Using the plane wave pseudopotential method we performed density functional theory calculations on the stability of steps and self-diffusion processes on Ag(100). Our calculated step formation energies show that the \{111\}-faceted step is more stable than the \{110\}-faceted step. In accordance with experimental observations we find that the equilibrium island shape should be octagonal very close to a square with predominately \{111\}-faceted steps. For the (100) surface of fcc metals atomic migration proceeds by a hopping or an exchange process. For Ag(100) we find that adatoms diffuse across flat surfaces preferentially by hopping. Adatoms approaching the close-packed \{111\}-faceted step edges descend from the upper terrace to the lower level by an atomic exchange with an energy barrier almost identical to the diffusion barrier on flat surface regions. Thus, within our numerical accuracy ($\approx \pm 0.05$ eV) there is no additional step-edge barrier to descent. This provides a natural explanation for the experimental observations of the smooth two-dimensional growth in homoepitaxy of Ag(100). Inspection of experimental results of other fcc crystal surfaces indicates that our result holds quite generally.

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I. INTRODUCTION

The study of the morphology of surfaces is one of the oldest areas of crystal growth and has attracted particular attention in recent years due to advances in epitaxy and the possibility of controlled growth of new materials and bulk quality surfaces. The structure of an epitaxial film is often thought to be determined by thermodynamic principles, in which the film is assumed to adopt the energetically stable thermal-equilibrium structure. However, there are many examples which demonstrate that under typical growth conditions growth is often governed by kinetics rather than thermodynamics. A lot of experimental works show that the growth mode (the evolution of film structure with coverage) can be altered by varying the growth conditions such as the substrate temperature and deposition rate, or by introducing defects or surfactants. A notable example is the study of homoepitaxial growth of Ag(111): Under clean surface conditions the growing surfaces are very rough with mountains as high as 30-40 atomic layers (multilayer growth). These studies revealed that the film structure is governed by the kinetics of surface diffusion. Hence, knowledge of the kinetics such as mass transport across terraces and steps and the diffusion parallel to steps is essential to reach understanding of the morphology and quality of growth.

To date most calculations of atomic diffusion on surfaces employ computationally fast semiempirical methods. They have been widely used by methodological simplicity and under the assumption that the results, although quantitatively not very accurate, may still explain general trends. The main approximation of these methods concerns the kinetic energy operator of the electron and the neglect of a self consistent adjustment of the electron density. Thus the essence of the mechanism governing the breaking and making of chemical bonds is missing. Obviously, quite often, as e.g., in the example discussed in this paper, quantitative results determine the qualitative features. For example, when the energy-barrier at the step edge is bigger than the diffusion barrier at the flat surface the growth mode is rough, and when the step-edge barrier is equal or smaller, the growth mode is flat. The proper treatment which gives quantitatively and qualitatively more accurate results and takes the quantum mechanical properties and the chemistry of interatomic interactions properly into account is density functional theory (DFT).

In this paper we report DFT total energy calculations of step formation and diffusion of Ag adatoms on the (100) surface of fcc silver, which extends work presented earlier. Homoeopitaxy of silver exhibits a different behaviour in the growth mode depending on substrate orientations: The growing surface of Ag(100) is smooth and flat whereas that of Ag(111) is typically rather rough. For Ag(100) surfaces reflection high-energy electron diffraction (RHEED) intensity oscillations have been observed in the temperature range from 200 to 480 K, which indicates that the growth proceeds by a smooth two-dimensional (2-D) mode. In contrast, for Ag(111) surfaces RHEED intensity oscillations are absent at all temperatures, suggesting that there is no 2-D growth but that the surface becomes very rough upon growth. This finding for Ag(111) was confirmed by x-ray reflection experiments and scanning tunneling microscopy (STM) measurements. The former study shows that the growth mode changes from multilayer to step-flow growth over the temperature range from 175 to 575 K. The latter studies show an STM topography of “mountain and canyon”-like structures with heights of 30-40 atomic layers.

From their analysis of STM images for Ag(111) Vrijmoeth et al. concluded that the multilayer growth is
attributed to an additional step-edge barrier. This is the barrier for a diffusing adatom descending steps minus the surface diffusion barrier. The authors obtained that the additional energy barrier is 0.15 eV. Bromann et al. developed a method to determine with high accuracy attempt frequencies and activation energies for terrace diffusion as well as for the step-down process. This analysis was done by measuring the nucleation rate on top of islands as a function of island size and temperature. They obtained for the additional energy barrier a value of 0.12 eV very close to the 0.15 eV by Vrijmoeth et al. Recently STM studies by Morgenstern et al. find the additional step-edge barrier to be 0.10 eV. This additional energy barrier which adatoms encounter at step edges explains why the growth of silver perpendicular to the (111) surface proceeds by a very rough multilayer mode. Interestingly, as noted above, the growth of the (100) surface is qualitatively different. As the calculations in Ref. 3 showed the additional step-edge barrier is practically zero. Below we extend our previous study and repeat convergence tests.

Furthermore, we consider the shape of islands formed on Ag (100) in thermal equilibrium. There are two types of monolayer-high steps for fcc (100) surfaces as shown in Fig. 1: One is a close-packed step running along the \( \langle 110 \rangle \) direction which has a \( \langle 111 \rangle \) microfacet at edges and the other an open step running along the \( \langle 100 \rangle \) direction which has a \( \langle 110 \rangle \) microfacet at edges. A ratio of formation energies of these two steps determines the equilibrium shape of islands on Ag(100) (as obtained by the Wulff construction). Here we apply the \textit{ab initio} total energy calculations to the energies of these two sorts of steps.

The paper is organized as follows. In Sec. II, we describe the method of calculation. In Sec. III, the equilibrium shape of islands is discussed as it follows from our calculated step-formation energies. In Sec. IV we present results for diffusion processes of a Ag adatom on flat and stepped Ag(100) surfaces, and discuss their implication on epitaxial growth. Finally the paper is concluded by Sec. V.

II. METHOD OF CALCULATION

The total energies and forces on atoms are calculated by the DFT. We use a norm-conserving pseudopotential method together with the Car-Parrinello-like technique for iterative minimization of the Kohn-Sham total energy. The electronic wavefunctions are expanded in a plane wave basis set. Most calculations have been carried out primarily using the local-density approximation (LDA) for the exchange-correlation functional. At important geometries we repeat the calculations using the generalized gradient approximation (GGA) of Perdew et al.

We use a repeating slab geometry to simulate the actual surface. A \((3 \times 3)\) periodicity is employed in the lateral directions, which we tested gives that artificial adatom-adatom interaction is sufficiently weak and in fact negligible for the questions of concern. An artificial periodicity is imposed along the perpendicular direction to the surface to construct a three-dimensional unit cell. We take a slab of three atomic layers and of a 10.35 Å vacuum region. This rather thin slab is acceptable, as we adsorb the adatom only on one side. We relax the adatom and the top-layer atoms according to a damped Newton dynamics, while the other atoms in the two bottom layers are kept at the bulk positions. The optimized geometries are identified by the requirement that the remaining forces acting on the atoms are smaller than 0.05 eV/Å.

The LDA (GGA) ionic pseudopotentials including the tightly bound 4\(d\)-electron state as valence states are created using the nonrelativistic (semirelativistic) scheme of Troullier and Martins. The fully separable norm-conserving pseudopotentials of the Kleinman-Bylander form are constructed with the \(s\) pseudopotential as the local component. We use a kinetic energy cutoff of 40 Ry to expand the wavefunctions in plane waves. The \(k\)-space integration is performed using nine equidis-
TABLE I. Structural properties of fcc silver obtained from the plane wave pseudopotential and all-electron linearized-augmented-plane-wave (LAPW) methods, for nonrelativistic (NR) and semirelativistic (SR) calculations in the LDA and GGA. The $T \rightarrow 0$ K experimental data are given for comparison.

|                  | This work (NR–LDA) | LAPW$^a$ (NR–LDA) | Expt.$^b$ |
|------------------|--------------------|--------------------|-----------|
|                  | LDA | GGA | LDA | GGA | LDA | GGA | Expt. |
| $a_0$ (Å)        | 4.14 | 4.18 | 4.00 | 4.17 | 4.07 |
| $B_0$ (GPa)      | 99  | 90  | 136 | 85 | 102 |

$^a$Reference 19
$^b$The experimental values are taken from Reference 19.

TABLE II. Calculated results for the properties of flat Ag(100): surface formation energy $\sigma$, work function $\phi$, and multilayer relaxation $\Delta d_{ij}$ relative to the interlayer spacing in the bulk $d_0$. It is noted that the experimental surface energy is an estimate from liquid surface tension measurements.

|                  | $\sigma$ (eV/atom) | $\phi$ (eV) | $\Delta d_{12}/d_0$ (%) | $\Delta d_{23}/d_0$ (%) |
|------------------|-------------------|-------------|-------------------------|-------------------------|
| This work (NR–LDA) | 0.57 | 4.39 | -2.2 | 0.4 |
| FP-LMTO (NR–LDA)$^a$ | 0.63 | 4.43 | -1.9 |
| FP-LMTO (SR–LDA)$^b$ | 0.62 | 4.77 | -1.9 |
| Expt.$^c$ | 0.65$^d$ | 4.64$^d$ | 0 ± 1.5$^e$ | 0 ± 1.5$^e$ |

$^a$Reference 21
$^b$Reference 23
$^c$Reference 22
$^d$Reference 21
$^e$Reference 23

is given by the difference between the electrostatic energy in the middle of the vacuum region and the Fermi energy. The multilayer relaxation $\Delta d_{ij}$ is defined by the change in spacing between layers $i$ and $j$ compared to the interlayer spacing in the bulk, $d_0$.

We calculate the properties of flat Ag(100), using the slab of 5 atomic layers, a vacuum region equivalent to 5 atomic layers, and 96 k points in the SBZ of the (1×1) cell. In this calculation we used the lattice constant 4.14 Å of k-sampling-converged calculation which differs only by 0.1% from the calculated lattice constant using the above k-points. The results are summarized in Table II. The results in our previous paper were obtained using a slab of 4 atomic layers, a vacuum region equivalent to 4 layers, and 64 k-points in the SBZ of the (1×1) cell. Due to these changes the present results differ slightly from those of Ref. 21. The calculated results are in good agreement with a previous full-potential linear-muffin-tin-orbital (FP-LMTO) calculation. Our calculations of the lattice relaxation give $\Delta d_{12}/d_0 = -2.2\%$ and $\Delta d_{23}/d_0 = 0.4\%$. The low-energy electron diffraction (LEED) analysis, in which the first ($d_{12}$) and second ($d_{23}$) interlayer spacings were determined, shows small relaxations with $\Delta d_{12}/d_0 = 0 ± 1.5\%$ and $\Delta d_{23}/d_0 = 0 ± 1.5\%$. This result is in good agreement with the present DFT-LDA results within the experimental accuracy, (see also the influence of surface vibrations, which is neglected here).

III. STEP FORMATION ON (100) SURFACES

A. Structure and energetics of the flat surface

Before we describe the step formation on Ag(100) it is worthwhile to study the properties of the flat Ag(100) surface. The surface formation energy per surface atom is given as

$$\sigma = \left( E_{\text{slab}} - N_{Ag} \mu_{Ag} \right) / N_{\text{surf}},$$

where $E_{\text{slab}}$ is the total energy of the slab of $N_{Ag}$ silver atoms and $N_{\text{surf}}$ is the number of atoms at the surface. In thermal equilibrium the silver chemical potential is equal to the energy of a silver atom in the bulk. In order to achieve an optimum of error cancellations the calculation of the bulk energy $\mu_{Ag}$ is done with the same k-points sampling as in the slab calculations. The work function $\phi$ is given as

$$\phi = \frac{E_{\text{slab}} - E_{\text{surf}}}{N_{\text{surf}}} - \mu_{Ag},$$

where $E_{\text{surf}}$ is the total energy of the surface and $\mu_{Ag}$ is the chemical potential of Ag atoms in the bulk.

B. Structure and energetics of steps

In this subsection we consider the stability of the two most densely packed monolayer-high steps on Ag(100): the close-packed $\langle 110 \rangle$ / $\langle 111 \rangle$ and open $\langle 100 \rangle$ / $\langle 110 \rangle$ steps (see Fig. 3). To compute step energies we use the slab geometry of the grooved surface sketched in Fig. 3.

The simulation cell has the periodicity of $N_{Ag}$ Å of $N_{Ag}$ silver atoms. The results derived from the Murnaghan equation-of-state fit to the calculated data are listed in Table II. Zero-point vibrations are not considered in these theoretical results. The calculated values are in good agreement with $T \rightarrow 0$ K experimental data.

The experimental values are given as $\sigma = 0.65$ eV/atom, $\phi = 4.64$ eV, $\Delta d_{12}/d_0 = 0 ± 1.5\%$, and $\Delta d_{23}/d_0 = 0 ± 1.5\%$. These results are in good agreement with the present DFT-LDA results within the experimental accuracy, (see also the influence of surface vibrations, which is neglected here).
and {110}-faceted steps, respectively. $L_y$ is treated as a variable, so that the ledge separation $l$ is equal to $L_y/2$ (see Fig. 2). The formation energy of the grooved surface $E_{surf}$ is extracted from the calculations of the $N$-layer slab shown in Fig. 2, by applying the formula

$$E_{surf}(N) = E_{slab}(N) - N\lambda_0 N_\Lambda_0 .$$

The step formation energy per unit length is

$$\lambda(N) = (E_{surf}(N) - N\sigma(N))/L_x .$$

In Eq. 3 $\sigma(N)$ is the surface energy per surface atom from the calculations of the $N$-layer slab of the flat (100) surface and $N_{surf}$ is the number of surface atoms at the grooved surface: $N_{surf} = L_x L_y/a_s^2$. The surface energy is evaluated by averaging the surface energies of the thin and thick region of the slab, i.e. $\sigma_{ave}(N) = (1-\alpha)\sigma(N) + \alpha\sigma(N+1)$ ($\alpha$ is a ratio of the number of surface atoms in the thick region and the total number of surface atoms). The averaging improves the accuracy of the calculated step energies.

Several calculations were done to test the dependence of the calculated step energies on the ledge separation $l$ and the number of atomic layers $N$. The results of the {111}-faceted step are summarized in Table III. It shows that the step energy decreases with increasing the ledge separation $l$. In particular, the step energy $\lambda$ can be expanded with respect to the ledge separation $l$:

$$\lambda = \lambda_0 + A/l^2 .$$

In this equation the first term is the energy of an isolated step, and the last term gives the effective interaction between steps. This term includes possible energetic contributions such as dipole-dipole or elastic interactions. For the 3-layer grooved surface we obtain $\lambda_0 = 0.150$ eV/$a_s$ and $A = 0.041$ eV/$a_s^2$ in the relaxed geometry by fitting the variation of the step energy with the ledge separation $l$ to Eq. 4. We find that the step energy already reach the isolated one at $l = 3a_s$ with an error of $0.005$ eV/$a_s$. The step energy decreases by $0.024$ eV/$a_s$ with increasing the slab thickness from 3 to 4 layers. We find that, while the step energy changed by 20% as the slab thickness is increased from 3 to 4 layers, a ratio of step energies changes only by 5%. Thus, we see that the slab of 4 layers is sufficient to obtain reasonably converged result of a ratio of step energies.

Using the 4-layer slab of the grooved surface and the ledge separation of $3a_s$, we obtain the formation energy of 0.130 eV/$a_s$ (LDA) for the close-packed {111}-faceted step. For the {110}-faceted step we take a 4-layer slab and ledge separation of $2\sqrt{2}a_s$. The obtained step energy is 0.156 eV/$a_s$ (LDA). Thus, the close-packed {111}-faceted step is more stable than the open {110}-faceted one. This confirms the experimental observation that the {111}-faceted steps are preferentially formed in thermal equilibrium. This result is not unexpected because of atomic geometries, i.e. the local coordinations of the two steps differ noticeably: Step-edge atom at the {111}-faceted step has seven nearest neighbors, while the step-edge atom at the {110}-faceted step has only six neighbors. Using the AFW (Adams-Foiles-Wolfer) EAM (embedded atom method) functions, Nelson et al. found $\lambda$ to be $0.102$ eV/$a_s$ and $0.142$ eV/$a_s$ for {111}- and {110}-faceted steps, respectively. With the VC (Voter-Chen) functions they obtained $\lambda$ to be $0.135$ eV/$a_s$ for {111}-faceted step.

When the formation energies of all steps were known,

![FIG. 2. Schematic representation of the N-layer slab of the grooved surface. Periodic boundary conditions are applied along the x and y axes.](image)

![TABLE III. Convergence of the formation energy of the {111}-faceted step in the relaxed geometry as a function of ledge separation l and the number of atomic layers N, calculated by DFT-LDA.](table)

| $N$ | 3 | 3 | 3 | 4 |
|-----|---|---|---|---|
| $l$ ($a_s$) | 2 | 3 | 4 | 3 |
| $E_{surf}$ (eV) [eq.2] | 4.951 | 7.258 | 9.593 | 7.172 |
| $\sigma_{ave}$ (eV/atom) | 0.579 | 0.579 | 0.581 | 0.576 |
| $\lambda$ (eV/$a_s$) [eq.3] | 0.160 | 0.155 | 0.152 | 0.130 |

![FIG. 3. Calculated shape of islands in thermal equilibrium. The close-packed {111}-faceted edges are longer with an edge length ratio $L_{(100)/(110)} : L_{(110)/(111)}$ of 3:10 than the open {110}-faceted ones.](image)
the equilibrium shape of an island can be obtained by finding the island shape with minimum free energy, or by applying the Wulff construction. For the (100) surface it is certainly plausible that only two steps are important. Thus we expect octagonally shaped islands as shown in Fig. 3. The calculated step formation energies imply that the {111}-faceted edges should dominate and that the edge-length ratio should be \( L_{(100)}/(110) = L_{(110)}/(111) = 3:10 \). This theoretical finding can be compared to experimental observations. In fact, for ion-bombarded Ag(100) surface the preferential formation of the close-packed (111)-faceted step edges has been observed at room temperature, and for Ir(100) Chen and Tsong, using the field ion microscope, also found that the equilibrium island shape is rectangular with {111}-faceted steps.

Next we consider the relaxations of the stepped surface. Figure 4 shows the geometry optimized structure of {111}-faceted steps. The relaxations of surface atoms in the upper terrace are nearly identical to those of surface atoms of flat Ag(100): surface atoms 1, 1', and 1'' relax toward the bulk by \( \sim 2\% \) of the bulk interlayer spacing \( d_0 \) [see Fig. 4 (a)]. Atoms 2 and 2' at step bottom slightly relax upward and toward atoms 3 and 3', but these relaxations of lower terrace atoms are nearly negligible. Figure 4(b) displays the bond lengths of step-edge atoms with their underlying nearest neighbors and the numbers show that the bond lengths are very close to those between surface atoms and their nearest neighbors in the subsurface sites of flat Ag (100). Similarly, at the grooved surface with the {110}-faceted steps downward relaxations of upper terrace atoms dominate.

**IV. SELF-DIFFUSION ON FLAT AND STEPPED (100) SURFACES**

**A. Adsorption and self-diffusion on flat surfaces**

We now present the results of adsorption and diffusion of a Ag adatom on the flat Ag (100) surface. For metals, metal adatoms on surfaces preferentially adsorb at the highest coordination site. Indeed the equilibrium adsorption site for a Ag adatom on Ag (100) is the fourfold hollow [Fig. 5(a)]. In the optimized geometry, the four nearest neighbors of the adatom slightly distort in the lateral directions, opening the hollow site even further. The lateral displacement from the ideal clean surface site is 0.02 Å. The adatom is located 1.84 Å above the surface layer, and 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.

In metal-on-metal surface diffusion, an adatom typically moves across a flat surface by a series of hops between adjacent equilibrium adsorption sites. For fcc (100) an adatom in a fourfold site moves over the twofold bridge site into a neighboring fourfold equilibrium site [see Fig. 5(b)]. An adatom may visit all of the fourfold surface sites, forming a \((1 \times 1)\) square pattern. An alternative mechanism for surface diffusion is atomic exchange where a diffusing atom moves by displacing a neighboring surface atom. For the fcc (100) surface the exchange process of an adatom with a surface atom occurs preferentially in the [010] and [001] directions. At the saddle point of the transition the adatom and surface atom are above a vacated surface-layer site [see Fig. 5(c)]. Subsequently the displaced surface atom becomes a new adatom in a next-nearest-neighbor fourfold site. When this diffusion mechanism is active, an adatom may visit only half of the fourfold surface sites, forming

![FIG. 4.](image4.png)

![FIG. 5.](image5.png)
 FIG. 6. Valence charge density at the transition state for the exchange diffusion. A schematic plot of the optimized atomic geometry is shown in (a). Panels (b) and (c) display the electron density. In (b) the plot is in the plane cutting atoms 5, 1, 2, and 6. In (c) the plot is in the plane cutting atoms 3, 1, 2, and 4. The value of the lowest-density contour is $3 \times 10^{-3} e/(\text{bohr})^3$ and subsequent contours differ by a factor of 2.2. Solid circles mark the second layer atoms.

Fig. 6(a), each of the two top-most adatoms has four bonds with neighbors. The distance between the two top-most adatoms is 2.75 Å, 1 % shorter than in the fourfold hollow. These two atoms are located 1.52 Å above the surface layer. The four atoms neighboring these atoms are pushed away by 0.06 Å and downwards by 0.05 Å. The bond length between the top-most and underlying Ag atoms is 2.71 Å, 3 % shorter than in the fourfold hollow. This again follows the well known trend: Each of the two bonds at the bridge site is longer than in the fourfold hollow, and 5 % longer than in the bulk. We note that at the (100) surface of aluminum, the exchange displacement is supported by the formation of covalent bonds, which is made possible (and indeed plausible) by the $sp$ valence of the group III element Al. For silver we find that the electron density does not reflect a pronounced covalency effect as shown in Fig. 6(b) and (c), which explains why the exchange displacement does not play a role at flat Ag(100).

B. Adsorption and self-diffusion on stepped surfaces

This subsection is concerned with the diffusion of a Ag adatom at the $\{111\}$-faceted steps which are prefer-
FIG. 7. Top and side view of the fcc (511) surface. The (511) surface has close-packed {111}-faceted steps and the number of atomic rows within the (100)-oriented terraces is three.

The {111} surface is vicinal to (100) (see Fig. 7). This surface consists of (100) terraces which are three atom rows wide. The step edges are perpendicular to the [100] and the [011] directions. The periodicity along the step edge is taken to be three surface lattice constants. Using a vicinal surface allows to consider a smaller number of atoms within the unit cell than that required for the ordered step arrays on flat surfaces (the grooved surfaces). Using the vicinal (511) surface of 4 atomic layers, we obtain the formation energy of 0.136 eV/a_s (LDA) for the close-packed {111}-faceted step, which is close to the corresponding value 0.130 eV/a_s (LDA) from the 4-layer slab calculations of grooved surface (see Table III). In Fig. 8(b) we display the total energy of a Ag adatom diffusing along the indicated path by a hopping (roll-over) process, calculated within the LDA. A top view of the vicinal (511) surface is shown in (a). The {111}-faceted edges are aligned along the [011] direction. The distance is given in unit of the surface lattice constant a_s.

Figure 8(b) clearly shows two stable adsorption sites: The hollow site (M) at the step, at which the adatom is fivefold coordinated and the hollow site (H) on the terrace, at which the adatom coordination is four. Due to the higher coordination it is indeed plausible that the DFT results give that the adsorption site M is more stable than site H. The energy difference between the M and H sites is 0.43 eV (LDA) and 0.32 eV (GGA). In the optimized geometry of the site M the distance between the step-edge atom and adatom is 2.89 Å, 1 % shorter than in the bulk. The bond length between the two step-bottom atoms and adatom is 2.78 Å, and that between the two lower-terrace atoms and adatom is 2.84 Å. It is also interesting to note that desorption of an adatom at the step edge to the flat region requires to overcome a very high energy barrier (LDA: 0.96 eV; GGA: 0.76 eV).

When the adatom rolls over the ledge from H site on the upper terrace to M site on the lower terrace, we obtain an energy barrier of 0.70 eV (LDA) and 0.55 eV (GGA). Thus, we find the “additional step-edge barrier” to be 0.18 eV (LDA) and 0.10 eV (GGA) to step down from the upper terrace by the hopping (roll-over) process. This value is by about 30 % (20 %) higher in the LDA (GGA) than the diffusion barrier at the flat region. At the transition state for the roll-over process the adatom is located near the bridge site at the ledge [S_h in Fig. 8(a)]. In the optimized geometry the two nearest neighbors of the adatom are slightly pushed away, and the adatom is located 2.27 Å above the upper terrace. The bond length between the step-edge atoms and adatom is found to be 2.72 Å, 1 % longer than in the bridge site at the flat region and 7 % shorter than that of a bulk atom: Each of the two bonds at site S_h is weaker than that at the bridge site on the flat region. At the bridge site on the flat terraces the adatom has four next-nearest-neighbors, while at S_h the adatom has two next-nearest-neighbors.
Thus, we could understand the additional energy barrier in terms of weaker bonds between the adatom and underlying surface atoms, and decrease of the number of the next-nearest-neighbors compared to the flat surfaces.

The other possibility to step down from the upper terrace is via an exchange, where adatom 1 displaces step-edge atom 2 and subsequently the latter moves to the fivefold coordinated site M [see Fig. 9(a)]. Figure 9(b) displays the results of the step-down diffusion by the exchange process. Within our numerical accuracy for energy differences ($\approx \pm 0.05$ 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 flat region. The transition state for the exchange process is identified to be near the bridge site formed by two step-bottom atoms 3 and 4 on the lower terrace [$S_{ex}$ in Fig. 9(a)]. The geometry of the optimized structure of the transition state is given in Fig. 10. The top-most adatom (no. 1) is located 1.26 Å above the upper-terrace atoms. The height is much lower than the value of 1.52 Å at the flat region. Inspection of the geometry at $S_{ex}$ shows that the local coordination of atoms 1 and 2 concerned with the exchange displacement remains high, since the atom 1 follows in close contact to atom 2 during the process: At $S_{ex}$ each of the two atoms 1 and 2 has five bonds with neighbors, while at the saddle point of the exchange diffusion on the flat region each of the two top-most atoms has only four bonds [Fig. 10(c)]. The origin of the lower diffusion barrier of the step-down motion by the exchange displacement compared to the flat region is thus the additional bonds formed at the obtained saddle point. Our finding that there is no additional energy barrier to descend from the upper to the lower terrace provides a natural explanation for the smooth 2-D growth of silver in the (100) orientation. By analyzing the STM images of Ag(100) during deposition Zhang et al. gave an estimate of 0.025 ± 0.005 eV for the additional step-edge barrier. Within our numerical accuracy ($\approx \pm 0.05$ eV) this is in good agreement with our result that the additional step-edge barrier is negligible.

Our finding that for Ag(100) an adatom goes down at step edges by an exchange process is expected to apply for other noble metals and other fcc transition metals as well. In fact, for homoepitaxial growth of Cu(100), Pd(100), and Fe(100) damped oscillations of the scattering intensity have been observed. In order to explain the intensity oscillations associated with smooth 2-D layer-by-layer growth, the step-edge barrier for the descent of adatoms was assumed to be negligible. For a hopping (roll-over) process we expect that an adatom generally encounters an additional (positive) step-edge barrier ($\sim 0.1$ eV for Ag(100)) because of the low coordination of the transition state. Thus, we expect that quite generally for fcc (100) metal surfaces step-down motion proceeds by an exchange process, similarly to Ag(100).

Finally we address the atomic motion along the close-packed {111}-faceted step to get ideas about the possible roughness of steps and kinetic growth shapes of islands. We find that the diffusion along step edge proceeds by a hopping process. An adatom in a fivefold coordinated adsorption site moves over a bridge site $E$ into a neighboring fivefold coordinated site [see Fig. 9(a)]. From Fig. 9(b) we see that the barrier (LDA: 0.30 eV; GGA: 0.27 eV) is significantly lower than the surface diffusion

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**FIG. 9.** Total energy of a Ag adatom diffusing across a step by an exchange process, calculated within the LDA. In (a) the adatom 1 is adsorbed at the fourfold hollow 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).

**FIG. 10.** Schematic view of the optimized atomic structure at the transition state $S_{ex}$ of the step-down diffusion by the exchange process, calculated within the LDA. $d_{18}$ denotes the bond length between the adatom 1 and second-layer atom below.
barrier $E_d$ (LDA: 0.52 eV; GGA: 0.45 eV). This lower energy barrier 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. In the optimized geometry of site $E$ the distance between the two step-edge atoms and adatom is 2.99 Å, 2% longer than in the bulk. We find the bond lengths of 2.66Å between the step-bottom atom and adatom and of 2.84 Å between the lower terrace atom and adatom and note that the coordination varies from five to four as the adatom moves from site $M'$ to site $E$ [Fig. 8(a)], while for diffusion on flat terraces the coordination varies from four to two. Thus, the lower barrier for diffusion parallel to steps can be understood in terms of smaller variation in coordination.

V. CONCLUSION

In the above Section, we presented results of first-principles total-energy calculations for the electronic structure and energies of steps and for various microscopic self-diffusion processes at Ag (100).

For fcc(100) surfaces two types of monolayer-high steps are of particular importance: the close-packed {111}- and more open {110}-faceted steps. Our total-energy calculations show that the {111}-faceted step is more stable than the {110}-faceted one. This is understood in terms of different coordination of step-edge atoms. In accordance with experimental observations, we find that in thermal equilibrium the shape of island should be octagonal but very close to a square with {111}-faceted edges. The edge-length ratio of the octagon is calculated as 10:3. The energy barrier for self-diffusion of a Ag adatom along {111}-faceted edges is found to be significantly lower than the surface diffusion barrier. Thus, we expect rather straight step edges and no fractally shaped islands.

At flat regions of Ag (100) Ag adatoms are found to diffuse by a hopping process. The obtained energy barrier is 0.45 eV in the GGA which is very close to the experimental estimates which are 0.40 eV [23] and 0.33 eV [24]. In contrast to atomic motion on flat region, the descent of adatoms at steps proceeds by an exchange process. The calculated energy barrier is almost identical to the barrier at flat region. This indicates that there is no additional step-edge barrier to diffuse across step edges. This finding is in sharp contrast to the additional energy barrier ($\Delta E_{\text{step}}^{\text{Ag}(111)} = 0.15$ eV [23] and 0.12 eV [24] and 0.10 eV [25]) experimentally found at Ag (111) actuating a rough growth morphology. The calculated result implies good interlayer mass transport at Ag (100) and thus explains the smooth 2-D growth experimentally observed in homoepitaxy of Ag (100). Inspection of experimental works indicates that the step-down motion at steps by an atomic exchange takes place quite generally for other fcc metals.

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