Strain Relief through Heterophase Interface Reconstruction: Ag(111)/Ru(0001)

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We report an experimental (scanning tunneling microscopy) and theoretical (embedded atom method) study of a heterophase interface reconstruction between Ag(111) and Ru(0001). Despite the large 7% mismatch, the second layer of Ag from the Ru exhibits a hexagonal structure with Ag bulk spacing, providing a close match to bulk Ag. The first layer of Ag (next to Ru) is reconstructed in a highly symmetrical and regular structure containing monolayer long threading dislocations. We argue that this structure may generally occur to relieve strain in a certain class of heterophase interfaces.

A heterophase interface is an interface between two crystals of different phase or composition. Although such interfaces occur wherever different solid phases are joined, relatively little is known about their structures compared to surface or grain boundary structures. This is because heterophase interfaces are intrinsically more complicated and because they are difficult to directly probe experimentally. High-resolution electron microscopy [1–3], x-ray diffraction [4], and scanning tunneling microscopy (STM) [5–8] have been the major experimental tools for examining structure of interfaces. One way to visualize a heterophase interface is to imagine taking two flat surfaces (of two different phases) and joining them together. The simplest possible resulting structure (and one that is often assumed) would have the two bulk-terminated surfaces meeting at an abrupt interface. Such a structure has been observed in a number of cases, for example Cu(111)/Ru(0001) [5]. In cases where the two joined surfaces have the same symmetry, but different lattice constants and/or rotations, such a structure is known as a moiré structure. If the bulk-terminated surfaces are hexagonal, the moiré structure includes regions where atoms are positioned directly over atoms in the adjacent layer. These energetically costly "on-top" regions are joined by Shockley partial misfit dislocations which separate regions of fcc and hcp stacking. In a moiré structure, misfit dislocations occur only at the interface between the two different phases.

In many cases, free surfaces reconstruct from their bulk-truncated structure to lower their surface energy. Similarly, it is likely that heterophase interfaces will sometimes reconstruct to lower their interface energy. There is some evidence for such behavior in Ag/Cu(111) [6], Co-Pt on Pt(111) [7], and $Pt_{25}Ni_{75}(111)$ [8] although these experiments were performed at thicknesses < 4 ML, raising the question of whether they are representative of a bulk-bulk interface. Two of these experiments are somewhat difficult to interpret due to alloying effects. In this Letter, we present a convincing observation of a heterophase interface reconstruction, which

persists to at least 9 ML of Ag on Ru(0001) and presumably applies for the bulk heterophase Ag(111)/Ru(0001) interface. Our STM observations show that this interface reconstruction effectively relieves the 7% misfit strain between the Ag and Ru bulk lattices. We use atomistic modeling to determine the arrangement of atoms at the interface, thereby revealing the dislocation structure associated with this interface reconstruction. Finally, we consider why this type of reconstruction occurs at the Ag(111)/Ru(0001) interface, but not the Cu(111)/Ru(0001) interface. Our observations demonstrate that the structure of heterophase interfaces can be very complex and that we are far from a complete understanding of the issues determining even equilibrium metal-metal interface structures.

The dislocation pattern present in 1 ML Ag/Ru(0001) has been studied in detail [9]. There are regions where Ag atoms occupy fcc sites on the Ru surface and regions where Ag atoms occupy hcp sites on the Ru surface. These areas are separated by lines several atoms wide, along which Ag atoms are near the bridge sites on the Ru surface. These lines correspond to Shockley partial dislocations. Similar structures have been observed for many strained film systems including the well known Au(111) reconstruction [10].

Here we will consider the pattern present in films of ≥ 2 ML Ag/Ru(0001). Ag was deposited by thermal evaporation at pressure below 2×10^{-10} Torr onto a ~150 °C Ru(0001) substrate cleaned by oxygen adsorption and ~1700 °C flashing. The Ag film was flash annealed to ~500 °C and cooled to room temperature for STM imaging. Films thicker than 1 ML present the highly ordered structure shown in Fig. 1. An important characteristic of this structure is that the top (second) layer of Ag is totally free of any edge dislocations (i.e., it is hexagonal except for small displacements). This point is illustrated by Fig. 1(b), which shows a closed Burger's circuit around one of the black line features of the atomic-resolution STM micrograph. Since there are no dislocations in the top layer, the contrast in the image presumably arises from vertical displacements or
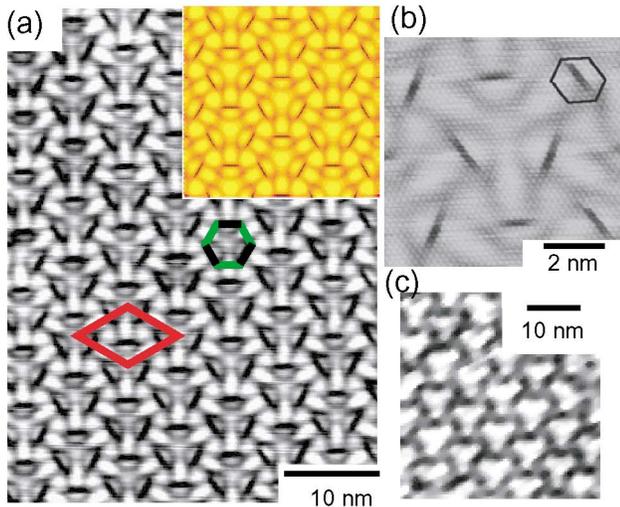
FIG. 1 (color). (a) STM image of a 2 ML film of Ag/Ru(0001). The entire area is covered by a single domain of the dislocation network. The primitive unit cell is indicated in red. A threefold symmetric feature is indicated in green. The color inset shows the height modulation of the EAM calculations. (b) Atomic resolution image with a closed Burger's circuit around black line feature in image, showing the absence of an edge dislocation at the surface layer. (c) STM image of a 6 ML area of Ag/Ru(0001). The structure appears identical to the 2 ML structure except that contrast is reduced.

electronic effects originating in the layers buried beneath the top layer.

From atomically resolved STM images [e.g., Fig. 1(b)], we determined the orientation and characteristic dimensions of the primitive unit cell [red in Fig. 1(a)]. The primitive lattice vectors are in the $\sqrt{3}$ directions and their length is $\sim 13\sqrt{3}$ times the nearest neighbor spacing of the Ag layer. Figure 1(a) also indicates in green a characteristic threefold symmetrical feature comprising three black line segments. By counting atomic rows, we determined the distance between the center of the threefold symmetric feature and the black lines as $\sim 4\sqrt{3}$ times the nearest neighbor spacing of the Ag layer. This measurement is duplicated by our theoretical calculations as will be described.

As previously mentioned, the second layer of Ag is hexagonal. Since it has the lattice constant of bulk Ag, it is expected that this second layer could serve as an ideal substrate for additional layers of bulk Ag. Images of thicker films [e.g., Fig. 1(c)] demonstrate that this is true. Upon adding Ag, the pattern remains largely unchanged except for progressive loss of contrast as the first layer structure is buried deeper by additional layers of Ag.

The STM micrographs suggest that a complex network of dislocations in the first Ag layer allows an excellent match between hexagonal planes of Ag(111) and hexagonal planes of Ru(0001) in spite of the 7% lattice mismatch. Our goal here is to understand how the interface atoms

and interface dislocations are arranged to relieve misfit at this heterophase interface. To this end, we used an atomistic model, specifically, the embedded atom method (EAM) with potentials for Ag and Ru developed previously [9].

Because the STM image had threefold features with black lines suggestive of buried edge dislocations, we constructed a first Ag layer that contained such features. Such threefold features have been called trigons in the literature [11] and we will follow that nomenclature here. (These features have also been called threefold stars [12].) Topologically, the first Ag layer consists of a periodically arranged array of monolayer Ag "islands" with hcp stacking arranged in a "sea" of monolayer Ag with fcc stacking [13]. The lattice vectors for the unit cell were chosen to match the lattice vectors of the STM patterns. (Later we will discuss how the size of the trigons is determined by the chemical potential of Ag.) The trigon structure can be created and relaxed for 1 ML of Ag on Ru(0001) although it is not the minimum energy structure for 1 ML. The atomistic structure of the trigon layer can be seen in the top left picture of Fig. 2. There are edge dislocations with an extra row of first layer Ag atoms at the ends of the three arms of the trigon. These edge dislocations are joined by Shockley partial dislocations.

The STM results show that a second layer of Ag with a perfect hexagonal arrangement can be matched to the trigon layer. To find the corresponding atomistic structure we constructed a second hexagonal Ag layer with the bulk Ag nearest neighbor distance. Considered from the viewpoint of the top Ru(0001) layer, this second Ag layer would have a moiré structure. Based on bulk lattice constants for Ru and Ag, the primitive unit cell for a moiré structure would have primitive lattice vectors in the nearest neighbor direction with length ~ 13 times the nearest neighbor spacing. This means that the primitive lattice vectors of the moiré structure are rotated 30° with respect to the primitive lattice vectors of the trigon structure seen in the experiment and that the area of the moiré primitive cell is one-third that of the trigon unit cell. In this manner, a hexagonal second layer of Ag can be matched to the trigon first layer while avoiding unfavorable on-top sites. Finally, we added a third hexagonal layer of Ag. The relaxed atomic structures are shown in the top pictures of Fig. 2. The densities of the three layers are ordered $D(Ag) < D(Ag_r) < D(Ru)$, where Ag_r denotes the first reconstructed silver layer. The trigons at the two different levels are linked only at the edge dislocations. Both the buried edge dislocations and the Shockley partial dislocations are visible in the STM micrograph and the EAM simulation [Fig. 1(a)]. The lower picture in Fig. 2 shows a perspective view of the structure.

It is common practice to discuss interface dislocation structures in terms of stacking sequences. In the case of heterophase interfaces, this can be quite confusing,

● Ru   ● 1st layer Ag   ● 2nd and 3rd layer Ag
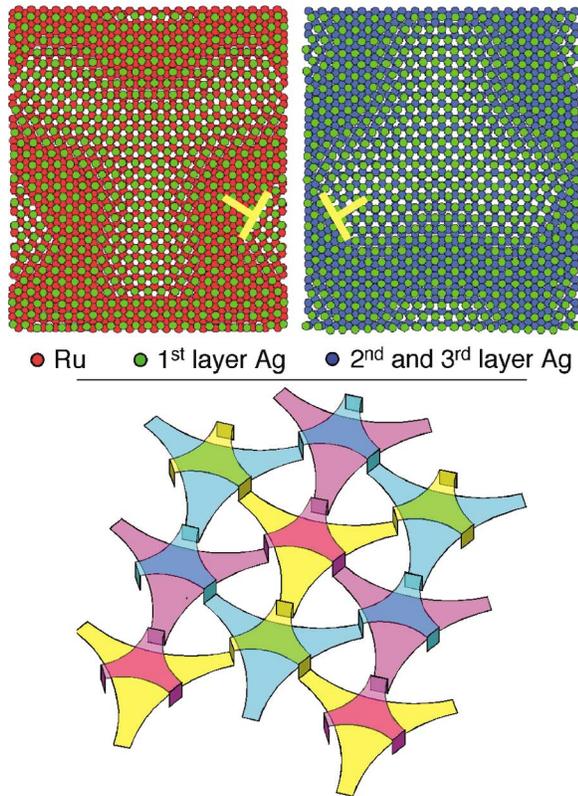
FIG. 2 (color). The top two pictures show the results of the EAM calculation for three layers of Ag on Ru(0001). The left picture shows a view from the reconstructed Ag interface layer into the bulk Ru. The right picture shows a view from the reconstructed Ag interface layer into the two layers of Ag. At the ends of the trigons, there are edge dislocations, one of which is marked in yellow in the two different views. The edge dislocations are identical in both views since they exist only in the reconstructed Ag layer. The Shockley partial dislocations link the edge dislocations and are different in the two views. The bottom picture shows a three dimensional representation of the heterophase interface reconstruction layer (Ag_r). The curved segments represent Shockley partial dislocations at the lower Ru/Ag_r interface and the upper Ag_r/Ag interface. The vertical segments are edge dislocations, which thread between the two interfaces. The network consists of three independent equivalent interwoven dislocation networks shown in yellow, magenta and cyan.

because the lattice vectors are different on the two sides of the interface. Nonetheless, we present a stacking sequence description for the Ag(111)/Ru(0001) interface in Fig. 3 as it shows clearly how on-top sites are avoided in the present configuration. In stacking sequence notation, bulk Ru (hcp) is designated $ABAB$. If one is to avoid the energetically costly on-top sites, the first Ag layer can be placed with stacking sequence $ABABa$ (hcp) or $ABABc$ (fcc). The first Ag layer has a topology of trigons with hcp stacking (green in Fig. 3) surrounded by a sea of fcc stacking (red in Fig. 3). As discussed previously, it is possible to add an additional Ag layer on top of this trigon

1st layer Ag
2nd layer Ag

■ Close packed stackings
relative to Ru(0001)
■ stacking
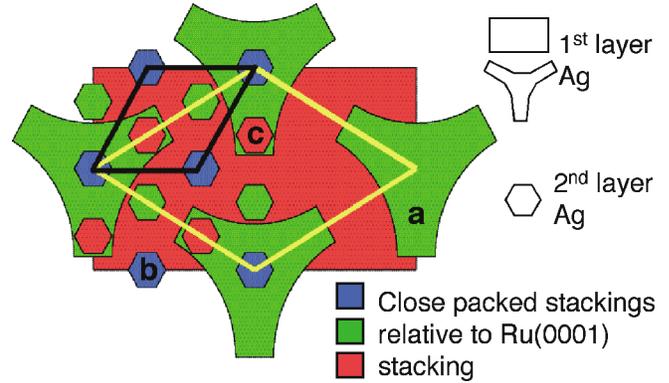
FIG. 3 (color). Schematic diagram of stacking sequences for two layers of Ag on Ru(0001) relative to the Ru stacking ($ABAB$). Small hexagonal areas on the left represent the stacking sequence of the 2nd monolayer. (In reality, the 2nd monolayer completely covers the 1st monolayer). The primitive cell of the moiré pattern between 2nd Ag layer and top Ru layer (before relaxation) is shown in black. Inside of the trigon areas, the stacking sequences are $ABABab$ and $ABABac$. Outside of the trigon areas, the stacking sequences are $ABABca$ and $ABABcb$. On-top sites (represented by a hexagon color superimposed on the same color) are avoided everywhere in the multilayer structure.

structure. With respect to the underlying Ru, this second Ag layer has a moiré structure. This moiré structure is shown schematically in the left-hand part of Fig. 3 by small colored hexagons indicating the stacking sequence of the second Ag layer with respect to the Ru. On-top sites are avoided due to the presence of the first Ag layer.

It is straightforward to calculate the size of the lowest energy trigons by calculating Ag chemical potentials using EAM. We vary the size of the trigons by adding or removing atoms at positions immediately adjacent to the edge dislocations. This process corresponds to edge dislocation climb and changes the number of Ag atoms in the system and the energy of the system. The definition of the Ag chemical potential in the interface layer is $\mu_{Ag} = dE/dN_{Ag}$, where E is the total energy of the system and
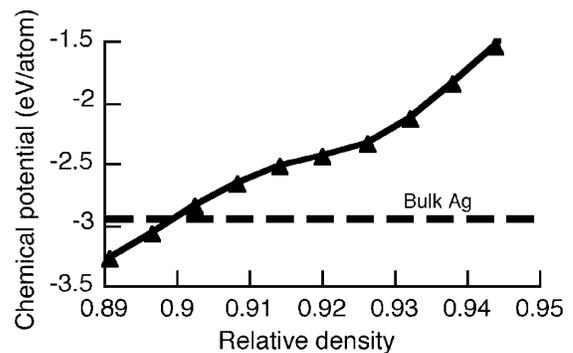
FIG. 4. Calculated chemical potential for Ag in the reconstructed interface layer as a function of its layer density.

N_{Ag} is the number of Ag atoms in the system. Figure 4 shows a plot of this chemical potential as a function of the density of the trigon layer (relative to the bulk Ru density). Since this structure exists in equilibrium with bulk Ag for the multilayer structures, the chemical potential of Ag in the interface layer (Ag_r) must equal the chemical potential of Ag in bulk Ag, which is the cohesive energy of Ag. The predicted density of the Ag interface layer is ~0.9 (relative to the density of the Ru layer), which is closer to the bulk Ag density than the bulk Ru density. This result indicates that the larger trigons are at the Ru/Ag_r interface, a fact not obvious from the experimental data. The predicted trigon size is in excellent agreement with experiment. The EAM calculations shown in Figs. 1(a) and 2 used this predicted trigon size.

We have demonstrated conclusively that a complex heterophase interface reconstruction occurs at the Ag(111)/Ru(0001) interface. This reconstruction involves three interwoven networks of dislocations, which relieve misfit strain in a very efficient manner. It remains to be seen how common this type of interface reconstruction may be. We mention that we have observed this interface reconstruction for Au(111)/Ru(0001) using STM. On the other hand it is not seen for Cu(111)/Ru(0001), in which a moiré pattern is seen for > 3 ML. There are also interface reconstructions previously reported that have apparently identical unit cells for the first and second layers [6,7]. Further experimental and theoretical work [14] will be required to determine the conditions under which heterophase interface reconstructions are favored.

Here we consider briefly why the structure described here is observed for Ag(111)/Ru(0001) whereas a moiré structure is observed for Cu(111)/Ru(0001) [15]. We argue as follows: Based on cohesive energies, a Ru-Ru bond is much stronger than that of a Ag-Ag or Cu-Cu bond, implying that Ru-Cu or Ru-Ag bonds will be stronger that Ag-Ag bonds or Cu-Cu bonds [16]. Thus, we would expect interface reconstructions increasing the density of Cu or Ag next to Ru to be favored since that will increase the number of stronger bonds in the system, thereby lowering the energy. The dislocation networks discussed here produce a layer of intermediate density between the two different metals at the heterophase interface. The density of a Cu(111) plane is higher than that of a Ru(0001) plane, which in turn is higher than that of a Ag(111) plane, due to the relative lattice constants. For Ag/Ru, this interface reconstruction increases the Ag density at the interface and is energetically favored. For Cu/Ru, this interface reconstruction would decrease the Cu density at the interface and thus does not occur.

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[13] Because of the small difference in stacking fault energy [V. Ozolins (private communication)], it is also possible to have fcc islands in an hcp sea. For the sake of clarity, we will discuss only one configuration.
[14] K. Thürmer and J. C. Hamilton (to be published).
[15] We compare these two systems because they have been thoroughly studied and because they have roughly the same percentage misfit, albeit with different signs.
[16] This assumption is based on the postulate of the geometric mean for bond strengths, as described in L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, NY, 1960), 3rd ed. It is also consistent with the thermal desorption temperatures for Ag and Cu from Ru(0001).