

SURFACE GEOMETRIC STRUCTURES OF CU DEPOSITED UPON α -Al₂O₃(0001)*

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Upon deposition of Cu on a 1×1 α -Al₂O₃(0001) surface at room temperature the surface structure was found to change with increasing amounts of Cu deposited, from two-dimensional monolayer islands through three-dimensional nuclei until reaching a thin film. Subsequent surface heat-treatment to 650°C produced a stable Cu(111)-R30° superstructure as observed by LEED.

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1. Introduction

The growth of copper upon alumina is of interest [1-3] due to its role as a catalyst in petrochemical processes. Studies by electron microscopy disagree [4, 5] as to whether or not a Cu(111) structure grows parallel to a sapphire α -Al₂O₃(0001) at high temperatures (900-1080°C).

In the previous work we have reported [6, 7] results on the development of the surface electronic structures and on the thermal stability of deposits of copper onto α -Al₂O₃(0001) surfaces. In the present paper we report on further Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) studies on the surface geometric structure of Cu deposited on this substrate.

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2. Experimental procedures

The experiments were carried out in a previously described [8] ultra-high vacuum system at pressures below 10^{-9} mbar. A single-pass cylindrical mirror analyzer was used for AES and 4-grid optics for LEED observation. The purity of the copper was 99.995% and the rates of Cu deposition were $1\text{--}3 \text{ \AA min}^{-1}$. The thickness of the deposited copper layers was monitored by a quartz crystal microbalance. A new high-temperature method of pretreatment of the sapphire was used, as previously described [6]. An atomic-level clean surface was then obtained.

Strong charging effects are occurring within a certain primary energy range for metal oxide insulators [9]. For the present substrate the LEED patterns cannot be seen at primary energies below 60 eV, and the surface-charging increased with the amount of deposited copper as also seen for the Cu/MgO system [9]. For temporary removal of the surface-charge disturbance a higher primary energy, 1–2 keV, was applied for a few seconds prior to photography. All Auger spectra and LEED patterns were recorded at room temperature.

3. Results and discussion

Figure 1 shows an ideal atomic arrangement from a (0001) sapphire surface with a hexagonal unit cell. The outermost layer consists of aluminum atoms, the second layer of oxygen and the third layer is again Al, but in a position off from that of the outermost Al atoms. The corresponding LEED pattern from a clean

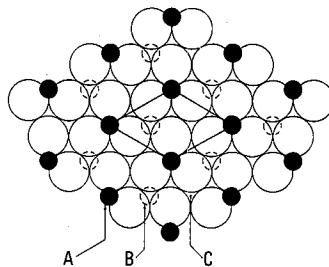


Fig. 1. $\alpha\text{-Al}_2\text{O}_3(0001)$ surface. Filled black circle: top layer (aluminum), large unfilled circle: second layer (oxygen), dashed circle: third layer (aluminum). A, B and C indicate different adsorption sites at the surface (see text). The unit cell is shown by bold lines.

$\alpha\text{-Al}_2\text{O}_3(0001)$ surface is a 1×1 structure; a hexagonal symmetry is seen.

Very small amounts of deposited copper, at average layer thicknesses $d_{\text{Cu}} < 2 \text{ \AA}$ deposited on the sapphire surface at room temperature, cause an increase in the background intensity from the substrate LEED pattern, and no new pattern was formed.

During the experiments it was observed that the surface charging increased with d_{Cu} . Within the 2–10 \AA range no LEED pattern could be obtained at primary beam energies below approximately 140 eV because of strong charging effects. For

thick layer deposits LEED patterns could not be obtained even at higher primary beam energies.

Heating samples with deposits in the 50–130 Å range on the substrate to temperatures within the 110–650°C range results in a LEED pattern indicating a Cu(111)R30°/1 × 1 α -Al₂O₃(0001) surface structure as shown in Fig. 2.

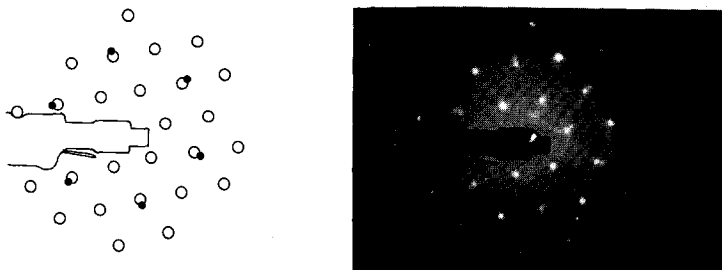


Fig. 2. LEED pattern from Cu/ α -Al₂O₃(0001) after an annealing at 650°C for 30 min. Primary energy 164 eV, taken at room temperature. Full circles: sapphire substrate, filled circles: copper.

The AES measurements indicate that the Auger aluminum (*KLL*)-to-oxygen (*KLL*) intensity ratio, I_{Al}/I_O , decreases during the initial Cu deposition, for $d_{Cu} < 2$ Å in comparison to those of higher Cu coverages. Taking into account that the inelastic mean free path λ in an Al₂O₃ film for 500 eV electrons (i.e. O(*KLL*)) is ~ 10 Å and that $\lambda \simeq 17$ Å for 1400 eV electrons (i.e. Al(*KLL*)), i.e. $\lambda_{Al} > \lambda_O$ in these measurements [10], then the results may perhaps indicate that the Cu atoms are positioned preferably at the top of aluminum sites, the A or B sites in Fig. 1 (and probably also at the C sites, see Fig. 1), during the initial stages of the copper depositions, resulting in a decrease in the I_{Al}/I_O AES intensity ratio.

The surface structure of the Cu/ α -Al₂O₃(0001) depends strongly on the cleanness of the substrate, and contaminants should be carefully removed, as controlled by AES.

Ideally, the outermost atoms of the 1 × 1 α -Al₂O₃(0001) surface are aluminum (see Fig. 1), but here the outermost atoms are expected to be oxygen due to the high-temperature oxidation pretreatment of the sample. This was confirmed by the measurement of the I_O/I_{Al} intensity ratio. Thus, based upon the LEED and AES results we propose the surface structure of Cu/Al₂O₃(0001) for coverages $50 \text{ \AA} < d_{Cu} < 130 \text{ \AA}$ after heat-treatment to 650°C to be as modelled in Fig. 4. The Cu–Cu distance of 2.56 Å of the Cu(111) plane was used in Figs. 3–4.

In summary, the surface geometric structure of Cu upon α -Al₂O₃(0001) changes with Cu coverage. For $d_{Cu} < 2$ Å, islands, i.e. two-dimensional clusters (see Fig. 4a), are formed. The copper islands are not uniformly dispersed over the surface at this stage, therefore no superstructure is formed. At increasing coverages, $2 \text{ \AA} < d_{Cu} < 50 \text{ \AA}$, 3-dimensional clusters are formed (Fig. 4b). In this range, and particularly for $2 \text{ \AA} < d_{Cu} < 20 \text{ \AA}$, no LEED pattern could be obtained due to charging effects. Further deposition at room temperature results in full coverage

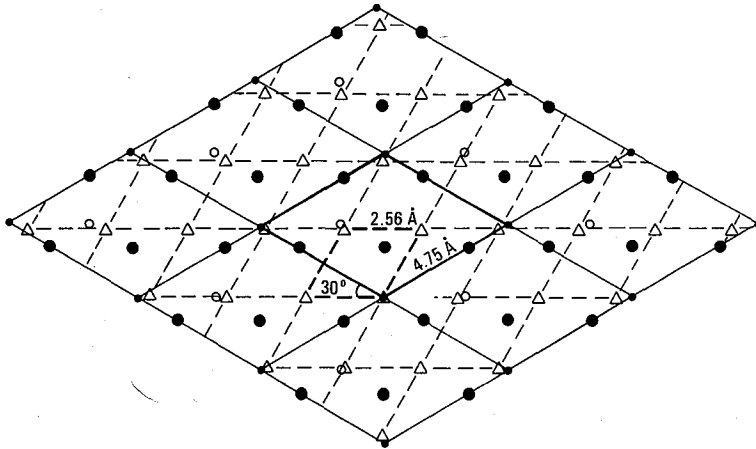


Fig. 3. Surface geometric structure of Cu/ $\text{Al}_2\text{O}_3(0001)$ after annealing for 30 min at 650°C for layer thicknesses within the 50–130 Å range. The lines show the unit cells for Cu(111) (dashed lines) and $\alpha\text{-Al}_2\text{O}_3(0001)$ (full lines), respectively.

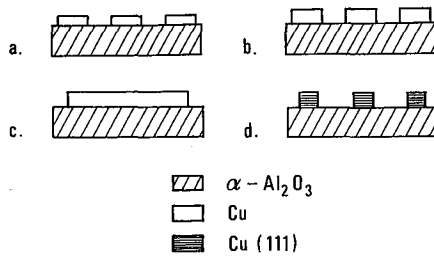


Fig. 4. Schematic diagram of surface structure for Cu deposited on $\alpha\text{-Al}_2\text{O}_3(0001)$. (a) 2-D islands (room temperature, $d_{\text{Cu}} < 2 \text{ \AA}$), (b) 3-D cluster (room temperature, $2 \text{ \AA} < d_{\text{Cu}} < 50 \text{ \AA}$), (c) whole substrate covered by Cu (room temperature, $d_{\text{Cu}} > 50 \text{ \AA}$), (d) Cu(111)/ $\alpha\text{-Al}_2\text{O}_3(0001)$ after annealing to 650°C .

of the substrate (Fig. 4c). Heating the 50–130 Å deposited samples to $110\text{--}650^\circ\text{C}$ for 10–30 min results in Cu agglomeration and formation of Cu(111) oriented nucleation centers, leading to a Cu(111) $\text{R}30^\circ/\alpha\text{-Al}_2\text{O}_3(0001)$ surface structure (Fig. 4d) as observed by LEED.

References

- [1] A.J. Pedraza, M.J. Godbole, D.H. Lowndes, J.R. Thompson Jr., *J. Mater. Sci.* **24**, 115 (1989).
- [2] E. Abonneau, G. Fuchs, M. Treilleux, A. Perez, *Nucl. Instr. Methods B* **46**, 111 (1990).

- [3] J.E.E. Baglin, A.G. Schrott, R.D. Thompson, K.N. Tu, A. Segmüller, *Nucl. Instr. Methods B* **19/20**, 782 (1987).
- [4] S.T. Lin, P.D. Ownby, *J. Mater. Sci.* **23**, 3187 (1988).
- [5] G. Katz, *Thin Solid Films* **33**, 99 (1976).
- [6] Q.L. Guo, P.J. Møller, *Surf. Sci.* **244**, 228 (1991).
- [7] Q.L. Guo, P.J. Møller, *Vacuum* **41**, 1114 (1990).
- [8] P.J. Møller, J.-W. He, *J. Vac. Sci. Technol. A* **5**, 996 (1987).
- [9] P.J. Møller, J.-W. He, *Nucl. Instrum. Methods B* **17**, 137 (1986).
- [10] F.L. Battye, J.G. Jenkin, J. Liesegang, R.C.G. Leckey, *Phys. Rev. B* **9**, 2887 (1974).