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Direct Observation of Interlayer Transport on Pt(111)

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The interlayer transport on Pt(111) has been investigated directly by observation in a field ion microscope. Although there is no effective step-edge barrier for Pt clusters containing more than two atoms, incorporation of a single atom is more effective at low temperatures. From the temperature dependence of the rate of escape of Pt single atoms from on top a monolayer height island, the additional barrier is found as 0.06±0.01eV, quite small compared to the barrier of 0.26eV for diffusion on a flat terrace.

1. INTRODUCTION

The step-edge barrier which inhibits interlayer mass transport at descending steps plays a significant role in the early stages of crystal growth[1,2]. If the step-edge barrier is small, atoms which landed on the island can readily escape to the lower layer. In this case a layer-by-layer growth is expected. On the other hand, if the barrier is so high that the adatoms on the island cannot escape rapidly, then the concentration of atoms on the island will rise until a stable nucleus is formed; growth will be three dimensional.

Following the first observations of adatom reflection at descending steps [3], some attempts were made to derive the value of step-edge barrier, but standard Arrhenius analysis of the rate of escape of adatoms proved unsuccessful [4,6-8]. Recently many detailed observations of growth on fcc(111) have become available and the height of the step-edge barrier have been estimated indirectly using simple models [9-15]. Quite recently, however, it has been suggested that step-edge barriers can be avoided altogether: on Cu(111), clusters have been found to decompose rapidly at step edge, providing a new route for interlayer mass transport [16]. A direct measurement of the step-edge barrier is clearly in order. The homoepitaxial growth on Pt(111) has already been intensively studied in nanoscale experiments [17-25], but comparison with atomistic information has so far not been possible for this or any other system. We have therefore undertaken quantitative measurements, using the field ion microscope (FIM) to examine the escape of platinum atoms and clusters from on top of the Pt(111) island.

2.INTERLAYER TRANSPORT OF ADATOMS AND CLUSTERS

The first question we address is whether atom clusters can incorporate readily into descending steps on Pt(111): is this an alternative mechanism for incorporation which can compete successfully with migration and escape of single atoms? To examine this possibility we have selected the pentamer Pt_5. The method of experiment is the same as described previously [26].

Platinum pentamers are found to migrate over Pt(111) on a time scale of 10s at T>260K. Measurement of the mean-square displacement at different temperatures yield the diffusivities in Fig.1 and give quite normal diffusion parameters in the Arrhenius plot of the diffusivity. As for the behavior of this cluster on an island, the pentamer is confined to the inner region of the island. There is an empty zone, roughly 3 nearest-neighbor distances 1 wide surrounding the inner region, in which the cluster is not observed, just as found previously for single atoms and dimers [27,28]. When the surface temperature is raised to 320K or higher, the pentamer escapes from the inner region and disappears from the island; it is never seen at the edges. This behavior is quite different from single atoms. Single adatoms, and also dimers, are observed at the island edge after escaping from the interior, which suggests that for these species there is an effective barrier at the step edge. We conclude that once the pentamer has left the inner region, there is in effect no additional barrier at the step edge.

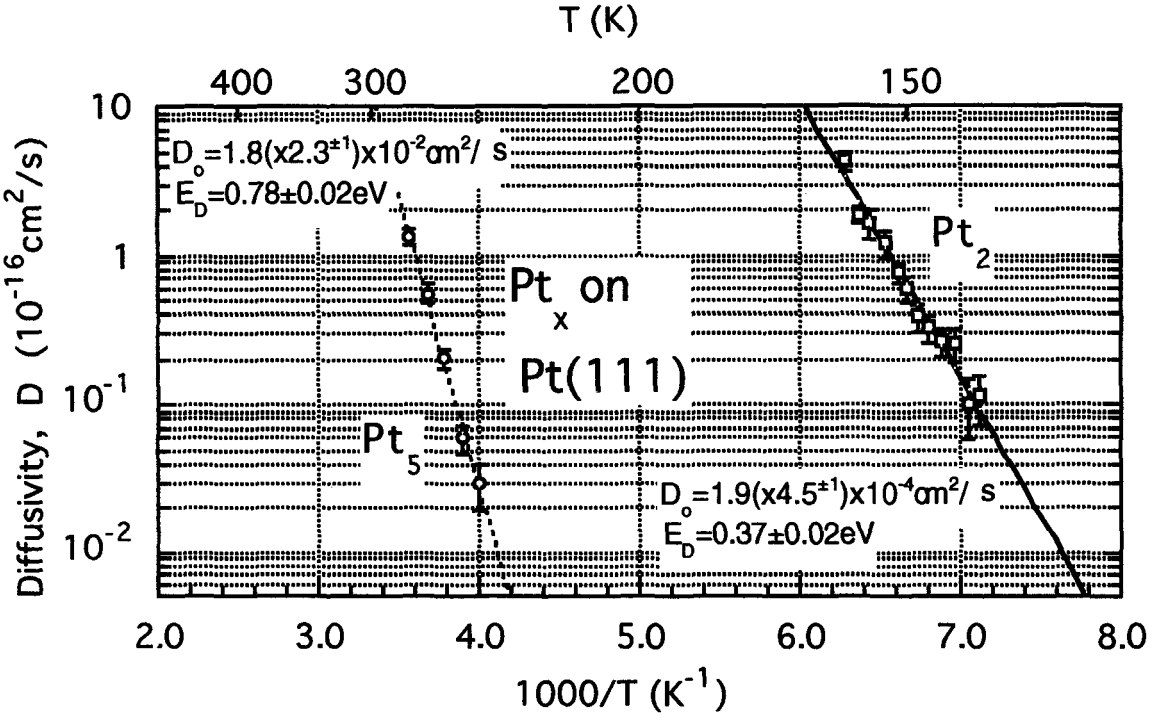

Fig.1 Temperature dependence of the diffusivity of Pt_2 and Pt_5 on Pt(111), derived from observations of the mean square displacement of single clusters.

Nevertheless, pentamers do not provide a rapid route for interlayer mass transport. Diffusion of pentamers starts at a temperature twice as high as that at which single atoms begin to incorporate into descending steps, and it is the barrier surrounding the inner region, estimated at ~0.95eV, that really limits incorporation of pentamers. Even the most mobile of clusters, dimers, only begin to diffuse at T~140K as shown also in Fig.1; incorporation is observed at T>190K. Single Pt atoms already incorporate into descending steps at much lower temperatures, T>120K; the primary vehicle for growth of platinum layers clearly must be Pt adatoms rather than clusters.

The question that now has to be answered is: What are the kinetics governing incorporation of Pt adatoms into a growing cluster? To this end we have made observations on monolayer height Pt(111) islands with radius of ~20l. In Fig.2 are shown the rates of incorporation $1/\tau$ at temperature from 120 to 140K, derived from observations on ~20 individual adatoms at each temperature. The activation energy of incorporation $E^{\ddagger}$ is found as 0.32±0.01eV. This is to be compared with the data for diffusion of Pt atoms on Pt(111) [28], for which an activation energy E_D=0.26±0.003eV have been derived from direct observations on individual adatoms, in agreement with deductions from studies of island formation on Pt(111) [18]. For incorporation, Pt adatoms therefore have to overcome a small additional energy barrier E_s of 0.06±0.01eV, above and beyond that for diffusion.

3. STEP-EDGE BARRIER AND GROWTH

What is most surprising is the disparity between the step-edge barrier E_s measured in direct observations of the escape of Pt atoms from a Pt(111) island, and the indirect results, deduced from observations of growth on Pt(111). Depending upon the particular analysis of the growth studies [17], the additional step-edge barrier E_s for Pt atoms on Pt(111) has been given as 0.21-0.25 [11], 0.15-0.21 [10], 0.31 [12], and 0.21eV [13,29]. Our direct measurements yield a much smaller value, E_s = 0.06 ± 0.01 eV.

Recently, however, two interesting papers appeared. P. J. Feibelman reported ab initio calculations showing a very small step-edge barrier, E_s, ~ 0.02 eV, for A-type edges on Pt(111). This is significantly lower than our measured E_s and implies incorporation even at ~ 100 K [30]. On B-type edges, however, E_s = .35 eV, a different order of magnitude

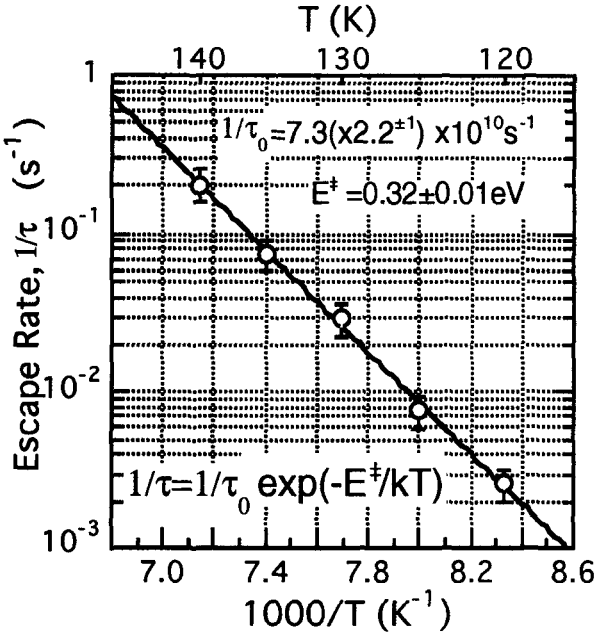

Fig.2 Arrhenius plot of the rate at which Pt adatoms escape from a Pt(111) island with a radius of ~20l.

than on A. More recently, M. Kalff et al. have found that previous growth experiments on Pt(111) were in fact marred by contamination which affected all aspects of homoepitaxy [31]. This presumably accounts for the high values of E_s previously derived from growth experiments; on "clean" Pt(111), Kalff et al. now estimate $E_s \sim 0.08$ eV.

At 205 K, the rate of adatom escape from islands with a radius of ~40Å, the maximum size before coalescence in the work of Bott et al. [17] is ~ $1x10^3$/s. At their deposition rate of ~ $3.3x10^{-3}$ monolayers/s , the rate of escape is more than two orders of magnitude higher than the rate of atom arrival at an island. Therefore the small step-edge barrier found by direct observation leads to the prediction of 2D growth below room temperature; the so-called reentrant layer-by-layer growth [21,24], reported in macroscopic studies at T~200K, is exactly what is expected from our barrier estimate.

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