

ANGULAR AND ENERGY DISTRIBUTIONS OF RH ATOMS DESORBED IN AN EXCITED STATE FROM ION-BOMBARDED RH{100}

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ABSTRACT

Multiphoton resonance ionization spectroscopy has been used to determine the polar-angle and the kinetic-energy distributions of rhodium atoms desorbed from ion-bombarded Rh{100} surface in the fine-structure components of the a 4F_J ($J=9/2$ and $7/2$) ground-state multiplet. The peak in the energy distribution of the metastable level ($^4F_{7/2}$ with excitation energy of 0.2 eV) is found to occur roughly at the same value as the ground-state ($^4F_{9/2}$) distribution but decays more gradually at higher energies. The measured spectra have been used to investigate the dependence of the excitation probability on the takeoff angle (θ) as well as the emission velocity (v). It is shown that the excitation probability depends strongly on these parameters, approaching an exponential dependence on $1/[v \cos(\theta)]$ at higher velocities ($> 5 \times 10^5$ cm/sec).

INTRODUCTION

Energetic ion bombardment of solid surfaces gives rise to the ejection of target species. A fraction of the desorbed particles leaves the surface in an excited state [1] which decays to ground state or to metastable levels via optical radiation. To investigate the desorption mechanism of the excited-state atoms, the spatial distribution [2-4] and the Doppler-broadened line-shape profile [5,6] of the emitted light were originally measured and used to determine the energy distributions of the ejected excited particles. With these techniques, extremely high values of mean kinetic energies (1 to 2 orders of magnitude higher than that for the ground state) were obtained, hence placing serious constraints on any models attempting to explain their mechanism of excitation. Based on these measurements, several excitation models were proposed. Some of these include excitation in early stages of collision cascade via knock-on collisions with target atoms [6], existence of a radiationless deexcitation process near the surface [7,8], resonance neutralization of sputtered ions into excited neutrals in the vicinity of the surface [9] and excitation via inelastic energy transfer to a target atom in the final collision leading to desorption [10].

More recently, Doppler-shift laser induced fluorescence (DSLIF) spectroscopy has been used to measure the velocity distribution of atoms desorbed in various metastable states [11-16]. With this technique, the energy distributions of atoms ejected in sublevels of ground-state multiplet or in low-lying excited states (with excitation energies less than 1 eV) were found to be very similar to the ground-state distribution [11,14]. Metastable particles with excitation energies above 1 eV were also investigated and shown to have broader energy distributions than the ground state, with the most probable energies 3-4 times higher than the sputtered ground-state atoms [12,13]. Another experimental approach that has provided a great deal of information about the sputtering process is multiphoton resonance ionization (MPRI) spectroscopy [17-20]. However, with respect to the excited states, this method, until now, has only been used to determine the relative populations of atoms desorbed in various excited states [17,18].

Despite the existence of a large number of measurements on the velocity distributions of the low- and the high-lying metastable- and excited-state neutrals, there has been, to our knowledge, no measurement of energy-resolved angular distributions of the particles desorbed in an excited state. In this paper, we employ the MPRI technique to measure the angular distributions of Rh atoms desorbed from Rh{100} surface in the sublevels of the a 4F_J ($J=9/2$

and $7/2$) ground-state multiplet. The measured spectra is used to determine the functional dependence of the excitation probability on the takeoff angle as well as on the emission velocity. It is found that for velocities greater than 5×10^5 cm/sec, the excitation probability depends exponentially on $1/[v \cos(\theta)]$ but deviates from this behavior at lower velocities.

EXPERIMENTAL SETUP

The Rh sample is an optically polished single crystal of 99.99% purity oriented to within $\pm 0.5^\circ$ of the (100) face. The cleaning procedure [21] and the experimental setup [22] have been described elsewhere. Briefly, the measurements are performed in an ultra-high vacuum chamber (2×10^{-10} Torr base pressure) equipped with a LEED/Auger surface analysis unit. The experiment proceeds as follows. A 200-nsec pulse of 5 keV Ar^+ is focussed, at normal incidence, onto a 2-mm spot on the sample. A given time after the ion impact, a ribbon-shaped laser pulse (1 mJ for 6 nsec) is used to ionize a small volume of the desorbed particles, thus defining the time of flight (TOF) of the probed species. The MPRI technique is employed to selectively ionize the ejected particles. Once the particles are ionized, they are accelerated toward a position-sensitive microchannel plate detector and are displayed on a phosphor screen located in the back of it. The image is, in-turn, monitored by a charge-coupled-device camera which is interfaced to a micro-VAX station II mini-computer for data storage and processing. For a typical spectrum, 30 to 60 images, each corresponding to a different TOF, are collected and sorted into an intensity map of kinetic energies and takeoff angles.

RESULTS AND DISCUSSION

The angle-integrated energy distributions of Rh atoms ejected from Rh{100} surface in the two fine-structure levels of the a 4F_J ($J=9/2$ and $7/2$) ground-state multiplet are shown in Fig. 1. The most probable energies, for both states, are roughly the same. This is in agreement with the results obtained using the DSLIF technique [11,14]. However, the excited-state ($^4F_{7/2}$ with 0.2 eV excitation energy) distribution decays more gradually than that of the ground state ($^4F_{9/2}$).

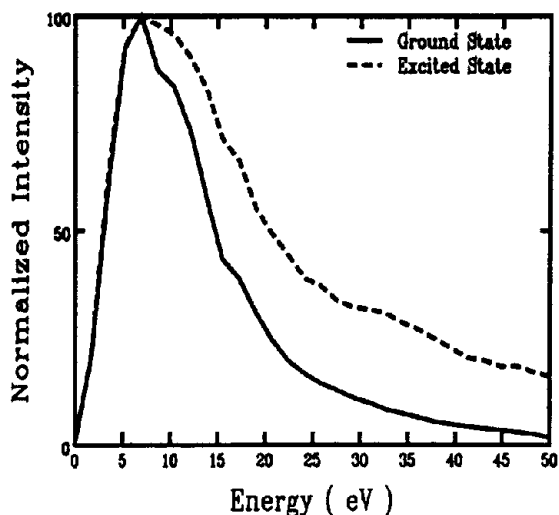


Fig. 1. Experimental angle-integrated energy distributions of the ground-state (solid curves) and the excited-state (dashed curves) Rh atoms desorbed from ion-bombarded Rh{100} surface along the $\langle 010 \rangle$ crystallographic direction. The distributions are normalized to the peak position.

The angular distributions of the ground-state and the excited-state Rh atoms ejected from Rh{100} surface along the $\langle 010 \rangle$ crystallographic direction are presented in Fig. 2. The ground-state angular distributions have already been presented and explained using the molecular dynamics (MD) simulation of the desorption process [21]. It was concluded that the angular anisotropies reflect, in a detailed way, the geometrical structure of the near-surface region. This structural sensitivity was shown to be a consequence of the surface atoms being channeled and blocked in particular directions along the surface while desorbing. However, as is evident in Fig. 2, the ratio of the intensity in the normal direction to that in the off-normal peak is measurably higher in the excited-state distribution and the higher the kinetic energy, the smaller the ratio. Moreover, the off-normal peak in the metastable distribution occurs closer to the surface normal than in the ground-state distribution.

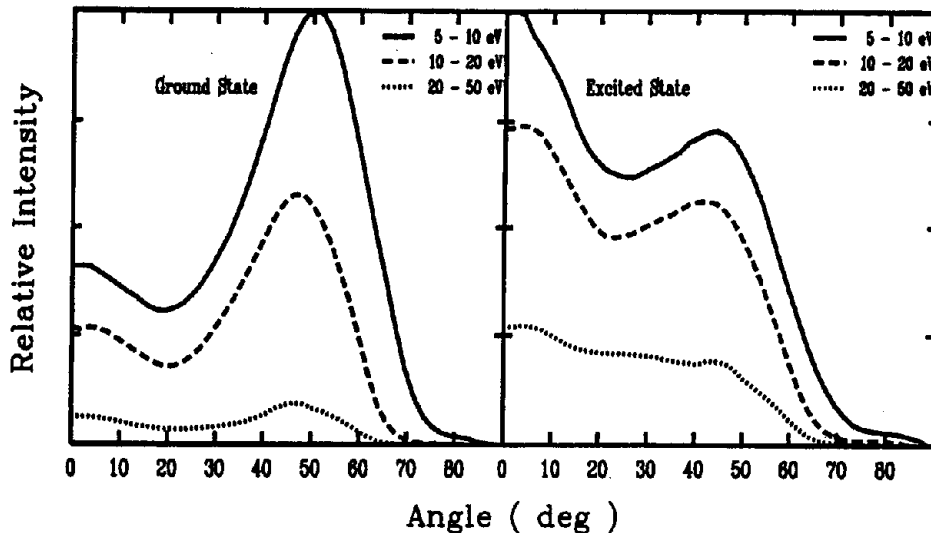


Fig. 2. Measured angular distributions of Rh atoms desorbed from Rh{100} surface along the $\langle 010 \rangle$ crystallographic direction. The left plot corresponds to the ground-state distributions and the right plot to the excited-state distributions for 5-10 eV (solid), 10-20 eV (dashed) and 20-50 eV (dotted) energy ranges.

The independent measurement of the energy-resolved angular distributions of the ground state and the metastable state allows the determination of the angular and the velocity dependence of the excitation probability. Assuming thermal equilibrium, the population density decreases exponentially with excitation energy, and hence the contribution of other higher-lying excited states decaying to the electronic levels investigated here is insignificant. The measured distributions are, therefore, directly proportional to the number of sputtered atoms in a particular state, and the ratio of the excited-state signal to that of ground state is proportional to the probability of excitation into the $^4F_{7/2}$ state during the desorption process.

It has been proposed [3,6,23] that this probability has a velocity, v , and angle, θ , dependence of the form $\exp\{-A/[av \cos(\theta)]\}$ where A is a transition rate and $1/a$ is a characteristic distance of atom-surface interaction. As is shown in Fig. 3, the ratio of the excited-state distribution to the ground-state distribution, indeed, approaches an exponential dependence on $1/[v \cos(\theta)]$ for velocities greater than 5×10^5 cm/sec. The coefficient A/a , obtained from the indicated straight line, is determined to be $(1.1 \pm 0.1) \times 10^6$ cm/sec. However, at lower energies, the distribution deviates from the simple exponential. This behavior has been previously observed for excited-state atoms [12] but the measurements were conducted at fixed ejection angle and consequently, the angular dependence of the excitation probability was not probed. Similar behavior has also been observed in the case of secondary ions [24] and has been attributed to the fact that the velocity of a particle, while desorbing, is not a

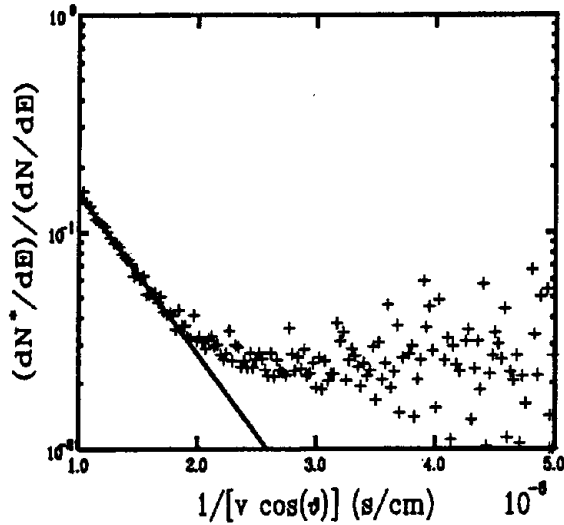


Fig. 3. Ratio of the excited-state distribution, dN^*/dE , to the ground state distribution, dN/dE , versus the reciprocal of the normal component of the emission velocity, $v \cos(\theta)$. The straight line indicates the best fit to the high-velocity part of the data points.

constant [24-26]. In other words, since the atom must overcome the surface binding energy, its velocity, near the surface, is larger than the measured velocity. This effect becomes particularly important, and must be taken into account, when the final energy of the particle is of the same order of magnitude as the surface binding energy. In the present investigation, the deviation occurs for $v_{\perp} \leq 5 \times 10^5$ cm/sec. This value corresponds to $E_{\perp} \leq 13.5$ eV, in contrast to 5.7 eV surface binding energy of Rh. In this regime, it is shown that the measured $v \cos(\theta)$ is not a good representative of v_{\perp} in the most important near surface region [25,26].

It is important to note that this is the first measurement where similar behavior has been observed for a low-lying excited state as compared to a high-lying level [12]. This is in contrast to the previous studies conducted on fine-structure components of ground state [11,14] where the excited atoms were found to behave in a similar manner as the ground-state atoms. It would be valuable to perform the same energy- and angle-resolved measurements on higher-lying excited states of Rh with excitation energies greater than 1 eV. However, since the short-lived excited states, with dipole-allowed transitions to lower-lying levels, will decay before interacting with the laser beam, only the metastable states can be probed with the present technique. Unfortunately, to our knowledge, the existence of such levels for rhodium is not known and hence such investigations must await the choice of a more appropriate target.

SUMMARY AND CONCLUSIONS

Angle-integrated energy distribution and energy-resolved angular distributions of the $4F_{7/2}$ excited-state Rh atoms ejected from 5 keV Ar ion-bombarded Rh{100} surface have been measured and compared to the $4F_{9/2}$ ground-state distributions. Consequently, the dependence of the excitation probability on the ejection angle (θ) as well as the emission velocity (v) is determined and shown to approach an exponential dependence on $1/[v \cos(\theta)]$ at high velocities.

The independent and simultaneous measurements of the energy- and angle-resolved distributions of atoms desorbed in various electronic states, possible with the present setup, enable the complete determination of the excitation probability. Such information is invaluable for unraveling the mechanisms leading to the ejection of excited-state atoms in sputtering process.

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