Detection of sputtered metastable atoms by autoionization

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We report on a scheme for the detection of sputter-generated metastable atoms that is based on the resonant excitation of an autoionizing state by single-photon absorption from a tunable laser. Using this technique, sputtered silver atoms ejected in the metastable $4d^9 5s^2\,{}^2D_{5/2}$ state with an excitation energy of 3.75 eV have been detected. This represents the highest excitation energy of sputtered metastable atoms observed so far.

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The ejection of surface particles from an ion-bombarded solid, i.e., sputtering, is not only connected with elastic, but also with inelastic atomic interactions. Such processes cause a certain fraction of the neutral atoms—which in most cases form the vast majority of the sputtered particle flux—to be ejected in electronically excited states. The investigation of such particles is of special interest, since the related processes are by far not yet completely understood. Therefore, a number of studies have been devoted to the state-selective detection of sputtered atoms, a review of which can be found in Ref. [1]. In principle, two experimental cases must be distinguished.

Short-lived excited states, on the one hand, decay radiatively within a distance of several millimeters above the sample surface and, hence, can be easily identified by the emitted photons [1–3]. In this case, however, a major difficulty arises from cascading transitions if the experimental results are to be interpreted in terms of excitation mechanisms occurring during sputtering [1].

Metastable states, on the other hand, must be detected by laser spectrometrical methods. Among these, laser-induced fluorescence has been extensively used to study atoms sputtered either in low-lying excited states belonging to the ground-state multiplet [4–11] (with excitation energies of typically 0.1 eV) or in higher metastable states outside the ground-state multiplet [7,12–14]. The highest excitation energy reported so far is 1.8 eV for Ca atoms sputtered in the $^3P_2$ state [13].

Another possibility for state selective detection of sputtered metastable atoms is by resonant-multiphoton-ionization (REMPI) spectroscopy. Using this technique, sputter-ejected metastable rhodium atoms have been investigated recently [15–17]. So far, however, only the $^2P_{7/2}$ state with a relatively low excitation energy of 0.2 eV above the ground state ($^2P_{9/2}$) could be detected. In the present Brief Report, we report on sputtered silver atoms ejected in the metastable Ag* $4d^9 5s^2\,{}^2D_{5/2}$ state with an excitation energy of 3.75 eV above the ground state. Since the population of a given excited state in sputtering has been found experimentally to decrease exponentially with increasing excitation energy [4,5], the detection of atoms in such a high-lying metastable state requires an extremely efficient detection scheme, which is described below.

The experimental setup is essentially the same one used for REMPI. A MARZ grade polycrystalline silver sample located in an UHV chamber (base pressure 10^{-9} mbar) is bombarded under 45° with a pulsed beam of 5-keV Ar^+ ions (pulse duration 1 μs). The plume of neutral particles sputtered from the sample surface is intersected by a photon beam from a pulsed tunable laser at a distance of approximately 2 mm above the surface. The photoions generated by laser ionization of sputtered neutral atoms are extracted toward a reflectron-type time-of-flight mass spectrometer providing good mass resolution ($m/\Delta m \cong 500$) and high transmission ($\cong 10^{-2}$). Details of the setup have been described elsewhere [18] and, hence, will not be repeated here.

The sputtered particles are ionized by means of a frequency-doubled tunable dye laser operated at wavelengths between 263 and 285 nm. Figure 1 shows the spectrum measured in this wavelength range if the mass spectrometer is tuned to the ^{107}Ag isotope. Apart from a continuous background resulting from nonresonant two-photon ionization of ground-state silver atoms, three distinct lines of different widths are found at wavelengths of 272.3, 279.7, and 282.5 nm, respectively. Due to the relatively large wavelength step of 8 picometers (pm) employed in Fig. 1, the maximum of line (1) was not exactly hit and, hence, the background is largely overestimated in Fig. 1. Therefore, Fig. 2 shows a high-resolution scan of the wavelength region around line (1) which reveals that the background is almost negligible.

Since no electronic levels of the silver atom exist at or even around the excitation energies corresponding to the observed lines (36724, 35740, and 35398 cm^{-1}, respectively), these structures clearly cannot be generated by resonant multiphoton ionization of *ground-state* silver atoms. Scanning through the literature, one finds that exactly the three lines observed here have been previously reported [19] when *metastable* silver atoms generated in a

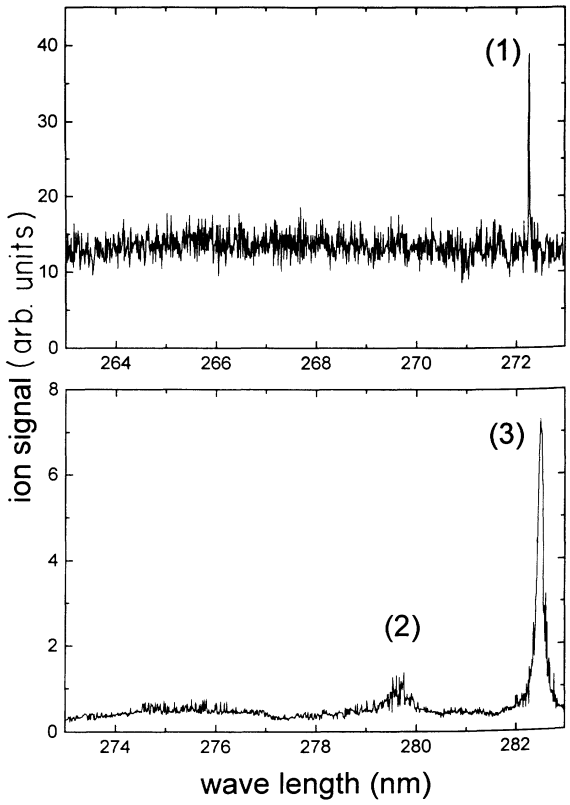

FIG. 1. Wavelength dependence of ion signal obtained for postionized neutral ^{107}Ag atoms sputtered from polycrystalline silver by 5-keV Ar^+ ions. Power density of the ionizing laser: 5×10^5 W/cm^2; wavelength step: 8 pm.

gas discharge were ionized by absorption of dipole radiation from a tunable laser. Following the classification given in Ref. [19], the observed ion signals correspond to resonant transitions between the metastable $4d^95s^2\,^2D_{5/2}$ state and the autoionizing $4d^95s(^3D)5p\,^2F_{7/2}$, $^2P_{3/2}$, and $^2D_{5/2}$ states of the silver atom, respectively. Apart from the exact agreement of the line positions, further evidence supporting this interpretation can be gained from their profiles. From Figs. 1 and 2, one finds experimental linewidths [full width at half maximum (FWHM)] which are listed in Table I. Also included in the table are the lifetimes of the corresponding autoionizing states which were taken from Ref. [19]. From these values, expected linewidths are estimated which agree surprisingly well with the values measured here. The remaining discrepancy, i.e., the fact that the measured FWHM of lines (2) and (3) are slightly larger than the estimated values, may be due to the power broadening of the resonant single-photon transitions, since the laser power density used in Fig. 1 was fairly high (approximately 10^5 W/cm^2). Note that the observed width of line (1) is essentially determined by the laser linewidth.

TABLE I. Experimental linewidths (FWHM) of the ion signals measured here and those estimated from lifetimes of corresponding autoionizing states (taken from Ref. [19]).

Autoionizing state	Measured linewidth (pm)	Lifetime (ps)	Estimated linewidth (pm)
$4d^95s(^3D)4p\,^2D_{5/2}$	3.5	>70	<0.5
$4d^95s(^3D)5p\,^2P_{3/2}$	571	0.21	198
$4d^95s(^3D)5p\,^2F_{7/2}$	126	0.52	80

We have also investigated the dependence of the observed intensities on the power density P_L of the ionizing laser. In order to estimate P_L from the measured pulse energy, a rectangular time profile of the laser pulse with a duration of 20 ns and a beam cross section of 1 mm in diameter (defined by an aperture in front of the beam entrance window) were assumed. Figure 3 shows the results obtained for transition (1) in Fig. 1. The dotted line also included in the figure corresponds to a fit according to

$$I-I_0(1-\exp[-\sigma I_L\tau])\,, \tag{1}$$

which is expected from standard rate theory of a single-photon ionization process [20]. In Eq. (1), σ denotes the photoionization cross section, I_L the laser photon flux

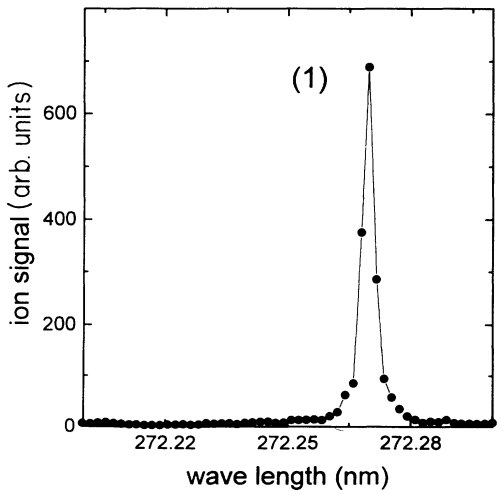

FIG. 2. High-resolution scan of line (1) in Fig. 1.

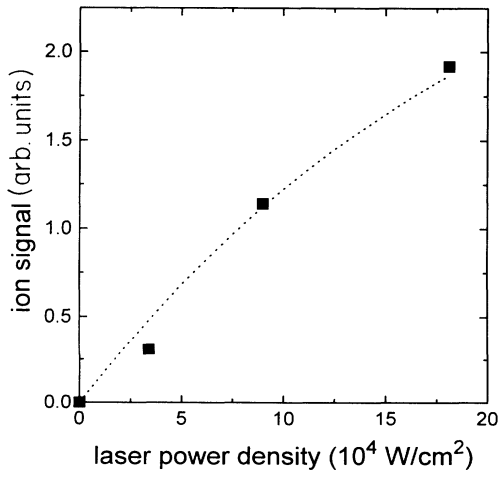

FIG. 3. Intensity of line (1) in Fig. 1 vs the power density of the ionizing laser.

density, and τ, the laser-pulse duration, respectively. From the fit indicated in Fig. 1, a value of σ around 1.7×10^{-16} cm^2 is estimated which means that the ionization will be saturated at laser power densities around 5×10^5 W/cm^2.

From the above, we conclude that we have detected sputtered neutral silver atoms which are ejected in a metastable excited $4d^9 5s^2\,^2D_{5/2}$ state by using single-photon ionization via autoionizing states. The corresponding excitation energy of 3.75 eV represents the highest metastable excitation of sputtered atoms observed so far. In future work, we will try to quantify the absolute fraction of metastable atoms within the flux of sputtered particles by saturating the ionization process for the metastable as well as for the ground-state atoms. This should be no problem for the metastables, since the above estimated power density required for saturation ionization should be easily attainable with the available laser system.

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[1] M. L. Yu, in *Sputtering by Particle Bombardment III,* edited by R. Behrisch and K. Wittmaack (Springer-Verlag, Berlin, 1991), p. 91 ff.
[2] I. S. T. Tsong and N. A. Yussuf, Appl. Phys. Lett. **33**, 999 (1978).
[3] P. Williams, I. S. T. Tsong, and S. Tsuji, Nucl. Instrum. Methods **170**, 591 (1980).
[4] B. Schweer and H. L. Bay, in *Proceedings of the International Conference on Solid Surfaces and 3rd European Conference on Surface Science,* edited by D. A. Degras and M. Costa (Société Francaise du Vide, Paris, 1980), p. 1349.
[5] C. E. Young, W. F. Calaway, M. J. Pellin, and D. M. Gruen, J. Vac. Sci. Technol. A **2**, 693 (1984).
[6] M. J. Pellin, D. M. Gruen, C. E. Young, and M. D. Wiggins, Nucl. Instrum. Methods **218**, 771 (1983).
[7] E. Dullni, Appl. Phys. A **38**, 131 (1985).
[8] R. B. Wright, M. J. Pellin, D. M. Gruen, and C. E. Young, Nucl. Instrum. Methods **170**, 295 (1980).
[9] R. B. Wright, M. J. Pellin, and D. M. Gruen, Surf. Sci. **110**, 151 (1981).
[10] M. J. Pellin, R. B. Wright, and D. M. Gruen, J. Chem. Phys. **74**, 6448 (1891).
[11] R. B. Wright, C. E. Young, M. J. Pellin, and D. M. Gruen, J. Vac. Sci. Technol. **20**, 510 (1982).
[12] D. Grischkowsky, M. L. Yu, and A. C. Balant, Suf. Sci. **127**, 315 (1983).
[13] W. Husinsky, G. Betz, and I. Girgis, Phys. Rev. Lett. **50**, 1689 (1983); J. Vac. Sci. Technol. A **2**, 698 (1984).
[14] B. Schweer and H. L. Bay, Appl. Phys. A **29**, 53 (1982).
[15] M. El-Maazawi, R. Maboudian, Z. Postawa, and N. Winograd, Phys. Rev. B **43**, 12 078 (1991).
[16] N. Winograd, M. El-Maazawi, R. Maboudian, Z. Postawa, D. N. Bernardo, and B.J. Garrison, J. Chem Phys. **96**, 6314 (1992).
[17] Z. Postawa, M. El-Maazawi, R. Maboudian, and N. Winograd, Nucl. Instrum. Methods B **67**, 565 (1992).
[18] A. Wucher, M. Wahl, and H. Oechsner, Nucl. Instrum. Methods B **82**, 337 (1993).
[19] S. Baier, M. Martins, B. R. Müller, M. Schulze, and P. Zimmermann, J. Phys. B **23**, 3095 (1990).
[20] V. S. Lethokov, *Photoionization Spectroscopy* (Academic, New York, 1987), p. 58.