Cu-O atomic chains observed on an ultrathin film of Cu(110)

Ruonan Guan
Laboratory of Atomic Imaging of Solids, Institute of Metal Research, Academia Sinica, Shenyang 110015, China

Ri-Sheng Li*
Laboratory of Atomic Imaging of Solids, Institute of Metal Research, Academia Sinica, Shenyang 110015, China; State Key Laboratory of Corrosion and Protection of Metals, Chinese Academy of Science, Shenyang 110015, China; and International Centre for Materials Physics, Academia Sinica, Shenyang 110015, China

Shu-Hua Xu† and Shu-You Li
Laboratory of Atomic Imaging of Solids, Institute of Metal Research, Academia Sinica, Shenyang 110015, China

H. Hashimoto
Okayama University of Sciences, 1-1, Ridai-Cho, Okayama 700, Japan
(Received 29 November 1994; revised manuscript received 21 March 1995)

The fringe contrast observed in a copper film with its Cu[110] parallel to the incident electron beam has been investigated by high-resolution electron microscopy (HREM). According to a geometrical analysis for these fringes, it was assumed that they originated from the Cu-O chains adsorbed on a Cu(110) surface. This assumption was confirmed by a multislice image simulation on the basis of the electron diffraction and imaging theory using an added-row reconstruction model. Our calculation indicates that an added-Cu-O-chain surface reconstruction can generate a regular fringe pattern with sufficient contrast in a thin copper film with a thickness of several nanometers. The present study demonstrates the potential of HREM to investigate surface structures and surface reaction of ultrathin films at the atomic level.

As demonstrated by numerous studies[1–7] the conventional high-resolution electron microscopic (HREM) images, i.e., the images in plan view, show simultaneously the bulk and surface information. In most cases, however, such information cannot be immediately obtained by simply looking at the images. If we can extract the surface information from this composite images with the aid of well-established simulation techniques, the plan view imaging mode in HREM may provide another approach to solve surface structure, as well as to investigate surface reaction at the atomic level.

It is well known that during electron microscopic observation many variations in the specimen will take place, the extent of which depends on the energy and the current density of the incident electron beam, the irradiation time, and the property of the target material. For example, when the energy of the electron beam is greater than 200 keV, a knock-on sputtering occurs, which is caused by direct collision of the energetic electrons with the nuclei of the target atoms.[8] Obviously, due to sputtering as well as other electron-beam-enhanced reactions, the contaminant adhered on the specimen surface will be removed, and the specimen will be further thinned. Furthermore, a clean metal surface may be oxidized during EM observation, despite the fact that the residual gases contain not only the oxygen-containing gases, such as water vapor, carbon oxides, and oxygen, but also hydrogen, hydrocarbon, and nitrogen. Such a phenomenon that a clean metal surface interacts preferentially with oxygen rather than with other gases to form surface oxide has been demonstrated by a number of experiments. For example, the formation of surface oxides during EM observations has been reported on silver[9] and palladium.[10] It was also reported that oxygen rather than carbon was readsorbed on a clean Ni (Ref. 11) and Cu (Refs. 12–14) surface under electron-beam irradiation in a ultra-high and a high-vacuum chamber. These experiments reveal a possibility that we can follow the adsorption process of oxygen on a clean metal surface during EM observation.

Recently, we have explored such a possibility. The HREM observations were carried out in a JEM 2000EX microscope. The thin copper film was prepared by Ar-ion thinning of a pure (with purity of 99.99 wt. %) copper sheet (with a thickness of 50–70 μm) under a 1.33×10^{-2} Pa Ar atmosphere. In order to investigate the reaction of oxygen with a clean copper surface, the cleaning effect caused by high-energy electron-beam irradiation was used, and the same field was under continuous examination. After observing for 350 min, most of the copper film in the previous field was removed, leaving an ultrathin film at the center, Fig. 1. Figure 2 shows, the magnified images of the region outlined in Fig. 1, where some extra fringes, in addition to the lattice image of the substrate, could be clearly observed. In this image, the two sets of Cu{111} planes, i.e., Cu($\bar{1}11$) and Cu($1\bar{1}1$), are marked by bars and the direction of Cu[001] and Cu[$1\bar{1}0$] are marked by arrows, to illustrate the geometrical and crystallographic features of the extra fringes with respect to the copper substrate. By carefully analyzing the observed results, the following points can be noted:

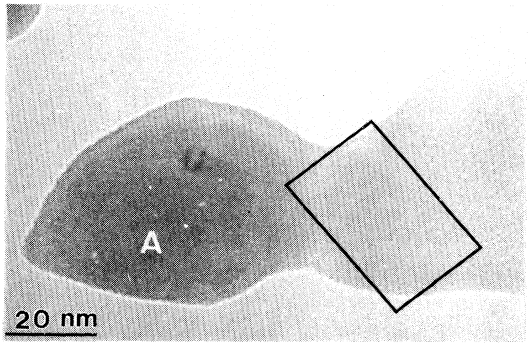

FIG. 1. Variations of a copper film during electron microscopic observation. After observation of 350 min.

(1) The extra fringes can be observed by HREM only when the copper film becomes sufficiently thin. This suggests that the fringe contrast depends sensitively on the thickness of the sample. (2) The arrangement of some fringes is regular. For example, those marked with 1–5 in Fig. 2 arrange themselves along the direction of Cu[001] with a fringe spacing of 0.51 nm, which equals to the double spacing of Cu{110}. (3) While the fringes generally arrange themselves as straight parallel lines, the linearity will change locally when these lines meet a surface or subsurface defect, as indicated by *J* in Fig. 2.

According to a number of recent scanning-tunneling-microscopy (STM) studies on oxygen-included reconstruction at the Cu(110) surface,[15–18] it is known that on a clean Cu(110) surface at 300 K, a finite concentration of mobile Cu adatoms is created by evaporation from step edges and terrace patches. These Cu adatoms on the Cu(110) surface diffuse rapidly even at room temperature. They are stabilized with dissociated O atoms, forming an added Cu-O row preferentially along Cu[001] on the Cu(110) surface. The arrangement of these Cu-O chains is shown in Fig. 3, where large circles represent the atoms of the first layer of Cu(110), the hatched circles and black dots represent, respectively, the Cu and O atoms in the Cu-O chains. We can see from this figure that the Cu adatom is situated at the twofold hollow sites consisting

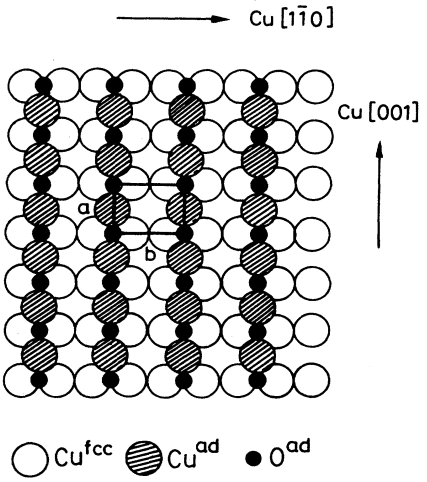

FIG. 3. Schematic diagram of an added-row model of the Cu(110)-(2×1)O reconstruction.

of four Cu atoms beneath it, while the coadsorbed O atom occupies the twofold bridge site. At the saturation oxygen coverage of 0.5 ML (monolayer), these added Cu-O chains arrange themselves parallel to each other with a spacing of 0.51 nm, establishing the well-known Cu(110)-(2×1)O reconstruction. Such an added-row model is equivalent to the missing-row model at saturation coverage, supports most previous results, and has been widely accepted. Comparing our results of a spacing of fringe of 0.51 nm shown in Fig. 2 with the added-row model, we can see that the spacing of the fringes equals also to the spacing of two adjacent Cu-O chains in this model. In addition, both the fringes and the Cu-O chains all arrange themselves parallel to Cu[001]. Therefore, we assume that the observed fringes originate from the Cu-O chains adsorbed on the Cu(110) surface.

The question is whether or not such an adsorption layer can be observed by HREM, because it may be too thin, as compared with its substrate, to be imaged with sufficient contrast? Second, if it can be observed, what is

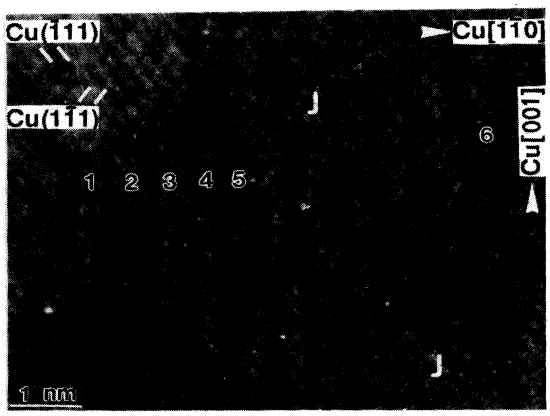

FIG. 2. Magnified image of the outlined part in Fig. 1.

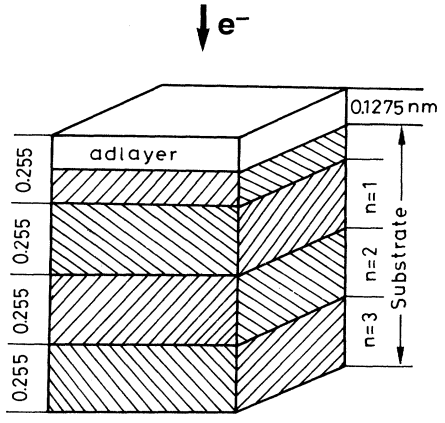

FIG. 4. Multislice model for image simulation.

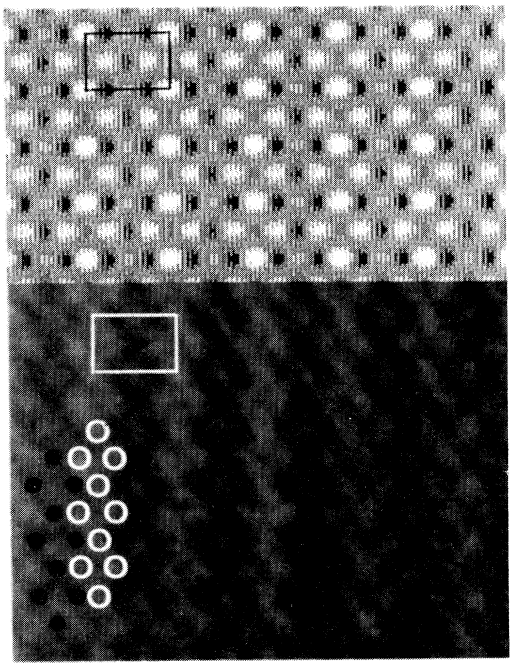

FIG. 5. Comparison of the calculated image (upper) with the observed image (lower).

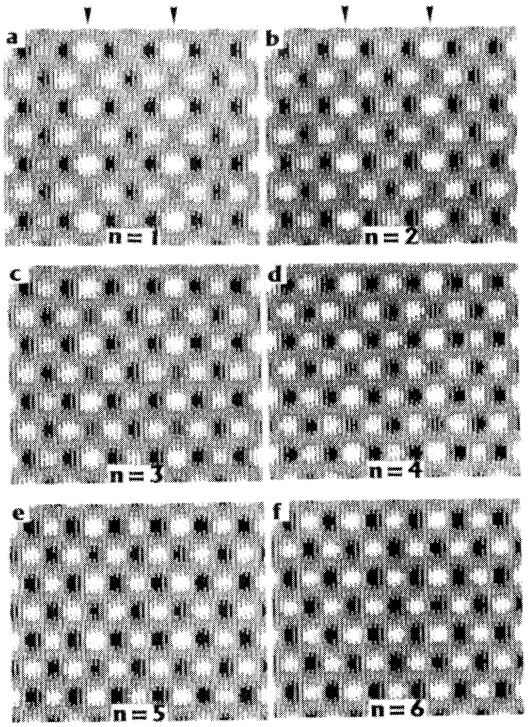

FIG. 6. Variation of the contrast of the imaging dots in the calculated images with different substrate thickness.

its image like? In other words, does an agreement exist between this image and the fringes observed presently? We will answer these questions using the simulation results calculated by the well-known multislice method on the basis of the electron diffraction and imaging theory. The program used in our calculation was provided by Beijing Laboratory of Electron Microscopy, Chinese Academy of Sciences. The parameters used in the calculation are given in Table I.

Figure 4 shows a multislice model used in our calculation. The first layer at the top of the figure represents phase grating 1, which consists of an adlayer and the top layer of the substrate. This overlapping layer has a thickness of 0.255 nm, assuming that both the adlayer and the top layer of the substrate all have a thickness of 0.1275 nm. The second layer also having a thickness of 0.255 represents the phase grating 2 beneath the phase grating 1, which consists of two Cu(110) layers. n indicates the number of the phase grating 2. We calculated ten images with n varying from 1 to 10. The case of $n=1$ represents the adsorption of Cu-O chains on a substrate consisting of three Cu(110) atomic layers. Obviously, in this case the substrate thickness is 0.3825 nm and the calculation thickness is 0.51 nm. Similarly, the case of $n=2$ represents the adsorption of Cu-O chains on a substrate consisting of 5 Cu(110) layers, with a substrate thickness of 0.6375 nm and a total thickness of 0.765 nm, including the Cu-O chains, etc. A thickness of each layer smaller than 0.255 nm has also been tried, but no appreciable influence on the calculated results has been found.

TABLE I. Electron optical parameters used.

Incident electron beam energy	200 keV
Energy spread	50 eV
Beam convergence	0.00075 mrad
Spherical aberration (Cs)	0.7 mm
Physical aperture minimum	0
maximum	0.6 Å^{-1}
Beam tilt away from zone axis	0
Defocus (Δf)	around 81 nm

The upper part of Fig. 5 shows the calculated result for $n=1$, the bottom part is the magnification of the observed fringes shown in the left part of Fig. 2. In Fig. 5, the black and white frames indicate, respectively, the corresponding unit cell in the calculated and the observed images. We show schematically the details of the fringe contrast in the observed image with white circles and black dots marked in the left part of the figure. They suggest that the observed bright fringe alternating with the dark fringes can be regarded as one that consists of a series of bright-dot rhombi alternating with a series of dark-dot rhombi along the Cu[001] direction. It is interesting to note that similar contrasting details can also be seen in the calculated image. Such a good agreement in the fringe contrasting details between the observed and the calculated images strongly suggests that the observed fringes with a spacing of 0.51 nm certainly originate from the added Cu-O chains in the Cu(110)-(2×1)O reconstruction.

We shall see how the contrast of the calculated image changes with the substrate thickness? Figures 6(a)–6(f) show six different calculated results for six different sub-

strate thicknesses. We can see from Fig. 6 that when the thickness of the substrate equals 0.3825 nm, the thickness ratio, i.e, the ratio of the thickness of the adsorption layer to that of the substrate is 33%, the fringe pattern caused by surface reconstruction as well as their contrast details are rather clear. This feature remains till the thickness of the substrate increases to 0.6375 nm, where the thickness ratio is 20%. Afterwards, this feature becomes smeared due to the increasing of the substrate thickness. However, even when the substrate thickness increases to 1.6575 nm, where the thickness ratio is only 7%, the contrast differences caused by surface reconstruction in the calculated images are still distinguishable.

Finally, we should point out the following three points: (1) We have also simulated for other three possible model. None could agree with our observation better than with the added-row model. In addition, in our simulation, the value of the defocus was varied from 70 to 100 nm and the best results was observed at $\Delta f = 81 \pm 1$ nm, which corresponds to our operating condition. This fact excludes a speculation that by changing the defocus, any reasonable model can be made to match experiment to the extent shown in this paper. (2) In the simulation, we excluded the role of the contaminant such as carbon responsible for the structure observed, because, as indicted in the introduction, in a previous study, we have demonstrated that oxygen rather than carbon readsorbed on a clean Cu surface under electron-beam irradiation in a vacuum chamber.[12] Furthermore, we have observed at some places, the observed structure transformed into a crystalline copper oxide rather than other compounds under electron-beam irradiation. (3) Although STM first gave the atom-resolved image of the Cu-O chains, the HREM can simultaneously reveal surface and subsurface structure, thus shedding new light on the relation between two. Indeed, we have observed many interactions of the subsurface defects with the Cu-O chains leading to their directions locally changing, one such example was indicated by *J* in Fig. 2. Since the aim of this paper is to reveal the potential of HREM to investigate the surface structure and surface reactions, a detailed analysis of such an interaction will be described in future paper.

This project is supported by the National Natural Science Foundation of China and the National Material Committee of China under Contract No. 592910003. The author would like to thank Professor K. H. Kuo for reading this manuscript.

*Author to whom correspondence should be addressed.
†Present address: Department of Applied Physics, South China University of Technology, Guangzhou 510641, China.

[1]W. Krakow, Surf. Sci. **111**, 503 (1981).
[2]K. Yagi *et al.*, *Crystals, Growth, Properties, and Applications,* edited by H. C. Freyhardt *et al.* (Springer-Verlag, Berlin, 1982), Vol. 7, pp. 48–74.
[3]G. Nihoul *et al.*, Ultramicroscopy **12**, 353 (1984).
[4]S. Ozawa *et al.*, in *Evolution of Thin Film and Surface Microstructure,* edited by C. V. Thompson, J. Y. Tsao, and D. J. Srolovitz, MRS Symposia Proceedings No. 202 (Materials Research Society, Pittsburgh, 1991), p. 311.
[5]Y. Haga and K. Takayanagi, Ultramicroscopy **45**, 95 (1992).
[6]P. Xu *et al.*, Surf. Sci. **285**, L479 (1993).
[7]D. N. Dunn *et al.*, Surf. Sci. **294**, 308 (1993).
[8]P. C. Townsend, Top. Appl. Phys. **52**, 147 (1983).
[9]E. A. Lodge and J. M. Cowley, Ultramicroscopy **13**, 215 (1984).
[10]H. Q. Ye *et al.*, Surf. Sci. **250**, 90 (1991).
[11]R. S. Li *et al.*, Appl. Surf. Sci. **8**, 465 (1981).
[12]R. Guan, R. S. Li, S. H. Xu, and Y. D. Yu, Chin. J Mater. Res. (Suppl. I) **533**, 486 (1994).
[13]R. Guan *et al.*, Scr. Metall. Mater. **30**, 889 (1994).
[14]R. Guan *et al.*, Surf. Sci. **326**, L467 (1995).
[15]D. J. Coulman *et al.*, Phys. Rev. Lett. **64**, 1761 (1980).
[16]J. Winterlin *et al.*, J. Vac. Sci. Technol. B **9**, 902 (1991).
[17]F. Jensen *et al.*, Phys. Rev. B **41**, 10 233 (1990).
[18]Y. Kuk *et al.*, Phys. Rev. B **41**, 12 393 (1990).

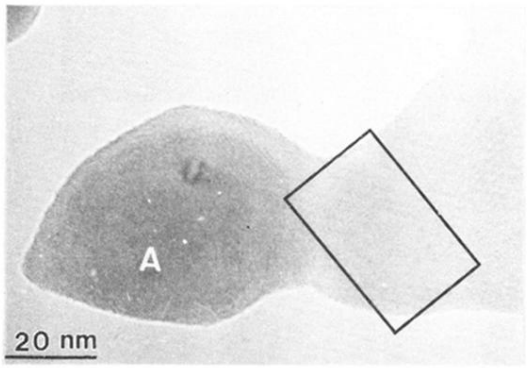

FIG. 1. Variations of a copper film during electron microscopic observation. After observation of 350 min.

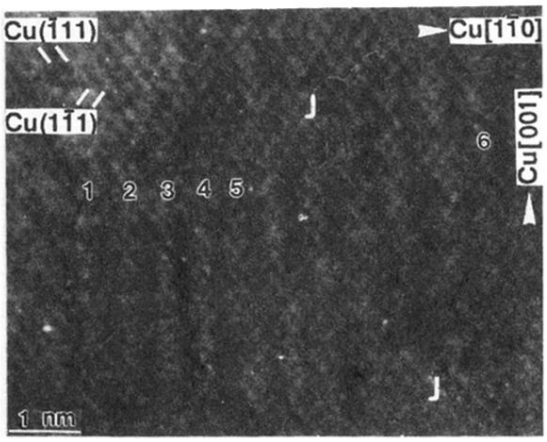

FIG. 2. Magnified image of the outlined part in Fig. 1.

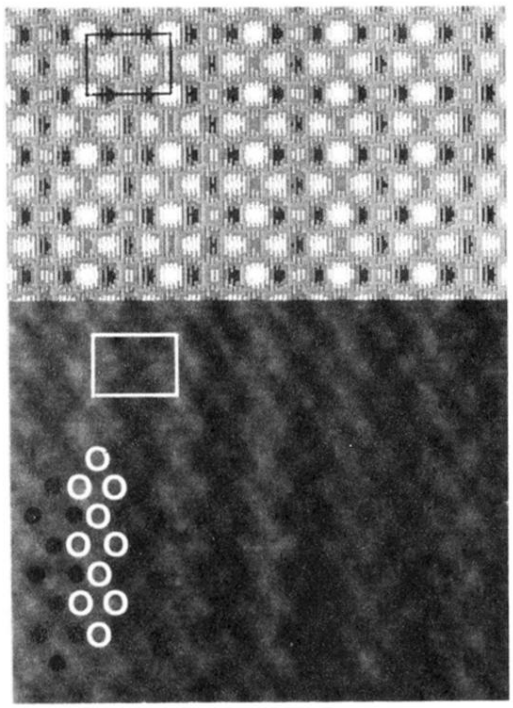

FIG. 5. Comparison of the calculated image (upper) with the observed image (lower).

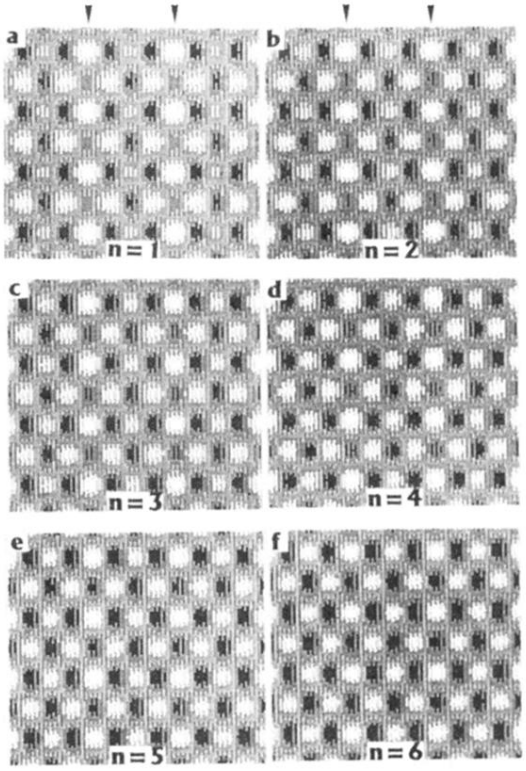

FIG. 6. Variation of the contrast of the imaging dots in the calculated images with different substrate thickness.