

## SECONDARY ION MASS SPECTROMETRY FOR THE STUDY OF SOLIDS

Within the past decade, secondary ion mass spectrometry for the detailed elemental analysis of solids has emerged as one of the most versatile and powerful analytical tools available to scientists. The APL instrument, one of several kinds being used for this purpose, is described along with examples of the type of results that are obtained.

### INTRODUCTION

A secondary ion mass spectrometer is an instrument that determines the elemental composition of a solid in both bulk and trace amounts. It has the advantage of providing, in a few minutes, a qualitative analysis for all the elements in a sample and, with suitable standards, of providing quantitative results down to the parts per billion (atomic) range. A continuous determination of atomic composition can be made as material is consumed during the analysis; thus, concentration profiles in solids (especially in thin film form) are obtainable. In addition, analysis of ion fragments can often lead to identification of compounds. These capabilities are what make secondary ion mass spectrometry so valuable to scientists.

### PRINCIPLES OF OPERATION

There are many kinds of secondary ion mass spectrometers, which vary in the way secondary ions are generated, separated, and detected. Secondary ions are ions that are ejected from a solid (this includes any gas or liquid that can be made solid by cooling) by such means as laser heating, passing a discharge through the solid, or, perhaps most effectively, impinging an energetic primary beam of ions against it. The last means of exciting the solid is known as sputtering; a common sputter-ion source is known as a duoplasmatron.

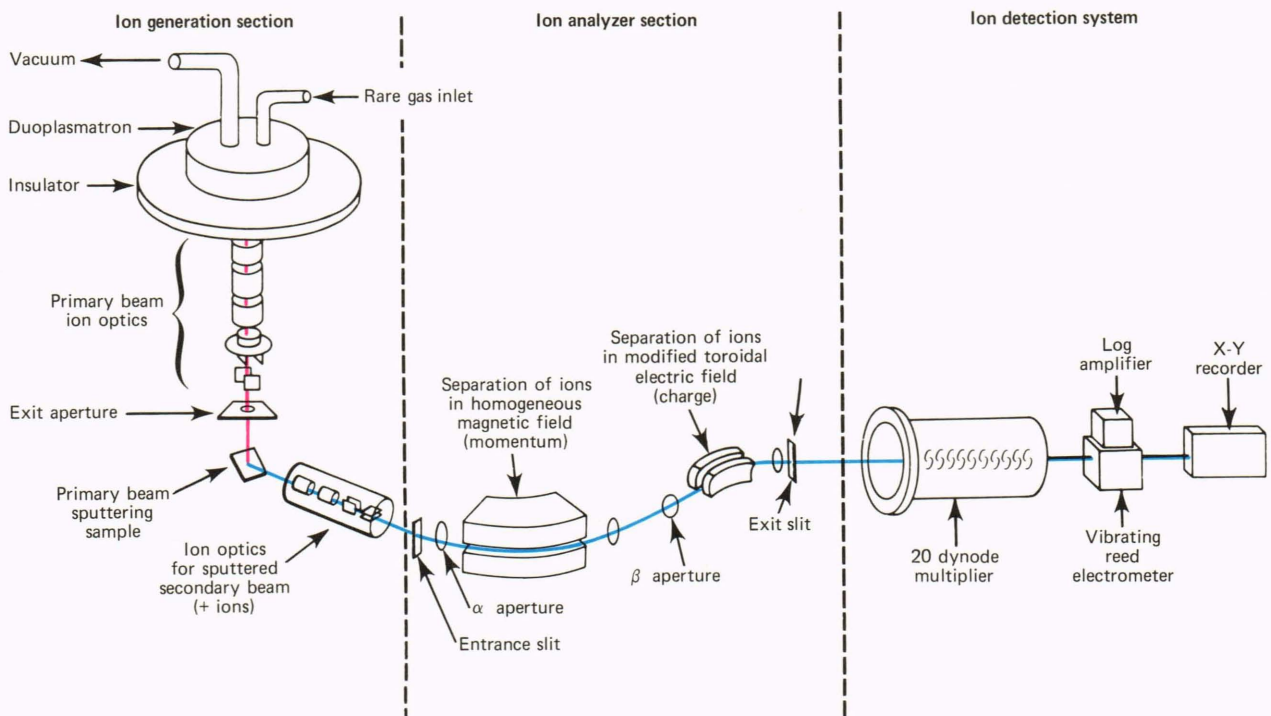
The secondary ion mass spectrometer (GCA IMS 101B)<sup>1</sup> at the APL Research Center uses such a source; it is shown schematically in Fig. 1. Positive ions of the primary gas generated in the vicinity of a hot filament (which serves as a source of ionizing electrons) are constricted in a permanent magnetic field, extracted, and accelerated through potentials of 1 to 15 keV. The resulting beam is then deflected and focused (in a manner analogous to an electron beam) using appropriate optics. In more sophisticated instruments, the ion beam can also be swept (rastered) across the sample, enabling one to obtain specific ion images of the surface being studied.

When the beam strikes a target, many ions penetrate the surface, exchanging momentum with

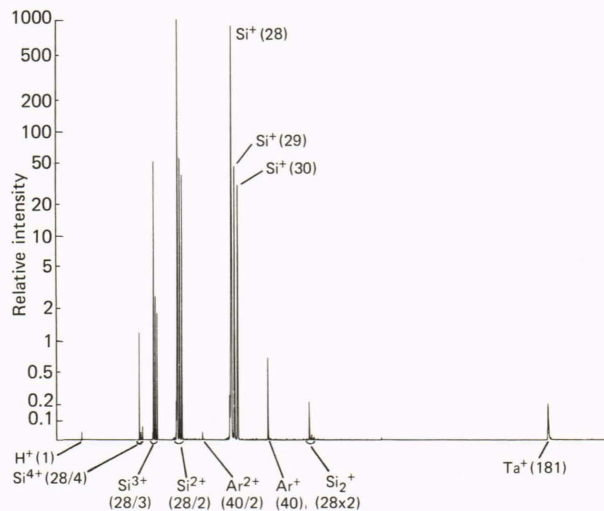
atoms of the matrix. The degree of penetration depends on the atomic number of the target material for a given set of primary beam conditions. Thus, for 10 keV argon ions ( $\text{Ar}^+$ ), the penetration into aluminum is approximately 10 nm (100 Å). The matrix bonding in the path of the entering ion is momentarily disrupted. In a complex succession of events, which are not entirely understood, the dissipation of the primary ion energy results in the ejection of atoms and atom clusters from the surface. (A mechanical analogue to this is the ejection of bits and pieces of a stone wall struck by a bullet or some other speeding object.)

In addition to the expelled neutral atoms and atom clusters, a fraction of the material removed is in the form of positive and negative ions; this constitutes the so-called secondary ion beam. This beam is a mixture of ions of different mass and energy and is of little use in diagnosing the composition of the solid unless subjected to a sorting, or unmixing, process in a mass spectrometer. In the APL instrument, separation by momentum in a magnetic field takes place, followed by separation according to charge. The secondary ions then leave the analyzer and impinge on a detector element. The amplified current from the detector is picked up by a vibrating reed electrometer whose output is normally displayed on an X-Y recorder.

A spectrum is obtained by sweeping the magnetic field from 100 to 11,000 gauss with a constant secondary acceleration voltage. Figure 2 shows an atomic ion spectrum obtained from the sputtering of pure silicon (Si). The Y axis shows the relative intensity of mass peaks. The indicated scale results from an amplifier that converts the electrometer output into logarithmic form (except for a linear portion at very low intensities); thus, peaks from impurities or trace elements as well as major components of the solid can be recorded simultaneously. The X axis represents ion masses starting with the lowest, viz., hydrogen, and ending at approximately 200. For specialized work, the mass range can be extended by reducing the secondary acceleration voltage.

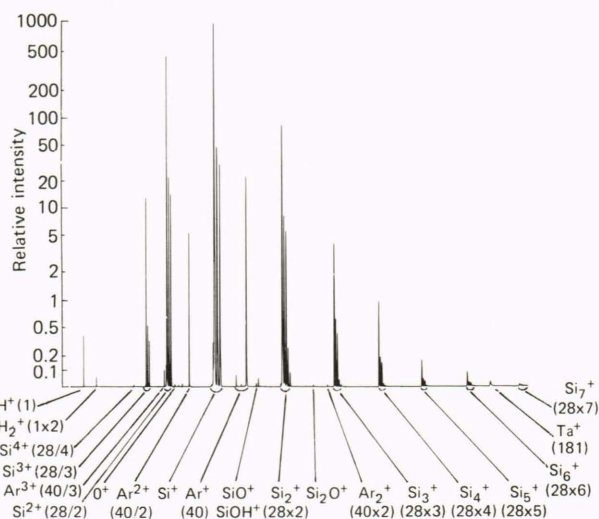


**Fig. 1—APL sputter-ion source secondary ion mass spectrometer (GCA IMS 101B).** The spectrometer is divided into three main sections: ion generation, ion analyzer, and ion detection. A primary beam (red) from a duoplasmatron sputters a target, producing secondary ions (blue) that are extracted and focused onto the entrance slit of a double-focusing mass spectrometer (analyzer) and exit onto the first dynode of a multiplier in the detection system.



**Fig. 2—An atomic spectrum of pure silicon sputtered with 10 keV argon ions.** Note the relative absence of cluster-ions (i.e., ions with many atoms). Numbers are mass-to-charge ratios of the main peak in the isotope sequences for silicon (masses 28, 29, and 30). Other elements have their characteristic isotope or isotopes.

Figure 3 shows a polyatomic ion spectrum of silicon. The richer spectrum reveals ions consisting of two or more atoms (clusters) ejected in the sputtering process. Also observed are argon (Ar) peaks derived from the resputtering of argon atoms embedded in the silicon matrix. The peaks associated with oxygen and hydrogen are partially



**Fig. 3—A polyatomic spectrum of pure silicon sputtered with 10 keV argon ions.** The spectrum is rich in cluster-ions. Multiplier gain has been reduced by 32 to compare with the atomic spectrum (Fig. 2). The extent of clustering for metals, i.e., the fraction of ions in cluster form, has been observed to correlate with the heat of sublimation. Clustering has also been observed in the sputtering of water and of other oxides such as magnesium oxide.

derived from the sputtering of water molecules chemisorbed on the silicon surface. Water molecules constitute a large part of the residual gas in the target vacuum chamber. The small tantalum (Ta) peak results from the structural components of the duoplasmatron.

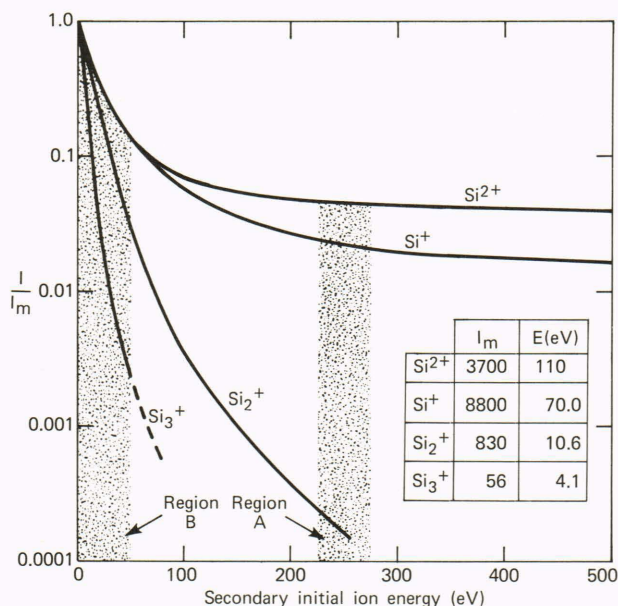


Fig. 4.—Secondary ion energy distribution curves from the sputtering of silicon with 10 keV argon ions. Curves are normalized to unity for ease in comparison. Simple ions such as  $Si^+$  and  $Si^{2+}$  have broad distributions; polyatomic ions such as  $Si_2^+$  and  $Si_3^+$  have narrow ones. By moving the 50 eV energy window (color bands) along the curves, atomic or polyatomic spectra are obtained. The mean energy of the ions becomes smaller as ion complexity increases.

The differences in the two spectra from the same material can be explained by a consideration of instrument design and the nature of sputtering. A study of the energy distribution of different secondary ions produced by sputtering has shown that, in general, simple elemental ions such as  $Si^+$  (or  $Al^+$ , aluminum) have broad tails in their distribution curves.<sup>1,2</sup> Polyatomic ions such as  $Si_2^+$  (and  $Al_2^+$ ), on the other hand, exhibit substantially narrower distributions. To illustrate this, secondary ion energy distribution curves from the sputtering of silicon are shown in Fig. 4. These curves can be readily obtained in the APL instrument since it is constructed so that it passes only a single band of energy at a time. The band is selected electronically, and its width is dictated by the size of the  $\alpha$  and  $\beta$  apertures shown in Fig. 1. By moving the band from low to high energies, a histogram of the energy distribution is provided. The narrower the bandwidth, the more accurate are the resulting curves. A bandwidth of 4 eV was used to obtain the curves in Fig. 4. However, a bandwidth of 50 eV is shown in the figure to illustrate the practical size for ordinary analytical use. When the band is in region A, the spectrum will consist of predominately atomic ions, but when it is moved to region B, the spectrum will include polyatomic ions as well.

The conversion of peak intensities to concentration remains one of the more serious problems in applying this analytical method. A calibration of some kind is usually necessary because the relative

ion yield of different species can range over several orders of magnitude.

It can be seen that spectra of the full mass range are readily obtained and identified, and, with suitable calibration, quantitative data can be calculated from the peak intensities. Very small amounts of material can be analyzed with little or no need for sample preparation. The spectra in Figs. 2 and 3 were obtained in 25 min of sputtering during which 12  $\mu g$  of material were removed. The sputtering rate depends on the primary beam parameters and the solid being analyzed, and can range from 2 to 1000 nm/min. For the silicon analysis, the rate of sputtering was 15 nm/min. Films as thin as 2 nm can be successfully examined by obtaining spectra in one mass range from one area of the film, translating to a new area for the next mass range, and repeating the process until the full mass range is covered. By presetting the magnetic field for a particular mass and turning the primary beam onto a desired area, an intensity profile from material within a few nanometers of the surface can be obtained.

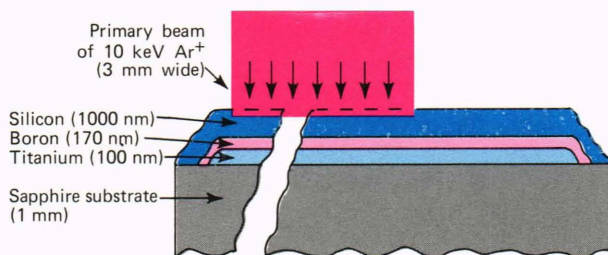
#### APPLICATION

The number of analytical problems that can be approached by secondary ion mass spectrometry is virtually endless, making it difficult to choose a single illustrative example. The spectrometer has been extensively used to determine composition and atomic distributions in complex thin films for polycrystalline silicon solar cells.<sup>3</sup> One such configuration, shown in Fig. 5a, represents a supporting substrate of sapphire on which successive overlapping layers of titanium, boron, and silicon have been deposited. The result of analyzing an actual sample is shown in Fig. 5b. As the beam removes the silicon layer, the boron profile appears. If the primary beam were perfectly homogeneous in cross section and the layers were perfectly separated or parallel, the initial slope of the boron profile would be infinite. In practice, the slope is finite and provides the basis for a calculation of the beam-depth resolution. In this instance, it was found to be  $\pm 2.5\%$  ( $\pm 15$  nm at a depth of 600 nm). The titanium profile appears somewhat sooner than this depth resolution would predict, suggesting that diffusion or mixing of the boron with the titanium had occurred. The rounded titanium profile results mainly from the diminished depth resolution at this point and from the fact that the titanium layer is thinner than the others. The profiles from this "unreacted" composite structure serve as a reference or calibration for the more complicated case in which the films are heated to diffuse or react the layers.

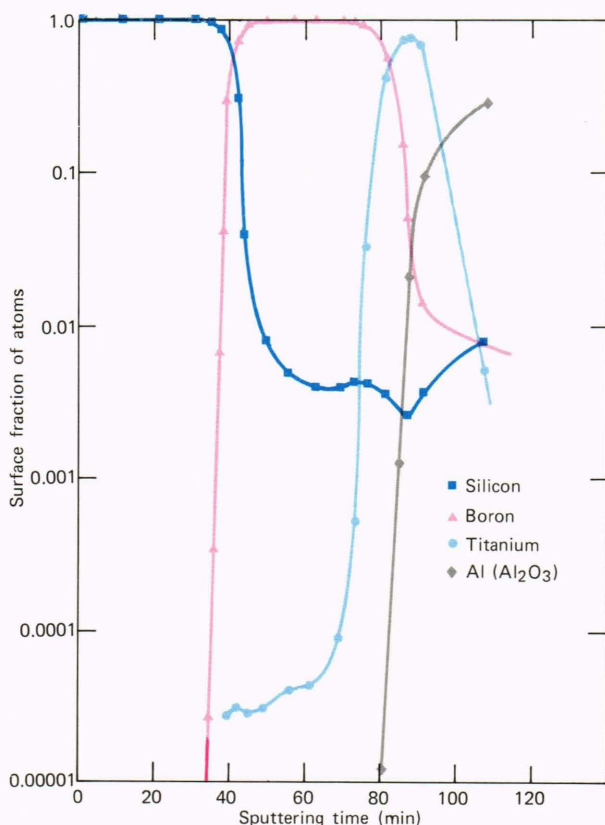
Although the extent of diffusion or reaction in this structure has been studied, discussion of the results is beyond the scope of this article. However, it can be said that the use of the energy window feature of the spectrometer (Fig. 4) was invaluable

in determining the diffusion coefficients of several species and in identifying reacted phases such as titanium diboride and titanium disilicide. The latter result was also confirmed by X-ray diffraction and scanning electron microscopy.<sup>4</sup>

This introduction to sputter-ion source mass spectrometry does not present to the reader many of the difficult but at the same time more interesting aspects of the subject. These generally fall into the category of basic research and include such



**Fig. 5a**—The primary beam (shown in red) is removing material (silicon) as the analysis of a composite-film solar cell sample proceeds. The more homogeneous the beam cross section, the less correction for crater shape is necessary. The greater the depth removed, the less distinct adjacent phase characterization becomes.

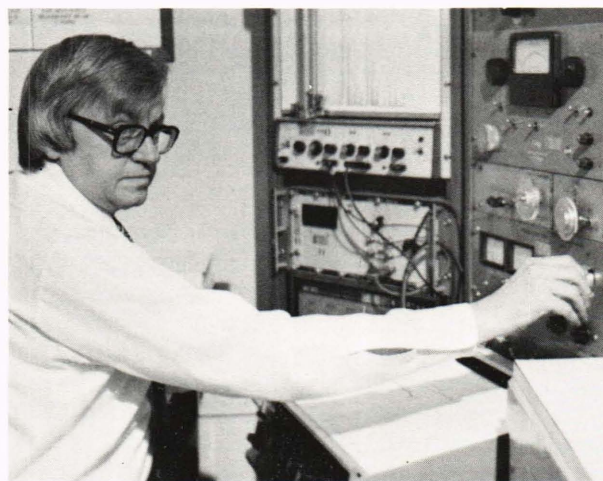


**Fig. 5b**—Concentration profiles of components of the composite film shown in Fig. 5a. (Concentrations have been calculated from such characteristic peaks in the spectra as Si<sup>+</sup>, B<sup>+</sup>, and Ti<sup>+</sup>.) This film experienced 500°C heating during the silicon deposition, which partly explains the limited interpenetration of the titanium and boron.

topics as bonding in solids and the phenomenon of secondary ion production. Studies that lead to a greater understanding of the sputtering phenomenon will ultimately provide a firmer theoretical basis for this technique and will no doubt have an even larger impact on solids analysis.

#### REFERENCES

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Prior to his Ph.D. studies, he was employed as a radiochemist at Tracerlab, Inc., working on ways to separate fission products as well to prepare isotopically labelled chemical compounds. Subsequently, he taught chemistry and mathematics for two years. After joining the Norton Co. as a research associate, Dr. Satkiewicz investigated ways of improving the mechanical properties of abrasives and refractories. He later worked as principal scientist for GCA Corp. in developing materials for space applications and as consultant in using the sputter-ion source mass spectrometry for studying solids. Since joining APL in 1973, Dr. Satkiewicz has concentrated on using and improving secondary ion mass spectrometry for the analysis of solid thin films.

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