The influence of projectile charge state on ionization probabilities of sputtered atoms

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**Abstract**

The ionization probability of atoms sputtered from a clean polycrystalline metal surface was measured for different charge states of the projectile used to bombard the sample. More specifically, a polycrystalline indium surface was irradiated with Ar\(^+\) and Ar\(^0\) beams of energies between 5 and 15 keV, and In\(^+\) secondary ions and neutral In atoms emitted from the surface were detected under identical experimental conditions regarding the sampled emission angle and energy. The resulting energy integrated ionization probability of sputtered In atoms is consistently found to be smaller for neutral projectiles, the difference decreasing with decreasing impact energy. The observed trends agree with those measured for kinetic electron emission, indicating that secondary ion formation is at least partly governed by kinetic substrate excitation.

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1. Introduction

The probability of a sputtered atom to leave the surface in an ionized state is of fundamental importance in the field of secondary ion mass spectrometry (SIMS). Although much work has been performed to determine the major factors determining this quantity, reliable experimental data are still rather scarce. For simple systems, the dependence of measured ionization probabilities on parameters like the surface work function and the emission velocity of the sputtered atom appear to be reasonably well understood in terms of either non-adiabatic ionization mechanisms or resonant electron transfer in combination with local electronic substrate excitations. In fact, the available (reliable) data have been analyzed in terms of theoretical predictions derived for both classes of excitation mechanisms [1,2], and the results clearly show that local substrate excitation must play a dominant role in the ionization process of most analytically useful secondary ions [2]. Therefore, it is of great interest to develop experiments where the local electronic excitation following the impact of an energetic projectile can be varied without changing the kinetics of the system. One possible scenario in this direction is to vary the charge state of the impinging projectile, since it is well known that kinetic observables like the sputtering yield are not influenced by projectile charge as long as metallic targets are investigated [3,4].

Using either external (see [5] for a review) or internal [6–8] electron emission as a probe, it was demonstrated that the local electronic excitation of a solid following an energetic particle impact depends on the charge state of the projectile. For slow multicharged ions, this is easily rationalized in terms of the potential energy introduced into the surface by such a particle [5,7]. Comparing neutral and singly ionized Argon projectiles, on the other hand, it was found that the difference in electron emission yields is induced by the kinetics of the interaction rather than the ionization energy of the projectile [6,9]. One possible scenario behind this is that at sufficiently large impact velocities the impinging ionic may survive above-surface neutralization and retain its charge state while penetrating through the first few monolayers below the surface, thereby experiencing a larger electronic stopping power than its neutral counterpart [9].

In the context of secondary ion formation, it is of interest to investigate how the changes of the local electronic excitation induced by different projectile charge states influence the ionization probabilities of sputtered atoms as well. This question is addressed in the work presented here. Similar to the work on electron emission [6,9], neutral and singly positively charged Argon atoms are used as projectiles bombarding a metal surface, and the resulting ionization probability of the sputtered atoms is measured. The results are compared with predictions of model calculations of kinetic electronic excitation.

2. Experimental

The experiments were performed using a laser postionization time-of-flight (ToF) mass spectrometer described elsewhere [10]. The velocity integrated ionization probability of single atoms...
sputtered from a clean metal surface under bombardment with atomic rare gas projectiles was measured using a protocol described in detail elsewhere [11]. Briefly, secondary ions and sputtered neutral atoms were detected under otherwise identical experimental conditions, and the ionization probability was determined from a direct comparison of both measured ToF signals [11]. Post-ionization of sputtered neutral atoms was performed using saturated single photon ionization in an intense pulsed UV laser beam. In order to allow single photon ionization with the available photon energy of 6.4 eV, indium was used as a target material due to the relatively low ionization energy of In atoms (5.6 eV). Moreover, the available laser intensity is large enough to ensure complete saturation of the photoionization process even though the laser was defocused to match the entire sensitive volume of the mass spectrometer. Secondary ions are detected from the same volume with the laser beam switched off.

The projectile beam was generated in a commercial rare gas ion source (Atomika WF 421) that was retrofitted with a gas cell neutralizer described elsewhere [12]. In ion mode, the source delivers a total beam current of about 300 nA into a spot of about 0.5 mm (FWHM). In neutral mode, Ar+ ions with energies between 5 and 15 keV were neutralized via resonant charge exchange in argon, and the remaining ions were deflected out of the beam. The flux of neutral projectiles impinging onto the sample surface was monitored by means of the signal of sputtered neutral atoms.

The investigated sample consisted of polycrystalline indium foil with >99% purity, which was sputter cleaned prior to each experiment by irradiating the surface with the projectile beam operated in dc mode for several minutes. Under the prevailing ultrahigh vacuum conditions (base pressure ~10^-9 mbar), this ensured a residual surface contamination well below the 1 at.% level, as substantiated by the absence of oxide molecule signals in the mass spectra. During data acquisition, the projectile beam was operated in a pulsed mode with a pulse length of about 1 μs and a repetition rate of about 100 Hz. Typically, about 10^8 shots were acquired and averaged per spectrum, rendering the total spectrum acquisition time about 100 s. Normally, no indication of additional surface contamination building up during this time could be discerned. Only at the highest argon gas pressure used while operating the neutralizer, an indication of such contamination build-up was found (see Section 3). All experiments were performed with the sample at room temperature.

3. Results and discussion

The signal measured for secondary In+ ions and neutral In0 atoms sputtered from a polycrystalline indium surface under different projectile source operating conditions is shown in Fig. 1. The data are plotted against the argon gas pressure in the neutralizer cell, which is monitored via the total pressure in the analysis chamber. At 2 × 10^-7 mbar, the In0 signal measured under ion and neutral impact is identical, indicating a neutralization efficiency of 50% in the cell. From the fact that the secondary ion signals cross at a higher gas pressure, it is already evident that the ionization probability must be different under ion and neutral bombardment. Fig. 2 shows an overlay of the normalized 115In+ signal measured under bombardment with 15 keV Ar+ or Ar0 projectiles versus gas pressure in the neutralizer cell.

![Fig. 1. In+ and In0 signal measured under bombardment with 15 keV Ar+ or Ar0 projectiles versus gas pressure in the neutralizer cell.](image1)

![Fig. 2. Normalized ToF peak of the 115In+ and 115In0 signal.](image2)

The resulting data are depicted in Fig. 3, again as a function of argon pressure. In principle, one would not expect the ionization probability to depend on the gas cell pressure, as is fulfilled in the low pressure regime. Above 2 × 10^-7 mbar, on the other hand, the ionization probability is found to increase with increasing gas pressure. This observation is presumably due to an increasing role of surface contamination, which may either arise from impurities in the introduced argon gas, or from a spatial broadening of the projectile beam by elastic scattering. In fact, our data indicate a scattering loss of about 2% of the usable projectile flux at 50% neutralization, increasing to about 11% at the highest pressure investigated. The broadened beam then illuminates a larger spot on the sample surface, which may include outer regions that have not been properly cleaned by the pre-sputtering treatment prior to the experiment.
Probably the most important observation in Fig. 3 is the fact that the ionization probability measured under Ar\textsuperscript{0} bombardment is consistently smaller than that observed under Ar\textsuperscript{+} ion bombardment. The difference is constant at low argon pressures, where it amounts to about a factor of three, and appears to increase in the high pressure regime. As shown in Fig. 4, it also appears to slightly increase with increasing impact energy. These findings are similar to those made for both external \cite{9} and internal \cite{6} electron emission yields. In both cases, a lower electron yield was found under bombardment with neutral projectiles. Using the same projectile source as employed here, the internal yield measured by bombarding the top silver surface of a metal–insulator–metal tunneling junction was found to decrease by roughly a factor of two upon transition from Ar\textsuperscript{+} to Ar\textsuperscript{0} projectiles at 15 keV \cite{6}. At impact energies below 7 keV, on the other hand, the difference was found to vanish, a finding which is consistent with the data plotted for 5 keV in Fig. 4.

These observations were interpreted in terms of differences in the kinetic electronic excitation of the solid induced by impinging projectile ions and neutrals. Following a scenario developed in \cite{9}, a fast projectile ion may approach the solid rapidly enough to sur-

![Fig. 3. Ionization probability of sputtered indium atoms versus argon pressure.](image)

![Fig. 4. Ionization probability of sputtered indium atoms versus projectile impact energy.](image)


give the efficient resonance and Auger neutralization processes and penetrate the surface still in a charged state. Calculations performed for H\textsuperscript{+}, H\textsuperscript{0} and H\textsuperscript{-} projectiles \cite{9} reveal that such a projectile ion will intrinsically experience a larger electronic stopping power than its neutral counterpart, thus leading to a more efficient energy transfer into the electronic system immediately upon traversing the surface. According to our model calculations of kinetic excitation processes \cite{13}, it is this initial energy loss during the first few femtoseconds after the projectile impact which is responsible for kinetic electron emission. After being immersed in the solid, both charged and neutral projectiles will undergo fast electron capture and loss processes and rapidly assume the equilibrium charge state \cite{9}. Shortly after the impact, the memory of the initial projectile charge state is therefore erased. Since most sputtered particles are emitted at later times, i.e. hundreds of femtoseconds after the projectile impact, secondary ion emission should in principle not be expected to be significantly influenced by the projectile charge state. In this context, the charge state dependence of secondary ion probabilities observed here is therefore surprising.

4. Conclusions

For the keV impact energy regime explored here, the ionization probabilities of atoms sputtered from a clean metal surface indicate that a singly charged Ar\textsuperscript{+} projectile ion is more efficient in generating kinetic substrate excitation relevant for secondary ion formation than a neutral atom of the same impact energy. In that respect, the observations made here point in the same direction as those made for both internal and external electron emission from metallic surfaces. These findings manifest that the ionization of sputtered atoms is at least partly governed by kinetic electronic excitation processes induced by the projectile impact. In fact, it is tempting to attribute the projectile charge state dependence observed for electron emission and secondary ion formation to the same physical origin. However, this notion must be regarded with care since both emission mechanisms probe the electronic excitation of the solid at different time scales after the projectile impact.

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References