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# ATOMIC-LEVEL STUDIES OF CLUSTER DIFFUSION ON METAL SURFACES

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G. L. KELLOGG

*Sandia National Laboratories*
*Albuquerque, NM 87185-1413 USA*
E-Mail: glkello@sandia.gov

Direct observations of atomic motion with the field ion microscope (FIM) are providing detailed information on the mechanisms and energetics by which small clusters migrate across metal surfaces. An important result to emerge from these studies is that the activation energies of surface diffusion for small clusters on fcc(100) surfaces are strongly correlated with their shape. For Rh clusters on Rh(100) this correlation leads to an oscillatory behavior in the cluster mobility as a function of cluster size. For Pt on Rh(100) the activation energy is constant as clusters increase in size from three to five atoms and is also correlated with shape. The atomic-level mechanism involved in cluster diffusion on fcc(100) surfaces is inferred from a comparison of the measured activation energies to previous theoretical calculations.

## 1. Introduction

Our ability to fabricate new materials by controlling microscopic growth processes requires a fundamental understanding of nucleation and growth at the atomic-level. Crucial to this understanding is a detailed knowledge of the mechanisms and energetics by which material transport takes place during the growth process. Much of the current work in this area is still based on classical nucleation theory, which typically assumes that clusters smaller than a critical size are unstable and that clusters larger than this critical size grow into islands.[1] In these models, material transport is accomplished exclusively by the diffusion of single atoms. The possibility that clusters themselves contribute to transport is often ignored, even though it has been known for some time that clusters can migrate across a surface without dissociation.[2] To achieve a comprehensive picture of growth at the atomic level, one therefore needs quantitative measurements of cluster mobility as a function of cluster size. Here, I report measurements of the activation energy of surface diffusion for Rh and Pt clusters migrating across (100)-oriented single-crystal terraces of rhodium.[3]

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## 2. Experimental Methods

The experimental methods used in field ion microscope studies of single-atom surface diffusion are well documented in several reviews.[4] The procedures used in the present studies were essentially the same as those described previously, with the exception that it was necessary to assemble clusters of varying size on the Rh(100) surface. This was accomplished by building the clusters one atom at a time following a sequence of steps including deposition from a thermal evaporator, sample annealing, and field ion imaging.[3] Some of the larger homogeneous clusters were also generated by termination of the field evaporation process (high field removal of surface atoms) just prior to final collapse of the topmost atomic layer. Data collection consisted of taking snapshots as the cluster performed a two-dimensional random walk across the surface. The images were recorded with the sample at 77 K. Migration occurred during fixed time intervals at elevated temperatures with the field-ion imaging voltage turned off.

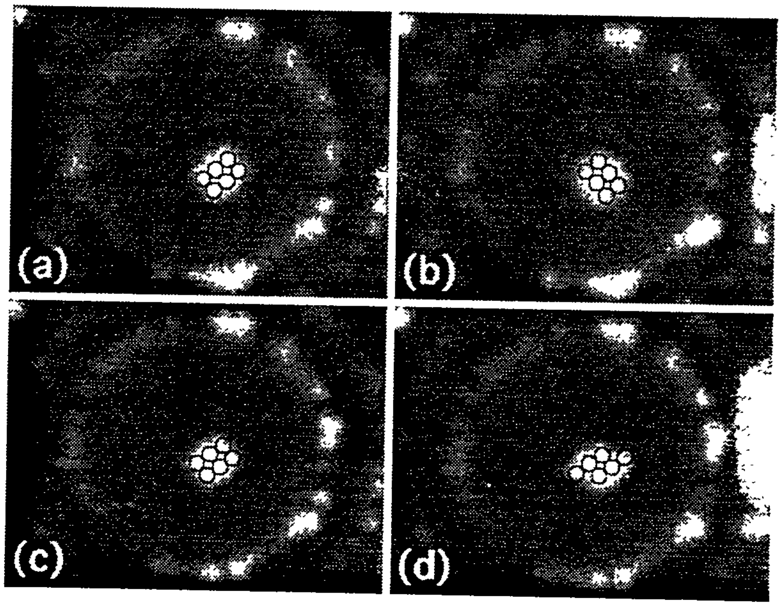

Fig. 1. Field ion micrographs showing the migration of a Rh hexamer on Rh(100). Between each photograph the sample was heated to 394 K for 30 sec. (From ref. 3)

An example of a Rh hexamer diffusing on the Rh(100) plane 394 K is shown in Fig. 1. The circular ring of spots towards the outside of the photographs defines the edge of the plane, with a step down in all directions. The superimposed circles indicate the arrangement of atoms within the cluster. Between each photograph the sample was heated to 394 K for 30 sec.

It is clear from Fig. 1 that the cluster changes its orientation and its configuration as it moves across the surface, but it does not dissociate. Diffusion without dissociation was observed for all Rh and Pt clusters investigated. At sufficiently high temperatures, the clusters migrated off the plane.

For each size cluster, the preferred (stable) atomic configuration was determined by counting the number of times a given configuration was observed. As a rule, one configuration dominated over all others. For example, the rectangular configuration for Rh hexamers seen in Fig. 1(a)-(c) was observed 74 times, whereas the metastable configuration seen in Fig. 1(d) was observed only once. In the case of Rh on Rh(100), clusters of 4-12 atoms always preferred the most compact two-dimensional island configurations. Trimers were the only Rh clusters found to be more stable in the linear configuration. In contrast, Pt clusters of up to five atoms preferred the chain configuration. Only when the clusters reached six atoms was the two-dimensional island configuration more stable. The identification of stable cluster configurations have been used in the past to provide detailed information on the atom-atom interactions involved in cluster nucleation.[5] Here, it is shown that the cluster configurations (or shapes) are also important in the energetics of diffusion across the surface.

## 3. Experimental Observations

The activation energy of surface diffusion was 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.[4] Investigations of single atoms indicated that diffusion of Rh and Pt on Rh(100) takes place by ordinary hopping displacements, not by the exchange displacements found for self diffusion on the (100) surfaces of Pt and Ir.[6] Due to the limited temperature range over which data could be collected, activation energies were determined with the assumption that the Arrhenius prefactor is independent of cluster size and given by $10^{-3}$ $cm^2/sec$, the generally accepted value for single atom diffusion.[4]

Figure 2 shows plots of the measured activation energies of surface diffusion as a function of size. Also shown on the graphs are schematic representations of the stable atomic configurations. 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 still correlated with shape. Clusters of three, four, and five atoms all have the same activation energy of surface diffusion (all are more stable in a chain configuration), whereas clusters of six atoms have a significantly higher activation energy (they prefer the compact island configuration). 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 (see below).

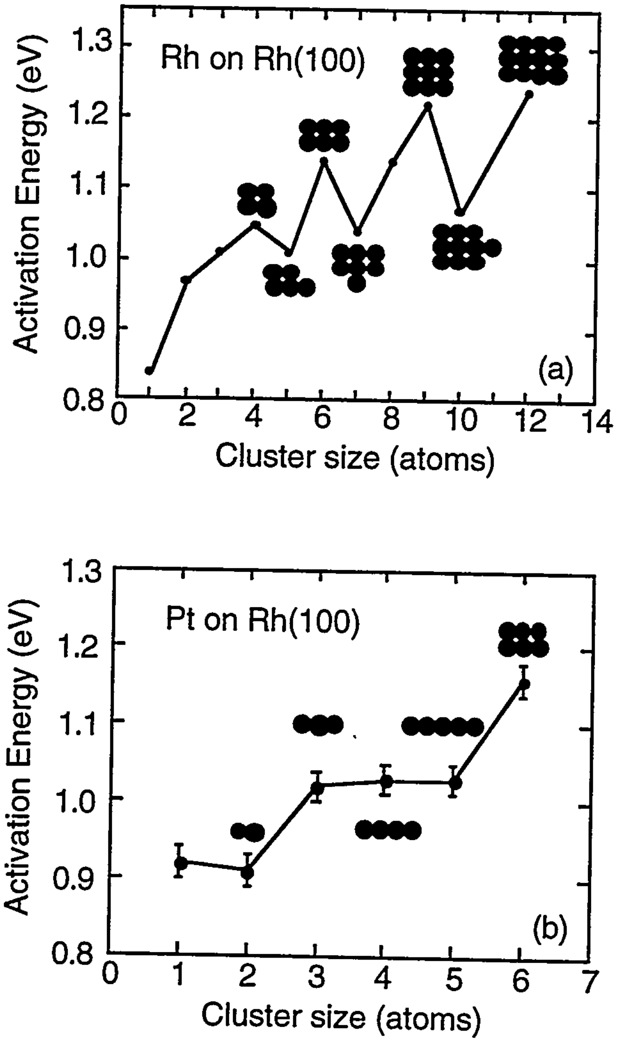

Fig. 2. Measured activation energies of surface diffusion as a function of cluster size for (a) Rh and (b) Pt clusters on Rh(100). The activation energy is correlated with the stable shape of the cluster as indicated in the inserted schematic drawings.

## 4. Discussion

Why do compact clusters have reduced mobility compared to clusters with extra atoms at the periphery and clusters in chain configurations? Previous theoretical investigations of cluster diffusion on other fcc(100) surfaces provide valuable insight. Molecular dynamics simulations of Ag cluster diffusion on Ag(100) by Voter[7] show 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 comparison of the calculated detachment energies for atoms from tetramers and pentamers illustrates this point. The calculations indicate that to detach an atom from the corner of a square tetramer requires an energy of 0.81 eV. To detach the peripheral atom of a pentamer, however, requires only 0.56 eV. A similar ratio of activation energies was found in more recent molecular statics calculations[8] using embedded atom-method (EAM) potentials for Ni on Ni(100) (viz., 1.0 and 0.68 eV). In all cases the energy to move the peripheral atom from the pentamer away from the cluster is significantly less than the energy required to remove a corner atom from a tetramer. The calculations[7,8] 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 low activation barriers associated with diffusion along edges were also observed in the present experiments. Fig. 3 shows field ion micrographs of an octamer, whose stable configuration is a square with one of the corner atoms missing. It is apparent that the corner vacancy (indicated by the arrow) moves from corner to corner during the heating intervals. This indicates that the peripheral atoms are moving around the cluster at 277 K. A net displacement of the entire cluster, however, does not occur until the temperature is increased to 390 K. Thus, consistent with the theoretical predictions,[7,8] it is possible for atoms to migrate along the edge of a cluster at temperatures well below those required for net motion of the entire cluster. This observation further supports the argument that the detachment of an atom from the edge is the rate-limiting step in cluster diffusion.

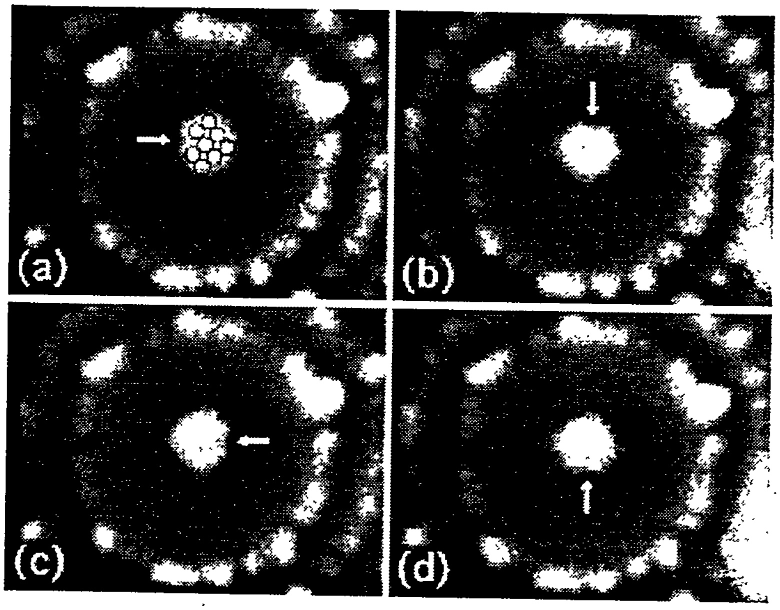

Fig. 3. Field ion micrographs illustrating the migration of a corner vacancy around a Rh hexamer on Rh(100). Between each photograph the sample was heated to 277 K for 30 sec. (From ref. 3)

Although calculations involving the diffusion of chain structures such as those seen for Pt on Rh(100) (Fig. 2(b)) have not been undertaken, the same qualitative arguments can be applied to explain the observed size dependence of the activation energy. The rate-determining step for migration of chain structures must involve the displacement of an end atom. 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. 2(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 their shape.

## 5. Summary

The key finding to emerge from these experimental studies is the direct observation that the mobilities of small clusters are correlated with their shape. This is markedly different from the general assumption that cluster mobility is related only to size. Compact clusters have a consistently higher activation energy of surface diffusion than clusters with extra atoms at the periphery. This means that the lower coordinated peripheral atoms actually destabilize the entire cluster leading to a net increase in its mobility. The excellent agreement between the experimentally measured size dependence of the activation energies and theoretical calculations[7,8] strongly supports models in which diffusion takes place by sequential displacements of edge atoms. The results are totally inconsistent with models in which the entire cluster glides as a unit across the surface.[9] The agreement 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 epitaxial growth processes required for the design of atomically engineered materials.

## 6. Acknowledgment

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