PHYSICAL REVIEW B VOLUME 62, NUMBER 23 15 DECEMBER 2000-I

Strain relief and island shape evolution in heteroepitaxial metal growth

V. S. Stepanyuk,[1,*] D. I. Bazhanov,[2,3] A. N. Baranov,[3,4] W. Hergert,[1] P. H. Dederichs,[4] and J. Kirschner[2]
[1]*Fachbereich Physik, Martin-Luther-Universität, Halle-Wittenberg, Friedemann-Bach-Platz 6, D-06099 Halle, Germany*
[2]*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany*
[3]*Solid State Physics Department, Moscow State University, 119899 Moscow, Russia*
[4]*Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich*

(Received 19 September 2000)

Atomistic scale calculations reveal that cobalt islands on Cu(001), as they grow in size, undergo unusual shape evolution. The strain relief in the Co islands is predicted to have a strong effect on the shape of the islands and the morphology of the substrate in the early stage of the film growth. We show that strain and stress at the interface vary strongly on an atomic scale. Our results demonstrate that the strain relief in the early stage of heteroepitaxy is more complicated than suggested by simple considerations based on the lattice mismatch of bulk materials.

The classical rule used to predict heteroepitaxial growth is based on the lattice mismatch between film and substrate.[1] However, several recent experiments[2–4] have shown that the scenario of the strain relaxation at metal interfaces is more complicated than expected from the lattice misfit. In contradiction to lattice mismatch consideration, a tremendous compressive stress in Ni on W(110) below 0.5 monolayer (ML) was measured.[2] Also, for Fe, Co, and Cu on W(110) compressive stress was found, while tensile stress is expected from mismatch arguments.[3] A giant compressive surface stress for the first few monolayers of silver on Pt(111) was reported, which is far beyond the stress induced by the misfit.[4] The results of stress measurements in the submonolayer range give clear evidence that continuum elasticity relying on bulk reference data is of questionable relevance for films thinner than 10 Å.[2] *Ab initio* studies have shown that for very thin cobalt films the comparison of the bulk lattice parameters of the two materials is inappropriate to study strained Co layers on Cu(001).[5]

In the initial stage of metal heteroepitaxy the lattice mismatch between film and substrate material leads to strain in islands. Strain-induced shape transitions in islands were predicted by Tersoff and Tromp.[6] Recently Muller *et al.*[7] have demonstrated that even at interfaces with square symmetry strain relaxation in islands can lead to growth of ramified islands. 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 the macroscopic one, which has a meaning only for infinite phases. It was shown that the mesoscopic misfit should depend on the size of nanostructures.[8] Relaxations of atoms in islands caused by the mesoscopic misfit can lead to in-plane lattice spacing variations, which cannot be predicted using macroscopic mismatch arguments. Recently in-plane lattice oscillations were observed during the heteroepitaxy and homoepitaxy of metals.[9,10]

In this report we demonstrate that even in systems with a small lattice mismatch the island growth in the initial stages of metal heteroepitaxy is drastically influenced by the size-dependent strain relaxation. We concentrate on Co islands on Cu(001). The growth of Co on Cu(001) is of general interest in the area of magnetoelectronics, because the quality of the Co/Cu interface has a strong influence on properties such as giant magnetoresistance, magnetic anisotropy, and oscillatory exchange coupling.[11] We demonstrate that cobalt islands, as they grow, undergo a size-dependent shape transition. The interplay of surface morphology, strain relief, and surface stress is revealed.

Atomic scale simulations are performed by means of the quasi–*ab initio* molecular static method recently developed in our group.[12] This approach is based on first principle calculations of selected cluster-substrate properties, which are used in the fitting of *N*-body potentials. The potentials are formulated in the second-moment tight-binding approximation. The combination of *ab initio* and semiempirical methods allows us to reproduce accurately the bulk and surface properties and to include implicitly magnetic effects in the interatomic forces. Details of the method and the parameters of the potentials can be found elsewhere.[12]

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, 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 length than that of Co fcc bulk. Small islands should adopt their intrinsic bond length, which can be different from that in the bulk. Therefore, the mesoscopic misfit between cobalt clusters and the copper substrate can also be different from the macroscopic misfit, which has a meaning only for infinite phases.

In order to quantify the view of the mesoscopic misfit and strain relaxations in the islands we calculate in the fully relaxed geometry the average bond length in the two-dimensional compact Co islands on Cu(001). Our results are presented in Fig. 1. One can see that average bonds in the islands are shorter than the bond length in fcc Co and Cu bulk due to the strong relaxation of edge atoms. With increasing size of the cluster, the effect of edge atoms becomes less important and the average bond length increases. Still in a Co island containing 100 atoms (Co_{100}) the average bond

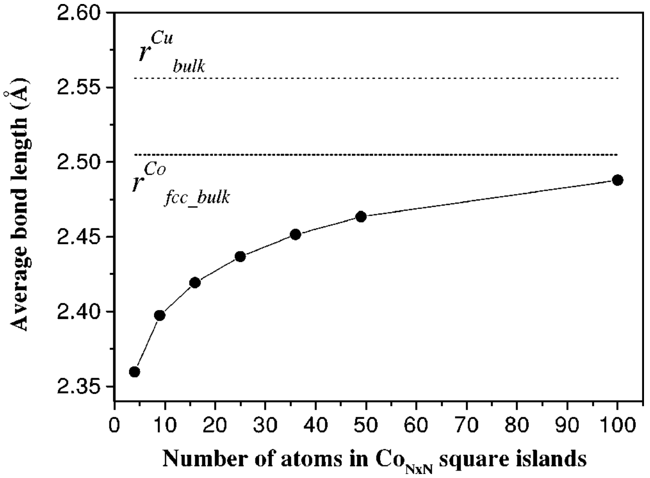

FIG. 1. The average Co-Co bond length in the two-dimensional compact Co islands on Cu(001).

length is smaller than that 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 order to get a deeper insight into the strain relief mechanism in the Co islands the shape of the islands and the surface morphology under the islands are determined. The evolution of the Co island shapes with increasing size is presented in Fig. 2. These results demonstrate that the islands and the surface layers are not flat anymore. The islands assume a platelike shape, and an adsorption ''hole'' appears in the surface under the island. The edge atoms in the Co islands are highest. In Fig. 3 we show the atomic displacement in the Co_{36} island and in the substrate along the $\langle 110 \rangle$ direction. The substrate atoms under the island are pushed down, while substrate atoms at the outer edge of the Co island are pushed up. This effect could provide an effective block to island mobility. The average strain (determined by measuring bond lengths) in the substrate layer under the cluster in the direction parallel to the surface 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 island 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.

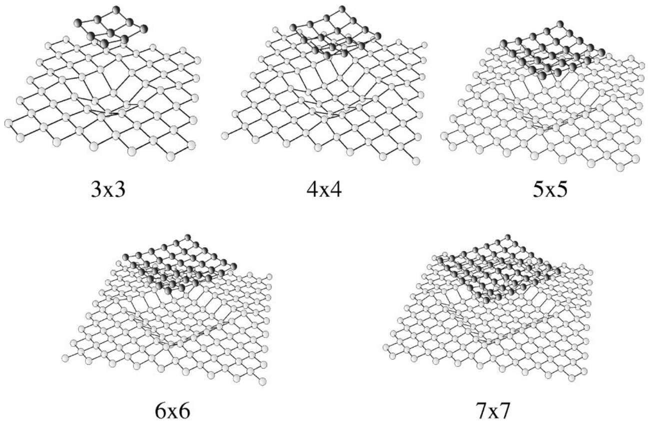

FIG. 2. The evolution of the Co island shape with increasing size.

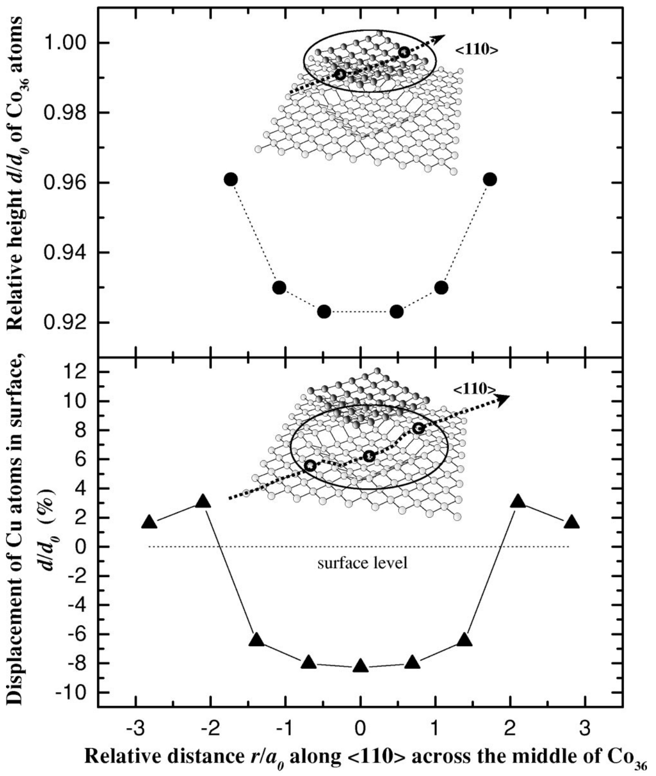

FIG. 3. The vertical displacement of Co atoms in the Co_{36} square island and the surface atoms in the topmost layer under the island in $\langle 110 \rangle$ direction; interlayer distance $d_0 = 1.8075$ Å and lattice constant $a_0 = 3.615$ Å.

It is important to note that the displacement fields on the Cu(001) under and near the Co islands are very similar to the results obtained for individual surface steps using elastic theory and atomistic simulations. Examples here include, but are not limited to, steps on Ni and Au surfaces.[13] It was found that the atomic displacement fields near surface steps exhibit a nontrivial behavior: there is a plane across which the out-of-plane atomic displacements change sign. This is the same effect that we have observed at the Co/Cu(001) interface (cf. Fig. 3). With increasing island size the hole in the surface under the island becomes smaller and ''bending'' of the island decreases. Thus, the growth of the Co on Cu(001) proceeds by a strong shape transition in the islands and a significant change of the surface morphology. Island coalescence will dominate for larger coverage, which reduces the strain relaxations in the islands and in the surface layer.

We should emphasize that step bending and island shape transitions have been predicted using elasticity theory.[14,15] Here these effects are investigated for transition metal heteroepitaxy by performing atomic scale simulations.

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 bond lengths, being shorter than the bulk bond length. The competition between Co-Co and Co-Cu interactions is also a driving force for the shape transitions in the clusters and the substrate. Our calculations show that the Co-Co interaction is stronger than Co-Cu and Cu-Cu interactions, and consequently we found a stronger relaxation of Co-Co interatomic distances in the Co cluster. The reported changes in the cluster shapes and the substrate are likely of general importance and should have a profound effect on island growth.

While we have used a particular system to illustrate island shape evolution in heteroepitaxial metal growth, it is generally true that strain makes the island shape size dependent.[15] Even in the case of homoepitaxy, where there is no macroscopic mismatch, the mesoscopic mismatch exists[8] because islands have different bond lengths compared to the bulk. Therefore, similar to heteroepitaxial growth, homoepitaxy at the mesoscale region can proceed by a shape transitions in islands.

Similar effects can exist in the case of a highly strained semiconductor heteroepitaxy. For example, recent experiments[16] on Ge/Si(100) islands have shown that an inhomegeneous strain distribution in the Si substrate at the base of the Ge island leads to the diffusion of the higly strained substrate material to regions of lower strain and trenches at the base of the islands are formed. The first molecular dynamics examination of a strained Ge/Si systems revealed a highly inhomogeneous nature of stresses and strains on an atomic scale.[17] In the case of Co/Cu(001), we find that the vacancy activation energy is drastically reduced near the cluster edge compared to a flat substrate[18] due to the increased tensile strain in the substrate at the cluster edge (cf. Fig. 3). Therefore, we expect that similar to the observation on Ge/Si(100) islands,[16] the Cu atoms will diffuse from near the island perimeter to regions of lower strain. Presumambly, such a mechanism can promote burrowing of Co clusters on the Cu(001) recently observed in experiments.[19]

We believe that the small film strain of the order of 0.1% can induce a significant change in magnetic anisotropy.[20] Thus, the shape evolution in the Co islands can have a strong effect on magnetic properties in the early stage of growth.

It is interesting to note that in calculations using the embedded atom potential a tentlike shape of Au clusters on a Ni surface[21] and Ag clusters on a Pt surface was revealed.[22] It was also shown[23] that adsorbate atoms Li, Na, and Mg on the (001) surface of Li induce a shallow hole in the substrate, while the Al adsorbate creates a low bump.

Finally, we turn to the stress distribution in the islands and in the uppermost Cu substrate layer. We perform calculations of the atomic level stress components:[17]

$$\sigma_{\alpha\beta}(i) = -\frac{1}{\Omega_0}\left[\frac{p_i^{\alpha} p_i^{\beta}}{m_i} + \frac{1}{4}\sum_{j}\left(r_{ij}^{\beta} f_{ij}^{\alpha} + r_{ij}^{\alpha} f_{ij}^{\beta}\right)\right], \qquad (1)$$

where $(\alpha\beta) \equiv (x,y,z)$, m_i and p_i are the mass and momentum of atom i, $\vec{r}_{ij}$ means the distance between atom i and j, $\vec{f}_{ij}$ is the force acting on atom i due to atom j, and Ω_0 defines the average atomic volume.

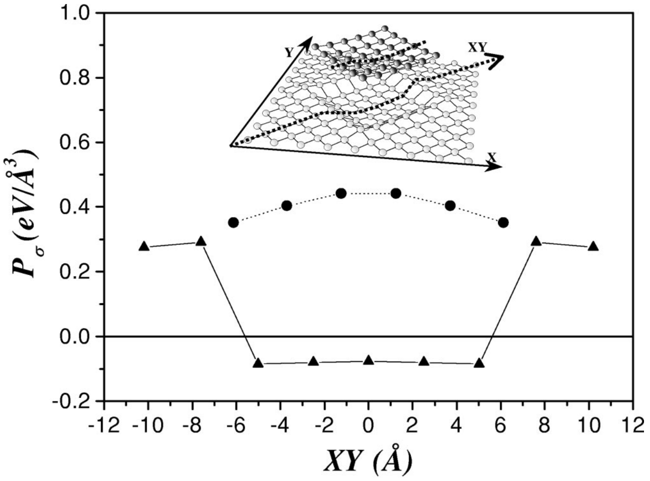

FIG. 4. The hydrostatic stress for the Co_{36} island and the uppermost Cu atomic layer along ⟨110⟩ direction.

Figure 4 shows the atomically resolved hydrostatic stress $P_\sigma = \mathrm{Tr}(\sigma_{\alpha\beta})$ in the Co_{36} island and in the surface layer. One can see the spatially varying nature of the stress on the Cu atomic layer. At the island edge, the stress is highly tensile, while the substrate layer under the island is seen to exhibit compressive hydrostatic stress. The tensile hydrostatic stress at the cluster center is different from that at the edge. We expect that the inhomogeneous stress distribution in the islands will influence the motion of atoms on top of the islands. It is worth noting that an empty zone found for atom diffusion on clusters[24] likely can be explained by the inhomogeneous stress distribution in islands.

In conclusion, the strain relief in the Co islands is predicted to have a profound effect on the shape of the islands and the morphology of the substrate in the early stage of the film growth. Small Co islands and the surface under these islands are not flat due to strain relief. A strongly inhomogeneous stress distribution in the substrate near Co islands has been revealed. This phenomenon is expected to be of general importance in transition metal heteroepitaxy and can have a strong effect on magnetic properties. We believe that strain fields at the mesoscale stage will be possible to detect using, for example, a new x-ray diffraction imaging procedure that has been recently proposed[25] for non-destructive determination of local strain with a high spatial resolution.

Calculations were performed on the Cray computer of the German supercomputer center (HLRZ). This project was supported by Deutsche Forschungsgemeinschaft (DFG).

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*Email address: stepan@valinux.physik.uni-halle.de

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