Metastable Excitation of Sputtered Silver Atoms

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Neutral atoms sputtered from a polycrystalline silver surface under bombardment with 15 keV Ar+ ions were investigated by resonant multiphoton ionization in combination with time-of-flight mass spectrometry. Electronically excited Ag atoms ejected in the metastable 4d⁰5s² 2D₃/₂ state (excitation energy 3.75 eV) were ionized by a frequency doubled tunable dye laser using a resonant single photon transition into the autoionizing 4d⁰5s(3D)5p 2D₅/₂ state. Ground state silver atoms were detected by means of a resonant two photon ionization scheme involving the intermediate 4d¹⁰(3S)5p 2P⁰ state. Both two and one color schemes were employed, the latter working via resonant excitation of Rydberg states and subsequent field ionization. The total population as well as the velocity distribution of sputtered metastable and ground state atoms were determined from the saturation behavior of the photoionization process and the flight time of the ejected neutral species between the ion bombarded surface and the ionization volume.

INTRODUCTION

If an energetic ion hits a solid surface, particles may be released into the gas phase by atomic collisions, a process which is usually called "sputtering". It has been long known that the flux of sputtered particles contains not only ground state atoms but also a (usually small) fraction of particles (atoms or molecules) which are released in electronically excited states (1). With respect to experimental detection schemes, these can roughly be classified into two categories. Short-lived states, on one hand, can easily be detected by the light emission due to radiative deexcitation closely above the surface. The interpretation of the data, however, is always complicated by the complex interplay between radiative deexcitation lifetimes and emission velocities as well as by the important role of cascading transitions from higher lying states. Metastable states, on the other hand, are less influenced by transient effects, and are therefore well suited to study the physical mechanisms leading to the excitation of atoms during the atomic collision cascade leading to their sputter ejection. They must, however, in general be detected by laser spectroscopic methods. Corresponding studies have been performed using either laser induced fluorescence (LIF) or resonance ionization mass spectroscopy (RIMS) to investigate the population of metastable excited Fe (2,3), Zr (4), Ti (5), U (6) or Rh (7) and Ni (8) atoms sputtered from the respective clean or oxidized metal surfaces. Typical quantities which are adressable by such experiments are the population of different excited states and the dependence of the excitation probability on the kinetic emission energy of the sputtered particles.

We have recently detected sputtered Ag atoms which are emitted in the first
metastable $4d^95s^2 \, ^2D_{5/2}$ state of silver with an excitation energy of 3.75 eV (9,10). To our knowledge, this is the highest lying metastable state of sputtered particles detected so far. In this paper, we will focus on the methods which were employed to identify Ag atoms in this state as well as in the electronic ground state among the total flux of sputtered particles. Results will be shown concerning the total fraction as well as the kinetic energy distributions of metastable and ground state atoms, respectively.

**EXPERIMENTAL**

The experimental setup used for mass and state selective detection of sputtered neutral atoms has been described in detail elsewhere (11). In short, particles which are sputtered from a polycrystalline silver sample under bombardment with 15 keV Ar$^+$ ions from a pulsed plasmatron ion gun are postionized by either one or two laser beams directed closely above and parallel to the sample surface. State selective postionization was achieved using either one or two tunable dye lasers employing the resonant photoionization (R2PI) process involving a resonant transition to the intermediate $4d^{10}5p \, (^2P_{3/2})$ state by an excitation laser (laser 1) tuned to a wavelength of 328.16 nm. Ionization from this state was achieved by two possible ways: First, a second, frequency doubled ionization laser (laser 2) operated around $\lambda \sim 272.2$ nm was employed to excite a non resonant transition to the ionization continuum. This two color scheme was used to determine the total population of the ground state within the sputtered atoms. Second, another resonant transition to a Rydberg state $[4d^{10}28d \, (^2D_1)]$ was induced by absorption of a second photon from the excitation laser. In this one color scheme, ionization was then achieved by the electric field ($\sim 215$ V/cm) used to Figure 1. Relevant energy levels of the silver atom and ionization schemes extract the photions into the reflectron type time-of-flight (ToF) mass spectrometer. Electronically excited atoms ejected in the first metastable $4d^95s^2 \, (^2D_{5/2})$ state of silver were detected by means of a resonant single photon transition to the autoionizing $4d^95s5p \, (^2D_{5/2})$ state (9,12). For this purpose, the excitation laser was blocked and the ionization laser was tuned to a wavelength of 272.27 nm.

For total population measurements, the two laser beams were crossed at an angle of $90^\circ$ and positioned at a distance of 0.5 mm above the surface. A relatively long primary ion pulse duration of $\tau = 5 \, \mu$s was chosen which ensured that the
measured signals did not increase with increasing \( \tau \), thus indicating that particles of all emission velocities are present in the ionization volume. The ionization laser was focused to a diameter of about 50 \( \mu \)m, while the excitation laser was strongly attenuated and defocused to a diameter of about 1 mm. Therefore, the ionization volume is determined by the spatial overlap of the ionization laser with the sensitive volume of the mass spectrometer (\( \sim 1 \) mm\(^3\)) and, in particular, does not depend on the excitation laser. This is important in order to ensure equal sizes of the effective ionization volume for both metastable and ground state atoms, since the detection of metastables involves the ionization laser alone. For the determination of the kinetic energy distributions, the primary ion pulse width was reduced to 100 ns and the lasers were backed off to a distance of 1.5 mm from the surface. In addition, both laser beams were now collinearly coupled into the chamber and shaped to identical spot sizes (50 \( \mu \)m). This was done in order to ensure that the same procedures could be followed during the somewhat critical alignment of the laser beam with respect to the ToF spectrometer and the ion bombarded spot on the sample surface. The emission velocity of the detected particles was selected via their flight time between the surface and the ionization volume. This was accomplished by introducing a variable time delay \( t \) between the primary ion and ionizing laser pulses. The velocity spectrum of sputtered neutral atoms ejected in a specific electronic state was then determined by unblocking the respective laser beam and following the photoion signal (i.e., the integrated \(^{107}\text{Ag}^+\) ion peak in the mass spectrum) as a function of \( t \).

RESULTS AND DISCUSSION

Wavelength Spectra

Fig. 2 shows the spectrum of the photoion signal as a function of the wavelength of the ionization laser. During acquisition of this spectrum the excitation laser was blocked. Three distinct resonances are visible, each of which exhibits a different spectral width. Both the energetic positions and the widths of the lines correspond to three resonant single photon transitions from the metastable \(4d^95s\text{ }^2D_{5/2}\) state into the autoionizing \(4d^95s(5D)5p \text{ }^2D_{5/2}, \text{ }^2P_{3/2}\) and \(2F_{7/2}\) states which have been observed previously (12). Since no electronic states of Ag exist at or even near the excitation energies corresponding to the observed lines, it is evident that the peaks in fig. 2 cannot be due to the ionization of ground state silver atoms, but must originate from the resonant ionization of the metastable excited state. In the following, we take the transition into the \(^2D_{5/2}\) state (line 1 in fig. 2) at a wavelength of 272.27 nm as representative for the metastable state.
Fig. 3 shows the spectrum which is generated if the ionization laser is detuned from the autoionizing resonance and the excitation laser is unblocked and scanned. The resonance at 328.16 nm corresponding to the transition from the ground state to the 4d_{10}(1S)5p \textsuperscript{2}P^0 state is clearly visible. Due to the relatively high power density of the excitation laser, this line is significantly broadened due to saturation. Since at the corresponding energy of 30472.71 cm\textsuperscript{-1} no autoionizing states are reachable from the metastable state, this configuration detects the silver atoms ejected in the electronic ground state by two color R2PI. As for the dependence on the wavelength of the ionization laser, unblocking the excitation laser simply adds a constant background to the spectrum of fig. 2 due to the non resonant character of the ionizing transition.

Of particular interest is the spectrum which is obtained when only the excitation laser is used. Fig. 4 shows the result if the electric field extracting the photoions into the mass spectrum is switched off during the ionization process. This was necessary since otherwise the extraction field largely complicated the spectrum by Stark-shift and -splitting. A variety of lines are seen originating from resonance enhanced two photon transitions into a number of Rydberg states which are close enough to the ionization limit to be field-ionized by the extraction field. The envelope of these lines follows the saturation broadened resonance into the intermediate \textsuperscript{2}P^0 state. By extrapolation of known states of the \textit{ns} and \textit{nd} Rydberg series (13) (n = 8...12), one can clearly identify each line in fig. 4 as indicated in the figure. Details of this identification procedure will be published elsewhere (14). Obviously the most efficient one color R2PI detection of ground state atoms is by resonantly exciting the 4d\textsuperscript{10}28d \textsuperscript{2}D\textsubscript{1} multiplet. The binding energy \(W_0\) of these states of about 160 cm\textsuperscript{-1} leads to a critical field strength for field ionization of about 68 V/mm which is well below the applied extraction field of 215 V/mm. We therefore expect an ionization efficiency of nearly 100 % once a Rydberg state is excited.

**Total population**

The quantitative determination of the population of a given electronic state from the measured photoion signal is hampered by the \textit{a priori} unknown photoionization cross sections \(\sigma_i\). One possible way to circumvent this problem is
to eliminate the influence of \( \sigma \), by driving the photoionization process into saturation. For the silver ground state atoms, Fig. 5a shows the measured photoion signal as a function of the excitation laser intensity, while the intensity of the ionization laser was kept at a fixed value. In order to reveal the true two color R2PI signal, the background induced by the excitation laser alone - which is due to the one color R2PI scheme (via Rydberg states) described above - was measured and subtracted. It is seen that already at very low power densities the resonant transition into the \( ^2P^o \) state is completely saturated. The dependence of both the ground state and the metastable state signal on the intensity of the ionization laser is displayed in Fig. 5b. It is obvious that in both cases no clear saturation plateaus are observed. This finding is due to signal contributions from the wings of the spatial laser beam profile, which lead to an increase of the effective ionization volume with increasing laser intensity. For the Gaussian beam profiles employed here, the influence of this effect can be included into the theoretically expected laser intensity dependence of the photoion signals. The solid lines depicted in Fig. 5b represent least square fits of this dependence to the measured data which include the saturation signal \( S_{\text{sat}} \) as a fitting parameter. A detailed discussion of the data displayed in Fig. 5b as well as the theoretical background behind the fitting procedure is given elsewhere (15). As a first approximation, the resulting ratio between the saturation signals evaluated for metastable and ground state atoms of approximately 7% can be taken as the relative population of these states among the total flux of sputtered silver atoms.

**Kinetic Energy Distributions**

The velocity distribution of sputtered atoms was measured by varying the time delay between the primary ion pulse initiating the sputtering process and the firing time of the ionization laser. Fig. 6 shows such a flight time distribution for both the silver ground state and metastable atoms. The geometric alignment was made such that only atoms ejected in a narrow solid angle around the direction along the surface normal were detected. It is seen that the velocity distributions largely differ. More specifically, the metastable atoms possess a lower average velocity than the ground state atoms. This finding is of particular interest since it appears to be at variance with all published data. Previous experiments on a number of different sputtered excited metastable atoms have revealed kinetic energy distributions which were either *identical* with or *broader* than that of the respective ground state atoms (16). These results have been interpreted in terms of a simple
deexcitation model: The particles which are excited during the collision cascade leading to their ejection are assumed to be more or less efficiently deexcited on their flight away from the surface. Due to the limited range of the electronic interaction with the surface, this model implies that faster particles are less efficiently deexcited and therefore predicts an apparent broadening of the velocity distribution. Here, the first case is observed where the velocity distribution of the excited state is narrower than that of the ground state and this model is therefore not applicable. Hence, the observed velocity distribution must be induced by a velocity dependent excitation rather than deexcitation mechanism. A possible way to explain the data is to assume that the metastable neutral atoms are formed by resonant neutralization of precursor ions containing a 4d-hole. As discussed in more detail in a forthcoming publication (17), the generation of such ions in the course of the collision cascade seems physically feasible. If neutralization occurs outside the solid, i.e. closely above the surface, a faster particle would be less efficiently neutralized, thus leading to an apparently narrower velocity distribution of the excited atoms.

**Literature**

14. Berthold, W. and Wucher, A., to be published
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