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Dynamics of Pt adatoms and dimers on Pt(110)-(1 × 2) observed directly by STM

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Abstract

The one-dimensional diffusion of Pt adatoms as well as the formation/dissociation kinetics of Pt dimers in the missing row troughs of the (1 × 2) reconstructed Pt(110) surface is monitored directly from atomically resolved time-lapsed STM images. For this self-diffusion system, it is found surprisingly that not only jumps between nearest neighbour sites but also long jumps, i.e. jumps between next nearest neighbour sites participate. The hopping rate for these long jumps is found to follow an Arrhenius dependence on temperature with an activation barrier for diffusion $E_{d2} = 0.89$ eV slightly larger than that for single jumps $E_{d1} = 0.81$ eV. It is found that dimers dissociate with a rate only slightly below that for single atom diffusion. Using the data obtained for the latter, the formation/dissociation kinetics of Pt dimers in the missing row troughs can be analysed and the binding energy of the Pt dimer is determined to be $E_b = 0.07$ eV.

Keywords: Growth; Nucleation; Platinum; Scanning tunneling microscopy; Surface diffusion

1. Introduction

A detailed understanding of adatom diffusion and adatom–adatom interactions on metal surfaces is crucial for our ability to predict and control processes in such diverse areas as crystal and thin film growth, heterogeneous catalysis and oxidation. The time-honoured technique for direct atomic-scale observation of diffusing and interacting metal adatoms is Field-Ion Microscopy (FIM), where adatom dynamics can be followed on small terraces at the apex of very sharp FIM tips [1,2]. In addition, more recently, Scanning Tunnelling Microscopy (STM) has provided valuable information on surface diffusion and adatom cohesion, but mainly in an indirect manner from nucleation and growth experiments [3–7]. With its capability of resolving individual atoms, however, STM also has a great potential for revealing dynamic processes directly at the atomic level [8–10]. This possibility has hitherto only been exploited to a very limited degree for metal-on-metal systems.

By means of atomically resolved time-lapse STM movies, we have studied the dynamic behaviour of Pt adatoms confined to the missing row troughs of the Pt(110)-(1 × 2) reconstructed surface [10,11]. The self-diffusion in this one-dimensional (1D) system is found surprisingly to incorporate a significant proportion of long jumps, i.e. processes where a diffusing adatom, once promoted to a transition state, spans two lattice spacings before

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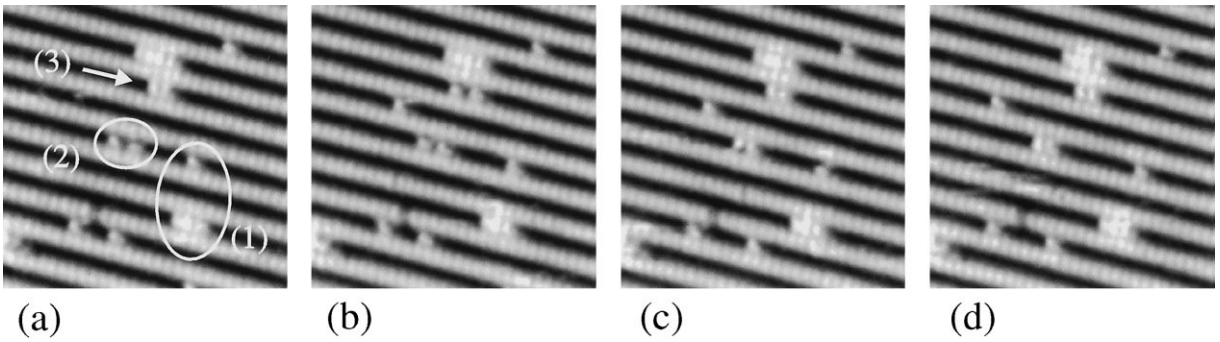

Fig. 1. Series of STM images showing the dynamic behaviour of Pt adatoms situated in the missing row troughs of the Pt(110)-(1 × 2) reconstructed surface. In image (a), an isolated adatom and an adatom trimer are marked by (1), and from image (a) to (d), the adatom can be seen to diffuse relative to the trimer which is stable. The adatom pair marked (2) in image (a) forms a dimer in going from image (b) to (c). Finally, the dimer (3) in image (a), situated next to a four-atom large island, dissociates from (a) to (b) and reforms from (b) to (c).

retrapping rather than migrating in the ordinary fashion between nearest-neighbour lattice sites ([12–16], and references therein). Pt dimers situated in the missing row troughs are found to be weakly bound, dissociating with a rate only slightly below that for adatom hopping.

Experimental details have been reported elsewhere [10]. In brief, a submonolayer amount of Pt is deposited, and the sample is transferred to the STM for imaging at temperatures ranging from 280 K to 380 K. The image acquisition time is varied according to the atomic mobilities, with values ranging from 2 to 20 s per image. Fig. 1 depicts a four-image excerpt from an STM movie. More extensive examples can be found at our WWW site (http://www.dfi.aau.dk/condensm/surface/stmlab/ptmovies/ptmovies.htm). The deposited Pt atoms are found in the 1D missing row troughs, and the close-packed Pt rows separating these troughs are imaged with atomic resolution. Several single adatoms can be found in the troughs, whereas others have nucleated and formed dimers or grown into a trimer or a larger 1D island. In the excerpt shown, diffusion of single adatoms as well as the formation and dissociation of dimers can be identified. In the investigated temperature interval, we did not observe any events in which an adatom traverses from one missing row trough to another, and therefore, the diffusion is truly 1D.

2. Adatom diffusion

From the determined adatom positions, a distribution of image-to-image displacements of the diffusing adatoms can be derived, as shown in Fig. 2. The observed displacements of adatoms cannot simply be equated with the actual adatom

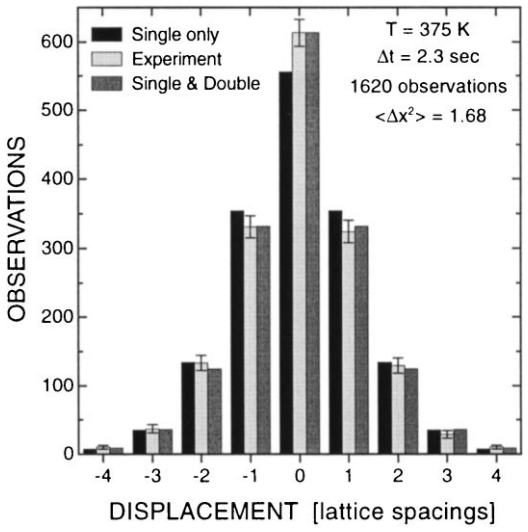

Fig. 2. Distribution of displacements for the self-diffusion of Pt on Pt(110)-(1 × 2) at 375 K. The best fit (dark gray) is obtained with a double to single jump ratio $h_2/h_1 = 9.5\%$. The distribution corresponding to diffusion by single jumps only is shown in black.

jumps, however. An adatom might perform several jumps between consecutive images, which could be observed as either a displacement over several lattice spacings or, if the atom jumped back and forth, no displacement at all. A suitable model thus has to be applied in order to unravel the adatom hopping rates and reveal a possible contribution from double jumps.

The appropriate analysis of a 1D random walk in continous time, including the possibility that an adatom can make long jumps, has been carried out in detail by Ehrlich and co-workers [17]. They found that the probability $P_x(t)$ of an atom, initially at position $x=0$ at time $t=0$, to be at lattice site x at some later time t is given by

$$P_x(t)=\exp[-(h_1+h_2)t]\sum_{j=-\infty}^{\infty} I_j(h_2t)I_{x-2j}(h_1t), \quad (1)$$

where I_n are the modified Bessel functions of the first kind of order n, and h_1 and h_2 are the rates for single and double jumps, respectively.[1] In the present context, t is the time-interval between consecutive images. The adatom hopping rates, h_1 and h_2, are determined by fitting the expression for $P_x(t)$ to the probabilities obtained from the measured distributions of adatom displacements. The validity of this approach has been thoroughly checked by fitting to displacement distributions obtained from kinetic Monte Carlo simulations of a 1D random walk incorporating single and double jumps. As shown in Fig. 2, the measured displacement distributions can only be accounted for by including significant contributions from double jumps.

The determined hopping rates for single and double jumps are plotted in Fig. 3 versus $1/T$. By fitting to the Arrhenius form, $h=\nu\exp(-E_d/k_BT)$, we obtain for the single jumps: $E_{d1}=0.81\pm 0.01$ eV, $\nu_1=10^{10.7\pm0.2}\,s^{-1}$ and for the double jumps: $E_{d2}=0.89\pm0.06$ eV, $\nu_2=10^{10.9\pm0.8}\,s^{-1}$.

The immediate way to think of a double jump is as a process where the diffusing adatom crosses

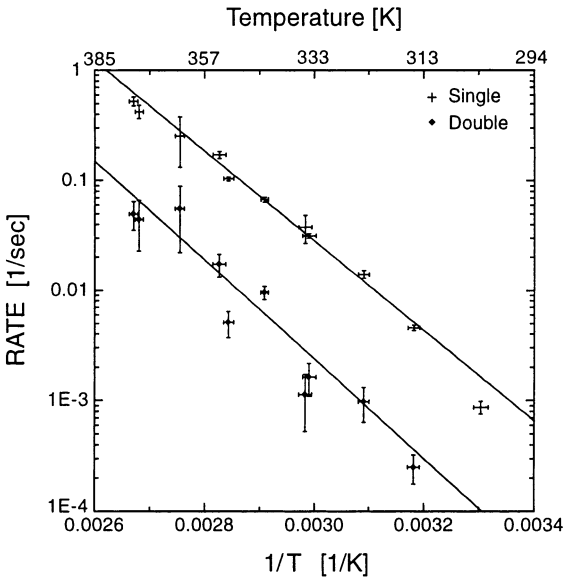

Fig. 3. Arrhenius plot of the determined rates for single and double jumps, h_1 and h_2.

the transition state between two adsorption sites with sufficient extra energy such that it can sustain some energy loss while still being able to overcome the next activation barrier [14–16]. In recent theoretical work by Jacobsen and coworkers [18], however, the smallest thermal fluctuation for which a double jump happens is shown to occur when energy, stored in lattice degrees of freedom at the time when the diffusing atom is at the first saddle point, is transferred to the adatom as it crosses the central well and conspires to push it on top of the second saddle point. Developing what they call Transition Path Theory, Jacobsen et al. show that the rate for double jumps is of the form $h_2\sim\sqrt{T}\exp(-E_{TP}/k_BT)$ with E_{TP} being the energy for this transition path. From molecular dynamics simulations of the Pt/Pt(110) system, they determined a value of $\Delta E=0.120$ eV for the extra energy required for a double jump to occur. This value is of the same magnitude as the $E_{d2}-E_{d1}=0.08\pm0.06$ eV derived here from the experiment.

Other experimental observations of long jumps are still very scarce. In a FIM study by Senft and Ehrlich [12], a significant contribution from long jumps was revealed for the diffusion of Pd on

[1] The actual fitting procedure allows for jump lengths up to 4 nearest neighbor spacings, yet it was found that triple and longer jumps do not play a statistically significant role in the temperature range investigated in this work.

W(211), whereas for self-diffusion of W on W(211), no long jumps were found to occur.

Interestingly, hopping rates for Pt on the unreconstructed Pt(110) surface reported by Kellogg from FIM measurements are roughly two orders of magnitude higher than the hopping rate h_1 determined here for Pt adatoms in the missing row troughs [19].

3. Dimer dissociation

Adatom–adatom interactions have been quantified from the acquired STM-movies by investigating the kinetics of dissociation and formation of dimers in the missing row troughs [11]. The rate by which adatom dimers dissociate is found to be only a factor of 2–3 below the hopping rate for isolated adatoms, h_1. The kinetics of dimer formation is quantified from the image-to-image evolution of adatom pairs situated in the missing row troughs and separated by a single empty lattice site (see Fig. 1). Such pairs are found to have roughly a 4:1 preference for forming a dimer compared to moving further apart. This is interpreted in terms of a reduced activation barrier for dimer formation compared to that for adatom diffusion.

From the described findings, the binding energy, E_b, for a Pt dimer situated in the missing row troughs of the Pt(110)-(1×2) reconstructed surface is determined to be $E_b = 0.07 \pm 0.02$ eV. This low value for E_b compared to 1/6 of the cohesive energy for Pt (5.84 eV per atom) is in line with previous findings for metal dimers on W surfaces [2]. The origins of such weak adatom–adatom cohesion has previously been addressed theoretically by Feibelman [20] in calculations for Al on Al(100). He found that as an Al dimer forms, the adatom bonds to the surface weakens, resulting in an overall low dimer binding energy.

Whereas dimers dissociate quite readily, trimers and larger islands are found from the STM movies to be stable towards decay by adatom detachment in the probed temperature interval.

4. Outlook

The Pt/Pt(110)-(1×2) system provides a highly interesting 1D case of homoepitaxial growth. The visualization provided by STM movies of dynamic processes involved in nucleation and growth enables one to obtain a unique insight into how these affect the resulting growth morphology. For instance, measured island size distributions may be related to the observed attachment/detachment kinetics of adatoms to/from islands and to direct observations of island coalescence. Analysis is currently in progress to further quantify such observations.

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