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# ENERGY- AND ANGLE-RESOLVED DETECTION OF NEUTRAL ATOMS DESORBED FROM ION BOMBARDED SINGLE CRYSTALS. Rh{111} and p(2 × 2)O/Rh{111}

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Measurements of energy- and angle-resolved distributions of neutral atoms desorbed from ion-bombarded single crystals are obtained using a novel multiphoton resonance ionization scheme. Experimental results are compared successfully to molecular dynamics calculations of the ion/solid collision event. This comparison suggests that the distributions from Rh{111} are sensitive to the crystal structure of the top atomic layer. Calculated distributions match experimental ones when oxygen atoms are assumed to adsorb in 3-fold hollow (c-site) bonding configurations.

The interaction of energetic particles with the near surface region of a solid has been widely studied with a growing body of applications, particularly in the modification of electronic materials through ion implantation [1] or reactive ion etching [2]. Molecular dynamics calculations of the ion impact event are now available which help to formulate the mechanisms of cluster emission as well as to unravel the origin of angular anisotropies for particles ejected from single crystal surfaces [3]. These models also provide an atomistic picture of the damage created within the material itself [4]. Experimental measurements of particle trajectories, however, have not been possible at the level necessary to make direct comparisons to theoretical predictions. Since the first studies of energy-integrated angular distributions 30 years ago [5], there has been much controversy and discussion regarding both the reliability of the measurements and the interpretation of the angular anisotropies themselves [6]. A major reason for this surprising lack of consensus is that there has been no method for detecting the direction and velocity of desorbed particles which

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is sufficiently sensitive to produce a signal before the physical nature of the target has been altered by the incident beam itself.

In this Letter, we present the first measurements of energy- *and* angle-resolved neutral-particle (EARN) distributions of atoms ejected from well-characterized surfaces under bombardment by energetic particles. To demonstrate the power of this novel approach, energy- and angle-resolved distributions of Rh atoms desorbed from ion-bombarded Rh{111} and Rh{111} covered with a p(2 × 2) oxygen overlayer are determined. The measurements are compared to molecular dynamics calculations of the expected response for this system. The ability to make such a comparison provides a convincing foundation from which it is possible to elucidate the complex nature of the ion bombardment event. In addition, as has been proposed and verified for the case of desorbed ions, the angular anisotropies are sensitive to the geometric arrangement of first layer atoms [7,8]. For Rh{111} we find that it is straightforward to distinguish the $\langle\bar{2}11\rangle$ direction (azimuthal angle $\phi = -30°$ in our notation defined in fig. 1) from the $\langle\bar{1}\bar{1}2\rangle$ direction ($\phi = 30°$) and that the calculated distributions agree well with the experimental ones if an adsorbed oxygen atom is placed in the 3-fold hollow (c-site) position.

The Rh{111} single-crystal surface was prepared by using methods previously documented [9]. Surface cleanliness and structure were monitored by low energy electron diffraction (LEED) and by Auger electron spectroscopy (AES) as well as by reproducibility of our surface-structure-sensitive EARN measurements. The optimal p(2 × 2) oxygen overlayer (measured by LEED) was found to occur at about 10 L $O_2$ exposure, consistent with previous studies of oxygen–Rh{111} interactions [9].

The EARN distributions are measured using a method which combines the position-sensitivity of a microchannel plate (MCP) detector, the collection efficiency of time-of-flight mass spectrometry, and the ionization selectivity and efficiency of multiphoton resonance ionization [10–12]. The apparatus used for these measurements is described in detail elsewhere [13]. A qualitative depiction of the experimental configuration is shown in fig. 1. A typical measurement is accomplished by the pulse sequence shown in the figure: (1) a 200 ns pulse of 5 keV $Ar^+$ ions ($\sim 2 \times 10^6$ ions) is focused through a 95% transmission Ni grid to a 2 mm diameter spot on the crystal surface; (2) upon impact of the ion pulse, a potential is applied to the Ni grid which sets up an extraction field of +1500 V between the sample and the grid and −800 V between the grid and the detector (the positive potential between the sample and grid serves to filter out positive secondary ions created by the ion bombardment event); (3) a cylindrically focused 6 ns laser pulse (~ 1 mJ at 3123.7 Å) ionizes a 0.5 mm thick volume of the neutral atoms above the grid after a time interval, $\tau_E$, which defines the Rh atom velocity; (4) the $Rh^+$ ions are then accelerated by the applied field toward the MCP detector which measures a spatially-resolved signal and displays it on a phosphor screen. The

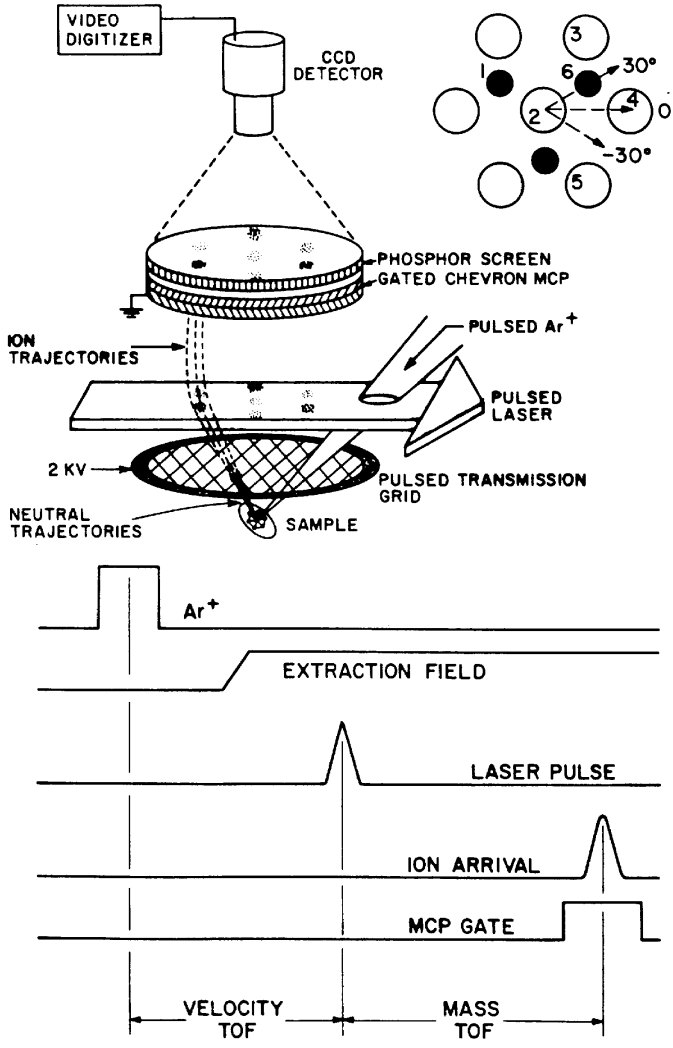


Fig. 1. A qualitative depiction of the EARN experiment with timing scheme. The crystallographic directions are defined in the inset. The open circles represent first layer atoms and the solid circles represent second layer atoms. The atoms are labeled with arbitrary numbers for reference purposes. The atop adsorption site is considered to be directly above any Rh surface atom. The b-site refers to adsorption in the 3-fold hollow position above a second-layer atom, for example 1 or 6. The c-site is the 3-fold hollow position above a third layer atom (not shown).

phosphor screen is monitored by an RCA model TC2911 video camera, and the signal is digitized by an LSI 11/23 computer system equipped with video-digitizing electronics. Typically about 600 measurements are integrated

to produce an ejection image for a given $\tau_E$. The image is corrected [13] for sampling volume, inhomogeneities in the detection, and for particle drift parallel to the MCO face during the period of time between ionization and detection.

A collection of approximately 60 corrected images for a range of $\tau_E$ values can be sorted into an intensity map over energies and angles. Examples of

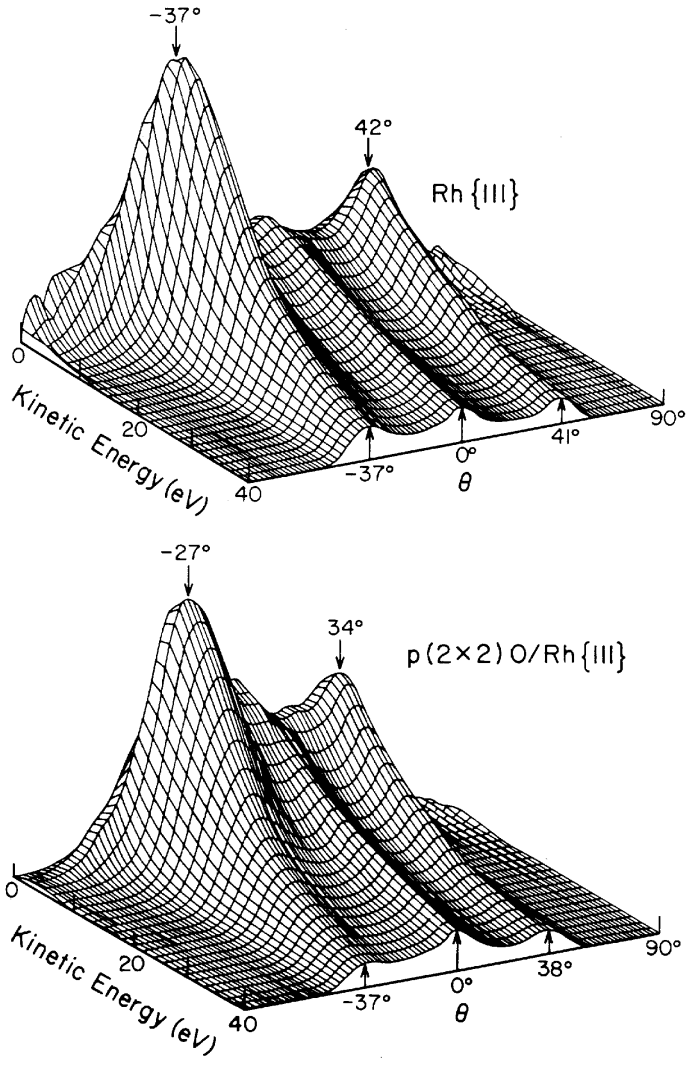


Fig. 2. The EARN intensity maps for clean Rh{111} and p(2×2)O/Rh{111}. The plots are normalized to the highest intensity peak in both cases. The positive values of $\theta$ are recorded along $\phi = 30°$ and the negative values of $\theta$ are recorded along $\phi = -30°$.

EARN intensity maps for clean Rh{111} and p(2 × 2)O/Rh{111} are given in fig. 2. These maps were obtained by recording information along one azimuth between polar angle $\theta = 0°$ (ejection along the surface normal) and $\theta = 90°$, then azimuthally rotating the crystal by 180°, followed again by acquiring data between polar angles of $\theta = 0°$ and $\theta = 90°$. Note that the incident flux required to construct an entire three-dimensional grid along one azimuthal direction is $\sim 2 \times 10^{12}$ ions $cm^{-2}$. Reproducibility of any given intensity in a map is about 5%. Both polar and azimuthal angle resolution is estimated to be $\pm 4°$.

The EARN intensity map for the clean Rh{111} surface along the open crystallographic directions $\phi = \pm 30°$ is shown in the upper part of fig. 2. It is possible to understand the important features of this map using the molecular dynamics simulations to extract dominant collision sequences that lead to particle ejection [14]. These sequences begin with the alignment of atomic motions inside the solid. As these motions cause ejection of first-layer atoms, further focusing is caused by channeling or blocking by other first-layer atoms. For example, the highest intensity is observed along the open crystallographic directions ($\phi = \pm 30°$ in our case) and the minimum intensity is observed along the close-packed crystallographic direction ($\phi = 0°$). If only surface processes were important, the peaks at $\theta = -37°$, $\phi = -30°$ and $\theta = 42°$, $\phi = 30°$ should be equal in intensity and not unequal as shown in fig. 3. The additional intensity at $\theta = -37°$, $\phi = -30°$ arises mainly from the ejection of atom 2 by atom 1 with first-layer focusing by atoms 4 and 5. The peak at $\theta = 42°$ and $\phi = 30°$ is lower in intensity by a factor of 0.5 at low kinetic energy (KE) since no such mechanism is available along this azimuth. The peak at $\theta = 0°$ arises mainly from ejection of the second-layer atom 6 which is focused upward by atoms 2, 3 and 4.

Several features of the angular distribution of ejected Rh atoms change in a systematic fashion when atoms with only high KE are detected. First, the intensity of the peak along $\phi = 30°$ now appearing at $\theta = 41°$ is only a factor of 0.7 lower than the peak appearing along $\phi = -30°$. The reason that these two peaks are more nearly equal in intensity is that other surface collisions between atoms 3 and 2 or between atoms 3 and 5 dominate the ejection process for the higher KE particles. Secondly, the peak at $\theta = 0°$ is relatively more important at high KE. The KE distribution at this angle is remarkably flat, indicating that the average energy of the particles is higher than those ejected in other directions. Previous molecular dynamics studies using Cu single crystals have predicted that the particles ejected at $\theta = 0°$ consist primarily of second-layer atoms with higher average KE [15].

A direct comparison of the calculated Rh distributions with the experimental ones obtained between 20 and 50 eV is shown in fig. 3. The agreement between experiment and theory is quite satisfactory considering the assumptions used to calculate interatomic forces during collisions [3]. The calculated

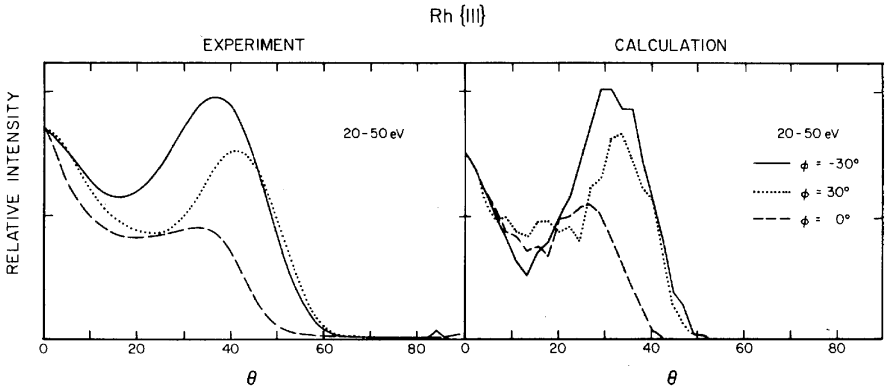


Fig. 3. Experimental and calculated EARN distributions for clean Rh{111}. A detailed account will be presented shortly [14].

peak shapes are somewhat sharper than those observed experimentally and the calculated angles corresponding to the peak intensity are 6°–9° smaller than observed. The source of this disagreement is currently not known, and represents a challenging problem for further refinements in the theory.

The important features of the EARN distributions are systematically altered by the presence of a p(2 × 2) oxygen overlayer as seen in the lower portion of fig. 2. At low KE the intensity of the peak along $\phi = -30°$ is preferentially reduced relative to the peak along $\phi = 30°$ and its peak angle is shifted 10° closer to the normal relative to the clean surface ($\theta = -27°$ versus $-37°$). This simple observation suggests that the oxygen atom bonds preferentially in the c-site since ejection of atom 2 is blocked by oxygen atoms only along $\phi = -30°$. Note also that the oxygen atom deflects ejecting Rh atoms toward the normal direction more strongly along $\phi = -30°$. The angular distributions at high KE approach those of the clean surface due to ineffective blocking of ejecting Rh atoms by the lighter oxygen atoms. These ideas are confirmed by preliminary molecular dynamics simulations as shown in fig. 4, where we have calculated expected Rh distributions for two different oxygen bonding geometries and have compared them directly to experimental results. It is gratifying that extensive LEED calculations also suggest that c-site adsorption is slightly favored over other possible bonding geometries [16].

To summarize, we have presented the first EARN distributions from ion bombarded single crystal surfaces. The measurements are made possible by a novel multiphoton resonance ionization detection scheme. The results suggest that the EARN data are sensitive to the crystal structure of the top atomic layer and that adsorbed species systematically alter these distributions. The experimental results are in excellent agreement with molecular dynamics calculations for both clean and adsorbate-covered surfaces.

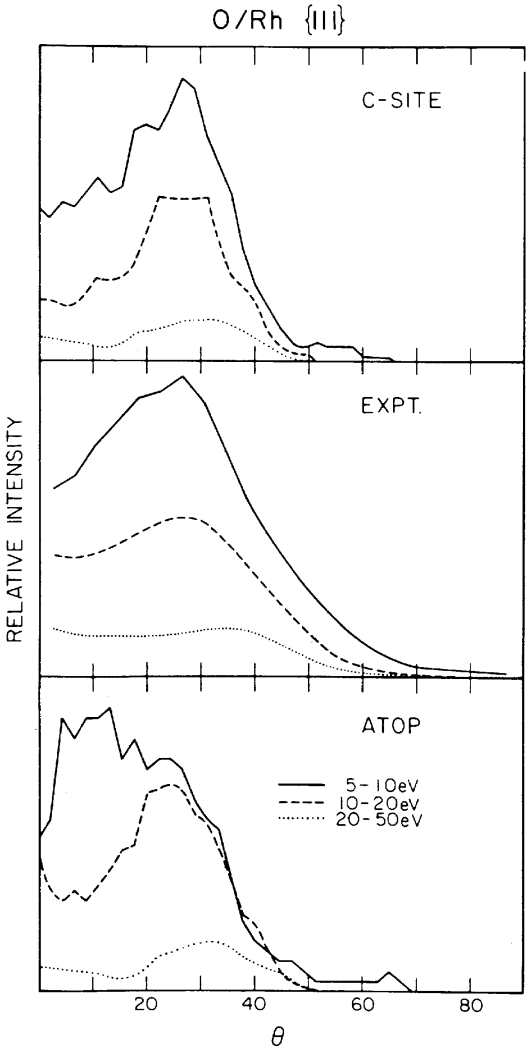


Fig. 4. Experimental and calculated EARN distributions for p(2×2)O/Rh{111}.

We believe these experiments are significant for the following reasons: (i) Detailed EARN trajectory measurements provide the most rigorous challenge for theoretical models of the ion/solid interaction. For example, it will be interesting to compare these results to calculations with utilize the binary collision approximation [17] and to other analytical models [18]. Further, energy- and angle-resolved trajectories allow unraveling of the mechanistic features of the ion/solid collision event in a much more reliable fashion than

is possible using only energy- and angle-integrated results. (ii) The structure sensitive nature of the ejection distributions suggests that this method may be a useful aid to the determination of bonding geometries of adsorbates on surfaces. Although actual bond-lengths may be more easily obtained by other methods, the simple channeling and blocking ideas provide a powerfully simple method for adsorbate-site determinations. In addition, we plan to measure the EARN distribution of the overlayer atom. This distribution more directly reflects the configuration of the adsorbate species [7]. (iii) The high sensitivity and selectivity of the detection scheme indicate that it will be applicable to related desorption experiments initiated by electrons or photons. A recent report, for example, demonstrates that the internal states of NO produced by electron bombardment could be accurately determined [19].

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