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Surface studies using ion beams and MPRI

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ABSTRACT

The study of the interaction of energetic particle beams with solids and surfaces has been of long-standing interest. These studies have ranged from fundamental investigations of the ion/solid collision event to the construction of microelectronic devices using ion implantation and reactive ion etching. Beam techniques have also been important in characterization of a wide range of materials ranging from semiconductors to high molecular weight proteins. In this work, we describe the use of MPRI as a valuable aid in allowing the study of neutral species which are desorbed from ion bombarded surfaces. This approach allows the trajectories of these species to be monitored with unprecedented accuracy sensitivity, and selectivity. The strategy behind our program involves the use of clean single crystal metal surfaces as targets so that the experimental results can be directly compared with theory. The theoretical method involves the calculation of the nuclear motion that leads to particle desorption using molecular dynamics procedures.

Introduction

Atomization of solids, followed by MPRI detection has proven to be a highly sensitive and selective solids characterization technique. Although the detection scheme is now fairly straightforward, many variations have been developed to optimize the atomization step. Initial efforts focussed on the thermal evaporation of material placed on a hot filament (Fasset 1985, Nogar 1985). This method has the advantage of generating a large number of atoms, but is somewhat inefficient due to difficulties in matching the timing of the thermal desorption to that of the laser ionization pulse. Another promising method utilizes a pulsed laser to desorb atoms or molecules from a solid. This approach solves the temporal matching problem between the desorption event and the ionization event. The potential sensitivity of this configuration is very large since an arbitrary quantity of the solid may be desorbed. A possible problem with this atomization method is that there may be matrix effects introduced into the system by the vaporization laser. There is only a limited amount of knowledge concerning the physics of the laser/solid interaction, making it difficult to correct for these effects. MPRI has been an important detection tool, however, in obtaining fundamental data about this phenomena. Several workers have reported successful analyses using laser desorption - MPRI detection for both atoms and molecules (Apel 1986, Hahn 1988).

In this work, we present a sampling of the latest results from our laboratory using energetic ion beams to desorb atoms and molecules from a solid surface followed by MPRI detection. There are three principal advantages of this method of sample atomization. (i) The ion beam may be pulsed to provide optimal temperal overlap with the ionization laser. (ii) There is a great deal known about the physics of the ion/solid interaction. For example, theories for electronic excitation, ionization and molecule

formation are well-developed. As will be seen in this paper, the trajectories of desorbing atoms may be accurately predicted. (iii) Approximately 90% of the desorbed atoms originate from the first layer of the solid (Harrison 1978). Although this aspect of the atomization process is a major disadvantage for bulk analysis due to difficulties in obtaining a representative sample and in desorbing a large number of atoms, it provides exciting opportunities for surface characterization.

Experimental Method

Kinetic energy- and angle-resolved neutral (EARN) desorbed atom measurements may be performed using an apparatus previously described (Kobrin 1986). In this experiment, desorbed neutral Rh atoms are ionized by MPRI using a pulsed photon source that is a tunable Nd:YAG-pumped dye laser with a frequency doubler, operating at a wavelength of 312 nm. Polar angle-resolved detection of the photoionized Rh atoms is achieved in the range θ=90° (grazing ejection) using photoion extraction optics and a multichannel plate. A 200-nsec pulsed 5-keV Ar^+ ion beam is focused to a 1-mm diameter spot and aimed normally at the Rh sample. After a time delay past each ion pulse, a 6-nsec laser pulse, focused into a thin ribbon, is aimed at a known distance from the ion impact point on the target. By varying the time delay between the incident ion pulse and the ionizing laser pulse, a time-of-flight measurement yielding kinetic energy-(KE)-resolved data in the range 0 to 50 eV is performed on desorbed neutrals. An LSI 11/23 microcomputer software-deconvolutes the KE and angular information, providing separately resolved KE and polar angular distributions. The KE resolution in ~4% for 5-eV particles and ~15% for 50-eV particles. The polar angle resolution is ~7%. These resolutions are adequate to measure commonly observed energy and angle distributions. The laser-ionization-based EARN experiment is highly sensitive. In a fifteen minute run, sufficient to collect a KE- and angle-resolved ejection spectrum, $5x10^{12}$ ions/cm^2 are incident on the sample, leading to erosion of less than a few percent of a monolayer. Thus, surface damage by the incident ions is negligible.

The experiments are performed in a cryopumped ultra-high vacuum system with a base pressure of ~$2x10^{-10}$ torr. The Rh crystals are mounted on a precision sample manipulator. The sample preparation consists of cycles of 5-keV Ar ion bombardment using an incident ion beam current of 2 μA, followed by annealing at ~870°C. Carbon is removed by exposure to $2x10^{-7}$ torr oxygen followed by heating to 650°C. Surface crystallography is verified using low energy electron diffraction (LEED).

Computer Simulations Using Many-body Interaction Potentials

A new model potential for classical dynamical simulations of keV-ion-induced desorption has recently been developed which is based on the embedded atom method (EAM) (Daw 1984). In the EAM, the potential energy of the i^{th} atom in the lattice is written as $E_i=F(\rho_i=\Sigma_{j\neq i}\rho_{atomic}(r_{ij}))+1/2\Sigma_{j\neq i}\varphi(r_{ij})$. In this expression, r_{ij} is the distance between the i^{th} and j^{th} atoms, $\varphi(r_{ij})$ is the potential energy of repulsion between the ion cores of the i^{th} and j^{th} atoms, $\rho_{atomic}(r_{ij})$ is the electron density at the position of the i^{th} atom due to the j^{th} atom, and ρ_i is the total electron density at the position of the i^{th} atom, excluding the electron density provided by the i^{th} atom itself. The embedding function, F, is a nonlinear function *which is taken not to depend on the source of the electron density*. Thus, once F is determined, it should be usable in an arbitrary configuration of Rh atoms.

The form of the EAM potential may be derived from density functional theory (Manninen 1986). With this theory, the embedding energy of the i^{th} atom is a

functional of the self-consistent electron density with the i^{th} atom removed from the lattice. Two approximations are then made. First, the functional is replaced by a function, and second, the self-consistent electron density is replaced by a homogeneous electron density, the value of which is taken to be the value of the correct density at the position of the i^{th} atom. Finally, a perturbation theory correction is added taking into account the nonuniformity of the electorn density near the atom. The result is an expression with the same form as the EAM. It should be noted that the EAM and the expression from density function theory are not rigorously identical, so that the EAM is empirical in nature. Also, an alternative interpretation exists for ρ_i. This parameter may be a measure of local density or coordination of atoms (Finnis 1984) rather than a measure of local electron density. In either interpretation, however, the atomic interactions are the consequence of many-body forces, which is more realistic for metals than the assumption of pairwise additive potentials.

Results and Discussion

The EARN experiments provide us with a unique opportunity to test the predictions of the EAM theory. As shown in figure 1, we have measured the polar angle distribution for Rh atoms ejected along various crystal azimuthal directions for Rh{111} and the atomically stepped Rh{331} surface for particles in the 10-20 eV range. The results of comparible computer simulations are also shown in the figure. The same potential parameters were employed for both crystal surfaces. The level of agreement is gratifying. The significance of the peak positions and relative amplitudes have been discussed in terms of the channeling and blocking of desorbing atoms by other surface atoms (Garrison 1988).

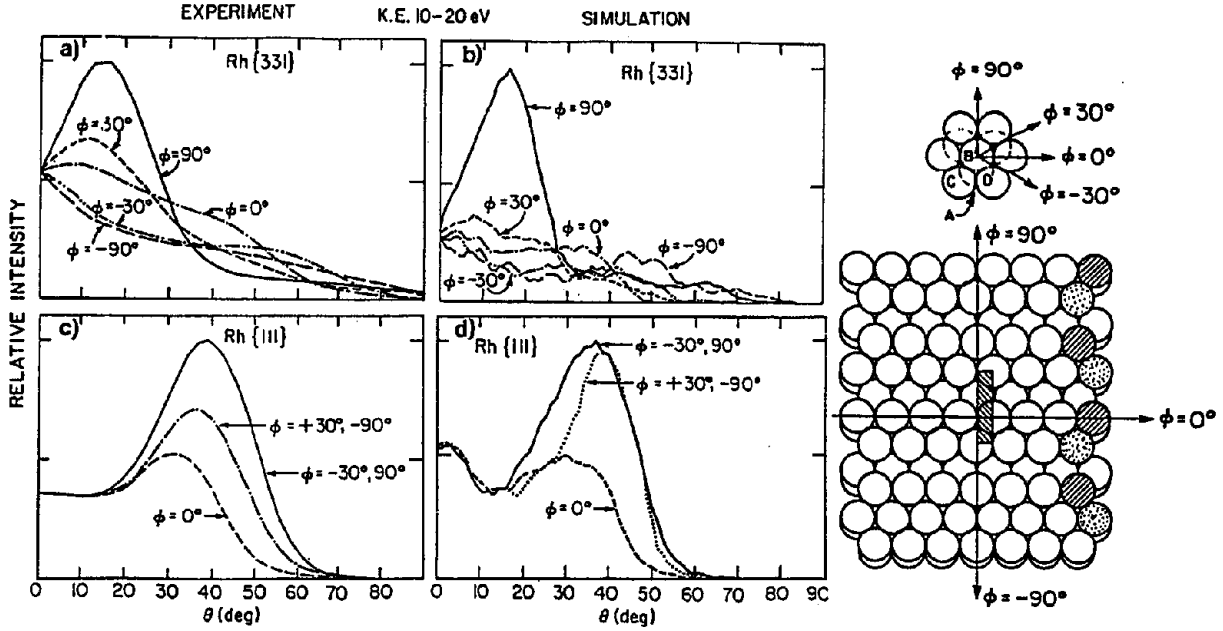

Figure 1. Polar angular distributions of Rh atoms desorbed from single crystal surfaces. The curves are energy-integrated in the range 10 to 20 eV. The azimuthal directions, ϕ, for Rh{111} are defined in the top crystal and for Rh{331} in the bottom crystal. a) Rh{331}, experimental desorption data; b) Rh{331}, simulated desorption data; c) Rh{111}, experimental desorption data; d) Rh{111}, simulated desorption data.

It is possible to chemically react these surfaces with a variety of small molecules to examine the influence of the overlayer on the desorbing Rh atom trajectory. In figure 2, for example, the KE and angular distributions for Rh{111}

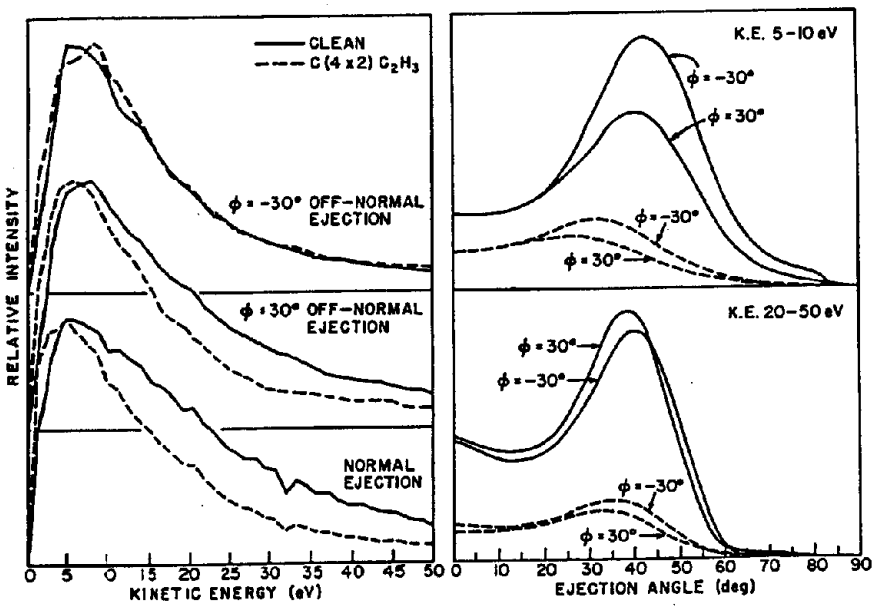

Figure 2. EARN distributions for Rh atoms ejected from Rh{111} covered with 50% of a monolayer of ≡C-CH_3. The azimuthal directions, ϕ, are defined in figure 1.

both clean and covered with 50% of a monolayer of ethylene (C_2H_4) are shown. The reaction product is believed to be the ethylidyne molecule, ≡C-CH_3, bound perpendicularly to the surface over a 3-fold hole site (Levis 1987). Note that the Rh intensity shown in the right two panels is significantly attenuated by the presence of the overlayer.

The KE distributions, shown in the left panel with intensities normalized to the peak values, are also effected by the adsorption of C_2H_4. The high KE tail for the normal ejection and along ϕ=30° may reflect specific blocking mechanisms along these azimuthal directions. Computer simulations are now in progress to attempt to elucidate the specific nature of the binding site.

As a final example, it seems that a powerful application of the MPRI detector will be in the analysis of the molecular species adsorbed on surfaces. In a preliminary experiment, we have adsorbed several layers of carbazole on a polycrystalline gold target and ionized the desorbed molecule using 285 nm radiation. As shown in figure 3, the results are very encouraging, with only the carbazole molecular ion observed with intensity many hundreds of times larger than obtained with SIMS. It will be interesting to see if the vibrational and rotational states of the systems may be determined via MPRI and compared to molecular dynamics simulations of ejected molecules.

Conclusions

The MPRI method for detecting neutral atoms desorbed from ion-bombarded surfaces has many unique areas of application. We have illustrated here how the spatial and temporal aspects of the experiment make it possible tod eternine energy and angle-resolved distributions and to probe for the presence of desorbed molecules. As has

been clear from a variety of papers presented at this conference, the trace analysis aspects of this configuration are extremely important. Using a slightly different detection configuration, for example, it has been possible to find just a few hundred atoms on a surface.

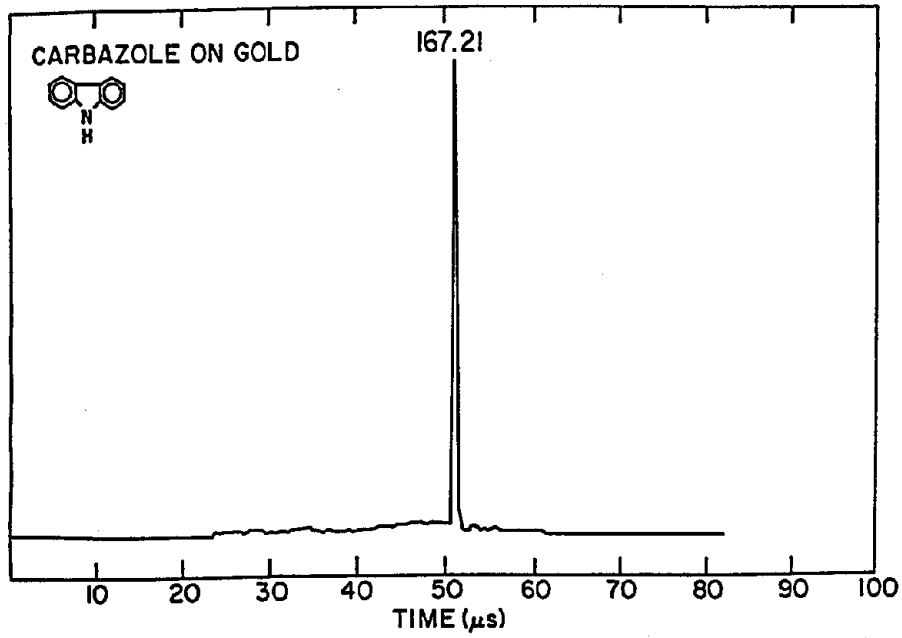

Figure 3. MPRI signal at 285 nm from carbazole deposited on gold, bombarded by 10 KeV Ar^+ ions. The small signals near the baseline are SIMS ions allowed to pass to the detector.

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