

On the Mechanism of Rapid Mound Decay

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Abstract

The observation of rapid mound decay events on Ag(111) is reported. As in the case of Cu(111), the critical terrace width for the onset of the rapid decay corresponds to about six atom rows. For Ag(111) this distance is incompatible with the surface state model proposed earlier for Cu(111). A new mechanism for the rapid decay events is considered which involves steps in close proximity. It is shown that the observed mean terrace width in the final, rapid decay of a mound is well described by a combination of the random walk and shape fluctuations of the islands with the proposed local decay mechanism. Approximate activation energies for the new process are determined for Cu(111) and Ag(111).

Keywords: Scanning tunneling microscopy, diffusion and migration, growth, surface diffusion, copper, silver, low index single crystal surface

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1. Introduction

Interlayer mass transport is frequently hindered by the Ehrlich-Schwoebel barrier (ES-barrier) [1, 2] which is known to exist in particular for the (111) surfaces of Cu and Ag [3-5]. In 1998 we reported on the surprising observation that on Cu(111) surfaces the decay rate of double layer and multilayer islands increases by several orders of magnitude when the distance between the island edges is below the critical width $w_c = 1.4$ nm (\cong 6 atom rows) [6]. This distance was found to be independent of temperature and the decay can be quantitatively accounted for by assuming that the Ehrlich-Schwoebel (ES) barrier vanishes for terrace widths below w_c [7]. On Cu(111), $w_c = 1.4$ nm is precisely the distance where also the occupation of the surface state vanishes because of quantum confinement [7]. Inspired by an earlier proposal of Bertel and Memmel [8] this has lead us to the conclusion that the effect of rapid mound decay was indeed due to a vanishing ES-barrier and that the existence of an ES-barrier is related to the occupation of a surface state on Cu(111) [9]. In order to put our proposition to a stringent test we have now extended our studies to Ag(111) where the same surface state exists, albeit closer to the Fermi-energy [10]. We find that for Ag(111) the critical distance for rapid decay corresponds again to about 6 atom rows which is at variance with the proposition that the effect of rapid mound decay and the occupation of surface states are related. In this paper, we show the mean terrace width of about 6 atom rows in the final, rapid decay of a bi- or multilayer mounds can be explained by a combination of the random walk and shape fluctuations of islands [11, 12] with a decay process involving two steps in close proximity. A quantitative analysis of the decay process at various temperatures furnishes an activation energy for the microscopic process involved in the rapid decay. A possible candidate for the process is discussed.

2. Experimental results

The experimental data concern the decay of bi-layer and multilayer stacks of islands on Cu(111) and Ag(111) which were produced by evaporation of Cu and Ag, respectively, at a large rate of up to 5 monolayers per second. For details of the experimental set up and the sample preparation see [13, 14]. After evaporation, the crystal surface was placed on the STM as quickly as possible (minimum about 2 min) and the coarsening was observed in repetitive images. Depending on the temperature, the decay times of islands ranged between 5 min and 10 h. In the upper panel of Fig. 1 the decay curves of a double layer island on Ag(111) at 303 K is shown. Both, the upper and the lower island decay, the upper one with a smaller rate of -0.035 atoms/s because of the ES-barrier limited decay. When the terrace width between the islands is below a critical distance the decay rate increases. From thereon, the mean terrace width stays constant at a distance corresponding to about 6 atom rows ($a_{\perp} = 0.25$ nm) and the mean decay rate is -0.25 atoms/s. In Fig. 2 the experimentally determined mean terrace width for Cu(111) and Ag(111) during the final stage of rapid mound decay are plotted vs. temperature together with the critical distance between steps where the occupation of the surface state vanishes because of the quantum confinement between the steps. For Ag(111), the critical distance for the occupation of the surface state is far above the experimental data. Hence, the data for Ag(111) are incompatible with the proposition that the rapid decay effect is related to the surface state. As in the case of Cu, the rapid final decay *could be* quantitatively described by assuming that the ES-barrier vanishes at $w_c = 6.5 a_{\perp}$, with a_{\perp} the distance between densely packed rows of atoms on the (111) surface. The data could also be fitted by assuming that the activation energies for adatom creation and/or for terrace diffusion are reduced at w_c by at least 0.1 eV. With the surface state honorably discharged, it is, however, difficult to understand why such a significant and abrupt change in activation energies should occur at a particular distance between the step edges and why the distance

should amount to about 6 atom rows on both surfaces. In the following we therefore explore the possibility to describe the rapid decay by an exchange of atoms between steps in close proximity.

3. A new model for the rapid decay

The basis for modeling the decay is the continuum theory of diffusion limited decay as described in [3, 13, 15]. Applied to the decay of the top layer islands in a stack of two islands and to the decay of islands in vacancy islands the analysis involves the numerical integration of a differential equation for the case of two concentric circular islands. It has been shown the solution describes likewise the decay of hexagonal islands [13] and, in the presence of an ES-barrier, the decay of islands which are not concentric [16]. With data in a sufficiently large temperature range, the sum of the energy for creation an adatom on the terrace from a kink site and the activation energy for diffusion $E_{ad}+E_{diff}$ can be determined as well as the pre-exponential factors for diffusion v_0 and for crossing the step edge v_{s0} , and the magnitude of the ES-barrier E_{ES} . The set of parameters is known also for Ag(111) [4, 17].

In Fig. 1 the result of the numerical integration in time steps of 1s is shown as a dashed line with the parameters taken from Morgenstern et. al [4, 17] and no parameter fitted to this data. The agreement is excellent until the terrace width approaches a critical distance of $\cong 6a_{\perp}$. A microscopic model for the rapid decay is now build into the code for the numerical integration in the following way. We firstly determine the center of mass for the top and bottom island from the experimental STM-images. The dashed line in the lower panel of Fig. 1 displays the difference between the centers of the upper and lower island $\Delta r_{center}(t)$ as a dash-dotted line. We note that the observed jitter in the position is smaller than expected from an unconfined random walk of an island of the same size [18], as it should. Secondly, we calculate the mean deviation of the shape from the equilibrium Δr_{shape} [12].

$$\Delta r_{\text{shape}} = \sqrt{\langle (\Delta r)^2 \rangle} = \frac{0.75 k_B T}{\pi \beta} R. \quad (1)$$

Here, R is the radius of the island and β is the step free energy. To be consistent the experimental values for β data were taken from the analysis of the shape fluctuations of Cu [12] and Ag [19] islands. We calculate the distance of closest approach somewhere along the perimeter as the mean terrace width w minus Δr_{center} and minus Δr_{shape} and assume that (for whatever reason) a rapid decay mechanism sets in if that distance is below one atom row.

$$w(t) - \Delta r_{\text{center}}(t) - \Delta r_{\text{shape}}(t) < a_{\perp}. \quad (2)$$

Since $\Delta r_{\text{center}}(t)$ is known only to the accuracy of the pixel size, (1 pixel $\cong 1.5 a_{\perp}$, in most cases) the condition above is relaxed by adding a random number to the right hand side between ± 0.5 pixel size. Once the rapid decay mechanism sets in, the model takes care of the change of the center of mass of the upper island due to the loss of atoms somewhere at the perimeter, until $\Delta r_{\text{center}}(t)$ becomes known at the next measurement. The rate of the rapid decay mechanism v_{rap} is assumed to follow an Arrhenius law

$$v_{\text{rap}} = v_{0,\text{rap}} e^{-E_{\text{rap}}/k_B T} \quad (3)$$

Lacking better knowledge, the pre-exponential factor is set as for the diffusion on the terraces ($v_0 = 10^{12} \text{ s}^{-1}$ [5, 15]). The activation energy for the rapid decay process is varied until an optimum fit to the experimental decay curves is found. The resulting activation energy is not

very sensitive to the exact distance assumed on the right hand side of eq. (2). Raising the distance by 50% adds about 0.03 eV to the activation energy. The full lines in the upper and lower panel of Fig. 1 shows the agreement between the calculation and the experimental data. The abrupt changes in the calculated island sizes is an artifact due to the finite time resolution. In reality, the island may loose only a single atom in each event of a local step contact and, while continuously being engaged in rapid fluctuations, loose the next atom at a different point along the perimeter. The activation energies determined from fitting all data available for Cu(111) and Ag(111) are plotted in Fig. 3. For Cu(111), the experimental data range over a sufficiently wide temperature range to allow the conclusion that the activation energy obtained from the analysis remains constant with T, as it should if the choice for the pre-exponential is roughly realistic. The mean values for the activation energies are

$$\begin{aligned} \text{Cu(111): } E_{\text{rap}} &= 0.69 \pm 0.04 \text{ eV} \\ \text{Ag(111): } E_{\text{rap}} &= 0.615 \pm 0.05 \text{ eV} \end{aligned} \quad \text{for } \nu_{0, \text{rap}} = 10^{12} \text{ s}^{-1} \quad (4)$$

In order to check the model for consistency with other data we have calculated the rapid island decay effect in a previously published case where the upper island is much smaller than the lower one and approaches the boundary of the lower one only occasionally to engage in the rapid decay as published in [6]. The later stages of the total decay curve are shown in Fig. 4. The solid line represents the calculation using the new model with the experimental positions of the islands and the mean activation energy of $E = 0.69 \text{ eV}$ taken into account. With no (!) parameter fitted to this data set, the calculation curve tracks the experimental data very well. It should be emphasized that in this case (for no particular reason as far as we know) the upper island stayed in close contact over the time period of several STM images. The fact that the experimental rapid decay rate matches the calculated rate in the rapid decay event shows that

the rate for the rapid decay is indeed quantitatively described by the model. We note further, that the rapid decay event at 240 K with a decay rate of 0.7 atoms/s reported for Ag(111) by Morgenstern et al. [20] is also consistent with the mechanism and the activation energy reported here. Extrapolation of our data to 240 K yields a rate of $0.12 \times 10^{+1}$ atoms/s.

4. Atomistic models

The activation energies obtained from the analysis (modulo the unknown pre-exponential factor) are lower than the activation energies for the creation of an adatom on the terraces from a kink site for both materials. This suggests a process in which an atom from a kink site in the upper island moves directly into a kink site of the lower without the intervening step of adatom creation as in the normal diffusion limited decay. A possible process involving a concerted motion of the kink atom in the upper island and an atom next to the kink of the lower island is shown in Fig. 5. The process was proposed by N. C. Bartelt in 1997 [21]. Concerted motion of atoms are known to be quite ubiquitous on surfaces. Diffusion on terraces and diffusion across the step edge are well studied examples [22-25]. Because of the concerted motion, the pre-exponential factor is likely to deviate from the 10^{12} s^{-1} assumed here which should be considered if the activation energies obtained here are compared with theory.

In summary we conclude that the decay curves of islands can be quantitatively described by invoking a local rapid decay mechanism when the experimentally observed fluctuations in the island positions are taken into account. The further reaching question as to why the terrace width in the final decay is independent of temperature at about $6.5 a_{\perp}$ remains open. The terrace width reflects a complex interplay of fluctuations in the shape and position of islands, step-step interactions, and the mechanism of atom transport across the step edge. While one has at least continuum models for the first, neither the step-step interactions at close distances nor the atomistics of the local rapid decay mechanism are known yet.

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Figure Captions

Fig. 1: Experimentally determined areas of the upper and lower islands in a double layer stack on Ag(111) are plotted in the upper panel as circles and squares, respectively, together with the numerical solution for the diffusion limited decay with the ES-barrier (dashed line) and with the new rapid decay mechanism discussed in the text (solid line). The lower panel displays the experimentally determined mean terrace width between the upper and the lower island (triangles) and the experimental difference in the positions of the centers of the islands. The full line is the mean terrace width calculated in the model for rapid decay.

Fig. 2: Experimental mean terrace width in the final rapid decay of Cu(111) (circles) [7] and Ag(111) (squares) islands and the critical distance between steps at which the electronic surface state is pushed above the Fermi-level (solid and dashed curve, respectively) [9, 10].

Fig. 3: Activation energies for the proposed rapid island decay mechanism. The pre-exponential factor is assumed to be as for diffusion on terraces $v_{0,rap} = 10^{12} \text{ s}^{-1}$.

Fig. 4: Decay of an island (circles) which is initially concentric with the lower layer island (squares). The dash-dotted line shows the difference Δr_{center} in the center of mass of both islands. The top layer island wanders to the edge to engage in a rapid decay [6]. The full line is calculated in the model using the instantaneous relative positions of the islands and the mean activation energy of 0.69 eV (Fig. 3) as ingredients.

Fig. 5: Model of a possible atomic process for the rapid island decay as first proposed by N.C. Bartelt in 1997 [1]: A kink atom (1) in the perimeter of the upper layer island next to a kink atom (3) in the lower layer island merges into the lower layer via an exchange process. This process involves the concerted motion of at least three atoms as indicated by the numbers. Similar processes are possible for kinks at A- and B-steps.

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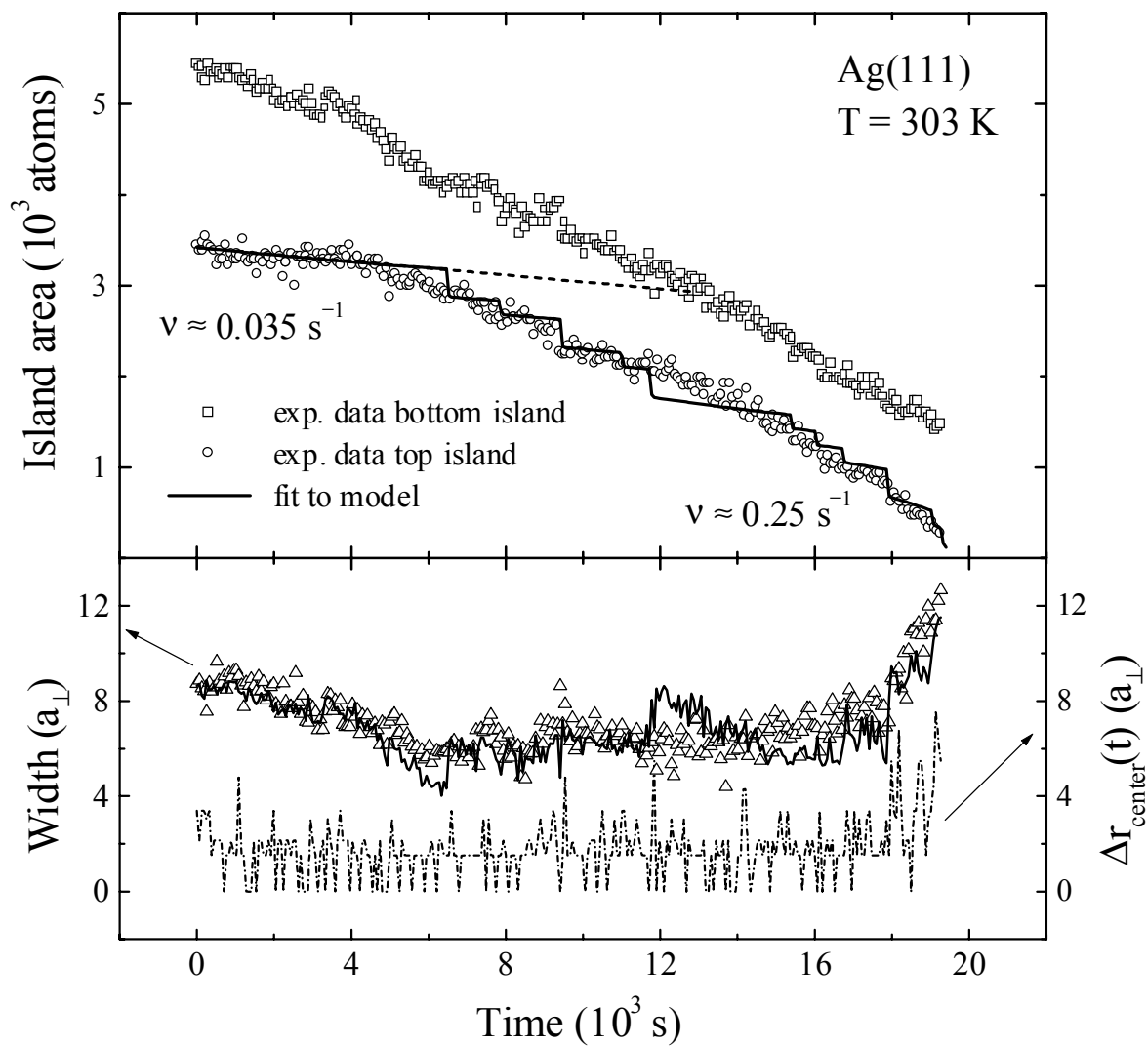


Fig. 1

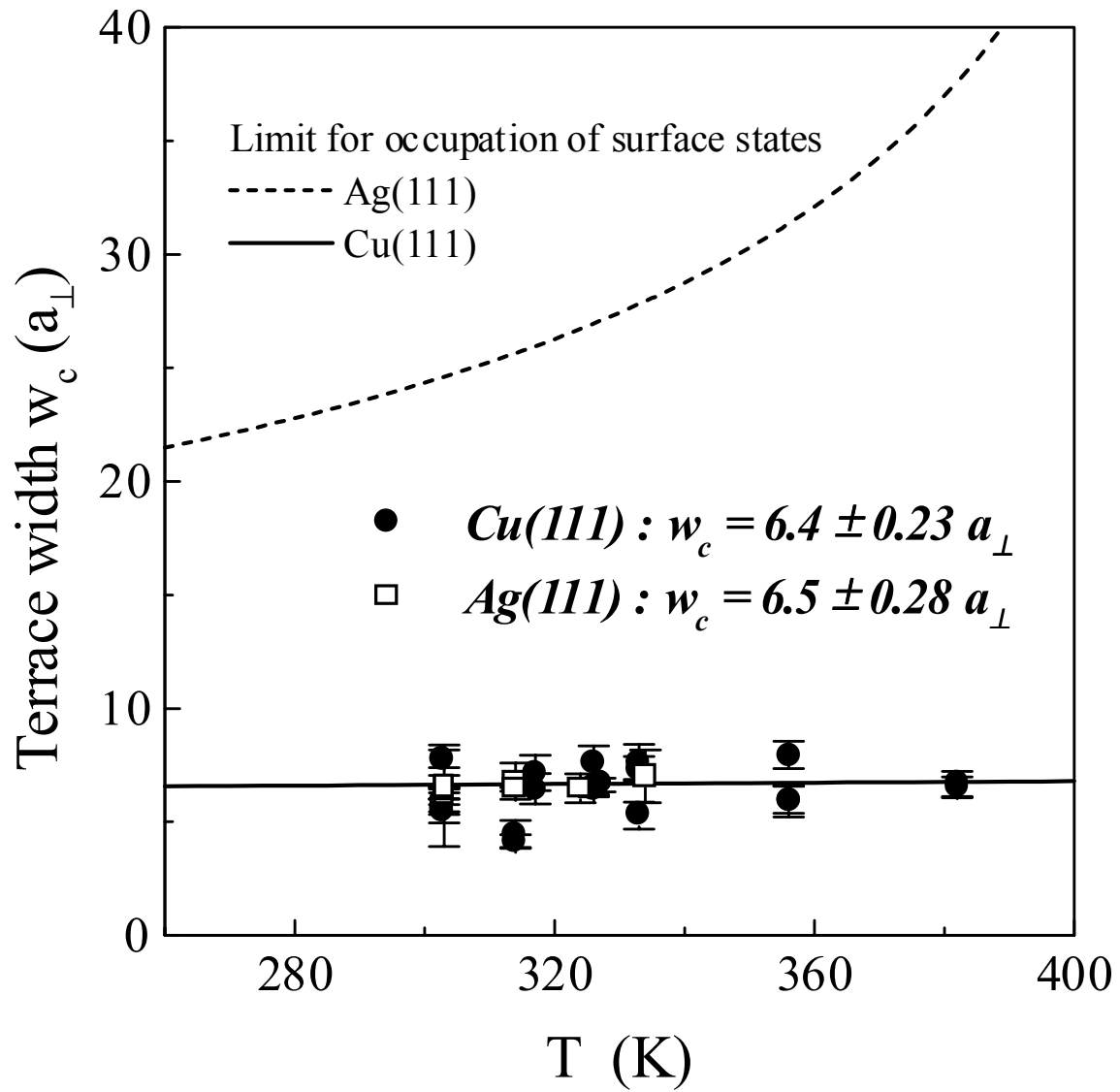


Fig. 2

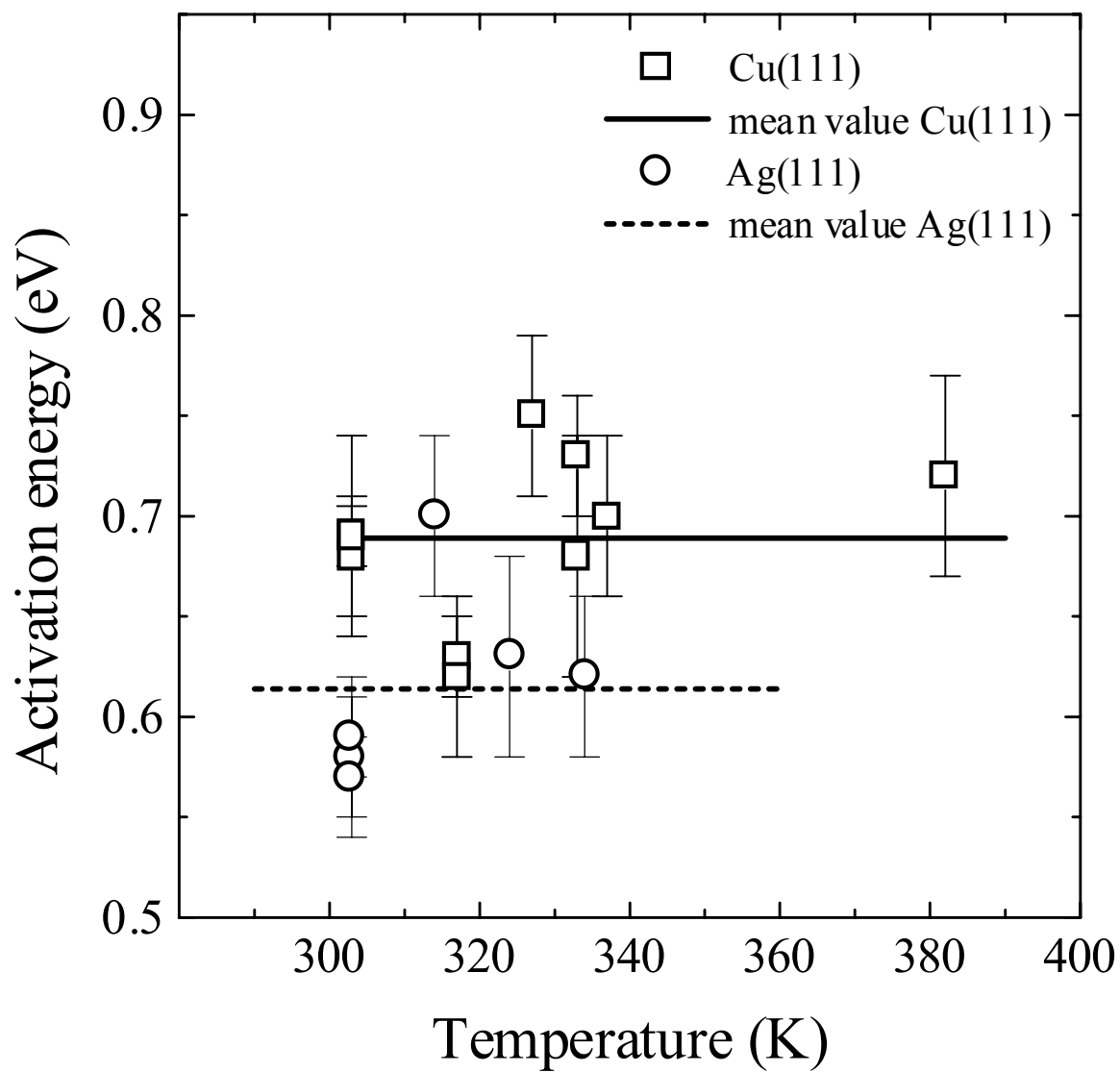


Fig. 3

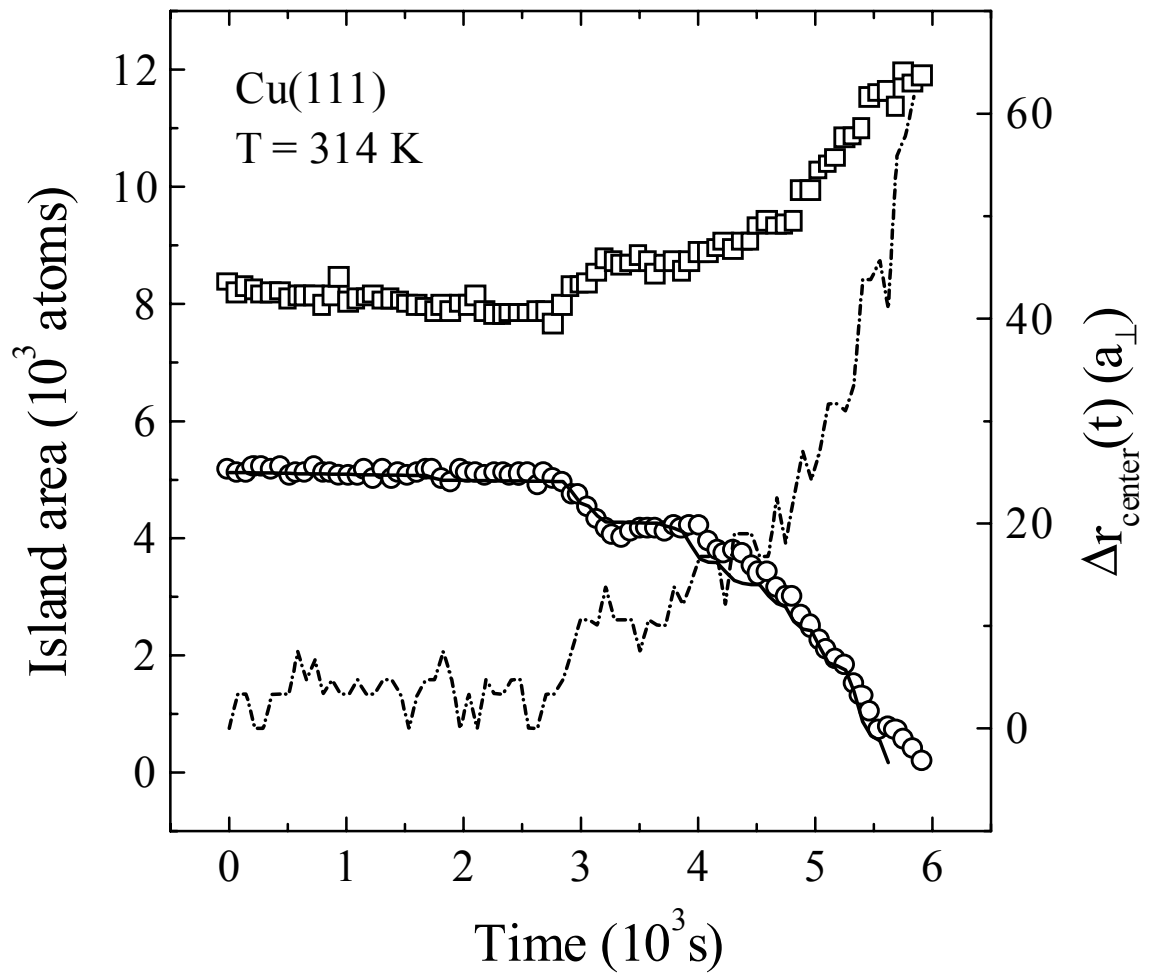


Fig. 4

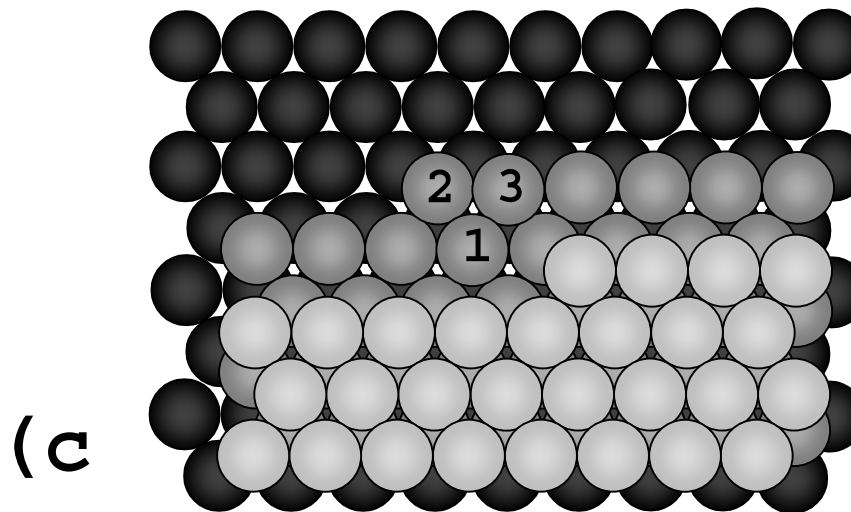
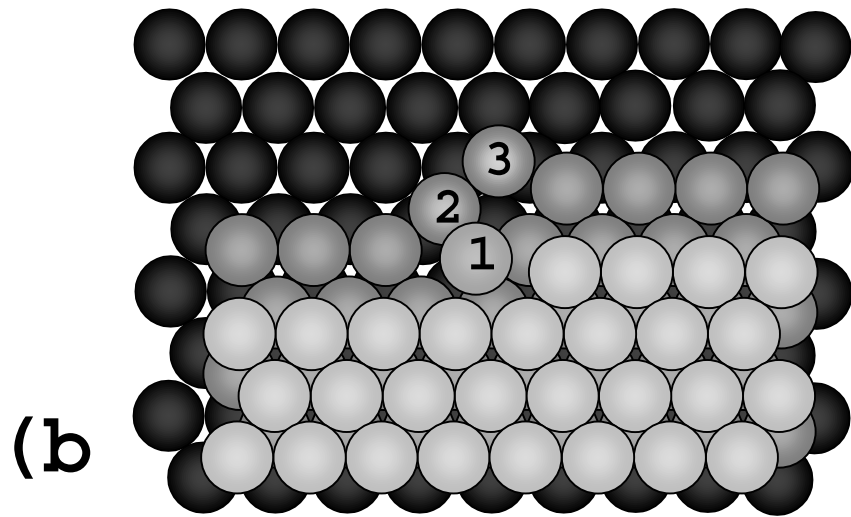
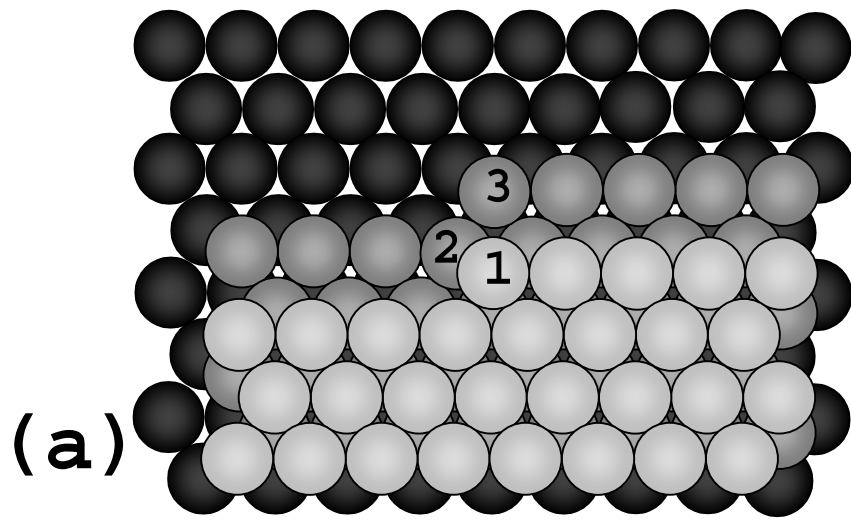


Fig. 5