Effect of mesoscopic relaxations on diffusion of Co adatoms on Cu(111)

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We demonstrate that mesoscopic relaxations in systems with low migration barriers significantly affect atomic motion in the vicinity of adsorbed islands. Atomic-scale calculations for Co islands and steps on Cu(111) reveal that adsorbate-induced strain in the substrate makes surface diffusion of Co adatom anisotropic. As the adatom approaches the island side, the migration barrier exhibits strong oscillations. Large energy barriers for the attachmnent of adatoms to islands are predicted by our calculations.

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Understanding film growth on the atomic level is critical for developing advanced materials and devices. In the early stage of growth stable and metastable islands are formed.[1] Atomic diffusion in the vicinity of the islands governs their size, shape, and density and finally the growth mode. Even after the deposition process surface diffusion can be decisive for the film morphology.[2]

At low island densities a two-dimensional random motion of isolated adatoms or tracer diffusion[3] takes place. When the thermal energies are much smaller than the migration barrier, i.e., $k_BT \ll E_m$, this process can be described in the framework of transition state theory (TST).[3] The corresponding diffusion coefficient is given by Ref. 4.

$$D = \frac{1}{2d} n \langle l^2 \rangle \nu_0 \exp\left\{ - \frac{E_m}{k_B T} \right\}, \tag{1}$$

where $\langle l^2 \rangle$ is the mean square hop length, d is the dimensionality of the motion ($d=2$ at the surface), n is the number of equivalent hop directions [for fcc(111) $n=3$], and ν_0 is the attempt frequency or prefactor. Experimentally, parameters E_m and ν_0 are determined by analyzing the dependence of island density on temperature and the deposition flux in the framework of mean-field nucleation theory (MFNT).[5] One of the key assumptions of the MFNT is that indirect interactions between adsorbates can be neglected. Recent theoretical[6] and experimental[7] studies revealed a complete failure of this approach for systems with low migration barriers. Existence of long-range interaction between adatoms affects nucleation in such systems and significantly modifies the predicted island densities.[8] Direct experimental observations prove that the interaction with steps[9] and islands[10] can influence adatom motion. This interaction can have either electronic[11,12] or elastic[13] origin.

Recently we have demonstrated that the island shape in the initial stages of transition metal homo[14] epitaxy and heteroepitaxy[15] is determined by the size-dependent mesoscopic mismatch. We have shown that the strain relaxation in Co islands on Cu(100) leads to stress oscillations during the epitaxial growth with a period of one atomic layer.[16] Atomistic simulations of Khalil *et al.*[17] suggest that the reduction of the strain energy can drive transition from single layer to bilayer Co growth on Cu(111) beyond a certain island size. Still little attention has been paid so far to the elastic strain in substrate near islands and it's role in atomic diffusion.

In this paper we demonstrate that the atomic motion near islands on metal surfaces with a weak corrugation is drastically influenced by the mesoscopic relaxation of the islands and substrate. As an example we present our results for the Co islands on Cu(111) which are model systems for structural, electronic, and magnetic studies.[18]

Performing atomic scale calculations we reveal a strong oscillation of adatom migration barrier near the Co islands. Anisotropy of adatom diffusion near the islands is found. Our results show that the size-dependent mesoscopic mismatch between the Co islands and the Cu substrate makes the migration barrier which also depends on the size of the islands.

Atomic scale simulations are performed using the *ab initio*-based many-body potentials recently developed by our group.[19] This approach is based on fitting of the potentials to accurate first-principle calculations of the surface and bulk properties of Co and Cu.[20] The potentials are formulated in the second moment approximation of the tight binding theory (TB-SMA). Parameters of the potentials were fitted to accurate first-principle results for Co clusters on Cu(001), as well as to the bulk properties of Co and Cu.[19,20]

To demonstrate the validity of the potentials for the Co/Cu(111) system we present in Table I binding energies for Co clusters on Cu(111) together with our *ab initio* calculations performed by means of the Korringa-Kohn-Rostoker (KKR) Green's function method for low-dimensional systems.[20] One can see that results obtained with our potentials are in good agreement with the *ab initio* calculations.

TABLE I. Binding energies (eV) of small Co clusters on Cu(111) calculated using the KKR Green's function method (*ab initio* data) and the TB-SMA potential. Details of the calculations and parameters of the potential are given in Refs. 19 and 20.

Configuration	*Ab initio* data	TB-SMA
Dimer	−1.18	−1.14
Triangle of three atoms	−3.06	−2.92
Chain of three atoms	−2.23	−2.13
Chain of four atoms	−3.10	−3.11

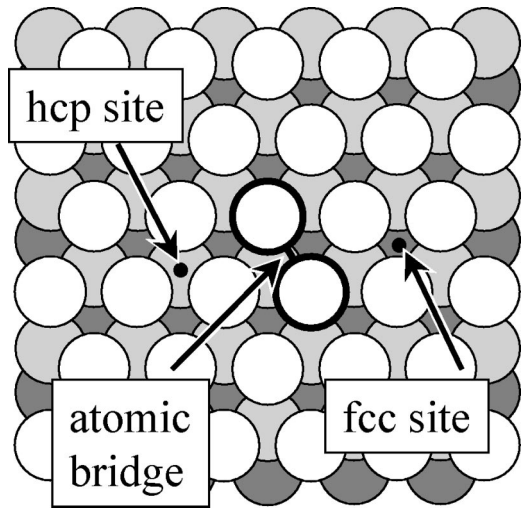

FIG. 1. Top view of the fcc(111) surface with two different types of adsorption sites corresponding to the fcc and hcp stacking sequence. The atomic bridge forms a twofold metastable adsorption site, which serves as a transition state for an elementary hopping process.

Atomic positions of clusters and the substrate atoms are determined in a fully relaxed geometry. The slab consists of eight layers with 1360 atoms in each layer. Two bottom layers are fixed and periodic boundary conditions are applied in the surface plane. Used interatomic potentials correctly reproduce the basic experimental finding for the Co/Cu(111) system—formation of three layer Co islands with one subsurface layer.[21] They also account for different binding energy of a ledge atom at Co steps of two possible types, thus explaining the triangular island form.[22,23]

First, we discuss the calculations of the migration barrier and prefactor for Co adatom on clean Cu(111) surface. Fig. 1 shows the schematic view of the fcc(111) surface with two different types of adsorption sites corresponding to fcc and hcp stacking sequences. The calculated energy difference between the two sites for Co adatom is less than 1 meV with fcc site being energetically more favorable. In the elementary diffusion event the adatom transfers from fcc site to the nearest hcp site (or vice versa) over a bridge formed by two Cu atoms in the substrate (cf. Fig. 1). The corresponding hopping barrier is found to be $E_m = 37$ meV. To calculate the value of prefactor we used the classical TST expression.[4]

$$\nu_0 = \frac{\nu_1 \nu_2 \nu_3}{\nu_1' \nu_2'}. \tag{2}$$

Here $\{\nu_1, \nu_2, \nu_3\}$ and $\{\nu_1', \nu_2'\}$ are the vibrational frequencies of the adatom in the equilibrium and transition (bridge) state, respectively. The calculated prefactor value for Co adatom on Cu(111) is $\nu_0 = 2.3 \times 10^{12}$ Hz. There is no distinguishable difference between the calculated parameters for the hopping from fcc to hcp site and from hcp to fcc.

In order to follow the experimental conditions we considered the diffusion of Co adatom in the vicinity of Co adsorbates. According to the experimental observations[22] adsorbed Co islands exhibit triangular shapes with their edges aligned along the close-packed $\langle 1\bar{1}0 \rangle$ directions of the Cu substrate. The macroscopic misfit between Co and Cu, defined as $m_0 = (r_{Cu} - r_{Co})/r_{Cu}$ is about 2% ($r_{Cu} = 2.56$ Å and $r_{Co} = 2.51$ Å are the first bond lengths in bulk Cu and Co). However, mesoscopic Co islands on Cu(111) do not have the bulk lattice spacing. Fig. 2 shows the calculated form of triangular Co_{36} island. The average bond length in the island is 2.47 Å, which is 3.4% smaller than Cu substrate. Strain relaxation at the island-substrate interface leads to deformation of both the island and the surface layers (cf. Fig. 2). Due to reduced interatomic distances in Co island compressive strain exists in the surface covered by the island. On the other hand, outside the island border Cu substrate undergoes tensile strain. Recent studies[24–29] have shown that atomic motion on strained and unstrained surfaces can be characterized by different migration barriers. Consequently, the expectation would be that migration barriers on Cu(111) surface are modified in presence of Co islands.

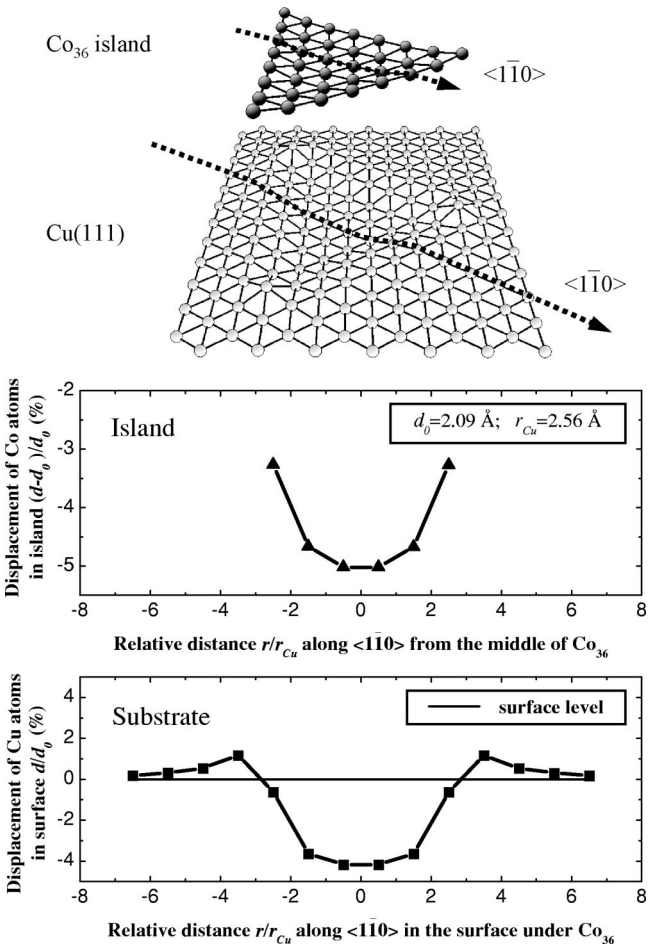

FIG. 2. Vertical displacements in Co_{36} island on Cu(111) and the substrate under the island calculated across the $\langle 1\bar{1}0 \rangle$ direction; d is the height above the surface level; $d_0 = 2.09$ Å is the interlayer distance in Cu(111); $r_{Cu} = 2.56$ Å is the bond length in Cu bulk.

In Fig. 3(a) we show schematically a sample diffusion path of Co adatom towards Co island. Numbers denote the elementary hops of the adatom along the $\langle 2\bar{1}\bar{1} \rangle$ direction. Energy barriers corresponding to the hops are plotted in Fig.

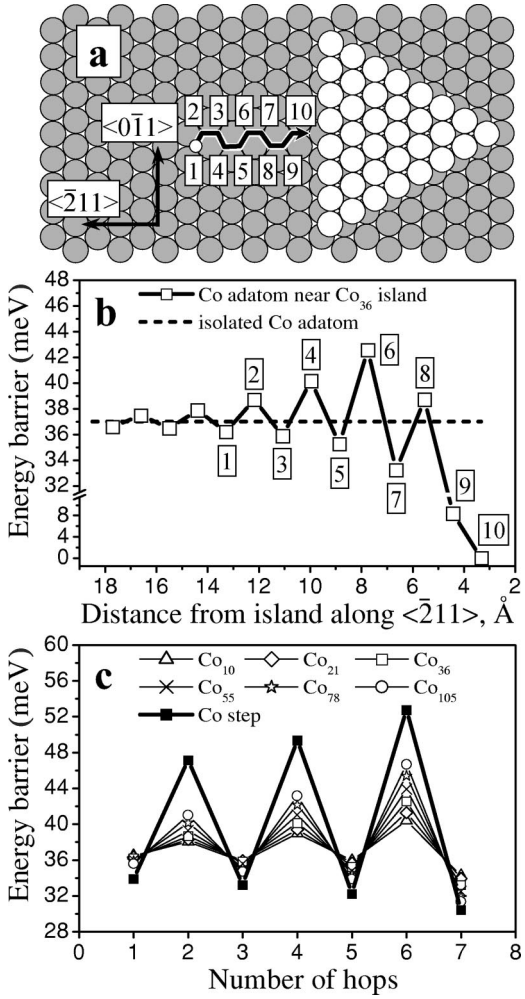

FIG. 3. (a) Schematic view of Co_{36} island (white circles) and the diffusion path of Co adatom. Numbers denote the hops of the adatom. (b) Plot of Co migration barrier near Co_{36} island. (c) Comparison of migration barriers for Co adatom near triangular Co islands of different sizes and near Co step.

3(b) as a function of the adatom-island separation. As the adatom approaches the island side, the migration barrier exhibits strong oscillatory changes. In the close vicinity of the island a direct attractive interaction with the adatom sets in. As a result, the last three energy barriers do not follow the common trend [see hops N8–10 in Fig. 3(b)]. Hop N10 has zero energy barrier and results in the attachment of at adatom to the island.

The deformation of the Cu(111) surface around Co islands is determined by the size-dependent mesoscopic mismatch between the island and substrate. Thus, the barrier oscillations should be different for different island sizes. In order to determine the role of the island size we considered the same diffusion path near several triangular Co islands and near Co step. The corresponding hopping barriers for Co adatom are plotted in Fig. 3(c). Clearly the same behavior is seen but the barrier oscillations become stronger for larger islands. In the limit of the step the amplitude of the oscillations is more than two times larger than for the Co_{36} island. In the close vicinity

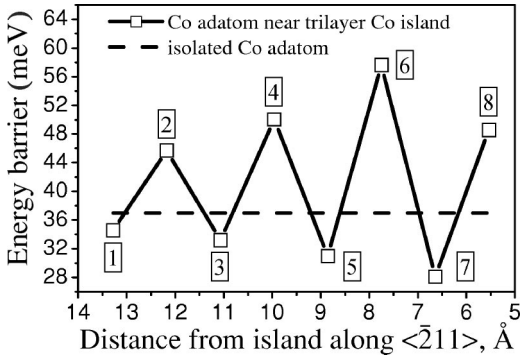

FIG. 4. Oscillations of the Co migration barrier near a three-layer Co island with one subsurface layer. The island consists of 45, 36, and 28 atoms in the consecutive layers.

of the step the barriers are strongly increased (upto 52 meV) as compared to the value for an isolated adatom (37 meV).

To understand these results we recall the recent calculations of adatom diffusion on strained surfaces.[24,25,27–29] The general trend for transition metals is the increase of hopping barrier with tensile strain.[25] This conclusion is supported by our calculations for the Co/Cu(111) system. Since outside the island border Cu substrate undergoes tensile strain, the hopping barriers in this area are raised. The nonmonotonic changes of the barrier are determined by the anisotropy of substrate deformation near the island edge. According to our calculations maximal tensile strain in Cu substrate corresponds to the direction perpendicular to the island edge [direction $\langle\bar{2}11\rangle$ in Fig. 3(a)]. Consequently, Co adatom hop in this direction and have the largest energy barriers [see Fig. 3(b), hops 2,4,6,8]. Strain in the direction along the island edge is slightly compressive [direction $\langle 0\bar{1}1\rangle$ in Fig. 3(a)]. The corresponding hopping barriers are reduced [hops 1,3,5,7 in Fig. 3(b)]. As the island size grows, the amount of Co adatoms, which have lattice spacing of Cu bulk increases. This implies that the average bond length in substrate near the island edge also increases. As a result, the hopping barriers near large islands turn to be higher than near small ones [cf. Fig. 3(c)].

Finally, we considered triangular Co islands with different orientation and height, as well as those occupying the metastable hcp adsorption sites. The behavior of Co migration barrier was qualitatively the same in all cases. As an example we show in Fig. 4 the barrier oscillations near a trilayer Co island with one subsurface layer. The amplitude of the oscillations is approximately two times larger compared to a single layer island of the same size.

Recently Bogicevic *et al.*[30,31] have studied the effect of adatom pair interaction on diffusion on (111) surfaces of Cu and Ag using density functional theory (DFT). For these systems separation and direction dependent energy barriers were reported. A similar result was obtained by Fichthorn and Scheffler[6] in the case of Ag adatoms on Pt(111). It was shown that a repulsive ring is formed about the adatoms, which can delay nucleation and drastically increase the islands density. In these studies modifications of the migration barrier about the single adatoms were attributed mostly to adatom-adatom interaction of the electronic origin. Accord-

ing to other DFT calculations adatom-step interaction on Al(111) is also mainly electronic.[32] Elastic effects in all cases were found to play a minor role. However, recent experiments suggest that the magnitude of electronic interactions can be significantly overestimated by DFT calculations.[33] On the other hand, according to our results adsorbed islands can significantly strain the substrate and thus, odsorbed islands stronger than adatoms can affect the migration barriers. In the limit case of the step the barrier assumes values in the interval from 30 to 52 meV. The changes are therefore as large as 60% of the migration barrier itself. It still remains unclear that how large the magnitude of electronic interaction between adatom and an island can be. Recently some new steps were made to answer this question.[34]

Apart from the adatom migration barriers, kinetics of island growth can also depend on the variation of adsorption energy or prefactor ν_0 near the island.[25,35,36] However, in our calculations Co adsorption energy in both fcc and hcp hollow sites on Cu(111) is affected to a very small extent by the island-induced strain in the substrate. For Co_{36} island the corresponding changes beyond the next-nearest-neighbor adatom-island separations are in the range of (2.039 ± 0.001) eV. In contrast, the energy barrier oscillations, presented in Fig. 3 are entirely determined by the variation of the adatom energy in the bridge position. The so-called compensation effect[35] from prefactor ν_0 is also not operative in our case. The prefactors for hops 1–8 near Co_{36} island are in the range of $(2.3 \pm 0.1) \times 10^{12}$ Hz. This result qualitatively agrees with recent atomic simulations of Kürpick for the Cu/Cu(111) system.[36]

Raised migration barriers about adsorbed islands should be accounted for, when analyzing the island density data in the Scanning Tunneling Microscope experiments. Apart from elastic interaction between adatom and island, a strong electronic interaction is expected.[8] Both these types of interactions should lead to a repulsive barrier for adatom attachment to islands and steps. We believe this can be the possible reason for a discrepancy between the experimental migration barrier value 190 meV reported in Ref. 37 for Co on Cu(111) and that calculated in the present work.

In conclusion, we have shown that energy barriers for bridge hopping of Co adatom near adsorbed Co island on Cu(111) are significantly different from those on clean surface. The island induces anisotropic strain in substrate which makes adatom motion parallel to the island side more preferable than in the direction to the island. The strain originates from existence of size-dependent mesoscopic mismatch between the island and substrate. This effect should be of general importance for homoepitaxial and heteroepitaxial systems with weak surface corrugation. Our calculations suggest that mesoscopic relaxations in such systems can be crucial for understanding the island growth and surface morphology.

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[1] Z. Zhang and M.G. Lagally, Science **276**, 377 (1997).
[2] A. Rabe, N. Memmel, A. Steltenpohl, and Th. Fauster, Phys. Rev. Lett. **73**, 2728 (1994).
[3] H. Brune, Surf. Sci. Rep. **31**, 125 (1998).
[4] D.E. Sanders and A.E. DePristo, Surf. Sci. **260**, 116 (1992).
[5] J.A. Venables, Philos. Mag. **27**, 697 (1973).
[6] K.A. Fichthorn and M. Scheffler, Phys. Rev. Lett. **84**, 5371 (2000).
[7] J.V. Barth, H. Brune, B. Fischer, J. Weckesser, and K. Kern, Phys. Rev. Lett. **84**, 1732 (2000).
[8] N. Knorr, H. Brune, M. Epple, A. Hirstein, M.A. Schneider, and K. Kern, Phys. Rev. B **65**, 115420 (2002).
[9] S.C. Wang and G. Ehrlich, Phys. Rev. Lett. **70**, 41 (1993).
[10] S.J. Koh and G. Ehrlich, Phys. Rev. Lett. **87**, 106103 (2001).
[11] K.H. Lau and W. Kohn, Surf. Sci. **75**, 69 (1978).
[12] V.S. Stepanyuk, A.N. Baranov, D.V. Tsivlin, W. Hergert, P. Bruno, N.Knorr, M.A. Schneider, and K. Kern, Phys. Rev. B **68**, 205410 (2003).
[13] K.H. Lau and W. Kohn, Surf. Sci. **65**, 607 (1977).
[14] O.V. Lysenko, V.S. Stepanyuk, W. Hergert, and J. Kirschner, Phys. Rev. Lett. **89**, 126102 (2002).
[15] V.S. Stepanyuk, D.I. Bazhanov, A.N. Baranov, W. Hergert, P.H. Dederichs, and J. Kirschner, Phys. Rev. B **62**, 15 398 (2000).
[16] D. Sander, S. Ouazi, V.S. Stepanyuk, D.I. Bazhanov, and J. Kirschner, Surf. Sci. **512**, 281 (2002).
[17] J. Khalil, G. Bozzolo, D. Farías, A.L. Vázquez de Parga, J.J. de Miguel, R. Miranda, Surf. Sci. (to be published).
[18] L. Diekhöner, M.A. Schneider, A.N. Baranov, V.S. Stepanyuk, P. Bruno, and K. Kern, Phys. Rev. Lett. **90**, 236801 (2003).
[19] N.A. Levanov, V.S. Stepanyuk, W. Hergert, D.I. Bazhanov, P.H. Dederichs, A.A. Katsnelson, and C. Massobrio, Phys. Rev. B **61**, 2230 (2000).
[20] K. Wildberger, V.S. Stepanyuk, P. Lang, R. Zeller, and P.H. Dederichs, Phys. Rev. Lett. **75**, 509 (1995).
[21] M.O. Pedersen, I.A. Bonicke, E. Legsgaard, I. Stensgaard, A. Ruban, J.K. Norskov, and F. Besenbacher, Surf. Sci. **387**, 86 (1997).
[22] J. de la Figuera, J.E. Prieto, C. Ocal, and R. Miranda, Phys. Rev. B **47**, 13 043 (1993).
[23] For example, we find that the embedding of Co_{36} island into the top layer of Cu(111) surface lowers the total energy by 0.23 eV/(Co atom), while 2D-3D transition in the island lowers by 0.036 eV/(Co atom). Binding energy of Co atom to Co *B* step is 32 meV larger than to *A* step.
[24] H. Brune, K. Bromann, H. Röder, K. Kern, J. Jacobsen, P. Stoltze, K. Jacobsen, and J. Nørskov, Phys. Rev. B **52**, R14380 (1995).
[25] R.F. Sabiryanov, M.I. Larsson, K.J. Cho, W.D. Nix, and B.M. Clemens, Phys. Rev. B **67**, 125412 (2003).
[26] E. Penev, P. Kratzer, and M. Scheffler, Phys. Rev. B **64**, 085401 (2001).
[27] C. Ratsch, A.P. Seitsonen, and M. Scheffler, Phys. Rev. B **55**, 6750 (1997).
[28] B.D. Yu and M. Scheffler, Phys. Rev. B **56**, R15569 (1997).
[29] M. Schroeder and D.E. Wolf, Surf. Sci. **375**, 129 (1997).
[30] S. Ovesson, A. Bogicevic, G. Wahnström, and B.I. Lundqvist, Phys. Rev. B **64**, 125423 (2001).
[31] A. Bogicevic, S. Ovesson, P. Hyldgaard, B.I. Lundqvist, H. Brune, and D.R. Jennison, Phys. Rev. Lett. **85**, 1910 (2000).
[32] R. Stumpf and M. Scheffler, Phys. Rev. B **53**, 4958 (1996).

[33] C. Polop, H. Hansen, C. Busse, and T. Michely, Phys. Rev. B **67**, 193405 (2003).
[34] P. Hyldgaard and T.L. Einstein, Surf. Sci. **532-535**, 600 (2003).
[35] G. Boisvert, L.J. Lewis, and A. Yelon, Phys. Rev. Lett. **75**, 469 (1995).
[36] U. Kürpick, Phys. Rev. B **66**, 165431 (2002).
[37] J.E. Prieto, J. de la Figuera, and R. Miranda, Phys. Rev. B **62**, 2126 (2000).