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Detection*

M. J. Pellin, C.E. Young, W.F. Calaway, K. R. Lykke, P. Wurz and D.M. Gruen
Argonne National Laboratory, Argonne, IL USA

D. R. Spiegel, A. M. Davis, and R. N. Clayton
Enrico Fermi Institute, University of Chicago, Chicago, IL 60637, USA

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M. J. Pellin, C.E. Young, W.F. Calaway, K. R. Lykke, P. Wurz and D.M. Gruen
Argonne National Laboratory, Argonne, IL USA

D. R. Spiegel, A. M. Davis, and R. N. Clayton
Enrico Fermi Institute, University of Chicago, Chicago, IL 60637, USA

ABSTRACT

Surface Analysis by Resonant Ionization of Sputtered Atoms (SARISA) has demonstrated the ability to detect trace elements at concentrations below 100 ppt. Use of energetic primary ions to desorb surface species is uniquely suited for elemental surface analysis because the ratio between the number of incident energetic ions and the number of ejected surface atoms is easily quantifiable as the sputter yield. Molecular surface analysis by ion desorption does not possess this advantage, however. In this case, laser desorption followed by resonant or near resonant ionization is often a better analysis tool. Here the power of resonant ionization detection of desorbed species is demonstrated on hibonite samples (for elemental analysis) and on fullerene samples (for molecular analysis).

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INTRODUCTION

Ultrasensitive, *surface* analysis is difficult both because of the few analyte atoms or molecules available and because of interference from the vast excess of bulk material. Surface Analysis by Resonant Ionization of Sputtered Atoms (SARISA) has demonstrated the ability to detect trace elements at concentrations below 100 ppt.¹⁻⁵ While the detectable concentration levels are impressive, recent results show that the strength of the SARISA technique may be found in analysis of naturally occurring samples with their wide compliment of minor and trace elements. Analysis of such samples is often complicated by several factors including sample charging due to poor sample conductivity, isobaric interferences, and lateral inhomogeneities. Here we will focus on the measurement of Ti in a naturally occurring oxide material (e.g hibonite). These results demonstrate the ability of SARISA to measure insulating samples without reduction in the Ti useful yield when compared to that of Ti metal.

The development of a straightforward method for the synthesis of macroscopic quantities^{6,7} of the truncated icosahedron called Buckminsterfullerene⁸, C₆₀, along with other stable closed shell clusters (e.g. C₇₀ and C₈₄) has triggered substantial interest in carbon cluster chemistry. Analysis by ion induced desorption (sputtering) of solid fullerene samples is complicated by their large masses. This report details time of flight mass spectrometry using laser desorption followed by laser ionization with a second laser. Of particular interest, a velocity distribution of C₆₀ is obtained by suitably delaying the desorbing laser with respect to the ionizing laser.

EXPERIMENTAL

Experiments involving Ti atoms were carried out in the SARISA time of flight instrument which has been described in detail elsewhere⁵. Three tunable wavelengths were generated using XeCl excimer pumped dye lasers. For Ti several schemes have been investigated, the

most suitable used a triply resonant scheme with $\omega_1 = 19323 \text{ cm}^{-1}$ ($a^3F_2 \rightarrow z^3F_2^0$) and $\omega_2 = 18216 \text{ cm}^{-1}$ ($z^3F_2^0 \rightarrow e^3F_2$). The third laser was then used to pump the excited populations into autoionizing resonances above the ionization potential of the Ti atom (55010 cm^{-1}). These resonances were not previously assigned and were found by scanning the third laser color and monitoring the photoion induced intensity in the presence of the first two lasers. Many resonances were observed, the most intense at $\omega_3 = 17668 \text{ cm}^{-1}$ above the ionization potential was utilized in these studies.

Ti samples were prepared by pressing chips of hibonite mineral into a gold foil which was subsequently pressed onto an Al electron microscope stub. The hibonite samples had dimensions between $90 \mu\text{m}$ and $300 \mu\text{m}$. A marz grade sample of Ti metal was also pressed into the gold foil approximately $300 \mu\text{m}$ from the hibonite sample. These samples were large enough to completely contain the primary ion beam of the SARISA apparatus ($\sim 100 \mu\text{m}$ beam diameter).

Hibonite is a naturally occurring mineral with the composition of $\text{CaAl}_{12-2x}\text{Ti}_x\text{Mg}_x\text{O}_{19}$, where x is the concentration of Ti which varies depending on the origins of the mineral. The Ti content of the hibonite sample used in these experiments was 1.2 at% as verified by electron induced X-ray fluorescence spectroscopy.⁹

For the fullerene measurements, a XeCl excimer laser was used for desorption and a frequency-doubled Coumarin 540A dye laser pumped by a second excimer laser was used for ionization. Both lasers are operated at 1 to 50 Hz repetition rates, with laser pulse widths of approximately 20 ns. The wavelengths are 308 nm and 270 nm for desorption and ionization, respectively. The fluence of the desorption laser was held constant at approximately $10\text{--}100 \text{ mJ/cm}^2$ for all experiments. The time delay between excimer laser firing times was controlled using a Stanford Instruments DG535 delay generator.

RESULTS

A comparison of the Ti signal from hibonite and from pure Ti was made by alternatively centering the Ti metal and then the hibonite sample under the primary ion beam in the SARISA apparatus. Comparison in signal could then be made without change in the instrument's transmission. Table 1 lists the relevant information. One key to this measurement is calibrating the gain of the channel plate detection system.^{2, 3} The sputtering yield of hibonite was taken to be equivalent to that of rutile¹⁰. Presently we are measuring precisely the sputtering yield of hibonite. The measurement presented here may be in error by as much as a factor of 2 because of the uncertainty in sputtering yield. Remarkably, the useful yield from the oxide is substantially *larger* than from the metal.

Table 1. The relative useful yield of Ti from hibonite and from Ti metal.

Material	Signal Level	Detector Gain	Sputtering Yield	[Ti]	Relative Useful Yield
Ti	2158.1	2	1.0	1	$Y_{\text{Hib}}/Y_{\text{Ti}} =$
Hibonite	2319.2	37	0.9	0.012	5.3

In another set of measurements we determined the velocity distributions for C_{60} and C_{70} clusters laser desorbed from a stainless steel substrate by allowing the desorbed neutral molecules to travel a short distance before being ionized and accelerated into the mass spectrometer. Several velocity distribution measurements for both samples were taken to

Fig 1. Velocity distribution for laser desorbed neutral C_{60} . Dashed curve gives the best fit for a Maxwell-Boltzmann temperature distribution.

insure reproducibility. These velocity distributions are fitted with a Maxwell-Boltzmann distribution giving reasonably good agreement with the measured data. Figure 1 shows a velocity distribution and a best fit Maxwell-Boltzmann distribution for laser desorbed C_{60} . Theoretical calculations are done to gauge the effect of angular and lateral distributions of the desorbed species on the measured velocity distribution for our particular setup. We found that these have only a small effect compared to other uncertainties encountered in the measurement, although there is a systematic underestimation of the temperature of about 50 K. Taking this into account, we obtain average values for the temperatures of 2100 ± 200 K for the C_{60} sample.

In conclusion, laser ionization detection of directed energy desorbed surface species can be a powerful tool for surface study. The exact nature of the optimum desorption source depends in detail on the information desired and on the sample of interest.

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