Interface intermixing in metal heteroepitaxy on the atomic scale

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We reveal the main mechanism of interface intermixing in the early stages of heteroepitaxy. Performing atomic scale calculations with *ab-initio*-based many-body potentials, we show that submonolayer inclusions of Fe atoms in the topmost layer of Cu(001) observed in experiments are caused by a collective process of atomic exchanges near small embedded Fe islands. We demonstrate that mesoscopic relaxations in the substrate depend on the size of embedded islands and drastically affect site exchanges.

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In the last few years considerable attention has been paid to different mechanisms of growth and intermixing in heteroepitaxial metallic systems. The complete knowledge of the properties of this kind of systems, especially when they have magnetic properties, is of crucial importance because of their potential technological applications.[1–3] Tersoff showed that surface-confined mixing can be expected quite generally in systems dominated by atomic size mismatch.[4]

There have been reported different mechanisms for intermixing in heteroepitaxial systems. The main known are the following: exchange of single adatoms with the substrate in order to stabilize the whole system [for example, Co adatoms deposited on the Cu(001) surface[5,6]] and burrowing of clusters into the substrate. The later effect was found for Co clusters on Cu(001), Ag(001), and Au(111) substrates.[7–9] A novel mechanism of intermixing has been predicted by Gómez *et al.*[10] Performing Monte Carlo simulations for Co islands of different sizes on the Cu(111) surface, they found that above a certain critical size the Co islands exhibit two-dimensional–three-dimensional transitions and form mixed Co-Cu clusters. Recently, Pentcheva *et al.*[11] have shown that intermixing during heteroepitaxial growth can lead to a bimodal growth and invalidates the predictions of the mean-field nucleation theory. Even in homoepitaxial systems, it is possible to find some effects of intermixing and subsequently mass transport; for example, the formation of surface crowdions in the Cu(001) substrate due to surface strain.[12]

In this paper we consider Fe heteroepitaxial growth on Cu(001). This system is taken as prototype in order to study the intermixing in heteroepitaxy on the atomic scale.

The puzzling structural and magnetic properties of Fe films grown on Cu(001) have been the aim of many studies for more than a decade.[13] Johnson *et al.*[14,15] reported that for submonolayer regimes Fe atoms deposited on the Cu(001) surface form submonolayer inclusions.

It was suggested that intermixing at the Fe/Cu(001) occurs due to an atomic exchange process. In a recent *ab initio* study,[16] the large barrier of 1.45 eV/Fe atom for the exchange process on Cu(001) has been reported. This energy was considered only as an upper limit, because the surface cell used for calculations was not sufficiently large.

Simple arguments to understand the atomic behavior at interfaces based on such macroscopic properties as surface and interface energies are rather questionable when applied to individual adatoms. To our knowledge, no studies have hitherto been performed to explain the mechanism of intermixing for Fe adatoms on the Cu(001) surface at the atomic scale.

The main goal of this paper is to reveal this mechanism and to show that intermixing is determined by a collective process of atomic exchanges near embedded small Fe islands. While we use a particular system, our finding is of general importance for understanding of heteroepitaxial growth.

We perform atomic scale simulations with *ab-initio*-based many-body potentials and demonstrate that mesoscopic relaxations near embedded islands strongly influence diffusion barriers of site exchanges.

Atomic scale simulations are performed by a molecular static method. Our system consists of 12 layers thick (001) slab. Each layer contains 2000 atoms. Periodic boundary conditions are employed in two orthogonal directions in the plane. The two atomic layers are fixed at the bottom. Atomic relaxation of Fe adatoms and clusters on the Cu(001) surface are performed with new many-body potentials constructed in the second-moment tight-binding (TB) approximation.[6,17] Our approach is based on fitting parameters of potentials at the Fe/Cu interface to accurate spin-polarized *ab initio* calculations of the Hellmann-Feynman forces acting on Fe adatoms on Cu(001) and binding energies of supported and embedded Fe clusters of different sizes and geometries. Forces and energies of clusters are calculated by means of the Korringa-Kohn-Rotoker (KKR) Green's-function method for adatoms and supported clusters.[6,18] We use the full-potential KKR Green's function to determine the Hellmann-Feynman forces. The combination of the first principles and the TB methods allows one to reproduce accurately properties of magnetic supported and embedded clusters, and to perform atomic relaxations for very large systems, which are still out of possibilities of *ab initio* methods.[19] We have to stress that we use only the *ab initio* results to determine the parameters

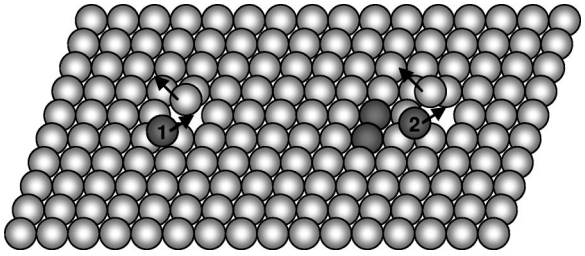

FIG. 1. Schematic view of two exchange processes. Left part (atom number 1): simple exchange on the flat surface. Right part (atom number 2): exchange with two atoms already embedded in the first layer of the substrate. For the system studied, Fe/Cu(001), the activation energy barriers for these two processes are, respectively, 0.78 eV and 0.60 eV.

of interactions at the surface. Details of our method and several applications can be found elsewhere.[6,18,22,23]

We consider first the energetics of the elementary exchange process at the Fe/Cu interface. The replacement of a substrate Cu atom by an Fe adatom is preferred by 0.44 eV (0.35 eV if we do not consider the relaxation of the system). This gain of energy reduces to 0.37 eV (0.31 eV without relaxation) if the displaced Cu atom lies far away from the embedded Fe atom. We have obtained that the energy barrier for this exchange intermixing process (see Fig. 1) is about 0.78 eV, which is considerably smaller than an upper limit found in Ref. 16. Our calculations show that the barrier for the jump diffusion (0.53 eV) is smaller than for the exchange process.

To explain experimental results on submonolayer Fe inclusions formed by deposition onto Cu(001) (Ref. 14) Chambliss and Johnson[15] suggested that an Fe adatom moves by hopping diffusion before exchange, and is more likely to exchange near another embedded Fe atom. Our study supports such model of intermixing at the Fe/Cu(001) interface. Indeed, we have obtained that the exchange energy barrier is reduced to 0.72 eV when we already have one Fe atom in the first layer of the Cu surface. Our calculations show that Fe atoms embedded in the topmost layer of Cu(001) attract each other at nearest-neighbor sites, and as a consequence Fe atoms should form clusters. Embedded clusters tend to stabilize the whole system. For example, when an Fe adatom, originally far apart from the embedded Fe cluster, is moved to the island, the energy gain is 1.43 eV. Therefore, embedded Fe clusters can be considered as preferential centers for growth. We have found that the cluster formation strongly affects an exchange process. For example, the barrier for the exchange is reduced to 0.6 eV near the Fe dimer in the topmost layer (cf. Fig. 1).

Figure 2 shows how the exchange barrier for the Fe adatom depends on the distance to Fe islands embedded in the Cu substrate. As an example, we present results for four different sizes of square Fe islands. Our calculations reveal a strong reduction of the exchange barrier near the island. This effect is caused by the increased interaction between the Fe adatom and the island at short distances (the main point is the number of atoms of the island which the adatom interacts to, therefore we choose, as a general example, a square shape

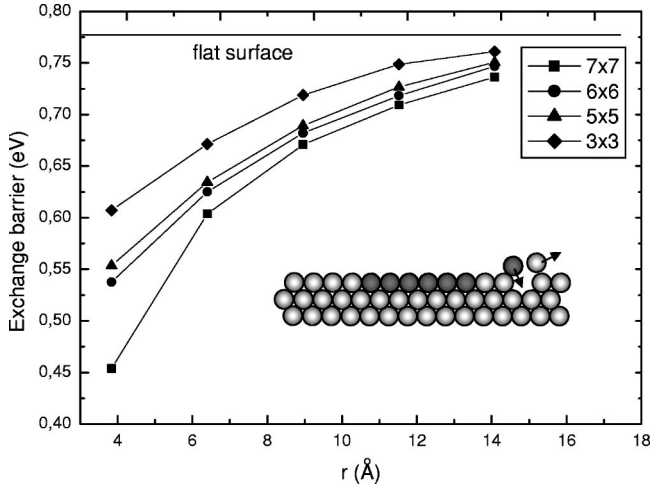

FIG. 2. Exchange barrier for the Fe adatom on the Cu(001) surface near embedded square Fe islands. The horizontal line represents the exchange barrier for a flat surface (Ref. 20).

for embedded islands), and by the local strain relaxations. At the same time, one can see the big difference that exists between the exchange barrier energy near the biggest island we have plotted (49 atoms) and the smallest one (9 atoms). This difference is due to the increasing number of Fe island atoms that the adatom interacts to and, also, to the fact, that the average bond length in the substrate near the embedded island increases with increasing size of the island.[21] As we will discuss later, the larger bond lengths reduce the exchange barrier.

Our recent studies have demonstrated that mesoscopic islands in heteroepitaxy and homoepitaxy introduce a strongly inhomogeneous strain distribution in the substrate which depends on the size of islands.[22–24] We revealed that strain relaxations at the mesoscale, determined by the size-dependent mesoscopic mismatch, can be much more stronger than predicted by the macroscopic approach based on the lattice mismatch between film and substrate. In the present case, we found an inhomogeneous strain distribution in the Cu substrate around embedded Fe islands. In Fig. 3 we show the total (color thermometer) and vertical and horizontal components of the displacement for an Fe square island of 36 atoms embedded in the substrate. These results indicate that strain relaxations in the embedded Fe island may lead to pronounced structural changes in the substrate. One can see that the surface layer and the embedded Fe island are not flat due to atomic relaxations. The edge atoms in the Fe island are highest. The substrate atoms, which are the nearest neighbors of the island, are strongly pushed down, while more distant atoms exhibit upward relaxations. Our calculations reveal a strong horizontal displacements of the substrate atoms in the direction to the island. Due to atomic relaxations the bond lengths in the substrate in the vicinity of the Fe island are increased compared to the flat surface.[25] According to results of Yu and Scheffler[26] the longer bond lengths lead to an enhanced corrugation of the potential acting on the adatom and reduce the exchange barrier.

The above results offer a consistent explanation of the

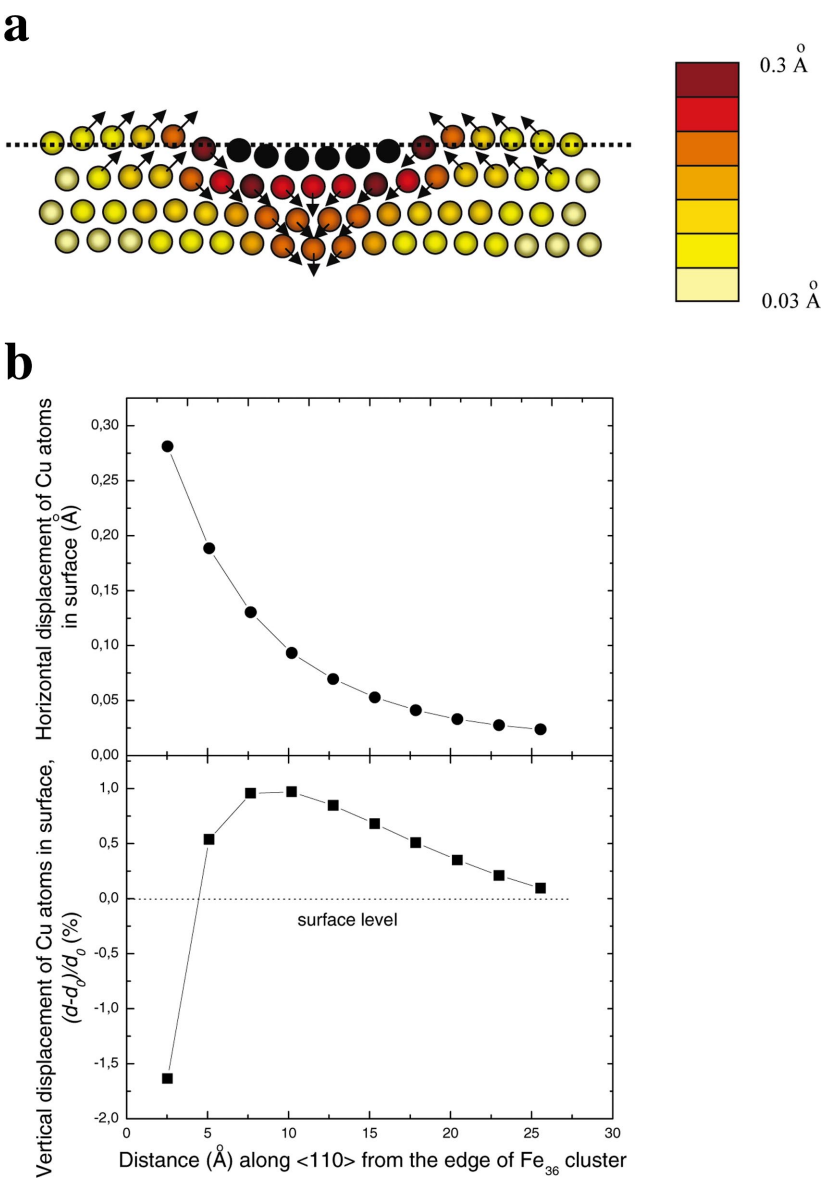

FIG. 3. (Color) (a) The shape of the embedded Fe island of 36 atoms and the Cu substrate (the dotted line represents the surface without the embedded cluster), the color marks the magnitude of the total displacement and the arrows the sense of this; (b) The horizontal (in the direction to the island) and vertical displacements of Cu atoms near the embedded Fe island for $\langle 110 \rangle$ direction; the interlayer distance is $d_0 = 1.8075$ Å and the lattice constant is $a_0 = 3.615$ Å.

mechanism of intermixing at the Fe/Cu(001) interface observed by Johnson *et al.*[14] This a collective process where, to stabilize the system, each new adatom deposited on the surface near the embedded cluster tends to exchange its position with an atom of the substrate. This is also corroborated by our finding that the energy barrier for the edge diffusion of one Fe adatom along the embedded Fe island (0.69 eV) is higher than the exchange barrier (see Fig. 2). Thus, the island formation around or above the embedded cluster is not favored energetically over the formation of embedded islands.

Finally, to clarify more this point, we have tested how strong is the above effect. It is clear that a decreasing of the exchange barrier energy can lead to an enhanced probability of this collective intermixing mechanism compared to another type of processes. If we choose an infinite embedded island (embedded layer) as a reference, the energy of the exchange process can be expressed as $E = E_0 + \Delta E(x,y)$, where E_0 is the energy of the process near the infinite embedded island and $\Delta E(x,y)$ depends on the local characteristics (local coordinations or strain fields). Then, the probability P of this mechanism at a temperature T near the island can be given by $P = P_0 \exp(-\Delta E/kT)$, with P_0 denoting the value for the reference state.[27] We have found, for example, that at room temperature, the probability for the intermixing directly near the embedded island of 36 atoms is more than ten times larger than the probability of this process for the Fe adatom at 6–7 Å from the island. This difference is even bigger if we compare it with the edge diffusion along the embedded island or with exchange on a flat surface. Therefore, we can conclude that the exchange process near embedded islands is the mechanism of the formation of Fe inclusions in Cu(001) found in experiments. We should also note that these results can be tested in the framework of new Kinetic Monte Carlo techniques, recently developed by Henkelman and Jonsson.[28]

To sum up, we have studied the energetics of Fe adatoms on the Cu(001) surface performing atomic scale calculations with *ab-initio*-based many-body potentials. Our results show that Fe adatoms tend to stabilize the system when they lie inside the substrate rather than when they are supported on it.

We have revealed that the exchange barrier of Fe adatoms with the substrate atoms strongly depends on the distance to embedded clusters and their sizes. Our results indicate that mesoscopic relaxations in the substrate around embedded islands strongly affect the atomic exchange at the interface. We have demonstrated that the Fe inclusions in the topmost layer of the Cu(001) substrate observed experimentally are formed due to collective atomic exchanges in the proximity of small embedded islands. This phenomenon is expected to be of general importance in metal heteroepitaxy.

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[1] G. Prinz and K. Hathaway, Phys. Today **48** (4), 24 (1995).
[2] H. Brune, M. Giovannini, K. Bromann, and K. Kern, Nature (London) **394**, 451 (1998).
[3] O. Fruchart, M. Klaua, J. Barthel, and J. Kirschner, Phys. Rev. Lett. **83**, 2769 (1999).
[4] J. Tersoff, Phys. Rev. Lett. **74**, 434 (1995).
[5] J. Fassbender, R. Allenspach, and U. Dürig, Surf. Sci. **383**, L742 (1997).
[6] N.A. Levanov, V.S. Stepanyuk, W. Hergert, D.I. Bazhanov, P.H. Dederichs, A. Katsnelson, and C. Massobrio, Phys. Rev. B **61**, 2230 (2000).
[7] C.G. Zimmermann, M. Yeadon, K. Nordlund, J.M. Gibson, R.S. Averback, U. Herr, and K. Samwer, Phys. Rev. Lett. **83**, 1163 (1999).
[8] S. Padovani, F. Scheurer, and J.P. Bucher, Europhys. Lett. **45**, 327 (1999).
[9] V.S. Stepanyuk, D.V. Tsivlin, D.I. Bazhanov, W. Hergert, and A.A. Katsnelson, Phys. Rev. B **63**, 235406 (2001).
[10] L. Gómez, C. Slutzky, J. Ferrón, J. de la Figuera, J. Camarero, A.L. Vázquez de Parga, J.J. de Miguel, and R. Miranda, Phys. Rev. Lett. **84**, 4397 (2000).
[11] R. Pentcheva, K.A. Fichthorn, M. Scheffler, T. Bernhard, R. Pfandzelter, and H. Winter, Phys. Rev. Lett. **90**, 076101 (2003); F. Nouvertné, U. May, M. Bamming, A. Rampe, U. Korte, G. Güntherodt, R. Pentcheva, and M. Scheffler, Phys. Rev. B **60**, 14 382 (1999).
[12] W. Xiao, P.A. Greaney, and D.C. Chrzan, Phys. Rev. Lett. **90**, 156102 (2003).
[13] J. Tomassen, B. Feldman, and M. Wuttig, Surf. Sci. **264**, 406 (1992); H. Jenniches, J. Shen, Ch.V. Mohan, S. Sundar Manoharan, J. Barthel, P. Ohresser, M. Klaus, and J. Kirschner, Phys. Rev. B **59**, 1196 (1999); R. Volmer and J. Kirschner, *ibid.* **61**, 4146 (2000); D. Peterka, A. Enders, G. Haus, and K. Kern, *ibid.* **66**, 104411 (2002).
[14] K.E. Johnson, D.D. Chambliss, R.J. Wilson, and S. Chiang, Surf. Sci. **313**, L811 (1994).
[15] D.D. Chambliss and K.E. Johnson, Phys. Rev. B **50**, 5012 (1994).
[16] D. Spisák and J. Hafner, Phys. Rev. B **64**, 205422 (2001).
[17] F. Cleri and V. Rosato, Phys. Rev. B **48**, 22 (1993); V. Rosato, B. Guillope, and B. Legrand, Philos. Mag. A **59**, 321 (1989).
[18] K. Wildberger, V.S. Stepanyuk, P. Lang, R. Zeller, and P.H. Dederichs, Phys. Rev. Lett. **75**, 509 (1995); V.S. Stepanyuk, W. Hergert, K. Wildberger, R. Zeller, and P.H. Dederichs, Phys. Rev. B **53**, 2121 (1996); N. Papanikolaou, R. Zeller, P.H. Dederichs, and N. Stefanou, *ibid.* **55**, 4157 (1997).
[19] The following parameters for Fe-Fe, Fe-Cu, and Cu-Cu interactions are obtained: Fe-Fe, $A^0=0.1658$ eV, $A^1=0.0$ eV, $\xi=1.7291$ eV, $p=7.9508$, $q=2.1719$, $r_0=2.3852$ Å; Fe-Cu, $A^0=-0.0342$ eV, $A^1=-0.7253$ eV, $\xi=0.8155$ eV, $p=7.1444$, $q=5.1248$, $r_0=2.4504$ Å; Cu-Cu, $A^0=0.0854$ eV, $A^1=0.0$ eV, $\xi=1.2243$ eV, $p=10.939$, $q=2.2799$, $r_0=2.5563$ Å. The potentials are used in the form of Rosato *et al.*; see Refs. 6 and 17.
[20] We have not included the nearest point to the islands because for sizes bigger than nine atoms, the adatom jumps over the island and does not undergo such an exchange process at such distance.
[21] For example, the average bond length near the island of 49 atoms is increased by about 20% compared to that near the island of 9 atoms.
[22] V.S. Stepanyuk, D.I. Bazhanov, A.N. Baranov, W. Hergert, P.H. Dederichs, and J. Kirschner, Phys. Rev. B **62**, 15398 (2000); D. Sander, S. Ouazi, V.S. Stepanyuk, D.I. Bazhanov, and J. Kirschner, Surf. Sci. **512**, 281 (2002).
[23] V.S. Stepanyuk, D.I. Bazhanov, W. Hergert, and J. Kirschner, Phys. Rev. B **63**, 153406 (2001).
[24] O.V. Lysenko, V.S. Stepanyuk, W. Hergert, and J. Kirschner, Phys. Rev. Lett. **89**, 126102 (2002).
[25] In the vicinity of the island the average bond length is increased by about 5% compared to the flat Cu substrate.
[26] B.D. Yu and M. Scheffler, Phys. Rev. B **56**, R15 569 (1997).
[27] These prefactors are more or less independent of the island size and of the distance between the adatom and the island. For example, the exchange prefactor for an adatom of Fe near an embedded Fe island of nine atoms is 1.69×10^{12} Hz (nearest position to the island) and 1.53×10^{12} Hz (for the most distant position calculated).
[28] G. Henkelman and H. Jonsson, Phys. Rev. Lett. **90**, 116101 (2003).