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AN ATOMIC VIEW OF CLUSTER DIFFUSION ON METAL SURFACES

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1. Abstract

Field ion microscope measurements show a strong correlation between the mobility and shape of small clusters on fcc(100) metal surfaces. For self-diffusion on Rh(100) this correlation leads to an oscillatory behavior in the activation energy of surface diffusion as a function of cluster size. Comparison of the measured activation energies to previous theoretical calculations indicate that the mechanism of cluster diffusion involves individual displacements of edge atoms (i.e., perimeter diffusion). The rate-determining step in the migration of clusters is the partial detachment of one of the perimeter atoms. The relative ease of adatom motion along straight edges of stationary clusters also permits measurements of diffusion barriers at steps -- measurements useful in the interpretation of fractal vs. compact island growth on fcc metal surfaces.

2. Introduction

A comprehensive understanding of the mechanisms and energetics by which small clusters migrate across single-crystal terraces is of both fundamental and technological importance. In addition to providing physical insight into the details of adatom-surface and adatom-adatom interactions on surfaces, information on the mechanisms and energetics of cluster motion can contribute to a better understanding of crystal and thin-films growth kinetics. Recent investigations of cluster diffusion by scanning tunneling microscopy [1, 2] and calculations of cluster energetics by semi-empirical theoretical approaches [3, 4] have stimulated considerable interest in the details of cluster diffusion on surfaces. Because the clusters examined by STM are typically quite large (>50 atoms), interpretation of the results tend to be model dependent. To assess the validity of such models and to test the accuracy of the various theoretical approaches, it is desirable to have direct measurements of the activation energy of surface diffusion for clusters whose size can be controlled and monitored. Past studies have shown that the field ion microscope (FIM), with its ability to resolve individual atoms and track their movements across surfaces, is ideally suited to investigate the energetics of surface diffusion [5, 6]. However, with only a few exceptions [7-9], the FIM has been applied to the study of single-atom and dimer diffusion on surfaces [10]. Here, I report measurements

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The activation energy of surface diffusion is obtained by measuring the mean-square displacement of the cluster's geometric center and following the standard Arrhenius analysis used in FIM studies of single-atom diffusion [5, 6]. Investigations of single atoms indicate that diffusion of Rh and Pt on Rh(100) takes place by ordinary hopping displacements [11, 12], not by the exchange displacements found for self diffusion on the (100) surfaces of Pt and Ir [16, 17]. It is reasonable to assume that exchange displacements are not involved in the diffusion of clusters as well. It should be noted that the temperature range over which data could be collected in this study was too small to permit a full Arrhenius analysis of mean-square displacement versus temperature. As a result, the activation energy for each size cluster was determined at a single temperature based on the assumption that the Arrhenius prefactor is independent of cluster size and is given by "standard value" for single atoms of 10^{-3} cm^2/sec [10]. This assumption is justified to a certain extent by previous measurements of Pt cluster diffusion on W(110) [7] and Ir cluster diffusion on Ir(111) [8, 9], where the prefactor is found to be relatively insensitive to cluster size. It should be emphasized, however, that the qualitative features of the results are not affected by this assumption.

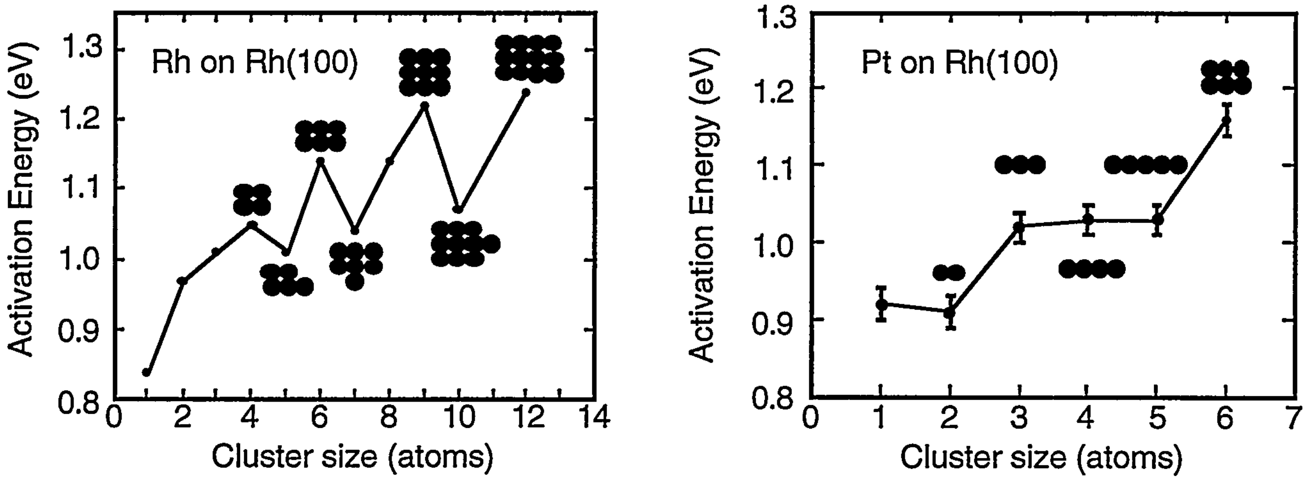

Fig. 1 Measured activation energies of surface diffusion as a function of cluster size for Rh and Pt clusters on Rh(100).

Figure 1 shows plots of the measured activation energies of surface diffusion as a function of size. Also shown on the graphs are the stable configurations of the clusters. For Rh clusters, an oscillatory behavior of the mobility as a function of cluster size is evident, as is the fact that clusters whose atoms are in compact configurations (squares and rectangles) have higher activation barriers than those with extra atoms at the periphery. Oscillations are not observed for Pt clusters, but the activation energy is also correlated with the shape of the cluster. Clusters of three, four, and five atoms, which are more stable in a chain configuration, all have the same activation energy, whereas clusters of six atoms, which prefer the compact island configuration, have a significantly higher activation energy. In neither the Rh nor the Pt system does the activation energy of surface diffusion simply increase as the cluster grows in size. This behavior leads to the conclusion that movements of individual edge atoms are of critical importance in defining the overall mobility of a cluster. The mechanism of diffusion is described in more detail in the discussion section below.

B. Edge atom and edge vacancy diffusion

The procedure used in the investigation of atom diffusion along the edge of Rh clusters on Rh(100) is illustrated by the field ion micrographs shown in Fig. 2. In this case a cluster of approximately 40 atoms is generated by terminating the field evaporation process and annealing the surface as discussed above. This procedure produces clusters approximately rectangular in shape although kinks may be present if the number of atoms is not exactly that required to produce a perfect rectangle. Adatoms are then deposited randomly on the surface. Those that land on top of the island are moved to the step edge by heating the surface to ~300 K. As the adatom moves across the surface (in a two-dimensional random walk), it eventually encounters the edge of the island. On Rh(100), the extra barrier for a Rh adatom to travel across the edge of an island (sometimes referred to as the Schwoebel [18] barrier) is negligible. Adatoms that descend from the island become incorporated at a site along the step. The surface is then heated and cooled as before and displacements of the atom are measured. Figure 2(a) shows a field ion micrograph of a Rh surface with an adatom (indicated by the short arrow) located at the edge of an island on the (100) plane. Subsequent micrographs (b)-(d) show the same surface after 30-sec. heating intervals at 236 K. At this temperature, the adatom moves back and forth along the step with the corners of the island acting as a reflecting boundary. The adatom does not detach from the island nor does it go around the corner as long as the temperature is below 330 K. Above 330 K, adatoms begin to move around the corners, but still do not detach from the island.

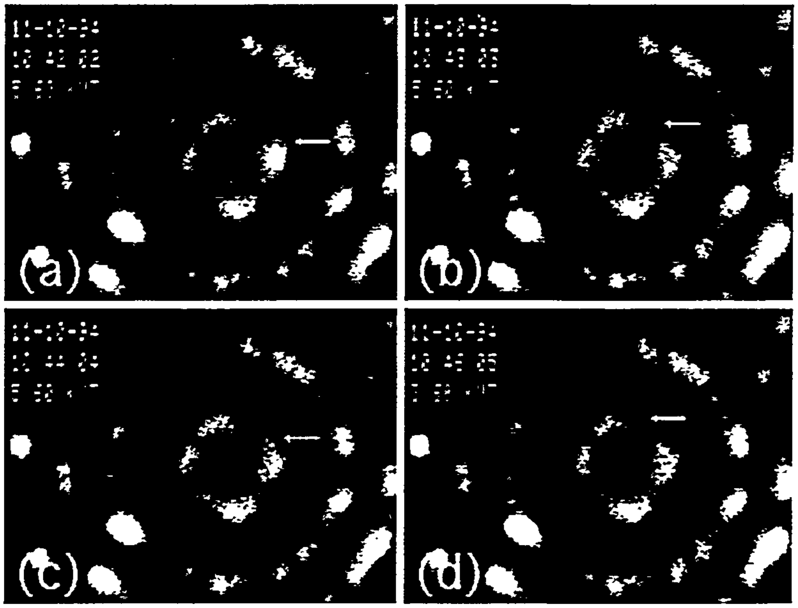

Fig. 2 Field ion microscope images showing the diffusion of a Rh atom at the edge of an island on Rh(100)

The measured mean-square displacements for a Rh adatom diffusing along the edge of a Rh(100) island at temperatures of 205 K, 212 K, 219 K, and 227 K are 1.45 ± 0.59 Å^2, 13.9 ± 4.9 Å^2, 20.5 ± 8.1 Å^2, and 27.5 ± 6.1 Å^2, respectively. Assuming the standard prefactor mentioned above, these values correspond to an activation energy of 0.58 ± 0.02 eV. The observation that adatoms diffuse around the corners of islands only when the temperature exceeds 330 K indicates that the activation barrier for this process is approximately 0.9 eV. It was not possible to gather enough statistics to measure a displacement rate for moving around corners because at this temperature, changes in the island configuration itself also occurred. The fact that the atoms did move around corners rather than dissociate from the island is consistent with the above observations of cluster diffusion without dissociation.

To gain information on the energetics of vacancy diffusion around the perimeter of islands, eight-atom clusters (octamers) of Rh on Rh(100) were investigated. The stable configuration of atoms for an octamer is a square with one of the corner atoms missing. The corner vacancy is found to move around the cluster at a temperature of 270 K, but the cluster as a whole does not move until the temperature is above 390 K. An onset temperature of diffusion of 270 K corresponds to an activation energy of approximately 0.8 eV for vacancy migration. This value is considerably less than the activation energy for center-of-mass motion of the cluster (1.14 eV).

4. Discussion

The most interesting observation related to the diffusion of Rh and Pt clusters on Rh(100) is that compact clusters have a significantly lower rate of diffusion than clusters with extra atoms at the periphery and clusters in chain configurations. Valuable insight as to why this is the case is provided by previous theoretical investigations of cluster diffusion on other fcc(100) surfaces. Molecular dynamics simulations of Ag cluster diffusion on Ag(100) by Voter [3] suggest that diffusion occurs by sequential displacements of individual atoms at the edge of the cluster. The calculations predict the same oscillatory size dependence of cluster mobility as observed in the present experiments for Rh on Rh(100). The mobility of clusters with compact geometric shapes is lower because the activation energy required to break an edge atom free from the cluster is higher. A similar result is obtained in more recent molecular statics calculations using embedded atom-method (EAM) potentials for Ni on Ni(100) [4]. In all cases the energy needed to move a peripheral atom away from the cluster is significantly less than the energy required to remove a corner atom from a compact square or rectangle. The calculations also indicate that the initial detachment-type displacements are rate-limiting. The remaining steps required to produce a net motion of the cluster involve either the return of the initially displaced atom to a site adjacent to the cluster or displacements of atoms along the cluster's periphery. The activation energies associated with these displacements, especially those for diffusion along the edges, are quite low. The prediction of a low activation barrier for atoms diffusing along the edge of an island is verified in the present experiments. As mentioned above in relation to Fig. 2, the activation energy of diffusion for an atom at the edge of an island on Rh(100) is 0.58 eV. This value is quite small compared to values greater than 1.0 eV for diffusion of the clusters as a whole. The low barrier for other displacement processes associated with diffusion at the perimeter is also evident from the low temperature required for vacancy diffusion around the perimeter of a cluster.

Although calculations involving the diffusion of chain structures such as those found for Pt on Rh(100) (Fig. 1(b)) have not been undertaken, the same qualitative arguments can be applied to explain the observed size dependence of the activation energy of surface diffusion. The rate-determining step for migration of chain structures must involve the displacement of an atom at the end of the chain. This displacement apparently is insensitive to the length of the chain. This is why trimers, tetramers, and pentamers all have the same activation energy of surface diffusion. The smallest-size cluster for a which Pt cluster is stable as an island is a rectangular-shaped hexamer. It is clear from Fig. 1(b) that the activation of energy of surface diffusion for the hexamer is considerably higher than the chain structures. Thus, consistent with the results for Rh, the mobility of Pt clusters can be correlated directly with the configuration of atoms within the cluster.

The low barriers for atoms moving along the edge of islands mentioned above also have interesting consequences related to the growth patterns of islands on fcc metal surfaces. STM measurements indicate that, within a given temperature range, submonolayer growth on fcc(111) surfaces typically proceeds in the form of dendritic- or fractal-like islands [19-22], whereas growth on fcc(100) surfaces under similar conditions proceeds in the form of compact islands [23]. The present measurements indicate that for Rh on Rh(100), the activation energy for an atom moving along the edge of an island (0.58 eV) is considerably less than that for an adatom on the open (100) plane (0.83 eV). Fast edge-atom diffusion compared to slow terrace atom diffusion is exactly what one would expect to lead to the formation of compact islands. Although similar measurements have not been carried out for atoms diffusion along the edges of islands on Rh(111), one might expect the edge-atom diffusion barriers to be comparable to those on Rh(100) due to the similarity of the atomic configurations at the step edges [at least for the (100)-faceted steps on Rh(111)]. The major difference between Rh(100) and Rh(111) is that the activation energy for terrace-atom diffusion on Rh(111) is very low (0.17 eV [6]). Thus, on (111) the situation is reversed with fast terrace-atom diffusion compared to slow edge-atom diffusion. These conditions are consistent with the dendritic- or fractal-like growth observed by STM. The reason for the difference in growth patterns on (111) vs. (100) fcc metal surfaces is therefore due to the large difference in terrace-atom diffusion barriers, not due to differences in edge-atom barriers for islands on (111) vs. (100) planes [24].

5. Summary

The primary conclusion from these experimental studies is that the mobilities of small clusters are correlated with their shape. This is markedly different from the intuitive view that cluster mobility is related only to size. For diffusion on Rh(100) compact clusters have a consistently higher activation energy of surface diffusion than clusters with extra atoms at the periphery or clusters that prefer a chain configuration. This means that the lower coordinated peripheral atoms actually destabilize the entire cluster leading to a net increase in its mobility. The qualitative agreement between the experimentally measured size dependence of the activation energies and theoretical calculations strongly supports models in which diffusion takes place by sequential displacements of edge atoms. This agreement along with the observation that the activation energy for diffusion of atoms along the edge of islands is much less than that for the cluster as a whole indicates that the rate-determining step in the diffusion of clusters is the partial detachment of atoms from the cluster core. The fact that the edge-atom diffusion barrier is intermediate between the terrace-atom diffusion barriers on the (100) and (111) planes is also consistent with STM observations of compact-island growth on fcc(100) planes and fractal-like growth on fcc(111) planes. The general agreement between the calculations and experiments also gives one confidence that the molecular dynamics and molecular statics approaches to the calculation of cluster energetics are valid and can be used to derive reasonable trends in the size dependence of diffusion energies. These calculations, as well as the direct measurements from this work, will provide much needed input into realistic simulations of thin-film growth processes required for the design of new materials.

6. Acknowledgment

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7. References

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