Diffusion Processes and Growth on Stepped Metal Surfaces

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(15 May 1995 (to appear in Phys. Rev. B Rapid Comm.))

We study the dynamics of adatoms in a model of vicinal (11m) fcc metal surfaces. We examine the role of different diffusion mechanisms and their implications to surface growth. In particular, we study the effect of steps and kinks on adatom dynamics. We show that the existence of kinks is crucially important for adatom motion along and across steps. Our results are in agreement with recent experiments on Cu(100) and Cu(1,1,19) surfaces. The results also suggest that for some metals exotic diffusion mechanisms may be important for mass transport across the steps.

PACS numbers: 61.50.Cj, 68.35.Fx, 68.55.Bd

Diffusion of adatoms on solid surfaces is an extensively studied subject [1]. In particular, adatom dynamics on vicinal metal and semiconductor surfaces has important implications to surface growth under non–equilibrium conditions [2]. However, barring a few special cases, the atomistic details of diffusion processes near steps and kinks are not known. Current experimental techniques are now able to yield atomistic information about adatom dynamics near steps and kinks [1], and growth of surfaces [3,4]. Clearly, careful microscopic calculations are needed to understand these phenomena.

Our aim in this Letter is to study models of surfaces of fcc metals vicinal to the (100) plane. The open structure of the (100) facets can be expected to give rise to some unconventional diffusion processes that are not seen for instance on stepped surfaces with fcc(111) terraces. First, we want to identify the various microscopic mechanisms relevant to self–diffusion near steps and kinks. Second, we shall discuss the implications of our results to the morphological stability of these surfaces under growth [5], and suggest a phenomenological model for step growth. Our results are consistent with experiments on Cu(100) [3] and Cu(1,1,19) [4] surfaces.

The geometric structure of an fcc(119) surface is shown in Fig. 1. An ideal fcc(11m) facet, with odd $m > 1$, consists of (100) terraces of width $(m - 1)r_{nm}/2$ separated by (111) steps of height $r_{nn}/\sqrt{2}$, where $r_{nn}$ is the distance between nearest neighbor atoms. Due to the geometry, only one kind of steps (of monolayer height) with close-packed edges exist on these surfaces. The metallic interactions between atoms in our model are derived from the semi–empirical Effective Medium Theory (EMT). The formalism of EMT is presented in Ref. [7].

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We shall divide the discussion of the microscopic mechanisms near step edges into three parts: standard hopping events (denoted by $H_1$), exchange and other exotic mechanisms ($X$), and the effect of kinks on diffusion near and across step edges ($K$). For each mechanism $M$ the activation barrier is denoted by $E_M$, and that of the reversed process by $E_M^{\text{rev}}$.

In Fig. 2(a) we show a contour plot of the adiabatic energy surface $E(x, y)$ experienced by a single adatom on the Cu(119) surface at zero temperature. The potential across the terrace is shown in Fig. 2(b), indicating the activation energy for diffusion on the terrace $E_A$, and the height of the Schwoebel step barrier $E_{H1}^{\text{rev}}$. It is evident that the barrier in the $x$ direction is appreciably modulated only at the immediate vicinity of the steps [3]. We have verified this for the Cu(1,1,15) surface also.

Activation energies for simple hopping mechanisms on surfaces of several fcc metals with different orientations, as given by EMT, have been extensively tabulated in Ref. [4]. Our results for copper are fully consistent. The barrier height for a single jump on a flat terrace far from step edges is found to be $E_A = 0.399$ eV, and that for diffusion of a vacancy in the first layer of the terrace is $E_V = 0.473$ eV. The lowest barrier is that of an adatom diffusing along a straight step edge, and has a value $E_{H2} = 0.258$ eV. As expected, on Cu(11m) surfaces we find $E_{H2} < E_A < E_{H1}^{\text{rev}} < E_{H1}$. The inequality $E_{H2} < E_A$ is consistent with experimental results [13].

In addition to ground–state calculations we have performed extensive MD simulations [14] to identify possible exotic diffusion mechanisms [15] and to study entropic contributions to the rates [16]. A well–known mechanism for step crossing, the replacement of an edge atom by an adatom from the terrace (mechanism X1) is observed in our simulations. In our model the activation energies for hopping and the simple exchange across the step edge are approximately equal: $E_{H1} \approx E_{X1}$ [16,17]. We have also found more complicated mechanisms for step crossing. In Fig. 3 we show two examples: a “coherent” chain transfer and an atom–by–atom replacement mechanism (vacancy...

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diffusion). A possible explanation for the first mechanism is the local close-packed-like order of the surface atoms in the second configuration of Fig. 3(a), which may lower the local free energy. This is obviously an effect characteristic to stepped surfaces with fcc(100) terraces: e.g. on an fcc(111) terrace the atomic rows are more densely packed and cannot easily slide with respect to each other. The second process shown in Fig. 3(b) can be described as a “popping up” of a surface atom onto the step edge and the diffusion of a vacancy towards the descending step. By reaching the step, the vacancy turns into a hole or a pair of kinks at the step edge, which can then be filled by a surface atom or an adatom from the terrace below. Repeating this procedure, e.g. under an external field driving the atoms into the negative x direction, can result in mass transfer across steps which can then enhance growth instability [1].

The activation energy of the first step of the process shown in Fig. 3(b), i.e. the pop-up of a surface atom, was reduced by the existence of a kink at the step edge. For the processes with and without a kink we find $E_{K3} < E_{X3}$, respectively (cf. Fig. 3). Indeed, the effect of kinks on the energetics of diffusion processes near step edges seems to be crucial. In Fig. 4 we show the most important diffusion routes near straight and kinked step edges. It turns out that the hopping of a single adatom across the step edge in the vicinity of a kink site (K1) is not much more favorable than climbing across a straight edge (H1). On the other hand, activation barrier for the escape of an adatom from a kink (K4) is higher than $E_A$, while going “around the corner” along a kinked step edge (K2) is even more expensive, i.e. $E_{H2} < E_A < E_{K4} < E_{K2}$. From experiments on Cu(111), the activation energy for mass transport along kinked step edges was determined to be $10300 \pm 1630$ K [6], which was assumed to be due to the process K4. For K4 we obtain 6011 K in agreement with Ref. [18]. However, if we assume that K2 is the rate-limiting process we get an activation energy of $E_{K2} = 9075$ K which is within the experimental error bars.

The activation barriers for the processes shown in Fig. 3 for Cu(11m) are summarized in Table I. For any mechanism of step crossing in either direction, the barrier height is found to be well above $E_A$, i.e. a clear Schwöbel barrier exists. Our results thus indicate that under growth conditions the currents should go upward which makes the (100) surface unstable [3]. This is consistent with the experimental results of Ref. [19] on growth of the Cu(100) surface.

In the case of our copper model, the activation barriers for H1, X1, and K3 across the step edge are almost the same. This means that a finite density of kinks promotes step crossing. Due to small differences in activation energy, the relative occurrence of the different mechanisms at low temperatures is expected to be strongly model and material dependent. In particular, our results suggest the possibility that for (11m) surfaces of other fcc metals, exotic mechanisms such as K3 could play a more important role in mass transport across step edges. In addition, some processes such as X2 are influenced by the step density. More systematic studies on the effects of inclination and finite temperatures will be published elsewhere [7].

As already mentioned, our results have important implications for growth processes on copper surfaces vicinal to the (100) plane. First, under molecular beam epitaxy (MBE) conditions step crossing should be very rare. Thus, our data can be used to construct a growth model for individual steps. In the case of copper, such a growth model [17] should include the following features: adatom motion along a straight step edge which is very fast, and motion through a kink site at the step edge which in turn is much slower than simple diffusion on a flat terrace. In the simplest approximation, step crossing and evaporation can be neglected. The activation energies for these processes are well separated from each other and well below those of the neglected ones, which makes the model simple and hopefully applicable to a variety of vicinal fcc metal surfaces. This is supported by experiments [3,14]. For some fcc metals step crossings could be more significant, and then the detailed interplay between different mechanisms at step edges and kink statistics has to be taken into account. Note that during growth a non-vanishing kink concentration is naturally provided by adatoms deposited on the terraces. The growth rules suggested above differ substantially from those expected to describe MBE on stepped surfaces of silicon [8], where the strong anisotropy of diffusion [21] results in an interesting step morphology [20].

Discussions with I. Bukharev and H. Hääkkinen are gratefully acknowledged. J. Krug and S. C. Ying are acknowledged for a critical reading of the manuscript. This work has been in part supported by a joint grant between the Academy of Finland and Deutcher Akademischer Austauschdienst (DAAD).

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FIG. 1. Ideal fcc(119) surface: (a) Perspective view and (b) top view. The size of the unit cell is shown by a dashed line.

FIG. 2. The adiabatic potential experienced by an adatom on the Cu(119) surface as given by EMT at zero temperature: (a) a contour plot of the potential, where the global minimum is at (0,0) and the energy difference between each contour is 0.1 eV, and (b) minimum energy route of an adatom diffusing in the x direction.

FIG. 3. Snapshots of two exotic diffusion events from MD simulations of the Cu(119) surface (a) at T = 700 K and (b) at T = 750 K. These events only include surface atoms which are colored black. Atoms in the adjacent layers are shown in grey. Only part of the simulation cell is shown. In (a), the surface atom marked with a cross is pushed up and a hole is left behind at the descending step edge. In (b), the surface atom marked with a cross is pushed up and the vacancy left behind diffuses to the lower step on the right.

FIG. 4. Dominant diffusion mechanisms at the step edge on an fcc(11m) surface (top view). Black circles are adatoms and open circles denote surface atoms. A shaded circle shows the position of an atom after the diffusion event has taken place. K1 is the mechanism with the lowest activation barrier of the several possibilities for hopping across a step near a kink. The five stages of the process X3 are shown by numbers in parentheses. The processes seen in Fig. 3(a) and 3(b) correspond to X2 and X3, respectively, albeit without an initial adatom on the lower terrace.

TABLE I. Activation energies of some diffusion mechanisms near step edges on Cu(11m) surfaces as given by EMT. The whole system around the adatom was allowed to relax in the calculations. The labels in the first column are those used in Fig. 4. The third column shows the barriers of the corresponding reversed processes. For the mechanism X3 the height of the highest barrier (stage 1) is given.

| M (mechanism) | $E_M$ (eV) | $E_{M}^{rev}$ (eV) |
|---------------|------------|-------------------|
| H1            | 0.867      | 0.578             |
| H2            | 0.258      | 0.258             |
| X1            | 0.909      | 0.631             |
| X2            | 1.310      | 1.310             |
| X3            | 1.074      | –                 |
| K1            | 0.842      | 0.573             |
| K2            | 0.782      | 0.492             |
| K3            | 0.879      | 0.143             |
| K4            | 0.518      | 0.239             |
Fig. 1 (Merikoski et al)
Fig. 2  (Merikoski et al)
Fig. 3 (Merikoski et al)
Fig. 4 (Merikoski et al)