Self-sputtering of silver using polyatomic projectiles

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Abstract

The self-sputtering of a silver surface under bombardment with Ag\(^n\)\(^-\) cluster ions \((n = 1-3)\) was investigated by means of time-of-flight mass spectrometry characterizing the composition of the sputtered flux. For that purpose, a simple ion source was set up in which projectile ions were generated by laser ablation of a silver rod, mass selected by a linear time-of-flight scheme and accelerated towards the investigated surface. Neutral particles sputtered from this surface are post-ionized prior to mass spectrometry by means of single photon ionization from an intense VUV laser beam. Particular emphasis was put on the investigation of the fraction of molecules and clusters among the sputtered material. It is demonstrated that the projectile intensity delivered by the cluster ion source is sufficient to permit the detection of silver clusters containing up to nine atoms under bombardment with 21-keV mono-, di- and tri-atomic silver projectiles. The ultimate goal of this work was to determine the role of possible non linear yield enhancement effects arising from the spatial and temporal overlap of individual collision cascades initiated by different constituent atoms of a cluster projectile. The results reveal that – in contrast to published experiments on sputtered ionic species – the relative abundance of neutral clusters among the sputtered flux is not significantly enhanced with increasing projectile nucularity. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

If a solid is bombarded with keV-ions, particles are released from the surface due to elastic collisions ("sputtering"). It has been known for a long time that the superposition of collision cascades initiated by several projectiles may lead to strong non-linear effects, provided the impinging particles hit the surface in a highly correlated manner both with respect to their impact location and time [1]. The use of polyatomic projectiles – for instance in form of ionized cluster beams – represents an elegant way to experimentally realize such conditions and study the effects of correlated atom bombardment in particle surface interactions. Using this technique, a number of mass spectrometric experiments have been published which indicate that the mass distribution of sputtered particles may be strongly influenced by the nucularity of the projectile. The basic result of these studies was that the contribution of complex molecules or clusters to the total flux of sputtered particles is generally enhanced if polyatomic instead of monoatomic projectiles are used, the effect being the more pronounced the larger the sputtered cluster [2-6]. In practically all of these experiments, however, only the charged fraction of the sputtered flux...
(“secondary ions”) have been analyzed. Since it is known that in most cases the majority of sputtered particles leaves the surface as neutrals, it is not clear whether these results reveal an enhancement of the partial sputtering yields of complex species or rather relate to their ionization mechanism which may be enhanced under polyatomic projectile bombardment. It is therefore highly desirable to perform similar experiments detecting the corresponding sputtered neutral species. We have recently developed a method to measure the yields of sputtered neutral particles under bombardment with mass selected mono- and polyatomic projectile ions using a tandem mass spectrometric arrangement [7]. Using this technique, it was possible to detect neutral atoms and clusters sputtered from a silver surface under self-sputtering conditions using mono-, di- and tri-atomic silver projectile ions. Due to the very low primary ion intensities achieved with the first version of the ion source, only very small clusters containing at most four atoms could be detected. In the present paper, we describe a modification of this setup which now allows to achieve much higher projectile intensities and therefore significantly expands the range of detectable cluster sizes.

2. Experimental setup

The scheme of the setup used in the present work is depicted in Fig. 1. The system comprises of an ion source generating cluster ions of a selectable element (here: silver) and a time-of-flight mass spectrometer with laser post-ionization used to detect the neutral species sputtered from a selectable target (here: also silver). All components are housed in an ultrahigh vacuum chamber with a base pressure of several $10^{-9}$ mbar. During the experiments, the pressure rises to about $2 \times 10^{-7}$ mbar (mostly Argon) due to the operation of a rare gas ion gun.

![Fig. 1. Schematic setup of cluster ion source and sputtered neutral mass spectrometer.](image-url)
2.1. Projectile ion source

The first version of the ion source invoked a sputtering process at target 1 which was initiated by bombardment with 5-keV Xe\(^+\) ions [7]. Since most of the atoms and clusters released this way are sputtered as neutrals, the particles have to be ionized which was accomplished by a focused laser beam intersecting the plume of sputtered particles in a direction parallel to the surface. In the present experiments, the sputtering process was substituted by an ablation process induced by bombarding the surface with an intense UV laser pulse. The laser employed for this purpose was a commercially available excimer laser (GamLaser model EX50F-1000) that was operated at a wavelength of 193 nm (corresponding to a photon energy of 6.4 eV), a pulse energy of about 1 mJ and a pulse length of ~10 ns. The beam was focused into a spot of about 0.5 mm diameter — resulting in a peak power density of about \(4 \times 10^7\) W/cm\(^2\) — onto a silver rod that was continuously turned in a spiral motion in order to avoid excessive erosion of deep craters at the surface.

The advantage of laser ablation compared to sputtering to produce the projectile ions is twofold. First, the silver target can be permanently kept on high potential which is necessary to accelerate the ions to their desired kinetic energy. This constitutes a major simplification in comparison to the sputtering mode, where the target must be kept at ground potential during the sputtering process in order to allow primary ions to reach the surface, and the extraction potential (up to 30 kV) must then be applied in a pulsed manner by means of a fast high voltage switch. Second, and more important, the number of ions created during an ablating pulse can be by orders of magnitude larger than that created in a sputtering pulse. In order to illustrate the operating specifications of the cluster ion source in laser ablation mode, Fig. 2(a) shows a typical time-of-flight spectrum of 7-keV projectile ions. The spectrum has been measured using a chevron dual microchannel plate detector (MCP 1) translated to the nominal position of the sputtering target (target 2) by recording the ion signal as a function of the delay time after the ablating laser pulse. In order to reduce statistical noise, the spectra have been averaged over 100 ablation pulses. It is seen that Ag\(^+\), Ag\(^+\)\(^+\) and Ag\(^+\)\(^+\)\(^+\) as well as multicharged Ag\(^+\)\(^+\) and some carbon containing ions are generated by the ablation process. The relative abundance of multiply charged ions depends on the intensity of the ablating radiation and increases with increasing laser intensity. The origin of the carbon contamination of the spectrum is not clear at the present time and will be further investigated.

Mass selection of the projectile species can be accomplished in a straightforward manner by means of a pulsed deflection voltage applied to a pair of blanking plates located downstream in the projectile path. Panels (b–d) of Fig. 2 depict the resulting spectra when the blanking pulse is timed such as to select specific projectiles. It is evident that the blanking device allows a practically
Table 1
Total number of ions $N_{ion}$, peak current $I_{max}$, flight time $t$ and half width (FWHM) $\Delta t$ of ion pulses extracted from the cluster ion source

<table>
<thead>
<tr>
<th></th>
<th>Ag</th>
<th>Ag$_2^+$</th>
<th>Ag$_3^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{ion}$</td>
<td>$5.9 \times 10^4$</td>
<td>$3.2 \times 10^4$</td>
<td>$8.8 \times 10^3$</td>
</tr>
<tr>
<td>$I_{max}$ (nA)</td>
<td>53</td>
<td>3.5</td>
<td>0.9</td>
</tr>
<tr>
<td>$t$ (ns)</td>
<td>15.3</td>
<td>20.6</td>
<td>24.9</td>
</tr>
<tr>
<td>$\Delta t$ (ns)</td>
<td>1700</td>
<td>1500</td>
<td>1500</td>
</tr>
</tbody>
</table>

complete suppression of unwanted ions. The oscillating structure visible in panels (c) and (d) arises from high frequency noise induced by the electronic device switching the blanking voltage. Integration of the flight time peaks reveals the total charge detected by the MCP 1 detector. In order to give a rough estimate of the relative intensities of different projectile ions, we convert this into the number $N_{ion}$ of projectile ions contained in a selected projectile peak by using the (particle specific) gain of the employed MCP determined as described elsewhere [8]. The resulting values are depicted in Table 1. Although these values may still contain some uncertainty (due to residual differences of the MCP gain between different clusters), it is worth noting that comparison with the data of Ref. [7] shows an enhancement of the absolute number of projectile ions per pulse delivered by the source by factors of 170, 29 and 12 for Ag$^+$, Ag$_2^+$ and Ag$_3^+$, respectively, as compared to the sputtering mode. Moreover, the temporal width of the projectile ion pulses is much larger than in the sputtering mode, a finding which is due to the spatial extension of the laser induced plasma and the kinetic energy distribution of ablated ions and which is desired very much in the present experiments (see below). It should be noted that both the relative intensities as well as the widths of the peaks depicted in Fig. 2 depend on the ablation laser intensity employed. In particular, the spectrum displayed in panel (b) was recorded at a higher laser intensity than that in panel a) in order to increase the temporal width of the Ag$^+$ pulse.

2.2. Laser ToF spectrometer

The projectile pulses leaving the cluster ion source are used to bombard a sputtering target (target 2) with kinetic energies up to about 25 keV under an incidence angle of 45° with respect to the surface normal. The diameter of the bombarded surface area is determined by the beam blanking aperture which in the present experiments was selected relatively large (~5 mm). The flux of neutral particles sputtered from the surface of target 2 is investigated by means of a laser post-ionization reflectron time-of-flight spectrometer that has been described in much detail earlier [8–11]. In short, neutral species leaving the surface are post-ionized employing a single photon ionization process using an intense ($5 \times 10^3$ W/cm$^2$) pulsed VUV laser emitting radiation at a wavelength of 157 nm. The laser beam is guided in a direction parallel to the target surface at a distance of about 0.5 mm. The time delay between the projectile ion pulse hitting the surface and the ionizing laser pulse is critical since it may act as an emission velocity selector for the sputtered neutrals. In order to integrate over the entire velocity distribution, it is necessary to use projectile pulses of at least several microseconds duration, which ensure that particles of all velocities are present in the volume illuminated by the laser. In that respect, it is advantageous that the laser ablation source delivers relatively long projectile ion pulses. In order to avoid any velocity discrimination, however, several mass spectra were taken at different delay times between projectile and laser pulses (separated by the half width of the projectile pulse) and added. Simultaneously with the ionizing laser pulse, the potential of target 2 is switched from ground potential to +1.6 kV, thus establishing an electric field which extracts the photo-ionized atoms and clusters into a reflectron type time-of-flight mass spectrometer (ReToF), where they are detected at a second microchannelplate detector (MCP 2 in Fig. 1). For a more detailed description of the experimental setup as well as of the procedures used to acquire mass spectra and yield distributions of sputtered neutral atoms and clusters with this system, the reader is referred to our previous publications [8–11].

The sputtering target used in the present experiments is a high purity polycrystalline silver foil. Prior to each experiment, the target surface was sputter cleaned by bombardment with 5-keV Ar$^+$.
ions at an ion current density of $3 \times 10^{-4}$ A/cm$^2$ for at least 5 s.

3. Results and discussion

Fig. 3 shows mass spectra of post-ionized sputtered neutral atoms and clusters which have been ejected from the polycrystalline silver surface under bombardment with Ag$^+$, Ag$_2^+$ and Ag$_3^+$ ions with a kinetic energy of 21 keV. The background mass spectrum recorded with the projectile beam completely blocked, which contains residual gas peaks, has been subtracted. The two spectra depicted on the left side of panels (a) and (b) were recorded by direct digitization of the MCP detector output, while the remaining spectra were taken by means of a single pulse counting technique. Although not displayed, the spectra measured with both detection methods overlap over a range including at least one cluster mass peak, which was then used in order to establish the relative detection probability of both methods. The displayed data therefore directly represent the dynamic range that could be achieved in the experiment. It is seen that in all three cases sputtered neutral clusters containing up to nine atoms can be observed, an achievement which is due to the large increase in intensity of the projectile pulses as compared to previous versions of the cluster ion source. The expansion in range of detectable cluster sizes with respect to our previous work [7] is the more important since a non-linear enhancement of sputtered cluster yields is expected to increase with increasing cluster size and therefore to predominantly manifest for clusters containing more than four atoms. As a consequence, it is now possible to investigate the occurrence of such effects for sputtered neutral clusters in order to complement the experiments performed on secondary cluster ions [3,12].

If the measured signals are to be quantified in terms of the respective sputtering yields, it is important to note that the data presented in Fig. 3 have been obtained with a relatively low intensity of the ionizing laser and must therefore be corrected for the photoionization cross-sections of the different sputtered neutral species. For that purpose, we can in principle use respective data for silver atoms and clusters that have been determined elsewhere [10]. In addition, possible differences between the emission velocity distributions of the different detected species must be taken into account since the laser post-ionization experiment detects the number densities of sputtered particles within the ionization volume rather than their fluxes. Unfortunately, the dynamic range of our experiment is still not sufficient to determine the velocity distribution of particles released under bombardment with mono- or poly-atomic silver projectile ions. Moreover, the technique employed

![Fig. 3](image-url)

Fig. 3. Mass spectra of post-ionized neutral atoms and clusters sputtered from a polycrystalline silver surface under bombardment with 21-keV Ag$^+$ ions ($m = 1$–3) incident under 45° with respect to the surface normal. Panels (a), (b) and (c) refer to mono-, di- and tri-atomic projectiles, respectively. Post-ionization laser: 157 nm, $4 \times 10^6$ W/cm$^2$. 

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to select the velocity of detected neutral species via their flight time between the sample surface and the post-ionization region ultimately requires short projectile pulses with a temporal duration of the order of 100 ns, which cannot be delivered with the cluster ion source operated in ablation mode. We therefore restrict ourselves to a qualitative discussion of the data presented in Fig. 3. Comparing, for instance, the relative signal of Ag₂ with that measured for sputtered Ag monomers, we find very similar ratios of 0.003, 0.006 and 0.003 for mono-, di- and tri-atomic projectile bombardment, respectively. At least for the condition of a constant projectile energy of 21 keV, the nuclearity of the projectile therefore seems to be of relatively minor importance with respect to the abundance distribution of sputtered neutral silver clusters.

This result is the more interesting since it appears to be at variance with relatively large yield enhancement effects detected for ionic species sputtered from Ta and Nb surfaces under bombardment with Auₙ projectiles (n = 1–3) [3,12]. At a constant projectile energy of 12 and 18 keV, this work reports a strong enhancement of the relative abundance of, for instance, Ta₆⁺ and Nb₅⁺ cluster ions with increasing nuclearity of the projectile ions, the observed enhancement factors upon changing from monoatomic to di- and tri-atomic projectiles being as large as 4–6 and 13–14, respectively. At present, we do not have a clear picture of what might be the cause of this discrepancy. For the case of a clean metallic sample studied here, neutral particles should in principle be more representative of sputtering yields and cluster formation processes than secondary ions, since the latter species may exhibit an a priori unknown ionization probability which may change as a function of projectile nuclearity. Certainly, more data of the type presented here are needed in order to clarify this point. Moreover, it is possible that a comparison of our data to the results obtained for Ta and Nb may not be particularly relevant, since the sublimation energy of both Ta and Nb is so high that nonlinear effects in the total yield of these metals may not appear at all. They have never been observed experimentally, and the Sigmund Clausen theory [13] would predict them to be negligible. In contrast, nonlinear effects have been found abundantly in Ag in the past [1], a distinction that may be responsible for the differences between the data presented here and in Refs. [3] and [12].

References