# New Approach for Determination of Diffusion Parameters of Adatoms

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A new approach for the determination of activation energy and attempt frequency for the diffusion of single adatoms on a surface is proposed and demonstrated for Pt adatom diffusion on Pt(111). The method is based on a combination of low temperature scanning tunneling microscopy (STM) measurements and kinetic Monte Carlo simulations. The method involves only a minimum of assumptions and is independent of classical nucleation theory. This independence allows one to analyze the applicability of the latter. In addition, it is found that the measurement of the mean square displacement of individual adatoms is influenced by the STM tip.

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Probably the most fundamental diffusion process in molecular beam epitaxy is the migration of the deposited atoms on the substrate, which enables the formation of deposit islands. The basic quantities characterizing adatom migration are the activation energy $E_d$ and the attempt frequency $\nu_0$. Besides the field emission microscopy approach [1] there are two methods to determine these parameters: the measurement of the temperature dependence of the mean square displacement adatoms by field ion microscopy (FIM method) [2] and the analysis of the temperature dependence of the island number density by the rate equation approach of the nucleation theory (nucleation theory method) [3–5]. While the FIM method involves only basic diffusion theory, the nucleation theory is rather sophisticated and its application always involves assumptions and approximations of the physical situation. Both methods have been applied successfully. In addition, Monte Carlo simulations of simple models were used to test and improve its formulation [6,7]. However, to the authors' best knowledge it has not yet been tried to test experimentally the applicability of the nucleation theory without presupposing its validity. Such a test of the nucleation theory might allow direct insight into the nature and relevance of the approximations to the physical situation involved in its application.

In this Letter we report a new method for determination of $E_d$ and $\nu_0$ in the temperature range just above the onset of adatom migration, based on scanning tunneling microscopy (STM) measurements and kinetic Monte Carlo (MC) simulations, involving only a minimum of assumptions. This method is independent of nucleation theory and enables us to perform a test of the nucleation theory method for the Pt adatom migration on Pt(111).

The experiments were performed in a variable temperature STM system with a base pressure of $5 \times 10^{-11}$ mbar described elsewhere [8]. The sample crystal was carefully prepared and cleaned before each deposition experiment according to standard procedures [8]. In order to remove gas atoms adsorbed during the initial cool down to 20 K, the sample is flashed prior to the low temperature deposition. After that, the density of impurities was less than $10^{-6}$ Å$^{-2}$ as checked by STM imaging. Pt deposition was performed by electron bombardment heating of a thoroughly cleaned Pt foil located in front of the sample. Immediately after deposition of the desired amount with the precisely controlled deposition rate $R = (6.6 \pm 0.7) \times 10^{-4}$ ML s$^{-1}$ (where ML denotes monolayer) at the specified sample temperature, the sample was cooled to 20 K for STM imaging.

In the MC simulations the deposition with a rate of $6.6 \times 10^{-4}$ ML s$^{-1}$ on a triangular lattice with $3 \times 10^4$ sites is chosen randomly in space and in time [9]. For temperatures below 245 K considered here (i) adatom migration on the Pt(111) surface and (ii) atom jumps from onefold coordinated to twofold coordinated sites at step edges are the only atomic processes relevant in the simulation. In particular, (iii) the diffusion of twofold coordinated atoms along step edges, (iv) dimer dissociation, (v) dimer diffusion, and (vi) transient mobility are either ruled out or irrelevant for the island densities obtained in the MC simulations. Assumptions (ii), (iii), and (iv) follow directly from a quantitative analysis of the temperature dependence of the average coordination number of atoms in large adatom islands (coverage $\approx$0.1 ML) [10] and are in agreement with the available FIM data for Pt and other fcc metals [2,11]. It has to be emphasized that due to the small island sizes in the main experiment, which establishes the new method, the corresponding MC simulations are *not* affected by the validity of assumptions (ii) and (iii). The assumption of the irrelevance of dimer diffusion up to 245 K [process (v)] needs a closer inspection. In order to test this approximation we performed MC simulations assuming not only adatoms but also dimers to be mobile. As long as the activation energy for dimer diffusion was at least 0.09 eV higher than for adatom diffusion, the island densities obtained from these simulations were identical within the limits of error to those assuming immobile dimers. Such a difference in activation energy of adatoms and dimers is in agreement with available FIM results [11]: Ir-dimer motion is found to have an activation energy of 0.16 eV higher than Ir-adatom motion. Finally a transient mobility of one or two lattice distances

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upon accommodation, as suggested by FIM experiments and effective mass theory calculations [12], was again found to have no measurable influence on the simulation results, thereby justifying assumption (vi).

In the main experiment to be described now we investigated the onset of nucleation due to the onset of the thermally activated migration of adatoms. At various fixed sample temperatures between 23 and 160 K an amount of $(4.2 \pm 0.4) \times 10^{-3}$ ML Pt was deposited (Fig. 1). This quantity has been chosen small in order to allow precise counting of the imaged objects. The "object" density upon deposition at 23 K is $(6.4 \pm 0.7) \times 10^{-4}$ Å$^{-2}$ and the adatom number density corresponding to the deposited amount is $(6.3 \pm 0.6) \times 10^{-4}$ Å$^{-2}$. Thus the bright spots seen in Fig. 1(a) are single adatoms. Even with a sharp STM tip as used in Fig. 1(a) the apparent diameter of an adatom is 7–8 Å. Repeated imaging of adatom distributions shows that at 20 K (1) adatoms are thermally immobile and (2) their locations are not affected by STM imaging. The decrease of the object density from Figs. 1(a) to 1(d) is apparent. Figure 2 shows quantitatively the temperature dependence of the object density as a "nucleation curve." It is constant up to 110 K, which demonstrates that under the given experimental conditions (rate, deposited amount) the adatom mobility at and below 110 K is insufficient for the adatoms to meet. With increasing temperature adatoms become mobile and during deposition and the 6 s before the sample is quenched, the adatoms start to meet, forming stable dimers. With further increasing temperature the chance of adatoms to attach to stable islands instead of forming new dimers increases, and thereby the object density decreases even further.

The MC simulations performed in order to reproduce the object densities involve besides the well-defined experimental conditions only two free parameters: $E_d$ and $\nu_0$. These two values were varied to reproduce the onset of nucleation at 110 K and the slope of the experimental object density above 110 K. Our best fit is obtained with $E_d = 0.26$ eV and $\nu_0 = 5 \times 10^{12}$ Hz (dotted line in Fig. 2). The dashed ($E_d = 0.24$ eV, $\nu_0 = 6 \times 10^{11}$ Hz) and dash-dotted ($E_d = 0.28$ eV, $\nu_0 = 4 \times 10^{13}$ Hz) curves in Fig. 2 demonstrate the sensitivity of the fitting procedure, from which we estimate the errors of our best fit to be $E_d = 0.26 \pm 0.01$ eV and $\nu_0 = 5 \times 10^{12 \pm 0.5}$ Hz. $E_d$ as determined here is identical within the error to that determined in a FIM experiment for the same system and lies in magnitude between embedded atom method and first principle calculations [13]. For $\nu_0$ no other experimental data are available, but its magnitude is in the expected range [13].

After having determined the diffusion parameters, independent experiments to test the new procedure were performed. First, the dependence of island density on coverage in the range between 0.002 and 0.15 ML was measured at 180 K. Examples of STM topographs are shown in Fig. 3. The island densities obtained from such topographs are plotted as full squares in Fig. 4. The dotted line represents the result of a MC simulation with $E_d = 0.26$ eV and $\nu_0 = 5 \times 10^{12}$ Hz as determined above. The simulation reproduces the experimental data accurately. Second, the dependence of the island density on temperature at a coverage of 0.1 ML was determined. At 0.1 ML the island density is saturated (i.e., it deviates less than a few percent from its maximum value) with the entire temperature range. The data (full squares) and the correspond-

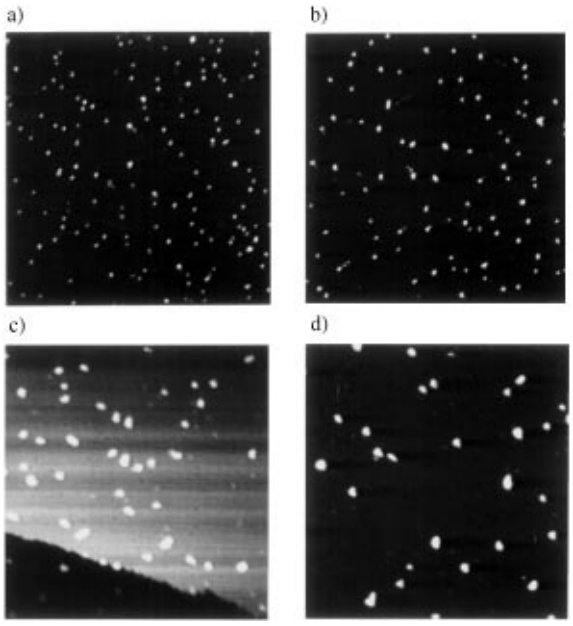


FIG. 1. STM topographs of Pt(111) surface after deposition of $4.2 \times 10^{-3}$ ML at sample temperatures of (a) 23 K, (b) 115 K, (c) 140 K, and (d) 160 K, respectively; scan size 480 Å and imaging at 20 K.

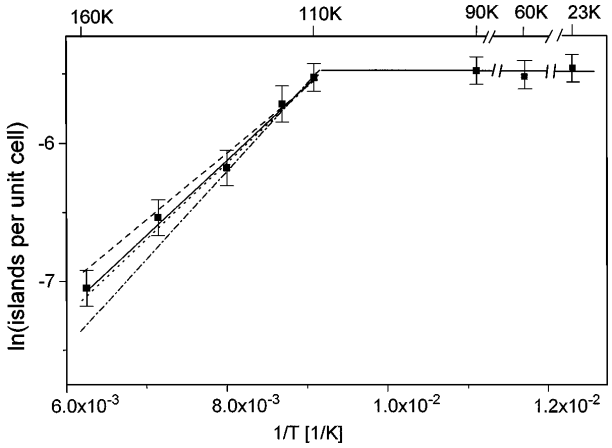


FIG. 2. Island density after deposition of $4.2 \times 10^{-3}$ ML vs $1/T$; experimental data (black squares) and corresponding linear regression (solid line); MC simulation with $E_d = 0.26$ eV and $\nu_0 = 5 \times 10^{12}$ Hz (dotted line); MC simulation with $E_d = 0.24$ eV, $\nu_0 = 6 \times 10^{11}$ Hz (dashed) and $E_d = 0.28$ eV, $\nu_0 = 4 \times 10^{13}$ Hz (dash-dotted), respectively.

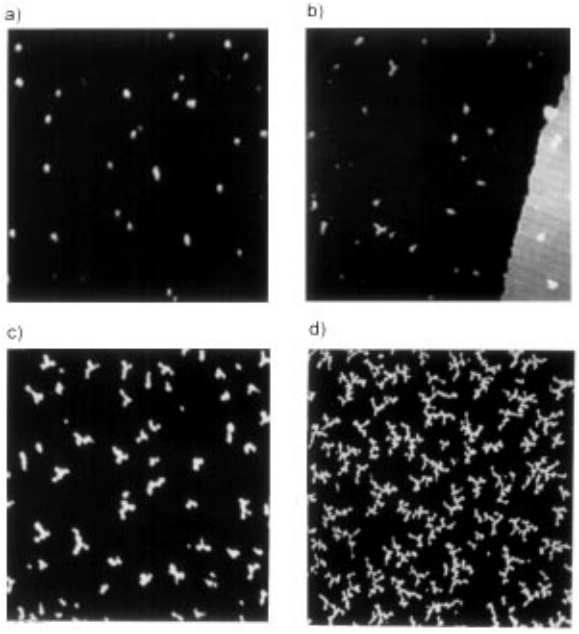


FIG. 3. STM topographs after deposition at 180 K of (a) $2 \times 10^{-3}$ ML, (b) $5 \times 10^{-3}$ ML, (c) $1 \times 10^{-2}$ ML, and (d) $1 \times 10^{-1}$ ML; scan size 960 Å and imaging at 20 K.

ing linear regression (solid line) are shown as an Arrhenius plot in Fig. 5. The result of the MC simulations obtained again with $E_d = 0.26$ eV and $\nu_0 = 5 \times 10^{12}$ Hz as determined above is represented by the dotted line. While the MC simulation tends to give slightly higher island densities than experimentally observed (10% higher), the slopes of the experiment and the simulation line are practically identical. Note also that the clear deviation of the experimental island density at 265 K ($3.77 \times 10^{-3}$ K$^{-1}$) indicates the breakdown of assumptions underlying the MC simulations at this high temperature. Probably either assumption (iv) (stability of dimers) or (v) (dimer diffusion) or both are not valid any more.

In conclusion, the two test experiments and the agreement of our results with independent FIM experiments [13] demonstrate that the take up of a nucleation curve and its fit by MC simulations is an efficient and accurate procedure for determining both diffusion parameters of adatom migration. The procedure is applicable for systems where adatoms are the diffusing species with the highest mobility. Its clue is that at the onset of nucleation all other activated atomic processes are either frozen out or irrelevant (all processes affecting cluster shape, cluster dissociation, etc.) such that the only two free parameters in the MC simulation are $\nu_0$ and $E_d$, which thereby can be unequivocally determined. Compared to the FIM method it has the advantage of being applicable not only to materials of large mechanical strength.

The new method also avoids some of the complications of the nucleation theory method as we will see now. The simplest way to use nucleation theory for the determination of $E_d$ and $\nu_0$ is with the help of the well-known scaling relation for the total island density $N = f(R/D)^{\gamma}$ with $D \propto \nu_0 e^{-E_d/kT}$ and $\gamma = \frac{1}{3}$ for the physical situation under consideration here [3,7]. The application of this relation is possible only for larger coverages where the island density is saturated. Therefore the function $f = f(\sigma)$ depends on the ability of the islands to incorporate free adatoms (capture number $\sigma$); it is not straightforward to determine $\sigma$ precisely, since it principally depends on island shape (specifically its dimensionality), as well as the lateral and the size distribution of islands [6,7]. Thus the nucleation theory method necessitates additional knowledge (e.g., on atomic processes at the island ledge) compared to the nucleation curve method (where, for instance, atomic processes at the island ledge are irrelevant). As an example of what is meant with these remarks we consider the

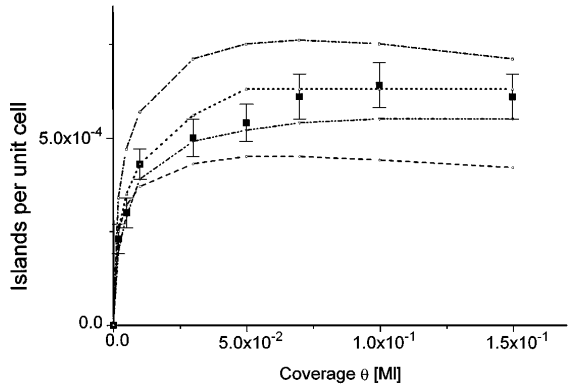


FIG. 4. Island density vs coverage, after deposition at 180 K: experimental data (black squares); MC simulation with $E_d = 0.26$ eV and $\nu_0 = 5 \times 10^{12}$ Hz (dotted line); numerical solution of the rate equations [14] with $E_d = 0.26$ eV and $\nu_0 = 5 \times 10^{12}$ Hz and with capture numbers $\sigma^{\mathrm{fr}}$ (dashed ) and $\sigma^{\mathrm{latt}}$ (dash-dotted), respectively. The dash–double-dotted curve is inferred from Fig. 2 of Ref. [7].

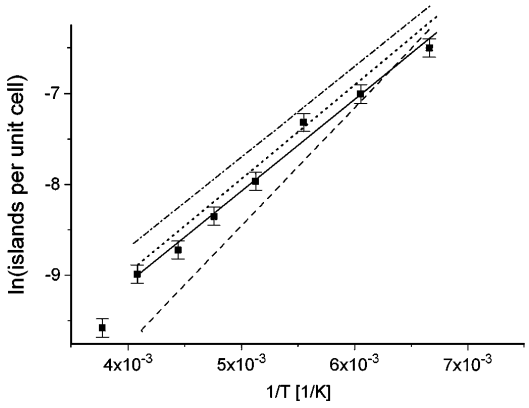


FIG. 5. Saturated island density at $1 \times 10^{-1}$ ML coverage vs $1/T$: experimental data (black squares) and corresponding linear regression (solid line); MC simulations with $E_d = 0.26$ eV and $\nu_0 = 5 \times 10^{12}$ Hz (dotted line); numerical solutions of the rate equation with the same parameters for the diffusion coefficient $D$ with $\sigma^{\mathrm{fr}}$ (dashed) and $\sigma^{\mathrm{latt}}$ (dash-dotted) as capture numbers (see text).

case of Pt-adatom migration on Pt(111) by using simplified rate equations [14]. These rate equations were numerically integrated with two different standard expressions for the capture number [14] $\sigma^{\text{latt}}$ (lattice approximation) and $\sigma^{\text{fr}}$ (geometrical concept for fractals) and with $E_d = 0.26$ eV and $\nu_0 = 5 \times 10^{12}$ Hz as an input. From Fig. 4 it is apparent that both capture number concepts show deviations from the experimental dependence of island density on coverage. However, both curves can be *fitted* to the experimental values by adjusting the attempt frequency. From Fig. 5 it can be seen that both solutions exhibit in fact a power law dependence on $R/D$. The use of $\sigma^{\text{latt}}$ reproduces the correct slope in the Arrhenius representation of Fig. 5 and therefore enables a correct determination of $E_d$. The use of $\sigma^{\text{fr}}$ leads in contrast to a wrong value for $E_d$ because $\sigma^{\text{fr}}$ and thus $f(\sigma^{\text{fr}})$ is strongly temperature dependent. Note that the determination of $E_d$ assuming a temperature *independent* function $f(\sigma)$ and the determination of $\nu_0$ by fitting with the coverage dependence of the island density with $\sigma^{\text{fr}}$ used in the rate equation—as done in Ref. [5]—is inconsistent. In the mean field approximation of nucleation theory better agreement with the experimental data for the coverage dependence of the island density may be achieved, if the island size, density, and structure dependence of the capture numbers is explicitly taken into account. Such a solution, as inferred from Fig. 2 of Ref. [7] for our experimental conditions ($D/R = 0.95 \times 10^8$), is represented by the dash–double-dotted line in Fig. 4.

The most direct method for determination of $E_d$ and $\nu_0$ by STM would be the monitoring of the displacements of individual adatoms in successive STM images at various fixed temperatures similar to the FIM method. However, we found, similar to the case of semiconductors [15,16], that the STM tip influences the adatom diffusion on Pt(111). The mean square displacement was too large (e.g., for $U = 30$ mV and $I = 0.2$ nA we determined $E_d = 0.17$ eV and $\nu_0 = 1.3 \times 10^{11}$ Hz) and increased with decreasing tip-sample distance. Minimization of the interaction of time of the migrating adatom with the STM tip and carefully chosen tunneling parameters might lead to useful results with this approach. However, an improved knowledge of the details of the interaction of the tip with the migrating adatom is necessary, which needs more detailed experiments [17].

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