

## Atomic excitations in ion induced sputtering of a Rh(100) single crystal

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Recently, we have measured the energy and angular distributions for ground- and excited-state Rh atoms emitted from a clean, oxygen- and cesium-covered Rh(100) surface. The results show that the excitation probability in all cases varies as  $\exp(-A/av_{\perp})$  at high velocities but is nearly constant at low velocities. The parameter  $A/a$  is found to be dependent on the state of the surface and on the azimuthal and the polar angles of ejection. A comparison between the experimental results and the molecular dynamics computer simulations indicates that the independence of the excitation probability on velocity at low velocities is caused by the effect of the surface binding energy and the existence of collisional excitations taking place *above* the surface. Both oxygen and cesium adsorption are found to enhance the relative emission of excited-state atoms. However, the magnitude of this enhancement is quite different for these two overlayers. The results are discussed in terms of the induced changes in the Fermi level and the creation of additional excitation channels.

### 1. Introduction

Bombardment of solid surfaces gives rise to a variety of inelastic collision events which lead to the ejection of the atoms, ions, and clusters in various excited states. It also leads to the emission of radiation from the surface. Although the absolute yields of particles sputtered in excited states are rather small, the implication of their existence is quite important. It has been known for many years that surface contamination could enhance these inelastic processes. To systematically study this process, many investigators have examined the effect of oxygen [1] and alkali metal [2] adsorption on the secondary ions and the excited states distributions and yields. However, most of these experiments have been performed under the so-called dynamic conditions. Typically, in these measurements, the chamber is filled with oxygen and the surface is bombarded with a continuous ion beam.

In the present work, we have investigated the dependence of the excitation probability on the emission velocity and the ejection angle of Rh atoms sputtered from the Rh(100) surface. Furthermore, the effect of oxygen and cesium adsorption on the excitation efficiency is examined. The measurements were performed under well controlled exposure conditions, and with low doses of bombarding ions ( $< 10^{13}$  ions/cm<sup>2</sup>). In this way, we were able to decouple the single

ion/surface interaction from the accumulative effect of ion-induced surface modifications.

### 2. Experimental

The Rh sample is an optically polished single crystal of 99.99% purity which is oriented within  $\pm 0.5^\circ$  of the (100) face. The cleaning procedure [3] and the experimental setup [4] have been described elsewhere. Briefly, the measurements are performed in an ultra-high vacuum (UHV) chamber ( $2 \times 10^{-10}$  Torr base pressure) equipped with a LEED/Auger surface analysis unit, and a Kelvin probe for monitoring the change in work function.

The experiment proceeds as follows. A pulse of mass-analyzed 5 keV ion beam is focussed onto a 2 mm diameter spot on the sample at normal incidence. A given time after the ion impact, a ribbon-shaped laser pulse resonantly ionizes a small volume of the desorbed neutrals, thus defining the time-of-flight of the probed species. The initial energy levels of interest are the  $^4F_{9/2}$  ground state and the  $^4F_{7/2}$  metastable fine structure state. The ionized particles are then accelerated towards a position-sensitive microchannel plate detector and are displayed on a phosphor screen. The image is, in turn, monitored by a charge-coupled-device camera which is interfaced to a micro-VAX Sta-

tion II computer for data storage and processing. For a typical spectrum, 30 images, each corresponding to a different time of flight, are collected and sorted into an intensity map of kinetic energies and take-off angles using a deconvolution procedure described earlier [4].

### 3. Results and discussion

The energy- and angle-resolved distributions of the ground- and the excited-state Rh atoms ejected from a 5 keV Ar<sup>+</sup> ion-bombarded Rh(100) are presented in fig. 1. In the ground-state distribution, the most intense peak is seen along the <100> azimuth ( $\varphi = 0^\circ$ ) at a polar angle  $\theta$  of about  $50^\circ$ . The observed anisotropies have been described previously [3]. However, the excited-state distribution is quite different. First, the most intense peak appears at normal ejection ( $\theta = 0^\circ$ ). Second, the peak position in the angular distribution is closer to the surface normal for the excited state than for the ground state. Third, the kinetic energy distribu-

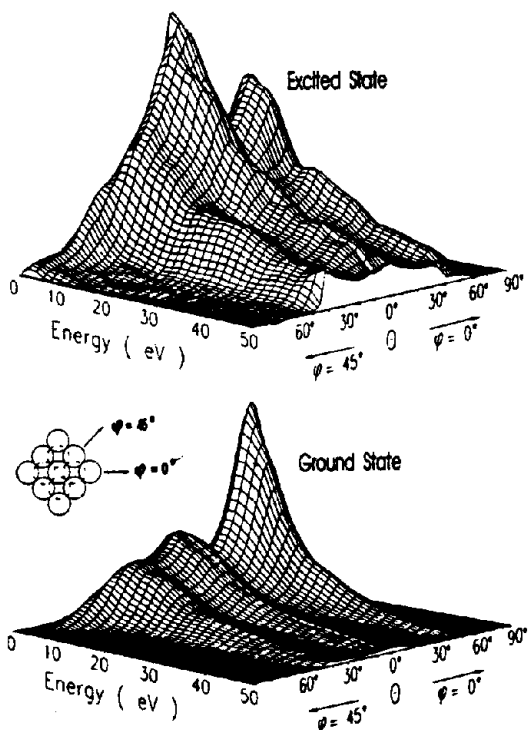


Fig. 1. Energy- and angle-resolved distributions of Rh atoms in the  ${}^4F_{7/2}$  excited state and  ${}^4F_{9/2}$  ground state, ejected from 5 keV Ar<sup>+</sup> ion bombarded Rh(100). The data correspond to ejection along  $\varphi = 0^\circ$  (<100>) and  $\varphi = 45^\circ$  (<110>) crystallographic directions, as defined in the inset. Both plots are normalized to the maximum intensity peaks. The dashed circles in the inset represent second layer atoms; polar angle  $\theta$  is measured from the normal to the surface, the ion beam is perpendicular to the sample.

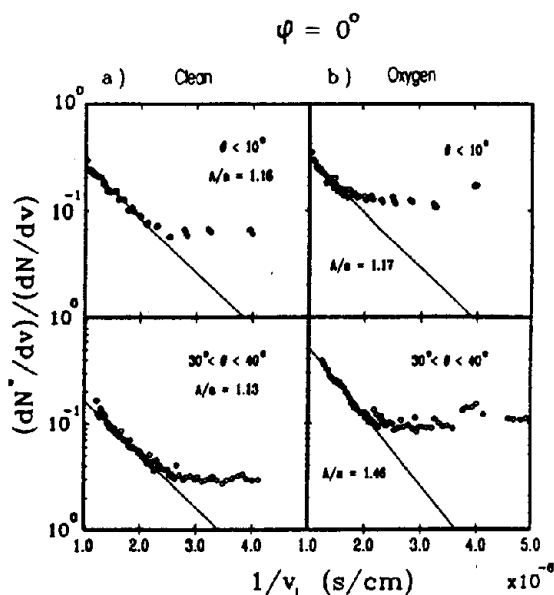


Fig. 2. Ratio of the measured intensities,  $(dN^*/dv)/(dN/dv)$ , vs the inverse of the normal component of velocity ( $1/v_\perp$ ) for different angles of ejection for (a) clean and (b) oxygen-covered surface of Rh(100). Straight lines have been fitted to the high-velocity portions of the data and have slopes,  $A/a$ , (in units of  $10^6$  cm/s), as displayed in each frame.

tion of the excited state ( ${}^4F_{7/2}$  with 0.19 excitation energy) decays more gradually than that of the ground state ( ${}^4F_{9/2}$ ).

The independent measurement of the energy-resolved angular distributions of the ground state and the metastable state allows one to determine the angular and velocity dependence of the excitation probability. Assuming that cascade transitions from higher-lying levels are insignificant in our measurements [5], the measured distributions are directly proportional to the number of sputtered atoms in a particular state, and the ratio of the excited-state signal to the ground state signal is proportional to the probability of excitation into the  ${}^4F_{7/2}$  state during the ion bombardment process.

It has been proposed that this probability has a velocity,  $v$ , and angle,  $\theta$ , dependence of the form  $\exp[-A/av_\perp]$  where  $A$  is the transition rate and  $1/a$  is the characteristic distance of atom-surface interaction [6,7]. As is shown in fig. 2a, the ratio of the excited-state distribution to the ground-state distribution, indeed approaches an exponential dependence on  $1/v_\perp$  at high velocities. However, the coefficient  $A/a$ , obtained from the indicated straight lines, depends on the angle of ejection. Furthermore, at low velocities, there is a sharp leveling off of the intensity ratios. The height of this plateau depends strongly on the polar

angle of ejection. Similar behavior has been previously observed in the case of secondary ions [2] and has been attributed to the fact that the velocity of the particle, while desorbing, is not a constant [8,9]. In other words, since the atom must overcome the surface binding energy, its velocity, near the surface, is larger than its measured velocity. The effect becomes particularly important when the energy of the particle leaving the surface is comparable to the surface binding energy. However, this effect alone is not sufficient to explain our results. For instance, at  $\theta = 0^\circ$ , the deviation occurs for  $v_{\perp} < 5 \times 10^5$  cm/s. This value corresponds to  $E_{\perp} < 13.5$  eV, which is much higher than the surface binding energy of Rh (5.7 eV). In addition, the low-velocity deviation occurs too abruptly to be simply a consequence of the surface binding energy. The results of our molecular dynamics computer simulations indicate that most of the excited atoms in the low velocity part of the spectrum have been excited by collisions above the surface ( $> 2 \text{ \AA}$ ) [10]. The calculations show that only about 4% of all emitted atoms undergo above-surface collisions. However, since this excitation process takes place outside the range of effective atom-surface interaction, the excited atoms have very high survival probabilities.

The results discussed so far are collected on a clean, contaminant-free surface. We then exposed the surface to 20 Langmuir (L) of oxygen, leading to a sharp  $p(2 \times 2)$  structure, as observed by LEED [11,12]. It is known that the contribution of excited atoms to the total sputtered flux can be increased by several orders of magnitude if oxygen is adsorbed on the surface [1]. We observed, on the contrary, that the ground-state signal was reduced by a factor of 2 and the emission of excited-state atoms remained almost unchanged (see table 1). A similar behavior has been reported by Pellin et al. from a Ti surface [13]. Our experiment differs

Table 1

The effect of oxygen and Cs exposure on the signal of ground- and excited-state Rh atoms emitted from Rh(100) along  $\varphi = 0^\circ$  azimuth. The data are normalized to the signal from the clean surface. The data for cesium are shown as a function of the exposure time. The work function was monitored with the Kelvin probe. The change of work function is measured relatively to the value of the work function on the clean surface

Surface	Ground state	Excited state	Ratio	Change of work function [eV]
Clean	1.00	1.0	1	0.0
20 L oxygen	0.55	1.2	2	+0.6
Cs 10 s	0.16	2.3	14	-0.3
Cs 20 s	0.08	5.6	70	-2.4
Cs 30 s	0.07	7.6	109	-2.0

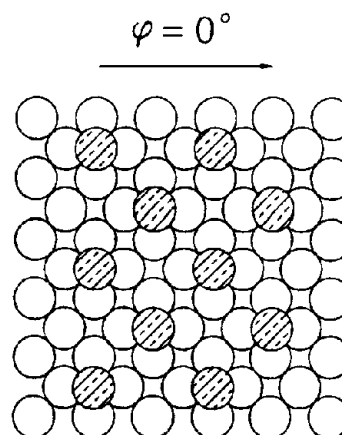


Fig. 3.  $p(2 \times 2)$  oxygen adsorption sites on the Rh(100) surface. The shaded circles represent oxygen atoms and the open circles are rhodium atoms.

from most of the previous measurements in which the vacuum chamber was filled with oxygen and the surface was exposed to a continuous ion beam. In these earlier experiments, it was found that the excited-state signal increased only when the surface was partially oxidized [1]. This observation led to the assumption that by oxidation, the electrons which are initially free become localized at the oxygen sites. This, in turn, leads to the creation of a band gap and, subsequently, inhibits the process of radiationless de-excitation [14] or to the creation of metal-oxygen molecules [15]. In the latter case the excitation takes place when the atom leaving the surface breaks M-O bonds.

Our experiment is performed under UHV conditions with a well controlled exposure to oxygen, and low doses of bombarding ions. Under these conditions, it is not possible to oxidize the rhodium surface [11]. It has been observed previously that oxygen reduces the emission of ground-state Rh atoms from Rh(100) [12]. Results were explained based on the concept of channeling and blocking of ejecting Rh atoms by the oxygen overlayer.

The effect of oxygen adsorption on the functional dependence of the excitation probability is shown in fig. 2b. Our computer simulations for the clean Rh(100) surface show that rhodium atoms departing at off-normal ( $\theta > 30^\circ$ ) angles can get re-excited via collisions with their neighboring atoms [10]. The process is more efficient as the distance between adjacent atoms becomes smaller. It is known that oxygen occupies the fourfold bridge site on the Rh(100) surface [12]. Hence, a Rh atom exiting at off-normal angles along the  $\varphi = 0^\circ$  azimuth finds an oxygen atom on its path (see fig. 3). In this way, the Rh atom can get re-excited via collision with the oxygen atom which, in turn, leads to an increase in the Rh excitation probability. This might

explain why the de-excitation coefficient ( $A/a$  factor) for an oxygen-covered surface increases with the polar angle in contrast to the data obtained on the clean crystal (fig. 2).

Much more pronounced changes are observed after Cs adsorption (table 1). As in the case of oxygen deposition, the ground-state signal is reduced. The reduction is considerably larger since Cs atoms are larger than oxygen atoms, and, hence, they can block the emission of Rh atoms more effectively. At the same time, the excited-state signal is found to increase drastically. We were not able to saturate the signal up to the coverage at which the ordered pattern of the Cs overlayer disappeared in the LEED image. It is known that the deposition of alkali atoms on metallic surfaces leads to the enhancement of negative secondary ion emission [2]. This effect is explained by the overlayer-induced changes in the Fermi level. A similar mechanism may operate in this case. To verify this conjecture, the change of the surface work function and the excited-state signal were monitored simultaneously. It may be seen from table 1 that at the beginning the surface work function decreases significantly. But after reaching a minimum at 20 s exposure, it increases slightly. In contrast, the excited-state intensity continues to increase. This implies that the variation in the Fermi level alone, is not sufficient to explain our results. Further measurements are needed to clarify these intriguing observations.

#### 4. Conclusions

The excitation probability of Rh atoms emitted from the Rh(100) surface has been measured. It has been found that the excitation probability has an exponential dependence on  $1/v_{\perp}$  at high velocities. The independence of the excitation probability on velocity at low velocities is explained by the effect of surface binding energy and the collisional excitation taking place above the surface.

Both oxygen and cesium adsorption are found to enhance the relative emission of excited atoms. However, the influence of cesium is much more pronounced.

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

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