

CONF-8709132--3

CONF-8709132--3

**LASER POST-IONIZATION SECONDARY
NEUTRAL MASS SPECTROSCOPY**

DE88 002979

by

D. M. Gruen, M. J. Pellin, W. F. Calaway and C. E. Young
Materials Science/Chemistry Divisions
Argonne National Laboratory
Argonne, IL

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:

6th International Conference
on Secondary Ion Mass Spectrometry
Versailles, France

September 13-18, 1987

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 supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

QSW

LASER POST-IONIZATION SECONDARY NEUTRAL MASS SPECTROSCOPY†

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

Materials Science/Chemistry Divisions
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439 USA

Abstract

Analytical techniques such as SIMS, LAMMA, PDMS, FAB, and ESDIAD, for example, detect only the ionized fraction of the flux of desorbed species. It appears however that in very many instances (e.g., clean metal surfaces, organic materials) the neutral/ion flux is of the order 10^4 . Furthermore, in order to increase detection sensitivity, surfaces are frequently bombarded with oxygen or cesium, thus profoundly altering not only the surface chemistry but frequently also the nature of the desorbed species. The above situation exists irrespective of the desorption mechanism, whether due to ion, electron, photon, or fission fragment interactions. Clearly, efficient postionization techniques could in principle enhance detection sensitivities by orders of magnitude with a concomitant decrease in surface damage and sample consumption. In addition, "matrix" effects would be minimized. Among the postionization methods (electron impact, plasma discharge, etc.) which have been applied, resonant and nonresonant laser ionization experiments have attracted much attention. Their recent introduction for the detection of sputtered neutrals has demonstrated that near 100% ionization efficiency can be achieved. Three different instruments using laser ionization techniques will be described.

Results from the SARI^{SA} instrument with a demonstrated figure of merit of .05 (atoms detected/atoms sputtered) for resonance ionization will be detailed. Detection of Fe at the sub-part-per-billion level in ultrapure Si will be discussed. Features of the instrument such as energy and angle refocusing time-of-flight (EARTOF) mass spectrometer and multiplexing for simultaneous detection of secondary ions and neutrals will be described.

1. Introduction

It has been recognized for a long time that effective postionization of sputtered neutrals would dramatically increase the sensitivity for detection of sputtered species and make the measurements much less dependent on surface ionization. Quantitative

†Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

elemental analyses based on sputtering techniques might therefore become more widely applicable. Mutatis mutandis, because of the higher detection sensitivity for minority constituents, sample consumption as well as surface damage due to ion bombardment could be reduced very substantially.

Experiments during the last few years in several different laboratories are beginning to show that laser post-ionization, particularly resonance ionization, is highly efficient for sputtered atoms and very well suited to UHV technology. Multiphoton resonance ionization by pulsed, tunable lasers provides, in addition to efficient ionization, very high selectivity for particular atomic species because of the unique energy level structure associated with each element. Disadvantages of laser post-ionization schemes are their low duty factor ($\sim 10^{-4}$) limited by the repetition rate of commercially available pulsed lasers as well as the cost and complexity of the lasers themselves.

Nonetheless, the availability of extremely sensitive techniques for the detection of sputtered species is of great importance, not only for basic research into the sputtering process itself, but also for the solution of certain classes of problems which are of critical technological significance. As an example of the former, one might mention the question of the depth of origin of sputtered species which is currently being studied with laser post-ionization methods in our laboratory. Examples of technological problems include the determination of semiconductor impurity levels at the sub-part-per-billion level.

In this paper, three laser ionization surface analytical instruments will be compared and contrasted. In this rapidly advancing field, it is impossible to consider in detail all of the excellent work which is being done. Rather than an exhaustive survey, we present an illustrative review of three instruments: sputter-initiated resonance ionization spectroscopy (SIRIS) [1], surface analysis by resonance ionization of sputtered atoms (SARISA) [2], and surface analysis by laser ionization (SALI) [3]. A more detailed discussion will be given of the sensitivity of the SARISA apparatus.

2. Secondary Neutral Mass Spectrometers Utilizing Laser Post-Ionization Techniques

The SALI (Fig. 1) apparatus has been used by Becker and Gillen [3] nonresonantly to ionize sputtered atoms and then to analyze the photoionized flux by a time-of-flight (TOF) mass spectrometer. The system is contained in a UHV apparatus with a base pressure of 10^{-9} mbar. The experimental sequence is initiated by an intense nonresonant laser pulse which ionizes the sputtered flux produced by a 2 keV pulsed Ar^+ or other primary ion beam. The laser pulse itself passes 1 mm in front of the target surface and is focused to a 0.2 mm waist. The ionizing radiation is usually of wavelength 193 nm or 248 nm with an intensity in the range 10^8 to 10^{12} W/cm². The photoions created are then extracted into a TOF mass analyzer of the reflectron type [4].

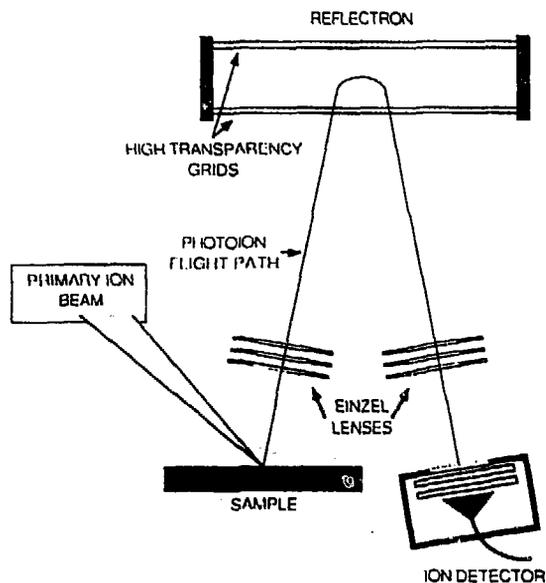


Fig. 1. A schematic diagram of the nonresonant laser ionization instrument of Becker and Gillen [3].

In the apparatus developed by Parks et al. [1] called SIRIS (Fig. 2), which is similar in some respects to resonance photoionization instruments used by other groups [10], the experimental sequence is initiated by a pulse of 5 to 30 keV Ar^+ ions, typically of 0.75 μsec duration with a peak current of 50 μamp . The sputtered flux contains both secondary neutral atoms and secondary ions. The neutral atoms of the element to be studied are then ionized in a resonant ionization scheme using two and sometimes three time-coincident laser pulses. The laser light is focused to a 1 mm dia. spot, 1 mm from the target surface. Ionization of the selected

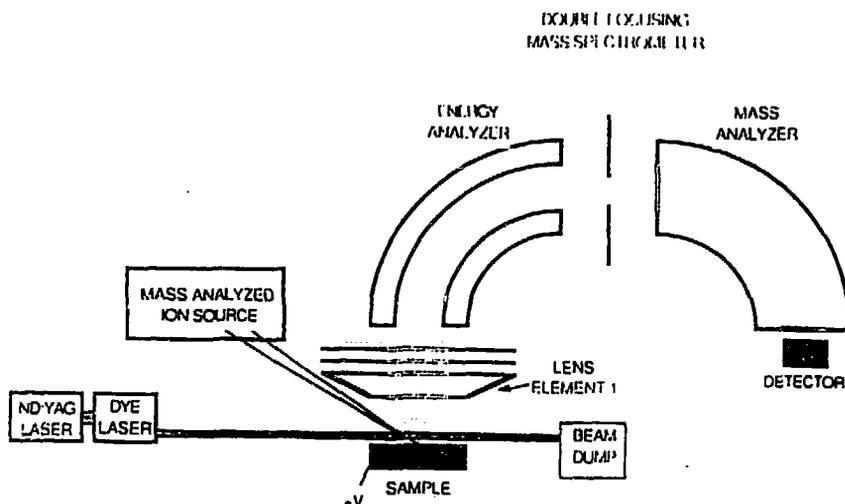


Fig. 2. A schematic diagram of the sputter-initiated resonance ionization spectrometer (SIRIS) system [1].

atomic component occurs because one of the lasers, referred to here as the resonant laser, is carefully tuned to a resonant frequency of the desired atomic component of the sputtered flux. A second laser, referred to here as the ionizing laser, is of sufficient energy to raise the energy of the resonantly excited atom to a value higher than its ionization potential. The electronically excited atom becomes an ion within a few hundred femtoseconds following absorption of an ionizing photon.

The photoion, once created, can be discriminated by energy and time selection produced during the sputtering process. The approximately 10 nsec long laser pulse creates the photoions a few hundred nanoseconds after the last secondary ions are produced by the primary ion pulse. The secondary ions have higher energy than the RIS ions because they are accelerated over the full distance between the sample and an extraction lens element. Photoions on the other hand are created from neutral atoms and molecules only in the laser excitation volume. The potential imparted to photoions created in this region is lower than for the secondary ions. Of course the actual energy of the secondary ions is the sum of their kinetic energy derived in the sputtering process and the potential energy of the applied target voltage. Similarly the energy of the photoions is a function of the sputtered kinetic energy, the distance from the target during laser ionization, and (because the lens has an extraction hole which distorts the potential field) the axial position.

The separation of secondary ions and photoions in the SIRIS apparatus following extraction occurs via a double focusing mass spectrometer. Subsequent detection uses an ion detector which can operate either in a single ion counting mode or in an analog current mode.

The data collection sequence in the SARISA apparatus [2] (Fig. 3) is initiated when a 0.5 to 2 μ sec long primary ion pulse enters an EARTOF system of special design. The ion pulse traverses a set of deflection plates and then passes through primary ion turning plates which merge the primary ions onto the EARTOF axis by means of electrostatic deflection. The beam is then focused onto the target by a high voltage Einzel lens. The primary ion pulse strikes the sample target during a time when the sample potential is held at 1400 V. At 300 ns following the primary ion pulse, the target potential is lowered to 1100 V and the two lasers are triggered. Resonant or nonresonant photoionization is used to generate positive ions in a spatial region 0.5 to 1.5 mm from the target surface with a 3 mm vertical dimension.

Once created the photoions are ejected away from the target and into the EARTOF by a large target potential. The photoions traverse the high voltage lens region. A unique lens design [5] allows them to be imaged through the primary ion beam turning plates (which are now at 0 V) onto the entrance aperture of the first resistive disk analyzer. The resistive disk analyzers are spherical energy analyzers constructed to have large angular and energy acceptance windows. This is accomplished using boundary electric field matching conditions similar to earlier designs [6,7].

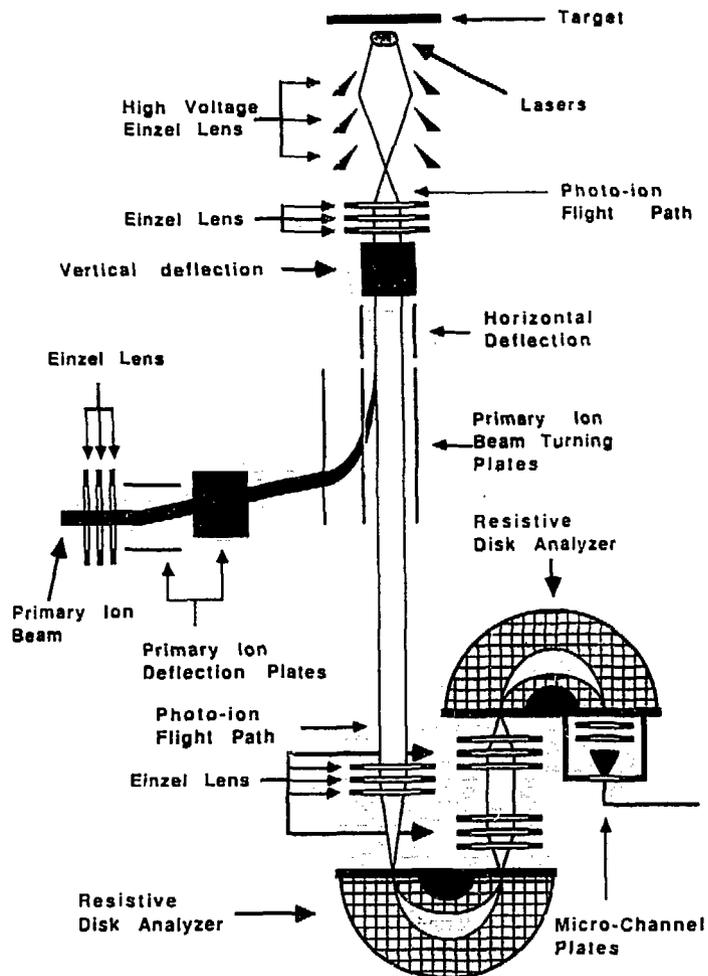


Fig. 3. The SARISA III Energy and Angle Refocusing Time-of-Flight (EARTOP) system [2]

The combination of two spherical analyzers provides two key functions in the SARISA system. First, they strongly suppress all high energy ions giving rise to noise produced during the sputtering process. Second, they serve to reduce the detrimental effects of the large photoion energy spread on the TOF mass spectrum. Several alternative energy refocusing systems based on spherical sectors have been designed and constructed [8,9]. Single laser pulse non-resonant ionization spectra of Mo atoms with the seven naturally occurring isotopes well-resolved have been measured in the SARISA apparatus with removal of about 10^6 Mo atoms.

3. SARISA Sensitivity

A principal distinguishing feature of the SARISA instruments [2] has been the emphasis on obtaining a high value for the following parameter: atoms detected/atoms removed from the sample (sometimes termed "useful yield") [16]. A high value of the useful yield is necessary for trace impurity measurements on small samples, where the total number of atoms is strictly limited. Trace surface

analysis at a depth resolution of one atomic layer and μm -scale spatial resolution is a good example of these stringent requirements. A 1 ppb impurity atom concentration corresponds to the presence of only ~ 1 such atom on the surface layer in a $10 \mu\text{m}^2$ area. Clearly, efficient use must be made of all the potential signal atoms under such circumstances. This is usually impossible to achieve when a laser ionization source is simply added to an existing mass spectrometer. In practice, the SARISA instrument has demonstrated a useful yield within a factor of two of the theoretical limits set by the initial distributions in direction and velocity distributions of the atoms desorbed from the sample prior to photoionization. This figure is believed to represent an improvement by orders of magnitude over current practice in the field of laser ionization mass spectrometry [2].

In addition to a high value of the useful yield, ultrasensitive trace analysis requires rigorous suppression of noise sources such as scattered primary ions, metastable excited neutrals and photons. The required noise rejection capability is an integral part of the design of our instrument. In fact, several aspects of the experimental design interact in a favorable manner, as will be briefly described. The high electric fields needed for efficient collection of photoions induce a large energy spread due to potential energy variation over the extended laser volume employed in our apparatus (and which is also crucial to efficient operation). Energy refocusing capability was included in the SARISA apparatus by the addition of sector-field elements to the flight path, according to existing analysis [9]. An innovative aspect of the present design was the use of resistive-film technology which permitted the construction of large-gap spherical sectors having near-ideal termination of the electric fields near the boundary. Consequently, a large range of ion trajectories could be transmitted. The use of highly transparent mesh for the outer electrode allows the escape of the various noise-inducing species mentioned above. Finally, operation with two 180° spherical elements, coupled by telecentric particle optics, enabled cancellation of time dispersion due to the initial angular spread of the photoions. The spatial refocusing property of the concatenated spherical deflectors means that very little signal is lost, while the noise rejection factor is compounded. A further notable advantage is the relative simplicity of construction of the required components. Further stages can be conveniently added within the existing concept for future enhancement of selectivity.

A study of the problem of iron impurity atoms in silicon was performed as a benchmark test of the SARISA technique for a problem of real importance to the semiconductor industry [2]. Key data are summarized below:

2 μA sputtering current	Sensitivity:	2.0 ppb (^{56}Fe)
2 μs ion pulse		0.5 ppb (^{54}Fe)
0.25 mm spot dia.	Useful yield:	0.055
20,000 laser pulses	Surface damage:	0.86 monolayer
(20 min. experiment)	Signal/noise ratio:	1

The standard analysis technique with commercially available equipment utilizes the secondary ion mass spectrometry (SIMS) technique. We give Fe/Si data for the CAMECA IMS 3-f, which is a state-of-the-art SIMS instrument.

	<u>SARISA</u>	<u>CAMECA</u>
Detectability limit	0.5 ppb	200 ppb
Useful yield	0.055	7×10^{-7}
Depth resolution	0.3 nm	10 nm

Also noteworthy is the insensitivity of the SARISA technique to the sample surface composition, the so-called "matrix effect," where the efficiency of secondary ion production can vary by several orders of magnitude depending on the state of oxidation of the surface [11], leading to substantial uncertainty in the measured composition. In contrast, laser ionization is a gas-phase process and matrix effects on neutral sputtering yields are normally very weak.

Recently, a multiplexed mode of SARISA operation has been introduced by us in which the dead time between laser pulses is utilized for taking SIMS spectra. By this means, one can infer information concerning the state of the matrix surface, while at the same time the laser ionization data provide quantitative elemental composition. Nonresonant laser ionization can be employed for comprehensive survey analysis of all surface species present. Absolute calibration can be achieved by occasional comparison against the quantitative RIS data. In the case of studies on desorbed molecular species, nonresonant laser ionization can be the preferable approach making possible the detection of chemical species which are too thinly distributed over a manifold of quantum states for the RIS technique to be applicable. In such studies, the high sensitivity (at good mass resolution) of the energy and angularly refocusing SARISA TOF mass spectrometer is retained. A fundamental investigation of the sputtering of Mo_n neutral and ionized clusters has recently been completed with this instrument [12]. This is another example of a new area of fundamental research opened up by the development of ultrasensitive laser detection techniques.

References

1. J.E. Parks, H.W. Schmitt, G.S. Hurst, and W.M. Fairbanks, Jr., *Thin Solid Films* **8**, 69 (1983); D.W. Beekman, L.J. Moore, H.W. Schmitt, M.T. Spaar, E.H. Taylor, J.M.R. Hutchinson, and W.M. Fairbanks, Jr., *Resonance Ionization Spectroscopy*, ed. by G.S. Hurst et al. (Inst. Phys. Conf. Ser. No. 00, Bristol, 1986) p. 000; 11th International Congress on X-ray Optics and Microanalysis, London, Ontario, Canada, Aug. 4-8, 1986.

2. M.J. Pellin, C.E. Young, W.F. Calaway, and D.M. Gruen, Surf. Sci. 144, 619 (1984); M.J. Pellin, C.E. Young, W.F. Calaway, and D.M. Gruen, Nucl. Instr. Meth. B13, 653 (1986); D.M. Gruen, M.J. Pellin, C.E. Young, and W.F. Calaway, J. Vac. Sci. Technol. A4, 1779 (1986); M.J. Pellin, C.E. Young, W.F. Calaway, J.W. Burnett, B. Jørgensen, E.L. Schweitzer, and D.M. Gruen, Nucl. Instr. Meth. B18, 446 (1987); C.E. Young, M.J. Pellin, W.F. Calaway, B. Jørgensen, E.L. Schweitzer, and D.M. Gruen in Resonance Ionization Spectroscopy 1986 (Inst. Phys. Conf. Ser. No. 84; Section 4, Bristol, 1987), p. 163, ed. by G.S. Hurst and C. Grey Morgan; C.E. Young, M.J. Pellin, W.F. Calaway, B. Jørgensen, E.L. Schweitzer, and D.M. Gruen, Nucl. Instr. Meth. B 27, 119 (1987).
3. C.H. Becker and K.T. Gillen, Anal. Chem. 56, 1671 (1984); Appl. Phys. Lett. 45, 1063 (1984); J. Vac. Sci. Technol. A3, 1438 (1985); in Secondary Ion Mass Spectrometry (SIMS V), ed. by A. Benninghoven, R.J. Colton, D.S. Simons, and H.W. Werner, Springer, Berlin, p. 85 (1986).
4. B.A. Mamyrin, V.I. Karataev, D.V. Shmikk, and V.A. Zagulin, Sov. Phys. - JETP 37, 45 (1973).
5. H. Liebl, Int. J. Mass Spectrom. Ion. Phys. 46, 511 (1983).
6. D. Lipinsky, R. Jede, O. Ganschow, and A. Benninghoven, J. Vac. Sci. Technol. A3, 2007 (1985).
7. M.W. Siegel and M.J. Vasile, Rev. Sci. Instr. 52, 1603 (1981).
8. W.P. Poschenrieder, Int. J. Mass Spectrom. Ion Phys. 9, 357 (1972).
9. T. Sakurai, T. Matsuo, and H. Matsuda, Int. J. Mass Spectrom. Ion Phys. 63, 273 (1985).
10. N. Winograd, J.P. Baxter, and F.M. Kimock, Chem. Phys. Lett. 88, 581 (1982); F.M. Kimock, J.P. Baxter, and N. Winograd, Surf. Sci. 124, L41 (1983); F.M. Kimock, J.P. Baxter, D.L. Pappas, P.H. Kober, and N. Winograd, Anal. Chem. 56, 2782 (1984); F.M. Kimock, D.L. Pappas, and N. Winograd, Anal. Chem. 57, 2669 (1985).
11. H. W. Werner, Surf. Sci. 47, 301 (1975).
12. M.J. Pellin, W. Husinsky, W.F. Calaway, J.W. Burnett, E.L. Schweitzer, C.E. Young, B. Jørgensen, and D.M. Gruen, J. Vac. Sci. Technol. A (1987), in press.