PHYSICAL REVIEW B, VOLUME 63, 165431

Determination of buried dislocation structures by scanning tunneling microscopy

J. de la Figuera, A. K. Schmid, N. C. Bartelt, K. Pohl,* and R. Q. Hwang
Sandia National Laboratories, Livermore, California 94551
(Received 5 September 2000; published 6 April 2001)

Using scanning tunneling microscopy on Cu/Ru(0001) thin films we have located the depth at which the cores of misfit dislocations lie below the film surface. The procedure is based on matching areas with unknown structure to areas with a known stacking sequence in the same film. Our results show that dislocations occur not only at the Cu/Ru interface, but also at various levels within the Cu films. Our analysis method should be applicable to the characterization of dislocation structures in other ultrathin film systems.

DOI: 10.1103/PhysRevB.63.165431 PACS number(s): 68.55.Jk, 68.37.Ef, 68.55.Ln

I. INTRODUCTION

Dislocations play a central role in defining many thin film properties. Determining their detailed structure continues to represent a challenging problem to experimentalists. For bulk samples, full characterization of dislocation networks at phase boundaries is sometimes possible through the examination of cross-sectional samples in transmission electron microscopy.[1] However, determining the structure of dislocations that are parallel to the interface is difficult. Recently, scanning tunneling microscopy (STM) has proven effective in imaging the in-plane structure of dislocations and their networks.[2,3] In this report we demonstrate that for close-packed fcc or hcp systems detailed information on the nature of buried dislocations can be extracted from controlled STM experiments. In particular, we are able to determine the atomic plane in which thin film dislocations reside through a careful geometrical analysis.

A basic mechanism for strain relief in thin films is the formation of misfit edge dislocations, thus permitting the atomic density of the film to differ from that of the substrate. In many ultrathin metal-film systems grown on surfaces with hexagonal symmetry[4–7] the misfit dislocations dissociate into stacking fault regions bounded by partial Shockley dislocations.[8] These partial dislocations arrange themselves in a variety of intricate patterns.[9,10]

A prototypical example of these patterns can be found in Cu films of various thickness grown on Ru(0001),[6] where there is a 5.5% in-plane lattice mismatch between the materials in bulk form. The structure of the surface layers of these films has been thoroughly investigated,[6,11–16] but the plane in which the dislocations reside has not yet been resolved by means of a local probe. Figure 1 schematically illustrates the basic problem: it is possible that dislocations at the different levels shown produce similar contrast in a STM image, making the STM measurement ambiguous about the depth of the dislocation cores. The purpose of this paper is to demonstrate how one can determine the depth of dislocations directly from STM using the case of Cu/Ru(0001) as an example. In principle the depth at which dislocations are located could also be extracted from the observed contrast within the STM images. But to do so would require decoupling structural from electronic effects in the topographic STM images and a thorough knowledge of the behavior of the film and the substrate. Our method, being purely geometrical, is free of such constraints.

In the equilibrium structure of one monolayer (ML) of Cu on Ru(0001), the Cu pseudomorphically matches the Ru lattice. In annealed submonolayer films, Cu is found wetting the Ru steps, as in Fig. 2. Additional deposition at room temperature can lead to incorporation of extra atoms into the film, creating edge dislocations[15] [see Fig. 3(a)]. It is energetically favorable to relax the edge dislocations into stacking fault ribbons separated from the unfaulted areas by Shockley partial dislocations on both sides, as seen in Fig. 3(b). This is very prominent in the structure of the 2 ML case as shown in Fig. 4. Arrays of Shockley partial dislocations are found oriented in three symmetrically equivalent domains. The inset shows an atomically resolved image of a pair of Shockley partials and the associated faulted and unfaulted regions. Note that they differ in width, reflecting the different energies of the two stacking sequences present.

To determine the depth of the dislocations we will analyze the stacking sequences of the film in the various faulted and unfaulted regions. The stacking sequences can be extracted by examining how areas of known stacking sequence match areas of unknown stacking sequence. In this way, solving the 1 ML case will provide enough information to solve the 2 ML case. This in turn will allow the analysis of the third monolayer, and so on.

II. EXPERIMENT

The experiments were performed in an UHV STM. The base pressure of the system is 4×10^{-11} torr. The UHV chamber is equipped with an electron spectrometer suitable

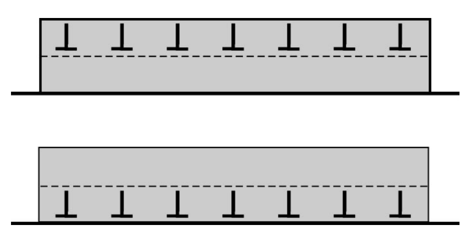

FIG. 1. Sketch of different possibilities of dislocation location in a film with a thickness of two atomic layers. The inverted T symbols mark the locations of the misfit dislocations.

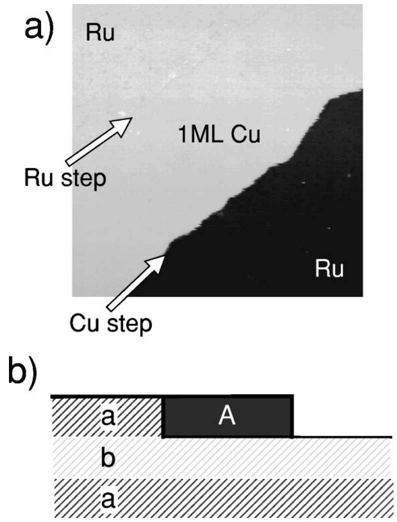

FIG. 2. (a) STM image of a 1 ML Cu island decorating a Ru step. The image size is 91×91 nm^2. (b) Schematic of the stacking sequence of the film.

for Auger electron spectroscopy (AES). The Ru(0001) substrate was cleaned by exposure to oxygen (9 L of O_2) followed by flashing to 1500 °C, repeated several thousand times. After a long series of cycles, Ru oxides form on the surface. These are removed by flashing in vacuum to 1600 °C. Cleanliness was checked by STM and AES. Terraces larger than 0.5 μm can be routinely found in the clean substrate. Cu films were grown by physical vapor deposition

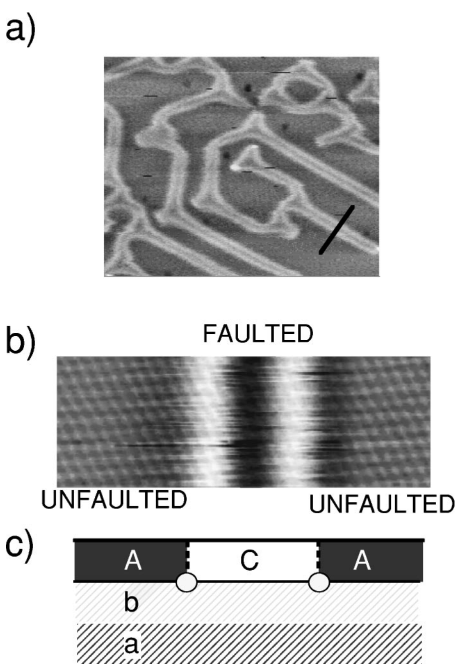

FIG. 3. Dislocation structure of a 1 ML Cu film after additional deposition of ~0.05 ML Cu. (a) 50 nm×45 nm STM image of the film. (b) Atomic resolution detail of the dislocation lines. (c) Schematic of the stacking sequences encountered when following the black line in (a). The white circles mark the positions of the partial Shockley dislocations.

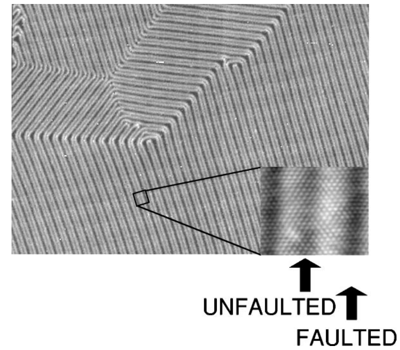

FIG. 4. STM image of a 2 ML Cu/Ru(0001) film. The size is 250 nm×175 nm. The inset shows the same structure with atomic resolution.

from a calibrated metal doser at rates of the order of 1 ML/min, during which the pressure in the system remained below 2×10^{-10} torr. All the films were annealed after growth to 600 °C for about 10 s, and allowed to cool to room temperature before imaging with the STM. In selected cases additional amounts of Cu were deposited on the previously grown film. The STM images are presented in gray scale. When it was necessary to increase the contrast in the presence of steps, either the derivative of the image was added to the original data or the contrast was increased on each terrace individually.

III. DISCUSSION

A. 1 ML Cu on Ru(0001)

The analysis described in this paper is presented in terms of the stacking of fcc and hcp crystals. To represent this stacking the labels *a*, *b*, and *c* will be used in the following to denote the three positions in which hexagonal layers can be stacked. Lower case labels a,b,c will indicate Ru layers and upper case labels A,B,C will refer to Cu layers: a hcp Ru terrace is described as $abab$, where the last letter corresponds to the surface layer. Additionally, a period will separate the substrate layers from the film itself, as in $a.B$. As a shorthand notation we will use a vertical bar to denote a transition in the same level, as in $a.B|C$, where on the same terrace we have both $a.B$ and $a.C$.

STM images of an annealed 1 ML Cu film show a perfect atomic hexagonal arrangement. Hence, two different stacking sequences might possibly describe the single monolayer Cu film: $ab.A$ or $ab.C$ (excluding the topologically possible but physically unlikely case of on-top stacking $ab.B$), where we assumed that the underlying Ru substrate ends in ab. The correct sequence can be determined by imaging the region of Cu film that is attached to a Ru step edge, as shown in Fig. 2(a). The stacking sequence of the Ru terrace on the upper side of the step is aba. If the stacking of the Cu layer were $ab.C$ then there would necessarily be a Shockley partial dislocation near the step edge marking the transition $ab.C|a$ (where the vertical bar indicates a stacking transition on the same level, C to a). As dislocations are not found in this area

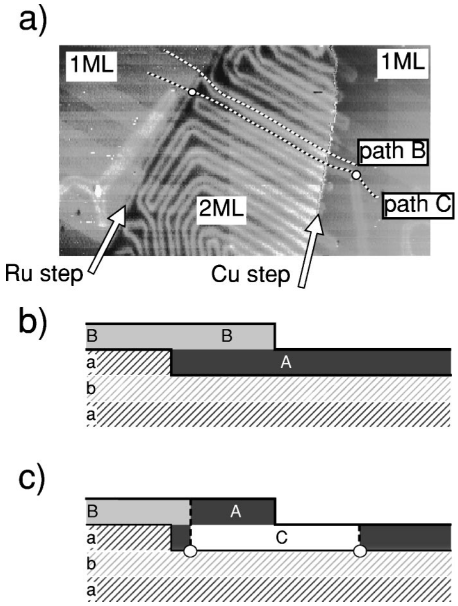

FIG. 5. (a) STM image of a 2 ML Cu island wetting a buried Ru step, surrounded by 1 ML Cu (113 nm$\times$64 nm). Also marked are two paths (B,C) along different dark stripes of the 2 ML island into the adjacent 1 ML Cu.(b) Schematic of the vertical structure of the film when followed along the path marked B in (a). (c) Structure of the film following the path marked as C.

the stacking sequence of the monolayer Cu film has to be $ab.A$, matching the upper terrace aba [as the schematic in Fig. 2(b) indicates].

If additional Cu is deposited at room temperature, dislocations are formed by the introduction of extra atoms in the first layer [see Fig. 3(a)]. The faulted regions must correspond to the $ab.C$ stacking sequence, and so the film must consist of $ab.A|C$ sequences, where the transitions between A and C are the Shockley partial dislocations imaged in the STM as bright lines. The stacking is represented in cross section in Fig. 3(c).

B. 2 ML Cu on Ru(0001)

The process can now be extended to the second Cu layer (Fig. 4). Two-layer-thick films might be composed of up to $3\times3=9$ different stacking sequences. Excluding the highly unfavorable cases of on-top stacking, four plausible possibilities remain: $ab.AB$, $ab.AC$, $ab.CA$, and $ab.CB$. To determine which two of these sequences represent the stripes in the 2 ML Cu films, again regions near steps are considered. The STM image shown in Fig. 5(a) contains a buried Ru step near the left. The flat regions on the left and right sides of the STM image are Cu monolayer regions, while the striped region in the middle is a two-monolayer island. Two dotted lines highlight paths along the narrow and wide dark stripes of the 2 ML island and into the neighboring 1 ML areas. By following these paths across the links to single-monolayer regions, we determine the stacking sequences as follows.

Since single-monolayer regions have hcp stacking, the left side of Fig. 5(a) corresponds to $aba.B$. There are dislocation-free paths starting from the left single-monolayer region, crossing the buried Ru step into the two-monolayer area of the next terrace, and then into the first monolayer area crossing the Cu step. Such a path is marked in Fig. 5(a) as path B and runs through a narrow dark stripe of the striped pattern. The stacking sequence of this region of the 2 ML island must match both the upper and the lower terraces of the pseudomorphic Cu first layer since it does not cross any partial dislocations. Only the bulk Ru hcp stacking sequence fulfills these requirements, so the sequence is $ab.AB$ [see Fig. 5(b)].

A path along a wide dark stripe in the two-monolayer island is indicated by path C in Fig. 5(a). At the right end, path C starts in the single-monolayer hcp region, which is stacked $ab.A$ (hcp stacking). Along the path C [see Fig. 5(a)], a Shockley partial dislocation must be crossed within the single-monolayer region at a point marked with a white circle. Therefore, after this point, the path runs along a faulted section of the single monolayer area. This faulted region has the sequence $ab.C$, as discussed for the 1 ML Cu film (see Fig. 3). Following the path onto the two-monolayer island, no other dislocation is crossed. Therefore the layer below the stripe shares the same C stacking as the faulted single-monolayer region. The stacking in this dark stripe of the island must be $ab.CX$, where X could be either A or B. As concluded in the previous paragraph, the neighboring stripe (upper dotted line) has the stacking sequence $ab.AB$. Therefore, if X were B, the entire second layer would have the same stacking sequence, leaving buried Shockley partial dislocations of opposite sense at the Cu-Ru interface and between the first and the second layers. This is not reasonable because the upper layer would then be pseudomorphic with the substrate and highly strained on top of a partially relaxed first layer. Hence the second layer in the region marked by the lower dotted line must be A and the stacking sequence must be $ab.CA$.

The stripes along paths B and C are separated by a stacking transition where $ab.AB$ is transformed into $ab.CA$. The Shockley partial dislocations in the stripe arrays of the 2 ML areas reside at the Cu-Ru interface: the same buried dislocation that generates the first-layer change $A\rightarrow C$ also changes $B\rightarrow A$ in the second layer. An important feature to note is that the wider dark regions of the stripe structure in the second layer match with the faulted regions of the first layer ($ab.C$). This is a key characteristic that will be used below.

As an alternative method of determining the stacking sequence of 2 ML islands, atomic resolution images across a Cu step [like Fig. 6(a)] can be examined. Following the rows of atoms across the step in Fig. 6(b) indicates the stacking in the upper layer relative to the lower one, giving further support to the sequence already described ($ab.CA$ connected to $ab.C$).

The stripes with the $ab.AB$ sequence are narrower than those with $ab.CA$, implying that $ab.CA$ stripes have lower energy. This experimental result can be compared with *ab initio* calculations of the energies of the four different stacking sequences.[17] The values obtained by both the local-density approximation (LDA) and the generalized-gradient approximation (GGA) are shown in Table I, obtained with

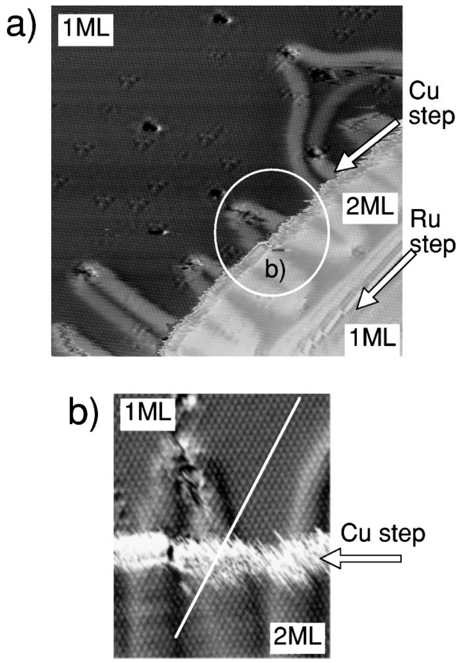

FIG. 6. (a) STM image of a 2 ML Cu region along a Ru step surrounded by a 1 ML high film. The image size is 24 nm $\times 24$ nm. Dislocations cross the Cu step. (b) Detail of the area marked by a white circle in (a), showing that one of the stacking positions of the last layer of the 2 ML part of the film ($ab.CA$) is the same as the pseudomorphic 1 ML Cu ($ab.A$).

the ultrasoft pseudopotential based code VASP.[18] The results follow the heuristic idea that the energies of ''fcc''-like sequences have lower energy than ''hcp''-like sequences when considering not only the two copper layers but also the topmost Ru layer. In the case of the 2 ML island of Fig. 5(a), the structures $ab.AB$ (narrower) and $ab.CA$ (wider) have energies of 21 (19) and 4 (0) meV, respectively, from LDA (GGA) calculations. The structures we determined from the STM data are indeed energetically plausible.

Further information about the competition between different stacking sequences can be gained by considering 2 ML Cu islands that are not attached to steps. Inspection of Fig. 7(a) reveals that there are two kinds of island that are easily distinguished by the orientation of their nearly triangular shapes, labeled in the figure as types I and II. Type I islands have wide dark stripes connected to stacking fault areas in the first layer, like the 2 ML islands wetting the steps described above. Therefore they have identical stacking se-

TABLE I. Calculated energies of the four expected stacking sequences in 2 ML Cu films on Ru(0001). Both LDA and GGA results are shown. All the results are in meV, relative to the lowest energy structure. Type I and type II refer to the sequences found in islands as described in the text.

	Type I		Type II	
	$ab.AB$	$ab.CA$	$ab.AC$	$ab.CB$
LDA	21	4	0	28
GGA	19	0	5	17

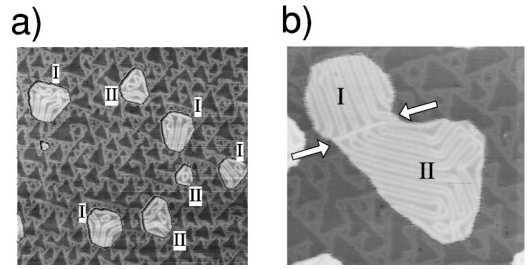

FIG. 7. (a) 85 nm wide STM image of the two families of 2 ML islands, designated as types I and II. (b) 72 nm wide STM image of coalescing islands of different types. Note the line along the boundary between them (marked by arrows in the image).

quences $ab.AB|CA$ separated by Shockley partials at the Cu-Ru interface. The stacking sequence of type II islands can be determined by observing how they join to 1 ML areas surrounding them. The two remaining possibilities for the stacking sequence of the type II islands are $ab.AC|CB$. Considering the connection of the stripes to the 1 ML Cu, it can be seen that the wide dark stripes of type II islands correspond to the ab.AC sequence and the narrow dark stripes to $ab.CB$. Again these dislocations are at the Cu/Ru interface. Further information can be gained by observing how islands of different types get connected, as in Fig. 7(b). At the border between the two types of island, an additional dislocation is present. In crossing this dislocation, wide dark stripes on one side connect to narrow dark stripes on the other. This boundary represents the stacking transitions $ab.AC|AB$ and $ab.CA|CB$. Therefore the dislocation separating the two island types does not reside at the Cu/Ru interface, but rather at the interface between the first and second Cu layers.

Again, *ab initio* calculations support the interpretation of the stacking sequence of the type II islands where the $ab.AC$ (wider) sequence has lower energy than the $ab.CB$ (narrower) sequence by about 28 (12) meV from LDA (GGA) calculations (Table I).

C. 3 ML Cu on Ru(0001)

To extend the procedure to 3 ML areas, a film with a thickness between 2 and 3 ML is grown. After annealing, the morphology of such a film [see Fig. 8(a)] is composed of patches of 3 ML areas wetting the Ru steps while the remainder of the substrate is covered by 2 ML. The structure visible on top of the 3 ML areas is a network of bright lines forming parallel lines, trigons and ''bright stars'' [see Figs. 8(a,d)].[6] The bright lines are again buried Shockley partial dislocations separating regions of different stacking. There remains a width difference between the dark stripes in the 3 ML islands: wide and narrow dark stripes alternate in the same way as in 2 ML Cu films. Our purpose is again to find the stacking sequence of those areas, and thus to locate the level at which the Shockley partial dislocations lie. Noteworthy in Fig. 8(a) is the presence of an additional type of line defect which crosses the 3 ML region, shown with atomic resolution in Fig. 8(d). It crosses the other dislocations in the film, joining wide to narrow dark stripes and vice versa. In the

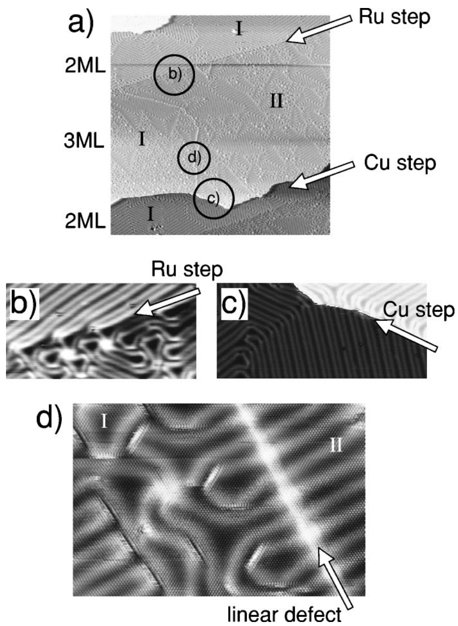

FIG. 8. (a) 490 nm wide STM image of an incomplete 3 ML film. The 2 ML area in the top of the image is on the next (upper) Ru terrace. (b) Smaller scale image (76 nm$\times$37 nm) of the connection of the upper 2 ML area with the 3 ML one. The wide dark areas are connected without dislocations across the buried Ru step. (c) The connection between the 2 ML lower area and the 3 ML upper area, where both are on the same Ru terrace (the size is 98 nm $\times$44 nm). (d) Atomic resolution detail of the linear defect found on the 3 ML area (40 nm$\times$27 nm).

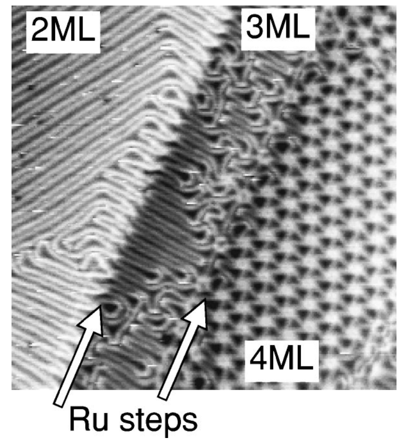

FIG. 9. (a) 150 nm wide STM image of a multilayer film. Shown in the image are 2, 3, and 4 ML areas on top of different underlying Ru terraces so the upper Cu surface is nearly at the same height.

upper left region of Fig. 8(a) the linear defect is seen to cross into the upper 2 ML part of the film where it becomes a dislocation between 2 ML areas. As discussed above, such a defect corresponds to a partial dislocation between the first and the second Cu layers. In order to resolve the stacking sequence problem we proceed to find the way in which the 3 ML film is connected to neighboring 2 ML areas.

The way the central 3 ML area joins the upper 2 ML area can be determined by looking near to the upper (buried) Ru step of Fig. 8(a). The wide dark stripes are continuously connected across the Ru step without crossing *any* dislocation [see Fig. 8(b)]. Figure 8(c) shows in detail the part of the film where the 3 ML part connects to the 2 ML area on the same terrace crossing the lower Cu step of Fig. 8(a). The narrow dark stripes in the 3 ML area are connected to the wide ones in the 2 ML area, and vice versa.

Both 2 ML areas on the top and bottom of Fig. 8(a) are of the same kind, i.e., they are both either type I or type II. This is indicated by the opposite orientations of the triangular joints of the wide dark stripes in the two 2 ML areas. This is expected on consecutive Ru terraces, due to the hcp nature of the substrate, which switches the last layer from b to a when crossing substrate steps.

We assume for now that both 2 ML areas are of type I. On the upper terrace [top of Fig. 8(a)], the stacking sequence has to include the bulklike sequence $aba.BA$ for the narrow dark stripes. The wider ones are then $aba.CB$. As the wide dark stripes in the 3 ML area are connected without dislocations to $aba.CB$, their sequence has to be $ab.ACB$. Now consider the Cu step, where dislocations (bright lines) appear to cross it. If the dislocations have the same character in the 3 ML region as they do in the 2 ML region, then as they are the boundary—in the 2 ML region—between $ab.AB$ (narrow dark stripe) and $ab.CA$ (wide dark stripe), they should also be the boundary in the 3 ML region between $ab.ACB$ (wide dark stripe) and $ab.CBA$ (narrow dark stripe), i.e., crossing the dislocation changes layers in the order $A\rightarrow C\rightarrow B\rightarrow A$. So the stacking sequence in the 3 ML part considered is $ab.ACB|CBA$. It should be noted that the lower two layers of this 3 ML sequence are the same as the type II 2 ML islands [and they have been labeled as such in Figs. 8(a,d)].

If we had done the same analysis on the left side of the linear defect in Fig. 8(d), the sequences $ab.ABC|CAB$ would have been found. The lower two layers are the same layers of type I 2 ML islands. Any other combination of stacking sequences would not be consistent with the crossings of all steps and boundaries considered (2 ML to 3 ML, 3 ML to 2 ML, 2 ML to 2 ML, and 3 ML to 3 ML).

The 3 ML film is composed of two stacking sequences separated by partial dislocations at the Cu-Ru interface. When crossing the linear defect in Fig. 8(d), the last two Cu layers are changed into their twin configuration, from BC to CB and from AB to BA. This defect can be considered the start of a twin boundary. Its orientation is perpendicular to the partial dislocations that lie at the Cu-Ru interface. For thicker films we would describe it as a $\Sigma 3\langle 112\rangle$ boundary.[8] A model for such a boundary has been proposed in terms of individual partial dislocations[19] lying in consecutive layers. Such a model is supported by our determination of the stacking sequence for 2 ML and 3 ML films.

The procedure can be continued in principle for thicker films through the use of incomplete films, as shown in Fig. 9 for the 4 ML case. The same structures found at 2 ML and up are consistent with the experimental observations, i.e., fcc continuation of pairs of sequences with the added complication of two different twinlike pairs that share the lowest Cu layer.

IV. SUMMARY

To identify the stacking sequence of Cu films on Ru(0001) we have examined films with incomplete layers. The structure of films with thickness between 1 and 3 ML has been determined by a step-by-step comparison of how unknown parts of a film match with regions of known stacking sequence.

The result from the analysis is the presence of several competing stacking sequences for each film thickness. The different stacking sequences are separated by Shockley partial dislocations at the Cu-Ru interface as determined also by means of reciprocal space techniques,[16] although some dislocations located at higher levels can also be found. For thicker films, all the stacking sequences correspond to fcc Cu.

ACKNOWLEDGMENTS

This work was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, of the U.S. Department of Energy under Contract No. DE-AC04-94AL85000. J.d.l.F. acknowledges financial support from the DGICyT through Grant No. PB96-0652.

*Permanent address: Dept. of Physics, University of New Hampshire, Durham, NH 03824.

[1] *Materials Interfaces*, edited by D. Wolf and S. Yip (Kluwer Academic Publishers, Dordrecht, 1992).
[2] R. Stalder, H. Sirringhaus, N. Onda, and H. von Kanel, Ultramicroscopy **42**, 781 (1992).
[3] M. Schmid, A. Biedermann, H. Stadler, and P. Varga, Phys. Rev. Lett. **69**, 925 (1992).
[4] J.V. Barth, H. Brune, G. Ertl, and R.J. Behm, Phys. Rev. B **42**, 9307 (1990).
[5] H. Brune, H. Röder, C. Boragno, and K. Kern, Phys. Rev. B **49**, 2997 (1994).
[6] C. Günther, J. Vrijmoeth, R.Q. Hwang, and R.J. Behm, Phys. Rev. Lett. **74**, 754 (1995).
[7] M. Hohage, T. Michely, and G. Comsa, Surf. Sci. **337**, 249 (1995).
[8] J.P. Hirth and J. Lothe, *Theory of Dislocations* (Krieger Publishing Company, Florida, 1992).
[9] R.Q. Hwang and M.C. Bartelt, Chem. Rev. **97**, 1063 (1997).
[10] C.B. Carter and R.Q. Hwang, Phys. Rev. B **51**, 4730 (1995).
[11] G. Pötschke *et al.*, Surf. Sci. **251**, 592 (1991).
[12] J.C. Hamilton and S.M. Foiles, Phys. Rev. Lett. **75**, 882 (1995).
[13] K. Meinel, H. Wolter, C. Ammer, and H. Neddermeyer, Surf. Sci. **401**, 434 (1998).
[14] S.D. Ruebush *et al.*, Surf. Sci. **387**, L1041 (1997).
[15] A.K. Schmid *et al.*, Phys. Rev. Lett. **78**, 3507 (1997).
[16] H. Zajonz *et al.*, Surf. Sci. **447**, L141 (2000).
[17] The energies of the different stacking sequences were computed for Cu layers adsorbed on a six-layer slab of hcp Ru with a supercell dimension of 12 layers. The bottom three Ru layers were held fixed; the coordinates of all the other atoms were relaxed until the forces were less that 0.02 eV/Å. A $12\times12\times1$ k-point mesh was used.
[18] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
[19] C.B. Carter, D.L. Medlin, J.E. Angelo, and M.J. Mills, Mater. Sci. Forum **207-209**, 209 (1996).