

## Tracing the Movements of Single Atoms and Molecules on Solid Surfaces

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Atoms and molecules on solid surfaces start to move at relatively low temperature. The dynamic behavior of atoms and molecules is responsible for crystal shape changes, crystal growth and thin film epitaxy, surface enhanced chemical reactions and many other surface phenomena where transport of atoms and molecules is involved. Identification of elementary atomic processes in the dynamic behavior, and finding their mechanisms and energetics are the key to understand these surface phenomena at the fundamental level. Using atomic resolution microscopy, it is now possible to trace the motion of single atoms and molecules on solid surfaces from which elementary atomic processes can be identified and studied. Here, we discuss a few of our recent results at metal and semiconductor surfaces where novel mechanisms of atomic and molecular movements have been found. We also discuss how our result can be used to explain different growth modes existing in epitaxy.

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### I. Introduction

Solid surfaces are by no means static. Atoms and molecules at the surface can move at relatively low temperatures. [1-3] This dynamic behavior of atoms and molecules is responsible for many surface phenomena where transport of atoms and molecules are involved. These phenomena include crystal shape changes, crystal growth and epitaxial growth of thin films, surface enhanced chemical reactions, adsorption and desorption, oxidation and chemical reactions and so on [4]. The key to understand these surface phenomena on atomic scale is that we identify first elementary atomic processes, and then find out their atomic mechanisms and energetics. For such purpose, atomic resolution microscopy is a powerful tool. The movements of single atoms and molecules can be directly observed and traced [5], thus their mechanisms and reaction pathways can be revealed and identified. From the temperature dependence of their rates of occurrence, the activation energies of these atomic processes can be derived.

Studies of random walk diffusion of single atoms and small atomic clusters were already reported in 1966 and 1969 [6, 7] using the field ion microscope (FIM) which achieved atomic resolution in 1957 [8]. Single atom tracing was, however, started only in 1972 [9]. At that time, I realized that adatoms on a surface can interact with each other, thus adatom

diffusion and adatom-adatom interaction have to be distinguished. This could be done by controlling the number of atoms deposited on a facet. In this study, the number of atoms on a small facet of a field ion emitter surface was controlled by repeated thermal depositions from a coil source and low temperature field desorption, or field evaporation, to remove excess adatoms. To study surface diffusion, one atom could be retained on the facet, whereas for studying adatom-adatom interaction, two atoms could be retained on the facet, and so on. For studying random walk diffusion, I was aware of the work of Jean Perrin in which he studied random walk of suspended particles in a colloidal solution by tracing the path in random motion of one particle from which quantitative data such as the mean square displacements at different temperatures were derived. But now the path of one atom in random walk could be traced using FIM. In the 1970's, no PC image digitizers were available. The positions of a diffusing adatom were determined from superposition of field ion images using an optical method where lattice atoms served as fiducial marks. The accuracy was very difficult to achieve, but it was concluded that a precision of about  $\pm 0.5 \text{ \AA}$  could be achieved. The power of single atom tracking achieved its potential only when PC image digitizers become generally available. With a modern PC image digitizer and improved vacuum technology, not only the adatom position can be more accurately mapped, the amount of data which can be collected from one adatom has increased tremendously, or both the data accuracy and statistical errors have improved greatly in recent years although the ideas and methods remain essentially unchanged. Only in the last year or so, we have succeeded in applying this same technique to a scanning tunneling microscope (STM) study of molecular diffusion and the power of single particle tracing is immediate. Here, I will describe a few of our recent works using this technique.

In random walk diffusion of single atoms on metal surfaces, adatoms usually move by hopping over a potential barrier via a saddle point of the twodimensional potential energy surface of the adatom-surface interaction. For some adatom-surface systems, however, an atomic displacement can occur by exchange-displacement where the adatom delves into the site of a nearest substrate atom, squeezing this atom out to the terrace at a nearby site. In Fig. 1 the displacements of a Pt adatom are found to form a  $c(2 \times 2)$  lattice of the substrate surface net which can only be explained in terms of the exchange-displacement *mechanism* [10] shown in Fig. 2. When the exchange-displacement mechanism occurs, one can expect that during the transition, a dimer-vacancy configuration will be formed temporarily although it may be a short lived state, and it may be too difficult to observe. For Re adatoms on Ir(001) surface, however, this intermediate state is found to be metastable [11] as shown in Fig. 2. The atomic configuration of the intermediate state can be observed within a narrow temperature range, from  $\sim 220 \text{ K}$  to  $\sim 280 \text{ K}$ . In fact, by field evaporating the Re-Ir dimer away, a vacancy can be found beneath the dimer. For this system, when the temperature goes beyond  $\sim 290 \text{ K}$ , the dimer will dissociate. Upon dissociation, the Re adatom will delve into the lattice site. The exchange-displacement mechanism is energetically favorable, since during the whole displacement process, atoms move in concerted motion. This mechanism always maintain the maximum number of nearest-neighbor atoms during the transition. The activation barrier height is derived from the Arrhenius plot shown in Fig. 3 to be  $0.74 \pm 0.02 \text{ eV}$ [12].

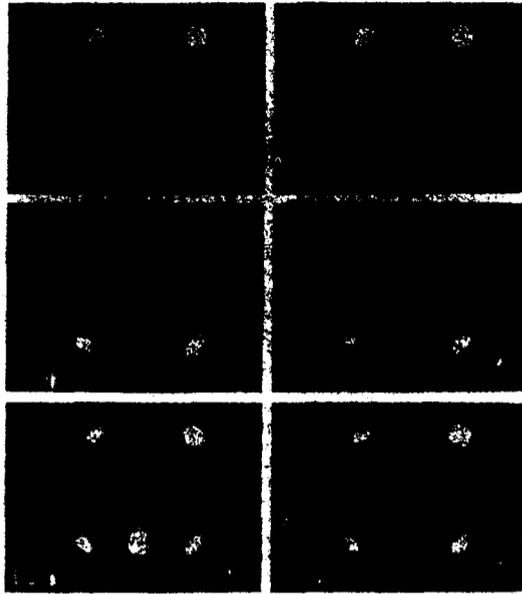


FIG. 1. This figure shows single atom tracing technique with a PC digitizer. (a) shows that a Pt atom is deposited to a nearly circular Pt(001) surface of about  $35 \text{ \AA}$  in diameter. The position of the adatom is digitized. The sample is then heated to 175 K without an applied field. After the surface is cooled and imaged again, the Pt adatom is found to be in a new position which is again digitized as shown in (b). By repeating this process for many heating periods of observation, the visited sites is found to form a  $c(2 \times 2)$  structure of the surface net, indicating that the shortest displacement of the adatom is in the diagonal direction of the surface unit cell.

When there is no driving force, adatoms will perform random walks. If one applies a driving force to an adatom, or if there exists a chemical potential gradient at the surface, then the adatom will drift toward the lower chemical potential region in the direction of maximum chemical potential gradient as constrained by the substrate surface channel structure. This, in fact, has been observed as early as 1975 in which the effective polarizability of 5-d transition metal adatoms on W(110) surface were derived by observing the velocity in the directional walk of single adatoms in an applied field [13]. A field gradient exists across a facet because of the step structure of the surface layer. This field gradient induces the directional motion of adatoms from the central region of the facet toward the step edge region of the facet. Field induced directional motion may in fact be the responsible mechanism of atomic manipulation with the scanning tunneling microscope [14].

It has already been thirty years since single atom diffusion can be studied by direct observation with the field ion microscope. This distinction has now been shared by the scanning tunneling microscope which is particularly powerful for studying semiconductor surfaces [15]. The surface area of the sample can be much larger also. Diffusion of single atoms and small atom-clusters has been successfully studied so far, but only in the last

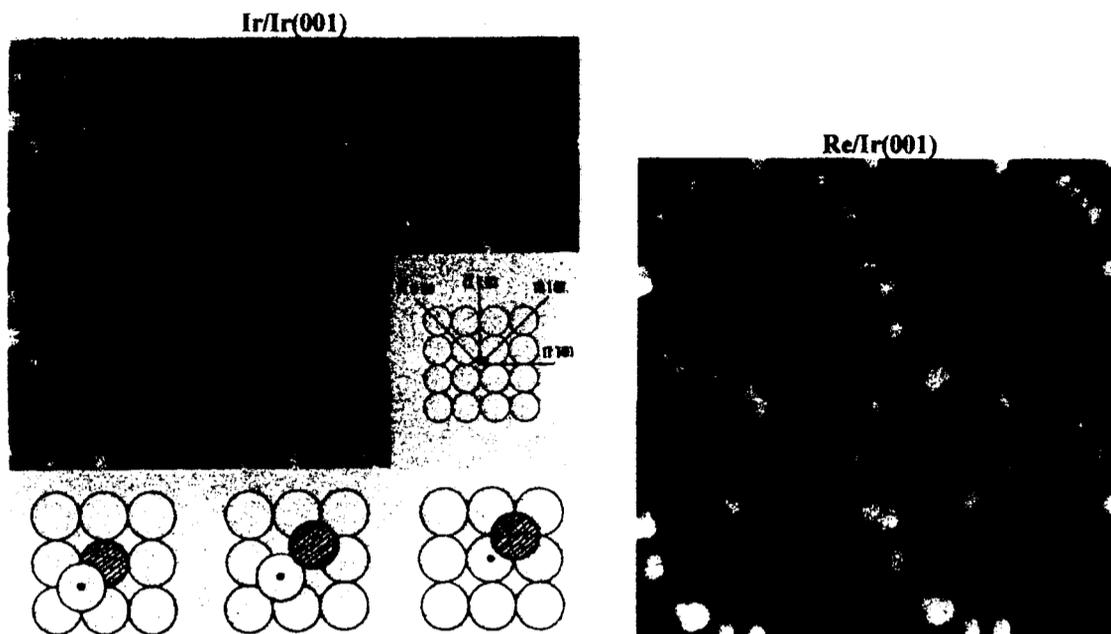


FIG. 2. FIM images show random walk diffusion of one Ir adatom on an Ir(001) surface of  $\sim 50 \text{ \AA}$  in diameter. A tracing of visited sites finds it to be a  $c(2 \times 2)$  structure of the surface net. This can be explained by an exchange-displacement mechanism of surface diffusion illustrated by the line drawing. If this mechanism is the correct one, then an intermediate state with a dimer-vacancy configuration may be observable. The lower FIM images show a similar experiment for one Re adatom on an Ir(001) surface. The dimer-vacancy configuration is indeed seen in the lowest two FIM images. The circular image spot changes to an oblong shape after heating, indicating it is now a dimer, which has two equivalent orientations (Images of Re and Ir atoms are indistinguishable). After field evaporating this dimer away, a vacancy can be found in the substrate layer.

year or so, this type of study has been successfully extended to a molecular species. We have succeeded in studying the dynamic behavior of oxygen molecules on silicon (111)- $7 \times 7$  surface using the single particle tracing method [16]. Our study not only derives site specific activation energies of molecular jumps, but more importantly, we have also identified the mechanism of molecular hopping as well as discovered two intermediate states mediating the hopping motion. It has been carefully established by an STM and UPS study that oxygen molecules adsorb first in a molecular state at the adatom site of this surface as bright image spots. When the sample is heated between 300 to 370  $^{\circ}\text{C}$ , the bright spot is found to hop within the unit cell, or the molecule can hop between adatom sites within the unit cell. The puzzling question is that adatoms are separated by nearly 7  $\text{\AA}$  apart, how can a molecule jump from one adatom site to another without desorption from the surface, and what is the atomic mechanism of the hopping motion. This question is answered from a very careful tracing of molecular movement at  $\sim 300 \text{ }^{\circ}\text{C}$  as shown in Fig. 4a. The oxygen

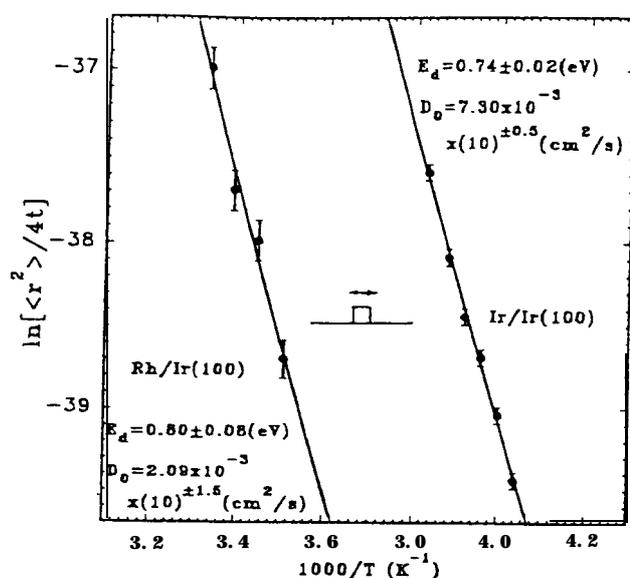


FIG. 3. Arrhenius plots for diffusion of Ir and Rh adatoms on Ir(001) surface. Diffusion of Ir adatoms occurs by exchange-displacement whereas that of Rh adatoms by atomic hopping. From the slopes and intercepts of the plots, activation energies and diffusivities are derived.

molecule is found to connect its dangling bond to that of a Si-rest atom, forming a metastable intermediate state as illustrated in Fig. 4b. This molecule can either return to the original adsorption state, or hop one more time to another intermediate state. In the later pathway, it will most likely hop to a new adatom site, thus complete a hop from one adatom site to another. All the activation barrier heights for these different pathways have been measured for hopping between two center sites in the faulted half of the unit cell. They are shown in Fig. 4c. This mechanism can be called bond-forming-breaking mechanism of diatomic molecular diffusion. We believe this type of extremely detailed studies of atomic and molecular motion will eventually shed some light on surface promoted chemical reactions, or heterogeneous catalysis.

Another subject of our recent study is the cross-step motion of diffusing adatoms and dissociation of step edge atoms. It is well known that real surfaces have many atomic steps. In crystal growth and growth of epitaxial layers, atoms will first aggregate into small clusters. These clusters have many steps also. Questions immediately arise when a diffusing adatom encounters a step what will happen to the adatom, and how the step-crossing property of diffusing adatom is going to affect the growth mode in epitaxy. In epitaxy, it is well known that there exist three dominant modes of growth, namely the 2-D layer-by-layer growth mode, the 3-D cluster growth mode, and the mixed growth mode, known respectively as Frank-Van der Merwe, Volmer-Weber, and Stranski-Krastanov growth modes [17]. Early FIM studies find that when adatoms encounter "descending steps", they are reflected. The importance of the reflecting property of steps [18], has recently being over emphasized

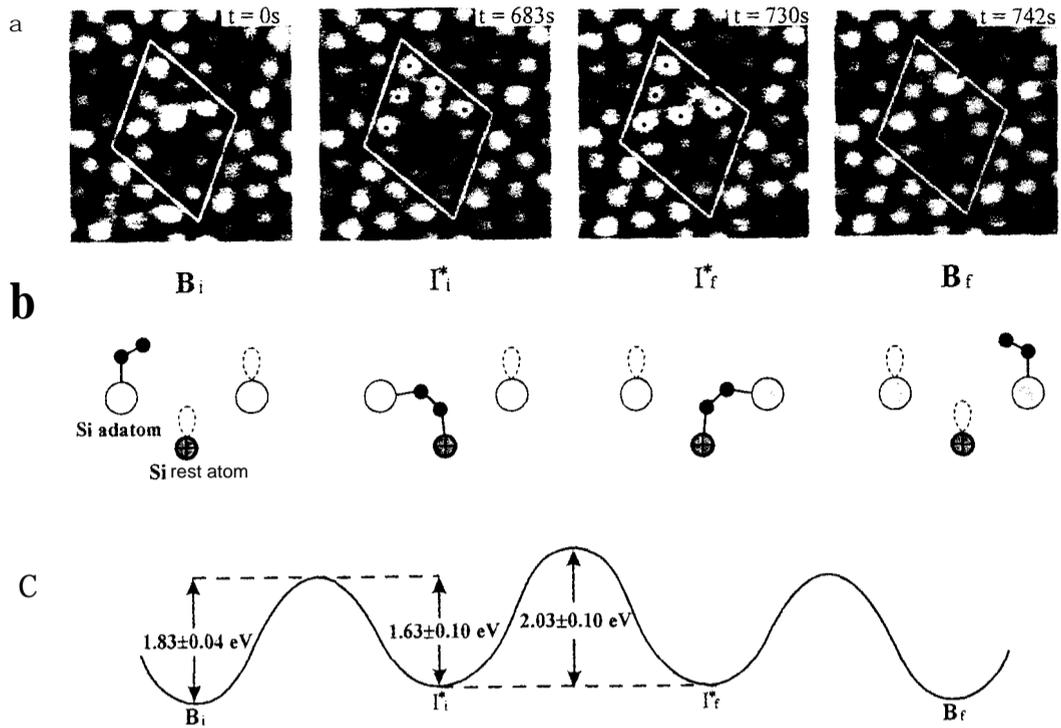


FIG. 4. (a) shows filled state STM images where an oxygen molecule is adsorbed on a center adatom site of the faulted half of the unit cell as represented by state  $B_i$ . Upon heating, the position of the bright spot shifts to a location, known as  $t_3$  site, between the adatom and a neighbor rest atom ( $I_i^*$  state). One more heating, the bright spot shifts position again to a new  $t_3$  site ( $I_f^*$  state). Another heating, the *oxygen* molecule *now* moves to a new center adatom site ( $B_f$  state). (b) shows the atomic configurations of all these states. (c) shows activation barriers measured for all these molecular transitions.

because of the lack of experimental values of the barrier heights of reflective step boundaries. In fact, many steps such as steps of Ir(001) layers do not reflect Ir adatoms at all [19]. Even for those steps which reflect, our earlier and recent measurements both give a barrier height of only  $\sim 0.2$  eV [20], which is effective in reflecting arriving adatoms, thus effective in affecting the growth mode, if and only if the sample temperature is below  $\sim 200$  K. The barriers are much too small to have a significant effect on the kinetics of growth at a typical growth temperature of several hundred K. In our studies, we also measure the dissociation energies of step edge atoms to both sides of steps. Surprisingly, they are nearly equal, and they are both  $\sim 1.5$  eV for Ir(111) surface. In other words, when a sample is heated to a temperature where step edge atoms can dissociate, they are equally likely to go to the "upper" terrace as to go to the "lower" terrace. The dissociation energy also represents the atom-trapping-strength for atoms coming to the steps. We can equally interpret *the existence of three growth modes in epitaxy in terms of the atom-trapping property of steps*. Consider the case where the atom deposition rate is low and diffusion speed is high. If,

at the temperature of growth, the trapping strength of steps is not strong enough to bind effectively arriving atoms, they can dissociate again to either the "upper" or the "lower" terrace. The growth should be three dimensional. On the other hand, if the atom-trapping strength of steps is strong enough, then all the arriving atoms from both sides of steps will be incorporated into the steps, or the layer can only grow two dimensionally by continuous trapping of arriving atoms, since the "upper" step edges do not reflect effectively step crossing atoms at this temperature. The step will flow continuously to fill up a layer before a new layer starts, thus the growth should be two-dimensional. In hetero-epitaxy, if hetero-steps, i.e. steps with different materials for the upper and lower layers, have a strong atom trapping strength, but homo-steps, i.e. steps with same material for the upper and lower layers, have a weak atom-trapping strength, then the first layer will grow in 2-D, but after that 3-D clusters will be formed. In fact, by changing the trapping strength of different layer structures, different growth modes can be explained in a most natural way. An important point is for different systems the trapping strength can range all the way from 0 to over 1.5 eV, thus is effective in affecting growth phenomena at the relatively high temperature where the growths are usually done.

What we have shown here is that if one can identify elementary surface atomic processes and clarifies their mechanisms and energetics, many surface phenomena can be understood in terms of these atomic processes in a very natural way. In this paper, I use a few of our recent works to illustrate the importance of such studies.

Finally, it is my great pleasure to contribute this article to commemorate the 91th birthday of Professor T. Y. Wu, who, through his teaching and writing, and his insistence of the importance of basic research and persistence in seeking funds to support basic research in Taiwan, has greatly contributed to its scientific progress. Personally, I am grateful to him for his trust and support over the years. Here I would also like to thank some of my coworkers from whose works this paper is based. They are Drs. C. L. Chen, T. Y. Fu, I. S. Hwang, R. L. Lo and others.

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