Velocity dependent electron transfer during emission of ion-beam sputtered Cu atoms

J. Bastiaansen, V. Philipsen, F. Vervaecke, E. Vandeweert,* P. Lievens, and R. E. Silverans
Laboratorium voor Vaste-Stoffysica en Magnetisme, K. U. Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium
(Received 30 April 2003; revised manuscript received 27 April 2003; published 29 August 2003)

We report on our investigations on the electronic processes during keV sputtering of metals. The population partition and the state-selective velocity distributions of Cu atoms sputtered in the ground and metastable states are obtained by *resonant laser ionization*. The *qualitative* trends in the observations are successfully interpreted assuming a resonant transfer of electrons between the bulk metal and the escaping particle to be the dominant mechanism to populate atomic states. We show that the velocity dependence of the population probabilities is in good agreement with the outcome of a rate-equation description of the resonant electron transfer process.

DOI: 10.1103/PhysRevB.68.073409 PACS number(s): 79.20.Rf, 32.80.Fb, 32.80.Rm

I. INTRODUCTION

The bombardment of a solid substrate with energetic particles results in the ejection of surface particles. A thorough understanding of this sputtering phenomenon is highly desirable as the sputter event underlies many experimental techniques in, e.g., surface characterization and vapor deposition. The main kinematic aspects, such as the energy or angle resolved distributions of the sputtered particles, are described in a satisfactory way by the transfer of impact energy and momentum during the collision cascade initiated by the incoming ion.[1]

On the other hand, the electronic processes, which distribute the sputtered particles over the different electronic states, are still under debate. Mechanisms such as dimer dissociation, collisional excitation at or above the surface, and nonradiative deexcitation have been invoked to interpret specific, state-selective observations of the ejected particles in neutral, atomic states.[2] Recently, studies of sputtered Co and Ni atoms suggested a resonant tunneling of electrons between the substrate conduction band and the sputtered particle to be the dominant electronic process determining the final quantum state of the neutral atoms sputtered in the ground and metastable states.[3–5] Trends in the population partitions and velocity distributions of the sputtered Co and Ni atoms agreed remarkably well with qualitative predictions from the resonant electron transfer (RET) model that describes the tunneling process.[6] Also, the anomalously high population on the excited states of Ag after sputtering has been explained by an electron transfer from the bulk metal to an escaping excited ion.[7] In this paper, we present experimental data on the relative population partition and state-selective velocity distributions of Cu atoms sputtered during keV ion bombardment. We demonstrate how these data reflect the *qualitative* trends of the RET model. Furthermore, we investigate whether the sputtering of atoms in different quantum states can also be *quantitatively* related to the RET process by comparing the experimental data of sputtered Cu atoms with the numerical outcome of a rate-equation description of the electron transfer.

II. EXPERIMENTAL PROCEDURE

The experimental procedure and setup are presented in detail elsewhere.[8] Here, we sketch the main aspects of the experimental procedure to measure population partitions and state-selective velocity distributions and give a brief description of the apparatus. To probe the sputtered atoms state selectively, we use two-color two-step resonant laser ionization. In a first step, Cu atoms sputtered in the ground state ($^2S_{1/2}$) or in one of the two excited metastable states ($^2D_{5/2}$ and $^2D_{3/2}$) are excited resonantly into the intermediate state $^2P^0_{3/2}$ at 3.82 eV by the absorption of a photon. Atoms in that intermediate state are photoionized via the autoionizing state $^4D_{5/2}$ at 7.8 eV. As the same intermediate state is used for all ionization processes, the measured photoion intensities are directly proportional to the populations on the initial states of the ionization processes. Only a saturation of the excitation steps is required, which is already obtained at moderate photon fluences.[8]

The sputtering experiments are performed in an ultra high vacuum chamber (base pressure below 2×10^{-10} hPa). An ion gun directs a 12-keV Ar^+ beam (1 μA/mm^2) at 45° incidence to the target foil. The plume of sputtered particles is intersected 4 mm in front of the target by the overlapping ionizing laser beams (diameter $\sim$1 mm). Two independent pulsed, tunable laser systems, an optical parametric oscillator and a dye laser both pumped by Nd:YAG (yttrium aluminum garnet) lasers, generate laser pulses with a duration of 6 ns and energies up to 50 mJ. The wavelength of the laser photons can be varied between 225 and 1800 nm.

The photoionized particles are accelerated into a reflectron time-of-flight mass spectrometer for mass-selective detection. Before each experiment, the polycrystalline Cu samples (Goodfellow, purity 99.9%) are sputter cleaned by continuous ion bombardment. The surface condition was checked by low energy ion scattering, which revealed no surface contaminants within the sensitivity of the method.[8] The ion beam can be operated either into a continuous mode or a pulsed mode. The continuous mode ensures that all velocities are present in the laser ionization volume and is therefore used for measuring population distributions. The pulsed mode is applied for measuring the velocity distributions, as the procedure becomes velocity selective. The delay time between the ion pulse (with a duration of 300 ns) and the laser pulse corresponds with the flight time that the sputtered particles need to travel the fixed distance (4 mm) between the sample surface and the ionization volume. The

TABLE I. Relative population of the ground and metastable states of Cu after 12-keV Ar^+ ion-beam sputtering.

Atomic state	Excitation energy (eV)	Electron configuration	Relative population
$^2S_{1/2}$	0.00	[Ar] $3d^{10}\ 4s^1$	1
$^2D_{5/2}$	1.39	[Ar] $3d^9\ 4s^2$	0.024(7)
$^2D_{3/2}$	1.64	[Ar] $3d^9\ 4s^2$	0.006(3)

delay time therefore determines the velocity of the atoms in the ionization volume.

III. EXPERIMENTAL RESULTS

The relative populations on the ground and metastable states of Cu after continuous ion-beam sputtering are presented in Table I. The population of the metastable states is about 3% of the population of the ground state. The velocity distributions of atoms sputtered in the $^2S_{1/2}$ ground state and the ^2D_J metastable excited states are shown in Fig. 1. The velocity distributions of atoms sputtered in the $^2D_{5/2}$ and $^2D_{3/2}$ atomic states are identical within the experimental uncertainty. The velocity distribution of atoms in the ground state is broader, and peaks at a higher velocity compared with the velocity distributions of metastable atoms. The total velocity distribution of all sputtered particles, which is approximated by summing the state-specific velocity distributions weighted with their respective populations, is in good accordance with the Thompson distribution developed for all particles sputtered from a linear collision cascade.[9] The value of the surface binding energy, obtained by a fit of the experimental total velocity distribution with the Thompson distribution, was found to be 3.3(5) eV, which is in close correspondence to the sublimation energy of Cu (3.5 eV). As the vast majority of sputtered particles ends up in the atomic ground state, the velocity distribution of the ground-state atoms also bears a close resemblance to the Thompson distribution.

The relative population probability P_i of an atomic state i as a function of velocity is extracted by weighting the normalized, state-selective velocity distribution $f_i(v)$ with the population n_i and dividing this by the total velocity distribution:

$$P_i(v) = \frac{n_i f_i(v)}{\sum_j n_j f_j(v)}. \quad (1)$$

These results are shown in Fig. 2, in which the total population probability of the metastable doublet ^2D_J is considered rather than the population probabilities of the individual states. This is reasonable since atoms sputtered in both states exhibit identical velocity distributions. Clearly, the population probability of the $^2S_{1/2}$ state increases with increasing velocity at the expense of the population probability of the ^2D_J states.

TABLE II. Parameter values for the atomic states of Cu used in the modelling of the experimental data shown in Fig. 2.

Atomic state	β_i	γ_i(Å^{-1})	Δ_0 (eV)
$^2S_{1/2}$	0.85	0.5	0.1
^2D_J	0.15	29	0.1

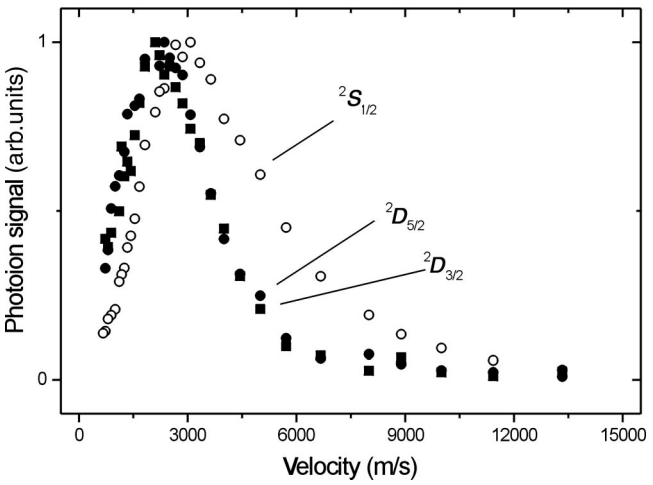

FIG. 1. State-selective velocity distributions of Cu atoms sputtered in the $^2S_{1/2}$ and ^2D_J atomic states.

IV. MODELING OF THE EXPERIMENTAL RESULTS

Most models that have been developed over the years to explain the formation of excited atoms during ion-beam sputtering predict that the velocity distributions of the atoms in the excited states are either identical to or shifted to higher velocities compared with the velocity distribution of atoms in the ground state.[2] Most (but not all) experimental results confirm this trend.[2,8,10] Our results, presented here, clearly demonstrate an opposite behavior: a higher average velocity for atoms sputtered in the ground state. A similar observation

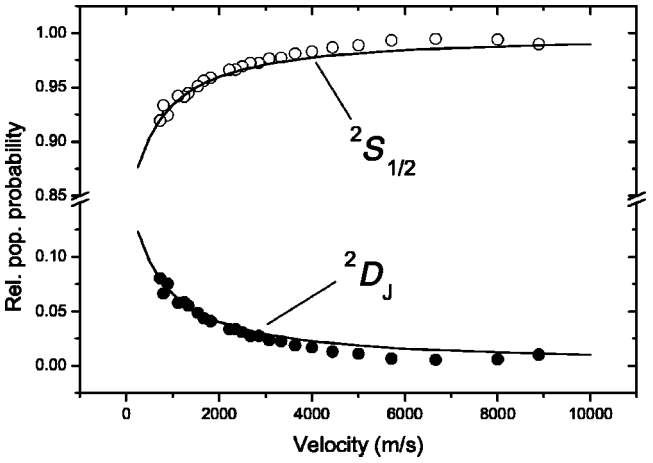

FIG. 2. Velocity-dependent population probabilities of the ground state and the metastable states of Cu extracted from the velocity distributions and the total populations. The solid line is the numerical outcome of the rate equations with parameter values listed in Table II.

was already made during the sputtering of neutral Ag atoms.[11] The RET model considers the electron configuration of the atomic state to be dominant in determining the state-selective velocity distributions of the sputtered atoms, and can account for the results presented in this paper.

In the RET model, the sputtering of a neutral atom is regarded as the evolution with time of an initially strongly coupled system consisting of a metal and an escaping atomic particle in which an electron nonadiabatically transfers from a valence-band state to a bound state of the atom.[6] If the escaping particle is ejected with a high velocity, the interaction time with the bulk metal is so short that an electron transfer into atomic states strongly coupled to the bulk metal is favored. Therefore, atoms sputtered in strongly coupled atomic states will have a higher average velocity.[4] The $^2S_{1/2}$ atomic ground state has an [Ar] $3d^{10}\ 4s^1$ electron configuration, while the ^2D_J excited states have an [Ar] $3d^9\ 4s^2$ electron configuration. The distribution of electrons in *d* and *s* levels for the bulk electron configuration, which is calculated[12] to be [Ar] $3d^{10.1}\ 4s^{0.5}\ 4p^{0.4}$, most resembles the distribution of electrons for the ground state. Therefore, the coupling of the $^2S_{1/2}$ ground state to the electron states of the metal will be larger. This is reflected in the increasing population probability of the $^2S_{1/2}$ atomic state with increasing velocity (see Fig. 2).

Now, we convert to a more mathematical description of the RET process to make a quantitative comparison with the experimental results. The energy level of an atom close to a metal surface will show an upward shift due to the classical image potential and a broadening Δ due to the interaction with the metallic electron states. This broadening is proportional to the magnitude of the interaction matrix element between the atomic state and the metallic states, which means that strongly coupled states will be strongly broadened. The level broadening decreases with increasing distance from the surface *z* due to the decreasing spatial overlap between atomic and metallic wave functions. Usually, an exponential dependence is assumed with a characteristic decay length γ^{-1}:

$$\Delta(z)=\Delta_0 \exp(-\gamma z), \tag{2}$$

with Δ_0 the broadening of the level at the surface.

The RET model was initially invoked in sputtering studies to describe the velocity-dependent ionization probability of sputtered particles.[13] In this case, only one atomic state well below the Fermi level is taken into account, for which a quantitative description can be formulated by a rate-equation approach:[6]

$$\frac{dP(t)}{dt}=[1-P(t)]\Delta(z)/\hbar. \tag{3}$$

The velocity-dependent occupation probability *P* of the shifted and broadened atomic level after complete decoupling at large distance *z* or time t_∞ is given by

$$P(t_\infty)=1-P_{ion}(t_\infty)=1-\exp(-\Delta_0/\hbar\gamma v), \tag{4}$$

with *v* the velocity of the escaping particle perpendicular to the surface and P_{ion} the probability that the particle is an ion.

To describe population probabilities during the sputtering process, more than one atomic level *i* needs to be taken into account, and one is confronted with a set of coupled rate equations, all similar to Eq. (3). So far, the transfer probability in the rate equations only depends on the coupling between the atomic states and the bulk metal states. However, the single-atomic level description based on the Anderson-Newns Hamiltonian predicts an exponential decrease of the level occupation as a function of excitation energy.[6] It has been observed experimentally that this trend survives a description with multiple atomic levels.[3] We insert the excitation energy dependence of the population probability in the rate equations in the following way. In the limit $v\rightarrow 0$, i.e., the adiabatic regime, *the transfer probability* to a certain atomic state *i* is dependent on the excitation energy and the broadening of the atomic state but no longer on the characteristic decay length γ_i^{-1}. Therefore, the *relative population probability* at $v=0$, β_i of a specific atomic state *i*, includes both the excitation-energy dependence of the atomic state as well as the broadening of the atomic state *i* relative to the broadening of the other states. Inserting the relative population probabilities at $v=0$ in the rate equations then yields the following:

$$\frac{dP_i(t)}{dt}=\left(1-\sum_i P_i(t)\right)\frac{\beta_i\Delta_0 \exp(-\gamma_i v t)}{\hbar} \tag{5}$$

$$\cdots$$

$$\sum_i P_i(t)+P_{ion}(t)=1. \tag{6}$$

By introducing β_i as the population probabilities at $v=0$, the parameter Δ_0 will be a state-independent measure of the initial level broadening.

As mentioned earlier, the total population of the excited doublet of Cu is considered rather than the population on the individual levels. This simplifies the set of equations in Eq. (5) to that of a two-level system. The rate equations are numerically solved for a fixed velocity to obtain the population probabilities after complete decoupling $P_i(t_\infty)$, which corresponds with the population probability experimentally recorded (Fig. 2). By repeating this procedure for different velocities, we obtain the velocity-dependent population probabilities of the atomic states. For this procedure, the parameters β_i can, through extrapolation of the data presented in Fig. 2, be deduced to be 0.85 for the $^2S_{1/2}$ state and 0.15 for the ^2D_J states. The characteristic decay length γ_i^{-1} of both atomic levels and the broadening Δ_0 are adjustable parameters.

With the values for the fitting parameters given in Table II, the overlap between the experimental data and numerical calculations is remarkably good (see Fig. 2). Theoretical calculations of energy level widths for light atoms (H, He) and alkali atoms (Li, Na) at various distances from metal surfaces have been reported.[14,15] The results revealed a very large sensitivity of the level width on the details of the electron-surface interaction potential. Typical values for Δ_0 were $\sim$ 0.5 eV at a distance equal to the Bohr radius, while γ ranged from 0.5 Å^{-1} to a few Å^{-1}. Although the system

under investigation (a Cu atom near a Cu surface) is very different, the parameter values that characterize the electron transfer into the *atomic ground state* of Cu are in reasonable agreement with these typical values. However, the value of the inverse characteristic decay length γ of the *excited doublet* resulting from the numerical fitting procedure is an order of magnitude higher, which would imply that the coupling between the metastable states and the metal states diminishes very rapidly. This could be an indication that γ for the excited states is merely a fitting parameter. To determine whether the parameter value has any physical sense, intricate *ab initio* calculations of a Cu atom in the vicinity of a Cu surface are needed.

The velocity-dependent ionization probability is another result from the numerical solutions of rate equations (4) that can be compared with experimental results. Traditionally, one models the velocity-dependent ionization probability with the function

$$P_{ion}(v) \propto \exp(-v_0/v), \tag{7}$$

where v_0 is the characteristic velocity.[16] The velocity-dependent ionization probability calculated with the parameters listed in Table II has a characteristic velocity of 3.1×10^4 m/s, which is in good agreement with the experimental value of 4.8×10^4 m/s obtained by Vasile.[17]

V. CONCLUSIONS

We reported the relative population partition and velocity distributions of ion beam sputtered Cu atoms. Atoms in the ground state and the two metastable excited states were state selectively probed using double-resonant two-color two-step laser ionization. The velocity distributions are interpreted qualitatively in terms of the resonant electron transfer model. Furthermore, we showed that the experimental velocity-dependent population probabilities can be adequately modeled by a rate-equation description of the RET process.

ACKNOWLEDGMENTS

This work was financially supported by the Fund for Scientific Research — Flanders (Belgium) (FWO), the Flemish Concerted Action (GOA) Research Program and the Interuniversity Attraction Poles Program (IAP) — Belgian State, Prime Minister's Office — Federal Office for Scientific, Technical and Cultural Affairs. E.V. is a postdoctoral research fellow of the FWO.

*Electronic address: erno.vandeweert@fys.kuleuven.ac.be

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