

Atomistic processes and the strain distribution in the early stages of thin film growth

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Abstract. Structural relaxations in small Co islands on the Cu(001) surface are investigated performing atomistic calculations. We demonstrate that the strain relief at the metal interface in the early stages of heteroepitaxy is more complicated than suggested by simple considerations based on the small mismatch between the Co and Cu bulk metals. We found that the strain distribution in the surface region near the islands varies strongly on an atomic scale. The effect of strain on the shape of the Co islands is revealed. Diffusion on the top of strained islands and edge diffusion are considered.

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A detailed understanding of film growth requires the study of the microscopic processes involved in epitaxy. Recent studies of submonolayer growth on metal surfaces have suggested that dimers can serve as the centers for growth of larger islands, as more adatoms diffuse to meet them [1–3]. Within the classic diffusion-limited aggregation (DLA) model once an adatom is attached to the growing cluster, it is trapped immediately with no further diffusion. However, this does not hold in general, even at low temperature. In real growth an adatom reaching an island will attempt to relax locally in order to find an energetically more favorable configuration. Due to local modifications at the cluster edges the classic hit-and-stick DLA model is inappropriate in many cases. For example, for Ag clusters on Pt(111) edge diffusion was found to be active down to at least 60 K [2]. The local diffusion processes along island edges lead to island formation during growth on the (100) surface of fcc metals, even in the absence of both thermal and nonthermal mobility of isolated adatoms [4].

The lattice mismatch between film and substrate material in heteroepitaxial growth leads to strain in islands. Recently Muller et al. [5] have demonstrated that even at interfaces with square symmetry strain relaxation in islands can lead to growth of ramified islands. Strain-induced shape transitions in islands were predicted by Tersoff and Tromp [6]. The shape

of islands is determined by the energy balance of the atomic bond energy within the islands and the strain energy due to the lattice mismatch. In small islands the mesoscopic misfit can be different from macroscopic one, which has a meaning only for infinite phases. It was shown that the mesoscopic misfit should depend on the size of nanostructures [7]. One can expect that even in systems with a small macroscopic misfit, strain effects in islands formed in the early stages of thin-film growth may be strong. Relaxations of atoms in islands can lead to in-plane lattice spacing oscillations. Recently such oscillations were observed during the hetero- and homo-epitaxy of metals [8, 9]. The growth of Co thin films on Cu(001) is of great importance, because the quality of the interface has a strong influence on properties such as giant magnetoresistance, magnetic anisotropy and interlayer coupling in Co/Cu(001) layers.

In this paper shape transitions in strained islands of Co on Cu(001) surface are investigated performing atomistic calculations with many-body potentials. We demonstrate that the strain relief in Co islands leads to inhomogeneous strain distribution in the surface. Unexpected shape transitions in the islands and the substrate are found. Edge diffusion and the diffusion on the top of islands are discussed.

1 Method of calculations

Atomic scale simulations are performed with finite slab with a free surface on the top and the two atomic layers fixed on the bottom. Periodic boundary conditions in the two directions parallel to the surface are used. The slab representing the substrate is 11 layers thick with 1058 atoms per layer. Molecular static calculations are performed to determine atomic positions of clusters and the substrate atoms in a fully relaxed geometry.

Our approach is based on fitting of the interaction parameters to accurate first-principles calculations of selected cluster-substrate properties and bulk properties of Cu and Co. The potentials are formulated in the form proposed by Rosato, Guiloep and Legrand (RGL) [10] with a modified form of the repulsive part. The cohesive energy E_{coh} is the

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sum of the band energy E_B and the repulsive part E_R :

$$E_{\text{coh}} = \sum_i (E_R^i + E_B^i), \quad (1)$$

$$E_B^i = - \left(\sum_j \xi_{\alpha\beta}^2 \exp \left(-2q_{\alpha\beta} \left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1 \right) \right) \right)^{1/2}, \quad (2)$$

$$E_R^i = \sum_j \left(A_{\alpha\beta}^1 \left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1 \right) + A_{\alpha\beta}^0 \right) \exp \left(-p_{\alpha\beta} \left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1 \right) \right), \quad (3)$$

where r_{ij} represents the distance between atoms i and j , and $r_0^{\alpha\beta}$ is the first-neighbor distance in $\alpha\beta$ lattice structure, whereas it is just an adjustable parameter in the case of the cross interaction. ξ is an effective hopping integral that depends on the material, and $q_{\alpha\beta}$ and $p_{\alpha\beta}$ describe the dependence of the interaction strength on the relative interatomic distance.

RGL potentials were derived in the second moment tight-binding approximation. It was shown in many calculations, that RGL potentials correctly describe surface relaxations, reconstruction and diffusion on surfaces of fcc transition metals.

In the present work, the parameters of Co–Co and Co–Cu interactions are optimized simultaneously to reproduce correctly the first-principles KKR Green's function calculations for binding energies of small Co clusters on Cu(001), the solution energy of the Co impurity in Cu bulk, the energies of interaction of two Co impurities in Cu bulk and in the surface layer and bulk properties of Co bulk. Parameters of Cu–Cu interactions are fitted to bulk properties of Cu bulk: lattice constant, cohesive energy, bulk modulus and elastic constants. For Co–Co and Co–Cu interactions magnetic effects are included implicitly by performing spin-polarized calculations for all clusters. The computational details and parameters of interatomic potentials have been presented in our recent publication [11].

2 Results and discussion

In this section we present results for Co islands on the Cu(001) surface. The interplay of surface morphology and strain relief in the islands is discussed. The energetics of isolated-atom diffusion on the terrace, edge diffusion along the islands and diffusion on top of islands is considered.

The macroscopic misfit between cobalt and copper is small ($\approx 2\%$). This would suggest a small tensile strain in Co nanostructures on Cu(001). However, small islands should adopt their intrinsic bond length, which can be different from the one in the bulk. Therefore, mesoscopic misfit between cobalt clusters and copper substrate can also be different from macroscopic misfit. Recently Pentcheva and Scheffler [12] have found that for very thin cobalt film the comparison of the bulk lattice parameter of the two material (macroscopic misfit) is inappropriate to study strained Co layers.

The reduced number of nearest neighbors near the island edges causes lower binding energies for edge atoms. These atoms are relaxing in the direction of the center of the island

and take other equilibrium positions with shorter bond than that of Co fcc bulk.

In order to get a deeper insight into the strain relief mechanism in small islands we calculate the bond length distribution in Co₃₆ square island on Cu(001), which is shown in Fig. 1. One can see that bonds in the cluster are shorter than the bond length in fcc Co and Cu bulk. Edge atoms exhibit strong relaxations in the direction of the center. Thus, the cluster is compressed with respect to fcc Co. With increasing size of the cluster the effect of edge atoms becomes less important and the average bond length increases (cf. Fig. 2). Still in a Co₁₀₀ island the average bond length is smaller than the one in fcc Co bulk. The above results indicate that strain relaxations in small Co islands may lead to pronounced structural changes in the substrate and the shape of clusters. In Figs. 3 and 4 we demonstrate that the cluster and the surface are not flat anymore. The cluster assumes a 'plate'-like

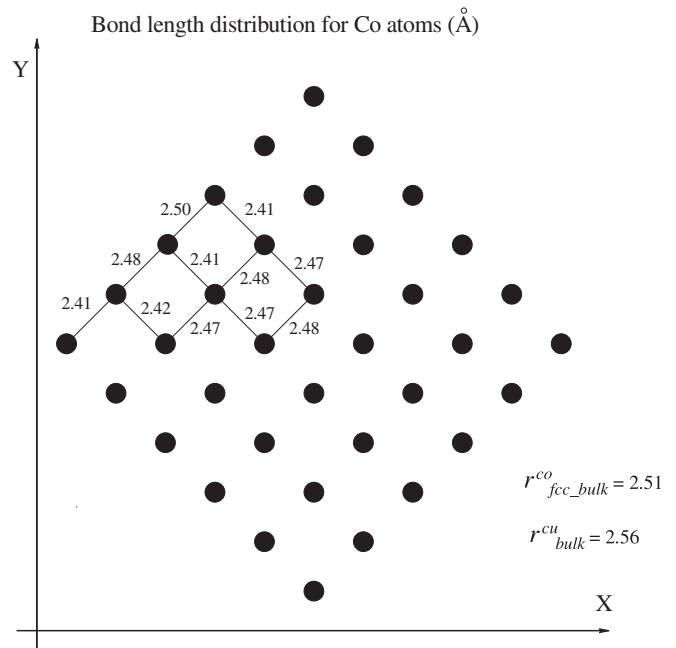


Fig. 1. Bond length distribution in Co₃₆ square island on Cu(001)

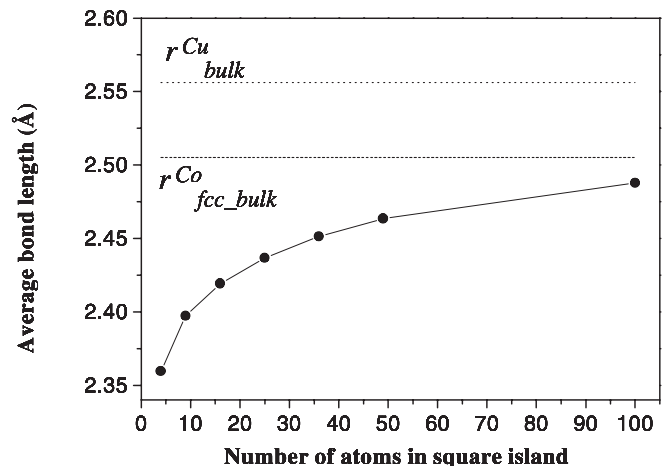


Fig. 2. Evolution of average bond length in Co plane islands on Cu(001) with increasing the size of the cluster (solid line)

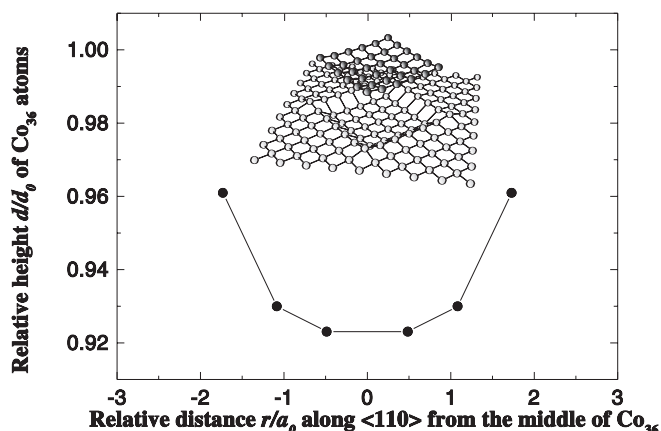


Fig. 3. The vertical displacement of Co atoms in Co_{36} square island due to the strain relaxation. The Co atoms are placed along the line in $\langle 110 \rangle$ direction from the middle of Co_{36} island (solid line). The relation to the Cu bulk parameters is used: interlayer distance $d_0 = 1.8075 \text{ \AA}$ and lattice constant $a_0 = 3.615 \text{ \AA}$ (in figure captions). The ‘plate’-like shape for Co island is demonstrated. Inset: schematic diagram for atomic arrangement of Co_{36} square island (black circle) on Cu(001) (white circles) in minimum-energy configuration

shape and an adsorption ‘hole’ appears in the surface under the cluster. The edge atoms in the Co cluster are highest (cf. Fig. 3). The vertical displacement of Cu atoms of the uppermost Cu(001) plane and average strain distribution in the substrate along $\langle 110 \rangle$ direction are shown in Fig. 4. The substrate atoms under the cluster are pushed down, while atoms at the outer edge of the Co cluster are pushed up. This effect could provide an effective block to cluster mobility. The average strain in the surface layer under the cluster is negative, i.e. the substrate atoms are under compressive strain. In contrast, the average strain of the substrate atoms at the outer edge of the cluster is tensile. Thus, small Co islands formed in the early stage of thin film growth introduce a strong inhomogeneous strain distribution in the surface layer. We think that the above results reflect the reaction of Co atoms on the large mesoscopic strain, i.e. Co atoms prefer to adopt their intrinsic bonds, being shorter than the bulk bond. The competition between Co–Co and Co–Cu bonding is also a driving force for the shape transitions in the clusters and the substrate. Our calculations show that Co–Co bonds are stronger than Co–Cu

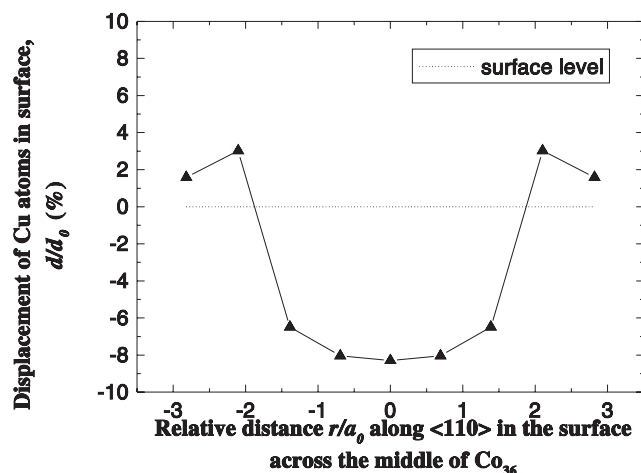


Fig. 4. The vertical displacement of Cu atoms of the uppermost Cu(001) plane under Co_{36} island (solid line). The Cu atoms are placed in the line in $\langle 110 \rangle$ direction across the middle of Co_{36} island (solid line). The relation to the Cu bulk parameters is used: interlayer distance $d_0 = 1.8075 \text{ \AA}$ and lattice constant $a_0 = 3.615 \text{ \AA}$ (in figure captions). The profile of ‘plate hole’ is demonstrated in the Cu substrate

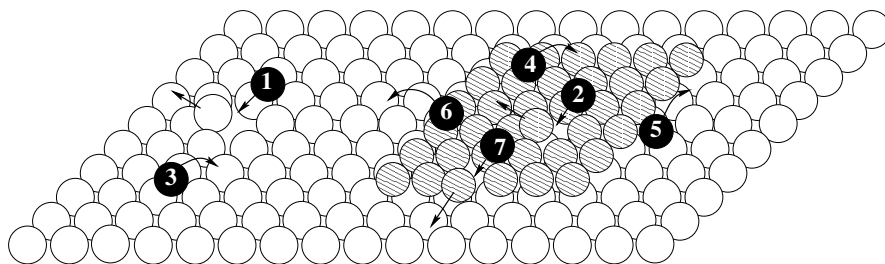
and Cu–Cu bonds and consequently we found a stronger relaxations of Co–Co interatomic distances in the Co cluster. The reported changes in the cluster shapes and the substrate are likely of general importance. We believe that the small film strain of order 0.1% can induce a significant change in the magnetic anisotropy [13].

We have also performed calculations for large Co islands (up to 200 atoms) and found that the hole in the surface under the island becomes smaller with increasing cluster size. The relaxation of the edge atoms is dominating only in small islands (up to 100 atoms). Island coalescence will dominate for larger coverage and the amount of Co atoms strained to the Cu lattice spacing will increase. Results for large Co islands will be published elsewhere.

Now we turn to the discussion of diffusion barriers for Co adatoms on Cu(001) surface. Our results are presented in Table 1. The Co adatom is found to diffuse preferably via a jump mechanism, the barrier for the exchange being much higher. It is important to note that the knowledge of the barrier heights is not sufficient to determine which process occur

Table 1. Diffusion processes of Co atoms for Co/Cu(001) system with deposited Co_{36} square island. (*) – index itemizes the diffusion process illustrated in schematic diagram below

| Processes (*) | Diffusion on flat surface | Diffusion on C_{36} island |
|-------------------------------|---------------------------|-------------------------------------|
| Exchange (1,2) | 0.86 eV | 0.90 eV |
| Jump (3,4) | 0.66 eV | 0.58 eV (0.69 eV) |
| Edge diffusion (5) | – | 0.20 eV (0.31 eV) |
| Ehrlich–Schwoebel barrier (6) | – | 1.03 eV (1.08 eV) |
| Edge exchange (7) | – | 1.25 eV |



most frequently on a given surface, because prefactors for the jump and the exchange processes can be different. To our knowledge, prefactors for Co diffusion on Cu(001) surface have not been determined. Nevertheless, surfaces with large activation barriers for diffusion compensate the difficulty in overcoming these barriers by increasing their prefactors (Meyer–Neldel rule) [14]. Recently, the interfacial intermixing at the Co/Cu(001) interface was found [15]. It is useful to recall our recent work on Co/Cu(001) [11]. We have shown that Co adatoms lower their energy by a direct-exchange mechanism with a Cu surface atom, thus residing in the terrace. The intermixing in the upper layers might not only be favored energetically, but also kinetically.

Finally we consider the diffusion near and on the top of Co islands. Recent kinetic Monte Carlo simulations [4] predicted that the activation energy for step-edge diffusion on the fcc(001) surface is lower than the barrier for isolated-adatom diffusion by hopping. It was suggested that such a mechanism leads to island formation in the absence of thermal mobility. Our results show that the barrier for edge diffusion of Co atoms along Co islands is significantly smaller than the barrier of the jump on a terrace (cf. Table 1). The preferential diffusion of Co adatoms along the cluster edge can result in formation of compact Co islands [16].

If deposited Co atoms can migrate from the top of Co islands down to the adsorption sites on the first layer, layer-by-layer growth will be promoted. The barrier for the jump on the top of the island, the Ehrlich–Schwoebel barrier for jump over the cluster edge and the barrier for an atomic exchange at the cluster edge describe the elementary process for interlayer mass transport. Our calculations for Co_{36} show (cf. Table 1) that the barrier height for the jump on the top of the island (0.58 eV) is less than the jump on the terrace (0.66 eV). For interlayer transport mechanism the barrier for jump over the cluster edge is lower than direct exchange. In Table 1 the barriers calculated without relaxation of the cluster are given in brackets. One can see that the effect of the cluster and substrate relaxations on diffusion is strong: relaxations reduce the barriers for all processes considered here. We have found that also the island size influences the activation barrier for adatom diffusion on the top of island [17].

3 Conclusion

We have predicted that the relaxation of lattice strain at the Co/Cu(001) interface can be much more complex than expected. Drastic strain effects on the atomic structure of both the island and the substrate have been found. Small Co islands and the surface under these clusters are not flat due to strain relief. A strongly inhomogeneous strain distribution in the substrate near Co islands has been revealed. A small barrier for edge diffusion of Co adatoms near the Co island can promote growth of compact Co islands on Cu(001) surface.

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