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Mesoscopic scenario of strain-relief at metal interfaces

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Abstract

Strain relaxations at metallic interfaces are usually predicted on the basis of macroscopic lattice mismatch. The new concept of mesoscopic mismatch is introduced, which will be more appropriate to discuss stress and strain fields near metallic islands on metallic surfaces. Using recently developed ab initio based many body potentials, the impact of mesoscopic mismatch on heteroepitaxial and homoepitaxial growth is investigated. Co and Cu islands on Cu(1 0 0) and Co islands on Cu(1 1 1) are studied.

Keywords: Mesoscopic mismatch; Quasi-ab initio molecular dynamics; Metal interfaces

1. Introduction

Interactions between atoms in bulk systems determine the intrinsic equilibrium bond length. If some material is grown on a substrate with a different bond length the lattice mismatch at the interface leads to strain fields. Strain can be relieved through the introduction of defects in the atomic structure, such as dislocations, or by an atomic rearrangement. The strain-relief patterns can be used for atomic engineering which allows one to fabricate fascinating materials at the nanoscale, such as quantum dots [1] and magnetic vertical pillars [2]. Usually strain relaxations are predicted on the basis of the macroscopic lattice mismatch between the two materials. However, if the deposited system is of mesoscopic size of several hundred atoms, its intrinsic bond lengths are different from the bond length in the bulk material. In this case the strain induced at the interface can locally distort the surface in an unpredictable way. Even in the case of homoepitaxy, where no macroscopic mismatch is present, the mesoscopic mismatch may lead to the drastic strain relaxations [3]. We demonstrate unexpected scenarios of strain-relief in mesoscopic islands in metal hetero- and homoepitaxy. Our results lead to the conclusion that the size-dependent mesoscopic mismatch, rather than the macroscopic one, is the driving force for strain-relieving effects at the mesoscale.

2. Mesoscopic mismatch in heteroepitaxial growth

2.1. Co islands on Cu(1 0 0)

We choose for our presentation Co islands on Cu(1 0 0) due to the importance of this system in magnetoelectronics. It has been believed that strain relaxations at the Co/Cu(1 0 0) interface are determined by the mismatch between Co and Cu bulk. This macroscopic mismatch m_0 between Co and Cu defined as $m_0=(a_{Cu}-a_{Co})/a_{Cu}$ (a_{Cu} and a_{Co} are lattice constants) is only $\approx 2\%$. This would suggest a small tensile strain in Co nanostructures on Cu(1 0 0). However, mesoscopic and macroscopic islands should adopt their intrinsic bond lengths, which can be different from the bond length in bulk. Therefore, the strain induced at the interface can locally be larger and may stronger affect structural, electronic and magnetic properties, than expected. For example, a small strain of order only 0.1% can produce significant changes in the magnetic anisotropy [4]. Several recent experiments have suggested that strain relaxations for the submonolayer coverage [5,6] or even for a few monolayers [7] cannot be explained by the macroscopic mismatch between bulk materials. Unexpected in-plane lattice spacing oscilla-

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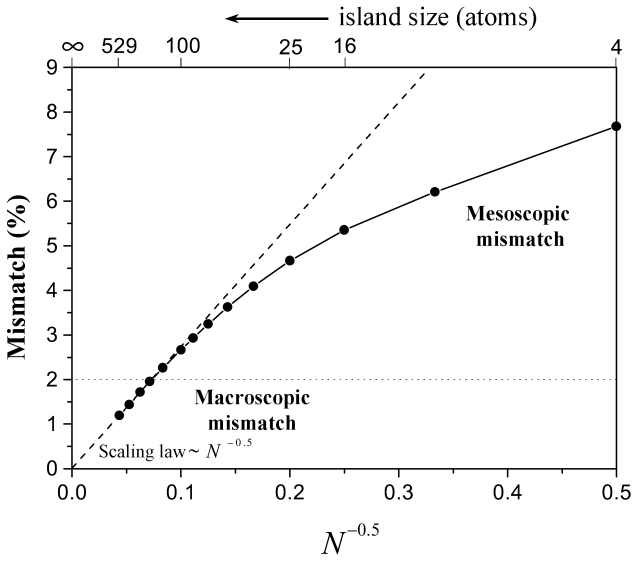

Fig. 1. Size-dependent mismatch $m=(r_b^{Cu}-r^{Co})/r_b^{Cu}$ for the Co square islands on Cu(1 0 0) (r_b^{Cu}—first bond length for Cu bulk; r^{Co}—average bond length in Co islands).

tions during the growth of Co on Cu(1 0 0) [3] and ramified copper islands on Ni(1 0 0) [8] are further examples of unusual strain relaxations at the nanoscale.

In order to get a deeper insight into the local strain relaxations on an atomic scale, the equilibrium geometries of plane square Co islands of different sizes (up to 600 atoms) on Cu(1 0 0) are calculated by computing the forces at each atomic site and relaxing the geometry of islands and the substrate atoms. We use a quasi-ab initio molecular dynamics method [9], which is based on the tight-binding approximation for many body potentials. Accurate first principle spin-polarized calculations of cluster–substrate properties [10] are performed to construct the interatomic potentials at the Co/Cu(1 0 0) interface. It has been shown that surface and bulk properties are well described by this method [9].

In Fig. 1 we show the change in the mismatch with the size of Co islands. It is seen, that the mesoscopic mismatch between small Co islands and the Cu substrate is considerably larger than the mismatch calculated from the lattice constants of the two materials.

Only for Co islands incorporating more than 200 atoms the local strain can be described by the macroscopic mismatch. We found that both the mesoscopic and macroscopic mismatch depend on the size of the islands and for the islands larger than 60 atoms mismatch scales as $N^{-0.5}$ (N—number of atoms in the island). Such scaling behavior is determined by the relaxations of edge atoms of the islands, whose number changes as $N^{0.5}$. For very small islands (for example, $N=9$) the mismatch is approximately 30% smaller than obtained from 'asymptotic' prediction based on scaling law, but extremely large, since practically all atoms are edge atoms. One very fundamental issue predicted by these results is the possible strong impact of the size-dependent mismatch on the local strain field. In particular, one might expect significant adsorbate-induced structural modifications on the surface, which will be different for

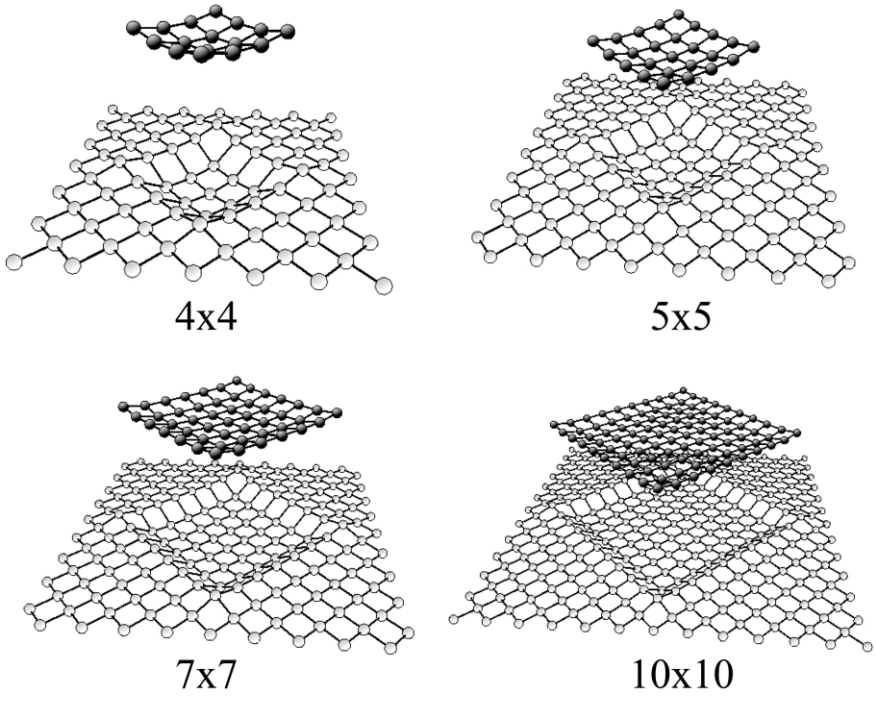

Fig. 2. Evolution in the shape of the Co square islands (dark) on Cu(1 0 0) and the surface under the islands (light).

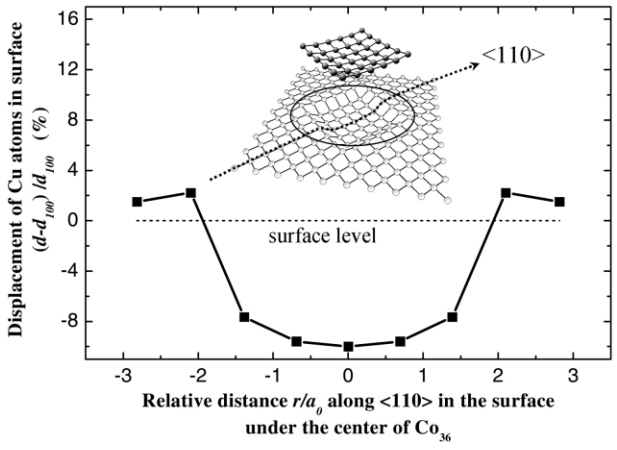

Fig. 3. Vertical displacement $(d-d_{1\,0\,0})/d_{1\,0\,0}$ in the topmost layer of Cu(1 0 0) surface under Co_{36} island calculated across the $\langle 1\,1\,0\rangle$ direction; $d_{1\,0\,0}=1.8075$ Å—interlayer distance in Cu(1 0 0); $a_0=3.615$ Å—Cu fcc lattice constant.

small and large islands. In other words, the substrate can dynamically respond to the growth of islands and can exhibit a strong inhomogeneous strain distribution during the growth process.

To give clear demonstration of the impact of the mesoscopic mismatch on the structure of Co/Cu interface, we show in Fig. 2 an evolution in the shape of the Co islands and the morphology of the substrate.

These striking results reveal 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 islands locally distort the surface and induce strongly inhomogeneous displacement pattern in the substrate. With increasing size of the islands the strain-depth profile in the substrate and the shape of islands show a dynamical behavior: the depth of the strain region in the surface and 'bending' of islands become smaller for larger islands. As an example, we present in Fig. 3 the lattice distortions for the Cu substrate atoms under and in the vicinity of the Co_{36} island. The surface atoms under the islands are pushed down, while atoms at the outer edge of the islands are pushed up.

None of the above observations could be predicted by the classical theory of monolayer growth based on the macroscopic lattice mismatch, while some interesting steps in the modification of this theory to the nanoscale were made [11]. The driving force for the strain-relief at the mesoscale is associated with the mesoscopic mismatch between Co islands and the Cu substrate, which is significantly larger than the macroscopic one (cf. Fig. 1).

2.2. Co islands on Cu(1 1 1)

In addition to the Co islands on Cu(1 0 0) also Co islands on Cu(1 1 1) have been investigated. STM experiments have shown [12], that stacking faults at the Co/Cu interface enhance the injection probability of electrons into the interface. Other experiments [13] observed a growth of trilayer cobalt islands on Cu(1 1 1) with one subsurface layer. The Co islands are surrounded by a brim of Cu.

We extended our analysis to Co islands on Cu(1 1 1) to demonstrate the general applicability of the concept of mesoscopic mismatch and to study the real structure of the islands in more detail. Fig. 4 shows the structure of a Co_{36} island on Cu(1 1 1). We observe a strong compressive strain at the Cu atoms below the Co island and a tensile strain at the boundary of the island. The triangular Co_{36} island on Cu(1 1 1) shows the same characteristic shape (platelike) as the quadratic island on Cu(1 0 0).

Fig. 5 shows the structure and displacements of a trilayer Co island on Cu(1 1 1). One layer of the island is embedded in the Cu surface. While the first two layers show the platelike shape the third layer has a tentlike shape. The calculated displacements for the particular layers show, that the tensile strain at the boundary of the island is reduced. A strong relaxation towards the Cu surface is obtained.

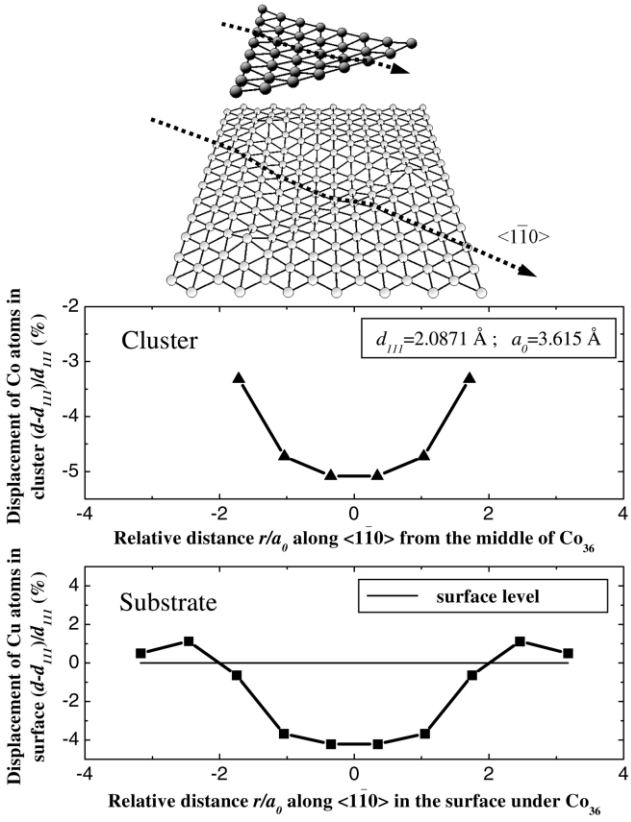

Fig. 4. Vertical displacement $(d-d_{1\,1\,1})/d_{1\,1\,1}$ in Co_{36} island on Cu(1 1 1) and the substrate under the island calculated across the $\langle 1\,1\,0\rangle$ direction; $d_{1\,1\,1}=2.0871$ Å—interlayer distance in Cu(1 1 1).

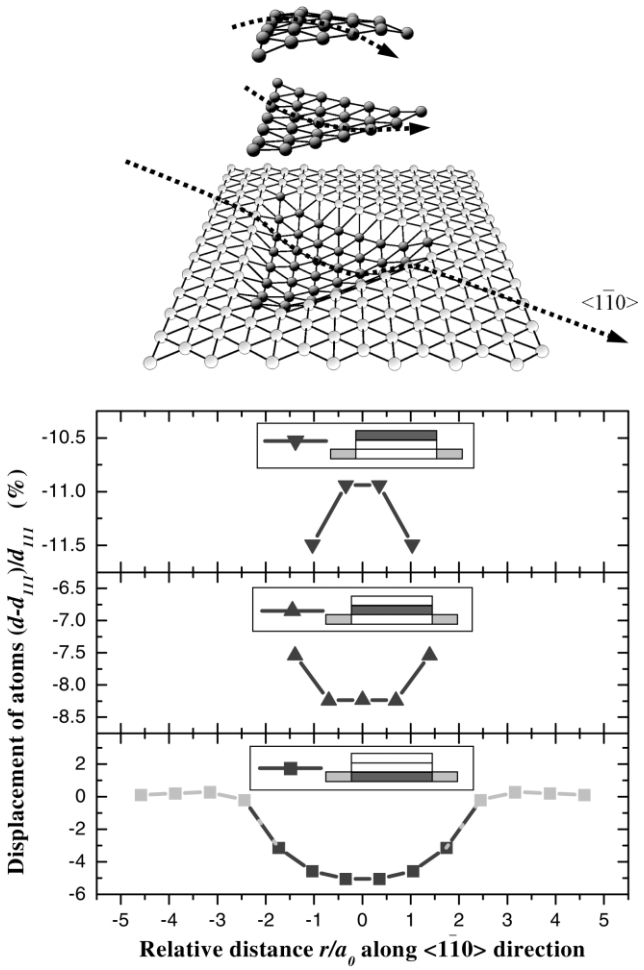

Fig. 5. Vertical displacement $(d-d_{1\,1\,1})/d_{1\,1\,1}$ in a trilayer Co island on Cu(1 1 1) calculated across the $\langle 1\,1\,0\rangle$ direction. One layer of the island is embedded in the Cu surface. The island consists of 36, 28, 21 atoms in consecutive layers.

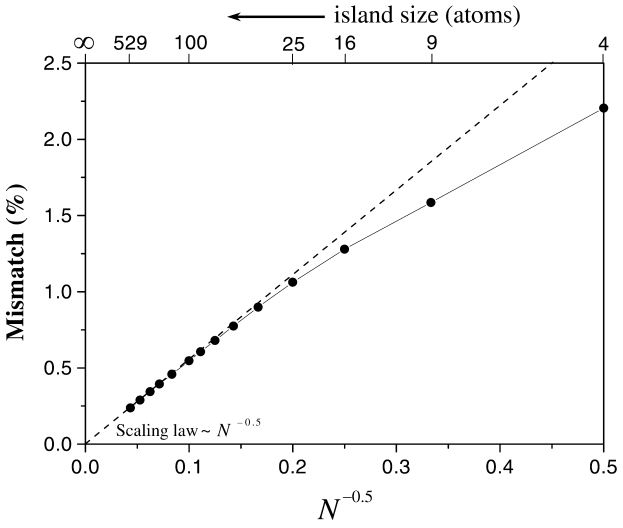

Fig. 6. Size-dependent mismatch $m=(r_b^{Cu}-r^{Cu})/r_b^{Cu}$ for the Cu square islands on Cu(1 0 0) (r^{Cu}—average bond length in Cu islands).

3. Strain relaxation in homoepitaxy

In view of these results one can expect that even in the case of homoepitaxy, where there is no macroscopic mismatch, the mesoscopic mismatch may lead to the drastic strain relaxations. We perform calculations for the Cu square islands on the Cu(1 0 0). The small Cu islands have different bond lengths compared to the Cu bulk, therefore the mesoscopic mismatch between the Cu islands and the Cu substrate exists. In Fig. 6 we present the size-dependent mesoscopic mismatch for the homoepitaxial growth.

The above results suggest that strain relaxations may be strong even in the absence of the macroscopic mismatch. We found that the mesoscopic Cu islands induce an inhomogeneous strain distribution in the Cu substrate. The strain-relief leads to the atomic distortions in the surface in the same manner as it was found for the Co/Cu system. The atomic rearrangement in the Cu substrate induced by the Cu_{36} island is shown in Fig. 7.

Similar to the heteroepitaxy, the homoepitaxy at the mesoscale proceeds by the same pronounced structural changes in the substrate and the shape of the island. The Cu island assumes a tentlike shape, where the edge atoms in island are the lowest. The Cu surface atoms under Cu island are pushed down into the substrate, while atoms at the outer edge of the Cu island are pushed up.

For islands larger than 25 atoms the scaling behavior is the same as for heteroepitaxy (cf. Fig. 1).

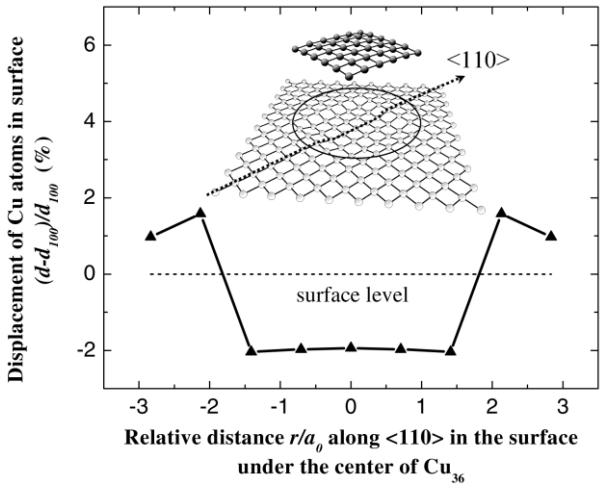

Fig. 7. Vertical displacement $(d-d_{1\,0\,0})/d_{1\,0\,0}$ of the atoms in the topmost layer of Cu(1 0 0) under Cu_{36} island calculated across the $\langle 1\,1\,0\rangle$ direction.

4. Conclusions

Our findings lead to the conclusion that the mesoscopic islands in homo- and heteroepitaxy grow in an unexpected fashion and cause significant displacements in the surface. Strain fields associated with these distortions in the island and substrate can have a profound effect on surface diffusion and can affect the growth modes. We think that it will be possible to detect strain fields at the mesoscale using, for example, a new X-ray diffraction imaging procedure recently presented in Nature [14]. Theoretical and experimental studies of the mesoscopic strain will be of a great importance in a variety of fundamental and technical problems. Recently the first experimental manifestation of the size-dependent mesoscopic mismatch has been found by Sander et al. [15]. It was demonstrated that stress oscillations in a growing metal film are determined by the relaxation of the size-dependent mesoscopic misfit.

Acknowledgments

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References

[1] H. Brune, M. Giovannini, K. Bromann, K. Kern, Nature 394 (1998) 451.
[2] O. Fruchart, M. Klaua, J. Barthel, J. Kirschner, Phys. Rev. Lett. 83 (1999) 2769.
[3] J. Fassbender, U. May, B. Schirmer, R.M. Jungblut, B. Hillebrands, G. Güntherodt, Phys. Rev. Lett. 75 (1995) 4476.
[4] D. Sander, Rep. Prog. Phys. 62 (1999) 809.
[5] D. Sander, R. Scomski, C. Schmidthals, A. Enders, J. Kirschner, Phys. Rev. Lett. 77 (1996) 2566.
[6] D. Sander, C. Schmidthals, A. Enders, J. Kirschner, Phys. Rev. B 57 (1998) 1406.
[7] A. Grossmann, W. Erley, J.B. Hannon, H. Ibach, Phys. Rev. Lett. 77 (1996) 127.
[8] B. Müller, L. Nedelmann, B. Fischer, H. Brune, J.V. Barth, K. Kern, Phys. Rev. Lett. 80 (1998) 2642.
[9] N.A. Levanov, V.S. Stepanyuk, W. Hergert, D.I. Bazhanov, P.H. Dederichs, A. Katsnelson, C. Massobrio, Phys. Rev. B 61 (2000) 2230.
[10] K. Wildberger, V.S. Stepanyuk, P. Lang, R. Zeller, P.H. Dederichs, Phys. Rev. Lett. 75 (1995) 509.
[11] R. Kern, P. Müller, Surf. Sci. 392 (1997) 103.
[12] A.L. Vázquez de Parga, F.J. Garcia-Vidal, R. Miranda, Phys. Rev. Lett. 85 (2000) 4365.
[13] M.O. Pedersen, I.A. Bönicke, E. Lægsgaard, I. Stensgaard, A. Ruban, J.K. Norskov, F. Besenbacher, Surf. Sci. 387 (1997) 86.
[14] S. Di Fonzo, W. Jark, S. Lagomarsino, C. Giannini, L. De Caro, A. Cedola, M. Müller, Nature 403 (2000) 638.
[15] D. Sander, S. Ouazi, V.S. Stepanyuk, D.I. Bazhanov, J. Kirschner, Surf. Sci. 512 (2002) 281.