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Title: RESONANT LASER ABLATION: APPLICATIONS AND MECHANISTIC ASPECTS

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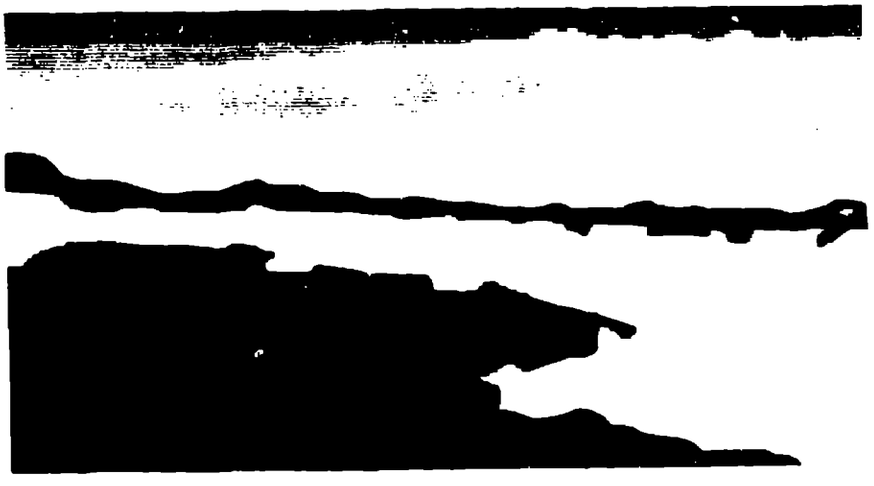

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Resonant Laser Ablation:
Applications and Mechanistic Aspects

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Abstract

Resonant laser ablation for depth profiling is described, along with absolute removal rates and detection limits. Possible mechanisms for low-power ablation are discussed.

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Introduction

Ever since the first report of laser action, it has been recognized that laser ablation (evaporation/volatilization) may provide a useful sampling mechanism for chemical analysis. In particular, laser ablation is rapidly gaining popularity as a method of sample introduction for mass spectrometry. Since its original description, numerous research papers and review articles have appeared on various aspects of laser mass spectrometry. While most laser ablation/mass spectrometry has been performed with fixed frequency lasers operating at relatively high intensities/fluences ($\geq 10^8$ W/cm^2, ≥ 1 J/cm^2), there has been some recent interest in the use of low-power tunable lasers to ablate and resonantly ionize selected components in the ablation plume. This process has been termed resonant laser ablation (RLA).[1] Potential advantages of RLA include: 1) simplification of the mass spectrum, by enhancement of signal from the analyte of interest; 2) improvement of the absolute detection limits by improving the ionization efficiency, and 3) improvement in relative sensitivity by reduction of spurious signal in the detection channel of interest (due to bleed through from adjascent mass channels or from isobaric interferences).

We report here on aspects of RLA behavior for a number of metals, alloys and thin films. The versatility of RLA is demonstrated, with results on a variety of samples and in several mass spectrometers. In addition, the application to depth profiling of thin films and multilayers is described; absolute removal rates and detection limits are also displayed. A discussion of possible mechanisms for low-power ablation is discussed.

Results and Discussion

Most experiments utilized an excimer-laser pumped dye laser for ablation/ionization, and either a linear time of flight (ToF) mass spectrometer, or an ion trap mass spectrometer (ITMS) for detection. The beam was typically passed through a variable attenuator to control the pulse energy, and a Soleil-Babinet compensator to control and rotate the plane of polarization.

a. General Considerations

RLA can be used to selectively address various elements in a multicomponent sample. Figure 1 shows typical mass spectra obtained with both the ToF and ITMS instruments. Each spectrum corresponds to irradiation of the surface at a different wavelength, corresponding to a "2+1" (photons to resonance + photons to ionize) ionization process for the labeled element. Several features are worth noting. First,

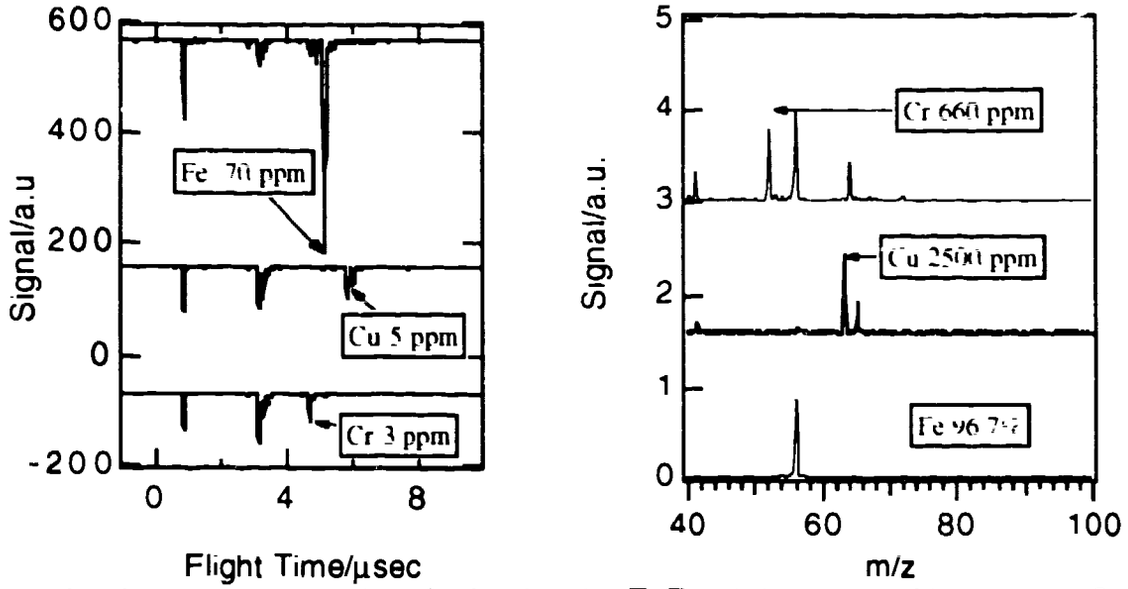

Figure 1a shows mass spectra obtained in the ToF with laser tuned to various "2+1" elemental resonances from a high-purity rhenium sample, while 1b shows similar results obtained with the ITMS from a high carbon steel sample.

signal was obtained with low pulse energies, typically 20 μJ (corresponding to a fluence ≈10 mJ/cm^2, or an intensity <10^7 W/cm^2). The observation of trace components at very low laser intensities is a significant virtue of this process; this sensitivity is due both to the resonant nature of the ionization process, and to the excellent overlap of the vaporized sample with the ionizing laser beam, as discussed below. Second, for very low concentration components, some interference may be seen: typically sodium and potassium, but in 1b (chromium) TiO is also observed. These components are presumably observed because of their high volatility and low ionization potential. They are thus easily vaporized, and ionized, by low-order non-resonant multiphoton processes. Last, using internal standards, we have been able to measure concentrations to an accuracy of ≈50%.

b. Thin film analysis and detection limits

A variety of metals have resonant transitions lying at similar energies, thus facilitating selective analyte ionization for a variety of components using the same laser dye. In addition, at the low fluences used, material removal rates are expected to be sub-monolayer per laser shot. With these characteristics, RLA has the potential for analysis of films and multilayer structures. We have demonstrated the use of RLA-mass spectrometry for the analysis of films using copper films of various thicknesses on Si(110) wafers, as a test case.[2] Figure 2a shows the copper RLA signal as a function of time for irradiation of a copper thin film (100 Å) on a silicon substrate. At a (rather high) pulse energy of 62 μJ, penetration of the film required 440 laser shots, resulting in a removal rate of ≈0.23 Å/shot. This removal occurs over a spot diameter ≈40μm, which allows us to calculate a total material removal per laser shot of 3.7 x 10^{-14} cm^3. If the copper film has the same density as bulk copper, this is a mass removal rate of 0.33 pg/shot.

To estimate the absolute sensitivity of RLA - ITMS, trace components of NIST standard reference materials (SRM's) were analyzed. The results for lead (26.5

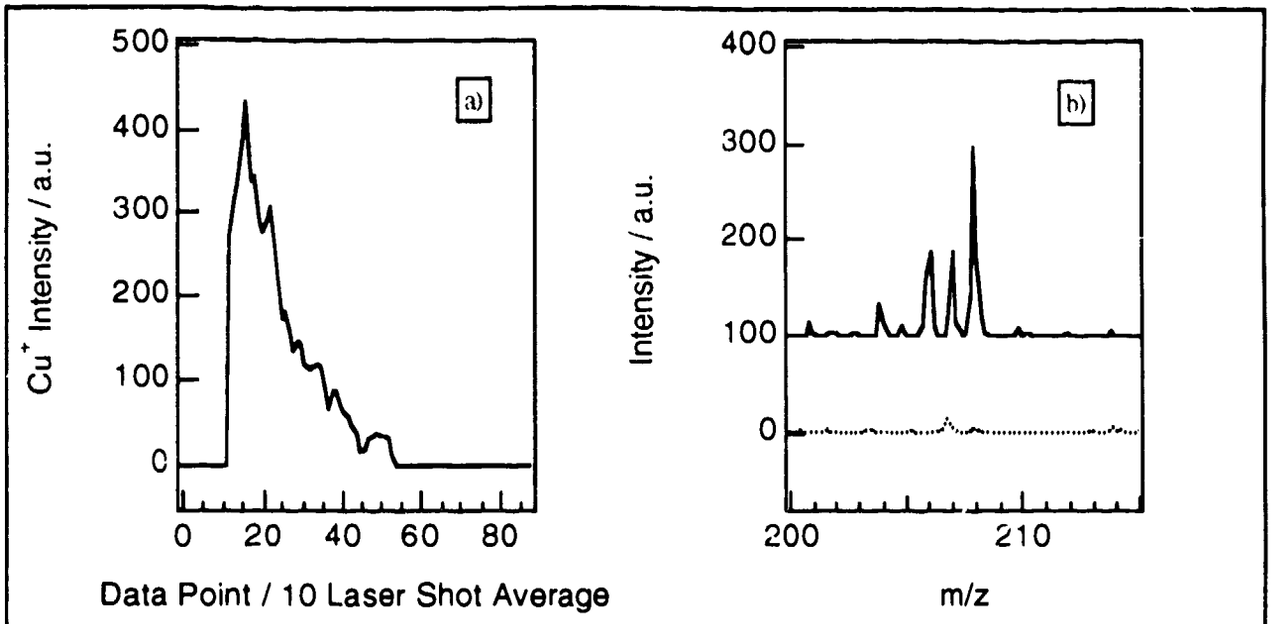

Figure 2a depicts removal rate for a 100 Å copper film from a silicon wafer; Figure 2b shows mass spectrum for lead on (upper) and off (lower) resonance.

ppm) in SRM 494 (unalloyed copper) are presented in Figure 2b. The high selectivity of RLA for the ionization of trace components in a complex matrix is observed, and when the mass removal rate determined above is factored in, the calculated absolute detection limit for RLA-ITMS is <9 attograms.

c. Mechanisms

Several observations suggest the observed ablation process may be nonthermal in nature.[3] The measured spot size of the laser and the ablation etch feature observed are significantly different, and may be seen as evidence of a nonlinear phenomena. In addition, microscopic examination of the laser ablated spots showed a series of lines in what appears to be an interference pattern, whose fringe spacing can be described by theoretical models based upon nonlinear growth processes. Laser polarization was observed to have a strong effect upon the RLA process, and was sample surface dependent. The variation in RLA intensity is consistent with the surface effects and polarization specificity of surface plasmon interactions. Based upon the experimental evidence and theoretical calculations presented, the desorption processes for RLA are non-thermal in nature, providing additional evidence for a nonlinear desorption mechanism based upon surface plasmon interactions.

References.

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