Step roughening effect on adatom diffusion

O. S. Trushin
Institute of Microelectronics, Russian Academy of Sciences, Universitetskaya 21, Yaroslavl 150007, Russia

K. Kokko*
Department of Physics, University of Turku, FIN-20014 Turku, Finland

P. T. Salo
Graduate School of Materials Science, Department of Physics, University of Turku, FIN-20014 Turku, Finland and Helsinki Institute of Physics, University of Helsinki, P.O. Box 9, Siltavuorenpenger 20 C, FIN-00014, Helsinki, Finland

W. Hergert
Fachbereich Physik, Martin-Luther-Universität, Friedemann-Bach-Platz 6, D-06099 Halle, Germany

M. Kotrla
Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 18040 Prague 8, Czech Republic
(Received 7 November 1996; revised manuscript received 17 June 1997)

Energy barriers for different movements of a single Cu adatom near steps on Cu(001) and Cu(111) surfaces are studied with molecular statics where an embedded-atom potential is used to simulate atomic interactions. The effect of step roughening on diffusion over step edges is investigated. In these calculations diffusion paths (jump, exchange) with low-energy barriers through kink sites are found. The presence of imperfections in a step ledge leads to a reduced Ehrlich-Schwoebel barrier in most cases and thus the obtained paths may serve as channels for adatoms to cross the descending steps. The possible consequences of these findings for growth processes are discussed. [S0163-1829(97)07743-6]

Surface diffusion on metals has attracted interest in recent years. This is due to the progress in experimental techniques [field-ion microscopy (FIM), scanning tunneling microscopy, and molecular-beam epitaxy (MBE)], and also due to the requirements of modern technology. To improve thin-film devices, it is essential to understand the epitaxial growth of metal films on an atomic scale.[1] Diffusion studies are important for the understanding of the microscopic nature of crystal-growth processes. Although a lot of work has already been done in this field, many questions have remained unresolved even in the case of simple homoepitaxial growth. Strong intensity oscillations have been found in a reflection high-energy electron diffraction (RHEED) experiment during epitaxial growth of Cu on Cu(001) at 77 K.[2] This observation has been explained with possible quasi-layer-by-layer growth model at low temperatures and interpreted as evidence of the transient mobility of adatoms at low temperatures. The recent discoveries, e.g., reentrant layer-by-layer growth phenomenon,[3] unstable pyramidlike growth,[4] and the ballistic exchange process,[5] are examples of problems in this field. The discovery of reentrant layer-by-layer growth during MBE of Pt on Pt(111) has stimulated the discussion on the role of the Ehrlich-Schwoebel (ES) barrier[6] in growth processes.[7]

Diffusion on Cu surfaces has been studied quite intensively with different theoretical approaches (see Ref. 8 and references therein). Recently discovered sophisticated exchange processes on metal surfaces[9] show that surface diffusion is a more complex phenomenon than was earlier thought. Modern surface diffusion models sometimes give contradictory predictions depending on the type of interatomic interactions used in calculations. An example of this is the estimation of energy barriers for jump and exchange diffusion on a Cu(001) surface. An investigation based on the effective-medium theory (EMT) with one-electron corrections predicted that the exchange diffusion is a more favorable process than the jump diffusion in Cu/Cu(001) systems.[10] However, the basic EMT (Ref. 10) and the embedded-atom method[11] (EAM) gave an opposite prediction. The latter result is even supported by recent first-principles calculations.[12]

Recently, Karimi *et al.*[13] made a detailed study on diffusion of Cu on Cu surfaces. They used molecular-statics (MS) simulations and the EAM to estimate energy barriers for different diffusion moves of a single Cu atom on flat and stepped Cu surfaces. The dominant mechanism of diffusion was predicted to be single vacancy migration on a Cu(011) surface and migration of adatoms on Cu(001) and Cu(111) surfaces. Regrettably, modern experiments do not allow a test of theoretical predictions for a single Cu atom diffusion on Cu surfaces on an atomic scale since most of the experiments use indirect methods [RHEED, low-energy electron diffraction, helium-ion and x-ray scattering] to observe the processes of epitaxial growth.[14,2,15] The diffusion characteristics are then extracted from the obtained separation of islands and size distribution data.

The epitaxial growth depends on external conditions like the flux of adatoms, substrate temperature, and surface im-

purities. The temperature of the substrate determines the mobility of the adatoms and the form of the steps. Because step ledges serve as sinks for adatoms, a high flux has an influence on the form of the steps. Step roughening due to adatoms and impurities changes the interlayer diffusion probability and consequently the growth mode can also change.

The influence of imperfections (steps, kinks, etc.) on single atom diffusion on a Cu(001) surface has also been discussed in literature.[13,16–18] Using the EMT, Merikoski *et al.* showed that kinks play an important role for diffusion both across and along step ledges in the case of Cu(001).[18] In this paper, we present a comparative study on different diffusion processes on flat and imperfect Cu(001) and Cu(111) surfaces. We study alternative diffusion paths close to a step in more detail. Furthermore, special attention is paid to the effect of step roughening on diffusion of adatoms over the step. The roughening of steps may occur when either temperature or the flux of adatoms are increased.[19,20]

The simulations were done with finite atomic slabs with a free surface on the top, two atomic layers fixed on the bottom, and periodic boundary conditions in the two directions parallel to the free surface. The slab representing the substrate was 11 layers thick with 128 atoms per layer. We used the classical *NVE* ensemble and molecular-dynamics cooling method for MS calculations of energy barriers. The equations of motion were solved using a leapfrog algorithm[21] with a time step of 10^{-14} s. A conventional spherical cutoff and a minimum image technique were used in the numerical simulations. The cutoff radius was 4.8 Å. The parameters for EAM were taken from Ref. 22. The energy barrier of a particular diffusion process was obtained by testing various paths of a diffusing atom and the path with the lowest diffusion barrier was chosen to be the optimum path. The adatom diffusion barrier E_d is defined as $E_d = E_{\mathrm{sad}} - E_{\mathrm{min}}$ where E_{sad} and E_{min} are the total energy of the system with the adatom at the saddle point and at the equilibrium adsorption site, respectively. Using the method above, two types of calculations were done. The minimum energy paths for both the jump and exchange processes of Cu on Cu(001) and Cu(111) were calculated. The minimum energy path for jump diffusion was determined by allowing the migrating atom to relax in a plane perpendicular to the path at each step. The rest of the atoms in the system were allowed to relax along all directions. The energy barrier of the exchange mechanism was obtained by moving the surface atom, which was to be replaced, by an adatom with finite steps along the direction of exchange. This atom was allowed to relax in the plane perpendicular to the exchange direction at each step, whereas the other atoms, including the adatom, were allowed to relax in all directions.

In order to understand how step roughening affects crystal growth, one has to compare first the diffusion barriers of imperfect steps with those of perfect steps and of flat surfaces. We calculated the barriers in all these cases. The diffusion barriers for a single Cu atom on a flat Cu(001) surface are 0.49 eV for jump and 0.69 eV for exchange. In the case of perfect steps on a Cu(001) surface, the diffusion barriers over a ⟨100⟩ step (0.33 eV for exchange and 0.57 eV for jump) are lower than those for the most closely packed step ⟨110⟩ (0.54 eV for exchange and 0.77 eV for jump). The barrier for diffusion along the ⟨100⟩ step ledge is much higher (0.83 eV) than that for diffusion along the ⟨110⟩ step (0.26 eV). The very-low-energy barrier for diffusion along the ⟨110⟩ step ledge suggests a large atomic transport along that step ledge which in crystal growth procedures leads to the formation of small monolayer islands which have borders consisting of steps with the orientation of ⟨110⟩. This prediction is supported by the recent LEED experiments for Cu(001).[14]

Adatom diffusion on Cu(111) differs drastically from that on Cu(001). Because an fcc(111) surface has a close-packed structure, it represents almost a flat surface for an adatom motion. The corresponding energy barrier for jump diffusion is very low (0.029 eV). Due to the close-packed structure of this surface the process of exchange diffusion has a very high activation energy and may be neglected when the adatom motion on a perfect Cu(111) surface is discussed.

There are two kinds of steps on fcc(111) surfaces: {100} microfaceted steps (A) and {111} microfaceted steps (B). As in the case of Cu(001), exchange diffusion is a more favorable process for crossing the descending steps on the Cu(111) surface. While both steps (A and B) represent almost equal barriers for jump diffusion (A, 0.51 eV; B, 0.50 eV) they differ drastically in the case of exchange diffusion (A, 0.28 eV; B, 0.085 eV). Compared to step A, step B has a very low barrier for crossing descending steps through the exchange mechanism suggesting that at normal conditions B-type steps should disappear while A-type steps should be predominant in a growth process. The lower barrier for exchange diffusion over step B is suggested to be due to the different geometry of the step ledge in these two cases. The movement of the exchanged atom in the case of step B can be related to jump diffusion on a flat Cu(111) surface which has a very low activation barrier. The energy barriers of crossing descending steps are much higher for fcc(111) surfaces than for fcc(001) surfaces compared to the flat surface case. Therefore the changes in ES barriers on a surface may have more important consequences for epitaxy in the case of fcc(111) than in the case of fcc(001). Our results for the diffusion on flat surfaces and near-perfect steps of Cu(001) and Cu(111) are in agreement with other EAM calculations.[13]

To discuss the effect of step roughening on energy barriers of descending steps we consider two extreme cases of imperfections on a ledge: a single atom and a kink. The diffusion paths considered in the present paper are shown in Fig. 1. We use the following notation hereafter: $j0$ and $x0$ refer to jump and exchange over a perfect step, $j1$ and $x1$ refer to jump and exchange over a step near a single atom on a ledge, and jk and xk refer to jump and exchange over a kink site. For each configuration the systematic MS calculations of the energy barriers (jump and exchange) of an adatom crossing the corresponding step were performed. The results are summarized in Table I.

In the following, we consider imperfections on the ⟨110⟩ steps on Cu (001). The presence of kinks on a ⟨110⟩ step on Cu(001) strongly influences the energy barriers for different diffusion moves close to the step. According to our simulations, a kink on a step changes the diffusion barrier only within the nearest-neighbor region of the kink atom. Impor-

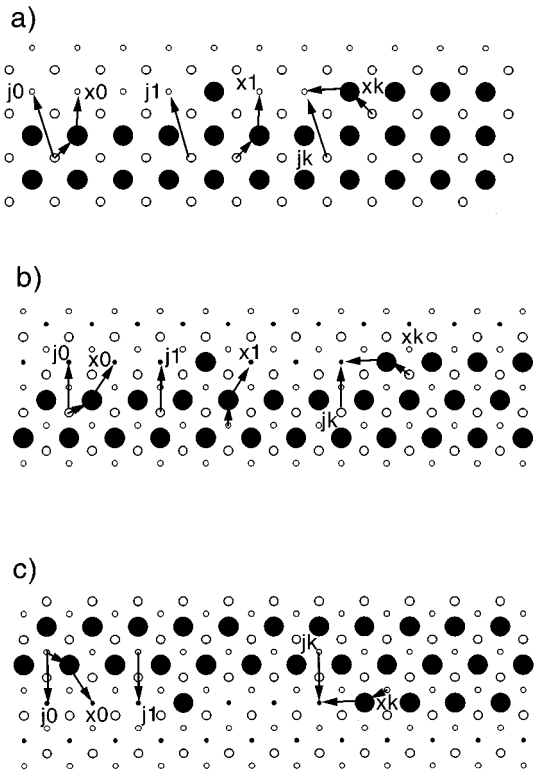

FIG. 1. Possible movements of adatoms near the steps with a single atom and a kink on the step ledge. (a) The ⟨110⟩ step on the Cu(001) surface. (b) The {100} faceted step and (c) the {111} faceted on the Cu(111) surface. The atomic layers from the surface to the bulk are large filled circles, large open circles, small open circles, and small filled circles.

tant changes take place especially for diffusion over the kink site. An interesting result is the very low barrier of the exchange diffusion as the corner atom of a kink is involved in the exchange process. This barrier (0.34 eV) is even lower than the one for diffusion on a flat Cu(001) surface (0.45 eV). The exchange diffusion over a kink site forms a channel through a potential barrier on the step edge, creating a drain for an adatom to cross the descending step. Somewhat surprisingly, even the presence of a single Cu atom on a step ledge lowers the step barrier almost as much as an ordinary kink.

In the case of Cu(111) we consider similar diffusion paths as for the Cu(001) case [Figs. 1(b) and 1(c)]. As for Cu(001) we observe that the diffusion barrier of jump diffusion for both *A* and *B* steps is reduced due to imperfections on a step ledge. An exception is exchange diffusion which shows the blocking effect for xk (step *B*) which means that the diffusion barrier is higher for the kink site than for the perfect step. The blocking effect in this case is due to the very low exchange barrier over a perfect step. The $x1$ for step *B* is omitted in Table I because in this case, we obtained a more complex diffusion process instead of a simple exchange.

The lowering of the energy barrier on a step ledge can be understood on the basis of the number of interatomic bonds. The ES barrier of a descending step is usually the number of interatomic bonds. The ES barrier of a descending step is usually explained as a result of a reduction of the number of the interatomic bonds when an atom crosses the step edge. If the adatom crosses the step near a kink atom, the number of bonds will not be reduced as much as in the case of a perfect step. Next, we discuss the possible effects of step roughening on growth modes. Because of the ES barrier on a descending step in both exchange and jump diffusion, the probability for adatoms to cross a descending step is low at low temperatures. This reduction in step crossing favors a three-dimensional growth mode during homoepitaxy at low temperatures. Our results suggest that the presence of kinks and even single atoms on a step ledge can open convenient channels for atoms to cross descending steps. Similar effects have been discussed recently in connection with the role of a surfactant in epitaxial processes.[23,24] Step roughening may occur, for instance, due to the fact that the edges of islands serve as sinks for adatoms during epitaxial growth or due to the high-temperature roughening of the steps. The latter has been observed recently in FIM experiments on an Ir(001) surface.[19] When an adatom has arrived at a step ledge it may move along the ledge until it is trapped on a kink site. The specific feature of the diffusion over the step with a kink makes it more favorable for adatoms to trickle from the upper terrace into a step-ledge corner where the ledge is blocked by the kink. Thus, the step roughening may contribute to quasi-layer-by-layer growth at low temperature especially in the case of high fluxes.

In conclusion, the effect of step roughening on adatom diffusion has been studied through MS calculations with EAM potentials for Cu(001) and Cu(111) surfaces. It was

TABLE I. Energy barriers for single Cu atom diffusion over descending steps with different imperfections on a step ledge of Cu(001) and Cu(111) surfaces.

Moves	$j0$	$x0$	$j1$	$x1$	jk	xk
Cu(001) step ⟨110⟩						
Present work (EAM)	0.77	0.54	0.55	0.36	0.57	0.34
EAM (Ref. 13)	0.77	0.51				
EMT (Ref. 18)	0.578	0.631			0.442	0.378
Cu(111) {100} faceted step *A*						
Present work (EAM)	0.51	0.28	0.38	0.20	0.40	0.20
{111} faceted step *B*						
Present work (EAM)	0.50	0.085	0.37		0.39	0.31
EAM (Ref. 13)	0.49	0.085				

shown that kinks and atoms on a step ledge lower the energy barriers so that adatoms can cross descending steps in most cases. This may affect growth modes during homoepitaxy on Cu(001) and Cu(111). Although our present results are for Cu surfaces, it is expected that the tendency of imperfections on a step ledge to lower the diffusion barrier over a step is a general feature based mainly on the geometry of the kink site rather than on the type of the atoms. This result is supported by the investigations on Ir diffusion on an Ir(111) surface[25] that show similar results as those discussed in the present paper.

Discussions with F. Máca are highly appreciated. We are also indebted to P. Ballone for providing the embedding functions and valuable advice. O.S.T. acknowledges the Center for International Mobility (Helsinki, Finland) for financial support during his stay in Turku. The work was partially performed during O.S.T.'s stay in the Institute of Physics, Academy of Sciences of Czech Republic, supported by Grant No. 202/96/1736 of the Grant Agency of the Czech Republic. K.K. acknowledges the financial support of the Academy of Finland (Grant No. 34942).

*Author to whom correspondence should be addressed. FAX: +358 2 3335993. Electronic address: kokko@utu.fi

[1] *Handbook of Thin-Film Deposition Processes and Techniques*, edited by K. K. Schuegraf (Noyes, Park Ridge, NJ, 1988).
[2] W. F. Egelhoff, Jr. and I. Jacob, Phys. Rev. Lett. **62**, 921 (1989).
[3] R. Kunkel, B. Poelsema, L. K. Verheij, and G. Comsa, Phys. Rev. Lett. **65**, 733 (1990).
[4] H.-J. Ernst, F. Fabre, R. Folkerts, and J. Lapujoulade, Phys. Rev. Lett. **72**, 112 (1994).
[5] G. L. Kellogg, Phys. Rev. Lett. **76**, 98 (1996).
[6] G. Ehrlich and F. G. Hudda, J. Chem. Phys. **44**, 1039 (1966); R. J. Schwoebel and E. J. Shipsey, J. Appl. Phys. **37**, 3682 (1966).
[7] A. C. Levi and M. Kotrla, J. Phys.: Condens. Matter **9**, 299 (1997).
[8] P. Stoltze, J. Phys.: Condens. Matter **6**, 9495 (1994).
[9] J. E. Black and Z.-J. Tian, Phys. Rev. Lett. **71**, 2445 (1993).
[10] L. Hansen, P. Stoltze, K. W. Jacobsen, and J. K. Nørskov, Phys. Rev. B **44**, 6523 (1991).
[11] C. L. Liu, J. M. Cohen, J. B. Adams, and A. F. Voter, Surf. Sci. **253**, 334 (1991).
[12] C. Lee, G. T. Barkema, M. Breeman, A. Pasquarello, and R. Car, Surf. Sci. Lett. **306**, L575 (1994).
[13] M. Karimi, T. Tomkowski, G. Vidali, and O. Biham, Phys. Rev. B **52**, 5364 (1995).
[14] H. Dürr, J. F. Wendelken, and J.-K. Zuo, Surf. Sci. **328**, L527 (1995).
[15] H.-J. Ernst, F. Fabre, and J. Lapujoulade, Phys. Rev. B **46**, 1929 (1992).
[16] C.-L. Liu, Mod. Phys. Lett. B **8**, 823 (1994).
[17] J. Merikoski and T. Ala-Nissila, Phys. Rev. B **52**, 8715 (1995).
[18] J. Merikoski, I. Vattulainen, J. Heinonen, and T. Ala-Nissila, Surf. Sci. **387**, 167 (1997).
[19] C. Chen and T. T. Tsong, Surf. Sci. **336**, L735 (1995).
[20] M. Giesen-Seibert, R. Jentjens, M. Poensgen, and H. Ibach, Phys. Rev. Lett. **71**, 3521 (1993).
[21] R. W. Hockney and J. W. Eastwood, *Computer Simulation Using Particles* (McGraw-Hill, New York, 1981), p. 540.
[22] S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986).
[23] H. A. van der Vegt *et al.*, Phys. Rev. B **51**, 14 806 (1995).
[24] M. Breeman, Ph.D. thesis, University of Groningen, 1993.
[25] O. S. Trushin, M. Kotrla, and F. Máca, Surf. Sci. (to be published).