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

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.

PACS number(s): 68.55.Jk, 68.35.Bs, 68.35.Fx

The diffusion of a single adatom on a surface is a fundamental process determining the surface morphology developing in epitaxial growth. For Ag on Ag (111) it has been demonstrated 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 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. 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 relation $N \sim (D/F)^{-\chi}$, where $F$ is the deposition flux, the diffusion barrier $E_b$ can be determined as long as the temperature is low enough so that the scaling exponent $\chi = 1/3$. Brune et al. find that the diffusion barriers are $E_b^{Ag-Pt} = 157 \pm 10$ meV for Ag on Pt (111), $E_b^{Ag-Ag} = 97 \pm 10$ meV for Ag on Ag (111), and $E_b^{Ag-Ag/Pt} = 60 \pm 10$ meV for Ag on one 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 argued that a metallic monolayer which 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 one 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 Gilmer found that the barrier for diffusion along the fast channel parallel to the dimer rows is lowered by approximately 10% for both, 3% compressive or 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 Wolf 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. 2 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 one 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 $E_b^{Ag-Pt} = 150$ meV, $E_b^{Ag-Ag} = 81$ meV, and $E_b^{Ag-Ag/Pt} = 63$ meV, which is in good agreement with the experimental data within the error margins.

We employ density-functional theory (DFT) together with the local-density approximation (LDA) for the exchange-correlation (XC) functional. The energy barriers are found to be only weakly affected when the
generalized-gradient approximation (GGA) is used instead of the LDA. In this study the GGA results for the barriers are typically higher but not more than 5% to 10% compared to the LDA results. Normal-conserving, fully-separable pseudopotentials have been employed that were generated according to a scheme proposed by Troullier and Martins. The computer code used is described by Bockstedte et al. The calculated bulk lattice constants are $a_{\text{Pt}} = 3.92$ Å for Pt and $a_{\text{Ag}} = 4.05$ Å for Ag with the LDA and $a_{\text{Pt}} = 4.01$ Å and $a_{\text{Ag}} = 4.19$ Å with the GGA. The LDA results are smaller than the GGA results which is the usual trend. 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 1. In calculation 1, 2, and 3 we varied the slab thickness $N_{\text{layer}}$ and conclude that $N_{\text{layer}} = 4$ is sufficient. The electronic wave functions are expanded in plane-waves that are truncated at a cut-off energy $E_{\text{cut}}$. From calculation 2, 4, and 5 we find that $E_{\text{cut}} = 40$ Ryd is sufficient if the desired accuracy is ±10%, but for a accuracy of ±2% a larger cut-off $E_{\text{cut}} = 50$ Ryd is necessary. For all the results reported below we choose a slab with a $(2 \times 2)$ cell as it can be justified from calculation 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 $k$-summation we used 10 $k$ points in the irreducible part of the surface Brillouin zone of the $(2 \times 2)$ cell that were generated according to Ref. 12. The $k$ points included the $\Gamma$-point but calculations with different $k$ points that did not include the $\Gamma$-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 $E_{b}^{\text{Ag}-\text{Ag}} = 81$ meV in good agreement with the STM results of Ref. 3. In the range of the lattice constants studied the diffusion barrier $E_{b}(a_{0}/a_{0})$ varies linearly within our numerical accuracy with a slope of $\sim 0.7$ eV. This is in contrast to the EMT.

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

![FIG. 2. The diffusion barrier as a function of the relative lattice constant $a_{0}/a_{0}$ 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 EMT results are taken from Ref. 3. The solid lines are a guide to the eye.](image)

| Calc. | $E_{\text{cut}}$ (Ryd) | $N_{\text{k}}$ | $N_{\text{layer}}$ | 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         |
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 $E_{b}^{Ag-Ag/Pt} = 63$ meV in good agreement with the STM value of $E_{b}^{Ag-Ag/Pt} = 60 \pm 10$ meV. For Ag on one ML of Ag on Pt (111) we have chosen $E_{cut} = 40$ Ryd and 3 Pt layers. We also checked the result with only 2 Pt layers and verified that choosing 3 Pt layers is indeed sufficient for this system. The diffusion barrier for Ag on one ML Ag on Pt (111) is almost identical to the value of $E_{b}^{Ag-Ag} = 60$ 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 one 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 1 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-ap) according to Ref. 12. Similarly the barrier increases by only $5 - 10$ meV for Ag on Pt (111) and Ag on one ML Ag on Pt (111). The negligible effect of the GGA is in agreement with results by Boisvert et al. for self diffusion of Pt on Pt (111) and results by Yu and Scheffler for diffusion via the hopping mechanism for Ag on Ag (100). 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 it has been found by the authors of Ref. 12 for Ag on Ag (100).

Brune et al. also measured the island densities of Ag on two ML of Ag on Pt (111) and found that the island density is much larger than it is for Ag on just one 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. 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 relief epitaxial strain. The experiments indicate that these domain walls act as repulsive

![Graph 3](image)

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.

results of Ref. 3 that are also shown in Fig. 2 where the dependence is sub-linear 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 the 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 dependence within a surprisingly large range of lattice constants. The change of the total energy $E_{ad}(a/a_0)$ with the adatom at the threefold coordinated fcc site is stronger than that at the twofold coordinated bridge site, and the slopes are $\sim 2.1$ eV for the bridge site and $\sim 2.8$ eV for the fcc site. The difference reflects that the 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 et al. recently pointed out that $\Delta E_b = (\sigma_{fcc} - \sigma_{bridge})\epsilon$ where $\epsilon$ is the strain and $\sigma_{fcc}$ ($\sigma_{bridge}$) is the surface stress with and adatom at the fcc (bridge) site. The slopes of the curves in Fig. 3 give these stresses $\sigma_{fcc}$ and $\sigma_{bridge}$.

The diffusion barrier for Ag on Pt (111) has been calculated as $E_{b}^{Ag-Pt} = 150$ meV with a $(2 \times 2)$ cell, a slab with 4 layers where the atoms of the top layer and the adatom are relaxed, and $E_{cut} = 40$ Ryd. The same result has been obtained for $i)$ a thickness of 3 layers, $ii)$ the top two layers relaxed, and $iii)$ a cell size of $(3 \times 3)$. We thus conclude that our result is converged. The value for $E_{b}^{Ag-Pt}$ is in excellent agreement with the STM value of $E_{b}^{Ag-Pt} = 157 \pm 10$ meV. Previous DFT-LDA results by Feibelman et al. who used the Green function theory gave a higher value of $E_{b}^{Ag-Pt} = 200$ meV.
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 \((1 \times 1)\) and a \((2 \times 2)\) cell (i.e. coverages \(\Theta = 1.0\) and \(\Theta = 0.25\)) 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 an Ag adatom on Pt (111) is 40 meV for a \((2 \times 2)\) cell (30 meV for a \((1 \times 1)\) cell), but less than 10 meV for an Ag adatom on one ML Ag on Pt (111). The reconstruction does not occur in the first layer because the Ag atoms are bound much stronger 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 linear with a slope of \(\sim 0.7\) 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 vary the diffusivity \textit{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.

---

1. G. Rosenfeld, R. Servaty, C. Teichert, B. Polsema, and G. Comsa, Phys. Rev. Lett. \textbf{71}, 895 (1993).
2. M. Scheffler, V. Fiorentini, and S. Oppo, In: Surface Science: Principles and Current Applications, eds. R.J. MacDonald, E. C. Taglauer, and K. R. Wandelt, Springer 1996, p. 219.
3. H. Brune, K. Bromann, H. Röder, K. Kern, J. Jacobsen, P. Stoltze, K. Jacobsen, and J. Nørskov, Phys. Rev. B \textbf{52}, R14380 (1995).
4. S. Stoyanov and D. Kachiev, in: Vol. 7 of Current Topics in Material Science, Ed. E. Kaldis (North-Holland, Amsterdam, 1981) ch. 2.