

Dislocation Structures of Submonolayer Films near the Commensurate-Incommensurate Phase Transition: Ag on Pt(111)

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Submonolayer films of Ag on Pt(111) exhibit parallel partial dislocations separated by narrow hcp domains and much wider fcc domains, the large difference in width being atypical of strained metal overlayers on close-packed substrates. Using a two-dimensional Frenkel-Kontorova model, we calculate the relative domain widths. We examine possible effects of dislocations on equilibrium island shape and calculate the energies of stable and metastable dislocation structures versus island size. Experimental results are explained by proximity to the incommensurate-commensurate phase transition. [S0031-9007(99)09291-1]

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Many close-packed metal overlayer systems show patterns of partial dislocations which form to relieve lattice mismatch between overlayer and substrate. Indeed, the well-known herringbone reconstruction of the clean gold (111) surface is a striking example of such a dislocation pattern, formed because the lower coordinated surface gold atoms have a closer equilibrium spacing than normally coordinated bulk gold atoms [1]. Similarly, bilayers of Cu on Ru(0001) form a striped dislocation pattern [2]. These patterns consist of alternating domains with fcc and hcp stacking separated by partial dislocations running in the $\sqrt{3}$ direction. In most systems, the fcc and hcp domains are similar in width, differing at most by a factor of 2.

The dislocation pattern formed by submonolayer Ag on Pt(111) is atypical for equilibrated heteroepitaxial metal overlayers on a metal surface in that it exhibits a dramatic difference in the widths of the fcc and hcp domains [3]. Figure 1 shows a scanning tunneling micrograph of the structure for submonolayer Ag on Pt(111). The inset is an experimental micrograph: The surrounding structure shows the result of the theoretical calculation described below. For Ag on Pt(111) the fcc domains are >3 times wider than the hcp domains. Differences in domain widths have been correctly attributed to the fact that the fcc sites are energetically favored relative to hcp sites. However, this "monolayer stacking fault energy" is not sufficient to explain the unusually wide fcc domain widths seen for Ag on Pt(111). We will show below that the major difference in domain widths is caused by the immediate proximity of this system to a commensurate-incommensurate phase transition.

The experimental work on this system has also examined the types of dislocation structures formed in Ag islands as a function of island size [3]. We find that a 2D Frenkel-Kontorova (FK) model can reproduce the three major types of dislocation structures seen in islands with diameters between 200 and 500 Å. The prediction

of the FK model is in agreement with the observation that dislocations do not form in islands until the island size is much greater than the dislocation spacing in continuous films. The FK model also suggests that dislocations have little effect on equilibrium island shapes for Ag on Pt(111).

The 2D Frenkel-Kontorova (FK) model provides a simple approach for modeling dislocation structures on surfaces. It has been applied to Au(111) [4] and to Cu on Ru(0001) [5] with considerable success. We model the Ag-Pt interaction using a 2D substrate potential:

$$V_{\text{Pt-Ag}}(\vec{r}) = V_0 + V_1 \sum_{\vec{G} \in G_1} \cos(\vec{G} \cdot \vec{r}) + V_2 \sum_{\vec{G} \in G_1} \sin(\vec{G} \cdot \vec{r}) + V_3 \sum_{\vec{G} \in G_2} \cos(\vec{G} \cdot \vec{r}),$$

where G_1 is a set of three reciprocal lattice vectors of length $4\pi/\sqrt{3}a$ along the x axis and spaced at 120°

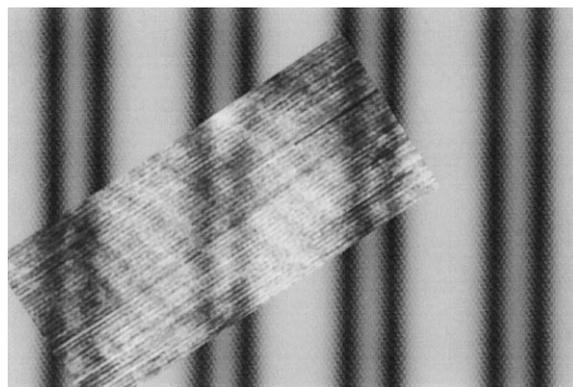


FIG. 1. Experimental and theoretical dislocation patterns for submonolayer Ag on Pt(111). The inset is a scanning tunneling micrograph. The surrounding area shows a simulated image based on the 2D Frenkel-Kontorova model. The dark vertical lines are partial misfit dislocations, the light vertical lines are narrow hcp domains, the light vertical areas are wide fcc domains. The horizontal length of the image is 370 Å.

angles to the x axis and G_2 is a set of three reciprocal lattice vectors of length $4\pi/a$ along the y axis and spaced at 120° angles to the y axis. [The y axis is the $\sqrt{3}$ direction of the Pt(111) surface.]

In order to determine values for the substrate potential parameters V_0 , V_1 , V_2 , and V_3 , we calculated the total energy of fcc, hcp, bridge, and on-top configurations of pseudomorphic Ag on Pt(111) using first principles calculations within the generalized gradient approximation (GGA) [6]. We used the plane wave ($E_{\text{cut}} = 191$ eV) and ultrasoft pseudopotential [7] based code VASP developed by Kresse and Furthmüller [8]. The calculated fcc-hcp energy difference was 21 meV, the fcc-bridge difference was 59 meV, and the fcc-top energy difference was 277 meV [9].

The Ag-Ag interactions in the overlayer were modeled using a Morse potential:

$$V_{\text{Ag-Ag}}(r) = D[e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}].$$

We proceed here by choosing physically reasonable values for D , a , and r_0 . We set the radius of the Morse potential, r_0 , to be 1.041 l.u. based on the relative experimental lattice constants of bulk Ag and Pt. [One lattice unit (l.u.) is defined by the platinum nearest neighbor spacing as 2.77 Å.] We set the depth of the Morse potential to the cohesive energy of Ag divided by 6, i.e., $D = 492$ meV. We then set the parameter, $a = 3.882$ (l.u.)⁻¹ to reproduce the bulk modulus of Ag. For this set of parameters, a pseudomorphic silver overlayer is the stable structure. However, the system is quite close to the pseudomorphic-incommensurate phase transition, thus small parameter changes allow dislocated structures to become stable. The period of the dislocation structure depends dramatically on small changes in the parameters, D , a , and r_0 . This is the major reason why we do not discuss the determination of these parameters from first principles here [10]. We found that first principles calculations of the Ag-Ag effective pair potential are in substantial agreement with the model presented here and show that the system is in immediate proximity to the phase transition.

The phase transition from a pseudomorphic to dislocated structure can be approached by adjusting the Morse potential or the substrate potential. To be specific, we describe the effect of varying the parameter, D . For a critical value, $D_c \cong 547$ meV, there is a phase transition. Below this value, the overlayer is pseudomorphic. Above this value, periodic dislocation pairs exist. The periodicity of the dislocation pairs is N l.u. For every N platinum substrate atoms there are $N - 1$ silver overlayer atoms. The stable value of N is plotted as a function of D in Fig. 2. The spacing of the dislocations diverges as D approaches the critical value. In order to reproduce the experimental domain widths, $D = 570$ meV was chosen. The resulting structure, plotted using a gray scale based on $V_{\text{Pt-Ag}}(\vec{r})$, is shown in Fig. 1. Adjusting D up from a bulk value is plausible since bond energy bond order arguments

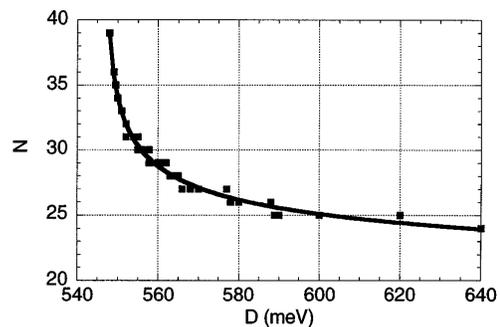


FIG. 2. Periodicity of calculated dislocation structure as a function of Morse parameter D . There is a critical value at $D = 547$ meV. As this value is approached from above, the dislocation spacing diverges. Below this value there are no dislocations.

predict that surface Ag-Ag bonds are stronger than bulk Ag-Ag bonds due to the lower coordination at the surface. The choice to adjust D is arbitrary. The key factors in fitting the domain widths are the value of r_0 and the immediate proximity to the commensurate-incommensurate phase transition.

The theory presented here is supported by the experimental observation that upon increasing the silver coverage to a monolayer the dislocation pattern disappears and a pseudomorphic film is formed. Experimentally, the phase transition from a dislocated to a pseudomorphic structure is driven by the discontinuous change in the silver chemical potential upon completion of a silver monolayer. As the second layer starts to form, additional silver is incorporated in the first layer and the dislocations are removed. This theory for the major difference in domain widths being associated with proximity to the phase transition is also supported by experimental work on clean Pt(111). Normally at room temperature, the Pt(111) surface shows no reconstruction. It is possible to create a dislocated structure on Pt(111) by increasing the chemical potential of Pt in the surroundings [11], or by heating the sample to $>65\%$ of the melting point [12]. At 65% of the melting point the clean Pt(111) surface undergoes a commensurate-incommensurate phase transition. Near the phase transition, the relative fraction of fcc domains is much larger than that of hcp domains, similar to the situation described here for Ag on Pt(111).

This FK model can also be applied to calculate equilibrium island shapes and equilibrium dislocation structures for Ag islands on Pt(111). These calculations are motivated by the experimental observation of different dislocation structures and island shapes in islands of different sizes. Experimentally, the following procedure was used to prepare a suitable range of island sizes [3]: First, 0.12 monolayer (ML) Ag was deposited at 50 K. Subsequently, the film was warmed to 300 K to enable 2D Ostwald ripening and another 0.25 ML Ag was added to the film. The resulting islands had a distribution of sizes and shapes. For islands less than 200 Å across, the

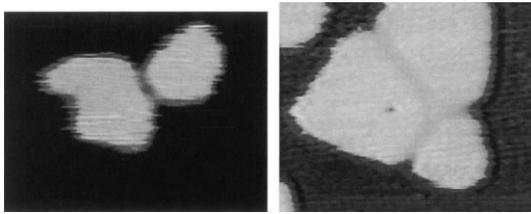


FIG. 3. Ag islands grown on Pt(111). Small islands (not shown) have no dislocations. The intermediate island on the left has a single dislocation running across the island. The larger island on the right has a Y-shaped dislocation pattern.

islands are invariably pseudomorphic. For islands more than 400 Å across, the islands invariably contained dislocations. From 200 to 400 Å there was a gradually increasing probability of dislocations. Figure 3 shows two islands with different dislocation structures observed after this growth process. These pictures motivate us to examine the issue of equilibrium island shape and dislocation structure as a function of island size.

We started by calculating the energies of hexagonal islands with several different metastable dislocation structures. The energies were calculated as a function of island size using the 2D FK model with the parameters listed above. Figure 4 shows four different structures for a 266 Å wide island. The first is a pseudomorphic structure, the second shows a single dislocation pair, the third shows two dislocation pairs, and the fourth shows a “Y”-shaped dislocation structure. The pseudomorphic, single dislocation pair, and Y-shaped dislocation are all observed experimentally for Ag on Pt(111). There are also beautiful transmission electron microscopy (TEM) photographs in the literature which show both multiple striped dislocation structures and Y-shaped dislocation structures (with multiple stripes) for reconstructed Au(111) surfaces on Au platelets grown on MoS₂ [13].

In Fig. 5, we plot the relative energies of the three dislocation configurations shown in Fig. 4 as a function of island size. The energies are plotted relative to that of a pseudomorphic configuration. For island widths less than about 240 Å, the pseudomorphic configuration is stable. For island widths between 240 and 320 Å, the structure with a single pair of partial dislocations is stable. For island widths somewhat greater than 320 Å, the structure with a double pair of partial dislocations is stable. These results are in qualitative agreement with the experimental observation that dislocations are never found in islands less than 200 Å in width, even though this is much greater than the 75 Å spacing of dislocation pairs in a continuous submonolayer film.

The above analysis applies only if the islands are nearly hexagonal, prompting consideration of the equilibrium shapes for pseudomorphic and dislocated islands. The equilibrium shape of a pseudomorphic island is determined by the step energies of the A- and B-type steps, and is easily calculated for this FK model. Starting from

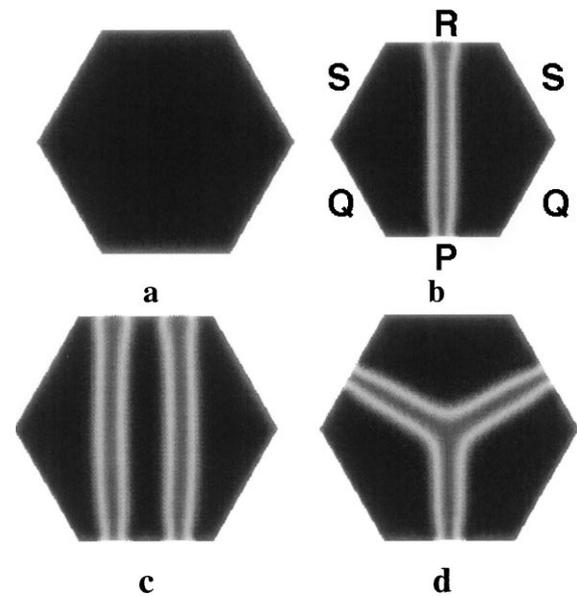


FIG. 4. Dislocation structures calculated for hexagonal island with a width of 266 Å. (a) Shows the pseudomorphic structure, (b) shows a single pair of partial dislocations, (c) shows two parallel pairs of partial dislocations, and (d) is a Y-shaped dislocation. The single pair of partial dislocations is the stable structure for this island size; the other structures are metastable. The gray scale in this figure is reversed relative to Fig. 1 and Figs. 3. The size of (b) is adjusted slightly to allow space for labels.

the unrelaxed step energy (570 meV for the Morse potential used here) and calculating the step relaxation energies, we obtain step energies of 487 and 473 meV for the A and B steps, respectively. For these step energies a Wulff construction gives islands with the B step length ~10% longer than the A step length. The pseudomorphic islands will be approximately hexagonal.

The equilibrium shape of a dislocated island is more difficult to calculate since the dislocation line energy and

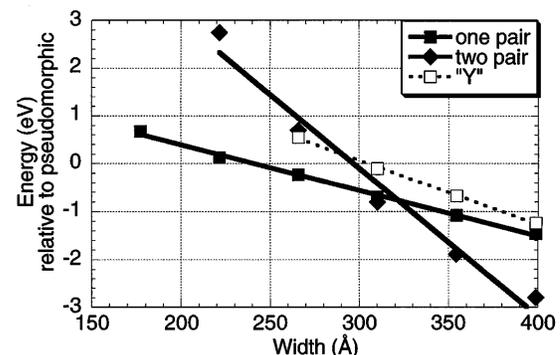


FIG. 5. Calculated hexagonal island energies for various dislocation structures as a function of island size. All energies are referenced to the energy of a pseudomorphic island. For widths less than about 240 Å, the pseudomorphic configuration is stable. For widths between 240 and 320 Å, the single dislocation pair configuration is stable. For widths greater than 320 Å, the double dislocation pair configuration is stable.

the relaxation of the strain field by the edges and the dislocation are involved and since the threefold symmetry is broken. Examination of the experimental island shapes (e.g., Fig. 3) suggests that necking may occur when dislocations reach the island perimeter. It is tempting to suppose that this might minimize the dislocation line energy. We have addressed this hypothesis by considering island shapes of the type indicated by the labels S , P , R , and Q in Fig. 4b. These labels represent the number of atoms in each island edge. They represent a class of six-sided polygons, with a vertical mirror plane as suggested by the dislocation pair, and with various aspect ratios (and thus different dislocation line lengths). We compared the energy for various islands with the same number of atoms but different values for S , P , R , and Q [14]. We found that for this particular system, the presence of a dislocation *does not* significantly affect the equilibrium shape of the islands. This suggests that the necking and other island shape effects seen in the experiment are due to kinetic effects. We conclude that the equilibrium island shapes in this system are nearly hexagonal with or without dislocations and that the analysis shown in Fig. 4 remains valid.

In conclusion, we have modeled the structure of dislocations both in submonolayer films and in islands of Ag on Pt(111). The system is found to be very close to the transition from a pseudomorphic to a dislocated structure. This accounts for the very wide fcc domain widths seen in this system. It also explains the fact that the pseudomorphic island structure is found for islands much larger than the dislocation spacing in a submonolayer film. We show that the equilibrium island shape is nearly hexagonal, with or without a dislocation across the island. This suggests that kinetics are determining the island shapes in the experiment, since the islands are far from hexagonal.

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- [10] In addition to the requirement that the Morse potential parameters must be determined (or chosen) very accurately, because the system is so close to a phase transition, there are other ambiguities, which arise in fitting the anharmonic potential from first principles. In order to make sufficiently accurate determination of the anharmonic potential, it would be necessary to calculate dislocation structures with larger unit cells than can presently be addressed with first principles. Although the FK model provides an excellent qualitative description, it is not clear that it would be sufficiently accurate to provide quantitative results this close to the phase transition.
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