Electronic Excitation during Sputtering of Silver Atoms

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The formation of metastable excited atoms during ion sputtering of polycrystalline silver was investigated by resonant laser postionization and time-of-flight mass spectrometry. It is shown that the metastable $4d^9 5s^2\,{}^2D_{5/2}$ state with an excitation energy of 3.75 eV is populated with a surprisingly high probability of several percent with respect to the ground state. The velocity distribution of the metastable atoms is found to fall off *more steeply* towards high emission velocities than that of the ground state atoms, thus indicating a new excitation mechanism of the sputtered silver atoms.

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If an energetic ion hits a solid surface, particles may be released from the solid into the gas phase by atomic collisions ("sputtering"). Besides neutral atoms in their respective ground state, the flux of these sputtered particles generally contains a (usually small) fraction of atoms which are emitted either as ions or in electronically excited states. While the elastic collision processes causing the mere ejection of particles seem to be reasonably well understood, our knowledge about the details of the inelastic processes leading to the ionization and excitation of sputtered atoms is still far from being complete. This is particularly true for the case of metastable excited states, where only a very limited amount of experimental data exist. A fairly recent review of this work is given in Ref. [1]. With regard to the elucidation of physical mechanisms responsible for the formation of excited states in sputtering, the most obvious quantities to be determined experimentally are the *total fraction* of the excited atoms within the flux of sputtered particles, on one hand, and their *velocity distribution*, on the other hand. While the former has been frequently interpreted in terms of Boltzmann-like population distributions involving "temperatures" of the order of 1000 K [2], recent measurements on sputtered excited Ni atoms [3–5] have revealed a pronounced population inversion and, hence, indicate that this interpretation is at least questionable. As for the latter, two limiting cases seem to exist, where the velocity distribution of the excited atoms is either identical to or significantly broader than that of the respective ground state atoms [1,2]. The physical interpretation of this finding in terms of theoretical models describing the excitation processes during sputtering is still under debate.

In this Letter, we report on an experimental study of ground state and metastable Ag atoms sputtered from a clean polycrystalline silver sample bombarded under 45° with a pulsed beam (duration 5 μs) of 15 keV Ar^+ ions. The beam current density during a pulse was 100 $\mu A/cm^2$ and, hence, low enough to ensure that all particle emission processes were caused by single ion impact events. The experiments were carried out under ultrahigh vacuum conditions (base pressure 10^{-9} mbar). Prior to the actual measurements the sample was sputter cleaned by cw ion bombardment for several minutes in order to achieve steady state surface conditions. The sputtered neutral particles were ionized by a laser beam directed closely above and parallel to the sample surface and detected by a reflectron type time-of-flight mass spectrometer. Details of the setup have been described elsewhere [6]. State selective photoionization of the emitted atoms was achieved using either one or two tunable dye lasers employing the ionization schemes sketched in Fig. 1. The ground state $[4d^{10}5s(^2S_{1/2})]$ atoms were ionized by a resonance enhanced two color two photon absorption process involving a resonant transition to the intermediate $4d^{10}5p(^2P_{3/2})$ state by an excitation laser tuned to a wavelength of 328.16 nm and a nonresonant transition to the ionization continuum by a second, frequency doubled ionization laser operated around $\lambda \sim 272.2$ nm. While the ionization laser was focused to a spot size of 50 μm (FWHM), the excitation laser was slightly defocused in order to ensure optimum overlap of the two beams. Electronically excited atoms in the first metastable $4d^9 5s^2(^2D_{5/2})$ state of silver were detected by means of a resonant single photon transition to the autoionizing $4d^9 5s5p(^2D_{5/2})$ state [7,8].

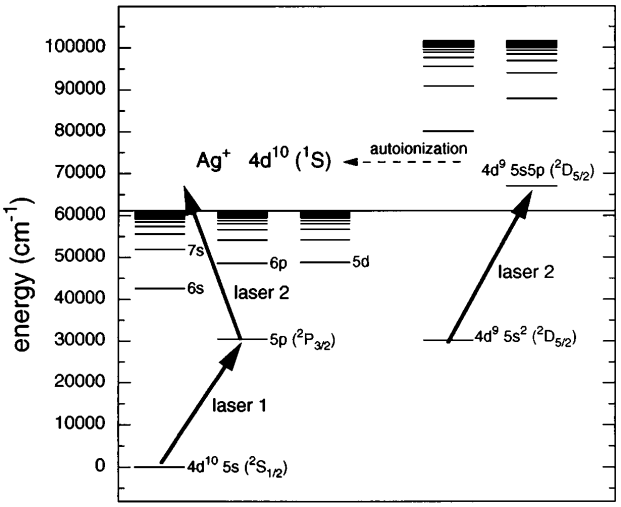

FIG. 1. Schematic diagram of relevant Ag atom energy levels and photoionization schemes.

For this purpose, the excitation laser was blocked and the ionization laser was tuned to a wavelength of 272.27 nm. By comparing the measured positions and widths of several spectral lines with available literature data, it can be unambiguously shown that the sharp resonance line observed at this wavelength originates from the ionization of metastable atoms [7].

In order to allow a quantitative discussion, it is of interest to determine the relative population of the metastable state within the total flux of sputtered silver atoms. This, however, requires the quantitative determination of state selective particle number densities which is often hampered by the—in general different—photoionization cross sections of atoms in different electronic states. This difficulty can, in principle, be circumvented in two different ways. First, the ion signals measured for sputtered atoms can be compared to those of thermally evaporated atoms, which can be assumed to exhibit a Boltzmann-like state distribution. This method, which has been successfully employed to determine the population of low-lying excited states of sputtered Ni atoms [3,4], is not applicable here due to the high excitation energy of the investigated metastable state. Second, one can try to saturate the photoionization process and thus eliminate the influence of different ionization cross sections [5]. This route has been followed here. Figure 2 shows the signal of ground state and metastable atoms as a function of the power density P_L of the ionizing laser. The difference between the two curves is that for the metastable state the excitation laser was blocked and the ionization laser was tuned to the autoionization resonance, while for ground state atoms the ionization laser was detuned from the autoionization resonance and the excitation laser was unblocked. This technique ensured that in the first case only metastable atoms could be detected, since no excited states are accessible from the ground state at the wavelength of the ionizing laser. In the second case mainly ground state atoms are detected with a small background of nonresonantly ionized metastables (which can be measured with blocked excitation laser and subtracted). From the data displayed in Fig. 2, it is seen that both curves do not show clear saturation plateaus in the regime of high P_L. This is due to the well-known fact that at high laser intensities more and more signal contributions from the wings of the spatial laser beam profile contribute to the measured signal, thus leading to an increase of the effective ionization volume with increasing P_L. 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 [9]. The solid lines depicted in Fig. 2 represent least-square fits of this dependence of the measured data, which contain the respective saturation signal and ionization cross section as fit parameters. For ground state atoms, the intensity of the excitation laser was high enough to completely saturate the excitation process, and an effective saturation behavior according to a single photon ionization process was assumed. Details as well as the theoretical background of the fitting procedure will be published elsewhere [10]. As a result, we find ratios of 0.06 and 4.6 between the saturation signals $S_0 = \rho T$ and ionization cross sections of metastable and ground state atoms, respectively. Since the mass spectrometer transmission T is identical for Ag^+ ions created from ground and excited state neutral atoms, the first of these values represents the ratio between the number densities ρ_m and ρ_g of metastable and ground state atoms within the ionization region. The ratio $\rho_m/\rho_g \cong 6\%$ indicates a relatively high population of the metastable state, which appears to be surprising for the case of a clean metal surface studied here. Assuming a Boltzmann-like population distribution, the corresponding "population temperature" of about 15 000 K is about an order of magnitude higher than similar parameters determined for lower-lying metastable states of atoms sputtered from other clean metal surfaces [2]. We therefore conclude that our present data cannot be interpreted in terms of quasithermal excitation models. This finding is consistent with a relatively large body of experimental data collected on atoms sputtered in short lived excited states (which, in contrast to the states investigated here, can radiatively decay after their emission). Although also in this case the data were often analyzed in terms of population temperatures, which were typically of the order of several thousand K [11], it was clearly demonstrated that the observed population distribution cannot be explained by local thermal equilibrium considerations [12,13]. For completeness, it should be added at this point that the observation of relatively large populations of high-lying metastable states in sputtering has, in principle, been reported previously. As an example, we refer to the published work on sputtered Ca, Cr [14], and Ti [15] atoms. These investigations, however, were

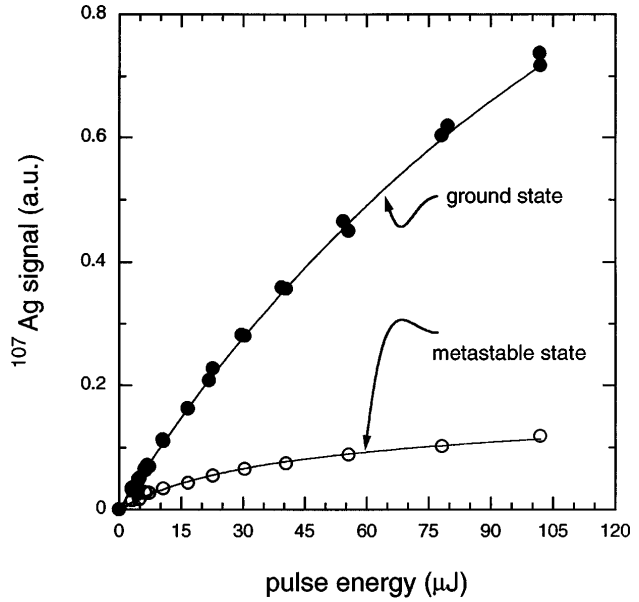

FIG. 2. Photoion signal measured for ground state and metastable Ag atoms sputtered from polycrystalline silver vs pulse energy of the ionizing laser.

performed under conditions where the surface was oxidized in order to enhance the metastable yield and therefore correspond to a significantly altered electronic surface structure as compared to the clean metal case studied here.

A second subject of great interest concerns the velocity distribution of the ejected excited atoms. In the present work, this was measured by reducing the temporal pulse width of the primary beam of Ar^+ ions to 100 ns and introducing a variable time delay between the ion pulse and the ionizing laser pulse. In addition, the laser beam was backed off from the sample surface to a distance of 1.5 mm and the sensitive volume of the mass spectrometer was restricted in the direction along the laser beam. Therefore, in contrast to the population determination where a relatively large fraction of the angular distribution of sputtered particles was probed, in these experiments only sputtered particles emitted into a small solid angle ($\sim$0.1 sr) around the surface normal with a certain selectable velocity are ionized and detected. By scanning the delay time, the velocity distribution can be measured in a state selective manner. Figure 3 shows the resulting flight time distributions for ground state and metastable excited Ag atoms ejected along the surface normal. It is seen that the two distributions clearly differ. In order to ensure that the detected metastable atoms are not by chance created by laser induced photofragmentation of sputtered silver dimers, the signal of Ag_2^+ ions generated by nonresonant two photon ionization of Ag_2 has been included in the figure. The distinct difference between the distributions measured for Ag_2^+ and the metastable atoms represents clear evidence that dimer fragmentation is not the source of the observed population of the metastable state, since otherwise the distributions would have to be identical [16]. The flight time distributions can be converted to kinetic energy distributions by

$$f(E) \propto S(t)t^2 \quad \text{with} \quad E = \frac{mr^2}{2t^2}. \tag{1}$$

Here $S(t)$ denotes the signal measured for a specific delay time t and r denotes the distance between laser beam and sample surface. It is of note that Eq. (1) assumes that the measured signals represent the *number density* of the sputtered neutral particles rather than their *flux*. For the focused lasers employed here, this condition is not necessarily fulfilled if the ionization is driven into saturation. The energy distribution experiments were therefore conducted far from saturation, i.e., with strongly attenuated laser beams. It can be shown that under these circumstances Eq. (1) holds for all laser focusing conditions [17]. Figure 4 depicts the resulting flux kinetic energy distributions of silver atoms sputtered in the ground or metastable state. It is seen that the distribution of metastable atoms falls off more steeply towards high emission energies than does that of ground state atoms. This finding is surprising, since it appears to be at variance with all literature data on the energy distributions of sputtered metastable atoms published to date. As mentioned above, these data show either identical distributions for metastable and ground state atoms or a significantly *broadened* energy distribution of the metastable atoms. This finding was interpreted by Winograd *et al.* [18] who proposed a qualitative deexcitation model taking into account the electronic structure of the specific excited atom. In essence, this model is based on the assumption that excited atoms, which are created, for instance, by collisional excitation in the course of the collision cascade, are more or less efficiently deexcited due to electronic interaction with the surface on their path away from the surface after sputtering. It is obvious that in this

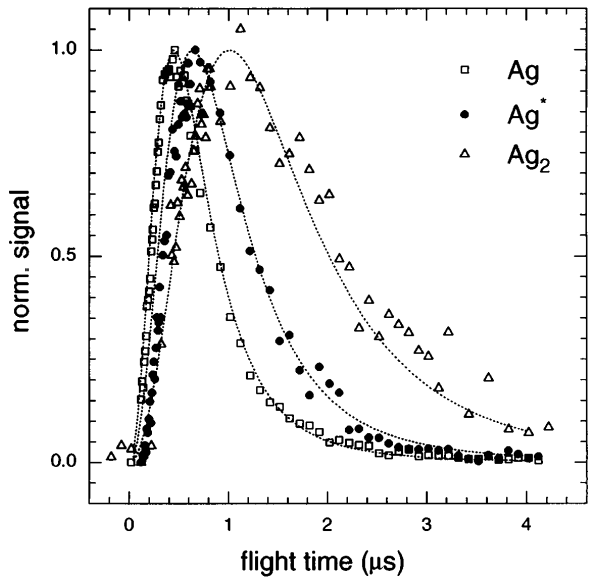

FIG. 3. Signal of sputtered positionized ground state and metastable Ag atoms and Ag_2 dimers as a function of the delay time between sputter pulse and ionizing laser pulse.

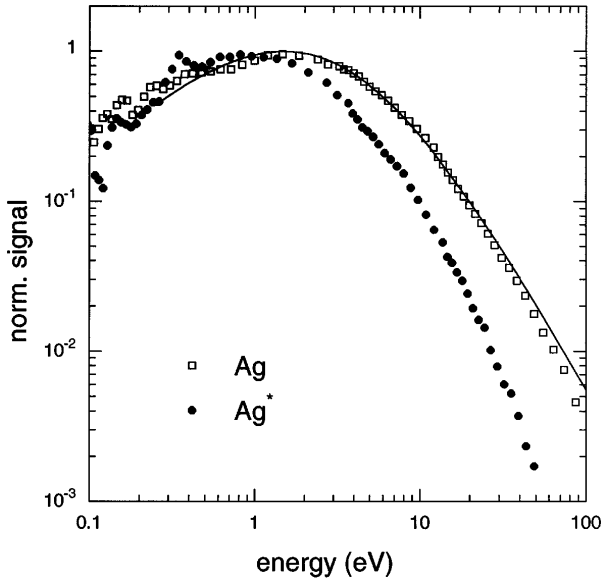

FIG. 4. Kinetic energy distribution of sputtered ground state and metastable silver atoms ejected along the surface normal. Solid line: theoretical prediction from linear cascade theory.

picture the degree of deexcitation will decrease with increasing emission velocity, since the atom spends less time in the vicinity of the surface and has therefore less time to deexcite. As a consequence, deexcitation leads to an apparent broadening of the (normalized) energy distribution measured for the excited atoms detected far away from the surface. In several cases, this expected behavior has indeed been observed. In other cases, no broadening with respect to the ground state distribution is observed and, hence, efficient deexcitation is obviously prevented. The idea is that this is always the case if the electronic configuration of the departing excited atom exhibits a closed outer shell, which then screens the interaction with the surface. Clearly, the excited metastable silver atoms investigated here would belong to that category, and therefore no broadening would be expected. The fact that we observe the *opposite* effect, however, cannot be explained by this model. If we plot the spectral excitation probability, i.e., the ratio of metastable and ground state population, vs the emission energy, we obtain the results depicted in Fig. 5, which show that at high energies the excitation probability decreases inversely proportional to the emission velocity [19]. This indicates that in the case studied here the *excitation* mechanism rather than deexcitation depends on the time spent by the atom near the surface. On the mechanism behind this excitation process we can only speculate. One possibility would be that the metastable state is created by resonant surface neutralization of a sputtered ion under simultaneous excitation of a *d* electron. This process, which is frequently observed in plasmas (where it is termed "dielectronic recombination"), would in the special case of silver atoms require surface electrons originating from occupied states well above the Fermi level. Because of the strong atomic disorder and/or a significant heating of the electronic system of the surface during the collision cascade initiating the emission of atoms in sputtering [20], however, the assumption of the existence of such states may not be as unphysical as it seems. As a second possibility, an outgoing ion, which—as a consequence of collisional excitation in the cascade—contains a hole in its *d* shell, may be neutralized above the surface by a resonant electron capture in to the $5s$ state. This mechanism, which also explains the observed velocity dependence, would predict an increasing yield of excited metastable ions (emitted in the $4d^9 5s$ configuration) with increasing emission velocity and could therefore in principle be checked in future experiments.

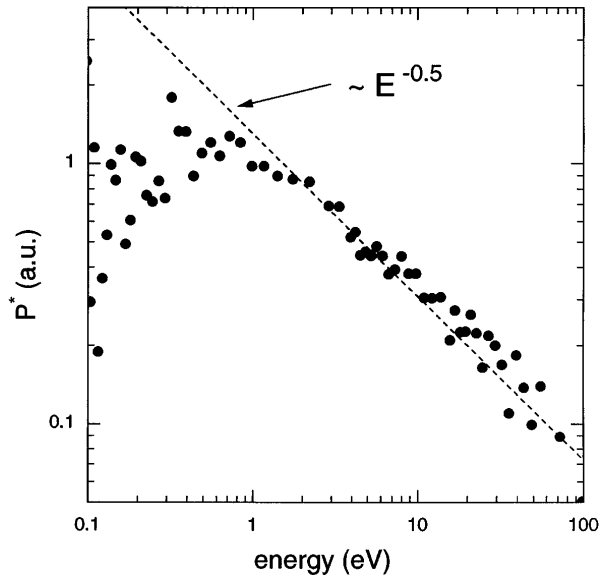

FIG. 5. Spectral excitation probability, i.e., relative population of metastable $^2D_{5/2}$ state with respect to the ground state vs kinetic emission energy of sputtered Ag atoms.

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