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SURFACE SELF-DIFFUSION OF Pt ON THE Pt(311) PLANE

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Abstract - The surface diffusion of single Pt atoms and Pt clusters on the channeled (311) plane of Pt has been investigated by field ion microscopy. Single atoms were found to migrate within a given channel of the (311) plane at temperatures above 215 K with an activation energy of 0.60 ± 0.03 eV and a diffusivity of \(1.9 \times 10^{-5}\) cm\(^2\)/sec. No cross-channel diffusion was observed for single atoms. Two atoms within the same channel associated into a dimer which was immobile and stable up to temperatures of 340 K. Subsequent addition of atoms to the same channel resulted in the formation of chains of atoms along the channel. The motion of two atoms diffusing in adjacent channels were not strongly correlated. However, occasional occurrences of cross-channel processes between adjacent channels to produce the stable dimer configuration were observed. Observations of atoms diffusing in next-adjacent channels suggested a weak attraction at separations from 9.2 to 12.4Å. Small clusters of atoms left on the plane after field evaporation were stable below 370 K, but at 370 K and above, the atoms rearranged to form a long chain within one channel. These results suggest that the mechanism for the formation of missing rows in the (1x2) reconstruction of channeled surfaces of Pt, Ir, and Au involves surface diffusion of atoms which are stabilized by short-ranged atomic interactions.

I - INTRODUCTION

Low Energy Electron Diffraction (LEED) studies of the (110)-oriented surfaces of Pt, Ir, and Au indicate a surface reconstruction which is characterized by a (1x2) pattern /1-5/. Of the several models proposed for the reconstruction, the "missing row" model has become the most popular. According to this model, every other close-packed [110] row in the outermost layer is missing. The missing-row model is supported by quantitative LEED analysis /2/, Rutherford Ion Backscattering measurements /6/, and direct images of the surface by Scanning Tunneling Microscopy (STM) /7/ and Transmission Electron Microscopy (TEM) /8/. In a recent paper Bonzel and Ferrer /9/ have questioned the missing row model based on problems associated with mass transfer. For the particular case of Pt(110), they observe a transition between an unreconstructed (1x1) surface and a reconstructed (1x2) surface taking place within 100 seconds at a temperature of 310 K. Their calculations of the mean diffusion distance for Pt by mass transfer surface diffusion using activation energies based on field emission measurements, however, indicate that the diffusion distance is much too small to explain the emptying of alternate rows of atoms. Instead, they propose a new model which does not suffer from the mass transfer problem. In an even more recent paper, Campuzano, et. al. /10/ argue that the (1x1) - (1x2) transition is an order-disorder transition and therefore does not require large mass transfer. Clearly, the role of surface atom migration in the (1x2) reconstruction needs to be defined.
In this paper we report observations of surface diffusion and atomic interactions on the Pt(311) plane which suggest that a (1x2) surface reconstruction could be driven by surface diffusion of atoms and stabilized by short-ranged interactions between the atoms. This mechanism is in accordance with the order-disorder explanation given for the transitions on the (110) plane /10/. Our experiments were carried out on the (311) plane of Pt, which is similar to the (110) in that it consists of close-packed rows of atoms separated by channels. The distance between rows is 4.62 Å on the (311) plane and 3.92 Å on the (110) plane. Our motivation for examining surface diffusion on the (311) plane stemmed from observations of missing rows of atoms in the (311) plane following thermal treatment of platinum tips. The occurrence of the missing rows in the (311) plane was very frequent if the annealing temperature was above 400 K. Unfortunately, surface atom mobility was so great at this temperature (the surface would begin its change from a field-evaporated endform to a thermal endform) that the detailed atomic steps leading to the formation of missing rows could not be directly observed. The observations did lead us to suspect that the chains of atoms were actually being formed by atoms diffusing on the plane and stabilizing in the chain formations, rather than rows of atoms within the plane diffusing out on to the steps. In order to determine whether or not such a process was possible, we undertook an investigation of the surface diffusion of Pt atoms and Pt clusters on the (311) plane. In this paper we report the results of that investigation which include studies of the diffusion of single atoms within a given (311) channel, two atoms within the same channel, two atoms in adjacent channels, two atoms in next-adjacent channels, and short chains of atoms in adjacent channels.

II - EXPERIMENTAL APPARATUS

The experimental procedures followed in field ion microscope studies of surface diffusion are well-documented /11/ and are not reviewed here. The experiments were performed in an all-metal field ion microscope pumped by a liquid-nitrogen-trapped, oil diffusion pump and a liquid-nitrogen-cooled titanium sublimation pump. After extensive vacuum processing, the background pressure with the tip cooled and the diffusion pump valved-off was \(4 - 5 \times 10^{-11}\) Torr. The background pressure was stable for several hours. Neon, purified by diffusion through a vycor bulb, was used for the imaging gas. Image intensification was accomplished with an internal channel plate cleaned by both ion and electron bombardment. Pt adatoms were supplied from deposition coils made from 0.005 inch Pt wire heated to a temperature just below their melting point. The Pt coils along with their support loops were extensively outgassed as a part of the vacuum processing. The Pt tip was prepared from 0.005 inch polycrystalline wire using the polishing procedure described in the literature /12/. It was cleaned using a combination of neon cathode sputtering, thermal annealing at 600 K and field evaporation.

The data collection and analysis were semi-automated. Field ion images were recorded from the internal phosphor screen using a RCA model TC1005 video camera and a JVC model 6060U video recorder. A home-built microprocessor controlled the alternate application of the imaging voltage, heating of the tip, and starting and stopping of the video recorder. The analysis of the recorded images consisted of marking the adatom position with a cursor generated by a Colorado Video Model 622 X-Y Digitizer. The digitizer transmitted the coordinates to an Dec LSI 11/03 minicomputer for analysis. Better-quality images were obtained for display purposes by photographing the phosphor screen with a 35 mm camera equipped with Kodak tri-x film. All of the field ion images displayed in this paper were recorded with the 35 mm camera.

III - EXPERIMENTAL RESULTS

Single Pt atoms on the (311) plane of Pt were found to migrate at temperatures above 215 K. The migration was confined to a given channel, i.e., no cross-channel diffusion such as that observed on the (110) plane /13/ was detected. Mean square displacements were obtained for six temperatures in the range from 217 K to 256 K. The data are plotted in Arrhenius form in Fig. 1. The slope and
intercept of the plot yield an activation energy for diffusion of $0.60 \pm 0.03$ eV and a diffusivity of $1.9 \times 10^{-4}$ cm$^2$/sec. These results are consistent with a previous study of Pt diffusion on Pt(311) by Bassett and Webber /13/ in which an activation energy for surface diffusion of $0.69 \pm 0.2$ eV was obtained by assuming

![Arrhenius plot for a single Pt atom diffusing within a channel of a Pt(311) plane.](image)

Fig. 1. An Arrhenius plot for a single Pt atom diffusing within a channel of a Pt(311) plane.

![Two Pt atoms migrating in the same Pt(311) channel (a,b) combine to form a dimer (c,d) which is stable to 340K.](image)

Fig. 2 Two Pt atoms migrating in the same Pt(311) channel (a,b) combine to form a dimer (c,d) which is stable to 340K.
the standard prefactor /11/. The frequency occupation for various sites along a
given channel measured for approximately 300 diffusion intervals indicated that the
binding along the channel was nonuniform, the adatoms were held more strongly at
sites near the edge of the plane than at the center. This phenomenon has been
studied in quantitative detail by Fink and Ehrlich /14/ for W and Re adatoms
migrating on the channeled W(211) plane.

When two Pt adatoms were deposited within the same channel of the Pt(311) plane,
the adatoms migrated freely until a close-packed dimer was formed. The
association of two atoms into a dimer is shown in Fig. 2. Once formed the dimer
did not migrate or dissociate until the surface was heated to temperatures of 340 K or above. At these temperatures, displacements of the dimer were occasionally
noted, but more often the dimer would simply be gone after the diffusion interval
indicating that the dimer had dissociated and the single atoms migrated off the
plane. It is worth noting that at these temperatures there was considerable
surface atom rearrangement occurring on the surface as a whole. This observation
means that this dimer configuration was more stable than the atoms at the various
plane edges. Additional atoms deposited in a channel with a dimer already present
would eventually associate with the dimer and form a chain structure.

In previous FIM studies of W and Re adatoms migrating on the channeled (211) plane
of tungsten, an interaction between atoms in adjacent rows was discovered /11/. This attractive interaction caused the atoms’ diffusion to be correlated, and
extensive analysis of the diffusion data yielded the interatomic potentials
involved /11/. In our measurements of Pt diffusion on Pt(311), this type of
correlated motion was not observed. Although our data are still somewhat limited,
if there is any attractive interaction at all, it occurs at distances greater than
the "straight" or "staggered" configurations. On several occasions, however, we
noted a different type of interaction. Atoms diffusing in adjacent channels were
observed to combine and form a close-packed dimer within the same channel. This
behavior is currently being investigated in more detail.

Our observation that missing rows of atoms in the (311) plane are produced by
thermal annealing of Pt suggested that an attractive interaction may exist between
atoms separated by a channel. To check this possibility, we examined the
diffusion of adatoms in channels one channel apart and looked for correlation.
The measurements were performed at a temperature of 239 K. Fig. 3 shows a plot of
the frequency of occupation at a given separation vs. the separation distance for
320 diffusion intervals. Also shown in Fig. 3 is the expected distribution for
non-interacting atoms. Although the number of observations are limited, the data
suggest a weak attraction at separations of 9.2 to 12.4\AA.

In all of the above measurements, the diffusing atoms were deposited from an
external sublimation source. It was also possible to field evaporate the (311)
plane to a very small size consisting of 4-8 atoms and examine the diffusion
properties of these atoms. The results were quite striking. No motion of surface
atoms generated in this fashion was detected at temperatures below 370 K. Again,
it is worth noting that significant diffusion occurs at this temperature on the
surface as a whole. At temperatures of 370 K and above, the small clusters were
observed to rearrange and form a long chain in a single channel. Fig. 4 shows an
example of this process. Between photographs the sample was heated to 370 K for 2
min. This rearrangement process was not an isolated observation, it happened
every time the experiment was performed (~ 10 times). The observation again
points to the very high stability of the chain configurations.

IV - DISCUSSION AND SUMMARY

Single Pt atoms freely migrate along channels in the (311) plane at temperatures
well below room temperature. If another atom is encountered, a dimer is formed
and the migration proceeds only if the temperature is 340 K or above. This high
stability results in the formation of chains if a number atoms are deposited in a
given (311) channel. Even atoms in adjacent channels will diffuse cross-channel
Fig. 3 The number of observations of atoms at a given separation vs. separation distance for two atoms migrating in next-adjacent channels of the Pt(311) plane. The histogram is the data and the liner plot is the expected distribution for non-interacting atoms.

Fig. 4. A cluster of atoms on the Pt (311) plane (a) rearranges to form a long chain (b) upon annealing at 370K for 2 min.
in order to achieve this stable configuration. (The actual mechanism for this cross-channel diffusion was not identified in this study, it may involve the same sort of exchange process proposed for cross-channel diffusion on the Pt(110) plane /13/.) The observation of chain structures with missing rows produced by thermal annealing at temperatures above 400 suggests that 400 K is the minimum temperature required for atoms to diffuse on to the (311) plane from steps below or it is the temperature at which the top surface layer of the (311) plane dissolves. This same type of process could lead to the "missing-row" reconstructions observed on macroscopic (110) surfaces. Atoms in channels of the (110) plane have the same close-packed separation (2.77 A) as atoms in the (311) plane and individual atoms have been found to diffuse on the (110) plane below room temperature /13/. The high mobility of surface atoms implies that mass transfer will not limit a reconstruction process. A mechanism in which atoms from edges and kinks diffuse out on to the terraces and are stabilized by the short-ranged interactions discussed here is clearly possible. In order to further explore this possibility we are initiating a study of the type reported here involving Pt diffusion on the Pt(110) plane.

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