A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.
TITLE
LASER DESORPTION/ABLATION STUDIES BY RESONANCE IONIZATION MASS SPECTROMETRY

AUTHORS
N. S. Nogar, R. C. Estler, M. W. Rowe, B. L. Fearey and C. M. Miller

SUBMITTED TO
Proceedings of the Fourth International Symposium on Resonance Ionization Spectroscopy and its Applications

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.

By acceptance of this article, the publisher recognizes that the U.S. Government retains a non-exclusive, royalty-free license to publish or reproduce the published form of this contribution or to allow others to do so for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.
Laser Desorption/Ablation Studies by Resonance Ionization Mass Spectrometry

N. S. Nogar†, R. C. Estler*, M. W. Rowe‡, B. L. Fearey§ and C. M. Miller

†CLS Division, MS G738; ‡INC Division, MS J514;  
Los Alamos National Laboratory, Los Alamos, New Mexico 87545  
*Chem. Dept., Fort Lewis College, Durango, Colorado 81301.  
§Chem. Dept., Texas A & M University, College Station, Texas

ABSTRACT: Theory and results are presented for RIMS diagnostics of a variety of laser-materials interactions.

1. Introduction

Resonance ionization mass spectrometry (RIMS) is becoming an accepted tool for chemical analysis (Fassett et al 1983). The use of laser ablation or desorption coupled with RIMS detection of sputtered neutrals has a number of interesting applications and advantages: 1) the duty cycle for analytical samples is vastly improved relative to thermal evaporation (Miller et al 1982); 2) no background is introduced due to bulk heating of the sample; 3) spatial resolution is limited only by diffraction (typically =1 μm in diameter); 4) little sample preparation is needed; 5) sensitivity is excellent, and the detection limit frequently falls in the femtogram to attogram (absolute) or sub-ppb range; and 6) the fundamentals of laser-material interactions can be studied (Estler et al 1987).

2. Experimental

Our apparatus has been described in detail previously (Estler, et al 1987). Very briefly, desorption is initiated by pulses from a Nd³⁺:YAG laser, operating with fitted-beam optics to produce 10 ns pulses of 1-100 mJ at 10 Hz. Ionization was affected by pulsed, variable delay, from an excimer-pumped dye laser propagating perpendicular to both the YAG laser and the flight tube of the mass spectrometer. A pair of deflection plates between the excimer and the flight tube maximized the transmission of ions and minimized transmission variations due to velocity components perpendicular to the electron beam. Detection electronics consisted of a range
Results and Discussion.

A schematic of the experimental geometry is shown in Fig. 1.

We have shown previously that for an isotropic $[\cos(\Theta)]$, thermal distribution, the collected signal at a given linear distance ($L_0$) from the surface will be given by:

$$ S(L_0,t) = \int S(L_0,\Theta) \, d\Theta = \int C(T) \, [L_0^{-3} (\cos^2(\Theta) t^4)] \cdot e^{-\left[\frac{mL_0^2 \cos^2(\Theta)}{2kT}\right]} \, dA dt d\Theta \quad [1a], $$

where $C(T) = kC'(T), C'(T) = n_0 \cdot (m/2\pi kT)^{3/2}, k$ is a measure of signal collection efficiency, $n_0$ is the desorbed number density, the integration limits are appropriate to the apparatus, and the rest of the terms have their usual meanings. Fig. 2 shows the calculated signals for a 100 au desorbate from a 2000K surface with $L_0 = D = 1$. Note that the distributions closely simulate a single Boltzmann population, although we are integrating over a substantial angular distribution. We have used this information to quantify laser desorption measurements. In initial experiments, tantalum was desorbed from a polycrystalline Ta foil. The velocity distribution we were able to attain under equilibrium (Godd, et al 1988), with a hydrodynamic and kinetic temperature of 1500K, and 1500K,
respectively. The atom vapor pulse is thus temporally narrow, so that the effective duty cycle is greatly increased relative to continuous thermal desorption. The total ionization probability for the desorption/RIMS detection process is \( \approx 2 \times 10^{-4} \), determined by convolving a geometric overlap of \( 5 \times 10^{-2} \), a temporal overlap of \( 10^{-1} \), a partition function of 0.5, and an ionization/detection probability for this three-photon process of \( 10^{-1} \).

In Al/Fe mixtures, there is a coincidence between a 1+1 ionization process for aluminum, \([4s)^2S_{1/2} \rightarrow (3p)^2P_{1/2} \) at 394.4 nm], and a variety of 2+1 ionization processes in iron, Fig. 3. This allows one to "tune" the ratio of ionization efficiencies, greatly increasing the measurement dynamic range. We were able to detect Al in iron at 1 ppt by tuning away from iron resonances, and on to the peak in the aluminum spectrum. Conversely, Fe was easily detected in Al at 10 ppm by tuning to a sharp iron feature in the aluminum spectrum tail.

We have also applied laser ablation/RIMS to the study of laser-material interactions, specifically in the optical damage process. Calcium fluoride was chosen for initial studies (Estler et al. 1997). Both the velocity distributions and internal energies of the cluster ejected from the surface during laser excitation (damage) were characterized. Irradiation at high intensity thermalizes energy, while lower intensity or weakly ionized.

Fig. 2. Calculated temporal distributions (left) for detection at normal incidence (solid line) and integrated (diamond) over the appropriate angular distribution, and spatial distribution (right) also integrated.
RIMS was also used in conjunction with Nomarski microscopy to characterize the initiation of optical damage in commercial optics (Estler et al 1988). The samples consisted of Sc₂O₃/SiO₂ multilayer coatings on glass substrates. At fluences above 100 mJ/cm², transient iron signals were observed, with the concomitant appearance of small circular (10µ) pits in the surface. The evidence suggests that the transients were due to the presence of small, iron-containing micro-inclusions in the optical coatings. Low fluence irradiation removed near-surface contaminants with minimal damage, while higher-fluence irradiation removed more deeply imbedded, or lower susceptibility, contaminants, with simultaneous removal of surrounding coating material.

It is apparent that RIMS will play an increasingly important role in the study of the laser desorption processes, especially as surface imaging capabilities become coupled to the ionization detection.

References: