THE EFFECT OF ADSORBATES ON THE ANGULAR
PATTERNS OF ION-INDUCED Rh ATOM EJECTION
FROM RH{111}: SURFACE STRUCTURE DETERMINATIONS

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Surface structure can be determined through various ion
beam techniques. Recently our research group has made detailed
measurements of target particle ejection (sputtering) from
single-crystal surfaces by incident low energy heavy ions. The
energy and angular distributions of desorbed ionic and neutral
species reflect details of surface structure[1] and adsorbate
location[2] and orientation.[3] If desorption mechanisms are
adequately understood, surface structure can therefore in
principle be obtained from careful measurements of the desorption
phenomenon.[1]

Material desorbed from ion-bombarded metals is dominantly
uncharged. Neutral atoms are easier to characterize than ionic
species[4] due to the presence of fewer matrix effects.[5] Therefore,
a high efficiency multiphoton resonance ionization (MPRI) detector
was recently built to simultaneously measure kinetic energy- and
angle-resolved neutral (EARN) desorbed atom distributions.[6] This
detector provides a detailed view of the desorption process and is
an invaluable aid to understanding how these processes relate to
surface structure.

We have examined bombardment of clean,[7] oxygen-[8] and
ethylene-dosed Rh{111}. The clean Rh{111} surface was prepared by
standard techniques.[9] A p(2x2) overlayer of atomic oxygen was
created by exposing the clean Rh{111} surface to molecular oxygen.
Exposing the surface to ethylene led to a c(4x2) overlayer of
ethylidyne, C_2H_3.[10] Oxygen atoms occupy three-fold hollows over
third layer Rh atoms;[11] and under low temperature conditions
ethylidyne is bonded vertically (one carbon on top of the other)
in three-fold hollows over second layer atoms.[10] It is not known
what site ethylidyne occupies at room temperature, which is the
temperature at which our studies are performed.

We briefly review the features of Rh ejection from clean
Rh{111}.[7] The relevant crystallographic directions are defined in
Fig. 1, as are the possible adsorbate sites discussed below. Some
examples of clean Rh{111} EARN data are shown by the solid curves
in Figs. 2 and 3. First, ejection in the "open" directions $\phi=\pm30°$
is favored. This is due to channeling of a moving surface Rh atom
by pairs of adjacent Rh atoms on the surface. Second, for low
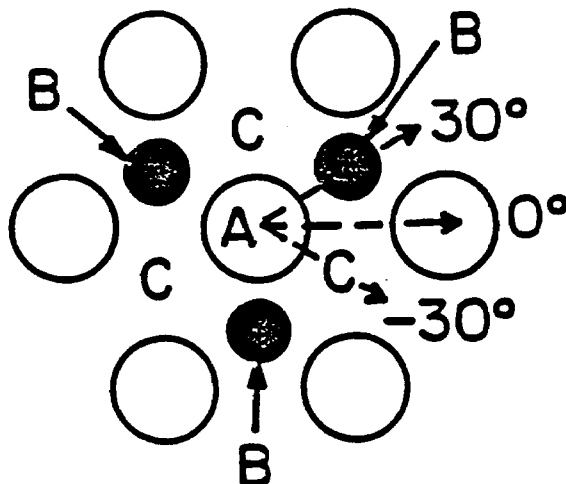kinetic energy (KE), ejection in the $\phi=-30°$ direction is favored

Fig. 1   Surface geometry of Rh{111}. Open circles
represent first layer atoms, closed circles represent
second layer atoms. The three azimuthal directions
$\phi=\pm30°$ and $0°$ are indicated, as are the three
important adsorbate sites A, B, and C.

over the $\phi=+30°$ direction; however for high Rh KE this favoritism
is only weakly expressed. The reasons for this trend are as
follows. At high KE, a Rh atom leaves the surface early in the
collision cascade and is therefore sensitive mainly to the first
layer, yielding approximately six-fold symmetric ejection
patterns. Low KE particles leave later on after the second layer
atoms start interacting with the surface. Therefore three-fold
symmetry characteristic of the first two layers results in the
ejection patterns. Second layer atoms efficiently push first layer
atoms in the $\phi=-30°$ direction, resulting in enhanced ejection in
that direction. Third and last, normal ejection is characterized
by relatively higher KE than is off-normal ejection. Simulations[12]
reveal that this is due to second layer atoms being channeled
straight up by triples of surface atoms after being hit from below
by incident ions which channel three or four layers into the
solid, and then undergo a hard collision of about 180°.

    With the above mechanisms in mind, we now treat the
adsorbate cases. EARN patterns from p(2x2) O/Rh{111} were
previously obtained.[8] Recently obtained data is shown in Fig. 2.
The distinguishing feature of this data is that ejection
off-normal in the $\phi=-30°$ direction is attenuated relative to
off-normal ejection in the $\phi=+30°$ direction. This immediately
suggests that oxygen atoms occupy the C-site, where they more
easily block ejection in the $\phi=-30°$ direction.

    We now switch attention to the ethylidyne overlayer. The
experimental results are summarized in Fig. 3. Focusing first on
the polar angular distribution, we see that $\phi=+30°$ and $\phi=-30°$
off-normal peaks are attenuated by about the same amount: 70% and
72% for the 5-10 eV case respectively and 80% and 74% respectively
for the 20-50 eV case. Evidently, to whichever site ethylidyne is
bonded, B or C, it stands tall enough to have some influence on
ejection in all directions. However, the kinetic energy spectra
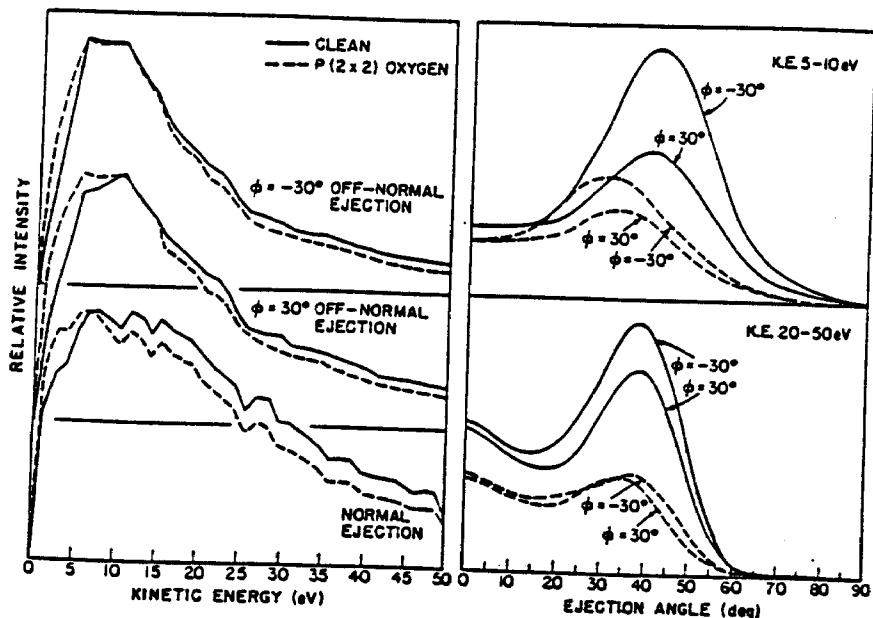provide an additional clue. The spectra are relatively depleted in

Fig. 2   Kinetic energy (KE) and polar angular distributions of Rh desorbed from clean Rh{111} and p(2x2) O/Rh{111}. Angular distributions are integrated over the indicated KE ranges. The KE spectra are peak normalized. The normal KE spectra were integrated over a 6° polar angle range centered at a polar angle of zero. The off-normal KE spectra were integrated over a 6° polar angle range centered at the off-normal polar peak of the appropriate low KE angular distribution.
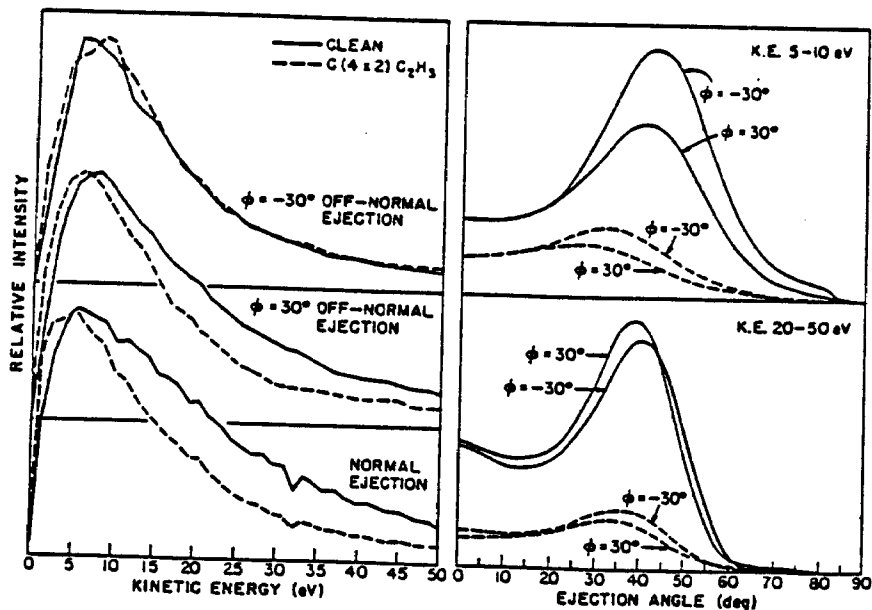

Fig. 3   Kinetic energy and polar angular distributions of Rh sputtered from clean Rh{111} and c(4x2) C₂H₃/Rh{111}.

the high KE ranges only off-normal in the $\phi=+30°$ direction and in the normal direction. The latter result particularly suggests that ethylidyne binds to the B-site where it can block second layer atoms ejected via the third mechanism discussed above for clean Rh{111}. This is a new site determination which is the same as the one observed for low temperature ethylidyne adsorption.

The EARN technique for surface structure determination should have some continued use in other cases which are being investigated now in our laboratory. We are also beginning a program of simulation of keV ion-induced desorption in the presence of adsorbed overlayers. Such simulations may provide additional insight into the details of how adsorbates alter the desorption patterns of single crystals.

1. N. Winograd, Prog. Solid St. Chem. <u>13</u>, 285 (1982).
2. S.P. Holland, B.J. Garrison, and N. Winograd,
    Phys. Rev. Lett. <u>43</u>, 220 (1979).
3. D.W. Moon, N. Winograd, and B.J. Garrison,
    Chem. Phys. Lett. <u>114</u>, 237 (1985).
4. B.J. Garrison and N. Winograd, Science <u>216</u>, 4548 (1982).
5. F.M. Kimock, J.P. Baxter, and N. Winograd,
    Surf. Sci. <u>124</u>, L41 (1983).
6. P.H. Kobrin, G.A. Schick, J.P. Baxter, and N. Winograd,
    Rev. Sci. Instrum. <u>57</u>, 1354 (1986).
7. J.P. Baxter, G.A. Schick, J. Singh, P.H. Kobrin, and
    N. Winograd, J. Vac. Sci. Tech. A <u>4</u>, 1218 (1986).
8. J. Singh, C.T. Reimann, J.P. Baxter, G.A. Schick,
    P.H. Kobrin, B.J. Garrison, and N. Winograd,
    J. Vac. Sci. and Tech. A. <u>5</u>, 1191 (1987).
9. L.A. DeLouise and N. Winograd, Surf. Sci. <u>138</u>, 417 (1984).
10. R.J. Koestner, M.A. Van Hove and G.A. Somorjai,
    Surf. Sci. <u>121</u>, 321 (1982).
11. P.C. Wong, K.C. Hui, M.Y. Zhou, and K.A.R. Mitchell,
    Surf. Sci. <u>165</u>, L21 (1986).
12. B.J. Garrison, C.T. Reimann, N. Winograd, and
    D.E. Harrison, Jr., Phys. Rev. B, in press.