LASER SPECTROSCOPY OF SPUTTERED ATOMS*

D. M. Gruen, M. J. Pellin, C. E. Young, and W. F. Calaway

Materials Science & Technology
and
Chemistry Divisions
Argonne National Laboratory
Argonne, IL 60439

DISCLAIMER

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, 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 or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

To be presented at:

32nd National AVS Symposium
Houston, TX
November 18-22, 1985

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy.

MASTER*Jsw*

LASER SPECTROSCOPY OF SPUTTERED ATOMS*

D. M. Gruen, M. J. Pellin, C. E. Young, and W. F. Calaway

Materials Science & Technology
and
Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

ABSTRACT

The use of laser radiation to study the sputtering process is of relatively recent origin. Much has been learned from this work about the basic physics of the sputtering process itself through measurements of velocity and excited state distributions of sputtered atoms and the effects of absorbates on substrate sputtering yields. Furthermore, the identification, characterization, and sensitive detection of sputtered atoms by laser spectroscopy has led to the development of in situ diagnostics for impurity fluxes in the plasma edge regions of tokamaks and of ultrasensitive methods (ppb Fe in Si) for surface analysis with ultralow (picocoulomb) ion fluences. The techniques involved in this work, laser fluorescence and multiphoton resonance ionization spectroscopy, will be described and illustrations given of results achieved up to now.

*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy.

Introduction

The use of laser radiation to study the sputtering process is of relatively recent origin.¹⁻⁶ Much has been learned from this work about the basic physics of the sputtering process itself through measurements of velocity⁷⁻⁹ and excited state distributions¹⁰⁻¹² of sputtered atoms and the effects of adsorbates on substrate sputtering yields.¹³ Furthermore, the identification, characterization, and sensitive detection of sputtered atoms by laser spectroscopy has led to the development of in situ diagnostics for impurity fluxes in the plasma edge regions of tokamaks¹⁴⁻²⁰ and of quantitative methods for surface analysis with ultralow ion fluences.²¹⁻²⁹

It is possible that this decade will see a demonstration of energy break-even in fusion machines such as TFTR (Princeton, NJ), JET (Culham, UK), and JT 60 (Tokyo) where impurity generation during long-pulse operation must be kept to a minimum. It is also an era which may see semiconductor devices based on submicron-sized structures requiring quantitative analysis of impurities at progressively lower impurity levels and high spatial resolution. The greatly increased sensitivity for the detection of sputtered products provided by laser-induced fluorescence (LIF) and resonance ionization spectroscopy (RIS) makes the rapid application of the techniques in these two advancing technological areas particularly attractive.

Depending on the details of an atom's energy level structure, LIF can measure sputtered fluxes of 10^5 - 10^8 atoms/cm³ while RIS sensitivity in terms of atoms detected/atoms sputtered can be

expected to reach 0.1 while employing picocoulomb ion fluences for a single measurement. A survey of the work which has been done in this field will be given here.

Sputtering

Sputtering occurs whenever an energetic particle, such as a kilovolt argon ion, transfers sufficient momentum to a lattice to exceed an atom's surface binding energy.³⁰ Sputtered products are a complex mixture of atoms, ions, and molecules in ground and excited electronic states. Because surface scientists are very familiar with the SIMS technique which measures only the secondary ions, it is often overlooked that in many instances the major fraction (>99%) of the sputtered flux consists of neutral atoms.⁸ Since the surface ionization coefficient is a very sensitive function of surface composition, the ion fraction is highly variable ("matrix effects") thus making it very difficult to interpret SIMS results quantitatively in terms of the concentrations of surface components. The neutral fraction, on the other hand, is much less sensitive to surface chemical composition.

Sputtering is an exceedingly surface-sensitive technique. Detailed calculations based on the TRIM Monte Carlo computer code have demonstrated that more than 90% of all sputtered atoms come from the very first or surface layer. More recently experimental evidence has also been deduced which verifies the theoretical calculations.³¹ However, to take advantage of the extreme surface sensitivity of sputtering, measurements must be made with very low ion fluences. At higher ion doses, displacement damage to surface and subsurface layers results in radiation-enhanced

segregation, ion beam mixing, recoil implantation and other effects which alter the surface composition.³²

The excellent detection sensitivity of LIF and RIS makes it possible to obtain meaningful results with ion fluences so low (picocoulombs in the case of RIS) that only a small fraction of a monolayer of surface atoms need be removed during a single measurement. With such low ion doses, ion-induced surface damage becomes negligible.

LIF and RIS of Sputtered Atoms

Tunable radiation from dye lasers is available to pump the resonance transitions of atoms for most elements in the periodic table.

In a typical experiment, narrowband laser radiation intercepts a beam of sputtered atoms coming from a target surface which is being bombarded by a pulsed ion beam in an UHV system ($\sim 10^{-11}$ Torr). Laser radiation tuned to a resonance transition excites electrons from ground to parity allowed states. In the case of LIF, spontaneously emitted fluorescence radiation is detected using photon counting techniques. For the RIS experiment, a second photon (308 nm) from a portion of the excimer beam, which is split out of the amplifying beam, is used to pump atoms in excited states to the still higher energy ionization continuum. Ions produced in such multiphoton ionization steps are extracted electrostatically from the ion production region and counted with high efficiency using spiraltron or multichannel plate detectors.²²

An illustration of the RIS and LIS detection schemes is given by a partial energy level diagram including transition rates (A coefficients), Lande g factors, and transition wavelengths for gaseous Fe atoms (Fig. 1). The resonance ionization transition sequence for Fe atoms in the a^5D_4 ground state is shown. The resonant photon of this two-photon, two-color sequence is labeled LASER and couples the a^5D_4 level to the y^5D^0 excited Fe state. The ionizing photon (308 nm, labeled RIS) couples the y^5D^0 state to the ionization continuum. For comparison, the LIF transition sequence is also depicted. Excitation (labeled LASER) is accomplished again using the $a^5D_4 \rightarrow y^5D^0$ transition. In the absence of an ionizing radiation, fluorescence photons are generated as a result of radiative $y^5D^0 \rightarrow a^5F_5$ decay and are detected.

Velocity Distributions of Sputtered Atoms

Atoms thermally evaporating from a metal, say iron atoms from metallic iron at 2000 K, have a Maxwellian energy distribution peaked at 0.1 eV. Iron atoms sputtered by 3 keV argon ions from an iron target at ambient (~300 K) temperatures, on the other hand, have energies peaked near 2 eV. In order to account for the velocity distribution of sputtered atoms, one can resort to the theory of collision cascade sputtering developed by Sigmund and Thompson.^{33,34} An important check on the accuracy of that theory are the experimental determinations of energy distributions which have been difficult measurements to make until the advent of LIF techniques. Using LIF, several determinations of velocity distributions of sputtered atoms based on

Doppler shift LIF have been made. The data shown in Fig. 2 on sputtered iron atoms are illustrative of such results.

A few percent of laser light near 302.07 nm corresponding to the wavelength of a resonance transition is sent to an iron hollow cathode lamp and the optogalvanic signal is digitized along with the fluorescence signal from sputtered atoms on each laser shot. The strong optogalvanic peak serves as a zero-frequency-shift marker, allowing the precise alignment of successive 30 GHz sweeps for averaging. A 3 GHz interferometer is used as a fixed etalon generating calibrating frequency markers as the laser scans.

The experiment was performed with a static argon gas pressure in the chamber of $\sim 6 \times 10^{-5}$ Torr producing a current of 18 μ A at the target. From sputtering yield data for iron and the known collection geometry, a density of $\sim 1 \times 10^8$ cm $^{-3}$ for Fe distributed over all electronic states is calculated at the center of the detection region. The laser was attenuated to 1.8 kW/cm 2 where power broadening of the measured distribution was not significant. A total of 100 laser shots per point were averaged in Fig. 2 which was obtained at an excimer laser repetition rate of 40 Hz.

The solid line through the points is the density distribution given by the Sigmund-Thompson theory constrained to the parameter $n=2$. The thermochemical value of 4.315 eV for the iron sublimation energy was used. No allowance for spatial averaging has been made. Model calculations indicate a peak shift of $<2\%$ for the actual geometry. The velocity distributions have now

been measured with LIF on a number of different atomic systems all of which confirm the general features of the theoretical predictions.

Excited State Distributions of Sputtered Atoms

As described above, sputtering is the result of a collision cascade initiated when the primary high energy ion impacts the target. In each collision event, whether between the primary ion and a lattice atom or between two lattice atoms, a fraction of the kinetic energy of the colliding partners is converted into electronic excitation. The latter inelastic process is referred to as electronic stopping as compared with elastic or nuclear stopping processes resulting in atomic displacements. Eventually, the collision cascade propagates to the surface where sufficient momentum is occasionally imparted to a surface atom in a final or "causal" collision to overcome its surface binding energy resulting in an ejection or "sputtering" event.

Electronic stopping manifests itself in the sputtering of a small fraction of atoms (10^{-4} - 10^{-6}) in highly excited electronic states (>2 eV) from which spontaneous fluorescence can be detected. Such "secondary photon" emission has been extensively studied for a very long time and has even been proposed as a method for surface analysis.^{35,36}

It turns out that atoms of many elements and particularly the transition elements have electronic energy levels at energies below 2 eV (see, e.g., Fig. 1) but until the advent of the LIF method, it had not been possible to obtain information about fractional occupations of sputtered atoms in these levels. The

reason for this state of affairs is that because of parity selection rules the lifetimes of the low-lying states is so long that atoms occupying them have left the observation volume before decay to a lower state produces a spontaneous fluorescent photon. With LIF techniques, however, these metastable states can be accessed by exciting atoms to higher lying states from which allowed transitions can occur. In this way, the details of electronic stopping mechanisms in solids can be probed by determining the state of electronic excitation of leaving atoms and deducing these from the fraction of kinetic energy converted to electronic excitation in the "causal" or final collision.

As can be seen by inspection of Table I and contrary to the situation for atoms sputtered in electronic states with energies greater than 2 eV, the fractions of atoms sputtered in low-lying levels can be quite large. The picture that emerges is of a continuum both in the fractional occupation of energy levels and in the most probable kinetic energy with which a given atom is sputtered: the higher the degree of electronic excitation, the higher the kinetic energy and the lower the fractional occupation.¹⁰

We now show that detailed considerations of electronic energy transfer in the binary collision approximation can rationalize the observations on atoms sputtered in low (0-2 eV) as well as high-lying states without making additional assumptions concerning energy partitioning.

It has already been pointed out that a very high fraction of sputtered atoms originates from the very surface layer or next to

outermost layer of atoms after suffering collisions which impart kinetic energy sufficient to overcome the surface binding energy. We will now briefly describe calculations of electronic energy transfer for the "causal" collision leading to sputtering using the TRIM Monte Carlo code.^{37,38}

One uses the binary collision approximation to follow the projectile and target atom trajectories collision by collision. The target is assumed to be amorphous and has an associated planar surface potential. Sputtered target atoms must overcome a surface binding energy.

Bulk atoms undergoing cascade (recoil) events are assumed to have binding energies equal to the monovacancy formation energy, ΔH_v . The Miedema model for ΔH_v has been invoked.³⁹

Nuclear scattering and energy loss is prescribed using the Moliere interatomic potential modified by a constant to approach the Biersack-Ziegler potential.⁴⁰ The constant, $C(r)$, is a function of the turning point. For Ar on Ti, $C(r) \approx .9$ for Ar-Ti and Ti-Ti interactions. Electronic energy loss makes use of a combination of Lindhard-Scharff and Oen-Robinson prescriptions.

Calculations of electronic energy loss in the "causal" collisions involving Ti atoms and resulting in sputtering are shown as a function of collision energy in Fig. 3.

The data in Table I are also plotted in Fig. 3. There is qualitative agreement between experiment and theory even though the experiments include a variety of different atomic systems while the calculations are for Ti sputtering only. The fractional population falls off somewhat more rapidly at low energies

of excitation than predicted by TRIM indicating that electronic energy loss is a stronger than linear function of the kinetic energy of the "causal" collision in the range 8-100 eV. It is entirely conceivable that this effect is in part due to de-excitation mechanisms which come into play at the lower end of the velocity spectrum for the departing atoms and which have been neglected in this treatment.

"Static Mode" Laser Fluorescence and Primary Adsorbate Layer Structures

As discussed above, LIF is so sensitive a detection technique that sputtering sufficient to give meaningful results can proceed at rates that do not change the surface composition during a measurement ("static mode"). It has also been pointed out that essentially all sputtered atoms come from the very first surface layer. Therefore, an overlayer one atom in thickness decreases, because of "shadowing," the sputtering yield of the substrate by an order of magnitude. We have recognized that this combination of circumstances allows one to use LIF as a surface structural probe. Recent work on oxygen monolayers on polycrystalline titanium metal is illustrative of this application of LIF.¹³

A Ti foil was oxygen-coated in a position facing an AES system after sputter-cleaning. The oxygen partial pressure ($\sim 10^{-6}$ Pa) was monitored with a quadrupole gas analyzer. In accordance with the high sticking coefficient for oxygen on titanium,⁴¹ one monolayer coverage was achieved at exposures of 1-2 L while 5 L was sufficient to produce an AES signal corresponding to about three monolayers. Desorption of oxygen by the

AES electron beam could be easily observed at coverages higher than two monolayers but could be kept to an acceptable rate by minimizing the electron beam current.

In the "static mode" LIF technique, the ion source is operated in a pulsed mode by application of a 4 μ s pulse producing a 600 V potential difference across the deflection plate system of the ion gun. During most of the 100 ms interval between laser pulses, the undeflected ion beam impacted the outer edge of the Ti target. This mode of operation minimizes sputtering of the central target area during LIF data collection and has been shown to result in virtually unchanged O/Ti ratios during a single run. After measurements at a given O/Ti ratio have been completed, the ion beam is allowed to bombard the central region of the target continuously until the next desired O/Ti ratio is established as indicated by the Auger monitoring system.

Experiments with LIF detection were now performed on the sputtering of Ti atoms as a function of oxygen coverage. First, successive members of the a^3F_J , $J=2,3,4$ ground state multiplet were accessed and fluorescence detected at wavelengths selected from the $a^3F \rightarrow z^3F^0$ system at 520 nm. The LIF signal was followed through diminishing oxygen coverage until essentially clean metal was indicated by Auger measurements. The relative normalization of the curves shown in Fig. 4 for the states of the ground state multiplet was obtained in separate experiments on the clean metal target for each of the $J=2,3,4$ levels. Several features emerge from an examination of Fig. 4. The steps in the Ti yield at or near integral monolayer coverages mirror those observed in

measurements on oxygen desorption yields by Auger spectroscopy. For the Ti yields, these steps are observed more clearly when a He^+ rather than an Ar^+ beam is used. The plateaus are present not only for atoms ejected in the a^3F_4 ground state but also in each of the other members of the ground state multiplet. They are less pronounced in Fig. 4 because of the way in which the data are plotted.

A remarkable result is the small change in yield for Ti atoms ejected from a clean Ti surface versus a Ti surface with one full monolayer of oxygen. For Ar^+ as the primary ion, a 20% decrease is measured while with He^+ no more than a 5% decrease was detected. A factor of two decrease over clean Ti is observed on completion of the second oxygen monolayer. With completion of the third oxygen monolayer, a much more pronounced decrease (factor of 6) in Ti sputtering yield is observed. This is in inverse correlation with the oxygen desorption yield which is small for coverages below two oxygen monolayers but increases dramatically above this level.

The clear implication of these results is that for coverages below two oxygen monolayers, Ti atoms are more accessible to sputtering than oxygen. Since sputtered atoms come nearly exclusively from the surface atomic layer, the primary surface structure must be one involving the formation of oxygen underlayers. Such a model is, in fact, suggested by LEED and XPS measurements of absorbed N on a single crystal Ti surface (0001) which found that the N atoms occupy the subsurface octahedral holes in the hcp Ti lattice in much the same manner as in the crystalline TiN

compound. Interestingly, the structure of TiO and TiN are nearly identical with O replacing N in the octahedral holes.

TRIM code calculations for the underlayer model show that at the one monolayer level good agreement with experiment is obtained lending further support to a structure involving an oxygen underlayer.

If the second oxygen layer is modeled as a surface layer giving an O/Ti/O/Ti/Ti structure, no reasonable set of binding energy parameters gives even marginal agreement with the experimentally derived oxygen and Ti yields. An oxygen adsorption model having two full oxygen underlayers of the form Ti/O/Ti/O/Ti/Ti gives much better agreement with the observed Ti result but is still in substantial disagreement with the oxygen yields. A final model makes use of information from XPS and chemical shifts in the Auger spectra which show a surface electronic structure which is best interpreted as arising from TiO_2 . The salient structural features of a " TiO_2 " layer can be modeled as $1/2 \text{ Ti/O}/1/2 \text{ Ti/O/Ti/Ti/Ti}$. Here, as in the anatase structure of TiO_2 , we assume a layered structure with Ti in the outer two layers occupying half the octahedral holes. This structural model gives excellent agreement to experimentally measured values for O and Ti ion-induced desorption.

Above two monolayers of oxygen coverage, good agreement can be found for a surface structure of $0/1/2 \text{ Ti/O}/1/2 \text{ Ti/O/Ti/Ti}$ with the surface oxygen layer assumed to be only weakly bound (SBE = 0.5 eV). This is not unreasonable since all available Ti atom valences have at this stage of oxidation been used in

binding. The first two oxygen monolayers appear to form a "passivating" layer at ambient temperatures with the third oxygen layer weakly physisorbed.

LIF as an Edge Diagnostic in Fusion Machines

High-Z impurities emanating from walls and limiters have been thought to cause serious disruption of the plasma in tokamak discharges.⁴² In the plasma interior, radiation from a small concentration of partially stripped atoms can seriously and adversely affect the power balance.⁴³ Despite intensive effort, it is not clear even today what mechanism or mechanisms (sputtering, arcing, vaporization) are responsible for impurity generation. LIF provides a powerful remote diagnostic for obtaining the concentrations and fluxes of atomic species in plasma devices and a method for helping to elucidate the impurity generation mechanism. Advantageous features of spatial localization, selectivity as to species, and sensitivity, as well as freedom from dependence on local plasma conditions for excitation rates, are noteworthy.

Since the fluorescence signal is essentially proportional to atomic density in most LIF experiments designed for fusion devices, measurement of the velocity distribution is necessary if atomic flux is to be determined. In particular, when there is the possibility of detecting LIF signal from atoms produced by both the mechanisms of sputtering and thermal evaporation, Doppler-scanned velocity spectra can provide a direct means for measuring the contributions to the total impurity flux from each source. However, when substantial spatial averaging is involved,

as will commonly be the case when probing the wall region of fusion devices, the most probable velocity is shifted toward zero for both the slow (thermal) and fast (sputtered) components. As a result, high resolution in velocity and good signal/noise ratio are required for assessing the relative contributions to the observed composite spectrum. Model calculations have been made for the case of Fe impurity atoms either evaporated at a characteristic temperature of 2000 K or sputtered with a distribution given by the Sigmund-Thompson model for a fully developed collision cascade.

Experiments on metallic impurities in fusion devices studied by LIF techniques^{15,16} are summarized in Table II. A majority have used laser wavelengths in the 300 nm region conveniently produced by doubling light from Rhodamine dyes. Repetition rates have been essentially one laser shot per tokamak shot for the flashlamp-pumped systems and in the 10-20 Hz regime for the Nd:Yag-pumped lasers. Only one experiment was reported with a broadband excimer-pumped laser reaching the 100 Hz regime.

Experiments listed in the upper half of Table II used a bandwidth equivalent to about 10 km/s sufficient to excite all thermal and sputtered atoms simultaneously. The authors of Ref. 18 were able to deduce the presence of sputtered Ti atoms from moderate changes in the line profile dominated by the exciting laser linewidth when tokamak shots were compared with thermal flux. Other experiments with the flashlamp-pumped system have used a bandwidth of ~2 GHz corresponding at $\lambda=300$ nm to a velocity width of 0.6 km/s. Although a higher resolution may be

useful, the main limitation for fusion diagnostics has been the single-shot sampling capability.

In the case of the c.w. laser experiments, the high duty cycle and scannable narrow bandwidth are advantageous, but the limitation to visible wavelengths and the low output power represent problems. It is desirable to be able to pump metallic atoms to upper states reached via near-UV wavelengths since radiative lifetimes in the 10 ns regime can be utilized minimizing the effects of electron collisions.

It can be seen that the ideal system for edge region LIF should combine several characteristics. It is desirable to utilize short UV pulses and lifetimes in order to reduce the complications in analysis caused when electron collisions and atomic transport are significant. High repetition rate is desirable in order to monitor real time variation in plasma behavior or to scan velocities during quiescent periods. The latter requires capability for rapid, continuous frequency shifts over a large range. It is also useful to have both narrow- and broadband modes available as well as high power for saturation studies.

Surface Analysis by Resonance Ionization of Sputtered Atoms (SARISA)

Recent trends, exemplified by stringent requirements in semiconductor processing, make quantitative surface analysis of impurities at impurity levels lower than can be achieved with LIF highly desirable. As such techniques are developed, it is useful to have a standard for comparison. Secondary ion mass spectroscopy (SIMS) can serve as such a standard for it is a well-established and widely-practiced technique. SIMS can achieve

remarkable sensitivity for detection of certain elements, down to the 10 ppb level⁴⁴ in favorable cases. Its ultimate sensitivity is limited by several factors. Very frequently, a SIMS apparatus detects only a small (10^{-5} to 10^{-1}) fraction^{45,46} of the sputtered flux which leaves the surface in an ionized state and thus does not sample directly the major component consisting primarily of neutral atoms. Furthermore, it is difficult in SIMS to determine quantitatively the concentrations of individual impurities in multicomponent systems because of significant differences in the sputtered ion fraction for each species and because these fractions vary depending on target surface chemical composition.^{45,47-50} Finally, the use of a mass spectrometer reduces the already small number (relative to the total sputtered flux) of secondary ions reaching the detector because of the low spectrometer transmission function.⁴⁴

Multiphoton resonance ionization spectroscopy (RIS) has been demonstrated to provide an extremely sensitive detection method for atoms in the gas phase. Indeed, single atom detection and detection of atoms of a particular species in a background of 10^{16} atoms of another species has been claimed.⁵¹ The key to the successful application of RIS to surface analysis lies in the development of an ion detection system, which discriminates between the signal due to multiphoton ionization of sputtered neutral atoms and noise sources due to backscattered primary ions, to secondary ions, and to ions produced by nonresonant multiphoton processes.²² Electrostatic mass spectrometric (quadrupole) detection of In^+ , produced by multiphoton ionization

of neutral In atoms sputtered from an indium target, has recently been used and appears to discriminate effectively against back-scattered primaries.²⁵ However, sensitivity is impaired in the same sense as in SIMS by the spectrometer transmission function. A similar comment applies to recent work employing a magnetic sector mass spectrometer.²⁷

An increase in sensitivity might be achieved by a detection scheme which obviates the need for a mass spectrometer by making optimal use of velocity selection between energetic backscattered primaries and less energetic sputtered atoms and by proper timing sequences of ion beam, laser pulse and detector to discriminate against secondary ions. Such a system has been operated recently²² and will be described here. For more detail, the reader is referred to the original paper.²²

A few words are in order concerning the complicated timing sequences employed. As Fig. 5 demonstrates, the 10 Hz clock signal initiates a data collection event. Some 13 ms later, the Nd:YAG flashlamps are triggered. Prior to the laser beams arrival at the vacuum chamber, the primary ion pulse has sputtered atoms from the target and has been shut off. While the sputtered atoms leave the target at energies ranging from 0 to 6 eV, the backscattered primary ions by contrast still have a significant fraction of their initial 3 keV energy and strike the detector long before the ions produced by resonance ionization arrive.

About 2 μ s after the ion pulse has been turned off, the sputtered atoms have reached the laser volume (~2 mm from the target surface). At this point, the timing sequence which

started the Nd:YAG laser pulse is terminated with a Q-switch trigger and followed by the almost simultaneous arrival of the resonant dye laser pulse in front of the target. At the same time, the previously triggered excimer laser pulse arrives at the target propagating along the dye laser axis but in a direction counter to the dye laser beam. The sputtered atoms are thus ionized in a period of 6-10 ns. Variations in trajectory and velocity combine to spread the arrival time of ions produced by resonance ionization at the detector to 300 ns. This RIS ion arrival time is then windowed with a 500 ns gating pulse to either the charge integrator or the pulse counter. A second 500 ns gating pulse provides the background signal for the data collection system.

Two samples were studied. A pure iron target (Marz grade foil; 500 μ m thick, 2 cm diameter) and an Fe-doped Si disk prepared from crystalline Si samples by ion implantation with a 500 keV Fe^+ beam.

Ion dose dependent properties such as radiation-enhanced diffusion, radiation-enhanced segregation, recoil mixing, and ion implantation can affect not only the surface concentration of alloy components but also their concentrations in the sample damage region.³² For this reason, it is necessary to use the lowest possible ion fluences in order to interpret the sputtering yield results in terms of an "undamaged" surface concentration. Ultimately, very high ion fluences lead to a quasi-equilibrium surface condition which brings the ratio of the alloy yields into an equality with the bulk concentrations. Thus, high fluence

measurements allow the measurement of bulk concentrations while low dose measurements must be used to determine surface concentrations.

The two samples present very different signal acquisition problems. For pure Fe targets, the large SARISA signal obviated data collection using a pulse counting mode. In this case, charge digitization was utilized. On the other hand, signal intensities generated from the Fe-doped Si targets allowed generally more sensitive particle counting techniques to be used.

Interestingly, the major source of noise in these experiments appears to depend on the oxygen contamination of the surface. It is known from other work that a monolayer oxygen coverage on Si causes a strong increase in the sputtered Si^+ ions. This manifests itself as a background signal contributing to the noise as the square root of the signal plus the background counts. As a result and even though the RIS ions are bunched in time, minor constituents such as a $^5\text{D}_0$ Fe atoms show a substantial signal-to-noise decrease for oxidized targets. This source of noise is being minimized in a new version of our spectrometer by taking advantage of the fact that the arrival times of the sputtered Si^+ ions depend not on the laser ionization pulse but only on the primary ion pulse.

Such a modification is necessitated by the fact that the velocity distributions of the sputtered secondary ions and the resonantly ionized neutral atoms are in general not sufficiently different to achieve an optimum separation solely by gating procedures. However, during the nearly 1 μs period following the

primary ion pulse and before the arrival of the laser ionizing pulses, a retarding potential may be applied to the target in order to sweep the secondary ions from the RIS ion extraction region well before the ionizing laser pulses arrive.

A nondestructive ultrasensitive surface analysis method based on multiphoton ionization of neutral sputtered atoms has therefore been developed. Its sensitivity has been demonstrated by determining surface Fe concentration in an ion implanted Fe in Si sample at the ppb level.

SARISA, by taking advantage of sophisticated timing techniques, eliminates the mass spectrometers used in earlier work and detects multiphoton ionized atoms directly by extraction into a spiraltron. The system described here discriminates against backscattered primary ions as well as against secondary ions and is expected ultimately to allow determinations to be made of impurities at the ppt level.

References

1. A. Elbern, E. Hintz, and B. Schweer, J. Nucl. Mater., 76/77, 143 (1978).
2. W. Husinsky and R. Bruckmüller, Surf. Sci., 80, 637 (1979).
3. R. B. Wright, M. J. Pellin, D. M. Gruen, and C. E. Young, Nucl. Instru. & Methods, 170, 295 (1980).
4. R. B. Wright, M. J. Pellin, and D. M. Gruen, Nucl. Instru. & Methods, 182/183, 167 (1981).
5. M. J. Pellin, R. B. Wright, and D. M. Gruen, J. Chem. Phys., 74, 6448 (1981).
6. R. B. Wright, M. J. Pellin, and D. M. Gruen, Surf. Sci., 110, 151 (1981).
7. M. J. Pellin, C. E. Young, M. H. Mendelsohn, D. M. Gruen, R. B. Wright, and A. B. DeWald, J. Nucl. Mater., 111/112, 738 (1982).

8. R. B. Wright, C. E. Young, M. J. Pellin, and D. M. Gruen, J. Vac. Sci. Technol., 20, 510 (1982).
9. D. M. Gruen, A. R. Krauss, M. J. Pellin, and R. B. Wright, Chemistry & Physics of Solid Surfaces, Vol. IV, pp. 107 (1982), Springer-Verlag (CONF-8108102-2).
10. D. M. Gruen, M. J. Pellin, C. E. Young, and M. H. Mendelsohn, Physica Scripta, T6, 42 (1983).
11. M. J. Pellin, D. M. Gruen, C. E. Young, and M. D. Wiggins, Nucl. Instru. & Methods, 218, 771 (1983).
12. C. E. Young, W. F. Calaway, M. J. Pellin, and D. M. Gruen, J. Vac. Sci. Technol., A2, 693 (1984).
13. M. J. Pellin, C. E. Young, D. M. Gruen, Y. Aratono, and A. B. DeWald, Surf. Sci., 151, 477 (1985).
14. C. E. Young, D. M. Gruen, M. J. Pellin, and W. F. Calaway, Fusion Tech., 6, 434 (1984).
15. C. E. Young, M. J. Pellin, D. M. Gruen, and J. H. Norem, J. Appl. Phys., 53, 4726 (1982).
16. C. H. Muller, D. R. Eames, and K. H. Burrell, J. Nucl. Mater., 111/112, 56 (1982).
17. B. Schweer, P. Bogen, E. Hintz, D. Rusbuldt, S. Goto, and K. H. Steven, J. Nucl. Mater., 111/112, 71 (1982).
18. E. Dullni, P. Bogen, E. Hintz, D. Rusbuldt, B. Schweer, S. Goto, and H. K. Stever, Phys. Lett., 88, 40 (1982).
19. E. Dullni, E. Hintz, J. B. Roberto, R. J. Colchin, and R. K. Richards, J. Nucl. Mater., 111/112, 61 (1982).
20. P. Bogen, B. Schweer, H. Ringler, and W. Ott, J. Nucl. Mater., 111/112, 67 (1982).
21. D. M. Gruen, M. J. Pellin, C. E. Young, and W. F. Calaway, Research & Development, 26, 153 (1984).
22. M. J. Pellin, C. E. Young, W. F. Calaway, and D. M. Gruen, Surf. Sci., 144, 619 (1984).
23. W. F. Calaway, M. J. Pellin, C. E. Young, and D. M. Gruen, 188th American Chemical Society National Meeting, Philadelphia, PA, August 26-31, 1984.
24. N. Winograd, J. P. Baxter, and F. M. Kimock, Chem. Phys. Letters, 88, 581 (1982).

25. F. M. Kimock, J. P. Baxter, and N. Winograd, *Surf. Sci.*, 124, 141 (1983).
26. F. M. Kimock, J. P. Baxter, D. L. Pappas, P. H. Kobrin, and N. Winograd, *Anal. Chem.*, 56, 2782 (1984).
27. J. E. Parks, H. W. Schmitt, G. S. Hurst, and W. M. Fairbanks, *Thin Solid Film*, 108, 69 (1983).
28. J. E. Parks, H. W. Schmitt, G. S. Hurst, and W. M. Fairbanks, *Inst. Phys. Conf. Ser. No. 71*, RIS 1984, Knoxville, TN, April 16-20, 1984.
29. C. H. Becker, and K. T. Gillen, *Anal. Chem.*, 56, 1671 (1984).
30. P. Sigmund, "Sputtering by Ion Bombardment: Theoretical Concepts," *Topics in Applied Physics*, Vol. 47, Springer, Berlin (1981).
31. M. F. Dumke, T. A. Tombrello, R. A. Weller, R. M. Housley, and E. H. Cirlin, *Surf. Sci.*, 124, 407 (1983).
32. H. Wiedersich, P. R. Okamoto, and N. Q. Lam, *J. Nucl. Mat.* 83, 98 (1979); N. Q. Lam, G. K. Leaf, H. Wiedersich, *J. Nucl. Mat.* 88, 289 (1980).
33. P. Sigmund, *Phys. Rev.*, 184, 383 (1969).
34. M. W. Thompson, *Philos. Mag.*, 18, 377 (1968).
35. C. W. White, E. W. Thomas, W. F. van der Weg, and N. H. Tolk, in *Inelastic Ion Surface Collisions*, eds. N. H. Tolk, J. C. Tolly, W. Heiland, and C. W. White, Academic Press, N.Y. (1977).
36. E. W. Thomas, *Progress in Surf. Sci.*, 10, 383-490 (1980).
37. J. P. Biersack and L. G. Hagmark, *Nucl. Instr. Methods*, 174, 257 (1980).
38. L. G. Hagmark and J. P. Biersack, *J. Nucl. Mat.*, 93/94, 664 (1980).
39. A. Miedema, *Z. Metallkunde*, 69, 455 (1978).
40. S. A. Cruc et al., *Nucl. Instr. & Methods*, 194, 659 (1982).
41. E. Fromm and O. Mayer, *Surf. Sci.*, 74, 259 (1978).
42. E. Oktay, "Atomic and Molecular Processes in Controlled Thermonuclear Fusion," ed. M. R. C. McDowell and A. M. Ferendeci [Plenum, New York, p. 114 (1980)].

43. R. W. Jensen, D. E. Post, and D. L. Jassby, Nucl. Sci. Eng., 65, 282 (1978).
44. H. W. Werner, Surf. Sci., 47, 301 (1975).
45. A. R. Krauss, D. M. Gruen, and R. B. Wright, J. Nucl. Mat., 89, 229 (1980).
46. K. Wittmack, Nucl. Instr. Meth., 168, 343 (1980).
47. C. M. Loxton, I. S. T. Tsong, and H. W. Pickering, J. Nucl. Mat., to be published.
48. H. Gaser, J. Nucl. Mat., to be published.
49. C. Bennedorf, R. Cortz, K. H. Gresman, and F. Thieme, Surf. Sci., 76, 509 (1978).
50. M. L. Yu and W. Reuter, J. Appl. Phys., 52, 1489 (1981).
51. G. S. Hurst, M. G. Payne, M. H. Nayfeh, J. P. Jusdish, and E. B. Wagner, Phys. Rev. Lett., 35, 82 (1975).
52. B. Schweer and H. L. Bay, Proc. Fourth Int. Conf. Solid Surfaces, Cannes, Vol. II, p. 1349 (Sept. 1980).
53. C. H. Muller, III and K. H. Burrell, "Time Dependent Measurements of Iron Impurity Densities in a Tokamak Discharge Using Laser Induced Fluorescence," GA-A15806, General Atomic Co. (1980).
54. C. H. Muller, III and K. H. Burrell, Phys. Rev. Lett., 47, 330 (1981).
55. B. Schweer, D. Rusbuldt, E. Hintz, J. B. Roberto, and W. R. Husinsky, J. Nucl. Mat., 93/94, 357 (1980).

Table I. Fractional Occupation of Low-Lying Electronic States of Sputtered Atoms with Ground State Population = 1.

Energy above Ground State (ev)	Fractional Occupation	Atomic Species	Spectroscopic State	Bombarding Particle and Energy (Kev)	Ref.
0	1.00	--	--	--	--
.021	.60	Ti	3F_3	Ar ⁺ , 3	7
.048	.40	Ti	3F_4	Ar ⁺ , 3	7
.052	.43	Fe	5D_3	Ar ⁺ , 10	52
.071	.39	Zr	3F_3	Kr ⁺ , 3	5
.077	.21	U	5K_5	Ar ⁺ , 3	3,4
.087	.21	Fe	5D_2	Ar ⁺ , 10	52
.11	.097	Fe	5D_1	Ar ⁺ , 10	52
.12	.029	Fe	5D_0	Ar ⁺ , 10	52
.15	.24	Zr	3F_4	Kr ⁺ , 3	5
.47	.005	U	5L_7	Ar ⁺ , 3	3,4
.48	.008	U	5H_3	Ar ⁺ , 3	3,4
.84	.015	Ti	5F_5	Ar ⁺ , 3	7
.86	.011	Fe	5F_5	Ar ⁺ , 10	52
.90	.008	Ti	1D	Ar ⁺ , 3	7
.91	.007	Fe	5F_4	Ar ⁺ , 10	52
.95	.004	Fe	5F_3	Ar ⁺ , 10	52
.99	.002	Fe	5F_2	Ar ⁺ , 10	52
1.01	.001	Fe	5F_1	Ar ⁺ , 10	52
1.46	.002	Ti	5P_4	Ar ⁺ , 3	7

Table II. Metallic Impurity Diagnostic Experiments by Laser-Induced Fluorescence Spectroscopy on High Temperature Plasma Devices.

Atom	Wave-length pump/det. (nm)	Minimum Band- width ^a (GHz)	Repetition Rate (Hz)	Pulse Length (ns)	Average Pulse Power (W)	Laser System Type ^b	Plasma Device	Reference
Fe	302/382	60	10	5	1×10^6	N	ISX-B	53,54
Ti	294/445							
Ti	294/445	52	17	5	6×10^5	N	D-III	16
Ti	294/445	28	1	500	800	F	ASDEX	17
		24	100	15	4×10^4	E		
Ti	294/445	24	1	500	800	F	ASDEX	18
Fe	302/382	2.0	1	500	700	F	ISX-B	55
Al	308/308	3.2	1	300	100	F	EBT-S	19
Mo	300/458	1.7	1	300	1.7×10^3	F	W VII-A	20
Zr	614/594	0.043 ^c	cw	5000 ^d	0.3	C	APEX	15

^aRefers to value actually used in indicated experiments.

^bAll systems used dye lasers and all except C used second harmonic generation in crystals. Pump sources were N:Nd:Yag laser, F:flashlamp, E:Excimer laser. C was an argon-ion pumped ring dye laser.

^cIncluding transit time and power broadening effects.

^dAcousto-optically modulated.

Figure Legends

Fig. 1 - Partial energy level diagram including transition rates (A coefficients), Lande g factors, and transition wavelengths for gaseous Fe atoms. The resonance ionization transition sequence for a^5D_4 Fe atoms is shown. The resonant photon of this two-photon, two-color sequence is labeled LASER and couples the a^5D_4 level to the $y^5D_4^0$ excited Fe state. The ionizing photon (308 nm, labeled RIS) couples the $y^5D_4^0$ state to the ionization continuum. For comparison, the LFS transition sequence is also depicted. Excitation (labeled LASER) is accomplished using the $a^5D_4 \rightarrow y^5D_4^0$ transition. Fluorescent photons generated during radiative $y^5D_4^0 \rightarrow a^5F_5$ decay are then detected.

Fig. 2 - Velocity distribution of ground state sputtered iron atoms.

Fig. 3 - TRIM calculations of electronic energy loss versus the kinetic energy of the "causal" collision leading to sputtering.

Fig. 4 - Ti^0 LFS signal as a function of O/Ti AES signal for the lowest multiplet.

Fig. 5 - Timing diagram used for SARISA experiments. The central portion of each timing curve (between breaks) is in one to one correspondence with the bottom time axis. All other relevant times are annotated with arrows. A detailed discussion of this figure may be found in the text.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

SARISA TIMING SCHEME

Fig. 5