Microsc. Microanal. Microstruct. **8** (1997) 167–174 JUNE **1997**, PAGE 167

Ag/Cu(111): An Incommensurate Reconstruction Studied with Scanning Tunnelling Microscopy and Surface X-Ray Diffraction

Bernard Aufray (1), Mats Göthelid (1), Jean-Marc Gay (1),
Christine Mottet (1), Erik Landemark (2), Gerald Falkenberg (3),
Lars Lottermoser (3), Lorenz Seehofer (3) and Robert L. Johnson (3)

(1) CRMC2-CNRS, Campus de Luminy, Case 913, 13288 Marseille Cedex 9, France
(2) Risø National Laboratory, Dept. of Solid State Physics, 4000 Roskilde, Denmark
(3) Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149,
22761 Hamburg, Germany

(Received June 3; accepted June 27, 1997)

PACS.61.16.Ch – Scanning probe microscopy: scanning tunneling, atomic force, scanning optical, magnetic force, etc.
PACS.68.55.Jk – Structure and morphology; thickness
PACS.61.10.-i – X-ray diffraction and scattering

Abstract. — We present the first results of a combined scanning tunneling microscopy (STM) and surface X-ray diffraction (SXRD) study of Ag monolayer deposited on Cu(111). The STM images of Ag monolayer show a periodic frame of triangles, 4 or 5 atomic row wide with 1 or 3 atoms protruding in the centre respectively. Away from the triangles, the corrugation of the atomic rows is about 0.05 Å while the depth of the triangles is about 0.5 Å. SXRD shows an "average" Ag surface unit cell (9.43×9.43) times the Cu(111) surface unit cell without rotation in good agreement with STM observations.

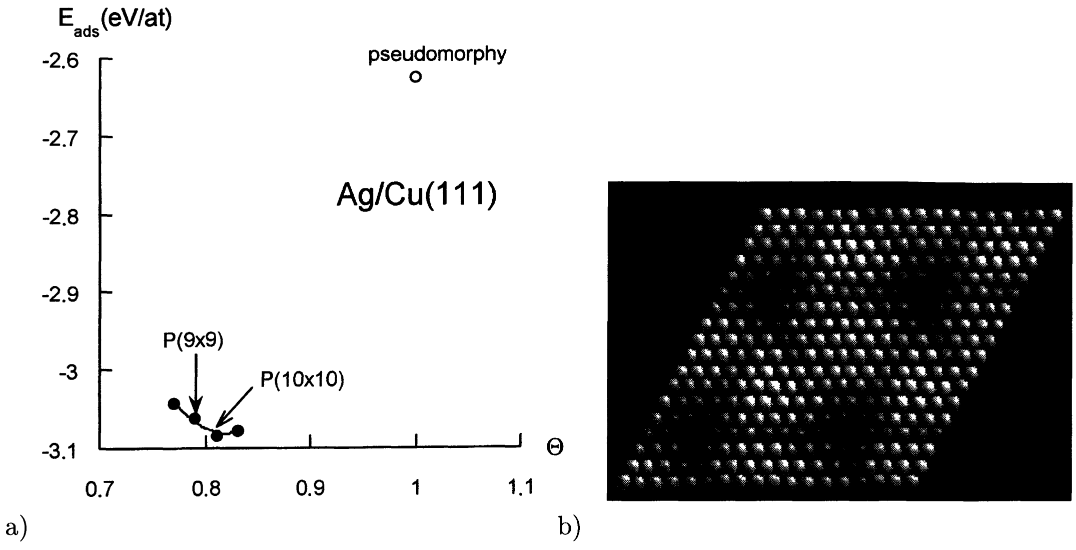
1. Introduction

It is well known that the Ag growth on a Cu substrate at room temperature is of layer by layer type [1]. This behaviour is a consequence of a lower surface energy of Ag compared to Cu, and also that the interface energy is even weaker than usual for metals [2]. The Ag monolayer on Cu(111) displays a ($9 \pm 1 \times 9 \pm 1$) Low Energy Electron Diffraction (LEED) pattern [3]. In this so-called pseudoepitaxy the deposited Ag layer adopts the same hexagonal closed-packed symmetry as the substrate surface with a lattice parameter very close to that of bulk Ag. The (9×9) surperstructure is explained considering the bulk lattice parameters of Ag and Cu which are almost commensurate with the ratio $d(\mathrm{Ag})/d(\mathrm{Cu})$ close to 9/8. Since in this type of superstructure many atoms occupy "less favourable positions" with respect to the substrate one can expect a strong process of relaxation.

The Ag submonolayer (0.5 ML) on Cu(111) has been previously studied by STM [4]. In that study, the authors observed Ag islands slightly compressed relative to bulk Ag. These Ag islands formed a mixture of superstructures close to 9×9 slightly rotated relative to the substrate axes. The corrugation observed on the Ag islands displayed an array of inverted triangles interpreted to be an electronic effect associated with structural modulations.

© EDP Sciences 1998

Article available at http://mmm.edpsciences.org or http://dx.doi.org/10.1051/mmm:1997116



a) b)

Fig. 1. — a) Variation of the adsorption energy with the Ag coverage (θ): from the pseudomorphy to the pseudoepitaxy structures b) Height map of the Ag adlayer for the p(10 × 10) superstructure. The grey scale illustrates the height variation from the lowest sites (black spheres: $\Delta z = -1$ Å) up to the highest ones (white spheres: $\Delta z = 0.3$ Å).

From a theoretical point of view the relaxed atomic structure of a complete monolayer of Ag on Cu(111) surface has been studied using an extended tight-binding quenched molecular dynamics simulation (ETBQMD) [5, 6]. These calculations clearly show that the lowest adsorption energy is obtained for a pseudoepitaxic p($n \times n$) superstructure with n equal to 10, see Figure 1a. It was also shown that the superlayer is strongly corrugated as seen in Figure 1b, where a corrugation map of the surface layer obtained from ETBQMD is shown. The perturbation extends up to the first ten surface layers.

In order to experimentally substantiate these theoretical simulations we have studied the structure of a complete ML of Ag deposited at room temperature on Cu(111) and annealed at low temperature to allow the reconstruction of the surface using both Surface X-ray Diffraction (SXRD) and Scanning Tunnelling Microscopy (STM).

2. Experimental

The experiments were performed in an ultra high vacuum (UHV) system, containing an Omicron STM, a LEED, a sputtering chamber and a molecular beam epitaxy (MBE) chamber for silver deposition and annealing. Two samples were prepared for STM and SXRD measurements respectively, with the same procedure and under the same conditions: electrochemically polished Cu(111) single crystals were used and the surface was cleaned by sputtering (500 V at 400 °C) followed by a short annealing at the same temperature in order to obtain a sharp (1 × 1) LEED pattern at room temperature. After deposition of approximately one monolayer of Ag the sample was annealed at about 100 °C for a few minutes. At room temperature the LEED showed the expected p($9 \pm 1 \times 9 \pm 1$) pattern. The samples were then transferred either into a portable UHV baby chamber for the X-ray measurements or into the STM.

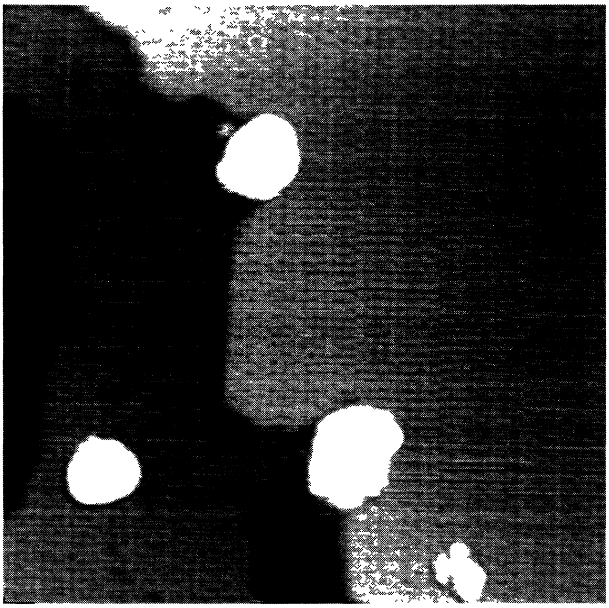


Fig. 2. — An overview STM image from the Ag/Cu(111) surface, recorded at $V_B = +8$ mV and $I_T = 0.5$ nA.

The X-ray diffraction experiments were performed at the BW2 wiggler beam line [7] at HASYLAB in Hamburg. The wavelength ($\lambda = 1.4586$ Å) used was selected by a water-cooled silicon crystal monochromator. A NaI detector was used to measure the intensities of the reflections. We recorded scans along the main Cu-surface symmetry axes, $[1\bar{1}0]$ and $[1\bar{2}1]$ which are indexed [11] and [10] respectively in surface notation, as well as in-plane ω-scans around the superstructure reflections. Additional rod scans perpendicular to the surface were also recorded. In this paper we will consider only the first in-plane measurements for the surface structure determination. The complete and detailed structural analysis of the diffraction data set will be discussed in a forthcoming article.

3. Results and Discussion

Figure 2 presents a 2000 × 2000 Å^2 overview STM image from the Ag/Cu(111) surface. The 1000 Å large flat terraces separated by monoatomic steps are in good agreement with the low disorientation (0.1 deg.) of the single crystal surface from the (111) plane. The surface atomic structure is not resolved on this scale, one faintly observes the surface reconstruction pattern uniformly covering the terraces. In addition, smaller (100 Å diameter) clusters or aggregates appear as white dots on the surface. These islands constitute most probably excess silver, further supported by the fact that we did not find any area exposing the bare Cu(111) substrate. The surface reconstruction does not seem to be strongly influenced by the presence of these islands, *i.e.* the structure close to the islands is the same as further away. The low impact of the tunnelling parameters; *i.e.* sample bias voltage (V_B) and tunnelling current (I_T), on the recorded images is shown in Figure 3 by a set of STM images obtained at different V_B and I_T (the tunnelling parameters can be found in the figure caption). Contrary to what is observed

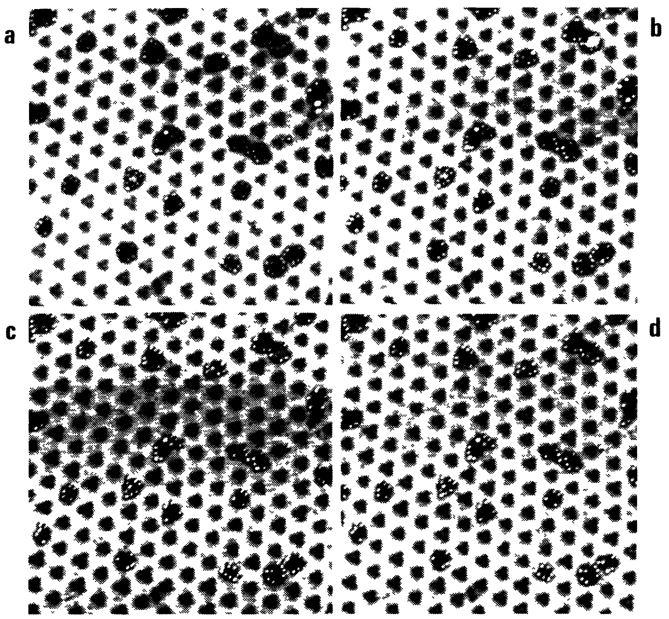
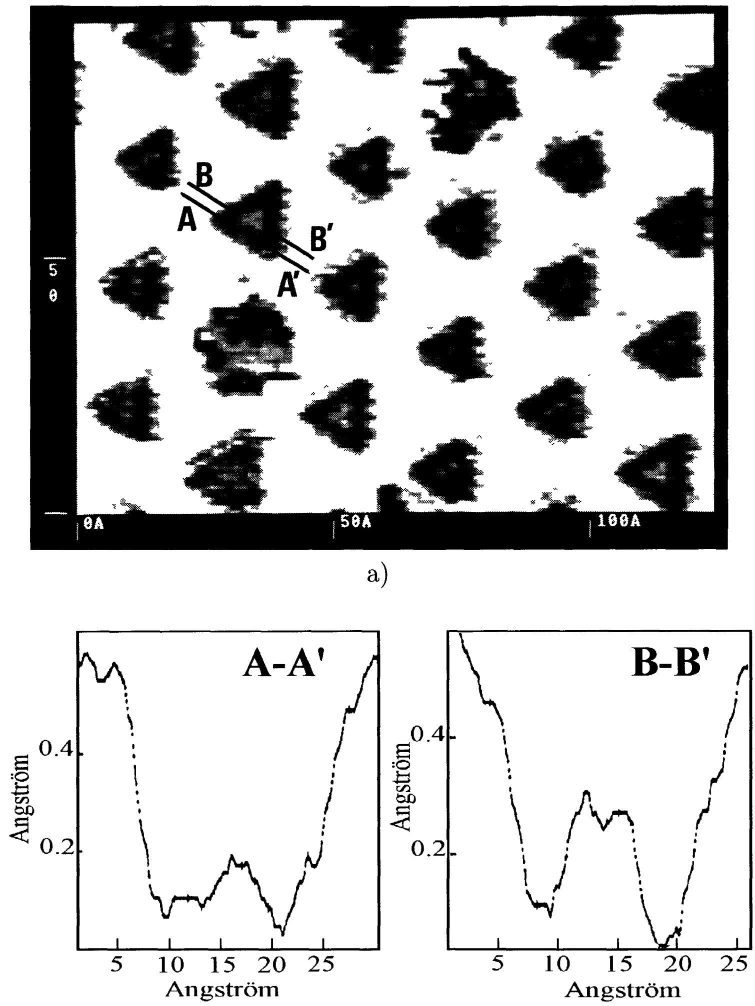


Fig. 3. — These images were recorded from the same surface area using different V_B and I_T, revealing the low influence of the image on the tunnelling parameters. a) −0.7 V and 3.6 nA, b) −0.46 V and 3.4 nA, c) −2 mV and 0.63 nA and finally in d) 8 mV and 0.63 nA.

on Ag islands at half-monolayer [4] the surface exhibits an array of triangular pits, all with the same angular orientation, occasionally replaced by defects, which probably play a role in the relaxation of the lattice mismatch. The rows of triangles display an in-plane wavy character, due to a difference in size between consecutive triangles and the presence of defects, as seen more clearly in the atomically resolved image in Figure 4a, recorded at 0.8 mV sample bias voltage and 0.63 nA tunnelling current. In this image one can see two kinds of triangles: large ones with 5 atoms on each side and 3 atoms protuding in the centre and small ones with only 3 atoms on each side and 1 atom in the centre. The line scans in Figure 4b illustrate clearly the details of the atomic corrugation in a triangle. Along a black side of a triangle (line A−A′) the corrugation is about 0.5 Å in each corner and 0.4 Å in the middle. The line scan B−B′ across a triangle reveals that the centre is about 0.3 Å lower than outside. The distance between two neighbouring large triangles corresponds to 9 times $d_{\text{Ag}-\text{Ag}}$ the interatomic distance in the Ag(111) plane while the distance between two neighbouring small triangles is only $8d_{\text{Ag}-\text{Ag}}$. No other distance than $8d_{\text{Ag}-\text{Ag}}$ or $9d_{\text{Ag}-\text{Ag}}$ was observed on the surface, and we do not find any ordering with respect to the size of consecutive triangles. On the flat areas between the triangles, the structure of the Ag monolayer is the expected hexagonal close-packed pattern with an "atomic" corrugation along the rows of about 0.05 Å. Since the bare Cu surface is not visible at this coverage it is not possible, from the STM pictures, to directly determine whether the cell is rotated or not with respect to the copper axes. We note, however, that the directions of the Ag atomic rows and the step edges, which are presumably aligned with the Cu(111) substrate axes, are found to be parallel which supports a non-rotated superstructure unit cell. Information about the rotation of the overlayer may be given by Surface X-Ray Diffraction as shown in the following.



a)

b)

Fig. 4. — a) Atomically resolved STM image from the Ag/Cu(111) surface. The image is obtained at 0.8 mV sample bias and 0.63 nA tunnelling current. b) Line scans along the A–A′ and B–B′ directions shown in the STM image.

In contrast with STM, SXRD is sensitive to both Cu and Ag lattices. The measurements were performed using the Cu surface reciprocal lattice as a reference. The combination of a radial h-scan and a transverse k-scan, reported together in Figure 5, clearly shows "extra" diffraction peaks originating from the Ag monolayer at positions (0.894, 0) and (0.894, 0.106) besides the (1, 0) copper reflection. The "average" Ag surface unit cell may be then deduced; it is $(9.43 \pm 0.02 \times 9.43 \pm 0.02)$ times the Cu(111) surface unit cell. ω-scans of the Cu (10) and Ag (0.894, 0) reflections are shown in the same figure (Fig. 6). The Ag peak is much broader than the Cu one (FWHM = 0.7 deg.), that corresponds to some relative disorder in the orientational epitaxy. Furthermore, it is worth noting that the Ag monolayer is aligned with the Cu surface axes, since the shift in the peak positions is precisely the difference of the Bragg angles of each reflection.

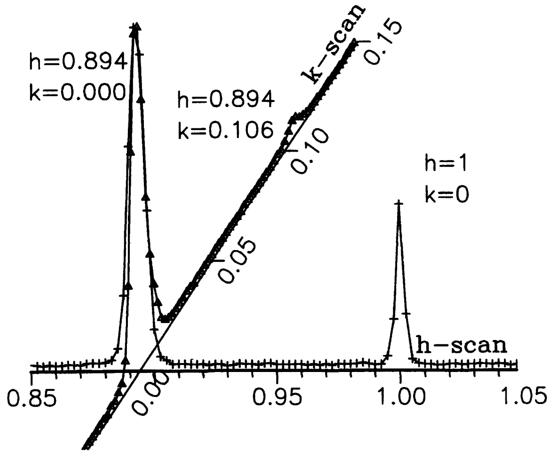


Fig. 5.

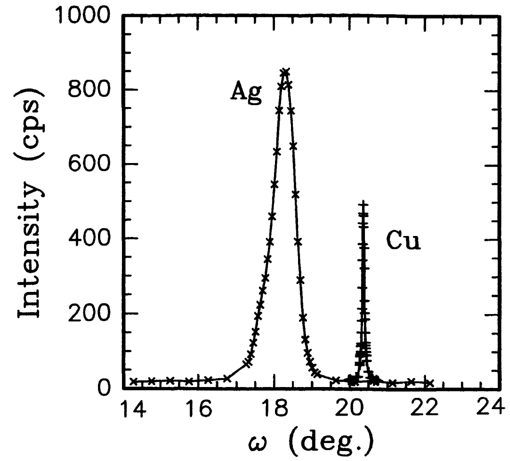


Fig. 6.

Fig. 5. — SXRD scans along the main symmetry *h* and *k* axes around the (1, 0) Cu-substrate reflection.

Fig. 6. — SXRD ω-scans of the Cu(1, 0) and Ag(0.894, 0) reflections.

The present study of the complete Ag monolayer reveals some differences with the previous work on Ag islands at half-monolayer coverage [4]. The STM images show a complete Ag monolayer made of an intimate mixture of two local superstuctures (8 × 8 and 9 × 9, with respect to the Ag lattice) without obvious phase relation among themselves (there is no phase boundaries) as shown in Figure 4a. Considering the natural lattice mismatch of Ag and Cu, the superstuctures indexed 8 × 8 and 9 × 9, with respect to Ag are in fact very close to 9 × 9 and 10 × 10 superstuctures relatively to Cu. The STM result is therefore in good agreement with the average unit cell (9.43 × 9.43) measured by SXRD. For 0.5 ML, the Ag islands display a mixture of superstructures close to (9 × 9) which are rotated and apparently slightly compressed relative to bulk silver. This compression and these rotations which do not exist for a complete monolayer (there is slight dilatation) show the role played by the borders of the islands which allow these rotations.

The STM image presented in Figure 4a is not very different from those obtained by the ETBQMD simulations. Nevertheless, the experimental corrugation appears to be more localized to only a few atoms. If one considers the STM images to be a direct "representation" of the surface crystallographic structure one can imagine that the black part of the triangles is due to the absence of silver atoms. Despite the difficulties to imagine a driving force for this mechanism, this structure can easily be obtained by removing 9 Ag atoms (or 12, in large triangles) and leaving 1 Ag atom (or 3, in large triangles) in the middle. Preliminary calculations performed by ETBQMD on these structures show that neither 1 nor 3 Ag atoms in the middle present stable structures. However, without Ag atoms in the middle, the simulations show that uncovered Cu atoms relax outwards to sit at a level close to the surface (as experimentally observed here) and the total energy obtained after relaxation is very close to the previous theoretical structure (Fig. 1a).

Keeping in mind that the STM images are not really a direct "representation" of the surface atomic structure but rather of its electronic structure, makes the interpretation of the images in terms of corrugation questionnable. Actually, the tunnelling current can be modified due to interference effects between the successive layers, so that the central atoms, which appear as protrusions in the images, could be geometrically "deeper". In this case only a theoretical calculation of the tunnelling current could give us an accurate answer [8].

The STM images of the Ag monolayer reported here are quite similar to those recently observed by the same technique for Au on Ni(111) [9]. In this latter study, at low temperature the structure observed is very similar to the theoretical simulation shown in Figure 1b. At higher temperature (100 °C) triangles quite similar to the ones presented here were observed but with a different periodicity which is certainly a simple effect of the difference in "lattice mismatch", 13% and 16% for Ag/Cu and Au/Ni systems respectively. The authors interpreted the triangular corrugation by the formation of dislocation loops in the top Ni layer (substrate). The scenario proposed is based on a removal of 1 row of 5 Ni atoms from the top substrate layer. That allows some Ni atoms to shift from fcc to hcp sites and Au atoms situated in the centre of triangles to keep a coordination with Ni atoms close to 3. In this model the removed Ni atoms are scattered over the Au layer and are seen in the STM images as single white dots on the surface. According to the authors this structure leads to an increased number of Au-Ni bonds which minimize the energy. Since the Ag-Cu system displays a very strong tendency to phase separation it is more difficult to imagine the same structure. From the STM images and from the first results of SXRD we are not yet able to confirm or to rule out the model proposed by [9]. Further X-ray diffraction analysis (rod scans) and theoretical calculations (ETBQMD) of the different possible structures including surface vacancies are needed to fully understand this complicated structure.

4. Summary

We have applied scanning tunnelling microscopy and surface X-ray diffraction to the Ag/Cu(111) surface. The STM images are in qualitative agreement with a theoretical prediction, revealing a strongly corrugated surface top layer consisting of an array of triangular depressions. The triangles are of two sizes, either 4 or 5 atomic rows wide with respectively one or three atoms protruding at 0.3 Å in the middle of the 0.5 Å deep holes. The presence of two different sizes can be explained by the misfit of the silver overlayer and the copper substrate, which gives an alternating preference of the direction of adjustment of the in-plane Ag adatom position with respect to the substrate. By use of SXRD we have determined the average surface unit cell to (9.43 × 9.43) times the substrate surface unit cell size without rotation. The slight rotation previously observed for 0.5 ML is no more possible when the Ag monolayer is completed.

Acknowledgments

This project was financed within the Large Installation Plan number II-95-09-EC under the direction of G. Lelay. M.G. and E.L. want to thank the Swedish Natural Science Research Council (NFR) for economical support.

References

[1] Borensztein Y., *Europhys. Lett.* **4** (1987) 723; Tokutaka H., Nishimori K. and Takashima K., *Surf. Sci.* **86** (1979) 54.

[2] Bauer E. and van der Merve J.H., *Phys. Rev. B* **33** (1986) 3657.

[3] Bauer E., *Surf. Sci.* **7** (1967) 351; Mitchell K.A.R., Woodruff D.P. and Vernon G.W., *Surf. Sci.* **46** (1974) 418.

[4] MacMahon W.E., Hirschorn E.S. and Chiang T.C., *Surf. Sci.* **279** (1992) L231.

[5] Mottet C., Tréglia G. and Legrand B., *Phys. Rev. B* **46** (1992) 16018.

[6] Mottet C., Tréglia G. and Legrand B., *Surf. Sci.* **287/288** (1993) 476.

[7] Feidenhans'l R., *Surf. Sci. Rep.* **10** (1989) 105.

[8] Sautet P., private communication.

[9] Jacobsen J., Pleth Nielsen L., Besenbacher F., Stensgaard I., Laegsgaard E., Rasmussen T., Jacobsen K.W. and Norskov J.K., *Phys. Rev. Lett.* **75** (1995) 489.