Using an empirical tight binding potential, we study the strain dependence of hopping and exchange diffusion barriers for Platinum on the unreconstructed Pt(100) surface. Also, adatom binding energies and Ehrlich-Schwoebel barriers are calculated as a function of substrate strain $\epsilon$. By analyzing the above quantities, we predict that for the growth of Pt on Pt(100) Layer by Layer growth should be improved under compressive strain.

1 Introduction

To improve the efficiency of electronic devices, the fabrication of highly ordered metal and semiconductor nanostructures is an important goal in technological applications.\textsuperscript{1,2} Molecular Beam Epitaxy (MBE) seems to be a promising method for the construction of such devices. Besides nanostructures, another important aim is the growth of smooth films and multilayer systems, which also play an important role in the fabrication of electronic devices.

In a simplified model the process of growth in MBE consists of adatom deposition with a flux $F$ and surface diffusion with a diffusion constant $D = \nu_0 \exp\left\{-(E_S - E_B)/k_BT\right\}$ (with $\nu_0 \approx 10^{12}/s$ being the so-called attempt frequency, $E_S$ the saddle-point or transition state energy, $E_B$ the binding energy, $k_B$ Boltzmann’s constant and $T$ the substrate temperature). The nucleation of islands will occur with an average distance\textsuperscript{3,4,5,6} $l \propto (D/F)^\gamma$. As the islands are growing, nucleations will also happen on top of existing islands, and island coalescence starts. Further on, the growth behav-
ior will fall in one out of three categories: Layer by Layer (Frank van der Merwe) growth, 3D-islanding (Volmer-Weber) and a mixture of both, known as Stranski-Krastanov mode, where after the growth of a few smooth layers 3D islands start to form.

If now the substrate is under compressive or tensile strain, saddle-point as well as binding energies are affected by strain. In the case of a homogeneously strained surface (e.g. in the middle of a large perfectly smooth terrace), this will simply result in an increased or decreased diffusion constant \( D \). On small islands or near island edges, the situation is more complicated. Islands try the relief stress at the edges, and therefore inhomogeneously strained areas occur, resulting in a gradient in binding as well as in saddle-point energies. This leads to an adatom current

\[
\dot{\mathbf{j}} = D \left( \nabla \rho + \frac{\rho}{k_B T} \nabla E_B \right).
\]

Beside the first term, Fick’s law, there is in general a drift towards positions of lower energy \( \rho \) (\( \rho \) is the adatom density).

Also, in systems which obey an additional barrier at step-edges, known as Ehrlich-Schwoebel barrier, this quantity will depend on the strain and will play an important role.

The aim of our work is to calculate the strain dependence of those three quantities important for surface diffusion: Binding and saddle-point energies and Ehrlich-Schwoebel barriers. By analyzing the strain dependence, we will try to make up a prediction for the growth of Platinum on Pt(100), whether Layer by Layer growth will be improved or hindered by a compressed or tensile strained substrate.

2 The model

Our calculations are based on an empirical tight-binding potential, which can be used to simulate various fcc metals and is given by

\[
E_i = A \sum_j \exp \left\{ -p \left( \frac{r_{ij}}{a_{NN}} - 1 \right) \right\} - \xi_0 \left\{ \sum_j \exp \left\{ -2q \left( \frac{r_{ij}}{a_{NN}} - 1 \right) \right\} \right\}^{1/2}.
\]

\( a_{NN} \) is the equilibrium nearest neighbor distance in the fcc lattice and \( r_{ij} \) is the distance of two atoms \( i \) and \( j \). The quantities \( A, p, q \) and \( \xi_0 \) are parameters which are used by the authors to fit the potential to the bulk properties of 10 different fcc metals.
We use a slab geometry with one free and one frozen (100) surface perpendicular to the z direction, and periodic boundary conditions in the x and y directions. By adjusting the lateral size of the simulation box, the system can be put under compressive or tensile strain. Diffusion barriers and binding energies are calculated using the molecular static method. We move a “test” adatom across the surface in small, discrete steps. In each of these steps we relax the whole system (with the constraints given above), with the exception that the adatom is fixed laterally and can relax only in the z direction. Relaxation is done using a conjugate gradient method, and is stopped when both an energy (\( |\Delta E| < 10^{-10}\) eV) and a force (\( |F_i| < 10^{-3}\) N) criterion are fulfilled. In each of these steps we record the minimal energy, and by analyzing the resulting energy landscape we can calculate the binding and saddle-point energies, and thus the activation energy \( E_A = E_B - E_S \).

To calculate the Ehrlich-Schwoebel barrier an additional island can be placed on the substrate before the calculation starts.

3 Pt/Pt(100) self-diffusion

In this paper we want to discuss growth and diffusion of Platinum on Pt(100). As observed for other fcc metals, like e.g. Iridium or Gold, under certain conditions the Pt surface obeys a (5x1) surface reconstruction, which shall be neglected for our calculations. This is valid if we restrict ourselves to small samples, like they are in use in field ion microscopy (FIM).

In general, two diffusion modes are possible on the fcc (100) surface: hopping and exchange diffusion (see Fig. 2).

![Figure 2. Possible modes for surface diffusion: hopping and exchange.](image-url)
Figure 3. Results for the activation energy $E_A$, Ehrlich-Schwoebel barrier $E_S$, and adatom binding energy $E_B$ as a function of surface strain. A negative $\epsilon$ denotes compressive isotropic strain parallel to the surface. In the reference state $\epsilon = 0$ the lattice constant along the surface is the same as in the unstrained bulk at zero pressure.

We calculated the important quantities for both diffusion modes. The results are shown in Fig. 3. Let us first look at the activation energy $E_A$. As observed before for Ag on Ag(100)$^{12}$ hopping and exchange diffusion behave totally different. While hopping diffusion is faster under compressive ($\epsilon < 0$) and slowed down under tensile ($\epsilon > 0$) strain, for exchange diffusion it is exactly the other way round. For vanishing strain the activation energy for hopping as well as for exchange is approximately $E_A \approx 0.87 \text{eV}$. In the case of hopping this is almost in agreement with recent$^{13}$ density functional calculations, which give a value of $E_A = 1.04 \text{eV}$.

To decide whether in the unstrained case hopping or exchange diffusion is the primary diffusion mode, it is not sufficient to look only at the diffusion barrier, but one also has to take the prefactor $\nu_0$ into account. Studies$^{14}$ show that this prefactor is about a factor 10 - 50 larger for exchange than for hopping. This, together with the fact that our barrier for hopping diffusion seems to be too small, can lead to the conclusion that exchange diffusion is the preferred diffusion mode is exchange diffusion, in accordance to what was found in FIM studies.$^{11}$

As observed before for hopping diffusion in various systems,$^{15,7,16}$ for
the activation energy of Pt on Pt(100) is an almost linear function of strain. This also holds in the case of exchange diffusion, however in this case we observe a negative slope.

Like the activation energy also the Ehrlich-Schwoebel barrier behaves completely different for hopping and exchange at an island edge. For exchange it is lowered and even gets negative for compressive strain, while under tensile strain it is increased. For hopping the strain dependence is the opposite.

Finally, the adatom binding energy is found to be lowered for tensile strain and increased for compressive strain. As we have shown before, this leads to a particle current. E.g. adatoms on strained islands on a compressed surface will drift to the island edge, as due to relaxation effects the island edges are weaker strained than the island center.

4 Prediction for Pt/Pt(100)

Now we summarize the results of the previous section and try to make a prediction under which type of strain Layer by Layer growth is preferred. Again, surface reconstruction will be neglected, and we stick to exchange diffusion, as this diffusion mode seems to be the relevant one from the experimental and theoretical point of view. It is important to note that we only need the fundamental trends we obtained in the previous section. While we do not claim that our values are close to the exact numbers for the diffusion barriers and binding energies, we trust the sign of the slope of their strain dependence. Our results are schematically summarized in Fig. 4

The first point to note is the island shape. Islands on a compressed surface will relax the edges outward, while on a tensile strained substrate they will relax inward. In the case of compressive strain the island relaxation leads to a decreased diffusion barrier on islands compared to the substrate, resulting in an increased interlayer transport of adatoms and better Layer by Layer growth.

Due to the reduced diffusion constant $D$ in the case of compressive strain, the island density is increased. Empirically one finds that an increased island density often favors Layer by Layer growth, which is the reason why techniques like a short sputtering or temperature drop at the beginning of each monolayer, or pulsed laser deposition are applied. One possible explanation is an effective reduction of the Ehrlich-Schwoebel barrier for small islands. On the other hand, simulations and analytical considerations show that in the absence of Ehrlich-Schwoebel barriers a reduced adatom mobility actually hinders Layer by Layer growth.

Analyzing the behavior of the binding energy, one can conclude that in...
the case of compressive strain the relaxation of the island edges leads to a net adatom current to the less compressed island edges, while under tensile strain adatoms drift to the island center. From this point of view compressive strain should improve the interlayer transport and therefore the Layer by Layer growth.

Finally we look at the additional Ehrlich-Schwoebel barrier at the step-edges. Assuming that adatom exchange processes also prevail at the step edges, we see that the activation energy for interlayer transport is reduced under compressive strain and raised for tensile strain, again leading to improved Layer by Layer growth in the case of compressive strain.

Putting this altogether, 3 out of 4 arguments predict improved Layer by Layer growth under compressive strain. Additionally, it has been shown in an example that the combined effects of particle drift and enhanced mobility on top of islands override the reduced average mobility of adatoms in favoring Layer by Layer growth. Both particle drift and inhomogeneous adatom mobil-
ity are due to strain relaxation at step edges. We conclude that compressive strain should lead to improved Layer by Layer growth for Pt on Pt(100), assuming exchange diffusion being the primary diffusion mode and neglecting the (5x1) surface reconstruction.

Acknowledgements

This work was supported by the DFG within SFB-166 and DFG grant No. WO 577/2-1.

References