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Growth and the diffusion of platinum atoms and dimers on Pt(111)

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Abstract

The diffusion of platinum adatoms and dimers on Pt(111) has been measured at different temperatures by direct observation in a low-temperature field ion microscope. The activation energy for single atom motion is found to be 0.260 ± 0.003 eV, while for dimers it is 0.37 ± 0.02 eV. Comparison with previous results obtained in STM studies of the density of islands after deposition from the vapor as well as with theoretical estimates are now possible. The former are in excellent agreement, the latter less so, but empirical extrapolation from the neighboring iridium proves useful. Contributions from dimer diffusion to growth at low temperatures can also be assessed, and are found to be minor. © 1998 Elsevier Science B.V.

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1. Introduction

In the growth of crystals and thin films, surface diffusion is now generally recognized as playing a vital role affecting the overall kinetics [1–3]. Despite that, little direct information about the movement of atoms and clusters over the surface is available for one of the more intensively studied systems, the growth of platinum layers on Pt(111) [4–11]. Platinum is also of obvious intrinsic interest because of its importance as a heterogeneous catalyst of chemical reactions [12].

Efforts have been made previously to directly characterize atomic behavior on Pt(111) by field ion microscopy [13,14]. However, technical problems have prevented the analysis necessary for independently determining the activation energy E_D and the prefactor D_0 which describe the temperature dependence of the diffusivity D in the Arrhenius relation $D = D_0 \exp(-E_D/kT)$. There have, however, been numerous attempts to characterize diffusion on Pt(111) by alternative methods. Various theoretical approaches have been tried in estimating the activation energy for diffusion [14–22]. More consistent results have been obtained by interpreting STM observations of the growth of islands in terms of kinetic models [23,24], and also in electron microscopic examination of Pt(111) after electrochemical treatment [25]. However, concerns have been raised about the role dimer diffusion may play in affecting the kinetics of growth [16,26–28], and therefore also in affecting indirect deductions about atom motion.

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In view of all the previous activity and the importance of platinum surfaces, we report here an extensive examination of diffusion on Pt(111), using a low-temperature field ion microscope to observe the behavior of individual adatoms as well as of platinum dimers (Pt_2) on the Pt(111) plane.

2. Notes on measurement and analysis

Measurements on individual adatoms are in principle simple, and the equipment and procedures used in our studies have all been described previously [29–31] To determine diffusivities, the displacement of an atom, after migration in the absence of any applied fields at a predetermined diffusion temperature, is measured at a low temperature ($T \approx 20$ K) Repetition eventually yields an estimate of the mean-square displacements such as $\langle \Delta x^2 \rangle$. The Einstein relation

$$\langle \Delta x^2 \rangle = 2Dt, \tag{1}$$

together with a knowledge of the diffusion interval t then leads to an estimate of the diffusivity D. The diffusion parameters (i.e. the activation energy E_D and the prefactor D_0 in the Arrhenius equation) are finally derived by repeating these operations at different diffusion temperatures. At least three practical problems must be solved to implement this scheme successfully.

(1) The Einstein relation (Eq. (1)) is valid for random motion on an infinite plane. Actual observations are made on a very finite surface, usually with a diameter of <100 Å. Corrections for the finite plane size must therefore be applied to the measured mean-square displacement [32].

(2) On heating the sample, the surface is not brought instantly to the diffusion temperature, and neither does the surface cool instantly once the heating current to the sample support is cut. Diffusion during these transient periods must be measured separately, by interrupting the heating as soon as the diffusion temperature is reached This heating transient correction is then subtracted from the measured mean-square displacement to obtain the value appropriate to the chosen diffusion temperature [33].

(3) Accurate knowledge of the temperature is crucial in deducing reliable values of the diffusion parameters, especially since diffusion of Pt atoms on Pt(111) is already noticeable at temperatures considerably below 100 K. The tungsten support loop on which the Pt sample is spot-welded is therefore used as a resistance thermometer. For this study, we have relied on the resistance versus temperature scale given by Desai et al. [34], and procedures have been newly optimized for measurements below room temperature.

3. Observations of Pt on Pt(111)

3 1. *Diffusion of single adatoms*

Displacements of individual Pt atoms over the central region of the Pt(111) plane [35] have been examined at eight temperatures ranging from 86 to 98 K. At each temperature, diffusivities have been calculated based on ~100 atom displacements. From the Arrhenius plot in Fig 1, obtained on surfaces with a radius of ~13 nearest-neighbor spacings l for the central region, we arrive at an activation energy for diffusion E_D of 0.260 ± 0.003 eV and a prefactor $D_0 = 2.0(\times 1.4^{\pm 1}) \times 10^{-3}\ \mathrm{cm^2\,s^{-1}}$ Earlier, less detailed studies were carried out on a separate sample, on

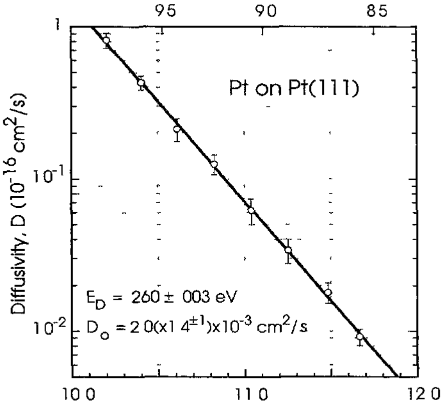

Fig. 1 Temperature dependence of the diffusivity of single Pt atoms on Pt(111) All values obtained on central regions with a radius of ~13l Only the statistical uncertainties of the diffusion parameters are indicated

surfaces with a central radius of ~8*l*. These studies gave an activation energy of 0.252±0.014 eV. It appears that in this range, the size of the surface on which diffusion actually takes place is not a significant factor.

Only the statistical uncertainties have been considered in these estimates of the diffusion parameters. Uncertainties of ±0.5 K in the absolute value of the temperature could change the activation energy by ~±4 meV, but the various corrections to the mean-square displacement measured in the experiments make only small contributions to the final values. Failing to compensate for the finite plane size lowers the activation energy by less than one tenth of the standard deviation. Without a correction for diffusion during heating transients, the activation energy would be ~5% higher.

3.2. Dimer diffusion

In order to examine platinum dimers, two Pt atoms are deposited on the (111) plane, and are then allowed to diffuse over the central region of the plane until they combine. Once this happens, the individual atoms are no longer distinguishable, but the dimer center is clearly imaged. No dissociation of dimers has been found after heating to temperatures $T<210$ K. However, binding sites for the dimers are observed to be consistently shifted in one direction compared to the grid describing single-atom sites. We attribute this to a reorientation of the dimer during imaging. Under our conditions, corrections for this effect are automatically included in the measurements of dimer displacement during heating transients. All observations have been made on central regions with a radius of ~13 nearest-neighbor spacings *l*. From the Arrhenius plot in Fig. 2 of measurements extending over 12 temperatures ranging from 140 to 159 K, the activation energy for dimer motion on Pt(111) appears as 0.37±0.02 eV, with a prefactor of $1.9(\times 4.5^{\pm 1}) \times 10^{-4}$ cm^2 s^{-1}.

3.3. Comparisons

Our direct observations of single Pt atoms diffusing on Pt(111) can be compared with the deductions of Bott et al. [23] from the density of platinum islands observed after deposition and diffusion for a fixed time interval on a macroscopic (111) plane. From measurements at different temperatures $T \geq 110$ K, they found an activation energy of $E_D = 0.26 \pm 0.01$ eV, in remarkable agreement with the present value from direct observations. They also give a frequency factor of $\nu_0 = 5 \times 10^{12 \pm 0.5}$ s^{-1}, which corresponds to a diffusivity prefactor $D_0 = 9.6 \times 10^{-4}$ cm^2 s^{-1}. Although this is roughly half the value from the present measurements, it is still within the expected uncertainty of the estimates.

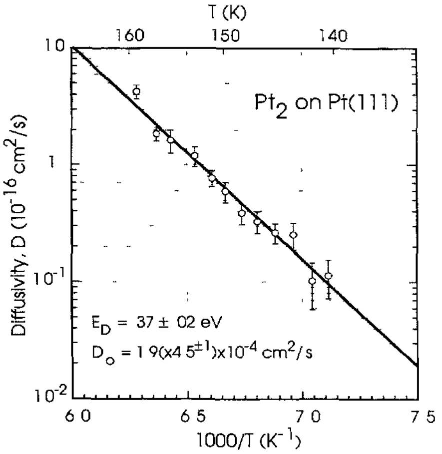

Fig. 2. Diffusivity of Pt$_2$ clusters on Pt(111). On the planes studied, the radius of the (111) central region is ~13*l*.

In carrying out their analysis, Bott et al. [23] assumed that diffusion of dimers did not occur to any appreciable extent at temperatures $T \leq 245$ K. Allowing dimer diffusion, but with an activation energy at least 0.09 eV higher than for single atoms, did not affect the island density found in simulations. Our results for the diffusion of Pt$_2$, which occurs over a barrier 0.11 eV higher than for single atoms, validates their simplifying assumption.

4. Pt atoms and dimers on Pt(111): some comments

4.1. Dimers in growth

A recently popular way of deducing diffusivities from growth experiments has been to measure the saturation island density N_S at different temperatures [1–3,36–40]. If it is assumed that dimers are the smallest stable clusters, and that clusters are essentially immobile, then the density of islands formed at saturation for a fixed coverage is given by the scaling relation [1,41]

$$N_S \propto (F/D)^{1/3}, \tag{2}$$

where F is the deposition flux Questions have, however, arisen concerning the validity of the assumptions about dimers [27,28], but we are now in a position to assess the conditions under which these assumptions are appropriate in the nucleation of Pt islands on Pt(111).

From our experiments, we know that platinum dimers are indeed stable entities: they do not dissociate at temperatures $T<210$ K. What about dimer mobility? This will have a significant effect upon the density of islands if dimer mobility leads to association with other islands at a rate faster than the rate at which dimers combine with single atoms. According to Villain et al. [26], this condition will prevail if the jump rates j_1 and j_2 for monomers and dimers, respectively, satisfy the requirement

$$j_2^3/j_1^2 > F. \tag{3}$$

Using the measured values for Pt adatom and dimer diffusivities, the critical flux $F_C = j_2^3/j_1^2$ is plotted in Fig. 3 at different temperatures For the experiments in which Bott et al. [23] measured the saturation island density (i e. with $F = 6.6\times10^{-4}$ monolayers s^{-1}), dimer diffusion will be important at $T>238$ K. This limit is above all except the two highest temperatures at which saturation densities were measured In fact, at the highest temperature ($T=265$ K), Bott et al noted that the island density observed lies below the predicted value, as would happen if dimer diffusion had become important. For the earlier experiments by Bott et al [42], with a deposition rate of 3.3×10^{-3} monolayers s^{-1}, dimer diffusion only becomes a significant factor at temperatures $T>252$ K. The estimate by Bartelt and Evans [24] of the diffusivity of Pt on Pt(111) at 205 K therefore remains unaffected. At the low tempertures at which saturation densities of Pt islands have been measured on Pt(111), diffusion of dimers does not significantly affect the kinetics.

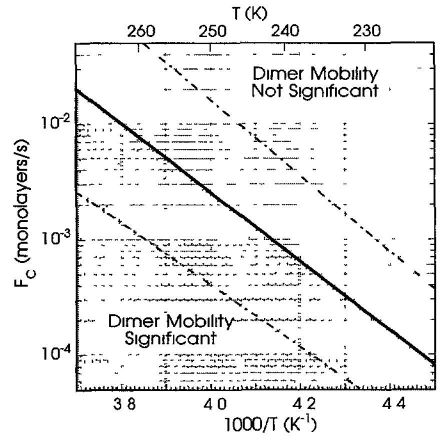

Fig 3 The effect of dimer mobility on island density, as predicted by Eq (3) for F_C, the critical value of the incident flux of Pt atoms on Pt(111) At fluxes below F_C, dimer mobility is significant in the kinetics of growth Dotted/dashed lines indicate the error limits of F_C Dissociation of the dimer is assumed to be negligible throughout

4.2. Diffusion

The activation energies for diffusion measured both for individual Pt adatoms and dimers are in some ways quite surprising. There is very good agreement in the activation energy for atom motion from direct observations and from experiments on the growth of platinum islands on Pt(111). More unexpected is the close coincidence of the activation energy for diffusion at the Pt(111)–vacuum interface (0.260±0.003 eV) and the value of 0.20±0.05 eV deduced by Twomey et al. [25] for diffusion on Pt(111) in 1M sulfuric acid More detailed studies at the (111)–electrolyte interface, to probe diffusion in greater detail, would certainly be desirable to establish whether the apparently lower diffusion barrier in solution is a general effect.

For comparison with the experiments, we list in Table 1 theoretical estimates of various sorts for the barrier to Pt atom motion on Pt(111). All are estimates of the static potential energy barrier to diffusion, which can differ significantly from the activation energies derived from Arrhenius plots

Table 1
Calculated self-diffusion barriers on Pt(111)[a]

Ref	Feibelman (FP, Pt)	Mortensen (FP, Pt)	Boisvert (FP, Pt)	C.L. Liu (SE, Pt)	S. Liu (SE, Pt/Pt_2)	Stoltze (SE, Pt)	Villarba (SE, Pt)	Wang (SE, Pt)	Li (SE, Pt)
E_D (eV)	0.38	~0.36	0.33	0.007	0.13/0.16	0.16	0.08	0.038	0.048

[a] Experimental values 0.260 eV for Pt, 0.37 eV for Pt_2.
FP first principles, SE semi-empirical

[43–45]. However, the indications are that on fcc (111) planes these differences are small at low temperatures [46–48]. It appears from Table 1 that effective medium theory and similar semi-empirical (SE) approaches [17] all quite significantly underestimate the barrier height to atom diffusion. Estimates for Pt dimers from effective medium theory are also considerably below the experimentally measured value of 0.37 eV. The three first-principles (FP) calculations for Pt adatoms on Pt(111) [14,21,22] yield values much higher than the measured activation energies, with the most recent calculations closer to the experiments but still ~25% too high. At the moment, it appears that calculations provide at best an uncertain guide to the diffusion of platinum on Pt(111).

Entirely empirical comparisons with diffusion on the neighboring element (i.e. iridium) fare better. Migration of single Ir atoms has been extensively examined on Ir(111) [49–51]. The currently most reasonable value for the activation energy to diffusion is 0.289±0.003 eV, while the prefactor is $3.5(\times 1.4^{\pm 1}) \times 10^{-4}$ cm^2 s^{-1} [52]. If, as has been done on other surfaces [30], we scale the activation energy by the ratio of the cohesive energy [53] of Pt (5.859 eV) compared to that for Ir (6.895 eV), then we can expect an activation energy for self-diffusion on Pt(111) of 0.246±0.003 eV. This estimate is only ~6% below the value actually measured, and is by far the best approximation presently available.

In looking for trends in the diffusion of dimers, it is useful to consider the ratio of the activation energy for motion of dimers to that of single adatoms. On Pt(111), this ratio is 1.43±0.08. For Ir on Ir(111), diffusion of dimers occurs over a barrier of 0.447±0.013 eV [54,55], a factor of 1.54±0.05 times the value for single Ir adatoms. The prefactor for dimer motion is $2.6(\times 2.2^{\pm 1}) \times 10^{-5}$ cm^2 s^{-1}, roughly an order of magnitude smaller than for Ir adatoms, as is the ratio of prefactors for Pt. Given the considerable uncertainty in these ratios, the agreement between iridium and platinum is reasonable, and it appears that empirical correlations also are useful for dimer diffusion.

The conclusion from the various comparisons of diffusion on Pt(111) is that the present capabilities for making quantitatively reliable predictions are quite limited. However, by exploiting similarities in the behavior of neighboring elements, it is possible to derive sensible if entirely empirical information about surface diffusion. The experimental situation appears most hopeful. entirely different methods for examining the diffusion of Pt adatoms on Pt(111) have produced diffusion parameters which are in quantitative agreement

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