

Anisotropy of Growth of the Close-Packed Surfaces of Silver

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The growth morphology of clean silver exhibits a profound anisotropy: The growing surface of Ag(111) is typically very rough while that of Ag(100) is smooth and flat. This serious and important difference is unexpected, not understood, and hitherto not observed for any other metal. Using density functional theory calculations of self-diffusion on flat and stepped Ag(100) we find, for example, that at flat regions a hopping mechanism is favored, while across step edges diffusion proceeds by an exchange process. The calculated microscopic parameters explain the experimentally reported growth properties. [S0031-9007(96)00820-4]

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The morphology and microscopic and mesoscopic qualities of surfaces are some of the major concerns in investigations of epitaxial growth. Often the growth mode and the resulting surface quality can be altered by varying the growth conditions, such as the substrate temperature and deposition rate, or by introducing defects or surfactants (see Ref. [1] and references therein). Interestingly, different substrate orientations sometimes exhibit a noticeably different behavior. Silver is probably one of the extreme examples: Homoepitaxy on clean Ag(111) gives rise to very rough surfaces, while on clean Ag(100) the growing surface remains smooth and flat. This result has been found by experimental studies using reflection high-energy electron diffraction (RHEED) intensity oscillations [2] showing for Ag(100) at temperatures between 200 and 480 K a smooth two-dimensional (2D) growth behavior. In contrast, for Ag(111) RHEED intensity oscillations are absent at all temperatures, suggesting that there is no 2D growth at all. This finding for Ag(111) was confirmed by x-ray reflectivity experiments [3] and scanning tunneling microscopy [4,5]. The latter studies exposed that the surface becomes deeply fissured with "mountains" as high as 30–40 atomic layers. The analysis gave that silver adatoms on top of existing islands encounter a step-edge barrier hindering their descent. This barrier is noticeably higher (by 0.15 eV [4]) than the diffusion barrier on the flat terrace which explains why deposited atoms which land on islands will stay on the island, giving rise to the observed multilayer growth of silver in the (111) orientation.

In general, the existence of a step-edge barrier [6] is plausible because of the low coordination of the step-edge atoms [7]. Thus, *a priori* a significant difference in growth mode between the two similarly close-packed surfaces of fcc metals is not to be expected, and, in fact, has not been reported so far for other systems. To date various semiempirical embedded-atom methods have been used to study fcc metals. However, we note that such semiempirical treatments may not be predictive, although it is often assumed that such approaches may explain general trends. Thus, a more elaborate and reliable theory

is necessary to find out if the growth anisotropy of silver is really special and what actuates the smooth growth of the (100) surface. Below we will answer these questions.

We performed density functional theory studies. Most calculations were done with the exchange-correlation functional treated in the local-density approximation (LDA); at the important geometries we repeated the calculations using the generalized gradient approximation (GGA) [8]. We used an updated version of the computer code described in Ref. [9] together with norm-conserving, fully separable pseudopotentials [10,11]. The surface was simulated by a repeating slab in which typically three atomic layers and a 10.35 Å vacuum region are included. In the lateral directions we took a (3×3) periodicity, which when tested gives that the artificial (unwanted) adatom-adatom interaction is sufficiently weak and, in fact, negligible for the questions of concern. The LDA (GGA) pseudopotentials were created using the nonrelativistic (relativistic) scheme of Troullier and Martins [10] and Kleinman and Bylander [11], as described by Fuchs *et al.* [12]. The details of the potential, such as presentation of its logarithmic derivatives and electronic hardness properties, will be published elsewhere [13]. The $4d$ states are included as valence states, and the basis set consists of plane waves up to a kinetic energy of 40 Ry. For the silver bulk this treatment gives a lattice constant $a_0 = 4.14$ (4.18) Å and a bulk modulus of $B_0 = 0.99$ (0.90) Mbar. These are the LDA results, and the values in brackets are obtained using the GGA. In these values the zero point vibrations are not taken into account. The agreement with $T \rightarrow 0$ K experimental data is good ($a_0^{\text{exp}} = 4.07$ Å and a bulk modulus of $B_0^{\text{exp}} = 1.02$ Mbar), as is that with other calculations [14,15]. For the \mathbf{k} summations in the surface calculations we took nine equidistant \mathbf{k} points in the surface Brillouin zone (SBZ) of the (3×3) cell (avoiding Γ point). We relaxed the adatoms and the top-layer atoms, keeping the other Ag atoms in their theoretical-bulk positions. All geometries were optimized until the remaining forces were smaller than 0.05 eV/Å. In order to attain fast convergence of

the iterative solution of the Schrödinger equation we found it important to start with initial wave functions obtained from a mixed basis set of pseudoatomic orbitals and plane waves with a 4 Ry cutoff, as developed by Kley *et al.* [16]. The number of substrate layers is admittedly small; we therefore note that the adatom is adsorbed only on one side of the slab (see also Ref. [17]).

We first summarize our LDA (GGA) results for the clean Ag(100) surface. The top-layer relaxation is $\Delta d_{12} = -2.0\%d_0$ ($-1.4\%d_0$), where d_0 is the interlayer spacing in the bulk. The surface energy per atom is $\sigma = 0.61$ eV (0.48 eV), and the work function is $\phi = 4.38$ eV (4.30 eV). The agreement with previous full-potential linear-muffin-tin-orbital (FP-LMTO) calculations [14] (only LDA results exist so far) is very good. We now address the energetics of adsorption and diffusion of a Ag adatom on the flat Ag(100) surface. We find that the stable adsorption site for a Ag adatom is the fourfold hollow [Fig. 1(a)], i.e., the highest coordination site, as would be expected for a noble metal. The four nearest neighbors of the adatom distort laterally, opening the hollow site even further. The bond length between the adatom and its neighbors is 2.78 Å, i.e., 5% shorter than the interatomic distance in the bulk. This follows the typical trend, namely, that bond strength per bond decreases with coordination and, correspondingly, bond length increases with coordination. Diffusion on the (100) surface of fcc metal may proceed by a hopping or an exchange process. For the hopping process the transition state is the twofold coordinated bridge geometry [see Fig. 1(b)]. For the exchange process the transition state consists of two atoms sitting over a surface vacancy [see Fig. 1(c)]. The exchange process has been theoretically predicted by Feibelman [18] to be active at Al(100) and stabilized by a covalentlike bonding in the transition state geometry. Experimental evidences for diffusion by exchange have been seen for Pt(100) [19] and Ir(100) [20]. For Cu(100) Hansen *et al.* [21], using the effective medium approach, predicted exchange diffusion to have lower energy barriers than a hopping.

For Ag(100) we find that the exchange process is clearly unfavorable. The energy barriers for hopping diffusion are 0.52 eV (LDA) and 0.45 eV (GGA) which is close to the results of the FP-LMTO calculation [22],

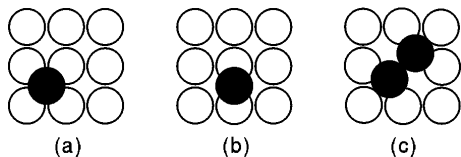


FIG. 1. Schematic top view of geometries at (a) the fourfold hollow site, (b) the transition state for the hopping diffusion (the twofold bridge site), and (c) the transition state for the exchange diffusion. The solid and open circles represent the adatoms and surface atoms, respectively.

which got 0.50 eV (LDA). The semiempirical study of Liu *et al.* [23] obtained with the embedded-atom method (EAM) a similar value, namely, 0.48 eV. The difference between the LDA and the GGA result is small (0.07 eV). In the bridge site the bond length between the adatom and its two neighbors is 2.69 Å, i.e., 3% shorter than in the fourfold hollow. This again follows the well known trend: Each of the two bonds at the bridge site is stronger than each of the four bonds at the hollow site.

For the exchange diffusion we obtain an energy barrier of 0.93 eV (LDA) and 0.73 eV (GGA) which is much higher than that for a hopping process. Thus, we can rule out that the exchange process will play a role for self-diffusion at flat regions of Ag(100). It is interesting that for the exchange geometry the difference between LDA and GGA is noticeable (0.20 eV). This is somewhat plausible, because in the transition state of the exchange process the bonds are more localized.

Some results of convergence tests for the diffusion barrier on flat surfaces are given in Table I. The tests have been done by additional calculations using a more extensive set of parameters, namely, a (2×2) cell, 4-layer slab, basis with 50 Ry energy cutoff, and 16 \mathbf{k} points in the SBZ. Increasing the cutoff energy from 40 to 50 Ry changed the diffusion barriers by less than 0.01 eV, and increasing the number of atomic layers from 3 to 4 results in changes of only 0.01 eV in the barriers. Increasing the number of \mathbf{k} points from 9 to 16 changed the results by less than 0.03 eV. Our calculations suggest that the results for the calculated energy barriers and other total-energy differences are accurate to 0.05 eV. Thus, for the present study our numerical accuracy is sufficiently high.

While at the flat regions exchange diffusion is found to be unimportant, the situation at steps is somewhat different. We considered a (511) surface which is vicinal to (100). This surface consists of (100) terraces which are 3 atoms wide. The step edges are perpendicular to the [100] and the [011] directions [see Fig. 2(a)]. The periodicity along the step edge is taken to be three surface lattice constants. Figure 2(b) displays the results obtained for the hopping process. There are two stable sites: The hollow site (M) at which the adatom is fivefold

TABLE I. Convergence tests for the LDA diffusion barriers E_d on flat surfaces with respect to the cutoff energy E_{cut} , the surface cell size, the number of atomic layers N_l , and the number of \mathbf{k} points in the SBZ N_k .

E_{cut} (Ry)	Surface cell size		E_d (eV)		
	N_l	N_k	Hopping	Exchange	
40	3×3	3	9	0.52	0.93
50	3×3	3	9	0.52	0.94
40	2×2	3	16	0.50	0.95
40	2×2	4	16	0.51	0.95
40	3×3	4	9	0.53	0.92
40	3×3	3	16	0.51	0.96

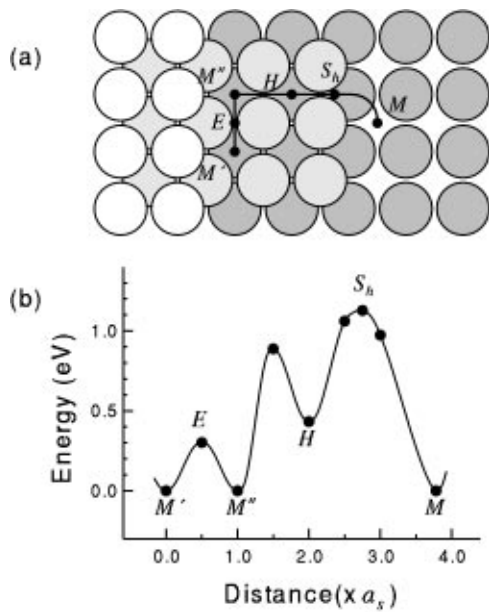


FIG. 2. Total energy of an Ag adatom diffusing along the indicated path by a hopping process, calculated within the LDA. A top view of the vicinal (511) surface is shown in (a). The step edges are aligned along the $[0\bar{1}1]$ direction. (b) The distance is given in units of the surface lattice constant $a_s = 2.92 \text{ \AA}$.

coordinated and the hollow site (H) on the terrace at which the adatom coordination is four.

It is plausible that at site M the adatom is bound best. The energy difference between the M and H sites is 0.43 eV (LDA) and 0.32 eV (GGA). The energy at the H site is, in fact, the same (within our accuracy of 0.05 eV) as that at flat regions of the surface. This result is found by comparing our total energies of the flat and the stepped surfaces and by doing additional calculations for a (711) surface, which has longer terraces. The “additional energy barrier” for rolling over the ledge from H to M is $\Delta E_{\text{step}}^{\text{Ag}(100)} = 0.18 \text{ eV}$ (LDA) and 0.10 eV (GGA). Thus, it is by about 30% (20%) higher in the LDA (GGA) than the diffusion barrier at the flat surface. The transition state for the roll over process is identified to be near the bridge site at the ledge [S_h in Fig. 2(a)]. The other possibility to reach the geometry M from H is via an exchange, where atom 1 replaces atom 2 and subsequently the latter moves to the fivefold coordinated site M (see Fig. 3). Within our numerical accuracy for energy differences ($\approx 0.05 \text{ eV}$) the calculated energy barrier of 0.52 eV (LDA) and 0.45 eV (GGA) is almost identical to that of the hopping diffusion at the terrace. At the transition state geometry atom 2 is located near the bridge site formed by two step-edge atoms 3 and 4 on the lower terrace [S_{ex} in Fig. 3(a)]. The interesting feature is that the step-edge atom 2 is situated closer to atom 4 to form a bond with atom 6. Each of the two topmost atoms 1 and 2 has five bonds with neighbors, while at the saddle point of the exchange diffusion on

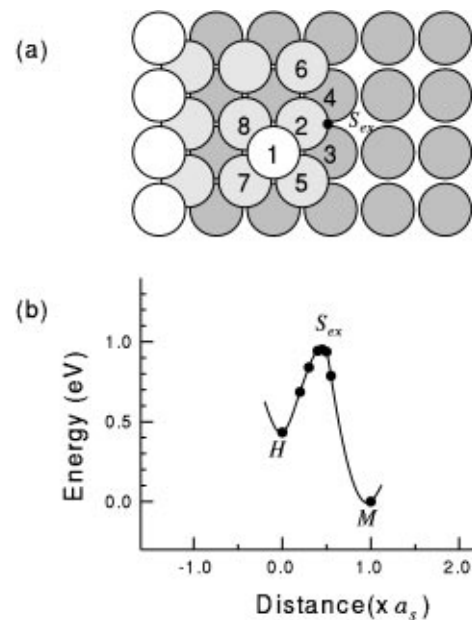


FIG. 3. Total energy of an Ag adatom diffusing across a step by an exchange process, calculated within the LDA. In (a) adatom 1 is adsorbed at site H . The total energy as a function of the distance of the step-edge atom 2 from the undistorted step edge is shown in (b).

the flat surface each of the two topmost atoms has only four bonds [Fig. 1(c)]. The origin of the lower diffusion barrier of the adatom at the edge is thus the additional bonds formed at the obtained saddle point. We have indeed found that *there is no additional energy barrier to descend from an upper to a lower terrace*. This finding provides a natural explanation for the smooth 2D growth observed in homoepitaxy on the Ag(100) surface.

Our total-energy calculations clearly show that the step-down diffusion proceeds by an exchange process. Inspection of the geometry (see Fig. 3) makes this theoretical finding very plausible. For this process atom 2 in Fig. 3 has to move only a short distance, namely, to the next hollow site, passing over a bridge position; this displacement is similar to the hopping at the flat surface. Because atom 1 follows in close contact to atom 2, the local coordination of atoms 1, 2, 5, and 8 always remains high, making the process energetically favorable. In contrast, the roll over process (see Fig. 2) is more involved; i.e., the diffusing atom has to proceed a much longer distance on which it even has to pass a nearly-on-top site, when turning from the S_h point towards M .

We note in passing that exchange processes will also play a role at steps at fcc (111) surfaces, but here the displacements are more complex and the additional step-edge barrier is not diminished. We also note that at aluminum surfaces, the system studied best so far, the exchange process is supported by the formation of covalent bonds, which is made possible by the sp valence electrons [18]. For silver we find that the electron density does not

reflect a pronounced covalency effect, which is indeed the expected behavior for a noble metal. This result explains why the exchange process does not happen at the flat Ag(100) surface and has only a minor effect at the close-packed steps at Ag(111).

Finally, we comment on the shape of islands. Key parameters that determine the shape of islands are the types of steps and the mobility of atoms along step edges. Since there are two different types of steps for fcc (111), in thermodynamic equilibrium islands have a hexagonal shape. For fcc (100) we find only one type of step as shown in Fig. 2(a) (the other step has a {110} microfacet and needs much higher energy to form). Thus, the expected equilibrium shape of islands is a square. The diffusion barrier along step edges determines the roughness of steps. We find that adatom diffuses along step edge by a hopping process. The barrier is significantly lower than the surface diffusion barrier E_d . This lower energy barrier (LDA: 0.30 eV; GGA: 0.27 eV) indicates that Ag islands formed on Ag(100) should be compact. Atoms which reach the step edges will certainly be able to diffuse parallel to the steps and thus local thermal equilibrium is attained. We therefore expect rather straight step edges and no fractally shaped islands. The lower barrier for diffusion parallel to steps can be understood in terms of variation in coordination from five to four as the adatom moves from site M' to site E [Fig. 2(a)], while for diffusion on flat terraces the coordination varies from four to two.

In summary, we presented density functional theory calculations for various microscopic diffusion processes at Ag(100). Ag adatoms are found to diffuse across flat terraces by a hopping process. Adatoms approaching step edges descend from the upper to the lower terrace by an exchange process and the obtained energy barrier is found to be 0.45 eV in the GGA, almost identical to the barrier at flat regions. Thus, there is no additional energy barrier to diffuse across step edges, in sharp contrast to the self-diffusion at Ag(111). This implies good interlayer mass transport for deposition at and growth of silver (100) giving rise to a smooth surface. In contrast, the additional step-edge barrier which exists at the silver (111) surface (and typically at other surfaces as well) gives rise to the rough growth of Ag(111). Also our finding that the step down motion proceeds by exchange is expected to apply for other noble metals and their left neighbors (but this is not a guarantee that the additional step-edge barrier vanishes completely).

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