

Strain dependence of surface diffusion: Ag on Ag(111) and Pt(111)

C. Ratsch*, A. P. Seitsonen, and M. Scheffler

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

(Received 2 October 1996)

Using density-functional theory with the local-density approximation and the generalized gradient approximation we compute the energy barriers for surface diffusion for Ag on Pt(111), Ag on one monolayer of Ag on Pt(111), and Ag on Ag(111). The diffusion barrier for Ag on Ag(111) is found to increase linearly with increasing lattice constant. We also discuss the reconstruction that has been found experimentally when two Ag layers are deposited on Pt(111). Our calculations explain why this strain driven reconstruction occurs only after two Ag layers have been deposited. [S0163-1829(97)06312-1]

The diffusion of a single adatom on a surface is a fundamental process determining the surface morphology development in epitaxial growth. For Ag on Ag(111) it has been demonstrated¹ that the substrate temperature can be lowered periodically for a short period of time so that diffusion is suppressed, and as a result the density of islands is increased at the beginning of the growth of a new layer. With this trick the growth mode can be changed from three dimensional to two dimensional (for a discussion of this and other approaches affecting the growth mode see Ref. 2). Growth of one material on a different material is of particular interest for a number of technological applications. In such a heteroepitaxial system the material to be deposited is under the influence of epitaxial strain, yet very little is known about the influence of strain on the surface diffusion constant. Additionally, strain is not only due to lattice mismatch but it is also present on surfaces of homoepitaxial systems as a result of the modified bonding configuration.

Experiments show that the diffusion constant follows an Arrhenius-type behavior $D \sim \exp(-E_b/k_B T)$, where E_b is the barrier for surface diffusion and T is the substrate temperature. In a recent scanning tunneling microscopy (STM) experiment Brune *et al.*³ measured the island density N of Ag on Ag(111), Ag on Pt(111), and Ag on one monolayer (ML) of Ag on Pt(111) for different temperatures. With the scaling relation⁴ $N \sim (D/F)^{-\chi}$, where F is the deposition flux, the diffusion barrier E_b can be determined as long as the temperature is low enough⁵ so that the scaling exponent $\chi = 1/3$. Brune *et al.* find that the diffusion barriers are $E_b^{\text{Ag-Pt}} = 157 \pm 10$ meV for Ag on Pt(111), $E_b^{\text{Ag-Ag}} = 97 \pm 10$ meV for Ag on Ag(111), and $E_b^{\text{Ag-Ag/Pt}} = 60 \pm 10$ meV for Ag on 1 ML Ag on Pt(111). Thus, the diffusion barrier for Ag on top of a pseudomorphic layer of Ag on Pt(111) is substantially lower than that for Ag on Ag(111). It has been argued⁶ that a metallic monolayer that is supported on a dissimilar substrate is electronically perturbed by the substrate, and that its chemical properties are altered. The question arises whether the low diffusion barrier for Ag on 1 ML Ag on Pt(111) is a result of the compressive strain of 4.2% or an electronic effect due to the Pt underneath the Ag layer.

There are only a few theoretical studies that investigated the effect of lattice mismatch on the diffusion barrier. In an

extensive molecular-dynamics study for Si on Si(001) that employed a Stillinger-Weber potential Roland and Gilmer⁷ found that the barrier for diffusion along the fast channel parallel to the dimer rows is *lowered* by approximately 10% for both 3% compressive and 2% tensile strain, while diffusion along the same direction atop the dimer rows is *increased* by about 10%, so that a general trend cannot be seen. Using Lennard-Jones potentials Schroeder and Wolf⁸ found that the diffusion barrier increases linearly as the lattice constant increases. For a metallic system we are only aware of results for Ag on Ag(111) where the authors of Ref. 3 find in an effective medium theory (EMT) calculation that the diffusion barrier increases with increasing tensile strain of the surface and decreases with increasing compressive strain. Comparison with experiment [for Ag on Pt(111), Ag on Ag(111), and Ag on 1 ML Ag on Pt(111)] confirms this trend but also shows that the EMT results are off with an error between 20% and 100%. For values of misfit larger than 3% the EMT diffusion barrier starts to decrease, which is in qualitative disagreement to our results described below.

In this work we present first-principles calculations of the dependence of the diffusion barrier on the lattice constant for Ag on Ag(111). This allows us to isolate the effect of strain from electronic effects caused by the difference of materials. The dependence of the diffusion barrier on lattice mismatch is found to be essentially linear. The diffusion barriers for the system Ag on Pt(111) are calculated as well. We find $E_b^{\text{Ag-Pt}} = 150$ meV, $E_b^{\text{Ag-Ag}} = 81$ meV, and $E_b^{\text{Ag-Ag/Pt}} = 63$ meV, which is in good agreement with the experimental data³ within the error margins.

We employ density-functional theory (DFT) together with the local-density approximation⁹ (LDA) for the exchange-correlation (XC) functional. The energy barriers are found to be only weakly affected when the generalized-gradient approximation¹⁰ (GGA) is used instead of the LDA. In this study the GGA results for the barriers are typically higher but not more than 5%–10% compared to the LDA results. Norm-conserving, fully separable pseudopotentials have been employed that were generated according to a scheme proposed by Troullier and Martins.¹¹ The computer code used is described by Bockstedte *et al.*¹³ The calculated bulk

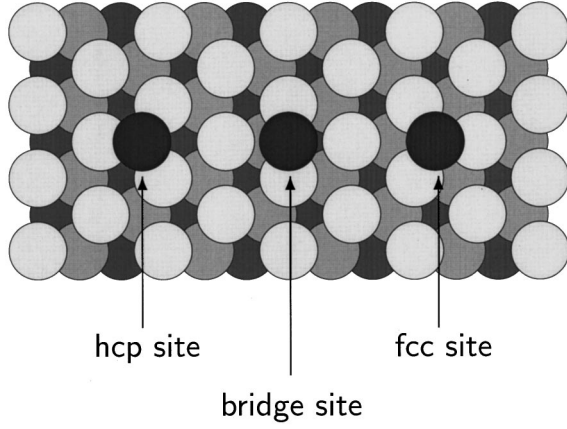


FIG. 1. A schematic representation of the adsorption sites (fcc and hcp site) and saddle point (bridge site) on the (111) surface.

lattice constants are $a_{\text{Pt}} = 3.92 \text{ \AA}$ for Pt and $a_{\text{Ag}} = 4.05 \text{ \AA}$ for Ag with the LDA and $a_{\text{Pt}} = 4.01 \text{ \AA}$ and $a_{\text{Ag}} = 4.19 \text{ \AA}$ with the GGA. The LDA results are smaller than the GGA results, which is the usual trend.¹⁴ For Ag the experimental value is slightly larger (smaller) than the LDA (GGA) result while for Pt the LDA result is identical to the experimental lattice constant. In the above theoretical values the influence of zero-point vibrations is not included; it would increase the lattice constant by less than 0.2%.

To simulate the surface we use the supercell approach. In the z direction slabs are separated by a vacuum region with a thickness that is equivalent to 6 layers, and it has been tested carefully that this vacuum region is thick enough. The adatom is placed on only one side of the slab. Because of the simple geometry of the (111) surface (cf. Fig. 1) only the fcc and hcp sites need to be considered as adsorption sites with the bridge site as the saddle point. It turns out that the fcc site is always slightly favored over the hcp site so that all barriers discussed are the differences between the total energies of the system with the adatom in the fcc site and the bridge site.

We carried out careful tests varying the slab thickness and surface cell size to ensure that interactions between neighboring adatoms are negligible. The tests for Ag on Ag(111) are summarized in Table I. In calculations 1, 2, and 3 we

TABLE I. Convergence tests for Ag on Ag(111). GGA is fully self-consistent GGA and GGA-ap is a posterior GGA as described in the text. The cell size used was (2×2) except in calculation 7, which was obtained with a (3×3) cell. N_k is the number of k points.

Calc.	E_{cut} (Ry)	N_k	N_{layer}	XC	E_b (meV)
1	40	10	3	LDA	82
2	40	10	4	LDA	73
3	40	10	5	LDA	73
4	50	10	4	LDA	81
5	60	10	4	LDA	80
6	50	8	4	LDA	81
7	40	5	4	LDA	73
8	40	10	4	GGA	78
9	50	10	4	GGA-ap	87

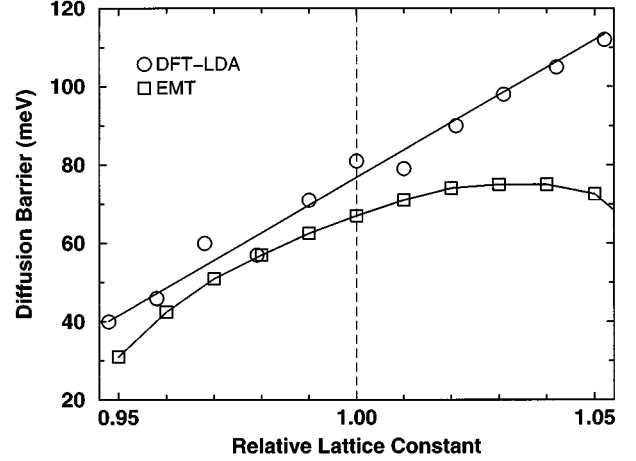


FIG. 2. The diffusion barrier as a function of the relative lattice constant a/a_0 for Ag on Ag(111). The lattice constant is normalized to the computed bulk lattice constants of Ag, $a_0 = 4.05 \text{ \AA}$ (DFT) and $a_0 = 4.075 \text{ \AA}$ (EMT). The EMT results are taken from Ref. 3. The solid lines are a guide to the eye.

varied the slab thickness N_{layer} and conclude that $N_{\text{layer}} = 4$ is sufficient. The electronic wave functions are expanded in plane waves that are truncated at a cutoff energy E_{cut} . From calculations 2, 4, and 5 we find that $E_{\text{cut}} = 40 \text{ Ry}$ is sufficient if the desired accuracy is $\pm 10\%$, but for an accuracy of $\pm 2\%$ a larger cutoff $E_{\text{cut}} = 50 \text{ Ry}$ is necessary. For all the results reported below we choose a slab with a (2×2) cell as can be justified from calculations 2 and 7. We always relaxed the positions of the adatom and the atoms of the top layer. A test revealed that the results remained unaltered upon relaxation of the second layer. For the \mathbf{k} summation we used 10 \mathbf{k} points in the irreducible part of the surface Brillouin zone of the (2×2) cell that were generated according to Ref. 15. The \mathbf{k} points included the $\bar{\Gamma}$ point but calculations with different \mathbf{k} points that did not include the $\bar{\Gamma}$ point (calculation 6) yielded identical results. Thus, the error in the Brillouin zone integration is negligible.

Results for the diffusion barrier for Ag on Ag(111) as a function of lattice mismatch are shown in Fig. 2. For the unstrained system we obtain $E_b^{\text{Ag-Ag}} = 81 \text{ meV}$ in good agreement with the STM results of Ref. 3. In the range of the lattice constants studied the diffusion barrier $E_b(a/a_0)$ varies linearly within our numerical accuracy¹⁶ with a slope of $\sim 0.7 \text{ eV}$. This is in contrast to the EMT results of Ref. 3 that are also shown in Fig. 2 where the dependence is sublinear and the diffusion barrier decreases for misfits larger than $\sim 3\%$.

To further explain the strain dependence of the diffusion barrier we show in Fig. 3 the strain dependencies of the underlying contributions, i.e., the total energies of an adatom at the fcc hollow and bridge sites. These are computed by subtracting the total energies of a clean surface and a free silver atom from the total energy of a surface with an adsorbed atom. The total energies of Fig. 3 show an approximately linear dependence¹⁶ within a surprisingly large range of lattice constants. The change of the total energy $E_{\text{ad}}(a/a_0)$ with the adatom at the threefold-coordinated fcc site is stronger than that at the twofold-coordinated bridge site, and the slopes are $\sim 2.1 \text{ eV}$ for the bridge site and $\sim 2.8 \text{ eV}$ for the fcc site. The difference reflects that the

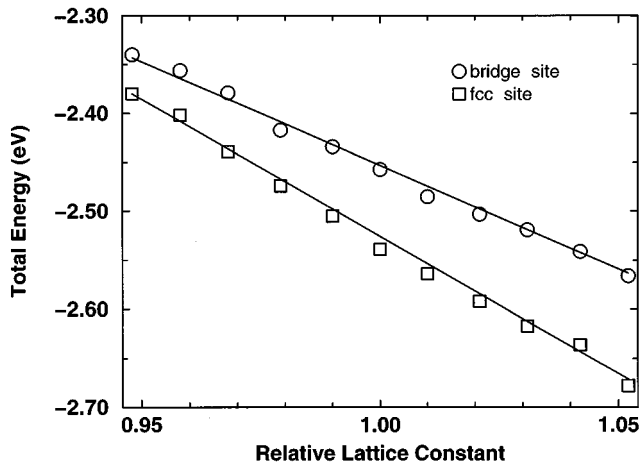


FIG. 3. The total energy of an adatom in the fcc site and bridge site as a function of the relative lattice constant a/a_0 for Ag on Ag(111). The lattice constant is normalized to the computed bulk lattice constants of Ag, $a_0=4.05$ Å (DFT) and $a_0=4.075$ Å (EMT). The solid lines are a guide to the eye.

corrugation of the potential energy surface gets more pronounced when the surface is expanded while under compression it becomes more flat. Obviously, the value of the difference equals the value of 0.7 eV obtained above from Fig. 2. We note that Dobbs, Zangwill, and Vvednensky¹⁷ recently pointed out that $\Delta E_b = (\sigma_{\text{fcc}} - \sigma_{\text{bridge}})\epsilon$, where ϵ is the strain and σ_{fcc} (σ_{bridge}) is the surface stress with an adatom at the fcc (bridge) site. The slopes of the curves in Fig. 3 give these stresses σ_{fcc} and σ_{bridge} .

The diffusion barrier for Ag on Pt(111) has been calculated as $E_b^{\text{Ag-Pt}} = 150$ meV with a (2×2) cell, a slab with four layers where the atoms of the top layer and the adatom are relaxed, and $E_{\text{cut}} = 40$ Ry. The same result has been obtained for (i) a thickness of three layers, (ii) the top two layers relaxed, and (iii) a cell size of (3×3) . We thus conclude that our result is converged. The value for $E_b^{\text{Ag-Pt}}$ is in excellent agreement with the STM value of $E_b^{\text{Ag-Pt}} = 157 \pm 10$ meV. Previous DFT-LDA results by Feibelman¹⁸ who used the Green-function theory gave a higher value of $E_b^{\text{Ag-Pt}} = 200$ meV.

Our calculations predict that the diffusion barrier drops dramatically for Ag on Pt(111) after one complete layer of Ag has been deposited. For this diffusion barrier we obtain $E_b^{\text{Ag-Ag/Pt}} = 63$ meV in good agreement with the STM value of $E_b^{\text{Ag-Ag/Pt}} = 60 \pm 10$ meV. For Ag on 1 ML of Ag on Pt(111) we have chosen $E_{\text{cut}} = 40$ Ry and three Pt layers. We also checked the result with only two Pt layers and verified that choosing three Pt layers is indeed sufficient for this system. The diffusion barrier for Ag on 1 ML Ag on Pt(111) is almost identical to the value of $E_b^{\text{Ag-Ag}} = 60$ meV we obtained for Ag on Ag(111) compressed to the lattice constant of Pt. This suggests that the small diffusion barrier for Ag on 1 ML Ag on Pt(111) is mainly due to the effect of strain and not an electronic effect because of the Pt underneath.

All the results discussed above have been obtained with the LDA for the XC functional. It is an ongoing debate whether the GGA is really an improvement over the LDA

and we investigated the influence of the GGA for all the systems discussed here. For Ag on Ag(111) we find that the effect of the GGA on the diffusion barriers is only about 5 meV. This can be seen in Table I from calculations 4 and 8 for a self-consistent GGA according to Ref. 10 and from calculations 2 and 9 where the energy has been computed with the GGA from a self-consistent LDA electron density (GGA-posterior) according to Ref. 12. Similarly the barrier increases by only 5–10 meV for Ag on Pt(111) and Ag on 1 ML Ag on Pt(111). The negligible effect of the GGA is in agreement with results by Boisvert, Lewis, and Scheffler for self-diffusion of Pt on Pt(111) (Ref. 19) and results by Yu and Scheffler for diffusion via the hopping mechanism for Ag on Ag(100).²⁰ The (111) surface is a close-packed surface with a very small surface corrugation and since LDA and GGA results are very close it is plausible to assume that for such a system LDA and GGA are both good approximations for the exact XC functional. This situation will presumably be different for diffusion events along and especially across steps as found by the authors of Ref. 20 for Ag on Ag(100).

Brune *et al.*³ also measured the island densities of Ag on 2 ML of Ag on Pt(111) and found that the island density is much larger than it is for Ag on just 1 ML of Ag on Pt(111). The reason for this increased island density is not a higher barrier for surface diffusion. The second layer of Ag on Pt(111) reconstructs in a trigonal network where domains with atoms in the fcc and hcp site alternate.²¹ This reconstruction occurs either during growth with high enough adatom mobility or upon annealing and it can be concluded that this trigonal network is the equilibrium structure. The periodicity of these domains is approximately two domain boundaries for every 24 atoms. This can be understood with purely geometrical arguments because the lattice mismatch is $\sim 4.2\%$ and every domain boundary implies that there is half of an Ag atom less, so that the domain network provides an efficient mechanism to relieve epitaxial strain. The experiments indicate that these domain walls act as repulsive walls so that the island density is determined by the size of the reconstructed unit cell and not the barrier for self-diffusion on the flat terrace. It was not clear, however, why this domain network is formed only after 2 ML Ag have been deposited and not already upon completion of the first Ag layer.

To answer this question we compared the total energy of an adatom in the fcc and in the hcp site. Calculations were carried out with a (1×1) and a (2×2) cell (i.e., coverages $\Theta = 1.0$ and 0.25) and slab thicknesses of up to 5 layers. We find that the fcc site is energetically more favorable than the hcp site in all cases. The energy difference between those two sites for a Ag adatom on Pt(111) is 40 meV for a (2×2) cell [30 meV for a (1×1) cell], but less than 10 meV for a Ag adatom on 1 ML Ag on Pt(111). The reconstruction does not occur in the first layer because the Ag atoms are bound much more strongly at the fcc sites but does occur in the second layer because the total energies for adatoms in the fcc and hcp site are almost indistinguishable.

In conclusion we found that in the range studied here the diffusion barrier $E_b(a/a_0)$ for Ag on Ag(111) increases approximately linearly with a slope of ~ 0.7 eV when the lattice constant increases. We propose that this result might

offer a possibility to change the diffusion barrier and thus the island density during growth by artificially straining the substrate. If this can be done periodically in a controlled manner it might be an alternative approach to varying the diffusivity *in situ*. Our LDA results show that careful DFT calculations with the LDA reproduce experimental values for the surface diffusion barrier for the system Ag on Pt(111) with very high

accuracy. Work to calculate the barriers for diffusion along and across steps and across domain boundaries and prefactors is in progress.

The authors would like to acknowledge helpful discussions with M. Bockstedte, G. Boisvert, A. Kley, E. Pehlke, P. Ruggerone, and B. D. Yu.

* Author to whom correspondence should be addressed: Electronic address: ratsch@theo22.rz-berlin.mpg.de

¹G. Rosenfeld, R. Servaty, C. Teichert, B. Poelsema, and G. Comsa, Phys. Rev. Lett. **71**, 895 (1993).

²M. Scheffler, V. Fiorentini, and S. Oppo, in *Surface Science: Principles and Current Applications*, edited by R. J. MacDonald, E. C. Taglauer, and K. R. Wandelt (Springer, Berlin, 1996), p. 219.

³H. Brune, K. Bromann, H. Röder, K. Kern, J. Jacobsen, P. Stoltze, K. Jacobsen, and J. Nørskov, Phys. Rev. B **52**, R14 380 (1995).

⁴S. Stoyanov and D. Kachiev, in *Current Topics in Material Science*, edited by E. Kaldis (North-Holland, Amsterdam, 1981), Vol. 7, Chap. 2.

⁵This assumes that the so-called critical cluster size is $i = 1$. This is generally true at low temperatures and a discussion of the validity of this assumption can be found, for example, in C. Ratsch, P. Šmilauer, A. Zangwill, and D. D. Vvedensky, Surf. Sci. **329**, L599 (1995).

⁶J. A. Rodriguez and D. W. Goodman, J. Phys. Chem. **95**, 4196 (1991).

⁷C. Roland and G. H. Gilmer, Phys. Rev. B **46**, 13 428 (1992).

⁸M. Schroeder and D. E. Wolf (unpublished).

⁹D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); parametrization by J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

¹⁰J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R.

Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

¹¹N. Troullier and J. L. Martins, Solid State Commun. **74**, 619 (1990); N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991). The exact scheme to generate the pseudopotentials used is described in Ref. 12.

¹²M. Fuchs *et al.* (unpublished).

¹³M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler (unpublished).

¹⁴A. Khein, D. J. Singh, and C. J. Umrigar, Phys. Rev. B **51**, 4105 (1995).

¹⁵H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

¹⁶We estimate the accuracy of our calculation for the total energies of the adatom at the fcc and bridge site and the diffusion barriers to be better than 10 meV. For the data at -2% misfit the errors for the total energies do not compensate each other (cf. Fig. 3) so that the value obtained for E_b appears to be too low (cf. Fig. 2); however, within the error margins it does not violate our assertion that the data can be fitted by a straight line.

¹⁷H. T. Dobbs, A. Zangwill, and D. D. Vvedensky, in *Surface Diffusion: Atomistic and Collective Processes*, edited by M. Tringides (Plenum, New York, in press).

¹⁸P. J. Feibelman, Surf. Sci. Lett. **313**, L801 (1994).

¹⁹G. Boisvert, L. Lewis, and M. Scheffler (unpublished).

²⁰B. D. Yu and M. Scheffler, Phys. Rev. Lett. **77**, 1095 (1996).

²¹H. Brune, H. Röder, C. Boragno, and K. Kern, Phys. Rev. B **49**, 2997 (1994).