Fast dimer diffusion near the island: A computational study

R.Z. Huang *, V.S. Stepanyuk

Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany

ARTICLE INFO

ABSTRACT

Performing atomic scale simulations, we study the diffusion of small Co clusters on Cu(111) surface in the presence of Co islands. It is revealed that mesoscopic relaxations at the island-substrate interface play an important role during the diffusion events of the clusters. The diffusion barrier of small Co clusters near the islands increases with increasing cluster size. Especially, we find that dimer diffusion near the island with B step is as fast as monomer's, which might be responsible for the formation of dendritic shaped islands at low temperature.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Understanding the surface diffusion of adparticles on metal surfaces is essential for a detailed understanding of numerous surface phenomena such as melting, roughening, crystal and film growth, catalysis and corrosion etc. A considerable amount of experimental and theoretical works are available on the energetics and mechanisms of single atom diffusion [1–4]. Single adatom diffusion mechanisms on metal surfaces are mostly well understood and can be classified as two different kinds: hopping and exchange mechanism. An adatom can hop from one hollow site to another hollow site, or exchange with a surface atom in the substrate.

It has been shown [5–8] that it is not enough to take just into account single adatom diffusion. Cluster diffusion also plays an important role in the process of crystal growth. Many growth models assume that once a cluster is nucleated it remains immobile or, at best, the mobility of the cluster simply decreases with the increasing cluster size. In fact, it was found that in metal-on-metal systems, not only small clusters but large clusters could have significant mobility at moderate temperature [5–8]. It was found that the energy barrier increases sharply from adatom, dimer, to trimer, but drops for tetramer, and then rises again for pentamer and larger clusters for self-diffusion of Ir clusters on the Ir(111) surface [6]. Similar behaviors were obtained by a systematic theoretical investigations on fcc metal (111) surfaces [8]. This

phenomenon of the break of the upwards trend in diffusion energy was predicted to be a general one. It was shown [7] that the activation energy of dimer diffusion was lower than that of monomer diffusion in the studies of self-diffusion of Cu clusters on flat Cu(100) surface. Dimer shear motion provided the easiest diffusion pathway for some compact clusters and interpreted better the oscillatory behavior of cluster mobility with cluster size found by Kellogg [9]. The barrier for dimer shearing along the edge of big clusters was lower than the barrier for adatom diffusion on a terrace.

In the early stage of film growth, stable and metastable islands are formed. Atomic and cluster diffusion in the vicinity of the islands will become complicated and governs the size, shape, and the growth mode of the islands. Lots of investigations [10–13] focused on the diffusion of single adatoms on and near the islands on metal surfaces. For examples, the upwards jumping of adatoms [11] was found to contribute to the Co bilayer growth mode on Cu(001) surface. The existence of fast edge diffusion along step edges was crucial to explain the surface roughness for unstable Cu/Cu(001) growth at low temperatures [12]. Corner diffusion anisotropy was found to control the shape of compact islands at intermediate temperatures [13]. However, little attention was paid to cluster diffusion on or near the islands [14, 15]. In our previous paper, we revealed [16] that mesoscopic relaxations in systems with low migration barriers significantly affect atomic motion in the vicinity of adsorbed islands. The migration barrier exhibits strong oscillations as approaching the adatom towards the island side. In this work, we investigate the diffusion of small Co clusters on and near Co islands on Cu(111) surface. It is found that mesoscopic relaxations at the

---

* Corresponding author.
E-mail address: hwangrz@googlemail.com (R.Z. Huang).

island-substrate interface significantly influence the mobility of the clusters near the islands. It is revealed that dimer migration can be as fast as monomer migration near the islands and steps, which might be responsible for the formation of dendritic shaped islands at low temperature.

2. Models and computational details

In this work, atomic scale simulations are performed using the Molecular Statics (MS) method with *ab initio* based many body potential [17]. This approach is based on fitting of many-body potentials to accurate *ab initio* data for surface and bulk properties. First, using the Korringa–Kohn–Rostoker (KKR) Green's function method [18], We construct an *ab initio* date pool by calculating surface and bulk properties of Co–Cu system. Then the many body potentials based on the second moment approximation of the tight binding theory [19] are fitted to this *ab initio* data. Recent studies [20–26] have shown that our method describes atomic relaxations in nanostructures in very good agreement with fully *ab initio* calculations. The technical details and parameters of interatomic potentials can be found in our previous works [17,26].

We concentrate on the diffusion of small Co clusters on and near the Co islands on Cu(111) surface. The Cu(111) substrate is typically modelled by a slab of nine-layer thick with 1400 atoms per layer. In experiments [27,28] the two monolayer (ML) Co nanoislands are formed on Cu(111) surface at room temperature. We consider two different kinds of 1 ML triangular islands with straight steps: A and B step with 100 and 111 microfacets respectively (see Fig. 1), aiming to investigate the effect of cluster diffusion on the growth of Co islands on Cu(111) in the early stages. Periodic boundary conditions are applied in the planes parallel to the surface and no such constraint is imposed along the direction normal to the surface. Atoms in the bottom two layers are fixed at their respective bulk positions in each relaxation, while atoms in the top seven layers as well as adparticles and clusters are free to move. When calculating the diffusion barrier of dimer, one of them moves ahead, leaving another one following it by the so-called "concerted motion" [8]. For other small clusters, we consider the possible diffusion paths and find that the "concerted motion" of atoms in these clusters is the easiest diffusion path along the $\langle \bar{2}11 \rangle$ direction. However, along the $\langle 0\bar{1}1 \rangle$ direction, these clusters diffuse in two separate steps. The "concerted motion" of a row of atoms in parallel to the $\langle 0\bar{1}1 \rangle$ direction follows that of another row of atoms in these clusters. We take the largest diffusion barrier in these two steps as the diffusion barrier along the $\langle 0\bar{1}1 \rangle$ direction.

In figures and Tables, "n-row" is defined as the distance of n-atom rows away from the island edge wherever clusters are on or near the islands. "towards" means the movement of clusters parallel to the $\langle \bar{2}11 \rangle$ direction while "along" means the diffusion of clusters parallel to the $\langle 0\bar{1}1 \rangle$ direction.

3. Results and discussions

The diffusion barriers of Co adatoms and clusters on flat Cu(001) surface are calculated and shown in Fig. 2. We also compare our results with those of Miron and Fichthorn [23] in Fig. 2. It is seen that our results have a good agreement with theirs. Dimers and trimers have a high mobility, comparable to that of the isolated adatom. This further check the reliability of our fitted potentials. It should be mentioned that the calculated diffusion barrier of Co adatom on flat Cu(001) surface is 0.63 eV using density functional theory (DFT) with generalized gradient approximation (GGA) for the exchange–correlation function. As we know, the lattice constant of Cu substrate will be overestimated using GGA. Accordingly the corrugation of potential energy surface of the Cu(001) surface becomes large. It has been demonstrated [29] that
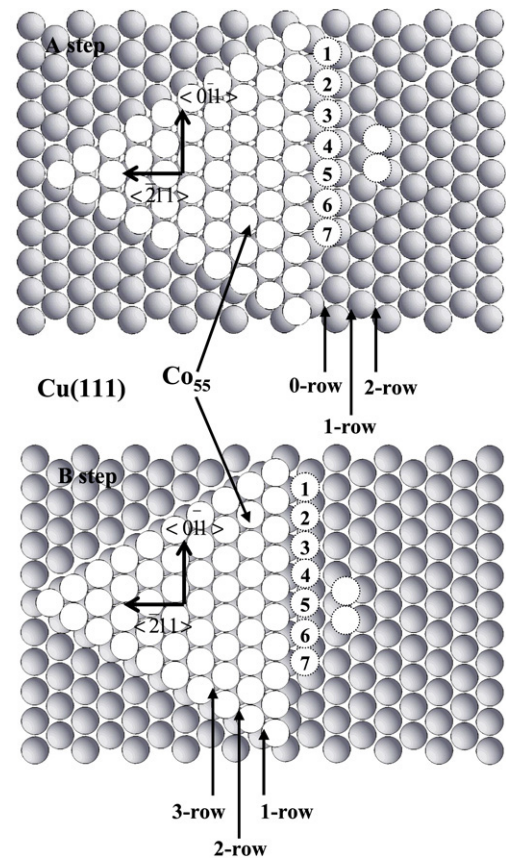

Fig. 1. Schematic view of Co$_{55}$ islands with A and B step on Cu(111) substrate. "n-row" (n is integer) is defined as the distance of n-atom row away from the island edge wherever clusters are on or near the islands. Numbers denote the position of the diffusing-ahead atom of a Co dimer.
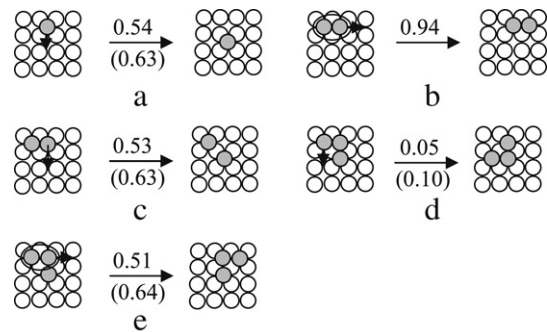
Fig. 2. Diffusion barriers (units: eV) of small Co clusters on Cu(001) surface: (a) adatom hop; (b) dimer collective motion; (c) dimer hop; (d) trimer rotation; (e) trimer hop.

when the corrugation of the potential acting on adatoms on a surface increases, the barrier for the jump diffusion also increases. Thus the diffusion barriers they calculated using DFT-GGA method should be a little larger than ours.

As mentioned previously, adsorbed Co islands on Cu(111) substrate exhibit triangular shapes with their edges aligned along the close-packed $\langle 0\bar{1}1 \rangle$ directions of the Cu substrate. Though the macroscopic mismatch between Co and Cu is small (defined as $m_0 = (r_{Cu} - r_{Co})/r_{Cu}$ is about 2%, where $r_{Cu} = 2.56$ Å and $r_{Co} = 2.51$ Å are the first bond lengths in bulk Cu and Co), mesoscopic Co islands on Cu(111) surface do not have the bulk lattice spacing. For the Co$_{55}$ islands with A or B step on Cu(111) surface (see Fig. 1), strain relaxation at the island-substrate interface leads to deformation of both the islands and the substrate surface layers
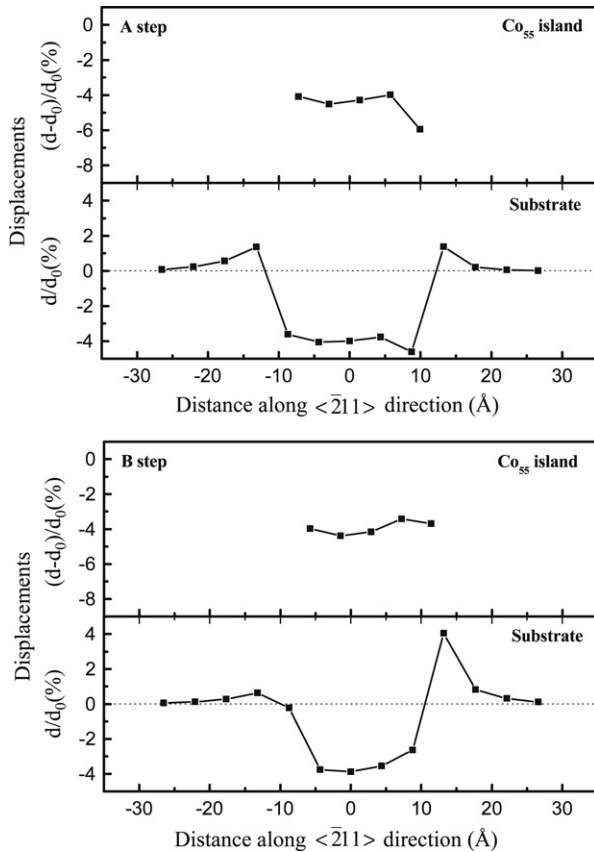
Fig. 3. Vertical displacements in Co$_{55}$ islands on Cu(111) and the substrate under the island calculated across the $\langle\bar{2}11\rangle$ direction; d is the height above the surface level; $d_0 = 2.09$ Å is the interlayer distance in Cu(111); The origins of the coordinate are shown in Fig. 1.

Table 1
Calculated diffusion barrier (units: eV) of Co dimer near Co$_{55}$ island on Cu(111) surface. The values in parentheses are the calculated diffusion barriers without taking into account the relaxation of the substrate.

Position	A step		B step	
	Along	Towards	Along	Towards
Edge	0.828(1.030)		0.761(1.132)	
1-row	0.069(0.153)	0.000(0.042)	0.033(0.068)	0.000(0.000)
2-row	0.087(0.126)	0.013(0.130)	0.089(0.126)	0.013(0.122)
3-row	0.090(0.138)	0.013(0.135)	0.090(0.138)	0.013(0.136)
4-row	0.091(0.138)	0.011(0.136)	0.091(0.138)	0.012(0.136)
5-row	0.092(0.138)	0.011(0.136)	0.093(0.138)	0.011(0.136)

(see Fig. 3). Due to reduced Co–Co bond lengths in Co islands, compressive strain exists in the substrate surface covered by the Co island. At the same time, the substrate surface outside the island undergoes the tensile strain.

First, let's see the diffusion of small clusters near the Co islands (with A or B step) on Cu(111) surface. Our investigations show that the edge diffusion barrier of Co dimer at the island edge is much higher than its diffusion barrier along the $\langle 0\bar{1}1\rangle$ direction when it is away from the island edge (see Table 1). This is easy

Table 3
Effect of cluster size on the diffusion barrier (units: eV) of clusters near Co$_{55}$ island.

Position	Cluster	A step		B step	
		Along	Towards	Along	Towards
1-row	Trimer	0.130	0.049	0.099	0.000
	Tetramer	0.184	0.084	0.193	0.000
2-row	Pentamer	0.242	0.094	0.200	0.000
	Trimer	0.141	0.141	0.140	0.136
	Tetramer	0.240	0.156	0.240	0.151
	Pentamer	0.286	0.215	0.264	0.205

to understand because much more bonds need to be broken for the edge diffusion. The diffusion barrier of Co dimer along the $\langle 0\bar{1}1\rangle$ direction is always larger than that along the $\langle\bar{2}11\rangle$ direction (see Table 1). With the increase of the distance to the islands, the diffusion barrier of Co dimer along the $\langle 0\bar{1}1\rangle$ direction increases while the diffusion barrier of Co dimer along the $\langle\bar{2}11\rangle$ direction decreases. The limits are the diffusion barriers of Co dimer on flat Cu(111) surface in the absence of islands (93 meV along the $\langle 0\bar{1}1\rangle$ direction and 10 meV along the $\langle\bar{2}11\rangle$ direction). If we don't take into account the relaxation of the substrate, the calculated barriers are much higher than those when we take it into account (see the values in the parentheses in Table 1). Thus it is demonstrated that mesoscopic relaxations of the island and substrate play an significant role in the diffusion events of the clusters near the islands.

It is seen from Table 1 that when the dimer is one-atom row away from the islands, the barrier of its diffusion towards the islands is zero. It is also found that in the local region near the island (the distance to the island is not far from 2-atom rows), the barrier of dimer diffusion near the island with B step is very lower (no more than 33 meV), which means that the dimer can easily diffuse towards the island edge when it is close to the island. The barrier of dimer diffusion near the island with A step (1-row away from the island) along the $\langle 0\bar{1}1\rangle$ direction is almost two times larger than that near the island with B step (see Table 2). One can see from Fig. 3 that the corrugation in the surface near the island with A step is larger than that in the surface near the island with B step, which is due to the different stacking sequence for the islands with A and B step. It is demonstrated [29] that when the corrugation of the potential acting on an adatom on a surface decreases, the diffusion barrier also decreases, and vice versa. The reduced corrugation of the potential in the surface near the island with B step decreases the diffusion barrier of the dimer. We also calculate the diffusion barrier of single Co adatom near the Co island in order to compare with that of the dimer. It is found that the diffusion of dimer can be as fast as that of monomer in the local region near the island with B step (see Table 2). When the cluster size increases from dimer to trimer, tetramer and pentamer, as we expect that the energy barrier increases with increasing cluster size (see Table 3).

Now, let's turn to the diffusion of small Co clusters on the Co islands. It is seen from Table 4 that the barriers of the cluster diffusion along both the $\langle 0\bar{1}1\rangle$ and $\langle\bar{2}11\rangle$ directions increase with increasing cluster size from the adatom to tetramer. The diffusion of Co adatom and dimer on the islands becomes more difficult compared to their diffusions on flat Cu(111) surface (see the corresponding values in Table 4). At the same time, we find that

Table 2
Calculated diffusion barrier (units: eV) of Co adatom and dimer near Co$_{55}$ island on Cu(111) surface.

Position	A step				B step			
	Along		Towards		Along		Towards	
	Adatom	Dimer	Adatom	Dimer	Adatom	Dimer	Adatom	Dimer
Edge	0.479	0.828			0.395	0.761		
1-row	0.024	0.069	0.000	0.000	0.011	0.033	0.000	0.000
2-row	0.032	0.087	0.043	0.013	0.031	0.089	0.035	0.013

Table 4
Calculated diffusion barrier (units: eV) of small Co clusters on Co_{55} island on Cu(111) surface.

| Position	A step				B step			
	Along		Towards		Along		Towards	
	Adatom	Dimer	Adatom	Dimer	Adatom	Dimer	Adatom	Dimer
1-row	0.075	0.219	0.626	0.576	0.072	0.207	0.636	0.584
2-row	0.050	0.144	0.014	0.010	0.047	0.135	0.021	0.016
3-row	0.049	0.150	0.041	0.016	0.049	0.146	0.047	0.020
Flat	0.037	0.093	0.011	0.010				
	Trimer	Tetramer	Trimer	Tetramer	Trimer	Tetramer	Trimer	Tetramer
1-row	0.210	0.331	0.877	0.699	0.203	0.327	0.883	0.703
2-row	0.164	0.176	0.095	0.118	0.155	0.174	0.104	0.130
3-row	0.168	0.278	0.158	0.177	0.173	0.292	0.173	0.189

the diffusion barriers of small clusters on the islands are generally larger than that near the islands if we compare Table 4 with Table 1. Actually the diffusion of Co adatoms on flat Cu(111) surface is easier than that on flat Co island due to the stronger Co–Co interaction compared to the Co–Cu interaction. Our study doesn't find evident difference of the mobility of Co clusters on the islands with A and B step (see Table 4). The big diffusion barrier of small clusters on the island should be responsible for the formation of 2 ML Co island.

We have checked the effect of dimer position on its diffusion barrier. The results are shown in Fig. 4. When the dimer is at the island edge, dimer position has little effect on its diffusion barrier. However, when it is located at the corner of the island, the barrier of dimer diffusion deviates from the value when it is at the island edge. This can be attributed to the big mesoscopic relaxations and diffusion anisotropy at the corner of the island. When the dimer is away from the island edge, dimer position at the same row has little effect on its diffusion barrier.

Now, let's try to describe the diffusion process of Co dimer near the Co island with B step. Supposing dimer is first located in the 2-atom row (both atoms of dimer occupy hcp sites) away from the island edge. One atom of the dimer moves ahead from hcp site to fcc site and then to hcp site again, leaving another atom staying its original hcp position and adjusting slightly with the movement of the diffusing atom (see Fig. 5(a)). The maximum barrier during this process is no more than 33 meV. Then both atoms move together from hcp site to fcc site (with a barrier no more than 33 meV). The atom moving ahead arrives at the island edge and stays here, waiting for the movement of another atom (see Fig. 5(b)). Another atom will move from fcc site to fcc site via hcp site and reach the island edge with a barrier less than 33 meV (see Fig. 5(c)). The diffusion of dimer from the 2-atom row away from the island to the island edge has finished in the end. The whole diffusion process will easily take place if a small disturbance occurs.

As we know, the shape of islands in epitaxial growth is influenced by many factors such as deposition rate, concentration of deposited adatom and temperature etc. In low temperature, most of diffusion processes are depressed, the shape of islands is usually dendritic. The main diffusion event is the jump of single adatom towards the island. Here our study has found that the migration diffusion of dimer in the local region near the islands can be as fast as monomer's. On the other hand, dimer slide along the island edge is more difficult than dimer migration to the island. Thus fast diffusion of dimer in the local region near the islands might be responsible for the formation of dendritic shaped islands during growth of thin film.

We have also investigated the effect of island size on dimer diffusion. The results shown in Table 5 reveal that the island size has hardly effect on the barrier of dimer diffusion along the $\langle 0\bar{1}1 \rangle$ direction when it is away from the island or step edge. But the barrier of dimer diffusion along the $\langle \bar{2}11 \rangle$ direction increases with increasing island size when it is 2-atom rows away from the island or step edge.
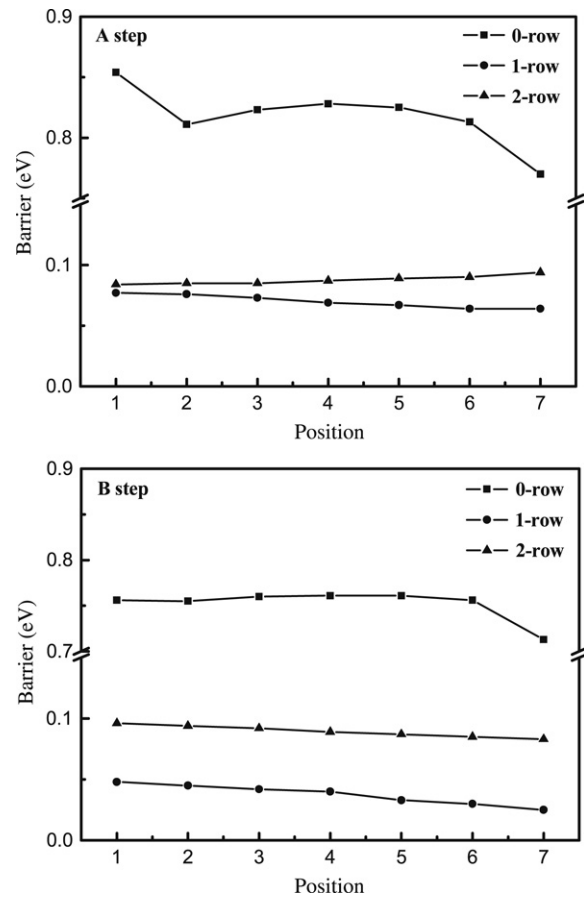
Fig. 4. Effect of the position of Co dimer on its diffusion barrier (units: eV) along the $\langle 0\bar{1}1 \rangle$ direction near the islands with A and B step.

Table 5
Effect of the island size on the diffusion barrier (units: eV) of the Co dimer near the island.

Position	Island	A step		B step	
		Along	Towards	Along	Towards
0-row	Co_{21}	0.782		0.790	
	Co_{55}	0.828		0.761	
	Step	1.011		0.734	
1-row	Co_{21}	0.068	0.000	0.030	0.000
	Co_{55}	0.069	0.000	0.033	0.000
	Step	0.067	0.000	0.041	0.000
2-row	Co_{21}	0.089	0.011	0.090	0.008
	Co_{55}	0.087	0.013	0.089	0.013
	Step	0.085	0.017	0.090	0.016
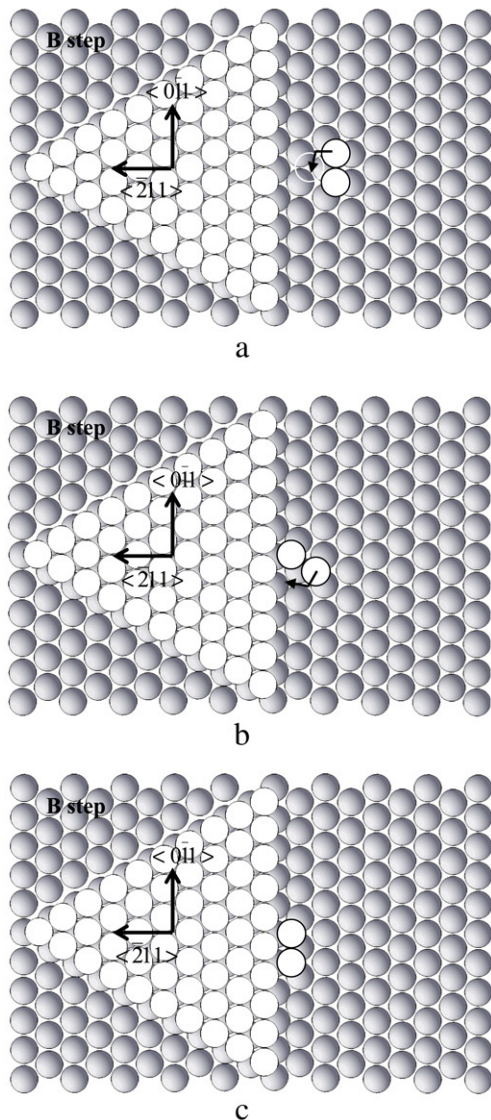
4. Conclusions

In summary, we have investigated the diffusion of small Co clusters on and near Co islands on Cu(111) surface. Our results show that mesoscopic relaxations at the island-substrate interface have significant influence on the migration barrier of small Co clusters towards the islands. It is revealed that dimer diffusion near the islands with B steps can be as fast as monomer's, which might be responsible for the formation of the dendritic shaped islands at low temperature.

References

[1] G.L. Kellogg, Surf. Sci. Rep. 21 (1994) 1.
[2] H. Brune, Surf. Sci. Rep. 31 (1998) 125.
[3] T.R. Linderoth, S. Horch, E. Läsgaard, I. Stensgaard, F. Besenbacher, Phys. Rev. Lett. 78 (1997) 4978.
[4] H. Bulou, C. Massobrio, Phys. Rev. B 72 (2005) 205427.
[5] W.W. Pai, A.K. Swan, Z. Zhang, J.F. Wendelken, Phys. Rev. Lett. 79 (1997) 3210.
[6] S.C. Wang, G. Ehrlich, Surf. Sci. 239 (1990) 301;   Phys. Rev. Lett. 79 (1997) 4234.
[7] Z.P. Shi, Z.Y. Zhang, A.K. Swan, J.F. Wendelken, Phys. Rev. Lett. 76 (1996) 4927.
[8] C.M. Chang, C.M. Wei, S.P. Chen, Phys. Rev. Lett. 85 (2000) 1044.
[9] G.L. Kellogg, Phys. Rev. Lett. 73 (1994) 1833.
[10] Q.V. Lysenko, V.S. Stepanyuk, W. Hergert, J. Kirschner, Phys. Rev. B 68 (2003) 033409.
[11] R.A. Micon, K.A. Fichthorn, Phys. Rev. B 72 (2005) 035415.
[12] Y. Shim, J.G. Amar, Phys. Rev. B 73 (2006) 035423.
[13] S. Ovesson, A. Bogicevic, B.I. Lundqvist, Phys. Rev. Lett. 83 (1999) 2608.
[14] M. Vladimirova, A.D. Vita, A. Pimpinelli, Phys. Rev. B 64 (2001) 245420.
[15] S.B. Lee, Phys. Rev. B 73 (2006) 035437.
[16] D.V. Tsivlin, V.S. Stepanyuk, W. Hergert, J. Kirschner, Phys. Rev. B 68 (2003) 205411.
[17] N.A. Levanov, V.S. Stepanyuk, W. Hergert, D.I. Bazhanov, P.H. Dederichs, A.A. Katsnelson, C. Massobrio, Phys. Rev. B 61 (2000) 2230.
[18] K. Wildberger, V.S. Stepanyuk, P. Lang, R. Zeller, P.H. Dederichs, Phys. Rev. Lett. 75 (1995) 509.
[19] F. Cleri, V. Rosato, Phys. Rev. B 48 (1993) 22;
     V. Rosato, B. Guillope, B. Legrand, Phil. Mag. A 59 (1989) 321.
[20] V.S. Stepanyuk, D.I. Bazhanov, A.N. Baranov, W. Hergert, P.H. Dederichs, J. Kirschner, Phys. Rev. B 62 (2000) 15398.
[21] V.S. Stepanyuk, A.L. Klavsyuk, W. Hergert, A.M. Saletsky, P. Bruno, I. Mertig, Phys. Rev. B 70 (2004) 195420.
[22] Š. Pick, V.S. Stepanyuk, A.L. Klavsyuk, L. Niebergall, W. Hergert, J. Kirschner, P. Bruno, Phys. Rev. B 70 (2004) 224419.
[23] R.A. Miron, K.A. Fichthorn, Phys. Rev. Lett. 93 (2004) 128301.
[24] K. Sastry, D.D. Johnson, D.E. Goldberg, P. Bellon, Phys. Rev. B 72 (2005) 085438.
[25] S.P. Ju, Y.C. Lo, S.J. Sun, J.G. Chang, J. Phys. Chem. B 109 (2005) 20805.
[26] V.S. Stepanyuk, A.L. Klavsyuk, L. Niebergall, A.M. Saletsky, W. Hergert, P. Bruno, Phase Tranit. 78 (2005) 61.
[27] J. de la Figuera, J.E. Prieto, C. Ocal, R. Miranda, Phys. Rev. B 47 (1993) 13043.
[28] L. Diekhöner, M.A. Schneider, A.N. Baranov, V.S. Stepanyuk, P. Bruno, K. Kern, Phys. Rev. Lett. 90 (2003) 236801.
[29] B.D. Yu, M. Scheffler, Phys. Rev. B 56 (1997) R15569.

Fig. 5. Schematic diffusion process of Co dimer near Co_{55} island with B step.

At the same time, we find that some corner diffusions of adatom and dimer have no barrier, which might enrich the diffusion behavior of small clusters near the islands.