Interlayer mass transport in homoepitaxy on the atomic scale

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We show that the atomistic structure of step edges is crucial for understanding of the interlayer mass transport in homoepitaxy. Performing atomic scale calculations for double layer Cu islands on Cu(111), we reveal that detachment energies of atoms from islands in the vicinity of the step edges are reduced. The interplay between diffusion barriers for the mass transport and the mesoscopic strain is demonstrated. Our study presents evidence that the mesoscopic mismatch between the upper and the lower islands leads to the shape transition at the edge and influences the interlayer mass transport.

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The classical concept of interlayer mass transport is based on the diffusion of single adatoms at step edges.[1–3] A smooth surface morphology can be maintained only if the interlayer mass transport is sufficiently fast to allow adatoms to leave the top of two-dimensional islands. An adatom may cross the step either by diffusion over the step [Ehrlich-Schwoebel (ES) barrier] or by the exchange process at the step. If the barriers of such processes are so large that adatoms cannot escape from the top of islands rapidly, growth becomes three dimensional and small clusters are formed on the top of islands in the initial stage of metal homoepitaxy and heteroepitaxy. Due to a random walk, small clusters can encounter the boundary of the larger island.[4] In this case a new channel for the interlayer mass transport caused by the decay of clusters at the edge may occur. Giesen, Schulze, Icking-Konert, and Ibach performing STM studies of the multilayer Cu islands on Cu(111), have found that when the distance between the edges of the upper and the lower islands is small, the decay rate of small islands increases by 2.0 orders of magnitude.[5] Similar results have been obtained for small and large Ag islands on Ag(111).[6] In a first interpretation of the results for Cu(111), the vanishing of the ES barrier for a close contact between island edges was suggested.[5] Furthermore, it was shown that for Cu(111) the existence of an ES barrier is related to the occupation of surface states.[5] However, experimental data on rapid interlayer mass transport for Ag(111) have demonstrated that the proposed breakdown of the step-edge barrier cannot explain the experimentally high decay rate.[6,7] The interplay between an ES barrier and quantum confinement of surface state electrons may be only coincidental.[4]

The above findings show that motion of clusters in the vicinity of step edges can affect the interlayer mass transport (see Fig. 1). It was suggested by Giesen that for small distances between island edges a local strain field may influence the exchange and the ES barrier.[4] Gölzhäuser and Ehrlich[8] have also noted about the possibility of strain effects on adatom and cluster motion on islands. Despite considerable efforts,[4] it is unclear what happens when a clusters approaches the descending step edges.

In this Brief Report we address this problem performing atomic scale calculations and demonstrate the effect of mesoscopic relaxations at step edges on the interlayer mass transport in homoepitaxial growth. As a model case, we discuss strain effects and the diffusion at the edge of double layer Cu islands on Cu(111). We find that detachment energies of atoms from islands in the vicinity of edges are significantly reduced. Our calculations reveal that the interlayer mass transport strongly depends on the distance between edges of islands. The limitation of the conventional approach to the interlayer mass transport based on the edge diffusion of single adatoms on a uniform surface is shown.

We carry out calculations of atomic relaxations and diffusion barriers using the molecular statics method with many-body potentials of Rosato, Guillope, and Legrand (RGL).[9] Potentials are formulated in the second moment tight-binding approximation. It was shown in many studies that RGL potentials correctly describe surface relaxations, reconstruction, and diffusion on surfaces of fcc metals.[9,10] However, the lack of a detailed description of electronic states is an obvious drawback of this approach. Therefore, the investigation of the effect of electronic confinement on the mass transport at step edges is out of the scope of this Brief Report.

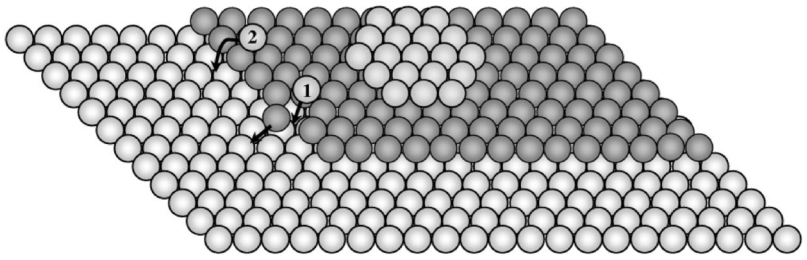

FIG. 1. Schematic view of atom incorporation at steps in a double layer island: (1) edge exchange, (2) Ehrlich-Schwoebel barrier.

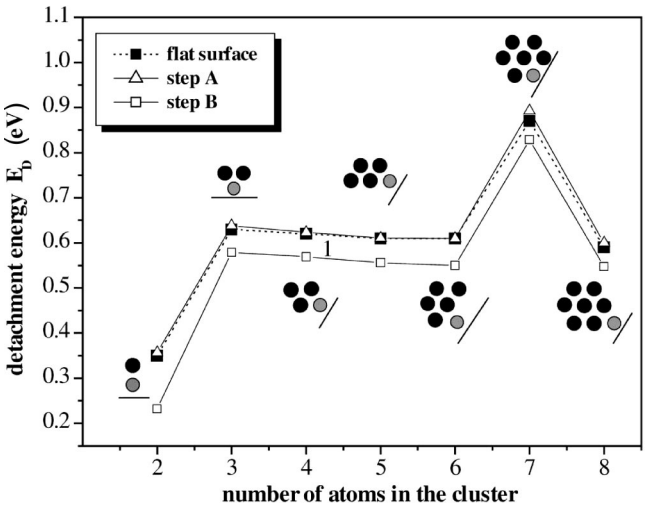

FIG. 2. The detachment energies for atoms of small stable Cu clusters at the step edges of Cu(111) and on the flat substrate; the step position is shown for a close contact between clusters and the step. Detachment energy is defined as $-(E_N-E_{N-1}-E_a)$, where E_N and E_{N-1} are the total energies of Cu(111) slab with the cluster of N and $N-1$ atoms, respectively, E_a is the adsorbtion energy of Cu adatom on the flat surface; the detaching atoms are marked as gray.

Atomic scale simulations are performed with a finite slab of 9 layers arranged according to the *ABC*-fcc sequence of (111) fcc surfaces. Each layer contains 1400 atoms. Periodic boundary conditions are imposed only along directions parallel to the surface. We consider the interlayer mass transport on Cu(111) with different kinds of straight steps: *A* and *B* steps, with (100) and (111) microfacets, respectively.

First, we show that the detachment energies of atoms from Cu islands are strongly reduced when the upper island touches a descending step of Cu island below. In Fig. 2 we compare detachment energies of Cu atoms from small Cu clusters at *A* and *B* steps with those for the flat surface, i.e., far away from steps. The detachment energy is characterized by the pronounced peak for the closed-shell cluster of 7 atoms (heptamer). The alternation between structures with twofold and threefold coordinations of the removed atom determines the behavior of detachment energies[11]. Atoms of the dimer are onefold-coordinated, therefore the detachment energy of the dimer is considerably smaller than for other clusters. The first cluster for which three bonds must be broken is the heptamer, therefore it has a high detachment energy. Similar results were found for Pt on Pt(111) and Ni on Ni(111).[11] Rosenfeld *et al.*[12] proposed that the heptamer has the largest probability of being observed at low coverages and for sufficiently high temperatures. One can see (Fig. 2) that the detachment energy of Cu cluster of 8 atoms is strongly reduced. It was suggested[12,13] that such behavior should lead to the stability gap, i.e., islands are restrained from growing larger than heptamers.

Our calculations reveal that at a *B* step the detachment energies of all clusters are reduced compared to the flat surface by 60–70 meV. For the dimer the reduction of the detachment energy at the edge is found to be more than 120 meV. The physical mechanism responsible for such strong effects is related to reduced local coordination at a *B* step (see Fig. 3) and mesoscopic relaxations.

To understand the nature of relaxations at the edge we recall our recent studies where we have shown that the size-dependent mesoscopic mismatch determines the morphology of islands, substrates, and the diffusion of adatoms on islands.[14] The mesoscopic mismatch between islands and a substrate exists even in homoepitaxy.[14,15] In the case of double layer Cu islands considered here the mismatch between the upper and the lower islands at the edge leads to local atomic displacements and reduces the detachment energy by 60–80 meV compared to the calculation without relaxations.

At the same time, the influence of an A step on the detachment energies is very small. In this case, the coordination of the atom which is detached from the cluster is the same on the flat surface and at the edge (see Fig. 3). Due to this fact, the local atomic relaxation around such atoms on the flat surface and near an *A* step is very similar.

The above effects are not specific to small clusters presented in Fig. 2. We have performed calculations for clusters of different sizes and found in general, that detachment en-

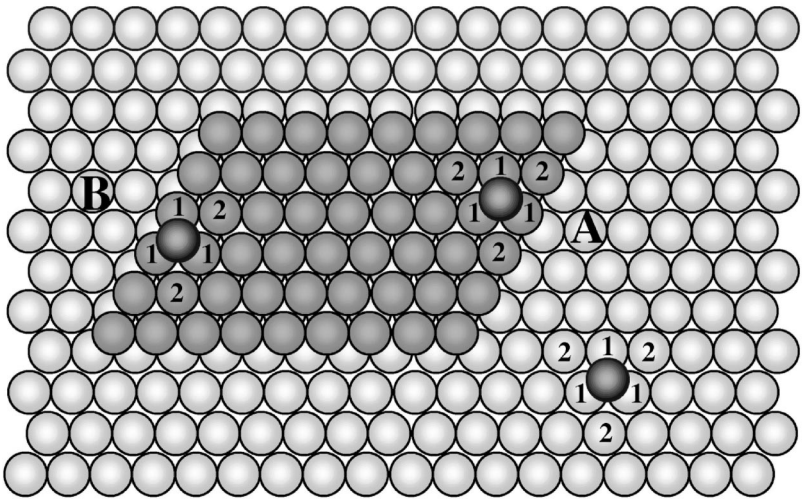

FIG. 3. Geometrical arrangement of atoms on top of an island near the step edges (*A* and *B* steps) and on the flat surface. The first and the second neighbors of an adatom are indicated.

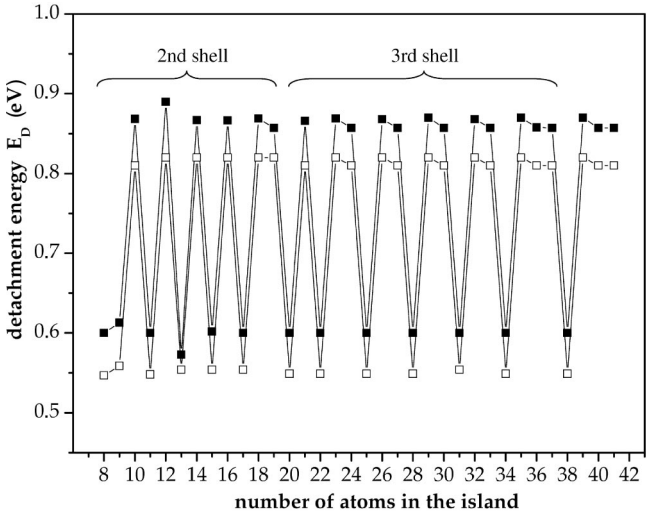

FIG. 4. Detachment energies of atoms from clusters with hexagonal shell arrangement at a *B* step and on the flat surface.

ergies of atoms from clusters near a B step are reduced compared to the flat surface. These results are presented in Fig. 4 for hexagonal Cu clusters with two and three shells. Each shell was calculated atom by atom and all obtained cluster configurations were relaxed. Similar to results for small clusters, the alternation between structures with twofold and threefold coordinations causes oscillations of detachment energies. It is well seen that changes in detachment energies near a *B* step are nearly the same for atoms with equal coordination in different clusters. In the case of large clusters, the trend of detachment energies will be determined by the variation of a local coordination of detaching atoms, i.e., it will be similar to results presented in Fig. 4.

Now we turn to the discussion of kinetic processes at edges of double layer islands. We have calculated the ES and the exchange barriers for Cu adatoms at *B* and *A* steps for different distances between the edges of the upper and the lower islands (see Fig. 1). Our results presented in Fig. 5 show that for both *A*- and *B*-type steps and for large distances between island edges, the downward mass transport via atomic exchange is considerably more facile than via hopping. While both steps represent almost equal barriers for the jump diffusion, they differ strongly in the case of exchange diffusion. These results suggest that there is asymmetry in the steps at which the mass transport occurs. To understand why the exchange barrier at a *B* step is drastically reduced (by a factor 3) compared to that at an *A* step, we calculated the average stress in the vicinity of both steps. Details concerning calculations of the atomic resolved stress can be found in our recent work.[14] We found that the average tensile stress near a *B* step (0.20 eV/A^3) is larger than near an *A* step (0.18 eV/A^3). These results can be explained by the fact the average bond length in the vicinity of a *B* step is increased compared to an *A* step. In other words, stress relief due to strain relaxations is larger for an *A* step. The shorter bond lenghts near an *A* step lead to a reduced corrugation of the potential acting on adatoms as compared to a *B* step.[16] According to Yu and Scheffler,[16] when corrugation of the potential decreases (increases), the barrier for exchange diffusion increases (decreases). Therefore, the mesoscopic stress at edges is the origin of the marked difference between the exchange barrier at *A* and *B* steps. Similar differences were found in calculations for Ag(111) and Pt(111), where the barrier for exchange turns out to be considerably lower at a *B* step than at an *A* step.[17] The interplay between diffusion barriers and strain field was also discussed by Schroeder and Wolf.[18]

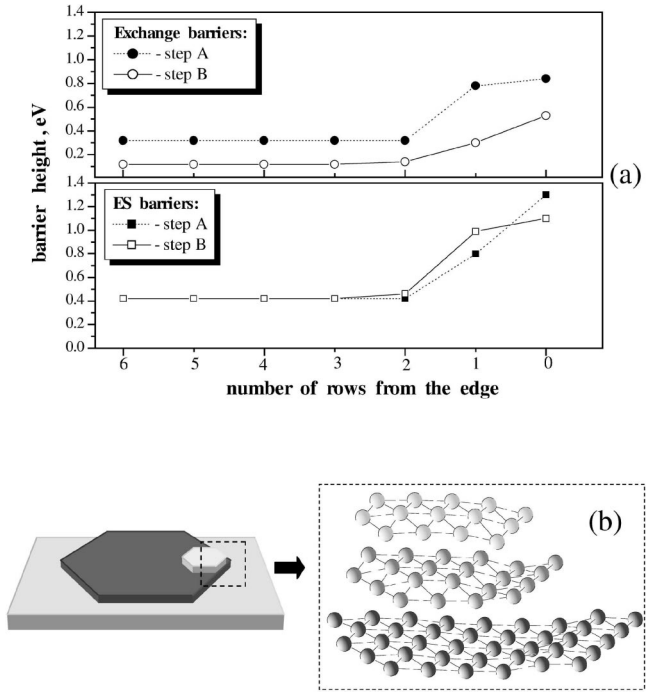

FIG. 5. (a) Dependence of energy barriers for hopping and exchange diffusion at *A* and *B* steps on the distance between edges of the upper and the lower Cu islands. (b) The shape of the step edge for a close contact between islands.

At the same time, our results show that barriers for the jump diffusion over steps are mainly determined by the loss of coordination at the saddle point position and they are very similar at both step edges. The above findings predict that for large distances between edges of islands the interlayer mass transport is most likely provided by the exchange mechanism at a *B* step with the barrier 0.12 eV. Haftel and Einstein have also found that exchange is favored over hopping diffusion on Ag surfaces[19]

It is interesting to note that the recent study of Li *et al.*[20] has shown that the any-site and the selective-site (kinks, for example) atom descent mechanisms at step edges lead to distinctly different mass transport. We believe that the difference in stress between such sites can play an important role.

Once the cluster is on the border (see Fig. 1), the scenario of the interlayer mass transport is dramatically changed. From the results shown in Fig. 5, it is immediately apparent that the downward movement of atoms at the edge is strongly suppressed. The barrier heights involved in the mass transport at both *A* and *B* steps are strongly increased. The smallest energy barrier is found for the exchange at a *B* step. The barriers for the ES process are very large, therefore we believe that the jump diffusion at steps is blocked for dis-

tances between island edges less than two atomic rows.[21]

A strong enhancement of all barriers is caused by the increased interaction between the adatom and the island as it approaches the edge, and by the local strain field. The stress relief at the edge strongly affects the shape of both islands, as it is illustrated in Fig. 5(b). One can see that edge atoms of the lower island are pushed up, while edge atoms of the upper island are pushed down. Our calculations show that vertical displacements of edge atoms range from 2 to 3 % relative to the unrelaxed positions. Due to the shape transition, the average bond length at the edge of the large island is reduced. This effect decreases the corrugation of the potential and increases the exchange barrier. Our results suggest that the interlayer diffusion of atoms detached from the upper island occurs if the distance between the edges of islands is larger than the one atomic row.

Finally, we note that recently Feibelman has performed *ab initio* calculations of the downward transport barriers for Cu adatoms at *A* and *B* kinks on Cu(111) and found that kinks can be crucial for the interlayer mass transport.[22] We expect that mesoscopic relaxations at kinks can affect the mass transport. The investigations of these effects are underway.[22]

In summary, our study shows that the atomistic structure of step edges is very important for understanding the interlayer mass transport. We have shown that the stability of islands at step edges and the diffusion barriers of adatoms are strongly affected by mesoscopic relaxations. Our calculations demonstrate that the interlayer mass transport at step edges depends on the distance between the edges of the upper and the lower islands. The nature of the underlaying physics suggests that effects found in our work may be of general importance.

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[21] For a close contact between the island edges the vertical displacement of atoms at the edge of the lower island for an *A* step is larger than for a *B* step, therefore the ES barrier for an *A* step is larger than for a *B* step [see Fig. 5(a)].

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