Inst. Phys. Conf. Ser. No 114: Section 11
Paper presented at RIS 90, Varese, Italy, 16–21 September 1990

451

Surface characterization and adsorbate-site determination using multiphoton resonance ionization detection of desorbed particles

M. El-Maazawi, Z. Postawa, R. Maboudian, B. J. Garrison, and N. Winograd

Department of Chemistry, The Pennsylvania State University
University Park, PA 16802, U.S.A.

Abstract: The high efficiency, sensitivity and selectivity of multiphoton resonance ionization (MPRI) coupled with energetic ion-bombardment and with a specially designed position-sensitive detector enabled us to simultaneously measure energy and angular distributions of neutral Rh atoms ejected from clean and oxygen covered Rh{001}. The results taken along $\varphi=0°$ (open) and $\varphi=45°$ (close) azimuthal directions are well reproduced by molecular dynamics computer simulations and are explained in terms of the geometrical structure of the very near-surface region. It is also found that oxygen adsorbs in the fourfold hollow sites of Rh{001}.

1. Introduction

Angular distributions of particles desorbed from ion-bombarded single crystals show characteristic anisotropies corresponding to preferred ejections along certain low-indexed directions. These anisotropies are perturbed by the presence of adsorbate atoms or molecules on the surface. By carefully studying these perturbations one can learn a great deal about the atomistic nature of the binding sites, coverages and possible ordering of the adsorbates. Computer simulations of the ion-impact process have offered a detailed picture of the mechanisms leading to the angular anisotropies. However, the progress has been hindered due to the lack of detailed experimental measurements. Although there have been a variety of techniques, such as LEED and SEXAFS, that have been used to study surface structures, our group has shown over the last few years that ion beam technique can be employed to get a detailed structural information through the simple concepts of atom channeling and blocking (Chang *et al* 1987, Blumenthal *et al* 1988, Reimann *et al* 1988 & 1989 and Maboudian *et al* 1990). We have also employed multiphoton resonance ionization (MPRI) process to simultaneously measure energy and angular distributions of desorbed species. This allows us to make direct and reliable comparisons to computer simulations using the molecular dynamics (MD) approach (Garrison *et al* 1988).

Despite the importance of oxygen in promoting the catalytic activity of Rh surfaces, only few investigations of oxygen adsorption on Rh exist (Fisher *et al* 1983 and Oed *et al* 1988). There has not been any detailed study of the interaction of oxygen with Rh surfaces at room temperature. In this paper we show that the angular distribution of the ejected atoms from clean Rh{001} is determined mainly by the relative positions of surface atoms which influence the trajectory of an ejecting particle via channeling and blocking. Furthermore, upon adsorption of oxygen, the angular distribution of the desorbing Rh atoms is affected in such a way as to suggest that oxygen adsorbs in the fourfold hollow site, in agreement with the LEED experiments done by Oed *et al* (1988).

2. Experimental Setup and Computer Simulations

The experimental arrangement is described in detail elsewhere (Kobrin *et al* 1986). Briefly,

it consists of a UHV chamber (2×10^{-10} Torr base pressure) equipped with LEED and Auger spectroscopy, a Nd:YAG pumped-dye laser with a frequency doubler to resonantly ionize the desorbed neutrals, a position-sensitive microchannel plate (MCP) detector with a phosphor screen in the back of it and an image processing system which includes a CCD camera interfaced to a micro-VAX station II computer via a real-time frame grabber. Molecular dynamics simulations of the ion-impact event are performed using 3 keV Ar^+ impact at normal incidence on a Rh{100} micro-crystallite. The interaction among the target atoms is described using the many-body potential based on the embedded-atom method (EAM) (Daw and Baskes 1984). It is already shown that the EAM potential developed originally for the Rh{111} surface by Garrison *et al* (1988), successfully accounts for the distributions obtained from the Rh{331} stepped surface (Reimann *et al* 1988). Here, the same many-body potential is further used to simulate the desorption process for Rh{001}.

3. Results and Discussion

The experimental polar-angle (θ) distributions of Rh atoms desorbed from Rh{001} surface along φ=0° (open) and φ=45° (close) azimuthal directions are shown in Fig. 1(b). The off-normal intensity for the 0° azimuth is higher than for the 45° direction indicating that there is a strong preference for ejection along the open channels of the crystal. In addition, ejection is focussed into a polar angle of about 50° along the open direction and 35° for the close-packed direction. The results of the classical molecular dynamics simulation of the desorption process are presented in Fig. 1(b). As can be seen, there exists a very good overall agreement between the measurement and the calculation in the high kinetic energy range. However, in the low energy regime, the agreement with the experimental data is less satisfactory. At this time, the reason for this discrepancy is not clear. The characteristics of the angular distributions along the two azimuthal directions emphasize the importance of the relative positions of surface atoms (Maboudian *et al* 1990). For an open surface such as {001}, the peak position in the angular distribution directly correlates with the nearest-neighbor distance. The larger this separation is, the larger is the peak angle, as is evident when comparing the distribution along φ=0° to that for the 45° ejection. Based on the above observations, one can conclude that the relative positions of surface atoms are the dominant factor in determining the angular distributions of desorbed atoms from an ion-bombarded single crystal.
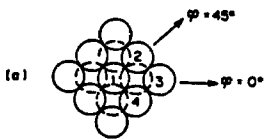

Fig. 1. (a) Rh{001} crystal face with φ=0° (open) and φ=45° (close) azimuthal directions shown. The dashed circles denote the positions of the second layer atoms. (b) Experimental (left) and calculated (right) angular distributions of Rh atoms desorbed atoms desorbed from Rh{001}. The curves marked "2nd layer" are the distributions obtained from simulations corresponding to the second layer atoms only.
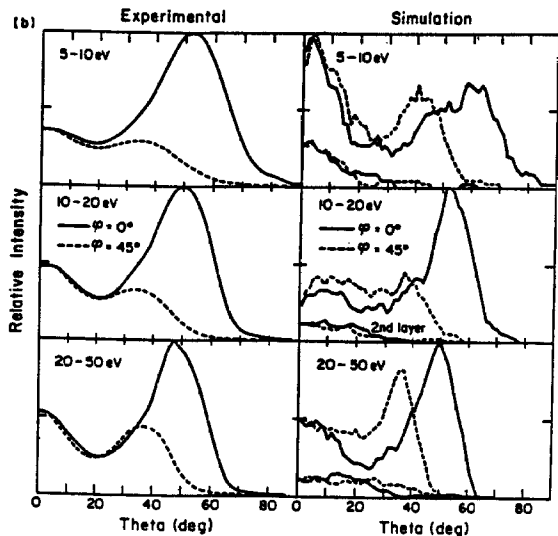
Kinetic energy distributions of Rh atoms emitted from clean and oxygen covered Rh{001} surface are shown in Fig. 2 for $\varphi=0°$ and $\varphi=45°$ azimuthal directions. Generally, no significant differences are visible between distributions taken before and after oxygen exposure. The small broadening of the spectrum for oxygen-covered surface is within the uncertainty of our measurements. Potentially, two processes can influence the energy spectra of emitted substrate atoms in the presence of oxygen overlayer. Oxygen can increase the surface binding energy which will shift the peak in the energy distribution to higher values (Thompson 1968). It can also cause an exiting particle to lose part of its kinetic energy due to collision with the adsorbed oxygen, moving the energy distribution towards lower values. These two processes compete with each other. The energy distribution then obtained is determined by the relative strength of these two processes. The lack of any change in the shape of the kinetic energy distributions differs from our previous measurements for Rh{111} crystal where a shift toward lower kinetic energies was observed after oxygen adsorption and explained by the dominance of the second process (Reimann *et al* 1989). One should, however, remember that the {111} surface has higher surface atomic density and higher oxygen coverage than the {001} and collisions between exiting Rh atoms and adsorbed oxygen atoms are much more probable and effective. More pronounced changes are visible in the energy-resolved polar angle distributions. In Fig. 3, such distributions are shown for atoms emitted along the open ($\varphi=0°$) and close ($\varphi=45°$) azimuthal directions. The position of the off-normal peak for the oxygen-covered surface is shifted closer to the surface normal for the open azimuth but is not altered in the spectrum measured along the $\varphi=45°$ azimuth. The magnitude of the shift depends on the energy of the emitted particle, being almost 10° in the 5-10 eV range and decreasing for higher kinetic energies. This trend is easy to be understood as Rh atoms with higher kinetic energies are less sensitive to the collisions with much lighter O atoms.
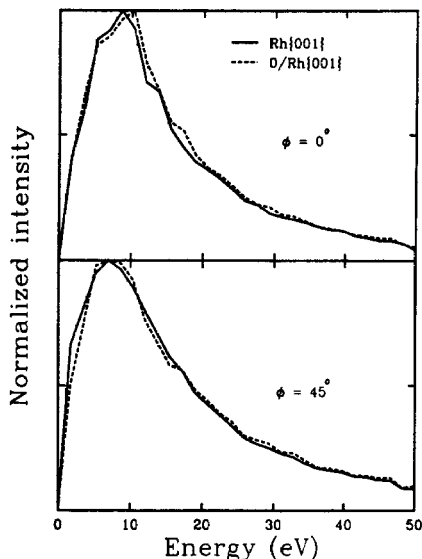

Fig. 2. Energy distributions of Rh atoms emitted along both azimuthal directions from clean and oxygen covered Rh{001}.
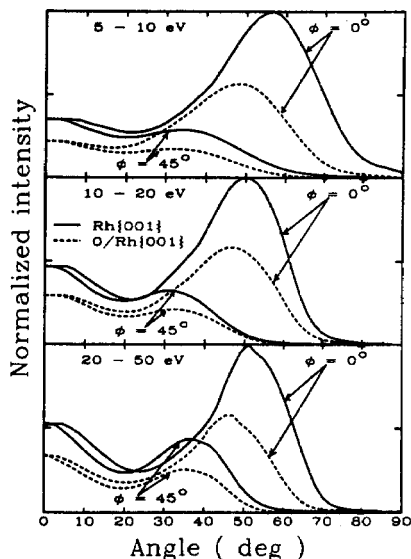
Fig. 3. Energy resolved polar angle distributions of Rh atoms emitted from clean and oxygen covered Rh{001}.

A careful inspection of Fig. 3 reveals an additional feature. The off-normal emission along the $\varphi=0°$ direction is suppressed more than the normal ejection whereas for the $\varphi=45°$, both components are reduced roughly by the same amount. The three possible high symmetry

p(2x2) oxygen overlayers on the Rh {001} surface are the A-top site, the twofold bridge site, and the fourfold bridge site. If oxygen atoms are located directly above the first layer atoms (A-top bonding site) they should equally influence the emission of Rh atoms. However, as we can see from Fig. 3, the angular distribution along $\varphi=0°$ is suppressed more than that along $\varphi=45°$. The total Rh signal is decreased roughly by 30%. Computer simulations for the O/Cu{001} system, which is analogous to the case discussed in this paper, suggest that in the case of the A-top oxygen adsorption the total sputtering yield of the emitted copper atoms is nearly unchanged whereas both twofold- and fourfold-bridge sites reduce the number of ejected copper atoms (Garrison *et al* 1978). Both arguments disqualify the A-top site as a possible bonding site for the adsorbed oxygen. Oxygen in both two- and fourfold bridge sites will partially block emission of second layer atoms. However, if the twofold-bridge sites are occupied, the emission along the $\varphi=45°$ azimuth should be shifted toward the surface normal since in this direction an additional atom is placed in the way of the exiting Rh atom, whereas the emission along the open direction should not be changed. The situation reverses if oxygen atoms are bonded in fourfold sites. As is shown in Fig. 3, the second alternative dominates and therefore we conclude that oxygen adsorbs in the fourfold bridge sites on Rh {001} at room temperature.

4. Summary and Conclusions

Energy-resolved angular distributions of Rh atoms ejected from ion-bombarded Rh{001} single crystal have been measured. Using the same many-body interaction potential developed originally for Rh{111}, a good agreement between the experimental results and the classical dynamics calculation of the desorption process has been obtained. By extracting the information available from the molecular dynamics simulations, we have shown that despite the complexity of the ion-bombardment process, the anisotropies observed in the angular distributions are mainly determined by the extreme local environment experienced by a surface atom. This causes the particle to preferentially desorb along certain crystallographic directions. Furthermore, the energy and the angular distributions of Rh atoms ejected from ion-bombarded oxygen-covered Rh{001} surface have been measured and used to identify bonding sites of adsorbed oxygen atoms. These observations are significant in terms of providing a simple and comprehensive picture of the mechanisms leading to the observed distributions. Moreover, they provide an important frame-work for future developments of any analytical models of the ion-bombardment process.

References

Blumenthal R, Donner S K, Herman J L, Trehan R, Caffey K P, Furman E, Winograd N and Weaver B D 1988 J. Vac. Sci. Technol. **B6** 1444
Chang C C, Malafsky G P and Winograd N 1987 J. Vac. Sci. Technol. **A5** 981
Daw M S and Baskes M I 1984 Phys. Rev. **B29** 6443
Fisher G B and Schmig S J 1983 J. Vac. Sci. Technol. **A1**(2) 1064
Garrison B J, Winograd N, Deaven D M, Reimann C T, Lo D Y, Tombrello T A, Harrison D E,Jr. and Shapiro M H 1988 Phys. Rev. **B37** 7197
Garrison B J, Winograd N and Harrison D E 1978 Phys. Rev. **B18**(11) 6000
Kobrin P H, Schick G A, Baxter J P and Winograd N 1986 Rev. Sci. Instrum. **57** 1354
Maboudian R, Postawa Z, EL-Maazawi M, Garrison B J and Winograd N 1990 Phys. Rev. **B42**(12)
Oed W, Dötch B, Hammer L, Heintz K, Müller K 1988 Surf. Sci. **207** 55
Reimann C T, EL-Maazawi M, Walzl K, Garrison B J and Winograd N 1989 J. Chem. Phys. **90**(3) 2027
Reimann C T, Walzl K, EL-Maazawi M, Garrison B J and Winograd N 1988 J. Chem. Phys. **89**(4) 2539
Thompson M W 1968 Philos. Mag. **18** 377