Strain dependence for microscopic growth parameters for Ag on Ag(100)

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I use density functional theory to study the strain dependence of microscopic growth parameters for the growth of Ag on Ag(100). Results are presented for the energy barrier for adatom diffusion, diffusion of adatoms along a step edge, detachment of atoms from a step edge, and dissociation of a dimer. Over a certain range of misfit values, these parameters vary almost linearly with strain. The most surprising result is a qualitatively different behavior for detachment of an atom from a step edge and dimer dissociation.

It is well known that strain in epitaxial systems leads to growth that is different than growth of unstrained structures. For example, strain is believed to facilitate the formation and self-organization of arrays of nanopatterns. These nanopatterns have an increasing relevance in many technological applications and have thus been the focus of many recent studies. Application can range from storage devices[1] and catalysts[2] for metallic systems to so-called semiconductor quantum dots (QDs) for next-generation optoelectronic devices.[3] It is important to understand how strain affects the growth of these systems and, therefore, on the most fundamental level, to understand how strain affects the microscopic processes that occur during growth.

It has been demonstrated in a number of recent papers that density functional theory (DFT) can be used to calculate many of these microscopic parameters from first principles and that, in fact, careful atomistic simulations (such as kinetic Monte Carlo simulations) can be used to model growth to a high degree of accuracy. This has been particularly successful for unstrained metallic systems.[4–7] In principle, this is also possible for semiconductor systems, but surface reconstructions and the exact atomic structure at the step edge make this a more complicated exercise. DFT has also successfully been used to study the strain dependence of adatom diffusion during epitaxial growth, for both metallic[8,9] and semiconductor systems.[10–13] But surprisingly, very little is known about the strain dependence of other microscopic parameters during growth, such as diffusion along an island edge, detachment from an island edge, or dissolution of a small island. In particular, the latter processes have been shown to be relevant for the ordering and distribution of islands and, ultimately, nanopatterns and QDs during epitaxial growth.[14,15]

I have performed DFT calculations that study the effect of strain on the energy barrier for adatom diffusion, edge diffusion, detachment from an island edge, and dissociation of a dimer for the model system Ag on Ag(100). I have chosen this system because some results for adatom diffusion were already known[7,9] and because a metallic system (in contrast to a semiconductor system) does not have complicated reconstructions, which also change as a function of strain.[16] However, the procedure and type of calculations presented here can be extended to a semiconductor system, which will be necessary for a detailed understanding of the growth of semiconductor QDs. I focus only on the strain dependence of the energy barrier and not the prefactor, as previous calculations have shown that the effect of strain on the prefactor is much smaller.[17]

All results presented below were obtained with DFT calculations, as implemented in the FHI-AIMS code.[18] This is an all-electron full-potential DFT code that uses numeric atom-centered orbitals as its basis set. I have carefully tested convergence of my results with respect to the basis set and the density of the (numerical) integration mesh and have used parameters as they are implemented in FHI-AIMS in the default setting "tight."[18] I use the generalized gradient approximation Perdew-Burke-Ernzerhof (GGA-PBE) for the exchange correlation functional.[19]

I used a periodic supercell with a thickness of six layers, where all but the bottom two layers were fully relaxed. The cell sizes were carefully tested for convergence, and the results presented below were obtained with cell sizes (3×3) for diffusion, (2×5) for dimer dissociation, and (3×7) for diffusion along a step edge or detachment from a step edge. For the latter two processes, the step edge was simulated by a partial seventh layer of width 4 that was also fully relaxed. All these geometries as well as the path of motion are depicted in Fig. 1. The vacuum was chosen to be about 20 Å for all calculations. The k-point mesh was equivalent to (8×8) k points in a 1×1 cell (or denser).

In Fig. 2 I show the results for the energy barrier for adatom diffusion of Ag on Ag(100). Results are shown for both the hopping mechanism and the exchange mechanism. In agreement with earlier studies,[9] I find that the energy barrier for diffusion increases with increasing misfit for the hopping mechanism, while it decreases for the exchange mechanism between -2% and 8% misfit. At 0% misfit, hopping is preferred, with an energy barrier of 432 meV, compared to 718 meV for the exchange mechanism. These numbers agree well with the GGA results reported in Ref. 9. Once the misfit exceeds approximately 4%, the exchange mechanism is preferred.

A simple explanation for this is that increasing tensile strain amplifies the variations on the potential-energy surface (PES) for diffusion via hopping, thus increasing the energy difference between the adsorption and the transition state. The strain dependence of the hopping mechanism is almost linear with a slope of approximately 16 meV per percent misfit. Such a linear increase of the diffusion barrier for adatom hopping
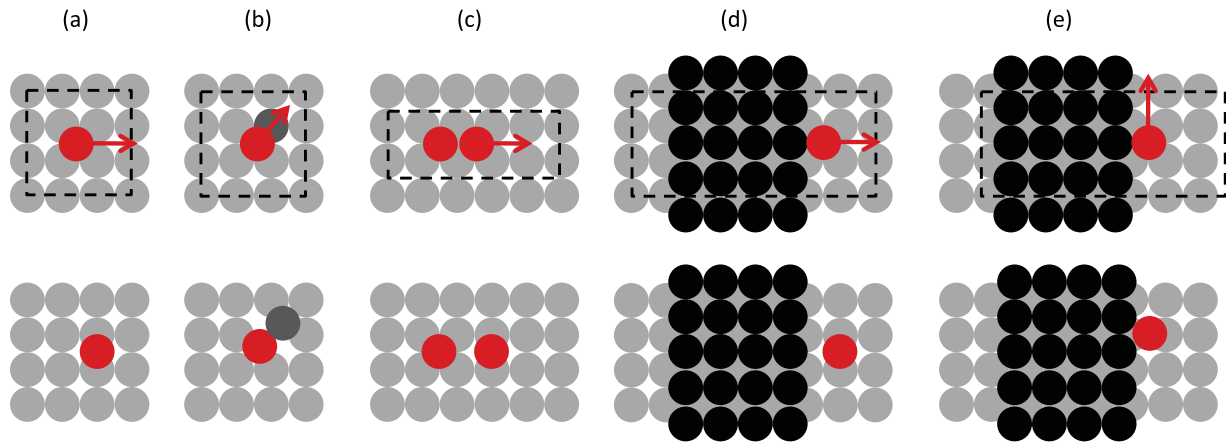
FIG. 1. (Color online) A schematic representation of all the microscopic processes discussed here. The top row shows the initial state, with an arrow indicating the direction of the move, while the bottom row shows the approximate transition state. The processes include (a) diffusion via the hopping mechanism, (b) diffusion via the exchange mechanism, (c) dimer dissociation, (d) detachment from the step edge of an island, and (e) diffusion along the step edge of an island. The island in (d) and (e) is shown with a darker shade for clarity. Also shown are dashed lines that indicate the size of the supercell.

has also been predicted in previous generic models.[20,21] In contrast, tensile strain creates more space, which is needed for the exchange mechanism, and also weakens the strength of the interatomic bonds in the substrate layer, thus favoring exchange. A similar trend has also been seen for other metal (100) surfaces.[9]

It is interesting to note that for −4% and −6% misfit, the energy barrier for exchange is lower again than it is for −2% misfit. I believe the reason is the following: The interatomic bonds between the surface atoms are a little stronger than they are in the bulk (because there are no atoms above). As a result, atoms prefer to be a little closer, by approximately 1%–2%. But when the system is compressed by more than 2%, the surface atoms do not have enough space, and the compression provides a driving force for atoms to "pop up" above the surface. Thus, for large compressive strain, the system can relieve some of the strain by forming the transition state of the exchange mechanism. This argument is supported by close

inspection of the relaxed geometries, which reveals that the two atoms participating in the exchange are much higher above the surface for −4% and −6% misfit.

The dependencies of the energy barrier for dimer dissociation and edge diffusion exhibit similar almost linear behaviors, as shown in Figs. 3 and 4. At 0% misfit, the barrier for dimer dissociation is 649 meV, which is approximately 200 meV larger than the barrier for surface diffusion. The slope for the energy barrier for dimer dissociation is approximately 13 meV per percent misfit. This is a slightly less pronounced dependence on strain than what we observed for diffusion via hopping. To understand this, one can think of dimer dissociation as a hopping event of one of the two atoms, except that this atom has an additional nearest-neighbor bond in the initial state. This bond to the neighboring atom increases the barrier for the atom to move, while at the same time it slightly weakens the bond to the substrate, and thus, the increased
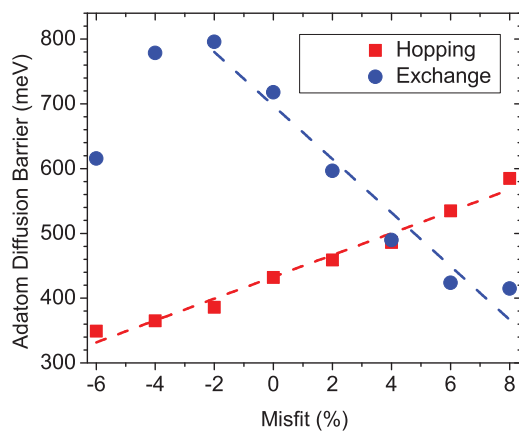

FIG. 2. (Color online) DFT results for the strain dependence of the energy barrier for diffusion of Ag on Ag(100). Shown are results for the hopping mechanism (squares) and the exchange mechanism (circles), as shown in Figs. 1(a) and 1(b). The dashed lines are a guide to the eye.
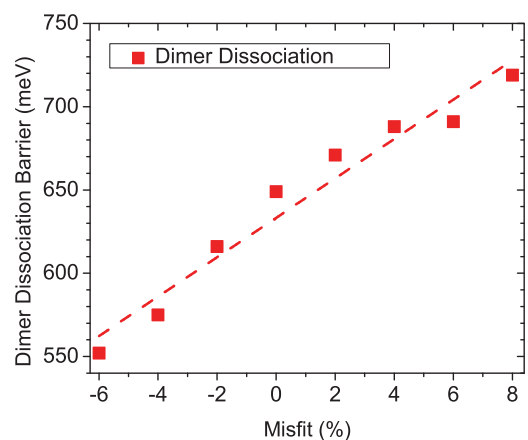

FIG. 3. (Color online) DFT results for the strain dependence of the energy barrier for the dissociation of an Ag dimer on Ag(100). The mechanism is illustrated in Fig. 1(c). The dashed line is a guide to the eye.
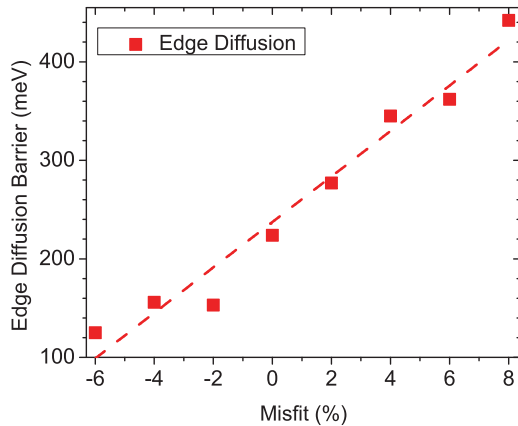
FIG. 4. (Color online) DFT results for the strain dependence of the energy barrier for diffusion of Ag along a step edge on Ag(100). The mechanism is illustrated in Fig. 1(d). The dashed line is a guide to the eye.

corrugation of the PES (due to the tensile strain) has a smaller effect.

Edge diffusion is a much more likely event and has an energy barrier of 277 meV at 0% misfit. The slope for the energy barrier for edge diffusion is approximately 23 meV per percent misfit. This is a much stronger effect than what is observed for adatom diffusion or dimer dissociation. I speculate that the reason for this is that, in a simple picture, the atom that moves has a bond to the substrate and to the step edge, and each of these two contributing bonds have similar strain dependencies, such that their effects amplify each other. But the bonds to the step edge are never completely broken, thus leading to an overall barrier that is smaller than the barrier for diffusion via the hopping mechanism.

The most intriguing result is the behavior of the energy barrier for detachment, which is shown in Fig. 5. For compressive strain, between −6% misfit and approximately 0% misfit, the energy barrier increases similarly to the results discussed above. The increase is almost linear, and the numbers for the barrier for detachment are very similar to
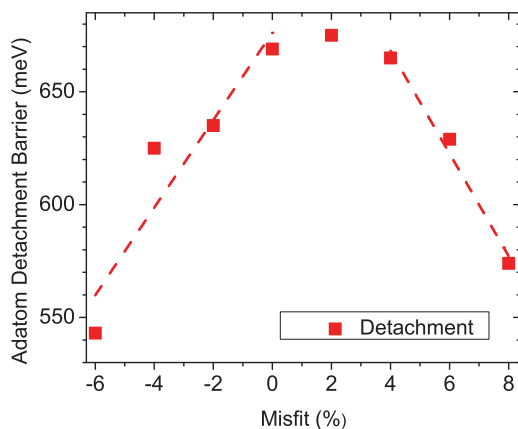

FIG. 5. (Color online) DFT results for the strain dependence of the energy barrier for the detachment of an Ag atom from a step edge on Ag(100). The mechanism is illustrated in Fig. 1(e). The dashed lines are a guide to the eye.

the numbers for dimer dissociation in this range. However, in contrast to the results for dimer dissociation (and all other mechanisms discussed in this Brief Report), the energy barrier decreases again for tensile strain between 4% and 8% misfit. In fact, it appears that the energy barrier has its maximum at approximately 2% misfit and that it decreases with similar slopes upon both compressive and tensile strain. I speculate that this unexpected result for tensile strain can be explained as follows: Increasing tensile strain leads to an increased corrugation of the potential energy surface, which leads to an increased barrier for hopping. At a step edge, the barrier is increased because of an in-plane nearest-neighbor bond (between the atom that is moving and the step edge). But this in-plane nearest-neighbor bond weakens upon tensile strain, and for strains larger than 2%, this weakening is more important than the effect of the increased corrugation of the potential-energy surface. For large enough tensile strain, this bond becomes negligible, such that the barrier for detachment from a step edge is close to the one for diffusion via hopping.

I have also investigated the effect of strain on the total binding energy of the moving atom in the adsorption site $E_B^{(ad)}$ and in the transition site $E_B^{(trans)}$. These energies are defined as the energy of the system with the atom in the adsorption (or transition) site minus the energy of a system without the atom that is considered for detachment minus the energy of a single, isolated atom. Interestingly, it turns out that $E_B^{(ad)}$ changes very little for strain values between −6% and 6% (the atom is bonded approximately 30 meV stronger for −6% and 6% strain, compared to the unstrained case), while the change in $E_B^{(trans)}$ is much more pronounced: It is bonded approximately 150 meV stronger for −6% strain and over 50 meV stronger for 6% strain (compared to the unstrained case).

It is interesting to note and discuss the qualitatively different behavior for dimer dissociation and detachment from a step edge. In simple nearest-neighbor bond-counting models, these two processes are often treated the same, as the moving atom has one bond to the substrate and one bond to one lateral nearest neighbor. But it turns out that these bonds are affected quite differently, in particular, upon application of tensile strain.

I have closely inspected the relaxed geometries and find the following in the transition state: For dimer dissociation, the atom that is not breaking away [i.e., the left one in Fig 1(c)] is displaced by approximately 0.03–0.07 Å to the right (with respect to its bulk position) for all strain values between −6% and +8%. It is basically "pulled along" by the atom that is breaking away. If one now considers the corresponding atom for detachment [i.e., the one to the left of the moving atom in Fig 1(e)], it is similarly displaced to the right for compressive strain. The reasons are that (i) the moving atom is "pulling it along" and (ii) the entire island is compressed, and the edge atoms are "squeezed out" to the right. This situation is quite different for tensile strain: The island is pulling this atom to the left (to keep it close to the island), while the atom that is detaching wants to pull it to the right. I find that for 8% tensile strain, the displacement of this atom (with respect to its bulk position) is 0.35 Å to the left, which is quite different than a displacement of 0.03 Å to the right for the corresponding

atom for dimer dissociation. As a result, the most relevant nearest-neighbor in-plane bond in the transition state is only 4.72 Å for dimer dissociation, at 8% tensile strain, while it is 5.21 Å in the case of detachment from the island. This explains why the barrier for detachment is reduced upon tensile strain and why this barrier approaches the energy barrier for diffusion.

The results presented here demonstrate that it is possible to calculate from first principles the strain dependence of all the relevant microscopic processes during growth. If different mechanisms are also needed, they can be computed in a similar way. For example, for multilayer growth on a simple metal surface, one might also need the strain dependence for the diffusion barrier of an atom moving over a step edge (that can occur either via hoping or exchange). To model such growth, one then needs a model such as an atomistic kinetic Monte Carlo model[22–24] or a level-set-based island dynamics model,[15] which includes all these processes. If one then also has an elastic model that computes the local strain (and thus the local lattice misfit) at every atomic position, one can faithfully model the growth of a strained system.

I also would like to note the following: In a typical growth model that includes strain, one needs to properly solve the elastic equations to obtain the local strain, ideally before every microscopic event. While this is still computationally expensive, there have been a number of recent growth models that illustrate that this is possible.[15,22–24] But the results presented here indicate that one should not simply calculate the elastic energy of the system before an event and the elastic energy of the system with one atom removed (the atom that is considered to move in the event) and then use the difference between these two elastic energies for the strain dependence of the microscopic event. In particular, such an approach does not include information about the direction of a move. This is problematic because, for example, the initial state for an atom diffusing along a step edge or an atom detaching from a step edge is the same (see Fig. 1), while, at the same time, it is clear from the results shown in Figs. 4 and 5 that the effect of strain on these two events is quite different (in particular, the effect of tensile strain).

In conclusion, I have shown that it is possible to calculate from first principles (using DFT) the strain dependencies of microscopic growth parameters that are relevant to understanding and modeling epitaxial growth. For Ag on Ag(100), I found that many of these parameters increase linearly, as the misfit increases. But I also found a somewhat surprising result for detachment of an adatom from a step edge. The barrier of this event first increases for negative misfits between −6% and 0%. It reaches a maximum at approximately 2% misfit and then decreases again with increasing positive misfit. In other words, starting at approximately 2% misfit, the barrier for this event decreases for both compressive and tensile strain. This is quite significant because it has been shown, for example, that detachment from a step edge and dimer dissociation are the two key processes that control the ordering and regularization of the size distribution in the submonolayer growth regime.[15] The results therefore suggest that such ordering might be qualitatively different for systems under tensile or compressive strain.

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[1] S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, Science **287**, 1989 (2000).

[2] M. Valden, X. Lai, and D. W. Goodman, Science **281**, 1647 (1998).

[3] J. Stangl, V. Holy, and G. Bauer, Rev. Mod. Phys. **76**, 725 (2004).

[4] R. Stumpf and M. Scheffler, Phys. Rev. Lett. **72**, 254 (1994).

[5] R. Stumpf and M. Scheffler, Phys. Rev. B **53**, 4958 (1996).

[6] A. Bogicevic, J. Strömquist, and B. I. Lundqvist, Phys. Rev. Lett. **81**, 637 (1998).

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

[8] C. Ratsch, A. P. Seitsonen, and M. Scheffler, Phys. Rev. B **55**, 6750 (1997).

[9] B. D. Yu and M. Scheffler, Phys. Rev. B **56**, R15569 (1997).

[10] E. Penev, P. Kratzer, and M. Scheffler, Phys. Rev. B **64**, 085401 (2001).

[11] M. Rosini, P. Kratzer, and R. Magri, J. Phys. Condens. Matter **21**, 355007 (2009).

[12] A. van de Walle, M. Asta, and P. W. Voorhees, Phys. Rev. B **67**, 041308(R) (2003).

[13] L. Huang, F. Liu, and X. G. Gong, Phys. Rev. B **70**, 155320 (2004).

[14] C. Ratsch, P. Smilauer, D. D. Vvedensky, and A. Zangwill, J. Phys. I **6**, 575 (1996).

[15] C. Ratsch, J. DeVita, and P. Smereka, Phys. Rev. B **80**, 155309 (2009).

[16] C. Ratsch, Phys. Rev. B **63**, 161306(R) (2001).

[17] C. Ratsch and M. Scheffler, Phys. Rev. B **58**, 13163 (1998).

[18] V. Blum, R. Gehrke, F. Hanke, P. Havuand, V. Havu, X. Ren, K. Reuter, and M. Scheffler, J. Comput. Phys. **228**, 8367 (2009).

[19] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[20] H. T. Dobbs, A. Zangwill, and D. D. Vvedensky, in *Surface Diffusion: Atomistic and Collective Processes*, edited by M. Tringides (Plenum, New York, 1997), p. 267.

[21] D. J. Shu, F. Liu, and X. G. Gong, Phys. Rev. B **64**, 245410 (2001).

[22] C.-H. Lam, C.-K. Lee, and L. M. Sander, Phys. Rev. Lett. **89**, 216102 (2002).

[23] J.-N. Aqua and T. Frisch, Phys. Rev. B **78**, 121305(R) (2008).

[24] A. Baskaran, J. Devita, and P. Smereka, Continuum Mech. Thermodyn. **22**, 1 (2010).