Sputtering of Ag atoms into metastable excited states

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We have investigated the processes that lead to the ejection of excited neutral silver atoms upon sputtering of a polycrystalline silver surface under bombardment with keV rare gas ions. Resonant multiphoton ionization in combination with time-of-flight mass spectrometry was used in order to allow a state-selective detection of the sputtered species. As a result, excited atoms in both states of the metastable multiplet $4d^95s^2 (^2D_{5/2})$ with excitation energies of 3.75 eV ($^2D_{5/2}$) and 4.30 eV ($^2D_{3/2}$) have been detected. The total population of both states is determined to be of the order of 1%, which is surprisingly high in view of the large excitation energy. The velocity distribution of atoms ejected in both states reveals that the metastable atoms are ejected with lower average velocity than those emitted in the electronic ground state, thus indicating a mechanism populating this state which becomes less efficient with increasing emission velocity. The results are discussed in terms of a two-step model describing the formation of an excited neutral atom as a combination of collective excitation processes within the collision cascade followed by resonant electron transfer between the surface and the escaping particle.

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I. 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 certain fraction of particles that the flux of sputtered particles contains not only ground-state atoms, but also a certain fraction of particles that are released in electronically excited states. In order to gain insight into the physical mechanisms leading to the emission of atoms in excited states, metastable states are of particular interest since they preserve their excitation until the atom has escaped far away from the surface and thus becomes eligible to experimental detection. To this end, quantum-state-selective detection of sputtered atoms can be accomplished by laser spectroscopic methods.

During the past decade, a relatively large body of experimental data on sputtered metastable atoms has been compiled using either laser-induced fluorescence (LIF) or resonance ionization mass spectroscopy (RIMS) to investigate metastable Fe, Zr, Ti, Cr, Ca, U, Rh, Ni, Co, and Ag atoms in various excited states which were sputtered from the respective clean or oxidized metal surfaces. A valuable source of information extractable from such experiments is the combination of (i) the population partition over different states and (ii) the dependence on the kinetic energy and angle of emission of the sputtered particles. While early experiments have frequently been interpreted in terms of Boltzmann-like population distributions with “temperatures” ranging from 980 to 2000 K (cf. Ref. 14 for a review), newer results indicate that the excitation energy alone is not sufficient to characterize the measured population partitions in sputtering. Instead, parameters like the electronic configuration of the departing particle as well as details of the band structure of the bombarded solid surface play a significant role in determining the final probability of detecting a sputtered particle in a specific electronic state. A comprehensive theoretical understanding of the whole entity of experimental data that have been collected to date is, however, still missing. It has nevertheless been shown recently that many of the observed data can be interpreted in terms of a resonant electron transfer model which assumes the population of excited states to proceed via resonant neutralization of ejected precursor ions.

A particularly interesting case has been found for Ag atoms sputtered from an ion-bombarded silver surface. In this case, a sizable fraction (several percent) of the sputtered atoms are ejected in the first metastable state $4d^95s^2 (^2D_{5/2})$ of silver with an excitation energy of 3.75 eV. Any quasi-Boltzmann distribution describing the observed population of this state would involve “temperatures” well above $10^4$ K, which are absolutely unrealistic. Since, in addition, the state is located well above the Fermi level of silver, it cannot be populated by resonant electron transfer from the conduction band into excited orbitals of an outgoing ground-state precursor ion either. Instead, a new population model was developed which assumes at least part of the excitation to be generated by collective electronic energy transfer processes occurring within the solid as a consequence of the collision cascade leading to the ejection of sputtered particles. In this context, the interesting question has remained as to whether other metastable states with even higher excitation energies might be detectable within the flux of sputtered particles ejected from an ion-bombarded silver surface. In this case, it would be very important to determine...
the relative population of such states as well as its dependence on the emission velocity in order to test the concepts of the newly developed model. The goal of the present work was therefore devoted to the detection and investigation of the population of the second state of the Ag $4d^95s^2$ ($^2D_J$) multiplet with $^2(D_{3/2})$ configuration and an excitation energy of $4.3 \text{ eV}$. To our knowledge, this is by far the highest-lying metastable excited state that has been detected in a sputtering experiment to date.

II. EXPERIMENT

The experiments reported in this work have been performed in collaboration between two laboratories. Although the experimental technique employed at both locations is identical, there are some subtle differences between the actual setups present at both laboratories. Both setups as well as the experimental methods employed for data acquisition and reduction have been described in detail elsewhere.\textsuperscript{17,19} In the present context, we will therefore restrict ourselves to a brief description of the method in general (a description which is common to both experiments) and then, where relevant in the context of this work, revert to the details which are different between both experiments.

State-selective detection of sputtered neutral species is accomplished by resonance ionization mass spectrometry. A sketch of the respective experimental setup is shown in Fig. 1. In essence, a polycrystalline silver sample located in an ultrahigh-vacuum chamber (base pressure $10^{-9}$ hPa or below) is bombarded with argon ions of energies between 5 and 15 keV impinging under $45^\circ$ with respect to the surface normal. Prior to each experiment, the sample was sputter cleaned by rastering a dc ion beam in order to remove any surface contamination. During data acquisition, the primary ion beam was operated in a pulsed mode in order to synchronize the sputtering and post-ionization processes. Neutral particles (atoms or molecules) ejected from a solid surface under ion bombardment are photoionized by a pulsed laser beam guided parallel to the surface. State-selective post-ionization is achieved using the resonant photoionization schemes depicted in Fig. 2. In particular, ground-state [$4d^{10}5s(^2S_{1/2})$] silver atoms are detected by a direct two-photon transition to the continuum using a laser wavelength of $327.80 \text{ nm}$. This transition is slightly resonance enhanced by the presence of the intermediate $4d^{10}5p (~^2P_{3/2})$ state and therefore exhibits a fairly large ionization cross section. Electronically excited atoms ejected in the metastable $4d^95s^2 (~^2D_{J})$ states, on the other hand, are detected in means of a resonant single-photon transition into an autoionizing state above the ionization threshold. We utilize a number of different transitions that have been observed and identified by Baier et al.\textsuperscript{20} using a plasma discharge source to generate the metastable atoms. The photoions generated within the ionization volume are extracted into a reflectron type time-of-flight mass spectrometer (TOF-MS) which can be operated either in linear mode (using the multichannel plate detector MCP 2 in Fig. 1) or in reflector mode (using detector MCP 1 in Fig. 1). In order to avoid any field ionization or static Stark splitting of the atomic energy levels, the extraction volume between sample surface and mass spectrometer entrance electrode is kept field free during the primary ion and laser pulses, and the extraction field is generated shortly ($\sim 10 \text{ ns}$) after the laser pulse by rapidly switching the target potential to high positive values.

The ionizing laser beam was generated by means of a tunable dye laser operated either with TMQ (tuning range 338–365 nm), a mixture of DCM and Pyridine I ($610–724$ nm), or Coumarin 307 ($479–555$ nm) dyes. Transitions at 347 and 364 nm could be accessed directly by using the fundamental wavelength, whereas all other transitions required frequency doubling using either a KDP or a BBO crystal. Due to different pumping sources (Nd:YAG laser in Leuven and Excimer laser in Essen, respectively), the temporal duration of the laser pulses varied from 6 ns (Leuven) to about 20 ns (Essen). During the measurements determining the total population of an excited state, the beam was shaped to a cross section of about $0.5–1 \text{ mm}^2$ and steered parallel to the sample surface at distances ranging from about 1 to 4 mm. As a result, particles emitted from the surface under polar angles up to $26^\circ$ with respect to the surface normal can interact with the laser and be detected. In addition, a relatively long primary ion pulse duration of $t_p \sim 10 \mu \text{s}$ in connection with a relatively short delay time between ion and laser pulse was chosen. This was done to ensure that the measured signals do not increase with increasing $t_p$, thus
indicating that particles of all relevant emission velocities are present in the ionization volume. In order to determine the emission velocity distribution of the sputtered particles, on the other hand, the laser was tightly focused to a beam waist of about 50 \( \mu \)m full width at half maximum (FWHM), the primary ion pulse width was reduced to \( t_p = 100 \) ns (Essen) or 300 ns (Leuven), and the time delay \( t \) between the primary ion and ionizing laser pulses was varied. This operation mode selects the emission velocity of the detected particles (sampling a polar emission angle interval of several degrees in the direction along the surface normal) via their flight time between the surface and ionization volume. The velocity spectrum of sputtered neutral atoms ejected in a specific electronic state was then determined by measuring the photoion signal (i.e., the integrated \( ^{107}\text{Ag}^+ \) ion peak detected in the mass spectrum) as a function of \( t \). The resulting flight time distribution \( f(t) \) can be converted into the velocity spectrum by means of

\[
f(v) \approx \frac{f(t) \Delta t}{\Delta r + v \Delta t},
\]

where \( \Delta r \) denotes the spatial width of the laser beam in the direction along the flight path of the sputtered neutrals and \( \Delta t \) is the temporal width of the ionizing laser pulse. The variable \( v \) denotes the selected emission velocity determined by

\[
v = r/t,
\]

where \( r \) denotes the flight path length between the surface and the ionization volume. The two terms in the denominator of Eq. (1) represent two different contributions to the measured signal. While the first term represents the contribution of the number density of sputtered neutral particles present within the ionization volume at the firing time of the laser, the second term corresponds to the contribution induced by the flux of sputtered particles across the ionization volume during the temporal duration of the laser pulse. The significance of the flux term depends on the selected velocity and cannot \textit{a priori} be neglected here due to the relatively small extension of the ionization volume. As shown in detail elsewhere,\(^{23}\) this term is only important if the photoionization process is driven into saturation, since otherwise the signal increase due to neutral particles flowing into the ionization volume and being ionized, is exactly balanced by the signal loss induced by neutral particles escaping the ionization volume without being ionized. Therefore, the velocity distribution measurements were performed with a strongly attenuated laser beam, thus ensuring that the photoionization efficiency was far from saturation, and the second term in the denominator of Eq. (1) was neglected.

### III. RESULTS AND DISCUSSION

As outlined in Sec. II, the identification of metastable excited atoms among the flux of sputtered neutral particles relies on their photoionization by resonant single-photon transitions into autoionizing states. The first step therefore naturally consists of an unambiguous identification of the corresponding resonances in the wavelength spectrum of the ionizing laser. In the first subsection, we therefore present spectral scans of the detected photoion signal which will then be compared to tabulated literature data. Once an observed resonance is identified to be representative of one particular initial state, it is essential to gather information about the ionization efficiency connected with the corresponding transition in order to determine the population of that state from the measured ion signal. In the second subsection, we therefore investigate the saturation behavior of the measured photoion signals as a function of increasing laser intensity in order to determine the ionization cross sections. The third subsection will then be devoted to the emission velocity distribution of atoms sputtered in specific electronic states. If compared to that of the respective ground-state atoms, this distribution reveals information about the velocity dependence of excitation probabilities, which in turn allows us to gain information about the mechanisms leading to the excitation of atoms in sputtering. Moreover, the velocity distribution is needed in order to convert the measured number density of excited atoms into particle fluxes and hence determine the population partition of different states among the sputtered flux.

#### A. Wavelength spectra

Figure 3 shows two typical spectral overview scans over parts of the wavelength regions of interest here. More specifically, the detected signal (i.e., the integrated TOF mass peak) of the \( ^{107}\text{Ag} \) isotope is plotted versus the wavelength of the ionizing laser, while all other experimental parameters were kept constant. Since the two scans of Fig. 3 have been taken at different laboratories (using different laser systems), the laser power density employed in both cases is different \( \sim 5 \times 10^5 \) W/cm\(^2\) in Fig. 3(a) and \( \sim 3 \times 10^7 \) W/cm\(^2\) in Fig.
The spectrum in Fig. 3(b) is dominated by a large peak at a wavelength of 327.80 nm. The corresponding photon energy is exactly half of the first ionization potential of Ag atoms in the $4d^{10}5s^2 \left(^1S_0\right)$ electronic ground state, thus indicating that this peak arises from the ionization of ground-state atoms by means of a direct two photon absorption. As shown in Table I all other spectral lines identified in Fig. 3 can be attributed to resonant single-photon transitions from higher-lying $4d^{10}5s^2 \left(^2D,^2F\right)$ states into excited neutral fragments. In principle, such a process may produce metastable excited atoms which can then be ionized by further absorption of another photon. By comparison of measured peak wavelengths with the data compiled by Baier et al.,

all resonances are superimposed by a nonresonant background signal which is generated either by nonresonant two-photon ionization of ground-state atoms (only possible for wavelengths below 327.80 nm) or by nonresonant single-photon ionization out of the metastable states. The assignment of the different spectral lines was performed by comparison of measured peak wavelengths with the data compiled by Baier et al.

Moreover, the measured linewidth of the spectral features can be compared with the autoionization lifetimes of the respective upper states which have been also determined in Ref. 20 (see Table I). Although all measured spectra displayed in Fig. 4 appear to be more or less power broadened, we find a clear correspondence which further validates the assignment given in Table I. While the lines labeled (1)–(3) have been observed earlier, the remaining transitions, and particularly those starting from the higher-lying $4d^{10}5s^2 \left(^2D_3/2\right)$ state, are detected here for the first time in a sputtering experiment. The mere existence of these spectral lines clearly shows that metastable atoms with a $4d^{10}5s^5p$ configuration in both fine structure ($^2D,^2F$) states are present in the cloud of sputtered particles. This finding is even more interesting in view of the relatively large excitation energy of 4.3 eV, which makes the $4d^{10}5s^2 \left(^2D_3/2\right)$ state the highest-lying metastable state ever observed in sputtering to date.

The above interpretation of the spectra depicted in Fig. 4 assumes that the photoionization process itself does not alter the population distribution of electronic states among the sputtered particles. The validity of this assumption is by no means trivial. One important possible mechanism that may falsify the data is photofragmentation of sputtered clusters in the ionizing laser beam. If silver dimers or even larger clusters are present in the ionization region and interact with the laser, absorption of one or more photons can in principle lead to excitation into repulsive states which may then dissociate into excited neutral fragments. In principle, such a process may produce metastable excited atoms which can then be ionized by further absorption of another photon. By comparison of the apparent emission velocity spectra of excited at-

### Table I. Assignment of the different spectral lines explored in this work by comparison with data published in Ref. 20. Initial and final states of observed transitions are given together with their excitation energy $E$ above the electronic ground state and autoionization lifetime $\tau$ of the upper state. The last column depicts the experimentally observed linewidth.

<table>
<thead>
<tr>
<th>No.</th>
<th>Wavelength (nm)</th>
<th>Initial state</th>
<th>Final state</th>
<th>Linewidth (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$4d^{10}5s^2 \left(^2D,^2F\right)$</td>
<td>$5p^2D_{3/2}$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>272.3</td>
<td>$\left(^2D_{3/2}\right)$</td>
<td>30242</td>
<td>5p $^2D_{3/2}$</td>
</tr>
<tr>
<td>2</td>
<td>279.8</td>
<td>$\left(^2D_{3/2}\right)$</td>
<td>30242</td>
<td>5p $^2P_{3/2}$</td>
</tr>
<tr>
<td>3</td>
<td>282.5</td>
<td>$\left(^2D_{3/2}\right)$</td>
<td>30242</td>
<td>5p $^2F_{5/2}$</td>
</tr>
<tr>
<td>4</td>
<td>313.1</td>
<td>$\left(^2D_{3/2}\right)$</td>
<td>30242</td>
<td>5p $^2D_{3/2}$</td>
</tr>
<tr>
<td>5</td>
<td>317.2</td>
<td>$\left(^2D_{3/2}\right)$</td>
<td>30242</td>
<td>5p $^2D_{5/2}$</td>
</tr>
<tr>
<td>6</td>
<td>322.6</td>
<td>$\left(^2D_{3/2}\right)$</td>
<td>34714</td>
<td>5p $^4F_{5/2}$</td>
</tr>
<tr>
<td>7</td>
<td>338.4</td>
<td>$\left(^2D_{3/2}\right)$</td>
<td>34714</td>
<td>5p $^2F_{5/2}$</td>
</tr>
<tr>
<td>8</td>
<td>347.0</td>
<td>$\left(^2D_{3/2}\right)$</td>
<td>34714</td>
<td>5p $^2D_{3/2}$</td>
</tr>
<tr>
<td>9</td>
<td>364.1</td>
<td>$\left(^2D_{3/2}\right)$</td>
<td>34714</td>
<td>5p $^4D_{3/2}$</td>
</tr>
</tbody>
</table>

*Data taken from Ref. 20.

![Fig. 4](image-url) Detailed scans of some of the spectral lines shown in Fig. 3 as well as two more lines not shown therein. The labeling of the lines corresponds to that used in Table I.
oms and sputtered dimers, Craig et al.\textsuperscript{15} have demonstrated that practically all of the apparent population observed for the metastable \((2P_{3/2})\) state of In atoms during ion sputtering of indium must be created by photofragmentation of In\(_2\). It is therefore extremely important to investigate and exclude this mechanism. In order to do so, we have heated the sample surface in order to produce a cloud of neutral particles above the sample surface that is generated by thermal evaporation. Figure 5 shows mass spectra that were taken under these conditions either with or without bombardment of the surface by 5-keV Ar\(^+\) ions. The ionizing laser was tuned to the resonance at 272.3 nm, which should selectively ionize the \((2D_{5/2})\) state, but is also capable of producing a nonresonant background signal by direct two-photon absorption from the ground state. It is clearly seen that silver atoms as well as dimers are detected under both conditions. Figure 6 shows spectral scans of the 107 Ag\(^+\) signal around the resonance for both cases. The most important observation is that the resonance is absent for thermally evaporated particles. This finding is largely expected, since under thermal equilibrium conditions at a temperature of about 1000 K one expects a negligible population probability of the order of 10\(^{-19}\) for a state with an excitation energy of 3.75 eV. It represents, on the other hand, the ultimate proof that the resonances observed in Fig. 4 are due to metastable atoms generated in sputtering. This argument is even more convincing since the mass spectra clearly show the presence of dimers in the ionization volume also under thermal evaporation conditions. From the data presented in Fig. 6 we can, therefore, also exclude the possibility that the metastable atoms detected in the sputtering experiment are created by photofragmentation of sputtered dimers.

The relatively large dimer signal observed under pure thermal evaporation conditions seems to be surprising at first sight. However, one should note that the relative intensities of atoms and dimers depicted in Fig. 5 are not necessarily representative of the respective number densities of neutral particles within the ionization volume. In the spectrum recorded with simultaneous ion bombardment, the atom signal is predominantly due to the selective ionization of metastable atoms, the relative population of which is fairly small with respect to ground-state atoms (see Sec. III D). In the spectrum without ion bombardment, on the other hand, metastable atoms are absent and the atom signal must therefore be due to nonresonant two-photon ionization of evaporated ground-state atoms. With the employed laser intensity of several 10\(^5\) W cm\(^{-2}\), such a transition is certainly not saturated and the ionization efficiency will be relatively low. Diatomic molecules or clusters, on the other hand, possess many intermediate electronic and rovibrational states and are therefore often ionized under practically resonant conditions. In particular, the photon energy corresponding to the employed laser wavelengths allows for accessing the \(B\) and \(C\) states of Ag\(_2\).\textsuperscript{22} As a consequence, we conclude that the photoionization efficiency of dimers must be significantly larger than that of atoms and, hence, the true contribution of dimers to the total flux of evaporated particles is largely overestimated by the spectrum displayed in Fig. 5.

Another interesting point concerns the temperature dependence of the signals displayed in Fig. 5. While one expects the number density of evaporated atoms to exhibit an Arrhenius-type behavior, the results obtained under ion bombardment may reveal any temperature dependence of the ex-
where \( n \) denotes the minimum number of photons that must be absorbed in order to overcome the ionization potential and \( \sigma_i^{(n)} \) denotes the generalized photoionization cross section.

As a consequence, the probability to convert a neutral atom into an ion during a laser pulse of duration \( t_L \) can be calculated as

\[
p_i = 1 - \exp(-\sigma_i^{(n)} \Phi t_L).
\]

Under conditions of low photon flux density, the measured ion signal will therefore be proportional to both the number density of neutral particles and the photoionization cross section, the latter quantity, however, being unknown for the different transitions depicted in Table I. If the laser intensity can be increased to large enough values, however, \( p_i \) approaches unity (i.e., the photoionization process is driven into saturation) and the influence of different photoionization cross sections may be eliminated. In order to arrive at quantitative conclusions regarding the absolute population of the detected states, it is therefore necessary to study the saturation behavior of the measured signals. In practice, the laser intensity and hence the photon flux density will exhibit a spatial profile and \( \Phi \) will therefore strongly depend on the geometrical location within the laser beam. Under the moderately focused beam conditions employed here, the intensity variation along the laser beam axis will not be important, since in this direction the spatial extension of the ionization volume is confined to a length \( z \) much smaller than the Rayleigh range by ion optical restrictions. In the direction perpendicular to the beam, however, the laser intensity variation must be taken into account. In order to simulate the saturation behavior of the measured ion signal, we assume a Gaussian beam profile and calculate the signal according to

\[
S = \rho T z \int_0^\infty \left[ 1 - \exp(-\sigma_i^{(n)} \Phi(r) t_L) \right]^2 2\pi r dr,
\]

where \( \rho \) denotes the number density of neutral particles in the interaction volume and \( T \) is the instrumental detection probability of the photoions.

Figure 8 shows the dependence of the measured photoion signal on the total fluence of photons in the ionizing laser pulse. In particular, the signal measured for the two resonances labeled (4) and (7) in Table I is shown since the corresponding two transitions start from the metastable \( ^2D_{3/2} \) and \( ^2D_{5/2} \) states, respectively, and therefore these signals represent the population of these states. For comparison, the signal obtained with the ionization laser tuned exactly to the resonance is shown along with the nonresonant background signal obtained with a slightly detuned laser. It is clearly seen that the resonant signals both exhibit a pronounced deviation from the linear behavior expected for a one-photon transition \( (n = 1) \) at low laser fluences, thus indicating that the resonant transitions are saturated towards high fluences. The nonresonant signals, on the other hand, behave strictly linear and must therefore be generated by a nonresonant one-photon absorption process. This finding is important, since it indicates that the background signals also stem from the ionization of metastable states rather than from the nonresonant two-photon ionization of ground-state atoms [which according to Eq. (3) would lead to a quadratic laser fluence dependence].

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Moreover, the nonresonant signal detected at a wavelength of 338.4 nm [Fig. 8(b)] can only be
due to ionization out of the \((^2D_{3/2})\) state, since the corresponding photon energy of 3.66 eV is not sufficient to ionize the \((^2D_{5/2})\) state by absorption of one photon. The ionization potential of Ag is 7.58 eV. Since both resonant and nonresonant signals represent transitions from the same initial state, it is therefore not necessary to subtract the background signal from that detected on resonance. The nonresonant signal detected at 313.1 nm [Fig. 8(a)] on the other hand, can be generated by one-photon ionization starting from both metastable states. In this case, it is in principle necessary to subtract that part of the signal which is due to nonresonant ionization out of the \((^2D_{3/2})\) state. Assuming the nonresonant ionization process to be independent of wavelength, we therefore take the signal depicted in the lower track of Fig. 8(b) and subtract it from the upper track of Fig. 8(a). The resulting photon fluence dependence of the corrected signals is displayed in Fig. 9. Employing a numerical procedure described in Refs. 23 and 24, the measured saturation behavior is fitted to the theoretical dependence of Eq. (5) taking the photoionization cross section and the quantity \(\rho T\) as fitting parameters. The resulting values of the photoionization cross section are displayed in Table II. Since the mass spectrometer cannot distinguish between Ag\(^+\) ions generated by both transitions, the instrument transmission \(T\) will be the same for both signals. The second fitting parameter therefore delivers the ratio between the number densities of atoms in the two metastable states that are present in the interaction region with the laser. From the data, we find a density ratio of

\[
\frac{\rho \gamma D_{5/2}}{\rho \gamma D_{3/2}} = 0.6.
\]

In order to attain a signal representative for the ground state atoms, we can utilize the dominating peak in the spectrum of Fig. 3(b) that arises from nonresonant two-photon ionization of these species. The saturation behavior of this signal is depicted in Fig. 10 together with a least-squares fit of Eq. (5) (now with \(n = 2\) as appropriate for a two-photon process). It is seen that the observed laser intensity dependence can be nicely reproduced by the fit: the resulting fitting parameters may serve as an indicator of the number density of ground-state atoms within the ionization volume.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength (nm)</th>
<th>Cross section ((cm^2))</th>
<th>(\sigma_{\text{resonant}}/\sigma_{\text{nonresonant}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>313.1</td>
<td>(7(1) \times 10^{-17})</td>
<td>10.7</td>
</tr>
<tr>
<td>7</td>
<td>338.4</td>
<td>(3.3(6) \times 10^{-18})</td>
<td>4.2</td>
</tr>
</tbody>
</table>
C. Emission velocity distribution

As outlined in Sec. II, the emission velocity of the detected neutral particles is selected by the temporal delay between the primary ion pulse and the ionizing laser pulse. In order to be accessible to photoionization, this delay must correspond to the flight time the neutral particles need to travel the fixed distance between the surface and the position of the laser focus. Figure 11 shows the resulting flight time distribution for two cases where the ionizing laser was tuned to the resonances labeled (1) and (9) in Table I and therefore allowed selective ionization out of the metastable \( ^2D_5/2 \) and \( ^2D_3/2 \) states, respectively. The geometrical arrangement of the bombarded spot at the surface and the laser beam was adjusted such as to selectively detect particles ejected along the surface normal. It is seen that the two distributions are identical within the experimental accuracy, thus indicating that the emission velocity distribution of atoms sputtered in both metastable states is the same. As seen in Fig. 12, however, this distribution is largely different from that of atoms emitted in the electronic ground state. This difference, which has been also observed earlier,\(^{13,17} \) clearly demonstrates that the physical mechanism leading to the excitation into metastable states in the course of the sputtering event becomes less efficient with increasing emission velocity. From the results presented in Fig. 11, we conclude that this effect does not depend on the excitation energy (note the relatively large energy difference of 0.55 eV between the two metastable states), but rather seems to reflect the electronic configuration of the outgoing particle (which is the same in both cases). A correlation of the latter kind is in principle predicted by a model put forward by Craig et al.\(^{15} \) who treat the formation of excited states in sputtering as a sequence of excitation within the solid and subsequent deexcitation outside the solid due to residual electronic interaction between the outgoing particle and the surface. Unfortunately, such a deexcitation model predicts an emission velocity dependence of the apparent excitation probability (which in this context rather denotes the survival probability of an excitation created within the solid than the excitation probability itself) which increases with increasing emission velocity, a prediction which is obviously inconsistent with the data presented in Fig. 12. Instead, the data indicate that the observed metastable states are populated by a velocity-dependent mechanism which seems to become less efficient with increasing velocity.
FIG. 13. Relative population of the metastable $^{2}D_{J}$ states among the neutral Ag atoms sputtered from a polycrystalline Silver surface under bombardment with 13-keV Ar$^{+}$ ions.

D. Population partition

In order to determine the relative population probabilities, two corrections must be added to the saturation signal determined in Sec. III B. First, it is important to note that the number density of neutral particles measured by the laser postionization experiment must be converted into sputtered fluxes. This conversion, in turn, requires knowledge about the distribution of emission velocities which may in principle be different for atoms sputtered in different electronic states. From the data presented in Sec. III C, we determine the average inverse emission velocity

$$\langle v^{-1} \rangle = \int_0^\infty v^{-1}f(v)dv \quad (6)$$

for sputtered atoms ejected in the ground state and the metastable excited $^{2}D_{J}$ states. While no correction is necessary between both metastable states, the population of ground-state atoms is underestimated by approximately a factor of 2 with respect to the excited states and must therefore be corrected accordingly.$^{13,17}$ Second, it is common practice to correct measured population probabilities with the statistical weight given by the degeneracy of the respective states. Although this is in principle only necessary when comparing the resulting population partitions to thermodynamic quantities, we adopt this practice and divide the measured population probability by factors of 2 and 3 for the $^{2}D_{3/2}$ and $^{2}D_{5/2}$ states, respectively.

With these corrections, the relative population of the metastable states with respect to that of the electronic ground state can be obtained by comparison of the respective signals measured under saturation ionization conditions. Regarding the resonant single-photon transitions displayed in Fig. 4 as representative for the metastable states and the nonresonant two-photon transition as representative for the ground state, we arrive at relative populations of the two metastable states which are depicted as open symbols in Fig. 13. There is, however, a fundamental problem associated with this procedure. Due to the largely different nature and cross section of the photoionization mechanisms, it is in principle possible that the effective ionization volume for resonant single-photon transitions used to probe the excited states is very much different from that of the nonresonant two-photon transition used to probe the ground state. This problem can be reduced if the ground-state atoms are detected via a resonant two-color scheme employing a first, resonant excitation step followed by nonresonant ionization into the continuum.$^{17}$ The big advantage of this technique is that the intermediate $^{2}P_{3/2}$ state is practically isoenergetic with the metastable $^{2}D_{5/2}$ state, and therefore the same laser can be used for the ionization from the intermediate state and from the $^{2}D_{5/2}$ state. The only difference between both cases is that the ionization laser is tuned to the resonance labeled (1) in Table I for detection of the $^{2}D_{3/2}$ state and detuned from this resonance in order to probe the intermediate $^{2}P_{3/2}$ state. Since the resonant transition into the intermediate state is easily saturated, this procedure allows a more quantitative comparison of ground- and metastable-state populations. The population partition obtained by combining the data of Ref. 17 [relative population of ground state and metastable $^{2}D_{5/2}$ state] with the data evaluated in Sec. III B (relative population of the two metastable states) is also displayed in Fig. 13 (solid symbols). It is seen that the two data sets show a remarkably good agreement, thus indicating that the ionization volume effect described above is not very large.

E. Excitation model

As already stated in the preceding subsections, neither the relatively large population of the metastable states investigated here nor the velocity dependence of the excitation probability can be understood in terms of the various excitation or deexcitation models published in the literature. Therefore, a simple model was developed, describing the formation of the excited metastable atom as a sequence of two steps.$^{18}$ First, an electronic excitation in the form of a $d$-band hole is supposed to be created within the solid by collective energy transfer processes in the course of the collision cascade initiated by the impinging primary ion. Due to the relatively strong atomic disorder induced by such a cascade, this excitation can stay localized in the cascade volume long enough to be carried away by a sputter ejected atom, thus yielding an outgoing particle which manifests itself as an excited ion containing a hole in the $d$ shell. As a second step, this ionic core is then neutralized on its path away from the surface by resonant electron transfer from the conduction band. Figure 14 depicts the one electron energy diagram relevant for such a transition. On the left-hand side, the electronic structure of the conduction band within the solid is shown with the Fermi energy $E_F$ and the work function $\Phi$. The solid line depicts the calculated density of states,$^{25}$ with the $d$ band located approximately 3–4 eV below the Fermi energy, occupied states are found in the hatched region. On the right-hand side, the $5s$ level of silver is shown, which is bent upwards and broadened close to the surface due to the interaction with the electronic system of the solid. In order to
arrive at a semiquantitative description of the energetic level position, we utilize the fact that far away from the surface the level shift must be described by the image potential \( e^2/4z \). In the other limit, where the outgoing particle is still part of the solid, the 5s level is broadened into the whole s band and centered around the Fermi energy.\(^{26,27}\) Close to the surface, the \( z \) dependence of the level center \( E_a \) is often empirically described as\(^{26}\)

\[
E_a(z) = E_a(\infty) + (E_a(0) - E_a(\infty)) \exp[-\alpha z],
\]

(7)

with \( E_a(\infty) \) corresponding to the level position at infinite distance. In order to arrive at a smooth transition between these limits, both the level position and its derivative can be matched at a distance \( z = \alpha^{-1} \) with the particular decay constant \( \alpha \) given by

\[
\alpha = \frac{4(E_a(0) - E_a(\infty)) \exp(-1)}{e^2}.
\]

(8)

From the known ionization potential and work function of silver (7.57 and 4.6 eV, respectively), one obtains \( \alpha = 0.3 \text{ Å}^{-1} \) and the level variation depicted as the dotted line in Fig. 14. It should be noted that typical values of \( \alpha \) introduced in the literature are larger, i.e., of the order of 2 Å\(^{-1}\).\(^{26} \)

The resulting level position described by Eq. (7), however, is located below the image potential shift for all \( z \) and therefore cannot be properly matched to the long-distance limit.

So far, the description is valid for a ground-state atom with an ionic core in the \( 4d^{10}5s^0 \) \((^1S_0)\) configuration and a one-electron 5s level. If the same one-electron picture is to be applied to the case of resonant neutralization of an excited ion, a different one-electron diagram must be used which depicts the one-electron states of an excited ionic core with \( 4d^{10}5s^1 \) configuration. A resonant transition into the 5s level of this core leads to the formation of an excited neutral atom with \( 4d^{10}5s^2 \) configuration. In order to determine the position of the 5s level relative to the conduction-band states, one must employ a multielectron picture and follow the electronic transition from the initial state (corresponding to a ground-state metal containing \( N \) electrons and an excited ion in front of the surface) to the final state (corresponding to a ground state metal with \( N - 1 \) electrons and an excited neutral atom in front of the surface) which can be viewed by the following energetic path:

\[
\text{metal}(N) + \text{ion}^* \xrightarrow{\Phi - I} \text{metal}(N) + \text{ion}
\]

\[
\xrightarrow{\Phi - I} \text{metal}(N - 1) + \text{atom}
\]

\[
\xrightarrow{E^*} \text{metal}(N - 1) + \text{atom}^*
\]

Here \( E^*_N \) and \( E^*_i \) denote the excitation energies of the ionic core and the neutral metastable atom, respectively, which can be taken from the literature.\(^{29} \)

With respect to the normally discussed case of a ground-state ion resonantly neutralized to form a ground-state neutral atom described by

\[
\text{metal}(N) + \text{ion} \xrightarrow{\Phi - I} \text{metal}(N - 1) + \text{atom},
\]

the 5s level in Fig. 14 must therefore be shifted by the energy difference

\[
\Delta E = E^*_s(4d^{10}5s^1 \rightarrow 4d^{10}5s^2) - E^*_i(4d^{10}5s^0 \rightarrow 4d^{10}5s^1).
\]

(9)

Since both the excited ionic and neutral states form a multiplet, we average over the fine structure connected with both electron configurations and find an average shift of \( \Delta E = -1.1 \text{ eV} \). The resulting \( z \) dependence of the 5s level corresponding to an excited ionic core is indicated by the solid line in Fig. 14. Probably the most important feature to note is that although the metastable neutral atom produced by the resonant neutralization process exhibits an excitation energy of several eV, the metal states which are in resonance with the 5s level of the outgoing excited ion are located below the Fermi level. The reason is that the excitation energy of the final state is already carried in the excited ionic core that is assumed to interact with the surface, and therefore no further excitation of solid electrons is necessary to produce the neutral metastable atom. Moreover, the qualitative discussion leading to the curves displayed in Fig. 14 implies that the 5s level faces the metallic band structure in the energy region where the density of states is high. We therefore expect the resonant neutralization of an excited ionic core to proceed at comparable or even larger rate as that of ground state ions. It is clear that in this picture the efficiency of neutralization and, hence, the probability of finding a sputtered neutral atom in a metastable \(^2D_2\) state depend on the time the ion interacts with the surface. A higher emission velocity will therefore lead to a lower population probability of the excited state, a prediction which is consistent with the data presented in Fig. 12. To a first approximation, one would...
assume the normal component of the emission velocity to be the essential parameter. Experimental data taken for the \((^{2}D_{5/2})\) state,\(^{13}\) however, indicate that the velocity spectrum of the excited atoms depends on the polar emission angle in a more complicated way which is still not fully understood.

In the frame of this model, the population partition found for the metastable atoms will essentially be determined by the probability of \(d\)-hole excitation and their localization time within the cascade volume from where the sputtered atoms originate. A rough estimate of the rate of \(d\)-hole production can be made on the basis of the available excitation energy produced by the electronic energy loss experienced by all moving particles in the cascade. In this picture, the excitation probability of an escaping ion can be described by\(^{18}\)

\[
p_{\text{exc}}(\tilde{E}_d) \propto \left| \frac{dE}{dt} \right| \tau_L \tilde{E}_d.
\]

where \((dE/dt)_e\) denotes the excitation energy which is deposited in the electron subsystem per unit time, \(\tau_L\) denotes the \(d\)-hole localization time, and \(\tilde{E}_d\) denotes a typical energy needed for \(d\)-hole production. Using the Lindhard formalism\(^{20}\) to describe the electronic stopping power, one finds that the resulting excitation probability of an escaping ion may suffice to explain the relatively high population probabilities depicted in Fig. 13.\(^{18}\) Moreover, even if the energy threshold \(\tilde{E}_d\) in Eq. (10) is assumed to scale with the final excitation energy of the detected metastable atom, one expects roughly comparable population probabilities for both metastable states observed here. Again, this finding is consistent with the data presented in Fig. 13. In contrast, any excitation model that does not invoke the preexistence of a \(d\)-hole prior to the resonant electron transfer process must necessarily involve conduction-band electrons in excited states far above the Fermi level. In this case, the population probability must drop exponentially with increasing excitation energy, thus leading to a dramatic difference between the population probabilities predicted for the two metastable states investigated here.

**IV. CONCLUSION**

In view of their large excitation energies of 3.75 and 4.30 eV, the observed population of the metastable excited \((^{2}D_{j})\) states of sputtered neutral silver atoms is surprisingly high. If such populations are to be explained by a Boltzmann-like distribution, unrealistically large temperatures of the order of \(10^4\) K and above would be required (see Fig. 13). From the results presented here, it is therefore evident that the generation of these excited states in sputtering must proceed in a nonthermal manner. Direct resonant electron transfer from the conduction band into the excited states, as originally proposed by Veje\(^{30}\) and successfully employed recently\(^{12}\) in order to interpret measured population partitions of metastable states in sputtering, is also not suited to understand the results presented here, since both investigated metastable states are energetically located well above the Fermi level of silver and therefore outside the energy window accessible to such a mechanism. Moreover, the energy difference between the higher-lying \((^{2}D_{3/2})\) state and the Fermi level (1.1 eV) is about twice that of the lower \((^{2}D_{5/2})\) state. The finding that the population of both states is about equal therefore clearly demonstrates that the observed excitation probability cannot be related to the statistical Fermi-population distribution of electronic states within the solid at any reasonable electron temperature. As a consequence, we conclude that the excitation energy must be transferred to the outgoing atom while it is still part of the solid. On the other hand, we observe a velocity distribution of the excited neutral atoms which is (i) the same for both metastable states and (ii) narrower than that of the ground state. In particular the latter finding excludes the possibility that the neutral excited atoms are formed by inelastic collisions occurring either within the solid or above the surface. This mechanism, which has, for instance, been proposed to be responsible for the formation of excited metastable rhodium\(^{31}\) and aluminum\(^{32}\) atoms, involves a collisional excitation mechanism by electron promotion that is characterized by a minimum collision energy and should, hence, result in a broader velocity distribution of the excited atoms. The same is true for any deexcitation mechanism involving velocity-dependent relaxation of an excitation carried away by a sputtered particle.\(^{15}\) From the results presented here, we are therefore forced to conclude that the excited particle which originally departs from the surface is not the neutral metastable atom that we detect far away from the surface, but, instead, some precursor particle which, however, must already carry the excitation energy. In this way, the metastable silver atoms investigated here are unique among all other metastable excited states detected in sputtering to date. One possible way to picture a population mechanism which is consistent with the experimental data is resonant neutralization of excited ionic cores ejected during the collision cascade.

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25 S. Cottenier (private communication).