Strain and adatom motion on mesoscopic islands

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We demonstrate that the concept of mesoscopic misfit, rather than macroscopic misfit, should be used to describe the atomistic processes in the early stages of metal heteroepitaxy. Atomic scale calculations reveal the drastic effect of the mesoscopic misfit on strain in Co islands on the Cu(001) surface. We show that atomic motion on strained islands is strongly affected by the mesoscopic misfit and depends on the size of the islands. The diffusion coefficient on top of small islands is found to be larger by 2 orders of magnitude than that on large islands.

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The fundamental processes occurring during the early stages of epitaxial growth include the adsorption from the vapor phase, diffusion of the adatoms on the substrate surface, and the formation of stable and metastable islands[1] (cf. Fig. 1). Subsequent diffusion of single atoms on top of islands is one of the most important processes that determines the growth mode. Two-dimensional growth is expected if adatoms can escape over the edge of islands. If deposited atoms cannot leave the tops of the islands, three-dimensional (3D) growth will be promoted. The barrier for the motion on the top of islands and the Ehrlich-Schwoebel barrier for the jump over the island edge describe the elementary processes for interlayer mass transport (cf. Fig. 1). In general, a delicate balance among these barriers, the deposition rate, and the size and shape of islands determines the growth mode. The interlayer transport can also occur by an exchange mechanism at the edge of the island.[1]

Direct observation of adatom movement on surface clusters was made first in the field ion microscope[2–4] (FIM). These experiments demonstrated that motion of adatoms on top of islands is not the same as on a flat surface. An empty zone separating the central region from the cluster edge was observed for Pt diffusion on Pt(111).[4] FIM experiments of atom incorporation at steps[2] revealed a different behavior for atoms on top of small and large islands. In STM experiments of Ag growth on Pt(111),[5] the strong decrease of the step-edge barrier with respect to the homoepitaxial system Ag/Ag(111) was found. Presumably, strain relaxations in islands cause these unexpected effects.

It has been believed that the strain relief in heteroepitaxy is determined by the lattice mismatch between the two materials. However, several recent experiments showed that the lattice mismatch arguments are often inappropriate for understanding the strain relief in the early stages of the heteroepitaxial growth. For example, compressive stress was revealed for Fe, Co, Ni, and Cu on W(110) for submonolayer growth, while tensile stress is expected from the mismatch between bulk materials.[6,7] A giant compressive stress for the first few monolayers of Ag on Pt(111) was found, which is far beyond the stress expected from the lattice mismatch between Ag and Pt.[8] It was suggested that the mesoscopic misfit, rather than macroscopic misfit, should be used to explain strain relaxation in heteroepitaxy in the early stages of growth.[9] Especially for small islands the mesoscopic misfit may be significantly different from the macroscopic misfit between bulk materials. To our knowledge, little attention, if any, has been paid so far to the impact of the mesoscopic misfit on monolayer growth in metal heteroepitaxy.

The following fundamental questions arise: What is the effect of the mesoscopic misfit on atomic motion on top of islands? Does the atomic motion depend on the size of islands? We believe that the answers to these questions are of fundamental importance for understanding the atomistic processes in heteroepitaxy.

In this paper the interplay among the mesoscopic misfit, the size of islands, and diffusion on top of islands is revealed by performing atomic scale calculations. Due to strong experimental and theoretical activities on the growth processes in Co/Cu(001), we concentrate on the strain and diffusion processes for the Co islands on Cu(001), while the main conclusions of our work are of general interest. We show that the mesoscopic strain in Co islands has a profound effect on the diffusion of atoms on top of islands.

Atomic scale simulations are performed using the quasi–*ab initio* molecular dynamics method recently developed in our group.[10] This approach is based on fitting of many-body potentials to accurate first-principle calculations of selected cluster-substrate properties and bulk properties of Cu and Co. Potentials are formulated in the second moment approximation of the tight binding theory. These potentials correctly describe surface and bulk properties in the Co/Cu system. Atomic positions of clusters and the substrate atoms are determined in a fully relaxed geometry. The computa-

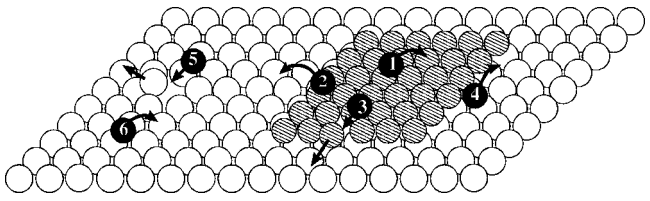

FIG. 1. Schematic view of diffusion processes: (1) jump on island; (2) Ehrlich-Schwoebel barrier; (3) edge exchange; (4) edge diffusion; (5) exchange on flat surface; (6) jump on flat surface.

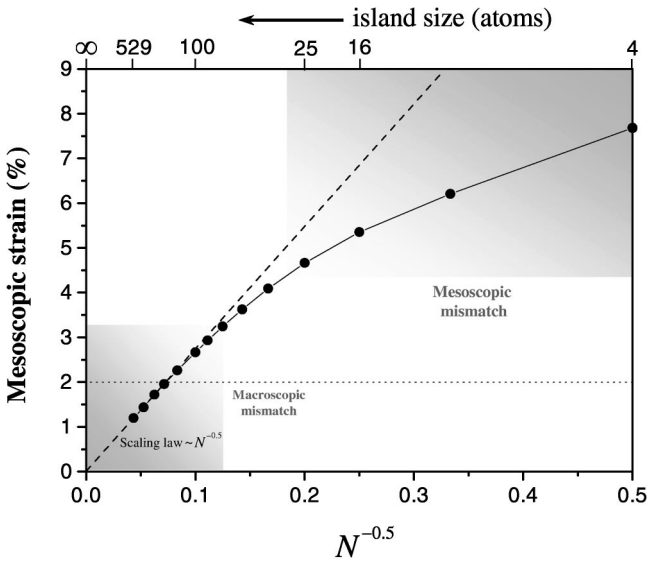

FIG. 2. Evolution of the average mesoscopic strain $m=(r_0-r_b)/r_0$ for Co square islands as a function of island size N (N number of atoms per island; r_b is the average first bond length in Co islands; $r_0=2.556$ Å is the first bond length for Cu bulk).

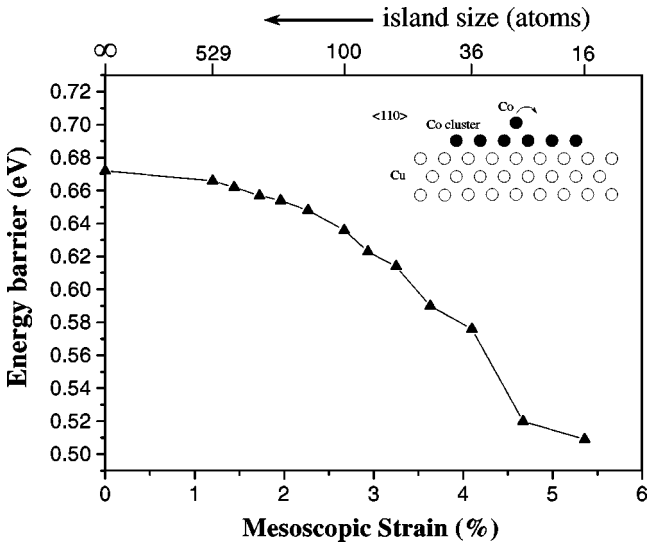

FIG. 3. Strain dependence of energy barrier for hopping diffusion on top of Co square islands. Since the strain depends on island size, the activation barrier for diffusion depends also on island size (see upper horizontal scale).

tional details and parameters of interatomic potentials have been presented in a recent publication.[10]

First, we discuss the size dependence of the mesoscopic strain in compact 2D Co square islands on the Cu(001). The macroscopic misfit m_0 between Co and Cu, defined as $m_0=(a_{\mathrm{Cu}}-a_{Co})/a_{\mathrm{Cu}}$ (a_{Cu} and a_{Co} are lattice constants) is small ($\approx 2\%$). However, Co islands on the Cu(001) surface do not have the bulk lattice spacing; therefore the mesoscopic strain m is not the same as the macroscopic one. The mesoscopic strain m is determined by measuring atomic bond lengths in Co islands and calculated as $m=(r_0-r_b)/r_0$ (r_b is the average first bond length in Co islands and r_0 the first bond length for Cu bulk). In small islands the relaxation of edge atoms can be the dominating process.[11] Since the perimeter of square islands scales as $N^{0.5}$ (N is the total number of atoms in the island), the expectation would be that the mesoscopic misfit m should scale like $N^{-0.5}$.

In Fig. 2 we show how the average strain in the Co islands changes with the size of islands. One finds that for islands larger than 60 atoms the strain scales like $N^{-0.5}$ indeed. In this region the mesoscopic misfit approaches the macroscopic one. It is clearly seen from Fig. 2 that for very small islands the mesoscopic misfit is not proportional to $N^{-0.5}$ and varies strongly with the cluster size. These results demonstrate that in the early stages of the growth the scenario of strain relief in islands is more complicated than expected from the lattice mismatch between bulk materials.

Now we turn to the discussion of the hopping diffusion of Co on top of Co islands. Contrary to the traditional view, we have found that the jump diffusion depends strongly on the size of islands. The barriers for the hopping on the small Co islands (16–50 atoms) are found to be about $\approx 20\%$ lower than those on the large islands (100–500 atoms) (cf. Fig. 3). The diffusivity D is related to the hopping rate of single adatoms by $D=D_0\exp(-E_d/kT)$, where E_d is the energy barrier for hopping and D_0 is the prefactor. We found that D_0 is nearly the same for all islands;[12] therefore the diffusion coefficient D on small Co islands at room temperature is found to be about two orders of magnitude larger than that on large Co islands. The physical mechanism responsible for such a drastic effect is related to the size-dependent mesoscopic strain in the islands. This is clear from Fig. 3, showing the diffusion barrier versus the mesoscopic strain. One can see that the large mesoscopic misfit between small Co islands and the Cu substrate corresponds to lower diffusion barriers compared to the large islands, where the mesoscopic misfit is considerably reduced. To understand these results we recall the recent calculations of atom diffusion on strained surfaces.[13–15] It was demonstrated that when the corrugation of the potential acting on adatoms on a surface decreases, the barrier for the jump diffusion also decreases, and vice versa. In Fig. 2 the large mesoscopic misfits correspond to a reduced average bond length in the islands. Shorter bonds lead to a reduced corrugation of the potential on the top of islands. It is useful to note that in the limit of very small bond length (i.e., strong compression) there are no more discrete binding sites and the hopping barrier vanishes. Therefore, the larger mesoscopic misfit (shorter bonds) leads to reduction of the hopping barrier. With increasing size of the islands, the amount of Co atoms, which have the Cu lattice spacing, will increase. This implies that the average bond length and the corrugation of the potential will also increase with increasing island size. The above qualitative consideration explains why the diffusivity on top of large islands is reduced compared to small islands.

It is worth noting that in the Co islands larger than 100 atoms the hopping barrier depends approximately linearly on strain (cf. Fig. 3). This finding is consistent with the calculations of the barriers for Ag self-diffusion on Ag(111).[14] It is interesting to note that in calculations using embedded atom potential the strain in Au clusters on a Ni surface was

TABLE I. Diffusion barriers for Co adatoms on a flat Cu(001) surface and deposited Co square island. The number in parentheses in the second column refers to the diffusion process illustrated in Fig. 1.

	Processes	Energy barriers
Flat	Exchange (5)	0.86 eV
surface	Jump (6)	0.66 eV
	Ehrlich-Schwoebel barrier (2)	1.03 eV
Strained	Edge exchange (3)	1.25 eV
islands	Edge diffusion (4)	0.20 eV

found to be a function of cluster size.[16]

We demonstrate that the diffusion of adatoms on top of islands depends strongly on the size of these islands. This may have important implications for epitaxial growth. Since reducing the compressive strain reduces the diffusivity on top of large islands, a higher nucleation probability is to be expected, which would promote 3D growth in the early stages of heteroepitaxy. However, if the kinetic energy of adatoms is sufficiently large to approach the island edge, the interlayer mass transport can occur in two ways (cf. Fig. 1): by the jump over the island edge or by an exchange process at the edge. The additional barrier at the edge (Ehrlich-Schwoebel barrier) exists because an atom reduces its coordination as it crosses the island edge. Our calculations show (cf. Table I) that for the Co islands, regardless of the size, the barrier for the jump over the island edge is lower than the exchange at the edge. In addition, we have found that there is no pronounced effect of the island size on the Ehrlich-Schwoebel barrier and on the edge exchange barrier. These results are presented in Table I together with the barriers for Co diffusion on the flat Cu surface. The Co adatom is found to diffuse on the flat surface preferably via a jump mechanism, the barrier for the exchange being much higher.

Finally we consider the diffusion on the substrate, but near the Co islands. We have found that the barrier for edge diffusion of Co atoms along Co islands of any size is significantly smaller than the barrier of the jump on a terrace (cf. Table I). We found that the strain relaxations in islands reduce this barrier approximately by 0.1 eV for all considered islands. The preferential diffusion of Co adatoms along the cluster edge can result in formation of compact Co islands. This finding is in agreement with recent kinetic Monte Carlo simulations[17] that predicted that the activation energy for step-edge diffusion on the fcc(001) surface is lower than that for isolated-adatom diffusion by hopping. It was suggested that such a mechanism leads to island formation in the absence of thermal mobility.

In summary, our results provide evidence that the mesoscopic misfit between two materials, rather than the macroscopic misfit, determines the atomistic processes in the early stages of thin-film growth. We have demonstrated that the mesoscopic misfit has drastic effects on atom motion on top of islands. This phenomenon is expected to be of general importance in metal heteroepitaxy. Our work clearly shows the limitation of the traditional concept of the macroscopic misfit for understanding of strain relaxations in the early stages of heteroepitaxy.

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