QUANTITATION OF SINGLE PHOTON IONIZATION LASER SNMS

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1. Introduction

The mass spectrometric analysis of neutral particles released from a solid surface by ion sputtering (SNMS) in connection with pulsed laser post-ionization (commonly referred to as "Laser-SNMS") is now a well established tool for quantitative surface characterization and depth profile analysis of thin films. As first pointed out by Becker et al. [1], the use of non-resonant ionization schemes offers the possibility to non-selectively ionize all ejected particles with the same laser setup. Due to the high photon flux densities achievable with present state-of-the-art UV lasers, it is in many cases possible to drive the post-ionization process close to saturation and, hence, detect different elements with comparable post-ionization efficiency. As long as ionization requires the non-resonant absorption of more than one photon, however, the quantitative interpretation of the saturation behavior in terms of simple perturbation theory is extremely complicated [2]. This situation is different if a single photon ionization (SPI) scheme is employed for post-ionization. As shown in our earlier work, an F₂ laser represents an ideal tool to study the saturation behavior of such an SPI process [3]. In the present work, we use a certified standard reference material of known composition as a test sample to evaluate the SPI cross sections and relative detection sensitivity for 7 elements as a function of the laser power density.

2. Experimental

The experimental setup employed in the present work has been described in great detail elsewhere [4]. A NIST standard reference material sample of certified composition (Inconel 1245a) was bombarded by a pulsed Ar⁺ ion beam of 5 keV impinging under 45° with respect to the surface normal. Neutral particles sputtered from the sample surface are ionized by a pulsed laser beam located 1 mm above the surface, the resulting photoions are extracted toward a reflectron-type time-of-flight mass spectrometer (TOF-MS) by an electric field which is switched on 20 ns after the laser pulse. The mass spectrometer was operated with a mass resolution of m/Δm = 600 at m = 27 amu.

Single photon ionization was accomplished with an F₂ laser operated at a wavelength of 157 nm (hν = 7.9 eV), which was coupled into the ultrahigh vacuum (UHV) chamber housing the TOF experiment by a CaF₂ window and a 200 mm focal length CaF₂ lens. The beam line was flushed with dry nitrogen to transport the VUV radiation. The laser pulse energy could be reduced in a controlled fashion
by a stack of two variable dielectric attenuators located in front of the lens and was monitored in situ by a homemade photoelectric detector described elsewhere /S/. The laser was fired at 200 ns after the end of the primary ion pulse (5 μs duration). The laser beam was shaped to a cross section of 0.7 mm x 1.5 mm (FWHM) in directions along and perpendicular to the surface normal, respectively. This way, the spatial beam profile was matched to the geometric volume accepted by the mass spectrometer, a condition which is essential to avoid laser intensity dependent variations of the effective ionization volume.

As an important modification of the setup, the micro channelplates (MCP) used for ion detection were replaced by a high output version with a larger dynamic range. This was done in order to minimize MCP gain saturation effects which may occur at high signal levels (see section 3).

3. Results and Discussion

Fig. 1 shows a plot of selected elemental signals, i.e. integrated mass peaks corrected for the natural isotopic abundance of the measured isotope, vs. the peak power density $P_L$ of the ionizing laser. It is seen that in most cases saturation of the ionization process is approached. As illustrated by the dotted lines in fig. 1, the theoretical saturation behavior of a single photon absorption process according to

$$S(P_L) = S_{sat} \left[ 1 - \exp \left( -\sigma_i \frac{P_L}{h\nu \Delta t} \right) \right]$$

($\Delta t$: laser pulse duration) can be fitted to the measured data. The resulting cross sections $\sigma_i$ for single photon ionization at 157 nm are displayed in fig. 2. It is seen that the majority of the values range from $10^{-18}$ to $10^{-17} \text{ cm}^2$. The cross section observed for Mo seems to be abnormally high, we therefore assume that in this case the ionization process is enhanced by an autoionizing resonance. Due to the limited power density delivered by our laser, the cross section given for Fe represents about the lowest value which can be determined in our experiment. Already in this case, the deviation from linearity even at the highest achievable power density is very small, and, hence, the fit according to eq. (1) bears a relatively large uncertainty. For Mn and Cu, we were not able to obtain a stable fit, the cross sections of these elements must therefore be smaller than $5 \times 10^{-19} \text{ cm}^2$. The relative sensitivity factors (RSF) calculated from the measured signals (with Ni as a reference element) are
displayed in fig. 3. In the limit of low $P_L$, the values are largely independent of $P_L$ and span a range of about three orders of magnitude, which basically reflects the range of $\sigma_i$ as displayed in fig. 2. For laser power densities between $10^5$ and $10^7$ W/cm$^2$, the difference between the observed RSF decreases with increasing $P_L$, thus indicating the onset of saturation. Ideally, one would expect a third regime in the limit of high $P_L$, where the RSF become constant due to complete saturation of the ionization process. Although our laser is not quite intense enough to reach this limit, we can use the saturation signal $S_{sat}$ obtained from the extrapolation by eq. (1) in order to determine the RSF expected in this regime. The resulting values have been included in fig. 3 at a hypothetical laser power density of $2 \times 10^8$ W/cm$^2$. It is seen that all extrapolated RSF are close to unity, the difference between the highest and lowest value being less than a factor of 3. Note that this finding is in marked contrast with our earlier experiments on the same sample [3], in which a much larger deviation had been observed. This discrepancy is mainly due to an experimental artifact in our earlier work which was induced by gain saturation of the MCP used for ion detection. More specifically, in the regime of high $P_L$ the signals of low masses reduce the MCP gain for those of higher masses occurring later in the TOF spectrum, thus leading to an overestimation of the RSF of low mass elements at high signal levels. In the present work, great care was taken to avoid these effects by reducing the MCP gain for each experiment until the measured mass spectrum was independent of the gain setting.

In principle, the extrapolated RSF depicted in fig. 3 represent conditions in which the influence of different photoionization probabilities has been eliminated. Since under steady state sputtering conditions the total flux of sputtered particles must represent the composition of the solid, deviations of the extrapolated RSF from unity must therefore reflect differences in the fraction of the sputtered neutral material which is intersected by the laser. Depending on the geometrical arrangement and the timing of the experiment, this fraction will be determined by the emission angle and velocity distribution of the sputter ejected particles. Since the laser ionization detects the number density of sputtered particles instead of their flux, the influence of the velocity distribution $f(v)$ manifests in form of the mean inverse velocity

$$\langle v^{-1} \rangle = \int v^{-1} f(v) dv$$

(2)

In order to estimate its influence, we have measured the velocity distribution of the sputtered particles by introducing a controlled time delay between the primary ion pulse and the laser pulse. Details of the experimental procedure have been given
elsewhere [6]. The resulting values of $<\nu^1>$ are given in table 1 together with the numerical values of the extrapolated RSF.

Although the relative variation of $<\nu^1>$ is of the same order as that of the RSF, no quantitative correlation is visible. In particular, the low extrapolated RSF of Ti apparently cannot be explained by the velocity distribution effect.

The influence of the angular distribution was investigated indirectly by varying the distance $d$ between laser and surface. In these experiments, the laser was tightly focused, thereby reducing the lateral extension of the ionization volume perpendicular to the laser beam to about 60 $\mu$m (note that the extension parallel to the laser is not restricted and therefore remains at about 1 mm). With $d$ being varied in the range 2.5...0.5 mm, the accepted solid angle was 0.02...0.48 sr. As shown in fig. 4, the resulting RSF of Al, Nb and Mo are virtually independent of $d$, thus indicating that the angular distributions of these elements are very similar to that of Ni. For Cr, an increase of the RSF with increasing $d$ indicates a slightly more forward peaked distribution. For Ti and Fe, on the other hand, a slightly decreasing RSF indicates a more sideward peaked distribution, which may in part be responsible for the low extrapolated RSF of Ti in fig. 3.

4. Conclusion

By extrapolation to complete saturation of the photoionization process, we have determined the cross section for 157-nm single photon ionization of a number of elements. As expected, the extrapolated RSF values are very close to unity. The remaining deviation, however, is not easy to explain. The experiments show that the influence of the velocity distribution of sputtered particles is small and, in particular, is not correlated with the RSF data. As a consequence, we conclude that the observed deviations must be due to differences in the spatial distribution of the sputtered neutrals. From the experimental data, however, it is at present not possible to unambiguously prove this assessment.

References