3.42	98	0.63	0.19	0.13
7	0.02	94.83	5.55	5.82	2.66	89	0.61	0.19	0.15

Figure 2.48 - AFM image of 4 damage sites on mica.

Figure 2.49 - AFM image of 7 damage sites on mica.

2.5. SYSTEM DEMONSTRATIONS

2.5.1. Micro-diamond tags

As was the case for automatic feature recognition and analysis, since we did not have a single application, the development of a complete system for deployment, recovery, and analysis of tags was not appropriate for this project.

We did, however, carry through some basic exercises on tag deployment and recovery, using two materials that are good candidates for actual applications. Microcrystals of diamond, individually grown and separated into 6 size classes (nominally 1, 5, 10, 25, 50, 100 μm), [Figure 2.50](#) shows SEM images of two samples of mixtures of different tag sizes.

A total of 36 identical samples of the powder, each 1 cc, were uniquely labeled by addition of varying amounts of the tag mixtures. Approximately 10^4 were used, amounting to 10^{-6} of the sample weight. Six samples were randomly selected and the tags were recovered using standard microtechniques and image with the SEM. Analysis of the images enabled correct identification of the samples by the tag size distributions.

Figure 2.50 - SEM images of two samples of mixtures of diamond tags.

2.5.2. Mica tags

This experiment was designed to demonstrate production of many tags with the same ion-induced bit pattern. If the ions penetrate deeply into a layered material such as mica, the same geometrical pattern of damage sites is produced in all layers. Subsequent delamination and track decoration with etching would produce a large number of tags with identical bit pattern. Approximately 10^3 - 10^5 tags could be produced with dimensions of 10-100 mm².

Figure 4.6 (Sec. 4.1.3.6) shows a schematic of this process.

We carried out a partial demonstration of this process. Uranium-free muscovite was used as the tag material. Uranium-free muscovite is desired because any nuclear tracks due to the presence of uranium in the muscovite will contaminate the bit pattern during the etching process. Alternatively, annealing of mica substrates prior to bit pattern exposure will erase any previous nuclear tracks. In addition, micaceous minerals with a high capacity for swelling, such as vermiculite, may delaminate easily in solution with the application of heat.

The bit pattern was produced using Xe⁺⁴⁴ ions. Techniques for ion track etching in micas are well established. The ion source and energy was picked to give a range greater than 1 mm in mica. Samples were damaged in a random or oriented pattern depending on the ion source. Density of damage sites was kept low (3-4% damage site coverage) to avoid exfoliation of the mica substrate.

A YAG laser was used to cut 10 mm x 10 mm squares from a 1 mm thick exposed substrate, resulting in a 1 mm long layered structure consisting of approx. 10^6 layers. Heat generated during cutting was a potential problem, resulting in exfoliation of the mica.

A combination of heat and ultrasound can be used to cause the 1 mm long layered tag structure to delaminate, resulting in 10^3 - 10^5 individual tags.

A quick etch in dilute HF acid will produce holes at ion damage sites. Some experimentation will be needed to control the hole size and reduce damage to the substrate. A stop bath and washing completed fabrication of the tags.

The tags were mixed with diamond powder substance to simulate actual deployment of tags in a hostile environment.

Electrostatic collection can be used to separate the mica tags from the diamond dust. They can be transferred to a microscope slide substrate with alcohol. The tags can be imaged with optical microscopy (1 mm resolution limit). After etching, the bit pattern can be easily read with the AFM,

3. PHYSICAL MODELS

We provide here a limited discussion of models that have been developed to account for some of the experimental observations. These models are not comprehensive; they are more preliminary explanations of our observations.

3.1. GENERAL PHYSICAL MODEL

The interaction of low-kinetic-energy, high-charge-state ions with condensed matter is currently a subject of intense study. It is becoming clear that the dominating parameters in an ion/solid interaction of this type are the ion velocity, its total potential energy, and to some degree (and less well understood), the electron distribution and mobility in the solid. The process is envisioned roughly as follows: As the ion approaches the surface, it polarizes the solid and begins to extract electrons by field emission. Some electrons are captured into high-lying bound states of the ion, some of which are re-emitted by Auger processes. To the extent that this process is fast compared with the resupply of electrons from the bulk, the surface is locally depleted of electrons and atomic displacements ("lattice damage") may occur. As the ion enters the solid, its electron shell is stripped away and it undergoes a series of fast collisions that neutralize and stop it. If the ion's projected range is small (i.e., low initial kinetic energy), all its energy, both kinetic and potential, will be deposited very near the surface. Any resultant damage will be confined to the near surface.

This picture is quite different from processes, such as sputtering or implantation, that occur when the kinetic energy of the ion is high (high KE), but its charge state is low (low Q). In that case, the ions penetrate into the solid, quickly establish an equilibrium charge state, and generate a collision cascade or damage track. Important parameters for this type of interaction are the angle of incidence, the masses of the collision partners, and the binding energy of the lattice atoms. There is a considerable literature on the surface expression of solid damage by such ions. Many effects can occur, such as changes in surface composition or formation of unusual surface structures (e.g., crater or cone formation). Recently, Tsong and co-workers observed craters on Si and PbS surfaces resulting from single ion impacts of Ge⁺, As⁺, and Kr⁺ at incident energies ranging from 8 keV to 1 MeV.

Thus, we have contrasting images of the two cases: Ions of high KE and low Q act as ion "bullets," penetrating deeply and doing damage by transferring momentum to lattice atoms along a relatively long track. Ions of low KE and high Q are expected to act more like ion "bombs," carrying internal energy that is released in an explosion at the surface.

3.2. COULOMB ENERGY

Most of the experiments described in this work used Xenon ions of charge state $Q=44$. The total potential energy of these ions is about 50 keV (Schmieder, 1990). Adding the kinetic energy (0.1-7 keV/ Q), the range of total energy available for deposition in the solid is about 55 keV (95% potential energy) - 360 keV (16% potential) from a single ion. Clearly this is enough to imply that permanent violent damage to the solid is inevitable, and furthermore, that the dynamics is almost certain to be strongly dependent, or driven by, the potential energy.

Except for the last stages of ionization, the coulomb Potential energy W_Q varies systematically with atomic number Z and ion charge Q . A semi-empirical formula for W_Q was developed by one of the authors (RWS):

$$W_Q \equiv Q^b \quad b = 3 - \frac{Z}{400} + \frac{1}{5} \left(\frac{2Q}{Z} - 1 \right)^2$$

Figure 3.1 shows a plot of this function for $Z=54$ and $Q=28-46$.

R. W. Schmieder, *Rev. Sci. Inst.* **61**, 1101 (1990).

Figure 3.1 - The total Coulomb energy of a Xe ion of charge Q , according to the semi-empirical formula given in the text.

3.3. LATTICE DAMAGE

The damage of the solid lattice by an incident ion is indicated by the amount of energy per atom deposited in the target. We have used the TRIM code, a widely-used tool for modeling ion penetration into solids, to calculate this quantity for various cases of interest to this work.

Figure 3.2 shows a typical case, Xe^{+44} incident on a plastic. As the ion kinetic energy increases, the deposited energy decreases. At the lowest energies used in this work, 0.1 keV/Q, the damage is about 20 eV/atom, far greater than the threshold for lattice damage. Clearly, these ions have the capacity for total disruption of the solid lattice. The subsequent rearrangement of the solid will almost certainly leave a scar. The region should be amorphous, and it probably will have lower density than the undisturbed solid. In other words, we expect a permanent defect that could be chemically different from the undisturbed solid.

Figure 3.2 - Average energy per carbon lattice atom deposited by a Xe^{+44} ion carrying both kinetic and potential energy in the half-ellipsoid volume determined by its range and lateral spread. At low kinetic energies, the deposited energy per atom throughout the volume greatly exceeds the sputter threshold.

3.4. ION RANGE IN SOLIDS

We have also used the TRIM code to calculate the ranges of ions in various solids. These calculations do not account for any possible charge state-dependence of the range. Figure 3.3 shows a typical result for Xe ions in CR-39 plastic. The range for ions used in this work is about 100 nm. Since the depth of the damage we observed in the experiments is considerably less than this, there apparently is some process that is either healing the damage or masking it from the AFM.

Figure 3.3 - Range of Xe at normal incidence in CR-39 plastic.

We also carried out calculations that predict that the ranges of high charge state ions will be significantly smaller than the same singly charged ion. The general picture of the implantation is as follows: As the ion approaches the solid, it undergoes a partial neutralization. So long as its velocity is not too low, it enters the solid with a substantial fraction of its initial charge. In the solid, the ion loses energy by collisions in which the atomic core feels the repulsive potential of the electrons in the solid. For ions of some 10's keV, the range is about 1 nm/keV.

We predict a charge-dependent range by the following reasoning: The collisional cross section, and therefore the ion energy loss rate (stopping power), will depend on the atomic configuration of the ion. We would expect an ion with many of its electrons in high-lying states to lose energy faster than the same ion in its ground state, principally because of the better match of electron velocities. Now, as the high-charge state ion enters the solid, it captures electrons principally into high-lying states. Thus, we would expect the ion to lose energy faster and stop shorter, due to the hollow atomic configuration.

The TRIM code contains a screening parameter that could reasonably simulate the effect of the hollow atom. We made calculations for Cs ions of energy 5 and 50 keV incident on Beryllium. For each case, the screening constant was taken as the code default value, which presumably therefore represents singly charged incident ions. Then we doubled the screening range (i.e., halved the amount of screening), to simulate the hollow atom. This factor of 2 was suggested by the author of the TRIM code, J. Biersack.

The results of the calculations are listed in Table 3.1. The energies listed are kinetic energy only. The code assumes that both charge state ions have the same velocity.

Table 3.1 - Predicted ranges of ions in Be

ion energy (keV)	Range in nm Be	
	low charge state Cs ions	high charge state Cs ions
5	7.7	1.2
50	36.3	13.5

3.5. CRATERING

3.5.1. Scaling law

At low incident ion velocities, the ion has sufficient time to extract electrons from the surface and become partially neutralized, re-emitting a fraction of the electrons as free Auger electrons. If the solid is an insulator, the local loss of electrons is uncompensated, and the surface becomes electrically charged, providing a repelling force on the incident ion and slowing it. In this approximation, all the ion kinetic energy is lost as the solid does work on it, but most of the potential energy will be dissipated when the ion actually arrives at the surface. The impact event thus resembles an explosion on a solid surface, a process with which we associate crater formation in macroscopic systems.

Crater formation is observed over an extremely large size range, from planetary impacts producing craters hundreds of km in diameter, to bullets producing craters of cm size, to cosmic dust impacts producing micro-craters 0.1 micron in diameter (Melosh, 1989). A remarkable observation is that the relationship between a few crucial descriptive parameters is sufficiently simple that several scaling laws are valid over essentially the entire range. The most important of these is

$$D \propto W^{1/3}$$

which relates the crater diameter D to the deposited energy W . The basis for this relation is the assumption that an impact produces first deposits the energy locally, and the material subsequently explodes.

We now ask whether this scaling law could be pushed all the way to the atomic limit: What size crater might we expect for a single ion "bomb" carrying, say, 50 keV? Meteor Crater in Arizona is about 1 km (10^{12} nm) in diameter and resulted from an initial impact-explosion energy of about 5×10^{16} J, or about 10^{34} keV. Scaling this to 50 keV, we predict

$$D(\text{ion crater}) = 10^{12} (50/10^{34})^{1/3} = 17 \text{ nm}.$$

This surely represents an upper limit, but even so, it is surprisingly consistent with our observed defect sizes (ca. 30 nm).

The application of a scaling law such as this is risky, of course, since the physical mechanism of fragmentation of the substrate is different, and the mechanism of retention of the ejecta is different. However, we do suggest that in analogy with the gravitational retention of ejecta in planetary cratering, the retention of atomic ejecta by intermolecular and possibly ionic forces also leaves most of the ejected mass on the substrate (just repositioned around the damage site). Thus, the "crater" diameter is properly described as the diameter of the damage, whether or not mass is left or redeposited in the site after the event.

3.5.2. Coulomb explosion sputtering

The energy source of the explosion that occurs on ion impact is the coulomb potential energy of the ion. The system is extremely far from any equilibrium configuration; it is the redistribution of this energy among many particles and degrees of freedom that produces the explosion. To the extent that the disturbed material is not electrically neutral, the coulomb force provides a very strong drive for ion and electron motion. Thus, the concept of "coulomb explosion" is natural. The possible existence of this phenomenon was recognized as early as the 1950's [Varley, 1954]. It has been recounted and reviewed many times [R. L. Fleisher, P. B. Price, and R. M. Walker, 1965]. In spite of its general acceptance, it was not clearly identified until the early 1990's.

It is generally assumed that four conditions are necessary for coulomb explosion to occur:

1. The local electrostatic stress must exceed the local mechanical strength. This is simply represented as the inequality

$$(1/4\pi\epsilon)(Ze/d)^2 > Y/10$$

where Y =Young's modulus. This relationship suggests that damage will occur in most dielectrics, semiconductors, and metals.

2. The free electron supply from the solid must be low. We can represent this as

$$\pi^2 d N_e < n_d$$

where n_d = # ionizations per atomic plane, r =diffusion length of electrons in the time (ca 10^{-13} s) before the ions fly apart. This relation excludes damage in metals, which is apparently correct: metals are not damaged, at least by singly charged ions.

3. The hole mobility in the solid must be small. This also predicts that metals will not be damaged.

4. The event must occur near a free surface if sputtering to occur. This requires that the kinetic energy of the incident ion must be sufficiently low that the range in the solid is small.

Until recently, the best evidence for coulomb explosion was the damage track left behind high energy ions as they penetrated deeply into the solid. These tracks were predicted and observed to have diameters ranging between 1 and 10 nm, depending on the conditions and the method of observation (electron microscopy and xray scattering provide different images).

The reason the surface explosion was not observed was that the impact of high energy low charge state ions do not produce sufficiently high local energy density. Only with the relatively recent development of sources of low energy, high charge state ions from sources such as the EBIS are we in a position to observe surface coulomb explosion, and not surprisingly, it was observed relatively soon after the sources became available.

The most extensive theoretical development of coulomb explosion has been by Parilis and co-workers [Bitensky and Parilis, 1989 and other references]. These authors have carried out detailed analysis of sputtering on non-metals by high charge state ions, and obtain the result that the sputtering yield can be very high (up to 100). Recent experiments have observed results consistent with these predictions.

These authors also proposed bombarding thick biomolecular layers to see if the intact biomolecules are desorbed or if the layer is fragmented. No experiments are yet reported on this prediction. These models are very relevant to the present work, in which we have proposed and examined ultrathin organic films (LB and SAM films) as a path to replication and pattern transfer.

Additional calculations of importance were done by Yamamura, Nakagawa, and Tarawa [preprint, 1994]. These authors used a combination of binary collisions and coulomb-driven molecular dynamics to follow the evolution of the impact of Xe^{+Q} ions on diamond, which is a prime candidate for micromechanical tags. These authors find that the sputtering yield of Xe^{+44} is 10 times that for Xe^{+1} . They were able to identify the sequence of high-lying bound states of Xe ions in which extracted electrons were captured, providing a detailed description of the extraction of electrons from the surface. These results are relevant to the present work when we attempt to account for the delamination of mica by electrostatic forces created by electron extraction.

J. H. O. Varley, *Nature* 174, 886 (1954).

R. L. Fleisher, P. B. Price, and R. M. Walker, *J. Appl. Phys.* 36, 3645 (1965).

I. S. Bitensky and E. S. Parilis, the sputtering of non-metals under slow multiply charged ions, *J. de Physique* 50, C2-227 (1989).

I. Bitensky, E. Parilis, S. Dell-Negra, and Y. Le Beyec, Emission of hydrogen ions under multiply charged ion bombardment, *Nucl. Inst. Meth.* B72, 380 (1992).

Y. Yamamura, S. T. Nakagawa, and H. Tarawa, Preprint [1994].

3.6. BLISTERING

It was natural to expect sputtering processes to produce craters in ion damaged materials. The appearance of convex features, "or blisters," was at first surprising, but in retrospect appears within the context of a large literature on closely related phenomena. There are many reviews of this subject, such as [Heiland, 1992]. The literature is almost uniformly concerned with singly charged ions, typically in the range 100 eV-10 keV. The models generally are built on single collision dynamics, and neglect electrostatic interactions.

Early models of blister formation (Mattern, Shelby, Thomas, and Bauer, 1976) envisioned a subsurface pocket of gas 10-1000Å in diameter produced by accumulation of implanted gas atoms. Presumably, expansion of the gas produces the blister by enlarging an initial defect into the void covered by a lid ("deckeldicke"). This process, however, cannot account for the well-defined size and shape of the blisters: it leads instead to exfoliation and ultimate rupture with release of the gas. Risch, Roth, and Scherzer [1977] have extended this gas-driven model to include the stress in the elastically distorted solid. Expansion of the blister halts at the transition from elastic to plastic strain. This model predicts a well-defined blister diameter and profile that is in broad agreement with experiment. In particular, they predict the observation that the deckeldicke thickness t is correlated with the blister diameter as $D \propto t^{3/2}$. This gas-driven blistering mechanism requires the deposition of a relatively large number of incident ions to form the gas pocket. It therefore cannot account for the blisters observed in this work, which are due to the impact of a single highly charged ion.

W. Heiland, The interaction of slow ions with surfaces, *Solid State Phenomena* 27, 107 (1992).

M. Risch, J. Roth, and B. M.U. Scherzer, Semiempirical theory of the dependence of blistering and exfoliation on radiation swelling and gas pressure, in: *Plasma Wall Interaction*, Pergamon Press, Oxford (1977).

3.6.1. Electrostatic delamination blistering

One of the present authors [EP] has examined the data from the present experiments on mica and adapted the model of coulomb explosion to provide a reasonable explanation of the blistering process. Figure 3.4 shows a diagram of this process. The incident ion extracts electrons from the surface, leaving the local region highly (positively) charged. The electrostatic stress exceeds the binding between mica layers, and they separate slightly, while maintaining integrity of the layer. The upper layer (deckeldicke) is elevated slightly less than the layer thickness, and appears as a low-profile blister.

Parilis applied this model to the conditions of the experiments on mica. His development is presented in the remaining sections of 3.6.1.

Figure 3.4 - Schematic of the electrostatic delamination process. (above) ion induced field emission; (below) electrostatic repulsion blistering.

3.6.1.1. Introduction

The investigation of sputtering and secondary ion emission under multiply charged ion bombardment has a relatively short history compared with the efforts spent to study sputtering by singly charged ions. In the first publications [1,2] some multiply charged ions with charge not exceeding +7 were used. Only with the development of new techniques did highly charged ions become available, and modeling of related processes become important [3].

The theory is based on the mechanism of Coulomb explosion of a domain on a non metal surface positively charged during step-by-step Auger neutralization of the multiply charged ion [4,1].

The goal of this work is to develop and apply a simple theoretical model to describe the surface damage produced by highly charged ion impact on an insulating, atomically flat surface of single nonisotropic mica crystal.

3.6.1.2. Summary of experimental results

The research is based on experimental findings by a joint group at Sandia National Laboratories, (Livermore) and Kansas State University (Manhattan). Nanometer-size shallow craters and blisters on mica surfaces exposed to slow highly charged Xe ions were observed.

The experimental data is:

Ions:	Xe ⁺⁴⁴
Energy:	E ₀ = 0.1-20 keV per Q
Ion flux:	I = 10 ⁷ ions/cm ² -s
Ion fluence:	F = 1-4x10 ¹⁰ ions/cm ²
Incidence:	normal
Crater or blister dia.:	D = 20 nm
Depth or height:	h = 0.3 nm
Crater or blister volume:	V = 40 nm ³
Number of atoms emitted or displaced:	N = 100-200
Dependence on ion kinetic energy:	D, h relatively insensitive to E ₀

Some relevant properties of Muscovite mica:

Composition:	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂
Structure:	pseudohexagonal alumino-oxygen-silicate layers formed by double (Si ₂) ₅ tetragonal structures in which one Si ion is replaced by Al ion, the layers being connected by Al(OH) ₃ forming negatively charged sheets with positively charged potassium ions between.
Atomic density:	δ=4 atoms/nm ³
elasticity of elongation:	μ=22,133 kg/mm ²
electrical resistance:	ρ=10 ¹⁵ - 2x10 ¹⁷ Ω-cm
breakdown strength:	F _b =300-400 kV/mm = 0.3-0.4 V/nm
work function:	φ=4 eV

The main conclusion made by the authors of the experiments [6] is that the shallow circular blister-like and crater-like features on mica produced by single slowly moving highly charged ions are due to local lattice disorder and layer deformation caused by local charge depletion.

3.6.1.3. The basic model for the damage sites

All the geometry of the phenomenon (the very thin pancake shape of the features, $h/D=0.015$, with the thickness of the damaged layer $h=0.3$ nm being comparable with the distance between mica atomic layers), leaves no doubt that the damage comes from outside the surface, rather than from the ion track within the solid. There are no secondary agents (electrons, recoil atom cascades, shock waves, etc.) connected to the nuclear or electron stopping power in solids that could be responsible for such a geometry.

In the meantime, for $Q=+44$, the electric field of the highly charged ion $F=Qe/x^2$ becomes equal to the electric breakdown strength of the best muscovite mica F_b at a distance $x=12$ nm from the surface, a length that gives an immediate estimate for the radius of the damaged spot. This is indeed found to be $D/2=10$ nm, in agreement with observations. The distance $x_f(Q) = Qe/\phi = 13.2$ nm at which the potential barrier for Fermi electrons disappears [7] is of the same order of magnitude.

The time $t=(2E_0/m)^{-1/2} x = 1.2 \times 10^{-14} - 1.5 \times 10^{-13}$ s that the ion needs to cover this distance is large enough to develop an avalanche-type breakdown in the upper layer of the solid, releasing free electrons to participate in Auger neutralization and leaving a charge depleted layer that screens deeper layers from the ion electric field. The electrons with typical energy $E_e = 5-10$ eV moving toward the ion cover this distance approximately $(mE_e/m_e E_0)^{1/2} = 1.2-7.8$ times faster than the ion does. The current density is $j = 4(Q+\gamma)e/t\pi D^2 = 2 \times 10^8$ A/cm² for secondary electron emission equal to $\gamma = 100$ electrons/ion. The Auger neutralization of the 18 upper O vacancies in Xe^{+44} releasing just 2-3 keV of the total amount of 50 keV neutralization energy, is quite enough to provide the observed surface damage and secondary electron emission.

The typical time τ for Auger neutralization by capturing electrons direct from the solid (S) into the vacant xenon shells via O-SS Auger transitions or by prior filling the upper, including Rydberg, ion states with subsequent autoionization of the hollow atom is $t = 10^{-15} - 10^{-14}$ s. Thus, $\tau < t$. Filling the remaining inner M and N vacancies is accompanied by emission of high energy Auger electrons and (with the fluorescent yield $> 50\%$) photons during $\tau = 2 \times 10^{-13}$ s $> t$, i.e., inside the solid. They add nothing, or very little, toward creation of the surface damage structures under discussion.

Therefore the estimates show that all the events described above are likely to be accomplished before the ion hits the surface. The experimental findings of the velocity independence of the damage site dimensions within the velocity range $v=8 \times 10^6 - 1 \times 10^8$ cm/s [6] is the most convincing evidence of this fact.

Of course, the ordinary sputtering of a solid due to development of collision cascades under heavy atom bombardment, known to increase with projectile energy, does contribute toward the creation of the damage sites, but the sputtering coefficients, typical for this energy [8] equal to $S=1-10$ atoms/ion, i.e., correspond to the amount of matter sputtered which is just about 1-10% of the damaged volume. This quantity, which is within the error bars on the experimental plots [6], cannot determine the energy dependence of the phenomenon.

The main source of the surface damage is the ion neutralization energy W_Q , equal to the sum of the ionization energies of the highly charged ion

$$W_Q = \sum_{i=1, Q} W_i$$

which is released in a series of step-by-step Auger neutralization processes and shared among the Coulomb repulsion energy W_c of a surface charged domain containing N_Q positive charges, appeared after double ionization of N_Q anions, emission of $(N_Q - Q)$ secondary electrons, and $N_{a,p}$ energetic Auger electron and photons. The relevant energy balance equation is

$$W_Q - Q\phi = W_c + (N_Q - Q) E_e + N_Q I_2 + N_{a,p}$$

For an extremely flat disk with diameter D and thickness $h \ll D$ containing N_Q positive charges,

$$W_c = 4 N_Q^2 e^2 (h - h_0) / \pi D^2$$

This formula reflects the nonuniform distribution of the charges due to specific anisotropic structure of the mica surface layers. After stripping electrons first from the anions and neutral atoms, the energy I_2 being spent to create cations K^+ in between will be created to form a 3-layer charged structure. The initial distance between anion and cation layers is h_0 . The Coulomb repulsion in this structure would cause a blister, if the dome will maintain its integrity, or a crater, if it will be fragmented.

In the earlier investigations [4,5,9], the number of electrons N_Q stripped from the atoms of the surface layers in partial outside-the-surface Auger neutralization of a Q -charged ion, was believed to be proportional to $W_Q \sim Q^2$. This assumption, based on a model of step-by-step Auger neutralization with energy steps equal to 15-25 eV gives for Xe^{+44} the numbers $N_Q = 2000-3000$. The corresponding secondary electron emission should be equal to $\gamma = k(N_Q - Q) = 600-1000$ electrons/ion. Actually, the model works only up to $Q=10-20$. For higher charges the dependence $N_Q(W_Q)$ is nonlinear due to emission of energetic Auger electrons. The emission $g = 70-90$ has been found for Xe^{+30} and Xe^{+44} on Cu and Au [10]. This corresponds to $(N_Q - Q) E_e = 2000-3000$ eV and $N_Q = 200-300$. This amount relates to the slow electrons emitted from the surface. The delayed high energy Auger electrons emitted inside the solid carry away a major part of the total W_Q and spend some of it in processes in the bulk. Yet there is no clear experimental evidence of the energetic Auger electrons outside the surface. Some simultaneous measurement of secondary electron emission and surface damage under highly charged ion bombardment would be very useful.

Returning to the energy balance, we can use the value $N_Q = 250$ to estimate W_c . If the final thickness of the damaged site h exceeds the initial distance between charged anion and cation layers h_0 by a factor of 2, i.e., $h_0 = a h$ with $a = 1/2$, then we get

$$W_c = 40.6 \text{ eV}.$$

Even if we would take into account the pre-existing charge of the K^+ cations to get $W_c = 160$ eV, still this amount of energy will remain a very small part of the total neutralization energy $W_Q = 50$ keV. Nevertheless, it is enough to provide the elastic deformation of both the upper and lower layers after the binding forces between cations and former anions will disappear due to stripping of electrons. Figure 3.5 shows a schematic of this process.

Figure 3.5 - Electrostatic delamination in mica due to Coulomb repulsion resulting from the impact of a high charge state ion.

This deformation consisting of a 10^{-4} increase of the area of the layer bent to form a dome needs in Muscovite mica just an amount of energy equal to 21 eV. No bonds need to be broken for the dome to be completely formed. Fragmentation of a dome, once formed, could be associated with point defects in the upper layer.

3.6.1.4. Charge dependence of the damage sites

Experiments at LLNL under similar conditions appear to show a linear dependence of the blister volume on total ionization energy W_Q . However, this does not mean that the total ionization energy (up to 180 keV for Th^{+74}) is spent to create the blisters. The blisters have volume $V = 200\text{--}800 \text{ nm}^3$, containing $N=800\text{--}2400$ atoms. If the entire energy W_Q were deposited in the solid, the hot domain would have energy density about 75 eV/atom.

Actually, the main part of W_Q is carried out by the high energy Auger electrons, or is deposited in bulk. The proportionality $V \sim W_Q$ is a manifestation that the electron capture in just the upper levels of the ion does play a role in the formation of blisters.

One can see from the distance $x_f(Q) = Qe/f = 13.2 \text{ nm}$ at which the potential barrier for Fermi electrons disappears is of the same order of magnitude as the blister radius $D/2 = 10 \text{ nm}$. If we take $D/2 = x_f(Q) \sim Q$, the damaged area $\pi D^2/4 \sim Q^2$. This gives an estimate of the charge dependence of the blister volume because the thickness is the same for all blisters: 1-2 atomic layers.

3.6.1.5. Conclusion

A model based on partial Auger neutralization of a highly charged ion outside the surface of mica crystal with consequent positive charge deposition in surface layers and their expansion due to Coulomb repulsion gives a reasonable explanation of the shallow features observed in the experiment using Xe^{+44} ions on mica. A more complete description of the process needs a more detailed knowledge of the mica crystal structure and ionization energies of the anions and cations in the solid as well as the elastic deformation constants and binding energies of the bonds.

3.6.1.6. References

- [1] U. A. Arifov, et al., *Izv. AN SSSR, ser. fiz.* 40, 2621 (1976).
- [2] S. T. De Zwart, et al., *Surf. Sci.* 177, L939 (1986).
- [3] R. W. Schmieder and R. J. Bastasz, *Nucl. Inst. Meth.* B43, 318 (1989).
- [4] E. S. Parillis, *Proc. IX Intern. Conf. Phenom. Ionized Gases.*, Bucharest, 1969, p. 94.
- [5] I. S. Bitensky and E. S. Parillis, *J. de Physique*, Coll. 2, suppl. 2, t. 50 (1989).
- [6] D. C. Parks, et al., *JVST paper*
- [7] P. Appel, *Nucl. Inst. Meth.* B23, 242 (1987).
- [8] R. Berish, ed., *Sputtering by particle bombardment I and II*, Topics in Applied Physics 52 (1983) and 57 (1981), Springer-Verlag, Berlin.
- [9] M. Delaunay, M. Fehrer, R. Geller, D. Hitz, P. Varga, and H. Winter, *Phys. Rev.* B35, 4232 (1987).
- [10] J. W. McDonald, et al., *Phys. Rev. Lett.* 68, 2297 (1992).

3.6.2. Plasma vapor-driven Blistering

The electrostatic delamination model of Parilis requires the solid to be a weakly bonded layered material. The gas-driven blistering model of Risch, Roth, and Scherzer [1977] makes no such assumption, but it does assume the gas to be cold and electrically neutral, and also that many incident ions would collect to form a gas pocket that expands to form the blister. One of the present authors (RWS) has proposed a modification of the RRS model that predicts single-ion blistering in nonlayered materials. We refer to this model as plasma/vapor-driven blistering.

3.6.2.1. Erasure as evidence for a void

A significant aspect of the present experiments is that the defect structures produced by single ions appear to be metastable: they persist for long periods (months) when undisturbed, but if stimulated, they apparently collapse and disappear. We visualize these structures as highly strained, plastically deformed, and containing at most a few hundred atoms. A simple image is that the site is a raised dome enclosing a void. The molecular bonds within the dome are strained; in the absence of a restraint, the dome would simply snap back to the flat surface. However, as the dome is raised, the material near the surface at the edge of the dome suffers plastic shear, and is unable to spread back radially when the pressure in the void disappears. The dome is thus left in a weakly stable configuration. Subsequent application of the AFM tip imposes a force on the dome, which is transferred to the metastable sheared region, reversing (at least partially) the shear, allowing the dome to collapse. This picture is also consistent with the observation that the site is erased in several incremental steps: each step provides an impulse sufficient for partial reverse shear.

3.6.2.2. Formation of the blister

We envision the process as occurring in two steps: First, the ion is implanted in the solid, carrying with it a significant fraction of its original coulomb potential energy, plus its kinetic energy. Dissipation of the total energy causes complete local subsurface vaporization of the solid and ionization of the atomic vapor. This collisionally-dominated mica plasma "blob" has nearly stoichiometric amounts of Si, O, Al, K, and possibly other species. Since the ions of higher kinetic energy enter the solid almost intact and are completely stopped in the solid within a distance of the order of 100 nm, all this energy is released within a cylindrical volume of about 100-1000 nm³, implying an energy density of the order of 1 keV/nm³. This is quite sufficient to completely dissociate and ionize the solid, producing a plasma with temperature of the order of perhaps 10 eV. To the extent that this process is fast compared to the rate of thermal diffusion in the mica, the blob will be isothermal. The plasma blob corresponds to the high-pressure gas pocket of the RRS model.

Second, the plasma blob expands, creating the blister. As the plasma cools, it is neutralized to become a hot vapor. Further expansion of this neutral vapor enlarges the blister, and this process is slowed by stress accumulating in the deckeldicke. When the vapor cools sufficiently, it suddenly condenses into a liquid or solid, and the vapor pressure suddenly drops to essentially zero. The blister is left in a highly stressed shape, and it may quickly relax to a less extended shape. Further cooling freezes the blister into a configuration that is stable at least over the period of observation, i.e., months, but which, with additional stimulation, might be induced to relax further.

3.6.2.3. Semiquantitative model of blisters

To quantify these ideas, we refer to the idealized diagram of a blister, Figure 3.6(a).

From RRS, the profile of the blister as a function of gas pressure is described by the deflection d of the deckeldicke as a function of radial distance r from the blister axis and other parameters:

$$y(r) = \frac{p}{S} \left\{ \frac{d^2 [J_0(kr/d) - J_0(k)]}{2kJ_1(k)} - \frac{(d^2 - r^2)}{4} \right\}$$

where J_0 and J_1 are Bessel functions, p is the vapor pressure, S is the stress in the deckeldicke, and

$$k = \sqrt{\frac{12Sd^2}{Et^3}},$$

where E is the elastic modulus. The deflection at $r=0$ (i.e., the blister height) is therefore

$$y(0) = \frac{pd^2}{2S} \left\{ \frac{[1 - J_0(k)]}{kJ_1(k)} - \frac{1}{4} \right\}$$

The normalized function $(2S/pd^2) y(0)$ is plotted in Figure 3.6(b). The model predicts that the blister will only be observable (i.e., $y(0)/d \approx 1$) when k is near 3.0, and that it will rupture when $k \geq 3.83171$. If we use the following values: $E=10^{11}$ N/m²; $k=3$; $d=5 \times 10^{-9}$ m; $t=10^{-9}$ m, we obtain from the equation for k the value for the stress, $S=3$ N/m. If we assume $y(0)/d=0.1$ then we obtain the pressure $p=4 \times 10^7$ N/m². This should be interpreted as the pressure of the vapor just prior to condensation.

The ratio p/S is related to the energy deposited by the ion E_0 . If we estimate the gas-dynamic work done on the deckeldicke as $W = (1/2) p V$, where V is the volume of the cavity, we obtain $W \sim 10^{-18-19}$ J, or about 1-10 eV. Since the incident ion carries about 10^4 eV, there is the weak suggestion in these rough numbers that the process of formation of the blisters is energy inefficient, i.e., most of the energy is being dissipated, rather than producing plastic deformation of the solid.

Figure 3.6 - Idealized diagram of a delaminate blister (a) the coordinate system; (b) the normalized function $y(0)$ for the blister profile.

3.6.2.4. Molecular granularity and metastability

While the classical bulk model of plastic deformation is consistent with the observations, in reality the damage sites have molecular granularity, and their dynamics probably resembles more the jerky, irregular motion of a pile of sticky balls held together by springs. We would expect the structure to contain some relatively weak parts that distort easily, while other parts resemble micro-clusters that remain relatively intact even during collapse. The image here is more like the collapse of an automobile being crushed in a compactor. Molecular simulations have, in fact, produced this kind of behavior: Muller [1989] presents diagrams of a bridge containing about 80 Ni atoms that is stimulated to almost complete catastrophic collapse by the impact of a single atom. We reproduce one of their diagrams in Figure 3.7. The bridge structure was metastable; after a relatively small stimulus, the dynamics was driven by purely intermolecular forces.

Figure 3.7 - Collapse of a metastable atom bridge due to ion impact. It is proposed that the blisters observed in mica are similar metastable structures that collapse when pressed by the AFM.

Molecular dynamics calculations by Ghaly and Averbach [1994], also give a more detailed picture of the process in the case of 10 and 20 keV Au ions impacting on Au. As shown in Figure 3.8, damage was due to viscous melting and flow. The damage was confined to a 6 nm diameter region. Evidently a raised blister somewhat shallower than 1 nm is left, consistent with the sizes of features seen in our experiments. Note that the damage in this metal is not predicted by the simple classic requirements listed above. We expect that careful AFM studies of any ion-irradiated material, including metals, will show evidence of damage, usually in the form of a blister.

- W. Heiland, The interaction of slow ions with surfaces, *Solid State Phenomena* 27, 107 (1992).
P. L. Mattern, J. E. Shelby, G. J. Thomas, and W. Bauer, *J. Nucl. Matls* 63, 317 (1976).
H. J. Melosh, *Impact Cratering: A Geologic Process*, Oxford University Press, New York, 1989.
K-H. Muller, Film growth modification by concurrent ion bombardment: Theory and simulation, in: J. J. Cuomo, S. M. Rossmagel, and H. R. Kaufman, *Handbook of Ion Beam Processing Technology*, Noyes Publications, Park Ridge, NJ (1989).
M. Risch, J. Roth, and B. M.U. Scherzer, Semiempirical theory of the dependence of blistering and exfoliation on radiation swelling and gas pressure, in: *Plasma Wall Interaction*, Pergamon Press, Oxford (1977).
J. Roth, Physical Sputtering of Solids at Ion Bombardment, in: *Physics of Plasma-Wall Interactions in Controlled Fusion*, D. E. Post and R. Behrisch, eds, Plenum Press, New York (1986).
M. Ghaly and R. S. Averbach, Effect of viscous flow on ion damage near solid surfaces, *Phys. Rev. Lett.* 72(3), 364 (1994).

Figure 3.8 - Damage due to ion impact, showing a low blister in the final state due to amorphotization of the solid. From Ghaly and Averbach [1994].

4. NANOTAG TECHNOLOGY

Micromechanical tag technology generally will involve the following steps:

- Fabrication
- Deployment
- Recovery
- Reading

In this section, we review these aspects and present the results of our investigation into available materials and processes that will be useful.

4.1. TAG FABRICATION

4.1.1. Ions

The ions used in this work have very low kinetic energy but high charge state. Production of such ions requires a special source, and there are only a few such sources in the world. These sources work by trapping the ions in an electrostatic trap, and subjecting them to prolonged intense irradiation by a high density electron beam. Naturally enough, the sources are called Electron Beam Ion Sources (EBIS).

There are several reviews available on the EBIS. There are about 10 working machines worldwide. The development of the technology described in this work would likely stimulate the development of more machines of lower cost.

Two EBISs were developed at Sandia California. The first was originally built at the Lawrence Berkeley Laboratory, and was moved to Livermore and extensively rebuilt. The second was a state-of-the-art machine designed to produce large numbers of Xe^{+44} and higher ions. This machine was shut down just as it reached completion. The publications produced from that program fairly indicate the nature of these sources and their involved technology.

"The Sandia EBIS Program" R. W. Schmieder, C. L. Bisson, S. Haney, N. Toly, A. R. Van Hook, and J. Weeks, *AIP Conf. Particles and Fields* 38, 45 (1988).

"Physics of the EBIS and its Ions." R. W. Schmieder, chapter in: *Physics of Highly Ionized Atoms*, R. Marrus, Ed., (Plenum, 1989).

"Status of the Sandia EBIS Atomic Physics Program." R. W. Schmieder, Proc. 1989 Particle Accel. Conf., Chicago, IL (1989).

"Enhanced Performance of the LBL/SNLL Leaky EBIS: Evidence for Cooling of Trapped Heavy Ions." R. W. Schmieder and C. L. Bisson, *Rev. Sci. Inst.* 61, 256 (1990).

"Sandia Super-EBIS." R. W. Schmieder, C. L. Bisson, S. Haney, N. Toly, A. R. Van Hook, and J. Weeks, *Rev. Sci. Inst.* 61, 259 (1990).

"Quightness: A Proposed Figure-of-Merit for Sources of Low-Energy, High-Charge-State Ions." R. W. Schmieder, *Rev. Sci. Inst.* 61, 1101 (1990).

"Ion Optical and Beam Energy Properties of the Electron Beam Ion Source." R. W. Schmieder, *Rev. Sci. Inst.* 61, 1104 (1990).

"Ion Collision Experiments with Slow, Very Highly Charged Ions Extracted from an Electron Beam Ion Trap." D. Schneider, D. DeWitt, M. W. Clark, R. Schuch, C. L. Cocke, R. W. Schmieder, K. Reed, M. H. Chen, R. Marrus, M. Levine, and R. Fortner, *Phys. Rev. A* 42, 3889 (1990). Material also presented at the Int'l Conf. Elect. and Ion Coll. and the Int'l Conf. on Atomic Physics.

4.1.2. Materials

4.1.2.1. Uses of Materials

Three types of materials of interest for developing tagging technology:

- Bit Pattern Materials: Material which actually receives the initial high charge state ion damage
- Replication Materials: Epitaxially grown, chemically deposited, or self-assembled materials used in the bit pattern replication process
- Tag Materials: Individual tag material substrate onto which bit pattern is transferred.

We have made an extensive search for materials that might prove suitable for use in one or more of these categories.

4.1.2.2. Types of materials

The following list includes materials we found that seem to have potential use in developing micromechanical tags. While not exhaustive, it probably covers most of the major groups.

- Native elements
- Sulphides
- Oxides
- Hydrides
- Halides
- Carbonates
- Sulfates
- Neosilicates
- Phyllosilicates
- Tectosilicates
- Polymers
- Non-minerals
- Organic molecular crystals
- Small pore zeolites

4.1.2.3. Material Properties

We have extracted salient property data from the various materials we believe will be of use in developing micromechanical tags. The materials are classified according to their mineralogical classes as listed above. Tables 4.1-12 give the names of mineral single crystal forms of materials are listed in brackets. References (such as EBN6) are in the Bibliography (Sec. 8). Abbreviations are as follows:

- R - resistivity (Ohm-cm)
- G - specific gravity
- H - hardness (Mohs)
- Mp - melting point (°C)
- D - density (g/cm³)

C. Palache, H. Berman, C. Frondel, *The System of Mineralogy*, 7th ed., 1944, John Wiley & Sons, New York, 843 pp.

Table 4.1 - Native elements

Graphite (HOPG)	Perfect {0001} cleavage. G: 2.23, H: 1-2, D: 2.20, R(par. to cleavage plane): 5×10^{-4} , R(perp. to cleavage plane): 0.8. Unattacked by acids. Good thermal insulator. Burns in air above 450.
Diamond	Perfect {111} cleavage. G: 3.51, H: 10, D: 3.52. Insoluble in acids and alkalis. Transforms to graphite above 1500. High electrical and thermal conductivity.
Si	Structure similar to cubic diamond. D: 2.33, Mp: 1410. Unreactive to O ₂ , H ₂ O, H halides (except HF). Dissolves in hot aqueous alkalis. Reactive to halogens.
Ge	Structure similar to diamond. D: 5.32, Mp: 945. No reaction with H ₂ O, dilute acids, or alkalis unless oxidant is present. Dissolves in hot, concentrated H ₂ SO ₄ . Oxidizes in air at 400. Brittle crystal.

Table 4.2 - Oxides

Al ₂ O ₃ [Corundum]	No cleavage. G: 4.02, H: 9.0, D: 3.97, Mp: 2320, R: $>10^{15}$. Very resistant to acids. Electrical insulator. Good mechanical strength. Al ₂ O ₃ has been suggested as a high resolution electron beam resist (EBN6). 2 nm diameter holes have been drilled up to 100 nm deep in Metal b-aluminas (Na ₂ O Δ Al ₂ O ₃ , etc...) using electron beams. These holes maintain a 2 nm diameter along their entire length and appear to be stable over time (EBN5). Atomically flat surfaces of the basal plane of polished and annealed Al ₂ O ₃ and the cleavage plane of Cr ₂ O ₃ were imaged using AFM (MOF3). Al ₂ O ₃ has been used as a substrate for growing single crystal ceramic thin films of TiO ₂ , VO ₂ , and TiO ₂ /VO ₂ multilayers (MOF2).
MoS ₂ , MoO ₃ =molybdate	The transition metal dichalcogenide, MoS ₂ , is a well-known solid state lubricant, and has semiconducting electrical properties. It has a layered structure consisting of covalently bonded S-Mo-S sheets held together by weak van der Waals forces. MoS ₂ crystal cleavage planes are thus atomically flat and relatively inert (B1). Damage pits from 13.4 MeV Au ion irradiation of a MoS ₂ single crystal surface have been studied with STM. Pits were 1-3.5 nm in diameter and approximately 1 nm deep. The spatial resolution of adjacent pits was estimated to be 3-5 nm (Mo1) A tribological study of the MoS ₂ surface indicates that MoS ₂ is relatively stable to wear from repeated AFM scanning and that wear occurs preferentially at surface defects, although freshly cleaved surfaces were defect free over large scan areas (Mo4). A thin film of MoO ₃ grown on a MoS ₂ single crystal substrate has been imaged, machined, and manipulated by AFM. 10 nm lines were machined in and completely through the 5 nm thin film using the AFM tip without causing any damage or wear to the underlying MoS ₂ substrate. The MoO ₃ film is easily grown by thermal oxidation of the MoS ₂ surface, resulting in a thin, rigid, non-deformable layer. The electronic properties of the film can be varied over an extraordinary range by doping (Mo2,3)
MgO [Periclase]	Perfect {001} cleavage. G: 3.56, H: 5.5, Mp: 2832, R: 10^{15} . Soluble in acids. Practically insoluble in H ₂ O. Insoluble in EtOH.
TiO ₂ [Rutile]	G: 4.18-4.25, H: 6-6.5. TiO ₂ has been used as a thin film resist for fast atom beam milling of nanometer scale patterns (MOF1).

Table 4.3 - Sulfides

MoS ₂ [Molybdenite]	Perfect {0001} cleavage. G: 4.62-4.73, H: 1-1.5, D: 5.0, Mp: 1185. Insoluble in H ₂ O, organic solvents, and dilute acids. Sublimes at 450. Diamagnetic semiconductor.
PbS [Galena]	Perfect {100} cleavage. G: 7.6, H: 2.5, Mp: 1114. Sparingly soluble in H ₂ O.

Table 4.4 - Hydroxides

Mg(OH) ₂ [Brucite]	Perfect {0001} cleavage layered structure. G: 2.39, H: 2.5. Dissolves in acids. Practically insoluble in H ₂ O.
-------------------------------	--

Table 4.5 - Halides

AlF ₃	AlF ₃ has been suggested as a high resolution electron beam resist (EBN6). Arrays of 2 nm diameter holes have been drilled on 4 nm centers in AlF ₃ using an electron beam. Arrays of 8 x 10 nm holes on 20 nm centers have been etched 30 nm deep into Si ₃ N ₄ using a CHF ₃ plasma etch and AlF ₃ e-beam patterned etch mask (EBN3).
NaCl [Halite]	Perfect {001} cleavage. G: 2.16, H: 2.5, Mp: 801. Soluble in H ₂ O. Sparingly soluble in EtOH
KCl [Sylvite]	Perfect {001} cleavage. G: 2.0, H: 1.99. Soluble in H ₂ O.
CaF ₂ [Fluorite]	Perfect {111} cleavage. G: 3.18, H: 4, Mp: 1418. Soluble in acids. Practically insoluble in H ₂ O.

Table 4.6 - Carbonates

CaCO ₃ [Calcite]	G: 2.71, H: 3, Mp: 1339. Dissolves in acids. Practically insoluble in H ₂ O.
CaMg(CO ₃) ₂ [Dolomite]	Perfect {10°10} cleavage. G: 2.85, H: 3.5-4.

Table 4.7 - Sulfates

BaSO ₄ [Barite]	Perfect {001} cleavage. G: 4.5, H: 3-3.5, Mp: 1580. Sparingly soluble in H ₂ O.
SrSO ₄ [Celestite]	Perfect {001} cleavage. G: 3.96, H: 3-3.5, Mp: 1605. Sparingly soluble in H ₂ O.
CaSO ₄ 2H ₂ O [Gypsum]	Perfect {010} cleavage. G: 2.32, H: 2.
CaSO ₄ [Anhydrite]	Perfect {001} cleavage. G: 3-3.5, H: 2.9.

Table 4.8 - Neosilicates

Al ₂ SiO ₄ (F, OH) ₂ [Topaz]	Perfect {001} cleavage. G: 3.4-3.6, H: 8. Insoluble.
Al ₂ SiO ₅ [Kyanite]	Perfect {001} cleavage. G: 3.55-3.66, H: 5.

Table 4.9 - Tectosilicates

SiO ₂ [Quartz]	G: 2.20, H: 7, D: 2.65, Mp: 1716-1736, R: 10 ¹⁸ . Chemically resistant to most reagents. Soluble in HF.
NaAlSi ₃ O ₈ [Albite]	Perfect {001} cleavage. G: 2.02, H: 6.

Table 4.10 - Phyllosilicates

KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂ [Muscovite]	G: 2.76-2.88, H: 2-2.5, D: 2.83, R: 10 ¹³ -10 ¹⁷ . Monoclinic layered micas with perfect {001} cleavage plane. Good resistance to chemical and molten materials except hydrofluoric acid. Oils cause delamination.
K(Mg, Fe) ₃ (AlSi ₃ O ₁₀)(OH) ₂ [Phlogopite]	G: 2.95-3.0, H: 2.5-3.0. Decomposes in H ₂ SO ₄ . Natural phlogopite is rare, but fluoro-phlogopite is commercially synthesized and has better chemical resistance properties than muscovite (G: 2.9, H: 3-4, R: 10 ¹³ -10 ¹⁷).
KMg ₃ (AlSi ₃ O ₁₀)(OH) ₂ [Biotite]	G: 2.95-3.0, H: 2.5-3.0. Decomposes in H ₂ SO ₄ .

Table 4.11 - Non-minerals

SiC	Hexagonal(a) and cubic(b) crystal structures. H: 9.5, D: 3.21. Insoluble in H ₂ O and acids. Soluble in fused KOH. Sublimes at 270. High thermal conductivity
Si ₃ N ₄	Hexagonal crystal structure. H: 9.5, Mp: 1900. Insoluble in H ₂ O. Soluble in HF. Chemically inert. Electrical insulator.
GeS	Layered structure. Mp: 530. Soluble in cold H ₂ O, HCl, NH ₄ OH, NH ₃ . Sublimes at 430.
LiF	
KBr	
AgBr	
BN (HOPBN)	
AlF ₃	
NiO	
Organic Molecular Crystals	
Tetracene	Defect-free surface over 1 mm ²)
Small Pore-Size Zeolites	(Clinoptilolite has < 1nm pore size)

Table 4.12 - Polymers

Poly(Tetrafluoroethylene)-Teflon (PTFE)	<p>PTFE has a low dielectric constant (≈ 2.0) and is physically and chemically inert.</p> <p>An AFM study of a teflon film created by rubbing commercial grade teflon across a glass microscope slide revealed a 15-40 nm thick, highly oriented polymer film with rows of 0.5 nm spacing and ridge structures 1-30 nm high spaced 25 nm - 1 mm apart (P2). These ordered teflon films have been used as a substrate to grow highly oriented thin films using a variety of materials (P3). This technique might be refined to produce smoother surfaces.</p> <p>Self-assembly of Poly(3-decyl-thiophene) on HOPG has been shown to occur due to matching of the HOPG lattice with the carbon structure in the polymer backbone (SAM2). Thus it might be possible to achieve self-assembly of a PTFE thin film by matching the polymer backbone structure to an appropriate substrate lattice [warrants further investigation].</p> <p>Focused ion beam damage of a 0.5 mm commercial teflon film spun onto a Si wafer has been demonstrated using 80 keV Ca^+ ions. A 0.1 mm deep structure was created using an ion flux of 10^{15} ions/cm². Thus the energy deposited per unit volume of material removed was $\approx 8 \times 10^{21}$ keV/cm³ which is the same order of magnitude as the energy deposited per unit volume for high charge state ion damage on mica ($\approx 2 \times 10^{21}$ keV/cm³). Ion exposure alters the properties of the teflon film so that either a SiO_2 film can be grown on the exposed areas, or AZ resist can be spun on and will only stick to the exposed areas. In addition, O_2 reactive ion etching (RIE) can be used to etch away teflon not covered by AZ resist (IBN1).</p> <p>Low level electron or x-ray radiation causes cross-linking of linear PTFE surface chains. Subsequent etching in sodium naphthalenide creates strong adhesive bonding sites in non-irradiated areas, while irradiated areas retain the usual inertness characteristic of PTFE. Copper deposited by electroless deposition or chemical vapor deposition (CVD) results in nucleation and growth of copper thin film on non-irradiated surface areas (P1). Although the irradiation from high charge state ions causes damage in the PTFE chains, a further process may serve to crosslink the bonds broken due to the ion damage.</p>
Polymethylmethacrylate (PMMA)	<p>PMMA is a commercial resist material commonly used in micron-scale lithography. Despite many claims that PMMA does not have the resolution needed for nanolithography, there are several examples: 12 nm lines in PMMA by Focused Ion Beam milling (IBN3), 5 nm lines transferred to nitride films by reactive ion etching using an electron beam-patterned PMMA resist thin film (EBN7), 30 nm diameter quantum dots constructed by e-beam patterning of PMMA and wet etching (QS4), and 10 nm pillars constructed using e-beam patterned PMMA, reactive ion etching, and wet HF etching (QS1,5).</p> <p>The order and thickness of PMMA films might be improved by using Langmuir-Blodgett techniques (LBF2), by growing the PMMA film on a highly oriented teflon surface (P2), or growing the PMMA film by self-assembly on a suitably matched substrate (SAM2).</p>

Alkanethiol and Organosilane Self-Assembling Monolayers	<p>Self-assembled monolayer films can be created with a thickness of $\approx 1\text{nm}$. While SAMs are not pinhole- or defect-free, defects larger than a few molecular diameters cannot be stable. A dot with a diameter of 20 nm, when placed on a monolayer surface, covers an assembly of ≈ 800 molecules. A SAM film is very stable in solvents and acids, but deteriorates in basic solutions. Alkanethiol films have been shown to be more highly ordered than organosilane films (B4).</p> <p>Organosilane precursors of the type RSiX_3 (R=organic functional group, X=Cl, OCH₃) self-assemble to form covalently bound thin films on Si substrates $\approx 1\text{nm}$ thick. Irradiation with x-rays transforms or removes the R group. Electroless deposition of Nickel results in a thin nickel film on the non-irradiated surface areas. Feature resolution has been demonstrated to linewidths of $\approx 0.25\text{ }\mu\text{m}$ (XRN1).</p> <p>A self-assembled OTS (n-octadecyltrichlorosilane) monolayer on SiO_2 has been shown to act as a self-developing positive electron beam resist. Features as small as 25nm (50 nm period) were etched 50 nm deep into the SiO_2 substrate using buffered HF (SAM13). OTS films have also been grown by self-assembly on a hydrated mica surface (SAM9). An OTS monolayer 2.8 nm thick on a Si substrate has been shown to be an excellent electrical insulating film (SAM15).</p> <p>A self-assembled ODT (n-octadecanethiol) monolayer on GaAs has been shown to act as a self-developing positive electron beam resist. Features as small as 25nm (50 nm period) were etched 30 nm deep into the GaAs substrate using ammonium hydroxide (SAM13,14). ODT monolayers on thin Au film on Mica substrate were examined by STM. Defects and pits in the SAM film were found with dimensions of 2-5 nm dia. and 0.5-0.8 nm depth. Simultaneous growth (SAM5,16).</p> <p>Simultaneous growth of two Alkanethiols of differing chain length on a gold surface has been demonstrated (SAM4,17). This might be of use in a self-assembly replication process.</p>
CR-39	See experimental section
Cronar	See experimental section
Rodyne	See experimental section

4.1.2.4. Summary of materials for use as tags

Table 4.13 presents the materials identified as candidate tag substrate materials along with various properties. Ideal tag materials are insoluble, mechanically hard, and either available as natural minerals with atomically flat cleavage planes, or synthesizable in ultra flat thin film layers.

Table 4.13 - Materials for use as tags

Common Name [Mineral]	Chemical Composition	Hardness (Mohs)	Comments
[Diamond]	C	10	Perfect cleavage, insoluble.
Cubic Boron Nitride	BN	10	Synthetic, insoluble.
Silicon Carbide	SiC	9.5	Synthetic, soluble in KOH, high thermal shock resistance.
Silicon Nitride	Si ₃ N ₄	9.5	Synthetic, soluble in HF, good high temp corrosion and wear resistance properties, demonstrated tag fabrication.
Alumina [Corundum]	Al ₂ O ₃	9	Naturally occurring or synthetic, insoluble.
[Eskolaite]	Cr ₂ O ₃	8	Naturally occurring or synthetic, low resistivity, insoluble.
[Topaz]	Al ₂ SiO ₄ (F,OH) ₂	8	Perfect cleavage, insoluble.
[Quartz]	SiO ₂	7	Naturally occurring or synthetic, soluble in HF.
[Albite]	NaAlSi ₃ O ₈	6	Naturally occurring, perfect cleavage.
Titania [Rutile]	TiO ₂	5.5	Naturally occurring or synthetic, reacts with H ₂ SO ₄ .
[Kyanite]	Al ₂ SiO ₅	5	Naturally occurring, perfect cleavage.
Mica [Phlogopite]	K(Mg,Fe) ₃ (AlSi ₃ O ₁₀)(OH) ₂	2.5 - 3	Naturally occurring or synthetic, perfect cleavage, layered structure, soluble in HF and H ₂ SO ₄ .
Mica [Muscovite]	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	2 - 2.5	Perfect cleavage, layered structure, soluble in HF, demonstrated ion damage / tag fabrication.
[Molybdenite]	MoS ₂	1-1.5	Perfect cleavage, layered structure, semiconductor, insoluble.
Teflon (PTFE)	-[CF ₂ CF ₂] _n -		Synthetic, insoluble.

4.1.3. Replication

The Passive Micromechanical Tag concept relies on the ability to manufacture millions of tags with identical nanobit patterns. Methods of lithography, anisotropic etching, epitaxial growth, and surface imprint polymerization are useful in the replication process.

4.1.3.1. Overview

Nanoscale bit patterns can be replicated by the following processes, among others:

- Physical
 - Multiplication
 - Lithographic printing
 - Deposition
 - Mechanical pressing
- Chemical
 - Etching
 - Template Patterning
 - Molecular imprinting
 - Epitaxy
 - Chemical pattern stamping

Physical replication involves lithography, deposition, etching, or mechanical pressing, while chemical replication involves site-specific thin film self-assembly. This is only intended as an outline of possible processes. Support for these processes can be found in the literature, but has not been referenced here (see bibliography).

4.1.3.2. Multiplication

Materials that show nanoscale structure that is characteristic of manufacture can be used as tag material in applications that do not require writing a predetermined message, i.e., tracking. The manufacturing process provides the information for the tag. Reading can be done automatically. Examples of these materials include polished surfaces that show scratch marks, and evaporated layers that show local aggregating.

4.1.3.3. Lithographic Printing:

In standard lithography, a mask is created that is used to print multiple (e.g., 10^8) copies of the bit pattern. Existing lithographic techniques include:

- Chemical vapor deposition
- Molecular beam epitaxy
- Metal film lift off
- X-ray lithography
- E-beam lithography
- Fast atom beam (FAB) milling
- Chemical etching (wet/dry)
- Reactive ion etching (RIE)

Lithographic printing techniques include scattering projection electron lithography (SCALPEL)¹ and X-ray projection lithography. X-ray lithography provides the small scale resolution necessary to replicate nanobit patterns. A tag material substrate is coated with an ultrathin, defect-free x-ray resist. Then a thin metal film containing the bit pattern is used as a shadow print mask to expose the resist. The substrate is preferentially etched through the exposed resist, transferring the bit pattern to the tag material substrate.

A single mask can be used to align and print multiple copies of the bit pattern. A new mask is then made from the multiple copy pattern and used to print more copies. In this manner, millions of tags are reproduced from a single bit pattern using a small number of x-ray exposures [Figure 4.1].

(a) Bit Pattern for individual tag is written on SAM film using high charge state ion surface damage.

(b) Thin metal film x-ray mask is produced from bit pattern.

(c) X-ray shadow print lithography is used to expose multiple copies of bit pattern on SAM film resist.

(d) Thin metal film x-ray mask is produced from exposed SAM film resist.

(e) Second x-ray mask is used for higher speed replication of bit pattern.

(f) Final x-ray shadow print exposure results in one SAM film containing millions of identical bit patterns, which are transferred to the underlying tag substrate by chemical etching.

Figure 4.1 - Replication using xray lithography.

Pattern transfer of 1 μm features has been demonstrated on an alkanethiol SAM film, which is etched to transfer the pattern to an underlying Au thin film [Kumar, 1993]. Hexadecanethiol SAM films were patterned on Au films on Si substrates. Etching (1 M KOH, 0.1 M KCN) removed the Au film in regions not covered by the SAM film. This method of transferring a nanobit pattern to a metal thin film, which is removed from its substrate through a lift-off process, can be used to produce an x-ray shadow printing mask [Figure 4.2].

(a) Alkanethiol SAM film on Au thin film on substrate.

(b) High charge state ion damage to SAM film.

(c) Etching of Au thin film.

(d) Liftoff of Au thin film x-ray mask.

Figure 4.2 - Mask fabrication by thin metal film x-ray lithography.

In another scheme, a bit pattern is created on an organosilane SAM film and a thin metal film is created through electroless deposition on the unexposed regions of the SAM film [Figure 4.3]. Pattern transfer of 20 nm features has been demonstrated using this method [Marrian, 1994; Dressick, 1994; Calvert, 1993]. Organosilane films of PYR, PEDA, and CMPTS were assembled on SiO₂ on Si and patterned using electron beam, x-ray, and UV lithography. Electroless metal deposition resulted in Ni thin films covering the unexposed regions of the SAM film. A lift-off process yields a patterned thin metal film x-ray shadow printing mask.

(a) Electron beam patterning alters SAM film.

(b) Catalysis occurs in non-patterned regions.

⊗ = Pd (II)

(c) Electroless deposition of Ni yields thin patterned film.

(d) SEM micrograph of CMPTS film plated with Ni. Width of lines is 20 nm [Marrian, 1994].

Figure 4.3 - Electrodeless metal deposition on patterned SAM film.

4.1.3.4. Deposition

Bit patterns are produced in a solid surface by high charge state ions. A combination of deposition, epitaxial growth, and etching is used to build up multi-layered structures which retain the bit pattern through crystal or thin film structure defects or through site-specific material substitution. A final etching process delaminates the layered structure releasing individual tags.

4.1.3.5. Mechanical Pressing

Bit patterns are produced in a solid surface by high charge state ions. Damage sites are modified by the addition of material or growth of crystallites to form hard protrusions which are chemically etched to form sharp tips. Modified surface is then used to stamp bit pattern onto tags. The bit pattern surface structure might resemble a two dimensional field of AFM or STM probe tips which could then be used for ballistic electron damage, E-field induced diffusion, or metal evaporation as a means of replicating the bit pattern.

4.1.3.6. Etching

Bit patterns are produced in an etch resist which is the surface layer of a multi-layered structure. Anisotropic etching results in vertical holes through the compound structure. A final etching process delaminates the layered structure releasing individual tags. Hole structures could be left as is or filled in with a different material.

Replication of patterns from an exposed resist material to an underlying substrate material has been demonstrated at the nanometer scale [Lercel, 1993; Tiberio, 1993]. In these studies self assembled monolayer films are patterned with an electron beam and used as etchant masks for pattern transfer to an underlying substrate. Patterns as small as 25 nm were created on *n*-octadecyltrichlorosilane (OTS) on SiO₂ on Si and on *n*-octadecanethiol (ODT) on GaAs [Figure 4.4]. Etching with NH₄F:HF:H₂O transferred the OTS pattern to the SiO₂ which was subsequently used as a KOH etchant mask to transfer the pattern to the underlying Si substrate. Etching with NH₄F:H₂O transferred the ODT pattern to the underlying GaAs substrate. In both cases, patterns as small as 25 nm were etched up to 30 nm deep in the substrate materials.

A demonstration of single replication pattern transfer by anisotropic etching of a high charge state ion damaged SAM film is currently in progress. Films of OTS on SiO₂ on Si are damaged with Xe⁺⁴⁴ ions. The damaged films are being examined with atomic force microscopy, and etched to transfer the damage pattern to the underlying Si substrate.

While these studies demonstrate single replication pattern transfer using anisotropic etching, multiple replications can be made by applying the same techniques to multi-layered structures. A bit pattern is etched through a structure composed of alternating layers of tag substrate material and separation layer material. A second etchant then dissolves the separation layers, releasing individual tags [Figure 4.5].

A demonstration of pattern transfer through a layered structure using nuclear track etching in mica is currently in progress. A muscovite mica layered structure is irradiated with low charge state, high kinetic energy ions, which leave latent tracks in the mica. The micrometer scale tag dimensions are defined by cutting with a high power pulsed Nd:YAG laser cutting tool and the layered mica structure is delaminated using a combination of heat and ultrasound to separate the loosely bound mica sheets. The individual tags are then briefly etched in HF, which develops the latent track bit pattern [Figure 4.6]. Due to limitations in bit pattern density and tag dimensions, nuclear track etched mica tags are not a substitute for high charge state ion tags.

Figure 4.4 - Electron beam patterned SAM film (OTS) on silicon showing 25 nm features.

(a) High charge state ion irradiation.

- Self assembled monolayer resist
- Tag substrate material
- Separation layer material

(b) Etching transfers bit pattern through layered structure.

(c) Final etch removes resist and separation layer material, releasing individual tags.

Figure 4.5 - Anisotropic etch transfer of bit pattern through layered structure.

Figure 4.6 - Demonstration of etch pattern transfer through a layered structure.

4.1.3.7. Template Patterning

Bit patterns are produced in a solid surface by high charge state ions. Damage sites from high charge state ions are chemically active and are used as nucleation sites for chemical synthesis and growth of self-assembling materials.

4.1.3.8. Epitaxy

The patterned growth of materials can also be used to replicate nanobit patterns. High charge state ion damage sites are chemically reactive and provide enhanced nucleation sites for growth of materials. Patterned epitaxial growth of materials has been demonstrated using a variety of techniques.

Enhanced binding of Cu to nanometer scale cavities formed through He ion beam implantation in Si has been demonstrated and is ascribed to the reaction of Cu with Si dangling bonds on the cavity walls [Myers, 1993].

Ceramic thin film growth on patterned self assembled monolayer films has been demonstrated [Bunker, 1994]. Ion or electron beam lithography is used to pattern etch the SAM film. An active monolayer film is then assembled in the etched regions, and ceramic thin film growth occurs only on the active regions [Figure 4.7].

Selective, maskless growth of InP on patterned GaAs has been demonstrated using focused ion beam implantation and vapor phase epitaxy [Lezec, 1993]. Local modification of the GaAs surface by Si ion bombardment leads to enhanced nucleation and growth of InP single crystals having dimensions of 500 nm.

Bunker, *Science* 264, 48 (1994)

4.1.3.9. Molecular imprint polymerization:

Molecular Imprint polymerization is a new technique which can be used in the replication of nanobit patterns. A functional monomer is attached to functional sites on a template molecule. Polymerization and subsequent removal of the template molecule results in an imprinted polymer [Mosbach, 1994]. By attaching functional monomers to chemically active nanobit sites and subsequent polymerization, a surface imprint of the nanobit is transferred to the polymer surface.

A molecularly imprinted polymer replication can cause pattern transfer through positive replication, in which a pit is transferred to the replicated surface [Figure 4.8], or negative replication, in which the negative image of a pit is transferred to the replicated surface [Figure 4.9].

K. Mosbach, Molecular Imprinting, *Trends in Biochemical Sciences* 19, 9 (1994). [123] review

4.1.3.10. Chemical pattern stamping

Bit patterns are produced in a solid surface by high charge state ions. Damage sites are modified by the addition of material to form a mechanical stamp. This stamp is used to lay down a patterned self-assembled monolayer on a substrate, which is subsequently etched, leaving a raised pattern on the substrate.

(a) Self assembled monolayer film.

(b) Patterning of SAM film with electron beam.

(c) Assembly of functional monolayer in patterned regions.

(d) Growth of thin film ceramic on patterned functional monolayer.

Figure 4.7 - Biomimetic lithography. (a) deposition of inert organic layer; (b) etching; (c) deposition of active organic layer in etched regions; (d) mineral growth from aqueous solution.

Figure 4.8 - Positive molecularly imprinted polymer replication.

Figure 4.9 - Negative molecularly imprinted polymer replication.

4.1.3.11. Summary of replication materials

Table 4.14 lists materials which can be used in the replication processes. These materials include resist material thin films, epitaxially grown films, and substrate materials with potentially useful properties.

Table 4.14 - Materials for replication of tags

Material Name	Chemical Composition	Comments
Aluminum tri-fluoride	AlF ₃	Demonstrated 2 nm electron beam milling resolution
Lithium Fluoride	LiF	Demonstrated track etching
Magnesia [Periclase]	MgO	Perfect cleavage, soluble in acids, partially insoluble in H ₂ O
Germanium Sulphate	GeS	layered semiconductor structure
[Molybdate]	MoO ₃	Demonstrated nanometer scale micromachining
Potassium Bromate	KBr	Demonstrated high resolution electron beam milling
[Paramontroseite]	VO ₂	Thin film layered epitaxy with aluminum oxide
[Kareliante]	V ₂ O ₃	Thin film layered epitaxy with aluminum oxide
[Galena]	PbS	Demonstrated high resolution electron beam milling
Graphite (HOPG)	C	Perfect cleavage, conductor
Silicon	Si	semiconductor
Germanium	Ge	semiconductor
Gallium Arsenide	GaAs	semiconductor
[Halite]	NaCl	Demonstrated high resolution electron beam milling
[Sylvite]	KCl	Demonstrated high resolution electron beam milling
[Fluorite]	CaF ₂	Demonstrated high resolution electron beam milling
PMMA	Polymethylmethacrylate	Demonstrated high resolution resist, LB thin film
OTS	<i>n</i> -octadecyltrichlorosilane	Demonstrated high resolution resist, SAM film
ODT	<i>n</i> -octadecanethiol	Demonstrated high resolution resist, SAM film
PEDA	(aminoethylaminomethyl) phenylethyltrimethoxy-silane	Demonstrated high resolution resist, SAM film
CMPTS	4-chloromethylphenyltri-chlorosilane	Demonstrated high resolution resist, SAM film

4.1.4. Tag machining

A variety of techniques are available for fabricating the chips that are to be used as tags. Normally, we would expect to write the label on a large substrate material, then separate it into individual tags, but this is not essential, and the method of choice will depend on the application. In this section we review several schemes for producing chips that can act as tags.

4.1.4.1. Lithographic micromachining

[The following was provided by Ned Godshall, Org. 1333]

A rapidly expanding technology that allows fabrication of very small mechanical devices using microelectronic processes and equipment. "Bulk" micromachining can produce thin objects by anisotropic etching of the silicon substrate. Conversely, "surface" micromachining can produce these objects by isotropic etching of an underlying "sacrificial" layer of silicon oxide, thereby freeing up any structures deposited above them.

Several methods exist for making the desired pieces. One of them would utilize our ability to deposit thin (0.1 to 1.0 micron), but well-defined, silicon nitride or polycrystalline silicon on a "sacrificial oxide" on substrate silicon. This could simply be photolithographically patterned, and subsequently plasma etched into 10×10 micron squares.

This would be followed by the standard surface micromachining wet HF etch, which would etch all the underlying oxide, consequently freeing all the squares in one step. The resulting pieces could be captured by some filtering device surrounding the wafer boat in the sacrificial oxide process.

A rough calculation illustrates that one 150 mm (6") diameter wafer would result in 140 million tags. A standard 25-wafer lot would therefore yield about 3.6 billion tags.

4.1.4.2. Grid Definition on Lithographic Bit Pattern Mask

Individual tags are fabricated during the replication of the bit pattern. This might occur in a process by which lithographic printing transfers a mask image of both bit pattern and border to a substrate material which is then somehow selectively etched to produce tags but not enlarge individual bits.

4.1.4.3. Lithographic Grid Definition Prior to Printing

Substrate material is masked and etched with large scale grid pattern prior to bit pattern transfer. Two examples are the following:

- 1 mm film of Si_3N_4 on Si is photolithographically etched to produce 0.1 mm wide by 1 mm deep troughs in a grid pattern with 10 mm spacing.
- Nanometer scale alignment techniques are used to align the bit pattern mask onto the substrate pattern for lithographic replication. A final etch releases the Si_3N_4 tags from the Si substrate.

4.1.4.4. Lithographic Grid Definition After Printing

Nanometer scale alignment techniques are used to super-impose a large-scale grid structure on the bit patterned substrate. This grid pattern is then etched to produce the individual tags.

4.1.4.5. Grid Definition During Chemical Replication

Chemical bit pattern replication occurs perpendicular to the substrate plane, defining tag dimensions during replication. Layered epitaxial growth of replicated tags includes layers of separation material, which is etched to release the individual tags.

4.1.4.6. Wafer bonding

[The following was provided by John Medernach, Org. 1333]

Wafer bonding requires the use of an ultra-flat (UF) silicon wafer, and a second less-flat silicon wafer. The wafers are cleaned, then a 0.5 micron - 1.0 micron thick oxide is grown on the UF wafer. The two wafers are joined under class 10 conditions or better, which reduced

potential particulate contamination. A high temperature oxidation, $>800^{\circ}\text{C}$ for 1 to 3 hours follows to complete the bonding process. At this point one side of the bonded wafers is thinned by lapped and/or polished to a thickness of 10 microns. A controlled chemical etch is used to thin the 10 micron layer to 1 micron. Photolithography is employed to define the 10 micron x 10 micro tag, and a brief etch with a dilute buffered HF solution should release the tags. Special precautions will be necessary to eliminate any agglomeration during the etching, post cleaning and drying. It should be noted that wafer bonded silicon on insulator (SOI) structures are commercially available with a 1 micron silicon layer. These structures are prepared by a slightly different process, but the end result is the same. The unit cost for a 150 mm diameter wafer bonded SOI structure can vary between \$1000 and \$2000 each, with a minimum quantity between 10 and 25. Submicron silicon layers will be proportionally more costly due to the individual processing that is required.

4.1.4.7. Polysilicon films

[The following was provided by Dave Palmer, Org. 1333]

The following steps could be used to produce tags of polysilicon films:

- Start with standard silicon wafer.
- Heavily oxidize (thermal and deposited) to a 1 or 2 micron thickness
- Deposit polysilicon film from 1000 to 10,000 Å
- e-beam pattern a grid with 0.1 micron details (a 6" wafer could take days for the patterning). Alternatively optically define the whole wafer pattern with a contact aligned (would take seconds)
- Anisotropically plasma etch throughout the polysilicon film
- Place in silicon oxide etch and float the tags off.
- Some work would be necessary to prevent the tags from warping.

4.1.4.8. Stochastic chip separation

The following schemes provide paths to fabrication of pseudo-random chips from the parent material

- Grinding
- Multicrystalline fracture
- Ultrasonic fracture
- Rollering (breaking along scratch lines)

4.2. INFORMATION STORAGE SCHEMES

4.2.1. Geometrical coding schemes

The simplest coding scheme is to place the nanobits in a regular array. The presence or absence of the bit would carry the information constituting the tag label. However, it is quite unnecessary to place the nanobits in a regular array; any geometric arrangement of the bits contains information, and therefore constitutes a label. The following list shows several ways to code the label by bit position:

- Binary bit coding Each bit represents a binary bit in the label. This provides the greatest information storage density, but requires position control approximately equal to the bit size.
- Pattern coding Bits are arranged in stripes, squares, or other areas differentiated from adjacent sites that have no nanobits. This scheme produces easily recognized patterns that do not require high precision position control. The overall label information density is much lower than binary bit coding.
- Random coding Bits pattern is random. No predefined message is encoded. Rather, once written, the bit pattern is permanent and unique; subsequent read operations will recover exactly the same bit pattern. In this operation, there is no randomness in the pattern, and there is very great capacity.
- Density coding The density of nanobits is position-dependent, with arbitrary resolution. This scheme obviates the need for high-precision positioning of the ions, and provides a label that had very low susceptibility to local damage.

These four coding schemes are illustrated in the Figure 4.10.

Digital Coding: Each damage site represents a binary bit in the tag name. High information storage density, but requires 2D ion steering.

Bar Coding: Pattern (stripe) of damage sites represents binary bit in the tag name. Provides reduced information storage density, but only requires 1D ion steering.

Random Coding: Random pattern of damage sites is read and recorded as a unique tag name. Large number of tagnames with no ion steering requirements.

Density Coding: Density of damage sites constitutes a unique tag name. Large number of tagnames with no ion steering required.

Figure 4.10 - Information storage coding schemes.

4.2.1.1. Random coding

Information can be stored in randomly positioned sites. This is because once the site pattern is laid down, multiple subsequent reads see exactly the same pattern; there is exactly zero randomness relative to the earlier read. In other words, a random pattern, once established, is no longer random; it may be considered addressable data. This is potentially important to ion nanotechnology, since in the absence of a technique for nanometer-precision steering the ions into ordered arrays, we are stuck with random arrays.

One procedure for using random arrays is to first write the array of sites, then scan the array with a scanning microscope (AFM, STM, etc.). Every time a site is encountered, the scanner writes a "0" or "1." This can be done by depositing charge (a volatile memory), or by causing an irreversible electrochemical change (producing a nonvolatile memory). Figure 4.11 shows how a sequence of sites is addressed; the width of the scan line indicates the precision of a typical commercial STM scan. Figure 4.12 shows how the number 1453 can be written using a regular linear array, a random linear array, and a random 2-dimensional array.

A simple way to take advantage of random-array information storage is to make an encrypted code, or key, especially on microscopic or extremely valuable objects, or as additives to controlled substances. A random pattern array of nanometer dots would be extremely difficult to read, alter, or counterfeit.

Figure 4.11 - Reading or writing onto a random array of sites.

Figure 4.12 - Representing the number 1453.

4.2.1.2. Density coding

Instead of considering the individual sites to be bits, the information can be coded as collective properties of the site arrays. For instance, the *density* of sites, regardless of distribution, could represent a number with a dynamic range of perhaps 100. Patterning akin to bar codes can be superimposed on site arrays to impose additional information. For instance, the scaling density of sites within each of 100 squares in a 10x10 array to a scale of 0-99 would give the capability of storing a single number from 1 to 10^4 . Coding in this way is useful, since even in the absence of techniques for detecting individual sites, techniques are available for reading average quantities such as the number of sites within an area (density), or the average size of the sites.

A specific density of damage sites represents a unique tag name. This scheme does not require ion steering capabilities. There is no pattern to be read and archived, and the continuum of densities allows unlimited unique tag names. Figure 4.13 shows a tag coded by bit density.

4.2.2. Whole-tag coding

Even without the application of a bit pattern produced by ion impact, many materials have characteristic nanostructure produced during manufacture. Structures such as striations, etch pits, fractures, and grain boundaries are all seen by scanning microscopy, and could form the basis for tag labels.

In addition, the size, shape, and other physical properties of the tag material, when differentiated from other materials, or combined to form contrast with any other materials, provides a basis for coding a tag label.

The following list gives a few of the properties which are available for whole-tag coding:

- Size
- Shape
- Specific gravity
- Microstructure (polishing scratches, etc.)
- Lattice defects (grain boundaries, etc.)
- Chemical properties (solubility, melting point, etc.)
- Optical properties (fluorescence spectrum, etc.)

As a simple example, Figure 4.14 shows a set of convex shapes provide a set of 9 tags, which require no further information.

Figure 4.13 - Density coding.

Figure 4.14 - Shape coding.

4.2.3. Bit characteristic coding

For the most part, we have assumed that all nanobits appear identical to the reader; it is only their pattern that contains information. However, the bit structures themselves can be varied within a limited range, thus providing another dimension for coding. For instance, the diameter and depth of etch pits in CR-39 plastic can be determined by the duration and temperature of the etch.

The following list gives some of the properties of nanobits that could be varied over a limited range to provide another dimension of coding:

- Diameter
- Depth
- Profile
- Shape
- Damage density (sensed by etch rate)

It may be noted that these properties can be combined, and that bits with various values of these properties can be combined to give a large label capacity. For example, we could use CR-39 to produce the pattern shown in [Figure 4.15](#). In this tag, the bit positions are random, but they are of 3 sizes. Furthermore, the numbers of the bits are as follows:

Thus, the bits are in the density ratios 1:2:1. If we were able to distinguish ratios with a resolution of 10, that is $x:y:z$ with $(x,y,z)=(1...10)$, we would have the capacity for $10 \times 10 \times 10 = 1000$ tag labels. In order to resolve the ratios to 1 part in 10, we would need at least 100 bits for each size.

The simplest possible tag might be one that has a characteristic shape. It would not carry any information beyond the simple fact that it was present in the sample. The characteristic shape would serve to make it unambiguously present. [Figure 4.16](#) shows one of the simplest tags we could imagine.

Figure 4.15 - Bit size coding.

Figure 4.16 - The simplest tag.

4.2.4. Chemical coding schemes

A completely different class of coding involves processing of the tag. In this case, it is not the geometrical arrangement of the nanobits that carries a message, it is the sequence of operations necessary to bring about some predefined tag configuration.

For example, suppose we embed a series of latent images in a tag, using several materials with particular chemical responses. In order to "read" this tag we would subject it to a series of chemical processes, stopping each when a desired result was obtained. The time necessary to reach each step would give the message. Obviously many variations of this theme are possible. Combined with geometrical coding, chemical coding introduces a high level of security, equivalent in some respects to a very complex geometrical code.

4.2.5. Coding schemes and tag capacity

The use of nanobits for information storage results in ultra-high storage densities. A 10 nm diameter nanobit has an area of $8 \times 10^{-13} \text{ cm}^2$ implying in a uniform storage density of 250 Gigabits/cm². This means that a passive micromechanical tag having dimensions of 10 mm x 10 mm could carry a tag name of up to 2.5 Megabits of information, or roughly the text of an 800-page book.

Various applications will have need of a certain resolution in tag names, i.e., complexity of the tags. For simple tracking applications, a small names is sufficient to distinguish all possible paths. For information-transmission applications, a large tag name is required. Therefore, it is worth listing the rough capacities for the various coding schemes.

Table 4.15 gives our estimates of the number of unique names available for various coding schemes.

In a particular application, it may be possible and desirable to combine two or more coding schemes to increase the label size, enhance security, facilitate reading, etc. For instance, a tag might have a shape, a bit density, and two bit sizes. This would provide a tag with $(100)(1000)(1000)=10^8$ possible labels.

4.3. TAGGING OPERATIONS

Table 4.15 - Number of names available with various coding schemes

Tag properties	Coding	Number
General	Size	100
	Shape	100
	Specific gravity	100
Bit pattern geometry	Bar code	10000
	Cross striping	10000
	Masked patterns	1000
Average bit characteristic	Diameter	10
	Depth	10
	Profile	10
	Bit density	1000
	Relative bit type densities (e.g., mark bits A or B)	1000
Bit blocks	Number within block	nM
Digital (every bit examined)	Presence or absence	2*N
	Bit type	2*(10N)
Chemical properties	Atomic composition	10*6
	Solubility	100
	Melting temperature	100
Optical properties	Fluorescence spectrum	100
	Polarization modification	100

N=number of bits; M=number of blocks; n=number of bits in a block

4.3.1. Matrix

Table 4.16 lists the major categories of matrices in which tags can be deployed, together with generic application.

Table 4.16 - Matrix for tag applications

Matrix	Applications
Powders	drugs raw chemicals explosives
Liquids	drugs gasoline water raw chemicals
Solids	microcircuits paper plastic glass
Gases	aerodynamic flows
Mixed materials	explosives
Organisms	insects, worms fecal pellet producers

4.3.2. Deployment

Table 4.17 indicates some of the deployment techniques that are available, together with generic applications.

Table 4.17 - Deployment techniques

Deployment technique	Matrix
Mixing	powders liquids
Attachment	insects documents computer chips gemstones
Injection	small organisms castings
Internal growth	precipitates
Ingestion	feeding organisms filter feeders

4.3.3. Processing

After deployment, the tag is subjected to a series of processes. The process could either leave the tag unaltered, or it can alter it in some way. We might be interested in the final state of an altered tag, or we might care only that it had been altered within a relatively broad range of alteration. For instance, we might look for tags that had experienced temperature above a threshold, but we might not care what that temperature was.

Table 4.18 lists some processes that we might expect to be relevant for the micromechanical tags.

Table 4.18 - Processing of tags

Process	Description
Aging	The tag spontaneously changes with time, providing a measure of its age.
Transport	The tag is collected at a location different from where it was deployed
Mixing	The tag is carried from one matrix into a mixture
Chemical processing	The tag experiences a chemically active bath but remains unaffected. The tag experiences a chemically active bath and undergoes a modification.
Melting	The matrix melts but the tag remains intact
Burning	The matrix is burned in a flame, leaving the tag unmodified.
Explosion	The matrix explodes, distributing the tag spatially but not altering it.
Digestion	The tag passes through the digestive system of an organism.

4.3.4. Location, Concentration, Recovery, Identification

Table 4.19 lists some techniques that can be useful for locating, concentrating, recovering, and identifying the tags. Location means finding the tag(s) with high certainty within a well-defined spatial region. Concentrating means reducing the spatial region without loss of tags. Recovery means separation of the tags from a potentially interfering matrix. Identification means validating that the object is a tag.

An example of a useful filter is the polycarbonate etched membrane filter, such as Nucleopore and Poretics filters, are readily available with flat, uniform surfaces and pore sizes of 0.1 - 10 mm. The quality of the polycarbonate filter surface allows direct AFM imaging of tags on the filter surface.

Table 4.19 - Locating, concentrating, recovering, and identifying tags

Procedure	Description
Filtration	matrix passes through a filter, leaving the tags
Centrifugation	matrix is dispersed in a liquid, which is centrifuged
Settling	matrix is dispersed in a liquid, which is centrifuged
Fluorescence	tag material incorporates an optical fluor, which aids location of the tag
Encapsulation	tag is chemically encapsulated and separated by filtration
Condensation	tag forms seed for condensate, which is separated by filtration or settling
Chemical trapping	tag attaches preferentially to substrate, e.g., zeolite
Electrostatic trapping	precipitator is size-selective
Magnetic precipitation	magnetic tag can be separated by magnetic field
Aerodynamic separation	vortex will cause concentration by weight, size
Optical microscopy	locate the tag by shape, texture, etc.
Radioisotope tracer	tag contains tracer
Companion tracers	material added to the matrix with the tags that will aid in locating the tag, e.g., a large mark on a small object that will identify it as tagged. The location of the tag within the object may not be obvious.

4.4. HANDLING THE TAG

Handling techniques for single micron sized particles are well developed [McCrone, 1973]. There is an extensive literature that appears under titles such as of aerosols, particulate matter, dust, and powder technologies.

McCrone, W. C. and J. G. Delly, *The Particle Atlas, Vol. 1*, Ann Arbor Science Publishers, Michigan, 1973.

4.5. PRE-READ PROCESSING OF THE TAG

Before the label on the tag is read, it may be desirable to pre-process it, perhaps to make the label reading easier. Table 4.20 lists some pre-processing steps that will have relevance to certain applications. All these processes would be done prior to actually reading the tag label.

Among these, we have used site enlargement by etching most often to enlarge the sites on CR-39 (cf. Sec. 2.3.1). Another technique that apparently works for CR-39 is shown in Figure 2.4. Before making this photograph, the SEM beam current was increased to slightly above the threshold for damage to the plastic. The result was that the edges of the etch site being irradiated were sharpened, i.e., the contrast of the nanobit was increased. Clearly this technique could improve the readability of the tag label.

Table 4.20 - Pre-read processing of tags

Pre-process	Description
Protective coating removal	Chemical dissolution of overcoat Mechanical opening of tag container Machining away of laminate
Latent image development	Chemical fixation of damage sites
Site enhancement (decoration)	Etch enlargement of damage sites Polymerization on site, altering surface topography Electron beam processing
Pattern transfer	Transfer to chemically active or inert substrate Transfer to enhance contrast

4.6. READING THE TAG

The actual reading of the tag label obviously depends on the nature of the label. The main emphasis in this work has been on ion-induced nanometer damage sites to create a bit-coded label. Reading such bits obviously requires a device with nanometer resolution, and we have used the scanning AFM as our main experimental tool. This is not the only tool available, however. Table 4.21 lists various types of labels and the tools that are available for reading them.

The read process is used in the sense that the tag properties are translated into a different image or bit pattern that is easily detected, recorded, and interpreted.

Table 4.21 - Reading tags

Property forming label	Process
Bulk properties	Filtration
	Density fractionation
	Solubility
	Refractometry
	Polarimetry
	Melting temperature
	Fluorescence
Bulk morphology	Optical microscopy
	Scanning Electron Microscopy (SEM)
Gross bit patterns	Optical microscopy
	SEM
	Optical scattering
Individual bit positions	AFM
	STM
	Anisotropic bulk electrical properties
	Intrinsic scanners (Gunn Effect)
Individual bit characteristics	AFM

4.6.1. Image processing

In images derived from atomic-resolution microscopy, noise will be a significant limitation to accuracy. Recognizing that a feature is a nanobit against a noisy background will be an ever-present challenge. However, there are some very powerful image-analysis algorithms that can be used to enhance the recognition of nanobits. The significant fact is that the size and shape of the nanobits are known a priori, or by calibration, thus providing a means for discriminating against morphologically dissimilar background. The automatic recognition of the bits was shown in an earlier section of this paper. In fact, the techniques can be far more sensitive and selective. As an example, Figure 4.17 shows a very noisy field, from which a pattern resembling nanobits is extracted. [Russ, 1994].

Russ, J. C., *The Image Processing Handbook*, 1994.

Figure 4.17 - Morphological image processing for feature extraction from noisy background. (a) Original noisy image; (b) Brightness thresholding shows bits plus small irregular features; (c) Erosion leaves only regular bit-sized features.

4.6.2. Latent images

Latent image nanobits provide for a large variety of potential covert uses for micromechanical tags. Table 4.22 lists several possible physical mechanisms that can be used to produce latent nanometer images.

Table 4.23 lists materials that can stably hold a latent image that can be read by etch enlargement. These materials have high etch sensitivity to ion track latent images. The primary damage sites are difficult or impossible to detect, even with AFM, but easy to see with an SEM or ordinary light microscope. For some materials, it is possible to arrange the conditions so that the correct etch procedure is narrowly defined, so that any etch that is not precisely correct will destroy permanently the image. This kind of function provides additional security.

Table 4.22 - Techniques for latent images

Mechanism	Description
Protective overcoat	
Polymeric chain breakage	Broken bonds are chemically active

Table 4.23 - Stable materials for latent images

Material Name	Chemical Composition	Comments
CR-39	Diethylene glycol bis(allyl carbonate)	Polycarbonate, etch with KOH or NaOH.
SR-86	80% CR-39 / 20% Diethylene glycol bis (allyl sulphate)	Polycarbonate, etch with KOH or NaOH, better etching sensitivity than CR-39.
Muscovite Mica	$KAl_2(AlSi_3O_{10})(OH)_2$	Naturally occurring, perfect cleavage, layered structure, etch with HF, demonstrated tag fabrication.
Cronar	Polyester	Rough surface for AFM
Rodyne	Polycarbonate	AFM imaging better than CR-39
PETP	Polyethylene terephthalate	Ion track etched membrane material
PP	Polypropylene	Ion track etched membrane material
PVDF	Polyvinylidene fluoride	Ion track etched membrane material

4.6.3. Nanochemistry

Nanochemistry describes the action of chemical transformations confined to nanometer size regions. Recently it was demonstrated using a scanning tip device (like the AFM). As an example of a nanoscale latent image, we note the work of Nagahara, et al., who observed etching of Si(100) localized with the STM tip while under HF. The mechanism suggested was stimulated oxide formation, followed by etch of the oxide.

This arrangement makes possible the selective etching of specific ion-induced damage features. Thus, we could imagine a series of partial selective reads of the tag. One envisions insertion of the tag in the reader, and application of a code for reading. The reader etches only those parts that constitute the message, leaving the remainder invisible as a latent image. If an unauthorized reader read the tag without the proper code, the message would be meaningless. This process is illustrated in [Figure 4.18](#).

L. A. Nagahara, T. Thundat, and S. M. Lindsay, Nanolithography on semiconductor surfaces under an etching solution, *Appl. Phys. Lett.* 57, 270 (1990).

Figure 4.18 - Nanochemical tag. (a) unetched tag; no message is apparent; (b) tag etched with correct code; message is meaningful; (c) tag etched with incorrect code; message not meaningful

4.6.4. Covert tags

The extremely small size of the tags studied in this project makes them ideal for covert operations. These tags can be incorporated in various materials and objects with very low probability of discovery.

If security even after discovery of the tag is needed, the lists of materials and processes given earlier provide many suggestion for covert tag labels. For instance, the tag could exhibit one bit pattern, but when etched, exhibit another (carrying the correct message). Or it could exhibit no pattern unless first subjected to heating.

4.6.5. Erasure

Our observations of the erasure of the blisters on mica provide the option of read-once tags. This would be useful for covert operations, or operations in which it was important to not repeat a tag reading. We believe there are other materials that will exhibit erasure.

4.6.6. Unstable tag

Unstable materials provide the option of a tag that is only useful for a specified duration. For instance, NaF has air lifetime of hours. We could make a structure with an extremely narrow window of readability, and therefore enhance security. For instance, we could stabilize a latent image in NaF with an overcoat; when overcoat was removed, we would have less than 1 hour to read message.

4.6.7. Environment sensing tags

If the tag itself is modified by the environment through which it passes, the tag label itself could represent that environment. For instance, HOPG tags will develop 20-30 nm diameter etch pits if exposed to 650°C for 5 minutes in air. Combined with an initially impressed message, this composite tag could be used to track combustibles.

5. EVALUATION OF THE TECHNOLOGY

5.1. ADVANTAGES AND DISADVANTAGES

The tags and tagging systems we have developed in this work have their domain of utility. The conspicuous advantages that led us into this technology include:

- small size
- nonperturbative
- nontoxic
- nonvolatile
- large label capacity
- chemically inert
- difficulty of counterfeiting
- large number of tags
- low cost per tag

After completing our investigation, we see several additional aspects that can be used to advantage:

- many coding schemes
- extensive covert capability
- interface with active electronics

On the other hand, the present approach has certain disadvantages, including:

- slow writing rate
- high error rate
- new technology must be implemented
- expensive ion source required
- technology is composite

The last point is elaborated in a later section

5.2. THE TECHNOLOGY IS COMPOSITE

Perhaps the single most important result of this study is that the technology is not monolithic: there is no one tag or tagging system that circumscribes all, or even most, of the foreseeable applications. At the outset, the concept seemed simple: make a tag, deploy it, collect it, read it. As we learned more about the available materials, invented tags and tagging schemes, explored options, and developed our ideas for applications, it became clear that this concept was naive.

Thus, the above lists of advantages and disadvantages must be used in a modular or compositional sense: some items in these lists might be taken as central for one application, while other items are de-emphasized. If we select one advantageous feature for a specific application, we may hinder or exclude other advantages. It is unlikely that any application could make use of all the advantages listed above simultaneously.

For example, suppose we have an application that requires very high density label on the tag. The material we select, say mica, might not have the stability in high temperature environments we would want. For durability, we might select diamond, but that choice obviates covert use of latent images or code-required reading. For latent imaging, plastics are good, but they may not withstand the chemical environment to which the tag will be subjected. In an attempt to optimize all these functions, we might envision a tag that encapsulates plastic inside a diamond case, or a mica-plastic-diamond sandwich. Clearly, the optimum balance between all available features cannot be determined until the specifics of the application are known.

We expect that some apparent disadvantages could be circumvented, obviated, or turned into advantages. We present here a brief summary of some of these aspects.

5.2.1. Precision steering of the ions is not necessary

There is a tendency to assume that a regular rectangular array of nanobits would be the only useful way to represent the tag label. However, as discussed elsewhere in this report, a random pattern would be *preferred* in certain applications. Aspects of random patterns that can be exploited include:

- A random pattern has exactly no randomness upon re-read. Thus, a very small number of bits is necessary for uniqueness. In operation, one would read each tag, record the pattern, deploy and recover the same tag, and read it again. The process can be done with a relatively small number of tags. This would be useful if the probability of recovering the tag were high. A typical application would be multiple path tracing: a set of tags is inserted at the beginning of a process, one tag in each channel. The tags are recovered at the end of the process, and the connections are thereby determined. An example would be tracking food material in small animal communities. Figure 5.1 shows a set of tags roughly to scale.

Figure 5.1 - A set of tags with random-pattern message. The spatial resolution of these tags as drawn is sufficient to make every tag unique—there is an effectively infinite number of labels.

- A random pattern subjected to a ciphering can contain an arbitrary message. The ciphered message acts as the key for deciphering the tag. Neither the tag nor the cipher is readable alone.

0100110011000110101001	TAG
BCABCD BACCBBADDEBCADABC	KEY
1001011000110111001010	Message

- A random pattern can serve as a code, for deciphering a separate message that was originally coded using that same pattern

010011001100011010100	TAG
E Y X X F K P	Message
M E S S A G E	Deciphered message

- A random pattern could be created as sensitized nanobits, and a scanning operation would write the label. Subsequent reads would recover the pattern. In this circumstance, the surface is essentially being sensitized to receive an image. The advantage of using ions for this is that they are intrinsically localized, hence provide automatic digitization. Figure 5.2 shows an example of this kind of tag.

Figure 5.2 - A tag with sensitized nanobits. An external device is used to alter the state of a subset of the bits, thereby writing the message. On this tag, the message is read along the stripes: the message is 1010000101110010101100.

- A pseudo random pattern can have a message coded within it in a covert way: a subtle modulation of the nanobit density as a function of position, the ratios of numbers of several types of nanobits, the presence of several types of latent nanobits for which particular chemical processing is necessary, etc. Figure 5.3 shows a covertly coded tag.

Figure 5.3 - A tag with a covertly coded message. The message here is not related to the four obvious groups; it is 71364.

5.2.2. An atomically smooth surface is not necessary

There is a tendency to assume that atomically flat surfaces are essential to creating and recognizing the nanobits, and we have spent considerable time in a search for such surfaces. While flat surfaces provide many advantages, rough surfaces can also be used under certain conditions. For instance, the impact of an ion can create chemically reactive sites on a rough surface. Subsequent etching will exhibit the bit pattern, in spite of the roughness. Of course, the bits must be etched to size larger than the characteristic roughness dimension. Figure 5.4 shows this process.

(a) Rough (noisy) surface on substrate provides cover for latent image.

(b) Ion damage creates chemically reactive sites which are not detectable over background noise.

(c) Etching at chemically reactive damage sites develops latent image.

Figure 5.4 - Latent image on a rough surface.

One could turn this around and *create* the rough surface from the ion bombardment. We envision bombarding the surface and then etching until the individual pits overlap. The roughness then will have certain statistical properties, such as fractal dimension, that can be used as the label. Roughness is normally specified by an RMS height variation:

$$s = \langle [h(x,y) - \bar{h}]^2 \rangle^{1/2}$$

The surface is called self-affine if s obeys the following relationship:

$$s \propto L^H$$

where L is the distance measured across the sample and $0 < H < 1$ is the affine exponent. The fractal dimension is

$$D = 3 - H$$

For iron bombarded with Ar^+ ions (Krim, et al., 1993), the exponent was found to be $H(\text{expt}) = 0.53$. In these experiments the surface was roughened by sputtering—it was not etched from individual damage sites.

For ion-induced damage, we expect H to be dependent on the density and extent of overlapping etch pits. Thus, the value of H , and therefore the label, will reflect the etching process.

The advantages of this kind of coding are:

- It allows for the tag to suffer damage without destroying the label, since the label is spread out over the tag
- It will not be immediately obvious how to read the tag label, hence could be used for covert operations
- It can be used on an initially rough surface: the modification of the roughness after etching will give the label.

J. Krim, I. Heyvaert, C. Van Haesdonck, and Y. Bruyneraede, Scanning Tunneling Microscopy Observation of Self-Affine Fractal Roughness in Ion-Bombarded Film Surfaces, *Phys. Rev. Lett.* 70, 57 (1993).

5.2.3. An atomic force microscope is not necessary

In this work we have made extensive use of the scanning atomic force microscope. It is, however, a research tool, and not at all essential for making or using tags. Many of the coding techniques and applications would use a much lower bit density than the ultimate attainable. For these cases, the bits can be etched to sizes that can be seen with the light microscope. Indeed, this was exactly how we first observed the phenomenon, using CR-39. In fact, the etched plastic appeared to the naked eye as crazed; under the light microscope, the individual etch pits were clearly resolved.

We can envision a whole class of chemical readout schemes, in which the damage pattern is processed to decorate and magnify the defects. Etching is but one type of decoration. One could expect to be able to attach functional groups to active sites, and to those attach a detectable structure. No imaging is done until the sites are modified to enhance contrast, or enlarge them to make that imaging easy.

An electron beam could be used for the readout device. Scanning the beam across the surface and measuring the current into the substrate would clearly indicate the locations of etch pits or other electronic defects. The advantage of the electron beam over the AFM is speed; the lower information about the detailed surface topography is of no consequence to the readout of digital information.

Still another approach to site detection is to create the sites on an intrinsically scannable substrate, e.g., a Gunn-effect oscillator. When biased with a voltage above a threshold, a Gunn device (typically GaAs) develops a negative-resistance domain that travels the length of the sample, reflects from the far end, and returns along the length of the sample. The round-trip transit time determines the oscillation frequency. If the material were subject to localized ion-induced damage, one would expect to see perturbations in the local potential as the domain travels, and from that to be able to derive the positions of those defects.

It should also be possible to process the defects into active circuit elements. A damage site can link two scannable planes, like a wire connecting two sides of a circuit board, hence provide a signal for its location.

Finally, if one wishes to continue to use scanning tip microscopy, one now has available microminiaturized versions of the AFM*. The size of the single device is about 100 microns. This would make possible use of arrays of the tips, thereby providing multichannel readout.

**Science* 252, 1252 (1992).

5.2.4. Writing predefined data is not necessary

It is natural to desire to write a predefined message on the tag, and this would certainly be one type of application of this technology. However, it is by no means necessary to be able to utilize the technology developed here. We have already described various coding schemes that can provide a very simple message. For instance, a tag coded by varying amounts of several bit sizes could have a capacity of 1000 patterns. One way to use this capacity would be to assign each of the 1000 numbers to a predefined message. Or we could assign each number to a predefined cipher key, enabling any message to be sent encoded. Or the number could simply be a unique name for use in tracking. In a subsequent section, we list categories of applications. From that list, it is clear that many applications do not require writing a predefined message.

5.3. LIMITS OF THE TECHNOLOGY

5.3.1. Bit size and bit density

We have found experimentally that mica faithfully records single nanobits. The individual damage sites are about 10 nm in size. If we adopt this as the spatial resolution, it implies an ultimate areal density of 10^{14} bits/cm². This implies that tags with a 10^6 -bit label could have area as small as 10^{-8} cm², i.e., a 1 micron square. Probably a more realistic goal would be a tag 10x10 microns, or the 1 micron tag carrying only 10^4 bits. In either case, this kind of tag far exceeds any similar tag in terms of information density.

The minimum size of the nanobits in our experiments is almost certainly determined by the high charge state of the ions. If we used high energy, low charge state ions, the damage sites would be long linear tracks about 1 nm in diameter (there is considerable literature on this). For instance, Tsong and co-workers have used AFM to observe individual defects due to impact of 3 keV Ar⁺ ions on Si(111) and Si(100). For Si(111), a 7x7 hexagonal structure, they found individual craters, each apparently caused by a single ion impact. The average sputtering yield (number of removed Si atoms per incident ion) was about 3.5. Also of interest in that work was the observation that thermal annealing at 950°C completely reversed the damage and restored the surface to its original state. These experiments extend the results from the present project into the domain of single atom removal, and show that, were it possible to steer the ions appropriately, near atomic surface densities of information could be stored, i.e., about 10^{15} /cm².

Note that these results were obtained with singly charged ions. The multiply charged ions create a larger, but better defined, damage site. When we attempt to work with very small sites, we will have only 100-1000 atoms in a site, and "atomic shot noise" on the structures will require a qualitatively different approach to storing the information. Thus, ion nanofabrication reaches the theoretical limit of density for conventional bit storage.

- H. J. W. Zandvliet, M. -H. Tsai, J. D. Dow, and I. S. T. Tsong, Random and ordered defects on ion-bombarded Si(100)-(2x1) surfaces, *Phys. Rev. Lett.* 69, 3076 (1992).
H. Feil, H. J. W. Zandvliet, H. B. Elswijk, E. J. van Loenen, and I. S. T. Tsong, Scanning tunneling microscopy and spectroscopy of ion-bombarded Si(111) and Si(100) surfaces, *Phys. Rev. B* 46, 7581 (1992).

5.3.2. Ion steering and bit density

When we began this work, ion beams could not be focused to smaller than about 100 nm. Currently, both electron and ion beams with focal spot size in the nanometer range are available. Therefore, we believe that we can relatively easily write a bit array on a tag with perhaps 100 nm spacing. This implies a density of 10^{10} /cm², and therefore a 1 micron-square tag could carry a 100-bit label. While not at the ultimate density we believe is possible, it is, of course, quite sufficient for many applications.

In a series of informal memos, one of the present authors (RWS) separately have developed a scheme for stochastic focusing. The basic idea is that the passage of a single low energy high charge state ion near a superconducting wire will induce a voltage in that wire, providing a signal that partially represents the ion trajectory. By feeding this signal to corrective optical elements, the trajectory can be modified to steer the ion to a desired target. Estimates indicate nanometer precision can be attained with this scheme. This scheme has not been experimentally demonstrated. It does, however, provide the dual features of steering the ions with great precision and imposing information, i.e., a pre-defined informational message, on the bit pattern.

Issues Related to the Gridded Wire Adaptive Ion Lens, R. W. Schmieder, Nov. 15, 1990.
Ion Steering with Wire Grids: Preliminary Technical Remarks, R. W. Schmieder, SNLL, Jan. 15, 1991.
Detecting Single Ions with Superconducting Wires, Preliminary Technical Remarks, R. W. Schmieder, SNLL, Feb. 15, 1991.
Experiments to Demonstrate Precision Steering and Detection of Single Ions, R. W. Schmieder, SNLL, and Ian G. Brown, LBL, Apr. 1, 1991.
Ion Trajectories in a Laplacian Potential, R. W. Schmieder, May 15, 1991.
Physics of the EBIS and its Ions. R. W. Schmieder, chapter in: *Physics of Highly Ionized Atoms*, R. Marrus, Ed., (Plenum, 1989).

5.3.3. Writing rates

The high charged state ions used in this work are difficult and expensive to produce, and presently are obtainable in small numbers. The expected performance of the EBIS is reviewed by one of the authors [Schmieder, 1990]. Typical performance of an EBIS is about 10^6 Xe⁺⁴⁴ /sec. This presents a major limitation to the total area that can be written directly with the ions. If we were to attempt to write 1 MB directly to each of 10^6 tags, we would require about 4 months. We could envision scaling the ion sources up by perhaps a factor of 100, but even with this advance, the tags probably would be too expensive.

This seems to point clearly to the idea that replication will be essential. We will need techniques for manufacturing large numbers of tags with essentially the same message. It should be evident from the descriptions in this report that there are various trade-offs to achieve this. First, we see the path to direct nanoscale replication via SAM films and similar ultra-thin lithographic masks. Second, few applications will require tags written at the highest possible density. For these applications, we can use other coding schemes, such as density or pattern coding, and replication schemes of lower resolution but greater ease.

5.4. TURNING APPARENT LIMITATIONS INTO ADVANTAGES

Another expression of the composite nature of the technology developed during this project is that the limits and boundaries of this technology are ephemeral: what appears to be a liability or limitation for one application can very often be turned into an asset or advantage for another. Probably this appears so because we have not yet completely encompassed the full range of applications for the micromechanical tags. To illustrate this process, we cite a few examples.

We have already mentioned the use of random bit patterns. What may appear to be a limitation is turned into an advantage by envisioning preferential use for the random patterns.

Another example is the use of materials with rough surfaces. What at first appears to be a limitation, can be used to advantage for covert operations, or simply to include additional materials with desirable properties.

Our primary concern was to find materials that are stable over long periods, say months or years. But unstable materials can be used to control unwanted access to the tag or its label, to sense extremes of the environment through which the tag passed, or to provide for the long-term degradation or disappearance of the tag. For instance, suppose we had a long-term tracking application in which the tags could not be easily removed from the system. Accumulation of old tags would require reading more and more useless tags, hence slow the process of tracking. If the tags were volatile, they could either disappear completely, or the message (or the entire surface) could become unreadable after a desired period. This situation might arise, for example, in tracking material transport within a community of small animals, where it is impractical to remove the old tags.

Another example is the erasure of the blisters observed on mica, in which the act of reading is destructive. If properly controlled, this kind of process could be a means of security: the tag would be read-once.

5.5. RELATION TO OTHER TECHNIQUES

There are several beam-based lithographic technologies that potentially compete with the single-ion approach investigated here. For completeness, we list reviews of these approaches.

Xray lithography:

J. R. Maldonado, Xray lithography system development at IBM:
Overview and status, *SPIE* 1465, 2 (1991).

Ion beam lithography:

R. L. Kubena, Resolution limits of focused-ion-beam resist patterning,
Mat. Res. Soc. Symp. Proc. 279, 567 (1993).

E beam lithography:

A. N. Boers, Resolution limits for electron-beam lithography, *IBM J. Res. Develop.* 32, 502 (1988).

5.6. CANDIDATE APPLICATIONS

In exploring the range of tag and tagging technology, we have also encountered a range of applications. While the following lists are not comprehensive, they do indicate the several areas

5.6.1. Categories of applications

The tags can have one or more of several uses:

- Connect two end points of a process (track)
- Enable sorting into groups of kind
- Convey a previously unknown message in readily understood form
- Convey a previously unknown message in coded form
- Identify one item on a list of predefined messages
- Provide a key for deciphering a separately sent message
- Provide validation or verification
- Record extremes of the environment through which the tag passes

It should be clear that the nature of the tag, and its operational scheme, will strongly depend on the use to which it will be put.

5.6.2. Material distribution

Tracking is an input-out operation: A process has multiple inputs and multiple outputs. The tag provides the diagram for connecting inputs and outputs. One of the most important uses of tracking is for material control and monitoring. We would like to be able to identify the origin of certain materials, and perhaps even determine something about the environment through which they passed.

Materials that are candidates for tracking are generally controlled substances: drugs, explosives, flammables, toxics, and radioactive materials. In addition, ordinary (uncontrolled) materials would find great value in tag tracking: quality control, interception of incorrect routing or use, impurity control, manufacturing and process control, law enforcement, etc.

For instance, suppose every batch of explosive was tagged. Forensics analysis of an explosion could recover the tag, read it, and thereby determine the origin of the material.

Prescription drugs could carry a tag, providing a record of the manufacturing unit.

Raw materials used in the manufacture of sensitive substances could be tagged, providing a trace to the origin of the materials.

Food products such as salt, sugar, flour, coffee, and spices would be particularly easy to tag, but the tag would have to be inert and biodegradable.

In addition to substances, objects can be tagged. For relatively large objects, say above a few mm, microtags probably would not be necessary. For small objects such as precious gems, computer chips, and insects, a microtag would be essential.

The vision generated by this capability is an economy in which all materials are tagged and tracked. Combination of several raw materials into a composite will generate composite tags. Any irregularity or deviation from specified use or quality would be traceable through the tags. It is obvious that such a scheme must make use of a wide variety of tags, all of which are sufficiently cryptic (small, chemically inert, etc.) to be unobserved and nonintrusive.

5.6.3. Information distribution

A second broad category of application is controlling the spread of information. Here the function is not to track a network, but generally to hide something (information). Motivations range from simple privacy to corporate competitiveness to national security.

The tag can assume any of several roles. It can carry the information itself. It can carry a key to interpreting the information carried by some other means. It can carry a yes/no message that amounts to verification or validation of the tag carrier. It can accumulate new information during its life.

The tag can explicitly display the information in a readily readable form. One could imagine that a precious stone such as a diamond could have a detailed description of its history written on it—when it was mined, who owned it, etc. The pedigree would be easily read by anyone with an appropriate microscope.

Or it can contain the message in visible but coded form. The tag shows a bit pattern that is easily seen, but means nothing without a key, held separately. A labeled diamond could carry a secret message that would be secure, even if intercepted. Carrying it in a microtag on a small object provides considerable security.

The tag can display the information only after a relatively simple processing of the tag. For instance, plastic tags must be etched to enlarge the damage pits. A foreign agent not knowledgeable about the processing will be unable to read the tag.

Taking this last idea to its limit, we can imagine a tag that requires very complex chemical processing to exhibit a predefined result, such as a simple message ("Gone to Roanoke"). Here, the chemical processing is part of the coding.

One reason why covert tags work is that they require a threshold technology to intercept and read them. To the extent that the originators of the tag have that technology and no one else does, the tags are secure and useful. In assessing the value of such operations, one also accounts for the motivation of the foreign agents: if there is little payoff but high cost to intercept and decode, the agent is unlikely to do it.

5.6.4. Natural science, esp. ecology

Population dynamics and the dynamics of ecosystems are large and growing subjects that are beginning to cut across interdisciplinary lines. Not only are biologists and ecologists interested in population dynamics; program managers, resource managers, and long-term planners also are finding it necessary to understand the dynamics of biological populations.

In the past few years, modeling of populations has undergone a major transformation. Previously, lumped, compartmental models tracking numbers of each species in the population were *de rigueur*. Now we are beginning to model the behavior of individuals in the population, extracting the dynamics from appropriate averages and lower-dimensional measures.

As an example, a population of smallmouth bass was simulated by simulating the behavior of individual fish, including their feeding, movement, mating, and other significant functions. The dynamics of the population was summarized by counting the number of individuals, their average position, and other descriptors as a function of time. It is generally acknowledged in the modeling community that these individual-based simulations are the future of the discipline. In the future, we must be able to track the behavior of individuals in order to understand the dynamics.

The main limitation to individual-based ecosystem models is field data on the behavior of the individuals. We are simply ignorant of much of the detailed behavior of even the megafauna (e.g., sharks), to say nothing of mesofauna (birds, fish, rodents, small reptiles, etc.) and microfauna (insects, spiders, other arthropods). While it is common knowledge that bees and ants carry out a complex sequence of operations thereby producing collective behavior of the population, we are totally ignorant of the behavior of individuals in such populations. We see a trail of ants, and describe the *average* ant as traveling between the food source and the nest, but we have virtually no knowledge of what the *individual* ant does. For instance, we do not know whether an individual ant that stumbles into a foreign nest will be incorporated into that colony or excluded. We do

not know what factors will make an individual ant more likely to wander from the trail. We do not know how different an ant must be for those differences to affect its functioning.

In the case of honeybees, in spite of a great body of knowledge about bee colonies and their behavior, we cannot write a model for an individual bee. We can write a model for an *average* individual bee, but such models will produce some sort of average emergent behavior. We know now that emergent behavior is usually chaotic: the exact time of swarming of the hive, its compass direction, its destination, and so on, are determined by extremely tiny differences in initial conditions. Models built from average individuals will not exhibit chaotic behavior, or that behavior will be grossly wrong.

Obviously the requirement is to obtain more detailed information about the behavior of individuals. It is a fact that the smaller the individuals in an ecosystem are, the more significant they are in determining the ecosystem dynamics. We take it as axiomatic that insect populations are among the most important to understand. But how can we learn more about the behavior of individual insects?

It seems obvious that tracking of individual insects could be a powerful tool. One could imagine monitoring the coming and going of individual bees, and perhaps their visits to certain flowers. For this, we would need a unique tag that could be attached to the individual insects, and read at appropriate intervals.

Tag would also be useful for tracking substances in the ecosystem. For instance, a rodent might eat some grain, be eaten in turn by a hawk. The spore of the hawk might be incorporated into a nest by another bird, which might be partially consumed by other predators. These material pathways are largely unknown and unsuspected, but they could be elucidated by tag tracking.

Obviously in all these applications, the tag must be very small, chemically inert, and capable of carrying a large label. The micromechanical tags developed in this project would seem to have advantages in these applications.

A few final remarks: For population tracking (whether it be biological populations or not), the need for many sensibly identical tags with different labels is central. It is this aspect that enables parallel data collection. Without this, the tracking process would be too inefficient to give sufficient data.

It should be remembered that what we are seeking is evidence for internal connections which are currently hidden from us. These connections are hidden because of the nature of the objects (flies fly fast and far). We need additional means for observing these connections, and tagging is one such means.

We reiterate that it is not enough to observe 1000 ants working cooperatively and say that we understand how they do it. The system is so sensitive to individual behavior, of which we are ignorant, that we cannot hope to succeed in all but the coarsest of lumped models.

Finally, what would be the motivation for doing all this work? Although we consider this self-evident, perhaps it is worth remarking that global and societal goals include reduction of pesticides, increase of crop yields, reduction of disease vectors, and conservation of natural resources. To the extent that population dynamics can contribute to understanding ecosystem dynamics, the kind of tool provided by these micromechanical tags will be a valuable tool.

- F. Lieutier, R. Ham, M. C. Ham, and J. Garcia, Individual tagging of bark beetles for laboratory studies, *Agronomie* 6(8), 773-776 (1986).
- F. Onder and F. Tezcan, Marking methods in entomological research, *Bitki Koruma Dergisi (Turkey)* 10(3), 185-192 (1986).
- G. F. Oster, Foraging energetics of Bombidae, Univ. Calif. Berkeley NSF Contract/Grant DEB77-27072, May, 1978-Sept., 1980. [Labeling of individual bees with micro-electronic tag].

6. EXTENSIONS OF THE TECHNOLOGY

During the course of this project, we have encountered a wide range of technologies and applications that have many aspects in common with the present work. Generally these fall into two categories: (1) nanofabrication; (2) active circuit devices.

The connection of micromechanical tags with nanofabrication is obviously very close: In order to record the tag label we are fabricating a nanometer structure. The tag material, matrix, and process, the contrast of the nanobit against the noisy background, the method of chemical processing and of reading the label, and many other aspects of tags and tagging depend on the ability to reliably fabricate nanometer structures. The interesting aspect here is that, given the ability to fabricate such structures, there are many applications of the techniques.

The connection with active circuit devices is not as direct, but just as significant. While this project has pursued *passive* tags, there is a wide field of application of *active* tags. In one approach, these tags would accept, store, and process information, and provide some facility for effecting a change in the outside world based on that processing. There are already such tags in wide use: in some countries, a chip on a credit-card is used as a local computer to manage the time and money for calls from public telephones. In another approach, we envision the active circuit elements to be an intrinsic part of the readout of the tag label. This would provide the option to alter the label during use, providing information about the process through which the tag passed.

Because of the nearness of these technologies to the present work, we include here some of that material.

6.1. NANOFABRICATON

The essential concept in ion nanofabrication is that the ion defines a nanometer-size region on the surface by causing permanent chemical change. This region is subsequently processed to produce a useful object (bit, active device, etc.). The technology is based on the simple fact that it takes some eV of energy to cause a bond break in the solid and there are some tens of keV of (total) energy available from an ion; the damaged region must be confined to a distance of some nanometers from the point of impact, and this is observed for both high-KE/low-Q and low-KE/high-Q ions. The extremely small size (comparable to, or smaller than, the best focused electron and ion beams) of the ion-induced chemical disturbance immediately suggests that this mechanism could be useful for nanofabrication, which is the basis for the present project.

- M. Sundaram, S. A. Chalmers, P. F. Hopkins, and A. C. Gossaro, New Quantum Structures, *Science* 254, 1326 (1991).
- W. P. Kirk and M. A. Reed, eds., *Nanostructures and Mesoscopic Systems*, Academic Press, London (1992).
- A. Ulman, *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly*, Academic Press, London (1991).
- R. W. Siegel, *Nanostructured Materials*, *Nanostructured Materials* 3, 1 (1993).
- G. A. Ozin, Nanochemistry: Synthesis in Diminishing Dimensions, *Adv. Mater.* 4, 612 (1992).
- G. M. Whitesides, J. P. Mathias, and C. T. Seto, Molecular self-assembly and nanochemistry: A chemical strategy for the synthesis of nanostructures, *Science* 254, 1312 (1991).

6.1.1. Characteristics

Ion nanofabrication has the following characteristics:

- The characteristic dimension is nanometers.
- The quantum efficiency is unity: every ion that reaches the surface creates a damage site. The event threshold is that the site must have sufficient chemical contrast against the surface material that subsequent chemical processing can produce discernible differences from the undamaged material.
- Damage sites are produced for a wide range of materials. Metals are difficult to damage, insulators are easy.
- All damage sites are essentially identical, given identical ions. This is important if we want to simply count sites (1 site = 1 binary bit).
- The geometry and nature of the damage sites depend on the ion charge, kinetic energy, mass, angle of incidence, and the nature of the solid surface and bulk.

In Figure 6.1 we compare the sizes of a laser CD bit, the smallest focal spot attainable with electron beam lithography, a damage site created by ion impact (a nanobit), and a single atom. Many of the potential applications described in this paper are enabled because of the extremely small size of the ion damage site, but in other cases it is the ability to chemically modify the site, to take advantage of its geometry or the fact that the damage is permanent, that offers unique advantages for certain applications. While this technique is only one of many being developed, it appears to have sufficient promise to motivate the present discussion.

Figure 6.1 - Comparison of bit sizes.

In Figure 6.2 we show some of the possible variations in geometry. In our experiments we have observed the general geometrical variations shown in these figures.

In implementing ion nanofabrication, the ability to precisely steer the ions is important (although by no means essential—there are applications that can use randomly positioned ions.). At present, there is no technology that can place ions with nanometer precision. However, one of the present authors (RWS) has proposed using micron-spacing grids of superconducting wires to determine the trajectory of individual ions and provide corrections to their trajectories. Low kinetic energy ions are required for this technique, since there must be sufficient time to calculate the corrections. A conceptual scheme for implementing the trajectory-control is shown in the reports by RWS.

Figure 6.2 - Altering the geometry of the damage site. (a) Varying the depth of damage; (b) Varying the shape of the damage.

6.1.2. Areas of Application

Once the idea that low-energy, high charge state ions can cause nanometer-sized surface-confined damage that can nucleate (and localize) subsequent chemical processing is realized, a host of applications is apparent. Table 6.1 lists a variety of such applications.

Table 6.1 - Applications of nanofabrication

Subject	Description
Image Storage	Archives, smart devices, mapping, climatology, large-scale calculations with images
Special Projects	Small number, high cost items (spacecraft, weapons, supercomputers)
Encryption	Coding, passkeys
Intelligence	Covert information transport
Tagging	ID of documents including currency and securities, art objects, gemstones, tracking controlled substances such as drugs, explosives
Entertainment	Audio, video, interactive games
Nanocircuits	VVLSI, CCD's, superlattice devices (neg. diff res.), quantum wires, ballistic point contacts
Imaging Electronics	Diode arrays, incl. preprocessing, IR detectors
Ion Detection	Low energy passive detector, absolute ion gauge
Ion Optics	Pits (pos. or neg.) as optical elements, aberration correcting devices, image mixing, real-time processing, single ion steering, detection
Nanomachining	Tuning resonances in mechanical filters, figuring
Optical Figuring	Xray optics
Electron Microscopy	Calibration, resolution testing, STM multilayer fabrication and scanning
Analysis	Chemical analysis, archaeology, forensics
Processing	Polymer etching, building, pit size control, multiple pit types, localized polymer breaking, insertion
Plasma Diagnostics	Ion identification, imaging
Chemistry	Electric field catalysis, nanopore filters, isotope separation
Mensuration	Calibrated roughness, texture
Alignment, Jigging	Lithography masks, mechanical stability, dynamic corrections
Gas Logic	Control of micro amounts of gasses by mechanical switching of micro-reservoirs
Vacuum Technology	Calibrated nanoleak
Crystal Growth	Nucleating sites

6.2. ACTIVE CIRCUIT DEVICES

There is currently an enormous effort worldwide to develop techniques for fabrication of useful electronic devices of nanometer size. Because conventional lithographic techniques are limited to dimensions of 100 nm or more, many alternative schemes are being sought. These techniques involve both destructive (e.g., mechanical damage, chemical etching) and constructive (e.g., polymerization, biosynthesis) mechanisms. Many techniques are being investigated, and every technique has its own advantages, disadvantages, and domain of applicability. It is not an exaggeration to say that any substantially new technique will have an impact on the technology. This proposal offers a new technique for fabrication of electronic devices of nanometer dimensions.

The central technical issue is how to alter some property of a solid surface within a region of some nanometers. One way is to increase the chemical contrast of the site against the substrate: if a nanometer sized site can be made chemically reactive to *something*, a series of chemical transformations can be envisioned that would build a nanometer device with desired electrical behavior. The key assumptions are that: (1) we have a means for defining a chemically active nanometer site; (2) the dimensions of the active site stay within acceptable limits through the desired chemical processing.

On the basis of our understanding of the ion-surface interaction, we believe that we are now in a position to fabricate a complete quantum circuit element.

We envision device fabrication as a 3-step process:

- (1) preparation of a suitable layered surface;
- (2) creation of a chemically active nanometer site by impact of a low energy ion;
- (3) fabrication of the device by chemical and/or physical processing.

6.2.1. Junction diode

A simple first step would be to construct a p-n junction diode using the process illustrated in [Figure 6.3](#) [from J. Gillaspay, NIST]. A layer of oxide on a silicon substrate is damaged by the impact of a high charge state, low kinetic energy ion. The damaged area is etched away, leaving a nm-sized circular mask opening. Boron is diffused into the silicon substrate through the opening, while the surrounding oxide provides the mask. The boron-doped Si is a p-type semiconductor; an evaporated metal electrode provides contact to the p-n diode.

It is clear that while the ion provides the intrinsic nanometer scale site definition, the success of this technique for device fabrication depends also on finding ultrathin layers that can act as masks, and appropriate chemical processing steps. In addition to oxides, we find that the most promising materials for this use are ultrathin self-assembled monolayer (SAM) films. Because of their potential importance to this project and to nanofabrication in general, we take some space here to review these structures and how they might be used to fabricate quantum devices.

Figure 6.3 - Proposed technique for synthesizing a p-n junction using ion nanofabrication.

6.2.2. Metal-insulator-semiconductor devices

SAM films form spontaneously on a variety of substrates and consist of: (1) a head group which covalently bonds to the substrate; (2) an alkyl chain; and (3) a surface functional group which can be engineered to provide specific characteristics. Typical SAM films are on the order of several nanometers thick, are highly insulating, and are resistant to most acids and organic solvents.

SAM films have been studied as high-resolution masks for nanometer scale lithography and replication. In one scheme the SAM film is patterned by an electron beam and used directly as an etch mask. The organosilane *n*-octadecyltrichlorosilane (OTS) and the alkanethiol *n*-octadecanethiol (ODT) have been used to transfer 25 nm patterns onto SiO₂ and GaAs, respectively. Another scheme involves x-ray, UV, electron beam, or ion beam cleavage of the SAM functional group followed by catalyzation and electrodeless metal deposition on the unexposed surface. Other materials known as PEDA, CMPTS, and PYR have been used to transfer patterns of several hundred nanometers onto SiO₂ substrate. An OTS film has been used as an ultrathin insulating layer in a metal-insulator-semiconductor (MIS) device. In that work, a 2.8 nm film of OTS was assembled on the native oxide layer of a p-type boron-doped Si (100) wafer, and a 1 nm thick dot of Al was laid on top of the OTS to complete the device.

Based on these results at somewhat larger scale, we believe that irradiation of an SAM film, resulting in nanometer scale modification of surface functional groups, and subsequent chemical processing could lead to nanometer scale junctions between highly insulating materials and metals or semiconductors. A process in which metal is deposited at exposed damage sites could be used to construct an active MIS device is illustrated in Figure 6.4.

Figure 6.4 - Proposed technique for fabricating a MIS device.

In addition to using SAM films as masks and ion impact to define the sites, we believe we can implement maskless fabrication techniques. This is based on the fact that the ion impact site is chemically active. Maskless growth and/or doping at high charge state ion damage sites would be an ideal means of building active devices, since eliminating mask materials and chemical etching would improve spatial resolution. In this regard, we note that selective epitaxial growth of InP single crystals on nanometer scale ion beam damage patterns in GaAs has recently been demonstrated.

Finally, alkanethiol SAM films have been used to bind CdS semiconducting nanocrystals to Au and Al surfaces, creating 1-10 nm diameter quantum dots. Free thiols in the SAM film bind readily to cadmium, suggesting another scheme for creating active devices: high charge state ions would be used to damage a surface, creating reactive sites onto which gold is deposited. Alkanethiol SAM films are assembled on the nanometer scale gold deposits, and CdS is bound to free thiols on the SAM film surface.

Metal Halides, including AlF_3 , NaCl , and LiF , have been studied as possible high resolution electron beam resists. E-beam irradiation causes dissociation of halide ions followed by formation of a metallic state. For AlF_3 it is found that Al coats the walls of the 10 nm diameter electron beam damage sites.

Since AlF_3 is an insulator ($\approx 10^{13} \Omega\cdot\text{m}$) and Al is a conductor ($\approx 10^{-8} \Omega\cdot\text{m}$), the possibility for an active device exists. Assuming it is possible to deposit a thin film of AlF_3 on a doped semiconductor substrate, a MIS device could be constructed. Figure 6.5 shows a process for fabricating a MIS device using this technique.

Figure 6.5 - Proposed techniques for fabricating an MIS.

6.2.3. Anisotropic conductors

Layered materials with high conductivity parallel to the surface and low conductivity normal to the surface may yield interesting device properties when damaged by high charge state ions. β -aluminas, which consist of alternating layers of insulating Al_2O_3 and conducting planes. Additional materials might include two dimensional conducting polymers such as polyacetylene or polypyrrole.

6.3. BIOSENSORS

A growing area of interest in chemical-specific biosensors. Since these devices must be as small as possible to be nonintrusive, and since arrays of them could be used to form a spatially-resolved detector, the techniques discussed here might find application in that field.

K. D. Wise and K. Najafi, Microfabrication techniques for integrated sensors and microsystems, *Science* 254, 1335 (1991).

7. SUMMARY

7.1. PROJECT ACCOMPLISHMENTS

This project has resulted in the following specific developments:

- The predicted damage in solids by low-energy, high charge state ions was experimentally observed.
- A large number of materials were examined for possible use as micromechanical tags, and a variety of appropriate materials were found.
- A new physical phenomenon, charge-induced delamination blistering, was observed in mica, providing a new mechanism for writing nanobits on surfaces.
- The minimum size of nanobits, and therefore maximum information density (10^{14} bit/cm²) was determined for several materials.
- Latent image formation and development was demonstrated using a plastic.
- A large number of new classes of tags and tagging were envisioned, broadening the range of potential applications far beyond the original concept.
- SAM films were identified as a route to replication and pattern transfer.
- A variety of techniques were identified for relaxing the technological requirements, such as obviating the need for the AFM, ion steering, and atomically smooth surfaces.
- A large number of coding schemes were invented to extend the range and flexibility of the tag label.
- Enhancement of the nanobits by preprocessing, e.g., by etching and by electron beam irradiation, was demonstrated.
- The link between tags and active quantum circuit devices was elaborated, providing a direction for future work that would enhance both technologies.

7.2. FUTURE DIRECTIONS

The following areas seem to us the most promising for future development of this technology:

- Search for additional materials with favorable properties, such as smooth surface, chemical inertness, and machinability.
- SAM films as a path to replication and pattern transfer.
- Stochastic ion focusing, possibly using a grid of superconducting wires, for controlling the locations of damage sites to nm dimension.
- Additional means for readout of the stored information, such as direct circuit connection, electron beam scanning, etc.
- Demonstration of nonlinear or quantum circuit devices fabricated with ion impact, and the integration of quantum circuitry with nm data storage.

8. ANNOTATED BIBLIOGRAPHY

8.1. GENERAL

8.1.1. Nanotechnology

- N1) R.W. Schmieder, R.J. Bastasz, **Potential Technological Applications of Low Energy, High Charge-State Ions**, in *Proceedings of the 6th International Conference on the Physics of Highly Charged Ions*, 274, 675 (1992).
- N2) R.W. Schmieder, **Comparison of Nanotechnologies: Why Should We Use EBIT Ions?** (1991).
- N3) R.W. Schmieder, **Notes on Nanotechnology**, (1990).

8.1.2. Atomic Force Microscopy

- AFM1) J. Frommer, E. Meyer, **Atomic Force Microscopy: A Tool for Surface Science**, J. Phys.: Condens. Matter, 3, S1 (1991).
[Review article: *Cadmium Arachidate LB film, AgBr single crystal*]
- AFM2) E. Meyer, J. Frommer, **Forcing Surface Issues**, Physics World, April 1991, p. 46.
[Review article: *Cadmium Arachidate LB film, AgBr single crystal*]
- AFM3) P.K. Hansma, V.B. Elings, O. Marti, C.E. Bracker, **Scanning Tunneling Microscopy and Atomic Force Microscopy: Application to Biology and Technology**, Science, 242, 209 (1988).
[Review article: *HOPG, GaAs, BN, Pt-C replicas*]
- AFM4) R. Pool, **The Children of the STM**, Science, 247, 634 (1990).
[Research News review]
- AFM5) D. Rugar, P. Hansma, **Atomic Force Microscopy**, Physics Today, October 1990, p. 23.
[Review: *HOPG, NaCl, Polyalanine*]
- AFM6) S. Hosaka, Y. Honda, T. Hasewaga, T. Yamamoto, M. Kondo, **Ultrahigh Vacuum Atomic Force Microscope Using a Pantograph Inchworm Mechanism**, Rev. Sci. Instrum., 64 (12), 3524 (1993).
[AFM atomic resolution images of MoS_2 and $\text{Si}(001)$ using new system]
- AFM7) G. Friedbacher, P.K. Hansma, E. Ramli, G.D. Stucky, **Imaging Powders with the Atomic Force Microscope: From Biominerals to Commercial Materials**, Science, 253, 1261 (1991).
[AFM images of CaCO_3 , SrCO_3]
- AFM8) M. Radmacher, R.W. Tillmann, M. Fritz, H.E. Gaub, **From Molecules to Cells: Imaging Soft Samples with the Atomic Force Microscope**, Science, 257, 1900 (1992).
[AFM review/imaging: *Cd-arachidate LB film*]
- AFM9) E. Meyer, H. Heinzelmann, P. Grütter, T. Jung, H.R. Hidber, H. Rudin, H.J. Güntherodt, **Atomic Force Microscopy for the Study of Tribiology and Adhesion**, Thin Solid Films, 181, 527 (1989).
[AFM review: *h (SAM5,15)*]
- AFM10) H. Heinzelmann, E. Meyer, L. Scandella, P. Grütter, T. Jung, H. Hug, H.R. Hidber, H.J. Güntherodt, **Topography and Correlation to Wear of Hydrogenated**

- Amorphous Carbon Coatings: An Atomic Force Microscopy Study, *Wear*, 135, 109 (1989).
 [AFM review: HOPG, amorphous carbon coatings]
- AFM11) C.M. Mate, An Atomic Force Microscope Study of Polymer Lubricants on Silicon Surfaces, (submitted to PRL, August, 1991).
- AFM12) G.S. Blackman, C.M. Mate, M.R. Philpott, Atomic Force Microscope Studies of Lubricant Films on Solid Surfaces, *Vacuum*, 41 (4-6), 1283 (1990).
- AFM13) Atomic Force Microscopy, A Current Perspective, *Digital Instr. Nanotips*, 5 (1), 1993.
- AFM14) B. Drake, C.B. Prater, A.L. Weisenhorn, S.A.C. Gould, T.R. Albrecht, C.F. Quate, D.S. Cannell, H.G. Hansma, P.K. Hansma, Imaging Crystals, Polymers, and Processes in Water with the Atomic Force Microscope, *Science*, 243, 1586 (1989).
 [AFM images of mica and polyalanine adsorbed on glass]

8.1.3. Micromechanical Tags

- MT1) R.W. Schmieder, LDRD progress reports and micromechanical tag notes (92-93).
- MT2) D. Palmer, correspondence with RWS regarding manufacture of individual tags (1992).
- MT3) E. Pennisi, Bolder Bar Codes: Squeezing More Information into those Black-and-White Symbols, *Sci. News*, 140, 106 (1991). [Two-dimensional bar code scheme]

8.1.4. High Charge State Ion Surface Damage

- HCSI1) D.C. Parks, R.J. Bastasz, R.W. Schmieder, M. Stöckli, AFM Imaging of Nanometer-size Surface Features Produced on Mica by Single High-Charge-State Ions, (in prep).
- HCSI2) R.W. Schmieder, R.J. Bastasz, Surface Damage Caused by Single, Low Energy, High-Charge-State Ions, in Proceedings of the 6th International Conference on the Physics of Highly Charged Ions, 274, 690 (1992).
- HCSI3) D.H. Schnieder, M.A. Briere, J. McDonald, J. Biersack, Ion/Surface Interaction Studies with 1-3 keV/amu Ions up to Th^{80+} , *Radiat. Eff. Defects Solids*, 127, 113 (1993).
- HCSI4) G. Schiwietz, D. Schneider, M. Clark, B. Skogvall, D. DeWitt, J. McDonald, Particle Emission Induced by the Interaction of Highly Charged Slow Xe-Ions with a SiO_2 Surface, *Radiat. Eff. Defects Solids*, 127, 11 (1993).
- HCSI5) D. Schneider, W. Siekhaus, M.W. Clark, J. McDonald, W. Bateson, J. Biersack, M.A. Briere, Atomic Displacement Due to the Electrostatic Potential Energy of Very Highly Charged Ions at Solid Surfaces, UCRL-JC-111718 Lawrence Livermore National Laboratory Report.
- HCSI6) J. Ackerman, S. Grafström, M. Neitzert, R. Neumann, C. Trautmann, J. Vetter, N. Angert, Scanning Force Microscopy of Heavy-Ion Tracks, *Radiat. Eff. Defects Solids*, 126, 213 (1993).
 [Etched tracks of: Pb^{26+} on polycarbonate, Xe^{21+} on polyimide, and Au^{24+} on glass]

HCSI7) H. Kemmer, S. Grafström, M. Neitzert, M. Wörtge, R. Neumann, C. Trautmann, J. Vetter, N. Angert, Scanning Tunneling Microscopy of Surface Modifications Induced by UNILAC Heavy-Ion Irradiation, *Ultramicroscopy*, 42-44, 1345 (1992).
[15 MeV/u Au^{24+} ions on HOPG]

HCSI8) S. Bouffard, J. Coutsy, Y. Pennec, F. Thibaudau, STM and AFM Observations of Latent Tracks, *Radiat. Eff. Defects Solids*, 126, 225 (1993).
[2.82 MeV/a U^{55+} ions on HOPG and Mica]

HCSI9) T. Hagen, S. Grafström, R. Neumann, J. Ackermann, J. Vetter, N. Angert, Scanning Force Microscopy of Heavy-Ion Irradiated Mica, *GSI-Nachrichten*, 3, 7 (1993).
[AFM study of 11.4 MeV/u Pb^{28+} damage sites on mica substrate]

8.1.5. Ion Tracks

IT1) P.B. Price, M.H. Salamon, Advances in Solid State Nuclear Track Detectors, *Int. J. Radiat. Appl. Instrum., Part D: Nuclear Tracks*, 12 (1-6), 5 (1986).
[α -particle tracks in mica, CR-39, Rodyne polycarbonate, and Cronar polyester]

IT2) R. Scholz, J. Vetter, S. Hopfe, Observation of Latent Heavy-Ion Tracks in GeS by transmission Electron Microscopy, *Radiat. Eff. Defects Solids*, 126, 275 (1993).
[11.4 MeV/n Au ions and 13 MeV/n Dy ions on GeS basal plane cleavage surface]

IT3) I.H. Wilson, N.J. Zheng, U. Knipping, I.S.T. Tsong, Effects of Isolated Atomic Collision Cascades on SiO_2/Si Interfaces Studied by Scanning Tunneling Microscopy, *Phys. Rev. B*, 38 (12), 8444 (1988).
[50 nm pits from 100 keV Ge^+ and As^+ ions in Si]

IT4) P.B. Price, M.H. Salamon, Fossil Tracks of α -Particle Interactions in Minerals, *Nature*, 320 (6061), 425 (1986).
[Nuclear decay fossil tracks in mica]

8.1.6. Books

B1) Y. Kim, I. Electron Transfer Reactions in Binuclear Model Systems. II. Scanning Probe Microscopy Studies of Transition Metal Dichalcogenides Materials: Atomic to Nanometer Scale Properties and Surface Modifications, Ph.D. Thesis, Harvard University, 1992.
[AFM studies and surface machining of MoO_3 / MoS_2 materials]

B2) W.P. Kirk, M.A. Reed, eds., Nanostructures and Mesoscopic Systems, Academic Press, London 1992. 551 pp.
[International symposium: May, 1991]

B3) M.A. Reed, W.P. Kirk, eds., Nanostructure Physics and Fabrication, Academic Press, London 1989. 523 pp.
[International symposium: March, 1989]

B4) A. Ulman, An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly, Academic Press, London 1991. 442 pp.
[Definitive modern reference]

B5) C. Weisbuch, B. Vinter, Quantum Semiconductor Structures: Fundamentals and Applications, Academic Press, London 1991. 252 pp.
[has not been examined]

B6) G.J. Ashwell, ed., *Molecular Electronics*, Wiley, New York 1992. 362pp.
[Definitive modern reference]

B7) G. Roberts, ed., *Langmuir-Blodgett Films*, Plenum Press, New York 1990.

8.2. MATERIALS

8.2.1. Mica (Muskovite)

M1) D. Snowden-Ifft, P.B. Price, L.A. Nagahara, A. Fujishima, *Atomic-Force-Microscopic Observations of Dissolution of Mica at Sites Penetrated by keV/nucleon Ions*, Phys. Rev. Lett., 70 (15), 2348 (1993).

[AFM study of 200 keV Ag alpha decay ion damage in mica]

M2) F. Thibaudau, J. Cousty, E. Balanzat, S. Bouffard, *Atomic-Force-Microscopy Observations of Tracks Induced by Swift Kr Ions in Mica*, Phys. Rev. Lett., 67 (12), 1582 (1991).

[AFM study of MeV/u Ar ion damage in mica]

M3) Y. Carmi, A.J. Dahm, S.J. Eppell, W. Jennings, R.E. Marchant, G.M. Michal, *Atomic Force Microscope and Auger Electron Microscopy Studies of Thin Film Ultrasmooth Au-Cr Films on Mica*, J. Vac. Sci. Technol. B 10 (5), 2302 (1992).

[AFM study of ultrasmooth Au-Cr films on mica]

8.2.2. Highly Oriented Pyrolytic Graphite (HOPG)

HOPG1) H. Chang, A. Bard, *Formation of Monolayer Pits of Controlled Nanometer Size on Highly Ordered Pyrolytic Graphite by Gasification Reactions as Studied by Scanning Tunneling Microscopy*, J. Am. Chem. Soc. 112, 4598 (1990).

[Controlled etching of graphite defect sites into nm-scale pits with monolayer depth]

HOPG2) J.D. Noll, J.B. Cooper, M.L. Myrick, *Analysis of Highly Ordered Pyrolytic Graphite Step Defects Via Scanning Tunneling Microscope*, J. Vac. Sci. Technol. B, 11 (6), 2006 (1993).

[Natural defects on cleavage surface of HOPG]

HOPG3) H. Chang, A.J. Bard, *Observation and Characterization by Scanning Tunneling Microscopy of Structures Generated by Cleaving Highly Oriented Pyrolytic Graphite*, Langmuir, 7 (6), 1143 (1991).

[Natural defects on cleavage surface of HOPG]

HOPG4) C.R. Clemmer, T.P. Beebe, Jr., *Graphite: A Mimic for Dna and Other Biomolecules in Scanning Tunneling Microscope Studies*, Science, 251, 640 (1991).

[Natural defects on cleavage surface of HOPG]

HOPG5) T.R. Albrecht, M.M. Dovek, M.D. Kirk, C.A. Lang, C.F. Quate, D.P.E. Smith, *Nanometer-scale Hole Formation on Graphite Using a Scanning Tunneling Microscope*, Appl. Phys. Lett., 55 (17), 1727 (1989).

[Mechanical Indentation of HOPG with STM tip]

HOPG6) E.A. Eklund, R. Bruinsma, J. Rudnick, R.S. Williams, *Submicron-Scale Surface Roughening Induced by Ion Bombardment*, Phys. Rev. Lett., 67 (13), 1759 (1991).

[HOPG surface roughening due to sputter etching]

8.2.3. Highly Oriented Pyrolytic Boron Nitride (HOPBN)

HOPBN1) T.R. Albrecht, C.F. Quate, Atomic Resolution of a Nonconductor by Atomic Force Microscopy, J. Appl. Phys., 62 (7), 2599 (1987).
[Atomically flat surfaces on HOPG, MoS₂, and HOPBN]

HOPBN2) T.R. Albrecht, C.F. Quate, Atomic Resolution with the Atomic Force Microscope on Conductors and Nonconductors, J. Vac. Sci. Technol. A, 6 (2), 271 (1988).
[Atomically flat surfaces on HOPG, MoS₂, and HOPBN]

8.2.4. Metal Films (Au, Au-Cr, Ti, Ta, Pt, Pt/C, Pt/Ir, Pt/C/Ir, Va, Cr, Ni, Ag, Zr, Nb)

MF1) Y. Carmi, A.J. Dahm, S.J. Eppell, W. Jennings, R.E. Marchant, G.M. Michal, Atomic Force Microscope and Auger Electron Microscopy Studies of Thin Film Ultrasmooth Au-Cr Films on Mica, J. Vac. Sci. Technol. B 10 (5), 2302 (1992).
[AFM study of ultrasmooth Au-Cr films on mica]

MF2) G. Devaud, K. Douglas, Microstructural Modification by Fast Atom Beam Milling of Nanotextured Ultrathin Metal Films, J. Vac. Sci. Technol. B 11 (1), 32 (1993).
[Thin metal film mask using biological pattern and a variety of metals]

MF3) P. Gadenne, C. Sella, M. Gasgnier, A. Benhamou, Structural, Optical, and Electrical Properties of Evaporated and Sputtered Au-Cr Thin Films, Thin Solid Films, 165, 29 (1988).
[abstract and references only - full article is 21 pgs.]

MF4) S. Buchholz, H. Fuchs, J.P. Rabe, Characterization and Modification of Conducting Substrates for Ultrathin Organic Films by Scanning Tunneling Microscopy, Adv. Mater., 3 (1), 51 (1991).
[Au film on HOPG as substrate for growing SAMs]

8.2.5. Polymers (Teflon, CR-39, PMMA, Epoxy, Poly-Carbonate, Poly-Styrene)

P1) R.R. Rye, A.J. Ricco, Patterned Adhesion of Electrolessly Deposited Copper on Poly(Tetrafluoroethylene), J. Electrochem. Soc., 140 (6), 1763 (1993).
[Cu film on non-irradiated areas of PTFE after subsequent etching]

P2) H. Hansma, F. Montamedi, P. Smith, P. Hansma, J.C. Wittman, Molecular Resolution of Thin, Highly Oriented Poly(Tetrafluoroethylene) Films with the Atomic Force Microscope, Polymer, 33 (3), 647 (1992).
[AFM study of thin, easily manufactured teflon film]

P3) J.C. Wittman, P. Smith, Highly Oriented Thin Films of Poly(Tetrafluoroethylene) as a Substrate for Oriented Growth of Materials, Nature, 352, 414 (1991).
[Oriented Teflon thin film is used to grow various oriented polymer thin films]

P4) A. Celerier, J. Machet, Metallization of Polytetrafluoroethylene Substrates by Ion Plating, Thin Solid Films, 148, 323 (1987).
[Cu thin film on PTFE by essentially RIE]

P5) S.P. Ahlen, G. Tarlé, P.B. Price, Studies of Relativistic Uranium Nuclei with Dielectric Track Detectors, Science, 217, 1139 (1982).
[Example of CR-39 being used as a nuclear detector]

- P6) B.G. Cartwright, E.K. Shirk, P.B. Price, **A Nuclear-Track-Recording Polymer of Unique Sensitivity and Resolution**, Nucl. Instr. Methods, 153, 457 (1978).
[Original source article for CR-39 as a nuclear particle detector]
- P7) R.W. Schmieder, R.J. Bastasz, **Surface Damage Caused by Single, Low Energy, High-Charge-State Ions**, in Proceedings of the 6th International Conference on the Physics of Highly Charged Ions, 274, 690 (1992).
[High charge state ion damage to CR-39 surface]
- P8) E. Hamada, R. Kaneko, **Micro-Tribological Evaluations of a Polymer Surface by Atomic Force Microscopes**, Ultramicroscopy, 42-44, 184 (1992).
[Mechanical properties of PMMA, Epoxy, and Poly-Carbonate]
- P9) H. Bu, E. Chen, J. Yao, S. Xu, Y. Kuang, **Scanning Tunneling Microscopy Studies of Single-Molecule Single-Crystals**, Polymer Eng. Sci., 32 (17), 1209 (1992).
STM Study of isotactic polystyrene on Au covered mica and HOPG]
- P10) J.M.J. Fréchet, **High Performance Resist Materials**, National Nanofabrication Facility Research Accomplishments 1991-1992, p. 134.
[Chemically amplified resist based on polymer crosslinking]
- P11) N. Stoffel, M. Calistri-Yeh, K.H. Dai, A. Dunne, E. Kim, L.J. Norton, P. Silberzan, E.J. Kramer, **Physical Properties of Polymer Films and Interfaces**, National Nanofabrication Facility Research Accomplishments 1991-1992, p. 144.
[Study of :Polymide, PS, PVP, OTS,UTS film adhesion to substrate]
- P12) F. Rodriguez, S.K. Obendorf, T.Long, C.P. Lei, **Polymer Resist Systems for Microlithography**, National Nanofabrication Facility Research Accomplishments 1991-1992, p. 151.
[Poly(4-hydroxystyrene) [P4HS] as a replacement for Novolac resist]
- P13) C.M. Mate, V.J. Novotny, **Molecular Confirmation and Disjoining Pressure of Polymeric Liquid Films**, J. Chem. Phys., 94 (12), 8420 (1991).
[AFM study of liquid fluorocarbon polymer films - not real useful]
- P14) D. Li, M.A. Ratner, T.J. Marks, C.H. Zhang, J. Yang, G.K. Wong, **Chromophoric Self-Assembled Multilayers. Organic Superlattice Approaches to Thin-Film Nonlinear Optical Materials**, J. Am. Chem. Soc., 112, 7389 (1990).
[Polymeris layers introduced into SAM to improve structural stability]
- P15) J. Brandrup, E.H. Immergut, eds., **Polymer Handbook**, Wiley & Sons, New York, 1989, v35-v44.
[Physical constants of PTFE]
- P16) L.C. Sawyer, D.T. Grubb, **Polymer Microscopy**, Chapman and Hall, London, 1987, 62-73, 109-121.
[Review: effects of radiation and etching on polymers]
- P17) L.H. Sperling, **Introduction to Physical Polymer Science**, Wiley & Sons, New York, 1986, 159-165.
[Polymer crystallographic data and single crystal polymers]
- P18) R.J. Young, P.A. Lovell, **Introduction to Polymers**, Chapman & Hall, London, 1991, 248-259.
[Polymer crystallographic data and single crystal polymers]

8.2.6. Minerals (Calcite, Albite, Hematite, Lizardite)

Min1) A.L. Rachlin, G.S. Henderson, M.C. Goh, An Atomic Force Microscope (AFM) Study of the Calcite Cleavage Plane: Image Averaging in Fourier Space, *Am. Mineral.*, 77, 904 (1992).

[AFM study of calcite cleavage plane in water - no atomic resolution]

Min2) B. Drake, R. Hellmann, Atomic Force Imaging of the Albite (010) Surface, *Am. Mineral.*, 76, 1773 (1991).

[AFM study of Albite cleavage plane]

Min3) M.F. Hochella, Jr., C.M. Eggleston, V.B. Elings, M.S. Thompson, Atomic Structure and Morphology of the Albite {010} Surface: An Atomic-Force Microscope and Electron Diffraction Study, *Am. Mineral.*, 75, 723 (1990).

[AFM study of Albite cleavage plane and surface features]

Min4) C.M. Eggleston, M.F. Hochella, Jr., The Structure of Hematite {001} Surface by Scanning Tunneling Microscopy: Image Interpretation, Surface Relaxation, and Step Structure, *Am. Mineral.*, 77, 911 (1992).

[STM study of Hematite cleavage plane - high step density]

Min5) P.A. Johnsson, C.M. Eggleston, M.F. Hochella, Jr., Imaging Molecular-Scale Structure and Microtopography of Hematite with the Atomic Force Microscope, *Am. Mineral.*, 76, 1442 (1991).

[AFM study of Hematite cleavage plane showing pits and steps]

Min6) F.J. Wicks, K. Kjoller, G.S. Henderson, Imaging the Hydroxyl Surface of Lizardite at Atomic Resolution with the Atomic Force Microscope, *Can. Mineral.*, 30, 83 (1992).

[AFM study of Lizardite cleavage plane]

Min7) C. Klein, C.S. Hurlbut, Jr., *Manual of Mineralogy*, Wiley & Sons, New York, 1985, p. 543-546.

[Table of prominent cleavage minerals]

8.2.7. MoO_3 / MoS_2 (MoO_3 , MoS_2)

Mo1) T. Xiaowei, Y. Junen, Z. Pengji, A Nuclear Detector with Super-High Spatial Resolution, *Nuc. Instr. Methods Phys. Res. Sect. A*, 320, 396 (1992).

[Single nucleon impacts on MoS_2 surface imaged with STM]

Mo2) C.M. Lieber, Y. Kim, Nanomachining and Manipulation with the Atomic Force Microscope, *Adv. Mater.* 5 (5), 392 (1993).

[Nanomachining of MoO_3 with AFM tip]

Mo3) Y. Kim, C.M. Lieber, Machining Oxide Thin Films with an Atomic Force Microscope: Pattern and Object Formation on the Nanometer Scale, *Science*, 257, 375 (1992).

[Nanomachining of MoO_3 with AFM tip]

Mo4) Y. Kim, J.L. Huang, C.M. Lieber, Characterization of Nanometer Scale Wear and Oxidation of Transition Metal Dichalcogenide Lubricants by Atomic Force Microscopy, *Appl. Phys. Lett.*, 59 (26), 3404 (1991).

[Compares physical characteristics of MoS_2 and NbSe_2]

Mo5) H. Permana, S. Lee, K.Y.S. Ng, Observation of Protrusions and Ring Structures on MoS_2 by Scanning Tunneling Microscopy, *J. Vac. Sci. Technol. B*, 10 (5), 2297 (1992).

[STM study of MoS_2 surface]

Mo6) T. Ichinokawa, T. Ichinose, M. Tohyama, H. Itoh, Scanning Tunneling Microscopy Observation of MoS₂ Surface and Gold Clusters Deposited on MoS₂ Surface, J. Vac. Sci. Technol. A, 8 (1), 500 (1990).

[STM/SEM studies of Au clusters on cleaved MoS₂ surface]

Mo7) M. Weimar, J. Kramar, C. Bai, J.D. Baldeschwieler, Tunneling Microscopy of 2H-MoS₂: A Compound Semiconductor Surface, Phys. Rev. B, 37 (8), 4292 (1988).

[STM study of MoS₂ surface]

Mo8) D. Sarid, T.D. Henson, N.R. Armstrong, L.S. Bell, Probing of Basal Planes of MoS₂ by Scanning Tunneling Microscopy, Appl. Phys. Lett., 52 (26), 2252 (1988).

[STM study of MoS₂ surface]

8.2.8. Metal Oxide Films (TiO₂, VO₂, TiO₂/VO₂, Cr₂O₃, NiO, Al₂O₃)

MOF1) K. Douglas, G. Devaud, N.A. Clark, Transfer of Biologically Derived Nanometer-scale Patterns to Smooth Substrates, Science, 257, 642 (1992).

[Thin metal film mask using biological pattern and TiO_x]

MOF2) H.L.M. Chang, Y. Gao, J. Guo, C.M. Foster, H. You, T.J. Zhang, D.J. Lam, Heteroepitaxial Growth of TiO₂, VO₂, and TiO₂/VO₂ Multilayers by MOCVD, J. de Phys., 4, C2-953 (1991).

[Single crystal films epitaxially grown on α -Al₂O₃]

MOF3) M.D. Antonik, R.J. Lad, Faceting, Reconstruction, and Defect Microstructure at Ceramic Surfaces Revealed by Atomic Force Microscopy, J. Vac. Sci. Technol. A, 10 (4), 669 (1992).

[AFM study of single crystal metal oxides: Cr₂O₃, NiO, Al₂O₃, and TiO₂]

8.2.9. Alkali Halide Crystals (NaCl, KBr, LiF)

AHC1) W. Krakow, Electron Microscope Studies of Vapor Deposited Materials: Nucleation, Epitaxial Growth and Surface Topography, NanoStructured Mater., 3, 115 (1993).

[Epitaxial growth of metal films/particles on NaCl crystal and C60 film on mica]

AHC2) F.J. Giessibl, G. Binnig, Investigation of the (001) Cleavage Plane of Potassium Bromide with an Atomic Force Microscope at 4.2 K in Ultra-High Vacuum, Ultramicroscopy, 42-44, 281 (1992).

[UHV AFM surface study of KBr crystal]

AHC3) G. Meyer, N.M. Amer, Optical-Beam-Deflection Atomic Force Microscopy: The NaCl (001) Surface, Appl. Phys. Lett., 56 (21), 2100 (1990).

[UHV AFM study of NaCl atomic resolution cleavage plane]

AHC4) E. Mayer, H. Heinzelmann, D. Brodbeck, G. Overney, L. Howald, H.J. Güntherodt, Atomic Force Microscopy: High Resolution and Contrast Mechanism, Frühjahrstagung der S.P.G., 63, 793 (1990).

[AFM study of LiF]

AHC5) H. Heinzelmann, E. Mayer, P. Grütter, H.R. Hidber, L. Rosenthaler, H.J. Güntherodt, Atomic Force Microscopy: General Aspects and Application to Insulators, J. Vac. Sci. Technol. A, 6 (2), 275 (1988).

[AFM study of LiF, HOPG, Quartz, Mineral glass optical lens]

8.2.10. Silicon

Si1) Cleaning Silicon Surfaces, Memo0521.tex, July 14, 1992.

Si2) U. Neuwald, H.E. Hessel, A. Feltz, U. Memmert, R.J. Behm, Initial Stages of Oxide Growth on Hydrogen Passivated Si(111) Surfaces Studied by Scanning Tunneling Microscopy, submitted to Appl. Phys. Lett., Nov 22, 1991.

Si3) J.I. Heinrich, C.L. Curtis, G.M. Credo, K.L. Kavanagh, M.J. Sailor, Luminescent Colloidal Silicon Suspensions from Porous Silicon, Science, 255, 66 (1992).
[Luminescent Si suspensions]

8.2.11. Quartz

Q1) L.C. Qin, L.W. Hobbs, HREM of Electron Irradiated Quartz, Mat. Res. Soc. Symp. Proc., 279, 387 (1993).
[Atomic scale images of quartz surface]

8.2.12. Organic Molecular Crystals (Tetracene)

OMC1) R.M. Overney, L. Howard, J. Frommer, E. Mayer, H.J. Güntherodt, Molecular Surface Structure of Tetracene Mapped by the Atomic Force Microscope, J. Chem. Phys., 94 (12), 8441 (1991).
[AFM study of cleaved Tetracene with defect-free surface over 1 mm²]

8.2.13. Misc. Materials(Pb₂P₂O₇, Ge, Clinoptilolite, C₆₀, Pt, 1T-TaS₂, 1T-TaSe₂)

MM1) T. Thundat, B.C. Sales, B.C. Chakoumakos, L.A. Boatner, D.P. Allison, R.J. Warmack, Atomic Layer-by-Layer Surface Removal by Force Microscopy, Surface Sci. Lett., 293, L863 (1993).
[AFM study of anisotropically corrugated cleavage plane of Pb₂P₂O₇]

MM2) S.A.C. Gould, B. Drake, C.B. Prater, A.L. Weisenhorn, S. Manne, H.G. Hansma, P.K. Hansma, J. Massie, M. Longmire, V. Elings, B.D. Northern, B. Mukerjee, C.M. Peterson, W. Stoeckenius, T.R. Albrecht, C.F. Quate, From Atoms to Integrated Circuit Chips, Blood Cells, and Bacteria with the Atomic Force Microscope, J. Vac. Sci. Technol. A, 8 (1), 369 (1990).
[AFM study of Germanium fracture surface - very little info for all those authors]

MM3) E. Mayer, R. Wiesendanger, D. Anselmetti, H.R. Hidber, H.J. Güntherodt, F. Lévy, H. Berger, Different Response of Atomic Force Microscopy and Scanning Tunneling Microscopy to Charge Density Waves, J. Vac. Sci. Technol. A, 8 (1), 495 (1990).
[Transition metal dichalcogenides: 1T-TaS₂ and 1T-TaSe₂]

MM4) A.L. Weisenhorn, J.E. MacDougall, S.A.C. Gould, S.D. Cox, W.S. Wise, J. Massies, P. Maivald, V.B. Elings, G.D. Stucky, P.K. Hansma, Imaging and Manipulating Molecules on a Zeolite Surface with an Atomic Force Microscope, Science, 247, 1330 (1990).
[AFM study of Clinoptilolite zeolite]

MM5) E. Pennisi, Buckyballs Still Charm, Science News, 140, 120 (1991).
[Popular overview of C₆₀ structure]

MM6) B.C. Schardt, S.L. Yau, F. Rinaldi, Atomic Resolution Imaging of Adsorbates on

Metal Surfaces in Air: Iodine Adsorption on Pt(111), Science, 243, 1050 (1989).
[STM study of Iodine on Pt single crystal substrate]

MM7) J.A. Switzer, R.P. Raffaele, R.J. Phillips, C.J. Hung, T.D. Golden, Scanning Tunneling Microscopy of Electrodeposited Ceramic Superlattices, Science, 258, 1918 (1992).
[Pb-Tl-O ceramic superlattice with regular corrugations of 10 nm scale]

8.2.14. Material Properties

MP1) Dictionary of Inorganic Compounds, Vol. 1 (Ac-C₁₀), Chapman & Hall, London, 1992, pgs. 63, 3813.
[Muscovite mica and silicon]

MP2) Materials Engineering: Materials Selector 1993, December, 1993, p. 144-148.
[Data sheets for muscovite, glass, graphite, silicon nitride/carbide]

MP3) E. Nadgorny, Dislocation dynamics and material properties of crystals, in Progress in Materials Science, 31, J.W. Christian, P. Haasen, T.B. Massalski, eds., Pergamon Press, Oxford, pgs. 513-517.
[Appendices listing crystallographic properties]

MP4) R. Riedel, Materials Harder than Diamond?, Adv. Mater., 4 (11), 759 (1992).
[Graph showing microhardness of several materials]

8.3. NANOLITHOGRAPHY

8.3.1. Nanolithography

NL1) H.I. Smith, H.G. Craighead, Nanofabrication, Physics Today, February, 1990, p. 24.
[Nanolithography review article]

NL2) R.F. Pease, Patterning Techniques for Sub-100 nm Devices, Circuits and Systems, W. Kirk, ed., Proceedings of the International Symposium on Nanostructures and Mesoscopic Systems, May, 1991 (Academic Press 1992).
[Review of nanolithography techniques: Conference paper]

8.3.2. Electron-Beam Nanolithography

EBN1) G. Bazán, G.H. Bernstein, Electron Beam Lithography Over Large Scan Fields, J. Vac. Sci. Technol. A, 11 (4), 1745 (1993).
[System for creating 20 nm scale patterns over large scan fields]

EBN2) E. Fratschmer, M. Isaacson, Nanostructure Fabrication in Metals, Insulators, and Semiconductors Using Self-Developing Metal Inorganic Resist, J. Vac. Sci. Technol. B, 4 (1), 361 (1986).
[AlF₃ as a self-developing e-beam resist for RIE of Si₃N₄]

EBN3) A. Murray, M. Isaacson, I. Adesida, AlF₃ - A New Very High Resolution Electron Beam Resist, Appl. Phys. Lett., 45 (5), 589 (1984).
[2 nm holes drilled on 4 nm centers in AlF₃. 10 nm holes replicated by RIE]

EBN4) M. Isaacson, A. Murray, In Situ Vaporization of Very Low Molecular Weight Resists Using 1/2 nm Diameter Electron Beams, J. Vac. Sci. Technol., 19 (4), 1117

- (1981).
[2 nm dia. holes drilled in NaCl up to 30 nm thick]
- EBN5) M.E. Mochel, C.J. Humphreys, J.A. Eades, J.M. Mochel, A.M. Petford, *Electron Beam Writing on a 20-Å Scale in Metal b-Aluminas*, Appl. Phys. Lett., 42 (4), 392 (1983).
[2 nm dia. holes drilled in b-Aluminas up to 100 nm thick]
- EBN6) A.N. Broers, *Resolution Limits for Electron-Beam Lithography*, IBM J. Res. Develop., 32 (4), 502 (1988).
[Review on e-beam resolution: suggests AlF₃, Al₂O₃, and MgF₂ as resists]
- EBN7) A.N. Broers, *Resolution Limits for Electron-Beam Lithography and Methods for Avoiding these Limits*, M.A. Reed, W.P. Kirk, eds., *Nanostructure Physics and Fabrication*, Academic Press, London 1989, p. 421.
[5 nm lines ion milled in metal films/ RIE etched in nitride films from PMMA]
- EBN8) C.R.K. Marrian, F.K. Perkins, S.L. Brandow, T.S. Koloski, E.A. Dobisz, J.M. Calvert, *Low Voltage Electron Beam Lithography in Self-Assembled Ultrathin Films with the Scanning Tunneling Microscope*, Appl. Phys. Lett., 64 (3), 390 (1994).
[SAMs: CMPTS (benzyl chloride) and PEDA (pem) functional groups are patterned with low energy electrons, then plated using electroless deposition of Ni. 20 nm linewidth]
- EBN9) A.E. Owen, P.J.S. Ewen, A. Zakery, M.N. Kozicki, Y. Khawaja, *Metal-Chalcogenide Photoresists for High Resolution Lithography and Sub-Micron Structures*, M.A. Reed, W.P. Kirk, eds., *Nanostructure Physics and Fabrication*, Academic Press, London 1989, p. 447.
[35 nm grid using As₃₃S₆₇ e-beam resist and wet chemical etching]

8.3.3. Projection Electron Lithography

- PEL1) S.D. Berger, J.M. Gibson, R.M. Camarda, R.C. Farrow, H.A. Huggins, J.S. Kraus, J.A. Liddle, *Fabrication of Nanostructure Arrays Using Projection Electron-Beam Lithography*, W. Kirk, ed., *Proceedings of the International Symposium on Nanostructures and Mesoscopic Systems*, May, 1991 (Academic Press 1992).
[Review of SCALPEL Technique: Conference paper]
- PEL2) S.D. Berger, J.M. Gibson, R.M. Camarda, R.C. Farrow, H.A. Huggins, J.S. Kraus, J.A. Liddle, *Projection Electron-Beam Lithography: A New Approach*, J. Vac. Sci. Technol. B 9 (6), 2996 (1991).
[Review of SCALPEL Technique: 1991]
- PEL3) S.D. Berger, J.M. Gibson, *New Approach to Projection-Electron Lithography with Demonstrated 0.1 μm Linewidth*, Appl. Phys. Lett., 57 (2), 153 (1990).
[Review of SCALPEL Technique: 1990]
- PEL4) J.A. Liddle, H.A. Huggins, S.D. Berger, J.M. Gibson, G. Weber, R. Kola, C.W. Jurgensen, *Mask Fabrication for Projection Electron-Beam Lithography Incorporating the SCALPEL Technique*, J. Vac. Sci. Technol. B 9 (6), 3000 (1991).
[Mask fabrication for SCALPEL Technique]
- PEL5) J.A. Liddle, S.D. Berger, *Choice of System Parameters for Projection Electron-Beam Lithography: Accelerating Voltage and Demagnification Factor*, J. Vac. Sci. Technol. B, 10 (6), 2776 (1992).
[System parameters for SCALPEL Technique]

PEL6) R.C. Farrow, J.A. Liddle, S.D. Berger, H.A. Huggins, J.S. Kraus, R.M. Camarda, C.W. Jurgensen, R.R. Kola, L. Fetter Mark Detection for Alignment Registration in a High-throughput Projection Electron Lithography Tool, J. Vac. Sci. Technol. B 10 (6), 2780 (1992). [mask alignment technique with 10 nm precision]
[10 nm mask alignment for SCALPEL Technique]

PEL7) R.C. Farrow, S.D. Berger, J.M. Gibson, J.A. Liddle, J.S. Kraus, R.M. Camarda, H.A. Huggins, Alignment and Registration Schemes for Projection Electron Lithography, J. Vac. Sci. Technol. B, 9 (6), 3582 (1991).
[Mask alignment for SCALPEL Technique]

8.3.4. X-Ray Nanolithography

XRN1) J.M. Calvert, T.S. Koloski, W.J. Dressick, C.S. Dulcey, M.C. Peckerar, F. Cerrina, J.W. Taylor, D. Suh, O.R. Wood II, A.A. MacDowell, R. D'Souza, Projection X-Ray Lithography with Ultrathin Imaging Layers and Selective Electroless Metalization, Opt. Eng., 32 (10), 2437 (1993).
[14 nm wavelength x-rays are used to pattern self-assembled-monolayers]

XRN2) J.R. Maldonado, X-Ray Lithography System Development at IBM: Overview and Status, SPIE Proc, 1465, 2 (1991).
[X-ray lithography feasibility study done by IBM]

XRN3) W. Chu, A. Yen, K. Ismail, M.I. Shepard, H.J. Lezec, C.R. Musil, J. Melngailis, Y.C. Ku, J.M. Carter, H.I. Smith, Sub-100-nm X-ray Mask Technology Using Focused-Ion-Beam Lithography, J. Vac. Sci. Technol. B, 7 (6), 1583 (1989).
[1.3 nm wavelength x-rays replicate 50nm scale pattern from FIBL mask]

XRN4) A. Moel, M.L. Schattenburg, J.M. Carter, H.I. Smith, Microgap Control in X-Ray Nanolithography, J. Vac. Sci. Technol. B, 7 (6), 1692 (1989).
[Technique to improve resolution by reducing mask/substrate gap]

XRN5) K. Ismail, D.A. Antoniadis, H.I. Smith, One-Dimensional Subbands and Mobility Modulation in GaAs/AlGaAs Quantum Wires, Appl. Phys. Lett, 54 (12), 1130 (1989).
[40 nm structures by x-ray lithography and Ti/Au liftoff mask for ion milling]

XRN6) K. Ismail, W. Chu, A. Yen, D.A. Antoniadis, H.I. Smith, Negative Transconductance and Negative Differential Resistance in a Grid-Gate Modulation-Doped Field-Effect Transistor, Appl. Phys. Lett, 54 (5), 460 (1989).
[60 nm structures by x-ray lithography and Ti/Au liftoff mask for ion milling]

8.3.5. Ion Beam Nanolithography

IBN1) J. Melngailis, D.A. Antoniadis, Nanofabrication by Focused Ion Beams, ARO 29631.2-EL/AD-A271 290. U.S. Army Research Office Report (1993).
[Review of several ion-beam lithography techniques]

IBN2) L.R. Harriott, In-Situ Nanostructure Fabrication Using Finely Focused Ion Beams, SPIE Proc., 1284, 132 (1990).
[Review of ion-beam lithography techniques]

IBN3) R.L. Kubena, F.P. Stratton, J.W. Ward, G.M. Atkinson, R.J. Joyce, Sub-20-nm-Wide Line Fabrication in Poly(Methylmethacrylate) Using a Ga⁺ Microprobe, J. Vac. Sci. Technol. B, 7 (6), 1798 (1989).
[12 nm features in PMMA with focused ion beam]

IBN4) R.L. Kubena, **Resolution Limits of Focused-Ion-Beam Resist Patterning**, Mat. Res. Soc. Symp. Proc., 279, 567 (1993).
[7 nm holes in PMMA using 50 keV Ga⁺ - lighter ions may increase resolution more]

8.3.6. Micromachining

Micro1) K.D. Wise, K. Najafi, **Microfabrication Techniques for Integrated Sensors and Microsystems**, Science, 254, 1335 (1991).
[Review: *Microfabrication techniques*]

Micro2) G. Stix, **Micron Machinations**, Scientific American, Nov. 1992, p. 106.
[Popular Review on micromachining]

Micro3) J.A. Stroscio, D.M. Eigler, **Atomic and Molecular Manipulation with the Scanning Tunneling Microscope**, Science, 254, 1319 (1991).
[Review on STM atomic manipulation]

Micro4) I.W. Lyo, P. Avouris, **Field-Induced Nanometer to Atomic-Scale Manipulation of Silicon Surfaces with the STM**, Science, 253, 173 (1991).
[Deposition and removal of single atoms on Si with the STM]

Micro5) A. Kobayashi, F. Grey, R.S. Williams, M. Aono, **Formation of Nanometer-Scale Grooves in Silicon with a Scanning Tunneling Microscope**, Science, 259, 1724 (1993).
[Nanomachining with the STM]

Micro6) O.M. Leung, M. C. Goh, **Orientational Ordering of Polymers by Atomic Force Microscope Tip-Surface Interaction**, Science, 255, 64 (1992).
[Ordering of Polystyrene film by repeated AFM scanning]

Micro7) J.P. Peyrade, F. Voillot, M. Goiran, C. Guasch, E. Bedel, C. Fontaine, H. Atmani, A. Rocher, **The Use of Dislocations as an "Atomic Saw" to cut 2D Structures - Interest for Plasticity Studies**, Solid State Phenomena, 35-36, 507 (1994).
[Method for making nm-scale quantum wires by dislocating layered crystals]

8.3.7. Quantum Structures

QS1) P.B. Fischer, K. Dai, E. Chen, S.Y. Chou, **10 nm Si Pillars Fabricated Using Electron-Beam Lithography, Reactive Ion Etching, and HF Etching**, J. Vac. Sci. Technol. B, 11 (6), 2524 (1993).
[Fabrication and photoluminescence of Si pillars]

QS2) I. Maximov, A. Gustafsson, H.C. Hansson, L. Samuelson, W. Seifert, A. Wiedensohler, **Fabrication of Quantum Dot Structures Using Aerosol Deposition and Plasma Etching Techniques**, J. Vac. Sci. Technol. A, 11 (4), 748 (1993).
[50-80 nm dots etched into GaInAs/InP using Metal-Organic-RIE]

QS3) K.J. Vahala, W.A. Saunders, C.S. Tsai, P.C. Sercel, T. Kuech, H.A. Atwater, R.C. Flagan, **Lower-Dimensional Quantum Structures by Selective Growth and Gas-Phase Nucleation**, J. Vac. Sci. Technol. B, 11 (4), 1660 (1993).
[Review of masked epitaxial growth and aerosol cluster growth of nanostructures]

QS4) P. Ils, M. Michel, A. Forchel, I. Gyuro, M. Klenk, E. Zielinski, **Fabrication and Optical Properties of InGaAs/InP Quantum Wires and Dots with Strong Lateral Quantization Effects**, J. Vac. Sci. Technol. B, 11 (6), 2584 (1993).
[30 nm dots by e-beam lithography of PMMA and wet etching]

- QS5) W. Chen, H. Ahmed, Fabrication of Sub-10 nm Structures by Lift-Off and by Etching After Electron-Beam Exposure of Poly(methylmethacrylate) Resist on Solid Substrates, *J. Vac. Sci. Technol. B*, 11 (6), 2519 (1993).
[10 nm dia. pillars by e-beam on PMMA, wet etch, or metal lift-off and RIE]
- QS6) D.A. Redman, D.M. Follstaedt, T. Guiling, M. Kelly, Photoluminescence of Silicon Nanostructures Formed by Ion Beam Implantation, *Mat. Res. Soc. Symp. Proc.*, 279, 201 (1993).
[Photoluminescence from 1-8 nm cavities in Si]
- QS7) D. Ralph, R.A. Buhrman, Fabrication and Studies of Metallic Nanobridges, National Nanofabrication Facility Research Accomplishments 1991-1992, p. 173.
[Growth of single-crystal Cu dendrite through 3 nm hole in Si₃N₄ film]
- QS8) J.G. Couillard, A. Davies, H.G. Craighead, Processing and Imaging of Silicon Based Nanostructures, National Nanofabrication Facility Research Accomplishments 1991-1992, p. 187.
[30 nm features through e-beam litho, RIE in SiGe and SiO₂]
- QS9) M. Sundaram, S.A. Chalmers, P.F. Hopkins, A.C. Gossard, New Quantum Structures, *Science*, 254, 1326 (1991).
[Review on quantum structure fabrication techniques]
- QS10) S.P. Beaumont, Fabrication and Overgrowth of Quantum Wires and Dots for Optoelectronic Applications, M.A. Reed, W.P. Kirk, eds., *Nanostructure Physics and Fabrication*, Academic Press, London 1989, p. 77.
[two fabrication schemes: masked ion implantation and annealing, or RIE and overgrowth]
- QS11) D.S. Chemla, Quantum Wells for Photonics, *Physics Today*, May 1985, p. 57.
[Epitaxial growth techniques for quantum well structures]

8.3.8. Epitaxy

- E1) V. Narayanamurti, Crystalline Semiconductor Heterostructures, *Physics Today*, October 1984, p. 24.
[Review of semiconductor epitaxy]
- E2) S.D. Berger, H.A. Huggins, A.E. White, K.T. Short, D. Loretto, A New Technique to Produce Single Crystal Epitaxial Nano-Structures, M.A. Reed, W.P. Kirk, eds., *Nanostructure Physics and Fabrication*, Academic Press, London 1989, p.401.
[Annealing after ion implantation in Si increases crystallinity]

8.3.9. Reactive Ion Etching

- RIE1) T. Matthies, C. David, J. Thieme, Trilevel Reactive Ion Etching Processes for Fabrication of 60 nm Germanium Structures with High Aspect Ratio, *J. Vac. Sci. Technol. B*, 11 (5), 1873 (1993).
[Az resist(45nm) on Ti(5nm) on Ni(12nm) on Ge(360 nm) on Cr(5nm). Az exposure, BCl₃ RIE of Ti, O₂ RIE of Ni, CBrF₃ RIE of Ge]
- RIE2) F.X. Campos, G.C. Weaver, C.J. Waltman, S.R. Leone, Enhanced Etching of Si(100) by Neutral Beams with Kinetic Energies up to 6 eV, *J. Vac. Sci. Technol. B*, 10 (5), 2217 (1992).

- RIE3) T.J. Sommerer, M.J. Kushner, Monte Carlo-Fluid Model of Chlorine Atom Production in Cl_2 , HCl , and CCl_4 Radio-Frequency Discharges for Plasma Etching, J. Vac. Sci. Technol. B, 10 (5), 2179 (1992).
- RIE4) R.A. Gottscho, C.W. Jurgensen, D.J. Vitkavage, Microscopic Uniformity in Plasma Etching, J. Vac. Sci. Technol. B, 10 (5), 2133 (1992).
- RIE5) N.G. Stoffel, Molecular Dynamics Simulations of Deep Penetration by Channeled Ions During Low-Energy Ion Bombardment of III-V Semiconductors, J. Vac. Sci. Technol. B, 10 (2), 651 (1992).

8.4. NANOCHEMISTRY

8.4.1. Nanochemistry

- NC1) G. A. Ozin, Nanochemistry: Synthesis in Diminishing Dimensions, Adv. Mater. 4 (10), 612 (1992).
[review article on nanochemistry]
- NC2) G.M. Whitesides, J.P. Mathias, C.T. Seto, Molecular Self-Assembly and Nanochemistry: A Chemical Strategy for the Synthesis of Nanostructures, Science, 254, 1312 (1991).
Review Article on Self-Assembly]
- NC3) R.W. Siegel, Nanostructured Materials - Mind Over Matter, NanoStructured Materials, 3, 1 (1993).
[Review on Nanostructured materials: Clusters, multilayers, nanophase materials]
- NC4) P. Ball, L. Garwin, Science at the Atomic Scale, Nature, 355, 761 (1992).
[Popular review on nanofabrication/nanochemistry]
- NC5) I. Amato, Where Chemists React: ACS Meeting in Atlanta, Research News, April 26, 1991, p. 511.
[Nanochemistry news article]

8.4.2. Ultrathin Organic Films

- UPF1) H. Fuchs, H. Ohst, W. Prass, Ultrathin Organic Films: Molecular Architectures for Advanced Optical, Electronic and Bio-Related Systems, Adv. Mater., 3 (1), 10 (1991).
[Review of applications of LB and SAM films]
- UOF2) J.D. Swalen, D.L. Allara, J.D. Andrade, E.A. Chandross, S. Garoff, J. Israelachvili, T.J. McCarthy, R. Murray, R.F. Pease, J.F. Rabolt, K.J. Wynne, H. Yu, Molecular Monolayers and Films, Langmuir, 3, 932 (1987).
[Review of applications of LB and SAM films]
- UOF3) G. Wegner, Ultrathin Layers: Innovation Through Research, Adv. Mater., 3 (1), 8 (1991).
[1 page review article]
- UOF4) A. Ulman, An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly, Academic Press, London, 1991, p.415-424.
[Author's final note: concluding thoughts on the future of ultrathin films]

8.4.3. Langmuir-Blodgett Films

- LBF1) L.L. Kosbar, C.W. Frank, R.F.W. Pease, **Multicomponent Langmuir-Blodgett Resists for Optical Lithography**, J. Vac. Sci. Technol. B, 8 (6), 1441 (1990).
[Novlac and poly(*p*-hydroxystyrene) LB films: UV lithography and wet etching]
- LBF2) S.W.J. Kuan, C.W. Frank, C.C. Fu, D.R. Allee, P. Maccagno, R.F.W. Pease, **Ultrathin Polymer films for Microlithography**, J. Vac. Sci. Technol. B 6 (6), 2274 (1988).
[LB PMMA films as e-beam resists]
- LBF3) D.K. Schwartz, R. Viswanathan, J.A.N. Zasadzinski, **Commensurate Defect Superstructures in a Langmuir-Blodgett Film**, Phys. Rev. Lett., 70 (9), 1267 (1993).
[AFM surface study of Ba Arachidate LB film]
- LBF4) Y. Lvov, F. Essler, G. Decher, **Combination of Polycation/Polyanion Self-Assembly and Langmuir-Blodgett Transfer for the Construction of Superlattice Films**, J. Phys. Chem., 97, 13773 (1993).
[DODAB and Poly-Vinyl-Sulfate LB film superlattice]
- LBF5) L. Bourdieu, O. Ronsin, D. Chatenay, **Molecular Positional Order in Langmuir-Blodgett Films by Atomic Force Microscopy**, Science, 259, 798 (1993).
[Heated Ba Arachidate LB Films organize into ordered structures]
- LBF6) J.Y. Josefowicz, N.C. Maliszewskyj, S.H.J. Idziak, P.A. Heiney, J.P. McCauley, Jr., A.B. Smith III, **Structure of Langmuir-Blodgett Films of Disk-Shaped Molecules Determined by Atomic Force Microscopy**, Science, 260, 323 (1993).
[AFM surface study of Discotic Mesogen LB film]
- LBF7) L.F. Chi, M. Anders, H. Fuchs, R.R. Johnston, H. Ringsdorf, **Domain Structures in Langmuir-Blodgett Films Investigated by Atomic Force Microscopy**, Science, 259, 213 (1993).
[Domain structures - not very useful]
- LBF8) D.K. Schwartz, J. Garnaes, R. Viswanathan, J.A.N. Zasadzinski, **Surface Order and Stability of Langmuir-Blodgett Films**, Science, 257, 508 (1992).
[AFM surface study of Cadmium Arachidate LB films]
- LBF9) E. Meyer, R. Overney, D. Brodbeck, L. Howald, R. Lüthi, J. Frommer, H.J. Güntherodt, **Friction and Wear of Langmuir-Blodgett Films Observed by Friction Force Microscopy**, Phys. Rev. Lett., 69 (12), 1777 (1992).
[Friction and wear of Cadmium Arachidate LB film]
- LBF10) E. Meyer, L. Howald, R.M. Overney, H. Heinzelmann, J. Frommer, H.J. Güntherodt, T. Wagner, H. Schier, S. Roth, **Molecular-Resolution Images of Langmuir-Blodgett Films Using Atomic Force Microscopy**, Nature, 349, 398 (1991).
[AFM surface study of Cadmium Arachidate LB films]
- LBF11) G.S. Blackman, C.M. Mate, M.R. Philpott, **Interaction Forces of a Sharp Tungsten Tip with Molecular Films on Silicon Surfaces**, Phys. Rev. Lett., 65 (18), 2270 (1990).
[Surface force studies of Cadmium Arachidate and perfluoropolyether LB films]
- LBF12) O. Marti, H.O. Ribi, B. Drake, T.R. Albrecht, C.F. Quate, P.K. Hansma, **Atomic Force Microscopy of an Organic Monolayer**, Science, 239, 50 (1988).
[Polymerized monolayer film on glass is highly oriented - good AFM of glass slide]

8.4.4. Self-Assembled Monolayers

SAM1) A. Kumar, G.M. Whitesides, Features of Gold Having Micrometer to Centimeter Dimensions Can be Formed Through a Combination of Stamping with an Elastomeric Stamp and an Alkanethiol "Ink" Followed by Chemical Etching, Appl. Phys. Lett. 63 (14), 2002 (1993).

[1 mm pattern transferred with elastomer stamp and SAM "ink"]

SAM2) A. Bonfiglio, R. Paradiso, E.D. Zitti, D. Ricci, A. Bolognesi, W. Pozio, Scanning Tunnelling Microscopy Investigations of Self-Assembled Monolayers of Poly(3-Decylthiophene) on Graphite, Adv. Mater. Optics Electron., 2, 295 (1993).

[Polymer assembled on HOPG surface]

SAM3) S.I. Stupp, S.Son, H.C. Lin, L.S. Li, Synthesis of Two-Dimensional Polymers, Science, 259, 59 (1993).

[Oligomers self organize into 2D layer - good article]

SAM4) G.P. López, H.A. Biebuyck, C.D. Frisbie, G.M. Whitesides, Imaging of Features on Surfaces by Condensation Figures, Science 260, 647 (1993)

[simultaneous growth of two alkanethiols on gold. Imaged by condensation figures]

SAM5) Y.T. Kim, A.J. Bard, Imaging and Etching of Self-Assembled *n*-Octadecanethiol Layers on Gold with the Scanning Tunneling Microscope, Langmuir, 8, 1096 (1992).

[ODT on Au on Mica: surface study and STM micromachining]

SAM6) P.E. Laibinis, R.L. Graham, H.A. Biebuyck, G.M. Whitesides, X-Ray Damage to CF₃CO₂ Terminated Organic Monolayers on Si/Au: Principal Effect of Electrons, Science, 254, 981 (1991).

[X-ray generated electrons (K α 1.5 keV) damage monolayer]

SAM7) P.E. Laibinis, G.M. Whitesides, D.L. Allara, Y.T. Tao, A.N. Parikh, R.G. Nuzzo, Comparison of the Structures and Wetting Properties of Self-Assembled Monolayers of *n*-Alkanethiols on the Coinage Metal Surfaces, Cu, Ag, Au, J. Am. Chem. Soc., 113, 7152 (1991).

[Extensive characterization paper on alkanethiols]

SAM8) P.E. Laibinis, J.J. Hickman, M.S. Wrighton, G.M. Whitesides, Orthogonal Self-Assembled Monolayers: Alkanethiols on Gold and Alkane Carboxylic Acids on Alumina, Science 245, 845 (1989).

[alkanethiols on gold and carboxylic acids on alumina as etch resists]

SAM9) D.K. Schwartz, S. Steinberg, J. Israelachvili, J.A.N. Zasadzinski, Growth of a Self-Assembled Monolayer by Fractal Aggregation, Phys. Rev. Lett., 69 (23), 3354 (1992).

[OTS layer on hydrated mica surface]

SAM10) N.L. Abbott, J.P. Folkers, G.M. Whitesides, Manipulation of the Wettability of Surfaces on the 0.1 to 1 Micrometer Scale Through Micromachining and Molecular Self-Assembly, Science, 257, 1380 (1992).

[Alkanethiol film on Au is micromachined and exposed regions covered with 2nd SAM]

SAM11) S.R. Wasserman, H. Biebuyck, G.M. Whitesides, Monolayers of 11-Trichlorosilylundecyl Thioacetate: A System that Promotes Adhesion Between Silicon Dioxide and Evaporated Gold, J. Mater. Res., 4 (4), 886 (1989).

[Sulfur-containing monolayer promotes adhesion between SiO₂ and Au]

SAM12) A. Ulman, Self-Assembled Monolayers of Alkyltrichlorosilanes: Building Blocks for Future Organic Materials, Adv. Mater., 2 (12), 573 (1990).

[Overview of SAM preparation methods for alkyltrichlorosilanes]

- SAM13) M.J. Lercel, R.C. Tiberio, P.F. Chapman, H.G. Craighead, C.W. Sheen, A.N. Parikh, D.L. Allara, **Self-Assembled Monolayer Electron-Beam Resists on GaAs and SiO₂**, J. Vac. Sci. Technol. B, 11 (6), 2823 (1993).
[ODT and OTS monolayers as self-developing e-beam resists]
- SAM14) R.C. Tiberio, H.G. Craighead, M. Lercel, T. Lau, C.W. Sheen, D.L. Allara, **Self-Assembled Monolayer Electron Beam Resists on GaAs**, Appl. Phys. Lett., 62 (5), 476 (1993).
[ODT monolayers as self-developing e-beam resists]
- SAM15) P. Fontaine, D. Goguenheim, D. Deresmes, D. Vuillaume, M. Garet, F. Rondelez, **Octadecyltrichlorosilane Monolayers as Ultrathin Gate Insulating Films in Metal-Semiconductor Devices**, Appl. Phys. Lett. 62 (18), 2256 (1993).
[ODT as insulating thin film]
- SAM16) L. Sun, R.M. Crooks, **Imaging of Defects Contained within n-Alkylthiol Monolayers by Combination of Underpotential Deposition and Scanning Tunneling Microscopy: Kinetics of Self-Assembly**, J. Electrochem. Soc., 138 (8), L23 (1991).
[2-5nm diameter x 0.5 nm deep pit structures in SAM films]
- SAM17) C.D. Bain, G.M. Whitesides, **Formation of Monolayers by the Coadsorption of Thiols on Gold: Variation in the Length of the Alkyl Chain**, J. Am. Chem. Soc., 111, 7164 (1989).
[simultaneous growth of two different sized thiols - replication???
- SAM18) W.J. Dressick, C.S. Dulcey, J.H. Georger, Jr., G.S. Calabrese, J.M. Calvert, **Covalent Binding of Pd Catalysts to Ligating Self-Assembled Monolayer Films for Selective Electroless Metal Deposition**, J. Electrochem. Soc., 141 (1), 210 (1994).
[Organosilanes containing a metal binding functional group are catalyzed and plated - see article on low voltage electron beam lithography by CRK Marrian]
- SAM19) G.A. Carson, S. Granick, **Self-Assembly of Octadecyltrichlorosilane Monolayers on Mica**, J. Mater. Res., 5 (8), 1745 (1990).
[Method for self-assembly of OTS on Mica - intro has good overview of SAMs]
- SAM20) C.S. Dulcey, J.H. Georger, Jr., V. Krauthamer, D.A. Stenger, T.L. Fare, J.M. Calvert, **Deep UV Photochemistry of Chemisorbed Monolayers: Patterned Coplanar Molecular Assemblies**, Science, 252, 551 (1991).
[UV exposure of organosilane film leaves hydrophilic reactive sites which can undergo a second chemisorption to build up orthogonal SAMs with similar substrate attachment]
- SAM21) V.L. Colvin, A.N. Goldstein, A.P. Alivisatos, **Semiconductor Nanocrystals Covalently Bound to Metal Surfaces with Self-Assembled Monolayers**, J. Am. Chem. Soc., 114, 5221 (1992).
[Free thiols on surface of SAM bind to CdS clusters]

8.4.5. Molecular Imprinting

- MI1) K. Mosbach, **Molecular Imprinting**, Trends in Biochem. Sci., 19, 9 (1994).
[Review article]
- MI2) F. Flam, **Molecular Imprints Make a Mark**, Science, 263, 1221 (1994).
[Popular Review]

- MI3) G. Vlatakis, L.I. Andersson, R. Müller, K. Mosbach, Drug Assay Using Antibody Mimics Made by Molecular Imprinting, *Nature*, 361, 645 (1993).
- MI4) O. Ramström, L.I. Andersson, K. Mosbach, Recognition Sites Incorporating Both Pyridinyl and Carboxy Functionalities Prepared by Molecular Imprinting, *J. Org. Chem.*, 58, 7562 (1993).
- MI5) T. Shimada, R. Kurazono, K. Morihara, Footprint Catalysis. V. Substituent Effects of Template Molecules on the catalytic Behavior of Imprinted Molecular Footprint Cavities, *Bull. Chem. Soc. Jpn.*, 66 (3), 836 (1993).
- MI6) J. Matsui, T. Kato, T. Takeuchi, M. Suzuki, K. Yokoyama, E. Tamiya, I. Karube, Molecular Recognition in Continuous Polymer Rods Prepared by a Molecular Imprinting Technique, *Anal. Chem.*, 65, 2223 (1993).
- MI7) E. Hedborg, F. Winquist, I. Lundström, L.I. Andersson, K. Mosbach, Some Studies of Molecularly-Imprinted Polymer Membranes in Combination with Field-Effect Devices, Sensors and Actuators A, 37-38, 796 (1993).
- MI8) I.R. Dunkin, J. Lenfeld, D.C. Sherrington, Molecular Imprinting of Flat Polycondensed Aromatic Molecules in Macroporous Polymers, *Polymer*, 34 (1), 77 (1993).
- MI9) K. Dabulis, A.M. Klibanov, Molecular Imprinting of Proteins and Other Macromolecules Resulting in New Adsorbents, *Biotech. and Bioengr.*, 39, 176 (1992).
- MI10) P.K. Dhal, F.H. Arnold, Metal-Coordination Interactions in the Template-Mediated Synthesis of Substrate-Selective Polymers: Recognition of Bis(imidazole) Substrates by Copper(II) Iminodiacetate Containing Polymers, *Macromolecules*, 25, 7051 (1992).
- MI11) K.J. Shea, D.Y. Sasaki, An Analysis of Small-Molecule Binding to Functionalized Synthetic Polymers by ^{13}C CP/MAS NMR and FT-IR Spectroscopy, *J. Am. Chem. Soc.*, 113, 4109 (1991).
- MI12) M. Glad, O. Norrlöw, B. Sellergren, N. Siegbahn, K. Mosbach, Use of Silane Monomers for Molecular Imprinting and Enzyme Entrapment in Polysiloxane-Coated Porous Silica, *J. Chromatography*, 347, 11 (1985).

8.4.6. Sol-Gel Matrices

- SGM1) J.L. Keddie, M.W. Russell, G.T. Kraus, V.K. Seth, E.P. Giannelis, Sol-Gel Thin Films, National Nanofabrication Facility Research Accomplishments 1991-1992, p. 136.
[Sol-Gel ceramic thin film deposition: TiN , TiO_2 , Ta_2O_5 , PZT, $\text{SiO}_2\text{-TiO}_2$]
- SGM2) K.M. Choi, K.J. Shea, New Materials for Synthesis of Quantum-Sized Semiconductors and Transition-Metal Particles. Microporous Polysilsesquioxanes as a Confinement Matrix for Particle Growth, *Chem. Mater.* 5, 1067 (1993).
[Metal cluster growth within sol-gel matrix]
- SGM3) T. Gacoin, F. Chaput, J.P. Boilot, G. Jaskierowicz, Complex Metal Clusters in Organically Modified Oxide Matrices, *Chem. Mater.* 5, 1150 (1993).
[Metal cluster growth within sol-gel matrix]
- SGM4) C.L. Schutte, P.M. Smith, G.M. Whitesides, Analysis of Depth Profiles of Sol-Gel Derived Multilayer Coatings by Rutherford Backscattering Spectrometry and by

Cross-Sectional Transmission Electron Microscopy, J. Mater. Res., 6 (4), 835 (1991).
[Multilayer ceramic thin films prepared using sol-gel techniques]

8.4.7. Impurity Gettering

IG1) S.M. Meyers, D.M. Follstaedt, D.M. Bishop, Binding of Copper to Nanocavity Surfaces in Silicon, SAND93-0244C Sandia National Laboratories Report (1993).
[Cu binds to dangling Si bonds on walls of nanocavities]

IG2) K. Graff, Transition Metals in Silicon and their Gettering Behaviour, Mater. Sci. Eng. B, 4, 63 (1989).
[Review on gettering of transition metals in Si]

8.5. MISCELLANEOUS

8.5.1. Replication

R1) G. Reznik, M. Issacson, A Technique for Fabrication of Textured Thin Carbon Films, Ultramicroscopy, 40, 181 (1992).
[Replication of 120 nm deep groove pattern in 10 nm thick carbon film]

8.5.2. Conducting Polymer Lateral Growth

CPLG1) M. Nishizawa, M. Shibuya, T. Sawaguchi, T. Matsue, I. Uchida, Electrochemical Preparation of Ultrathin Polypyrrole Film at Microarray Electrodes, J. Phys. Chem 95, 9042 (1991).
[lateral electrosynthesized growth of conducting polymer]

CPLG2) M. Okano, K. Itoh, A. Fujishima, K. Honda, Generation of Organic Conducting Patterns on Semiconductors by Photoelectrochemical Polymerization of Pyrrole, Chem. Lett.
[lateral electrosynthesized growth of conducting polymer]

8.5.3. Metrology

MET1) M. Noguchi, Y. Kembo, 40-nm Particle High Probability Detection for Bare Wafer Using Side-Scattered Light, SPIE, 1926, 536 (1993).
[Optical noise scattered from Si wafer detects 38nm high particles on the surface]

INITIAL DISTRIBUTION:

R. Skinner
c/o Limit Point Systems
Sandia California

Kansas State University (2)
Department of Physics
Attn: D. Parks
M. Stockli
Manhattan, KA 66506

National Institute of Standards and Technology (NIST)
Attn: J. Gillaspay
Bldg. 221, Room A167
Gaithersburg, MD 20899

California Institute of Technology
Department of Physics
Attn: E. Parilis
Pasadena, CA

MS 0320	C. E. Meyers, 1011
MS 0986	N. A. Godshall, 2665
MS 9001	J. C. Crawford, 8000; Attn: E. E. Ives, 5200 J. B. Wright, 5300 R. J. Detry, 8200 P. N. Smith, 8500 L. A. West, 8600 D. L. Crawford, 8900
MS 9004	M. E. John, 8100
MS 9054	W. J. McLean, 8300
MS 9105	L. A. Hiles, 8400
MS 9141	M. Dyer, 8800
MS 9161	R. H. Stuhlen, 8342
MS 9162	A. E. Pontau, 8347
MS 9162	R. J. Bastasz, 8347 (10)
MS 9162	J. Whaley, 8347
MS 9163	W. Bauer, 8302
MS 9163	R. W. Schmieder, 8302 (10)
MS 9401	R. C. Wayne, 8700
MS 9402	M. W. Perra, 8714
MS 9402	G. J. Thomas, 8715
MS 9403	M. I. Baskes, 8712
MS 9404	J. C. Wang, 8713

MS 9022	Mail Distribution Team, 8533-1/for OSTI (10)
MS 9022	Mail Distribution Team, 8533-1/Technical Library, MS 0899, 13414
MS 0899	Technical Library, 13414 (4)
MS 9018	Central Technical Files, 8523-2 (3)