PROPERTIES AND APPLICATIONS OF ION-IMPLANTED ALLOYS*

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ABSTRACT

Ion implantation is a controlled and versatile means for near-surface alloying of metals. Supersaturated solutions, metastable compounds, amorphous phases, and equilibrium alloys have been produced. Uses include the investigation of new metastable phases, characterization of alloying reactions occurring in conventional materials, and improvement of surface properties such as hardness, wear, and corrosion. A brief review is given of the physical processes occurring during ion implantation, the types of alloys which result, and representative applications.

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DISCLAIMER

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I. INTRODUCTION

Alloying of metals by implantation of high-energy ions (≥ 10 keV) has several features which distinguish it from more conventional methods. First, it produces an intimate atomic mixture within the near-surface region whose composition is not limited by thermodynamics. Moreover, concentration-versus-depth profiles may be tailored by varying ion dose and energy, subject to an upper bound of typically 5 - 30 at.% on the concentration which is a consequence of sputtering. A second important feature is the generation of atomic displacements by the incident ion beam. This usually results in extensive lattice damage, and it may also induce significant atomic transport. Third, since ion implantation is an athermal process, thermally activated phenomena may be independently regulated via the host temperature.

The above characteristics allow a high degree of control and versatility in the formation of near-surface (≤ 1 μm) alloys. Highly supersaturated solid solutions,¹⁻⁶ metastable intermetallic compounds,⁷ amorphous phases,^{5,8} and equilibrium-phase alloys^{9,10} have been produced. In addition, the low-temperature evolution of reacting systems has been greatly accelerated.^{11,12} These capabilities have been used both in basic studies of alloying processes and to achieve desired

macroscopic properties. As compared to the highly developed applications of ion implantation to semiconductor doping and to radiation damage studies, implantation metallurgy is relatively new, having expanded greatly in the past five years.

The present paper briefly summarizes the properties and uses of ion-implanted metals. Section II outlines the physical processes which are believed to underlie the observed behavior. In Section III, the various types of alloy states are discussed. Then, in Section IV, applications are illustrated by several examples.

II. PHYSICAL PROCESSES

A. Ion Damage

High energy ions dissipate a portion of their kinetic energy in atomic displacements, thereby producing vacancy-interstitial pairs. The defect generation rates are usually high: typically, except for the lightest ions, about one displacement occurs per lattice spacing along the ion track. The character of the damage is illustrated in Fig. 1, which shows the observed vacancy distribution in W resulting from implantation of three different individual ions.¹³ These data were obtained by field ion microscopy at a temperature of 10 K, below the onset of thermally activated lattice recovery.

When the temperature is sufficiently high, irradiation defects undergo thermally activated migration, and lattice recovery occurs. The principal features of the recovery process are illustrated by considering a pure fcc metal subjected to low-level irradiation near absolute zero and then isochronally annealed at a series of increasing temperatures. This particular case has been extensively studied,^{14,15} and it is broadly representative of metallic systems. Self-interstitials become mobile first, causing a portion of these point defects to recombine with vacancies and the remainder to form clusters. As the temperature is increased further, the interstitial clusters coarsen into dislocations observable by electron microscopy. Next, vacancies become mobile, with some annihilating at the interstitial agglomerations and others forming clusters. Additional increases in temperature then cause the vacancy clusters to coarsen into observable dislocations. Finally, all of the dislocations anneal out through self-diffusion processes, and the lattice recovery reaches completion.

In most intermetallic systems the following rules of thumb are applicable: interstitials become mobile below room temperature, vacancies may begin to diffuse either above or below room temperature depending on composition, and the dissolution of extended defects occurs at an

elevated temperature. Consequently, implantation into metals at room temperature usually results in a dense array of dislocations. An example is given in Fig. 2, which shows a transmission electron micrograph of Al following room-temperature implantation of Ni.¹⁶

The relatively high implanted fluences often used in metals work, typically $\geq 10^{16}$ ions/cm², may produce many atomic displacements per host atom. Under these conditions the damage cascades overlap, and a saturation level of defects is produced. Depending upon composition and temperature, the recovery processes (either spontaneous or thermally activated) may maintain crystallinity; alternatively, the alloy may become amorphous. The latter condition is always metastable, and recrystallization takes place above some characteristic temperature. Among metallic systems which have been implanted at room temperature, a majority have remain crystalline.¹⁻⁶ Those which are driven amorphous^{5,8} often have a metalloid element as a constituent, following a trend observed in alloys quenched from the melt.¹⁷ There are a number of exceptions, however, such as amorphous Cu-W and Ni-Dy.

Ion irradiation may substantially alter atomic transport, particularly at temperatures below the onset of appreciable perfect-lattice self-diffusion. Three

mechanisms are observed most frequently.¹⁸ First, atomic collisions within the ion damage cascade produce athermal atomic motion. Second, at temperatures sufficiently high for thermally activated diffusion of irradiation-produced vacancies and interstitials, the defect migration enhances atomic diffusion. This effect is mostly observed for substitutional solutes. It may be much larger than the above athermal collisional mixing, since a point defect often migrates many lattice spacings before annihilation. The third mechanism affecting transport is solute trapping by defects, which inhibits diffusion. This process is important principally for interstitial solutes, which usually become mobile at a temperature below that of complete lattice recovery.

B. Configuration of the Implanted Atoms

Implanted atoms are initially dispersed on an atomic scale. Discrete precipitates or clusters are generally not observed, even if the alloy is thermodynamically supersaturated, unless the temperature is high enough for thermally assisted solute migration to occur. This solutionized condition often persists at room temperature, and here the lattice location of the implanted atoms has been determined by ion channeling in a number of systems.¹⁻⁶

The measured site is frequently well defined and unique, particularly when the implanted concentration is no more than several at.%, and may be either substitutional or interstitial.

The physical processes which lead to these lattice location results are not well understood. One contributing mechanism is probably the replacement collision, in which an incident ion loses the last increment of its energy by exchanging with a host atom, thereby assuming a substitutional site.¹⁹ It is also possible that lattice agitation produced by the damage cascade, i.e. the "thermal spike",²⁰ assists the implanted atom in moving to a local minimum in positional energy. In room-temperature experiments, thermally activated processes probably play a role. For instance, if the implanted atom is initially interstitial, it may be sufficiently mobile to diffuse into a nearby vacancy produced by the irradiation.⁶ Detailed consideration of the lattice location results suggests that no one process is always dominant.

When an implanted alloy is held at a temperature where all of the constituents are mobile, the system approaches thermodynamic equilibrium.⁹ Precipitation occurs in conformance with the phase diagram, and, as discussed in Section II. A, the lattice damage anneals out. An important

feature of the equilibration process is that it usually goes nearly to completion within the implanted layer before there is significant solute diffusion into the underlying bulk of the host. This occurs simply because the diffusion lengths for local thermal evolution are small compared to those for dissolution into the bulk.

In certain cases, specific solutes may become mobile at temperatures well below the onset of general diffusion. This occurs particularly for small interstitial species such as H or C. Under these conditions precipitation can occur, but the system does not necessarily achieve the equilibrium state described above.⁹ The phases which form may be metastable, and the level of lattice damage may remain high.

III. IMPLANTED ALLOY STATES

A. Supersaturated Crystalline Solutions

At temperatures where thermally activated transport is negligible, the initially dispersed distribution of implanted atoms may persist for concentrations orders of magnitude above the equilibrium solubility. A number of highly supersaturated crystalline solutions have been produced at room temperature in various metallic hosts, including Be, Al, Fe, Ni, and Cu.¹⁻⁶ As indicated earlier, the implanted solutes frequently occupy a single substitutional or interstitial site, even at concentrations

of several at.%. For example, implanted Ag in Cu was found to be nearly 100% substitutional at 17 at.%²¹, although its room-temperature solubility is < 0.1 at.%.

The lattice position occupied by the implanted atoms cannot generally be predicted at present, although systematic trends are observed as a function of host and implanted species.⁵ The greatest success in theoretical treatments has been achieved for the host Be.⁴ The behavior of heavy ions implanted into this light metal is believed to be considerably simplified by the complete absence of one process, the replacements collision,¹⁹ which is precluded by the disparity in atomic masses. The theoretical calculations were based on the Miedema approach.²² Minimum-energy configurations were determined as a function of the two known parameters ϕ^* and n_{WS} , which are related respectively to elemental work functions and to the elemental electron density at the boundary of the Wigner-Seitz cell. The results are compared with experiment in Fig. 3, where the solid lines delineate the predicted regions of substitutional, tetrahedral interstitial, and octahedral interstitial occupation. The agreement is seen to be excellent. It suggests that, in the absence of replacement collisions, the lowest-energy local site is preferentially occupied.

B. Metastable Crystalline Structures

Under certain conditions ion implantation leads to a metastable crystalline structure. Such phases range from randomized solutions with a wide composition range to stoichiometric compounds. Depending upon the nature of the system, their occurrence is variously attributed to the high levels of lattice damage, to mobility of only certain constituents of the material such as light interstitials, and to athermal production of a composition closely corresponding to a metastable compound.

The wide variety of implanted alloys in this category is illustrated by several examples. In one instance, P implantation of fcc Ni apparently produced small hcp inclusions.⁸ Solid-state slip mechanisms induced by implantation damage were cited as the cause, presumably with the P stabilizing the hcp configuration. Another experiment entailed implanting C into Fe at room temperature, followed by annealing at 603 K.²³ Martensite, a metastable, distorted bcc Fe lattice with interstitial C, was reported at room temperature. Annealing then produced precipitates of the metastable compound Fe_3C . These results correspond qualitatively to the behavior of bulk C steels quenched and then tempered. In a final example, deposited Pt films on Si substrates were irradiated with Xe ions at room

temperature to produce a Si-rich Pt-Si mixture.⁷ Annealing at 673-773 K then yielded the metastable compounds Pt_2Si_3 and Pt_4Si_9 in separate layers.

C. Amorphous Phases

The high atomic displacement rates and composition changes produced by ion implantation drive certain alloys amorphous. It has been argued⁵ that this method for amorphization is exceptionally effective as compared to techniques such as splat cooling. For example, in analogy with quenching from the melt, an effective cooling rate has been defined as the melting temperature divided by the lifetime of an ion collision cascade; the resulting rate is extremely high, typically $\sim 10^3\text{K}/10^{-12}\text{s} = 10^{15}\text{K/s}$. Another useful feature of implantation is that both composition and the level of disorder may be varied continuously, thereby permitting the amorphization process to be studied in some detail.

Alloy layers which appear amorphous in transmission electron diffraction have been reported from a number of implantation experiments.^{5,8} In most cases these studies were carried out at room temperature. The injected species and hosts included the following: B or F into Fe, Co, or Ni; P into 316 stainless steel; Dy into Fe or Ni; Bi into Ni; Ta or W into Cu; and Au into Pt. (The amorphization of

semiconductors and insulators is beyond the scope of this paper.) At present it is not possible to predict precisely which implanted alloys will undergo a crystalline-to-amorphous transition. However, two features of the above results may be noted: first, in initially pure metals, the amorphous condition occurred only at implanted concentrations ≥ 10 at.%; and second, this state was consistently achieved when the implanted species was a metalloid.

D. Equilibrium Alloys

When metals are implanted and then heated so that the diffusion lengths $\sqrt{Dt}$ for all constituents are large compared to the lattice spacing, a state close to thermodynamic equilibrium is usually achieved within the implanted region. Irradiation damage anneals out, and additional phases expected from the phase diagram are observed to precipitate. As an example, Fig. 4 shows a transmission-electron dark-field micrograph of ϵ -FeSb precipitates in Sb-implanted Fe after heating to 873 K.²⁴ Similar conformance to the phase diagram following annealing has been found for various implantations into the hosts Be, Al, Fe, and Cu.²⁵

Annealing also causes the implanted species to diffuse into the underlying bulk of the host. Typical behavior is illustrated in Fig. 5, where measured depth profiles of

Implanted Cu in Be are given before and after annealing at 673 K.²⁶ Migration into the bulk is evidenced here by the emergence of a lower-amplitude tail from the peak. The region of the peak contains Be₃Cu precipitates, while the tail reflects Cu in solution within single-phase Be, and the two profile segments intersect at a concentration equal to the Cu solubility at the annealing temperature. It should be noted that, in principle, such continuing solute transport does not allow full thermodynamic equilibrium within the implanted layer. The departure is usually negligible, however, because diffusion-limited communication between closely spaced precipitates is rapid compared to long-range migration into the substrate. Thus, the rates of these two processes typically differ by a factor of $\sim 10^4$.

In the above equilibrium regime ion implantation provides a high degree of control over precipitation. Size, volume fraction, and depth distribution may be independently varied over wide ranges. Very high particle densities and volume fractions have been achieved, sometimes greatly exceeding the capabilities of conventional alloying. For example, TiC precipitates have been introduced in Fe to a density of $\sim 10^{20}$ particles/cm³ and a volume fraction of $\sim 30\%$.²⁷

IV. APPLICATIONS

Implantation work with metals has included the production of new metastable alloys, elucidation of reactions occurring in conventional materials, and development of the technique as a production tool. In the area of metastable alloys, a notable example is the discovery of several new amorphous systems. These include Cu-W, Cu-Ta, Fe-Dy, Ni-Dy, and Pt-Au.^{5,6}

The control and versatility of ion implantation make it a powerful tool with which to investigate alloying processes in technologically important conventional materials. Moreover, the microscopic scale and the possibility of using radiation-enhanced diffusion facilitate measurements at lower temperatures. Studies in the equilibrium regime (Section III. D) have yielded information on diffusion rates, phase diagrams, and new impurity trapping mechanisms.²⁵ For example, experiments in ion-implanted Fe have shown that TiC precipitates are effective traps for Sb impurities.²⁸ The depth profiles in Fig. 6 exhibit one key observation of this work. Here the TiC precipitates and the Sb were initially located at different depths within the Fe host. Annealing then caused the Sb to redistribute in conformance with the TiC precipitate distribution. Discovery of this trapping

mechanism may provide a means for immobilizing Sb and other metalloid impurities within ferritic steels, thereby reducing the embrittlement which results from their grain-boundary segregation.

Ion implantation now seems a realistic tool for altering the surface properties of small components such as bearings and cutting edges. Hardness, wear resistance, and resistance to corrosion have been improved by an order of magnitude in certain cases.^{29,30} As an example, Fig. 7 shows the wear rate of a type 416 stainless steel cylinder pressed onto a rotating, lubricated cylinder of 304 stainless steel.³⁰ The erosion rate of the fixed cylinder is seen to drop ~ 50 times upon N implantation of the rotating cylinder. The responsible mechanism has not been established, but is believed related to an interaction between the N and dislocations which impedes the motion of the latter. The effect persists to depths much greater than the implantation range, perhaps because the N migrates before the advancing wear front.

Recently, the irradiation-induced transport mechanisms discussed in Section II. A have been exploited to accelerate thin-film reactions. For example, the temperature of silicide

formation from various Si-metal couples has been reduced several hundred °K by inert gas or Si ion bombardment.^{7,11,12} This may prove to be a significant capability in future low-temperature fabrication of semiconductor devices.

V. SOME FUTURE DEVELOPMENTS

Prospects seem good for overcoming several widely accepted constraints on ion implantation of metals. First, the limit on compositional changes imposed by sputtering, typically 5 - 30 at.%, has already been circumvented by ion-induced mixing of predeposited films.^{7,11,12} Additional work is needed to determine whether the mixing rate is sufficient in all systems at all temperatures, and to what extent the mixed and implanted alloys differ in microstructure. Second, pulsed surface heating by lasers or electron beams may permit damage recovery while retaining other metastable characteristics such as supersaturation. Highly super-saturated and defect-free solutions have been achieved in Si,³¹ and similar experiments are now being conducted in metallic hosts. Finally, a new generation of high-flux implantation accelerators is being planned, and with these machines the feasible implanted areas should be measured in square meters rather than centimeters.

References

1. H. de Waard and L. C. Feldman, in Applications of Ion Beams to Metals, edited by S. T. Picraux, E. P. EerNisse, and F. L. Vook (Plenum, New York, 1974), pp. 317-351, review paper.
2. J. A. Borders and J. M. Poate, Phys. Rev. B 13, 969 (1976).
3. D. K. Sood and G. Dearnaley, in Applications of Ion Beams to Materials 1975, edited by G. Carter, J. S. Colligon, and W. A. Grant (Institute of Physics, London, 1976), pp 196-203.
4. E. N. Kaufmann, R. Vianden, J. R. Chelikowsky, and J. C. Phillips, Phys. Rev. Lett. 39, 1671 (1977).
5. J. M. Poate, J. Vac. Sci. Technol. 15, 1636 (1978), review paper.
6. E. N. Kaufmann, R. Vianden, T. E. Jackman, J. R. MacDonald, and L. G. Haggmark, J. Phys. F 9, L23, (1979), and references therein.
7. B. Y. Tsaur, Z. L. Liau, and J. W. Mayer, Phys. Lett. A 71, 270 (1979).
8. W. A. Grant, J. Vac. Sci. Technol. 15, 1644 (1978), review paper.
9. S. M. Myers, J. Vac. Sci. Technol. 15, 1650 (1978), review paper.
10. R. A. Kant, S. M. Myers, and S. T. Picraux, J. Appl. Phys. 50, 214 (1979).

References (Continued)

11. B. Y. Tsaur, Z. L. Liau, and J. W. Mayer, Appl. Phys. Lett. 34, 168 (1979).
12. S. Matteson, J. Roth, and M. A. Nicolet, Radiat. Eff., 1979, in press.
13. C. Y. Wei and D. N. Seidman, Appl. Phys. Lett. 34, 622 (1979).
14. W. Schilling, P. Ehrhart, and K. Sonnenberg, in Fundamental Aspects of Radiation Damage in Metals, edited by M. T. Robinson and F. W. Young (National Technical Information Service, Springfield, Va, CONF-751006), pp. 470-492, review paper.
15. F. W. Young, J. Nucl. Mater. 69 & 70, 310 (1978), review paper.
16. S. T. Picraux, D. M. Follstaedt, P. Baeri, S. U. Capisano, G. Foti, and E. Rimini, Radiat. Eff., 1979, in press.
17. See, for example, Rapidly Quenched Metals, edited by N. J. Grant and B. C. Giessen (M.I.T. Press, Cambridge, Mass., 1976).
18. S. M. Myers, Nucl. Instrum. and Methods, 1979, in press, review paper.
19. D. K. Brice, in Applications of Ion Beams to Materials 1975, edited by G. Carter, J. S. Colligon, and W. A. Grant (Institute of Physics, London, 1976) pp. 334-339.

References (Continued)

20. See for example, P. Sigmund, Appl. Phys. Lett. 25, 169 (1974).
21. J. M. Poate, J. A. Borders, A. G. Cullis, and J. K. Hirvonen, Appl. Phys. Lett. 30, 365 (1977).
22. A. R. Miedema, Phillips Tech. Rev. 36, 217 (1976), and references therein.
23. F. L. Vogel, Thin Solid Films 27, 369 (1975).
24. S. M. Myers and H. J. Rack, J. Appl. Phys. 49, 3246 (1978).
25. See, for example, Ref. 9 and references therein.
26. S. M. Myers and J. E. Smugeresky, Metall. Trans. A 8, 609 (1977).
27. D. M. Follstaedt and S. M. Myers, Radiat. Eff., 1979, in press.
28. S. M. Myers, D. M. Follstaedt, and H. J. Rack, Appl. Phys. Lett. 33, 396 (1978).
29. G. Dearnaley, Trans. Inst. of Metal Finishing 56, 25 (1978), review paper.
30. J. K. Hirvonen, J. Vac. Sci. Technol. 15, 1662 (1978), review paper.
31. See, for example, C. W. White, P. P. Pronko, S. R. Wilson, B. R. Appleton, J. Narayan, and R. T. Young, J. Appl. Phys. 50, 3261 (1979).

Figure Captions

1. Observed spatial distribution of vacancies within three individual ion damage cascades in W. The data were obtained at a temperature of 10 K using field ion microscopy. The arrows give the direction of the incident ion, and bars connecting the vacancies have a length equal to one nearest-neighbor lattice spacing. (Ref. 13)
2. Transmission-electron dark-field micrograph of Al following room-temperature implantation of 2×10^{15} Ni/cm² at an energy of 150 keV. The dislocations appear as bright regions. (Ref. 16)
3. Miedema plot of lattice location for various elements implanted into hcp Be at room temperature. The experimental data points were obtained by ion channeling, and theoretically predicted regions for occupation of the three sites are separated by solid lines. (Ref. 4)
4. Transmission-electron dark-field micrograph of ϵ -FeSb precipitates in Sb-implanted Fe. Room-temperature implantation of 6×10^{16} Sb/cm² at 200 keV was followed by a 0.5 hour anneal at 373 K. Phases were identified by transmission electron diffraction.
5. Depth profiles of implanted Cu in Be before and after 94 hours at 673 K. The concentration scale is expanded 2.5 times on the right-hand plot.
6. Redistribution of Sb to TiC precipitates in Fe during annealing. The Fe host was alloyed by ion implantation at room temperature prior to annealing. The TiC precipitates

Figure Captions (Continued)

- had a mean size of ~ 2 nm, and their depth distribution is reflected in the measured Ti profile. (Ref. 28)
- 7. Normalized wear rate for a stationary stainless steel cylinder held against a rotating stainless steel cylinder as a function of implantation conditions. (Ref. 30)

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Sb, Ti - IMPLANTED Fe

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