Misfit Dislocation Structure for Close-Packed Metal-Metal Interfaces

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We describe theoretical calculations applying a 2D Frenkel-Kontorova (FK) model to the heteroepitaxial system Cu on Ru(1000). The experimentally observed variation of structure with layer thickness is simulated by scaling the adatom-adatom interaction. The minimum energy configurations are in exceptional agreement with recent scanning tunneling microscopy results showing four distinct structures as a function of thickness. These metal on metal films present a new realization of the FK model which complements previous investigations of rare gas adsorption on graphite.

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Structure and phase transitions of overlayers on surfaces have been the subject of intense experimental and theoretical study for many years. Perhaps the most studied system is the adsorption of rare gases on the basal plane of graphite at cryogenic temperatures [1–5]. Because solid rare gases have a considerably larger lattice spacing than a graphite lattice, all of the hollow sites cannot be occupied and in many cases domains with a $\sqrt{3} \times \sqrt{3}$ structure are formed. The atoms in these domains can occupy one of three fully equivalent lattice sties, generally denoted A, B, and C. Depending on the density of the gas layer, a variety of phases including striped and hexagonal domains are formed. The hexagonal structure of the incommensurate solid phase is shown in Fig. 1(a). The domains are separated by walls variously described as misfit dislocations, partial dislocations, or solitons.

An equally active area of research is the structure of metal-metal interfaces. For close-packed metal-metal overlayer systems, there are generally two favorable sites, fcc and hcp. There is a large energy penalty associated with occupation of an on-top site. As shown in Fig. 1, the difference between the three-site (rare gases on graphite) and the two-site (metal on metal) cases results in basic topological differences in possible domain and misfit dislocation structure. Figures 1(b) and 1(c) show two possible topologies which could occur for the latter systems. The Au(111) surface which reconstructs to form a "herringbone" structure [6,7] is a special case of a metal-metal interface since the surface gold atoms have a preferred spacing different from that of the bulk atoms. The herringbone structure has been shown to be due to substrate elastic strain effects [8].

In this paper we model and describe the energetically favorable structures for monolayers and multilayers of Cu on Ru(0001). The nearest neighbor spacing of bulk copper is 5.5% smaller than that of the Ru(0001) plane. The structure of this overlayer system has recently been examined using scanning tunneling microscopy (STM) to determine the equilibrium structures of Cu monolayers, bilayers, trilayers, and thicker layers on Ru(0001) [9]. For the monolayer, a pseudomorphic structure was observed with the copper atoms sitting in the hollows of the ruthenium surface. For the bilayer, a striped dislocation pattern, closely related to the Au(111) reconstruction, was seen. For the trilayer, a pattern with triangular symmetry was observed with significant local variations in structure. For four or more layers, a "moiré" pattern was observed with the copper layer at close to the bulk copper spacing. The authors of Ref. [9] suggest that this sequence of structures should be attributed to the balance between elastic strain in the copper overlayer and misfit strain occurring at the copper-ruthenium interface. We examine this assertion with a detailed theoretical model which reproduces all of the experimentally observed structures as a function of overlayer thickness.

We model the ruthenium-copper interaction using a Frenkel-Kontorova (FK) model [10] with a 2D substrate potential of the form [8,11]

$$V_{\text{Ru-Cu}}(\mathbf{r}) = V_0 + V_1 \sum_{\mathbf{G}\in\mathbf{G}_1} \cos(\mathbf{G}\cdot\mathbf{r}) + V_2 \sum_{\mathbf{G}\in\mathbf{G}_2} \cos(\mathbf{G}\cdot\mathbf{r}), \quad (1)$$

where $\mathbf{G}_1$ is a set of three reciprocal lattice vectors of length $4\pi/\sqrt{3}a$ along the x axis and spaced at 120° angles to the x axis and $\mathbf{G}_2$ 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

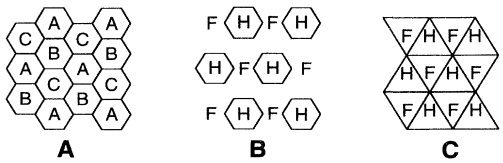

FIG. 1. Domain configurations for 2D incommensurate structures in the FK model. (a) shows the ground state structure for a three state rare gas on graphite incommensurate solid phase. (b) and (c) show two possible structures for the two site close-packed metal on metal incommensurate phase. F and H represent fcc and hcp domains, respectively.

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hcp Ru(0001) plane.] V_0, V_1, and V_2 were chosen to give hcp and fcc site energies of zero meV, a bridge site energy of 76 meV, and an on-top site energy of 400 meV. These values were obtained from an embedded atom method (EAM) calculation for a single Cu atom on Ru(1000) [12]. As expected, this EAM calculation showed the fcc and hcp sites to be favored with a moderate barrier for the bridge site and a large barrier to occupancy of the on-top site. We selected the energy scale so that the zero of energy would occur for a Cu atom in the fcc or hcp sites. $V_{\text{Ru-Cu}}$ is a measure of the misfit energy due to displacement of copper atoms from the fcc or hcp sites.

For the copper-copper interactions within a single monolayer, we used a Lennard-Jones potential of the form

$$V_{\text{Cu-Cu}} = 4\varepsilon_0[(r_0/r)^{1/2} - (r_0/r)^6]. \quad (2)$$

The value $r_0 = 2.30$ Å was chosen to give the lattice spacing for a (111) Cu monolayer equal to the Cu bulk lattice spacing. The value $\varepsilon_0 = 0.192$ Å was chosen to fit the bulk vacancy energy of copper. This potential was truncated at 5.5 Å and shifted by the value of the potential at the cutoff.

The total energy for the overlayer is given by a sum over all copper atoms of the Ru-Cu interaction and the Cu-Cu interaction. We choose a zero for this energy by adding a term NE_{Cu}, where N is the total number of copper atoms in the monolayer and E_{Cu} is the cohesive energy per copper atom in a (111) Cu monolayer with the Cu bulk lattice spacing:

$$E(\mathbf{r}_1, \mathbf{r}_2, \ldots) = \sum_j V_{\text{Ru-Cu}}(\mathbf{r}_j) + \frac{1}{2}\sum_{i \neq j} V_{\text{Cu-Cu}}(\mathbf{r}_i - \mathbf{r}_j) + NE_{\text{Cu}}. \quad (3)$$

The first summation gives the total misfit energy of the Cu monolayer. The other two terms give the total strain energy of the monolayer.

The above discussion pertains to the case of monolayer coverage. We have treated the multilayer case making the following approximations:

(1) the strain of the ruthenium due to stress produced by the copper overlayer is zero,

(2) the elastic constant of the copper layer is independent of thickness, and

(3) dislocations in the copper thread from the buried interface to the surface; thus the local strain in each copper layer is virtually identical.

In the spirit of these assumptions we approximate p layers of copper by a monolayer of adatoms with an adatom-adatom interaction equal to p times that of Eq. (2). The energy per copper atom in the multilayer structure is $E(\mathbf{r}_1, \mathbf{r}_2, \ldots)/(pN)$, where pN is the total number of copper atoms in the multilayer. We treat p as a continuous variable and investigate the minimum energy configurations as a function of p, where $0.5 < p < 15$. This is equivalent to treating the copper interactions using a mean-field approximation. We emphasize that the correspondence between p and the number of layers is expected to be semiquantitative at best.

Our calculations are performed using periodic boundary conditions. A starting overlayer configuration was input for the calculation and E was minimized using the conjugate gradient method. In order to find the minimum energy structure (for a given value of p), the starting configuration (including periodic boundary conditions) was varied systematically until a global minimum of the energy per Cu overlayer atom was found. In practice, the energy per Cu atom was calculated and plotted as a function of p for a given starting configuration (e.g., Fig. 2). The minimum energy configuration for a given value of p was determined from such a plot. In this manner different structures and periodicities (and thus different overlayer densities) were determined to be the lowest energy configurations for different values of p.

All of the minimum energy structures found were generated from a periodic overlayer starting configuration with primitive lattice vectors $\mathbf{a}$ and $\mathbf{b}$ only slightly different from those of (111) copper or (0001) ruthenium. For a pseudomorphic layer the primitive lattice vectors would be $\mathbf{a} = a_0\hat{\mathbf{x}}$ and $\mathbf{b} = a_0\hat{\mathbf{x}}/\sqrt{2} + \sqrt{3}a_0\hat{\mathbf{y}}/2$, where a_0 is the nearest neighbor spacing of the Ru surface. The starting configuration for generating the striped layers was $\mathbf{a} = ra_0\hat{\mathbf{x}}$ and $\mathbf{b} = ra_0\hat{\mathbf{x}}/\sqrt{2} + \sqrt{3}\hat{\mathbf{y}}/2$, where $r = n/(n+1)$, the ratio between the starting periodicity of the Ru substrate and the starting periodicity of the Cu overlayer. The starting configuration for generating the moiré and bright star patterns was $\mathbf{a} = ra_0\hat{\mathbf{x}}$ and $\mathbf{b} = ra_0\hat{\mathbf{x}}/2 + r\sqrt{3}a_0\hat{\mathbf{y}}/2$.

In Fig. 2 we plot the energy per copper atoms as a function of p for some of the starting configurations which gave minimum energy structures for some value of p. Three structural transitions are seen as a function of overlayer thickness. From $p = 0$ to $p = 1$, the pseudomorphic configuration is the minimum energy

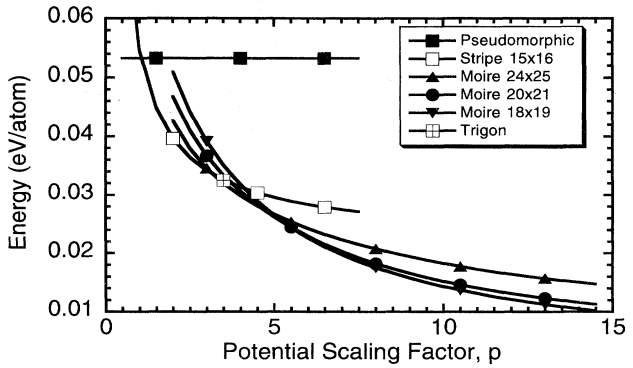

FIG. 2. Energy per Cu overlayer atom for some of the minimum energy structures. The starting configurations are labeled $n \times m$, where $r = n/m$ is the ratio of the starting periodicities of the Cu overlayer and the Ru substrate. For some r and p, the bright-star structure results from the moiré starting configuration (see text).

structure. From $p = 1.5$ to 3, the striped configuration is the minimum energy structure. From $p = 3.5$ to 5, the bright-star configuration is the minimum energy structure [we started with a moiré configuration with large unit cells which relaxed to the bright star, Fig. 3(b), for this range of p]. For $p > 5.5$, the moiré configuration is the minimum energy structure.

Figures 3(a), 3(b), and 3(c) show blackbody scale plots of the minimum energy configurations for $p = 1.5$ (striped), $p = 3.5$ (bright star), and $p = 6$ (moiré). The color for each atom position is plotted from the substrate potential, $V_{\text{Ru-Cu}}$, thereby showing the dislocation structure which is observed by measuring tip height in a STM. This model gives very good agreement with experiment reproducing both the sequence of structures observed as a function of layer thickness (p) and the repeat distances (periodicity) for these configurations. The values of p at which these configurations are predicted are not in precise agreement with the experiment, presumably because of the crude interatomic potentials which do not reproduce the thickness variation of the elastic constant of copper in this thickness regime. The spiral bright-star structure shown in Fig. 3(b) is of particular interest. It is related to the moiré structure, however, the unit cell is much larger than the relative lattice constants of copper and ruthenium would predict. Detailed examination of the atomic positions near the bright stars shows that the spirals occur because the atoms are attempting to avoid energetically unfavorable on-top sites. This bright-star structure has no counterpart in the rare gas–graphite systems where three different energetically favorable sites exist and three different domains can meet at a point forming a hexagonal structure [Fig. 1(a)]. In the present case with only two energetically favorable sites, the hexagonal domain structure cannot exist and the lowest energy configuration involves several atoms near energetically unfavorable on-top sites.

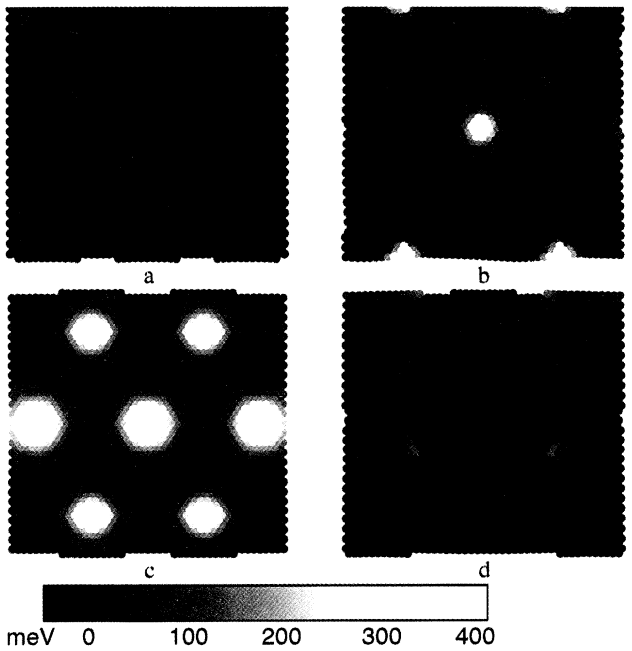

FIG. 3 (color). Plots of the misfit energy for dislocation structures formed in Cu on Ru(0001). The plots show 120 Å × 120 Å areas. Atoms in on-top sites have energies close to 400 meV. Atoms in bridge sites have energies close to 76 meV. (a) shows the striped structure formed for $p = 1.5$, with $r = 17/16$. (b) shows the bright-star structure formed for $p = 3.5$ and $r = 26/25$. (c) shows the moiré structure formed for $p = 6$ and $r = 19/18$. (d) shows a trigon structure formed for $p = 3.5$. Edge dislocations are found in the vicinity of the "orange atoms" ($V_{\text{Ru-Cu}}$ about 200 meV) for the trigon structure.

In addition to the bright-star structure shown in Fig. 3(b), the experimental results for Cu on Ru show other structures which have been called "trigons" [13]. The bright-star configuration of Fig. 3(b) is generally seen for three monolayers of well-annealed Cu on Ru. If the copper is not well annealed, a variety of other structures are seen including the trigons [14]. In order to model trigons, a starting topology shown in Fig. 1(b) was used. We varied the size of the periodic cell over a wide range and varied the size and shape of the six-sided hcp polygons while retaining their threefold symmetry. Unfortunately, it was not possible to be exhaustive in this search due to the wide range of possible starting configurations. Nonetheless, we are confident that we are reasonably near to the minimum energy configuration for the trigons. The blackbody scale plot for the trigons is shown in Fig. 3(d). The energy of this structure for $p = 3.5$ is plotted in Fig. 1. This structure is only slightly higher in energy (<1 meV/atom at $p = 3.5$) than the bright-star configuration [Fig. 3(b)], in accord with the experimental observations showing coexistence of the two structures. The trigon structure is fundamentally different from the other structures described here in that it contains edge dislocations within a single copper layer. Because of these defects, the in-plane local environment of some copper atoms is fundamentally different from the others. More specifically, some of the copper atoms have five or seven nearest neighbors in the vicinity of the edge dislocation cores.

The FK model involves a trade-off between the strain energy of the overlayer and the misfit energy of the overlayer. In Fig. 4 the strain and misfit energies (per Cu overlayer atom) of the structures shown in Fig. 3 are plotted as a function of p. The strain and misfit energies for the metastable trigon configuration are also plotted for $p = 3.5$. Figure 4 also shows the Cu atomic density for the minimum energy states as a function of p. A dramatic feature of these curves is the large increase in misfit energy (along with a minor increase in overlayer density) with increasing p at the structural transition from the bright star to the moiré configuration. This occurs because significant numbers of atoms are moving into the on-top configuration as the moiré pattern is formed, thereby increasing the misfit energy while decreasing the

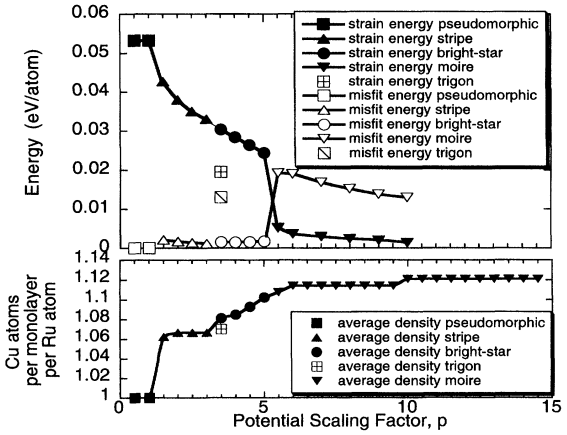

FIG. 4. Top plot shows misfit and strain energies of minimum energy structures as a function of the potential scaling factor, p. The misfit and strain energies for the metastable trigon structure are plotted for $p = 3.5$. Bottom plot shows average atomic density of minimum energy structures as a function of p. The atomic density for the metastable trigon structure is also plotted for $p = 3.5$.

overlayer strain. This result emphasizes that the bright-star structure is a new structure characteristic of this 2D FK model, which has not been discussed in previous theoretical treatments.

We anticipate that the results described here will be applicable to a wide range of close-packed metal overlayer systems and that the results are not critically dependent on the potentials used or the magnitude of the overlayer mismatch. (We *do not* expect this sequence of structures for adatoms larger than substrate atoms because adatom-adatom repulsions will be much stronger for such systems than the adatom-adatom attractions operating here.) To verify the generality of these results, calculations were also performed for a springlike potential model. We also ran calculations for a mismatch of 3.5%. In both cases the same sequence of structures shown in Fig. 3 was observed. We note that structures similar to those shown in Fig. 3(a) have been calculated for Au(111) [11]. Structures similar to those shown in Fig. 3(b) and 3(d) have been observed on Pt(111) [15] and modeled theoretically [16].

Some other tentative conclusions can be drawn from this model. The minimum energy structures are defect-free (except of course for partial dislocations) over the whole range of potential strengths p. Thus each copper atom has a local in-plane environment of copper atoms which is only slightly perturbed from the bulk structure. The success of the mean-field approximation used to represent multiple copper layers, suggests that all or virtually all of the multiple copper layers have nearly the same structure. Thus, for example, the experimentally observed moiré pattern is likely due to four overlayers, all having nearly the bulk copper spacing and not to one or more layers of pseudomorphic copper with the remaining overlayers being bulk copper. This hypothesis is consistent with one- and two-dimensional treatments of the FK model for fourfold symmetric systems which predict pseudomorphic growth up to a critical thickness and incommensurate phases above that thickness [17]. For the striped two overlayer structure, we have verified this hypothesis using a full EAM calculation, which shows the same structure for both copper layers with the partial dislocation extending from the buried interface to the surface. Final confirmation of this hypothesis for the other structures must await more detailed experimental data or theoretical modeling.

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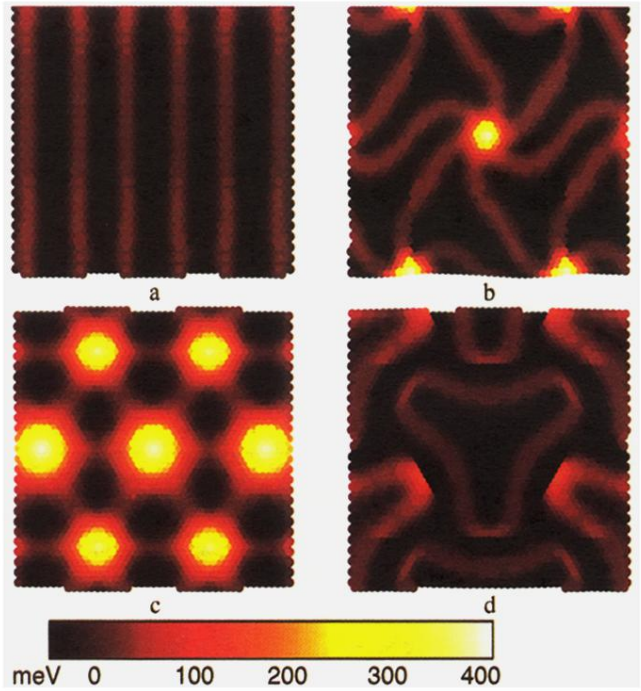

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