Geometric and electronic structure of Cu on corundum (0001) surfaces

Qinlin Guo*, E.G. Wang

State Key Laboratory for Surface Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People’s Republic of China

Received 16 March 2005; accepted 26 May 2005
Available online 12 September 2005

Abstract

In recent years, we have been focused the attention on the metal growth on (0001) surfaces of dimetal trioxide, M₂O₃ (M = Al, Cr, V and Fe), with corundum structure including ordered films and single crystals. The surface geometric and electronic structure of Cu on M₂O₃(0001) has been studied by use of various ultra high vacuum surface analysis techniques, including X-ray photoelectron spectroscopy, Auger electron spectroscopy, high resolution electron energy loss spectroscopy, low energy electron diffraction and ultraviolet photoelectron spectroscopy. This brief review paper shows the main results and highlights that the surface symmetry and chemical interaction between deposit and substrate play an important role in Cu epitaxial growth on M₂O₃ (0001).

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Copper growth; Ordered oxide films; Corundum surfaces; Surface geometric structure; Electronic structure; Epitaxial growth; Dimetal trioxide

1. Introduction

Research on the growth of metals on oxide surfaces has been attracted considerable attention due to their fundamental importance in applications such as metal ceramic interfaces, gas sensors, oxide-supported metal catalysis and solid state electronic devices. In particular, the oxides with corundum structure, alumina is a very good example, are widely used in many areas. In order to gain further insight into the mechanism, it is important to have a better understanding of the geometric and electronic structure, especially the interface formation.

Investigations at the interface of metal and oxide by electronic spectroscopies under ultrahigh vacuum (UHV) are often limited due to surface-charging problems and the difficulty of sample heating and cooling. To circumvent all these problems and offer the basic studies, ordered, thin metal oxide films supported on refractory metals have been successfully prepared [1–6]. As model samples the oxide films have been used for various fundamental studies, especially the growth of metal clusters on the oxide films.

For the last years we have made studies of the growth of metals (Au, Ag, Cu, Cr and V) on the (0001) surfaces of thin dimetal trioxide films of M₂O₃ (M = Al, Cr and V) with hexagonal symmetry structure (Al₂O₃(0001)/Mo(110), Cr₂O₃(0001)/Re(0001), V₂O₃(0001)/Re(0001)), and the results were compared with the same surfaces of single crystals. The various UHV surface techniques including X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), high-resolution electron energy loss spectroscopy (HREELS), low energy electron diffraction (LEED) and ultraviolet photoelectron spectroscopy (UPS) are applied in situ in those studies. In this brief review paper, we show the main results of surface geometric and electronic structure of Cu growth on M₂O₃(0001) surfaces and emphasize that the chemical bonding at the interface is one of the important factor for an epitaxial growth of Cu.

2. Experimental

The experiments are carried out in our laboratory under UHV condition using ESCALAB-5 multifunctional spectrometer (VG Scientific Ltd), ELS 22 spectrometer (LEYbold-Heraeus GmbH) and QMI 156 system (Riber). The ultra thin films with corundum (0001) orientation were in situ prepared on the Re(0001) or Mo(110) surfaces in the UHV chambers. More information on the experimental details can be found in Refs. [7–11].
3. Results and discussion

Fig. 1 shows XPS result and a hexagonal LEED pattern after a \( \sim 20 \) MLE (monolayer equivalent) \( \text{Cr}_2\text{O}_3(0001) \) film is grown on the \( \text{Re}(0001) \) surface. The data from XP spectra are consistent with former XP studies for single-crystal samples of \( \text{Cr}_2\text{O}_3 \), powder samples of \( \text{Cr}_2\text{O}_3 \) [12,13], and \( \text{Cr}_2\text{O}_3 \) films formed on \( \text{Cr}(110) \), \( \text{Pt}(111) \) and \( \text{Cu}(110) \) [14–20]. Then, the Cu was grown on the \( \text{Cr}_2\text{O}_3(0001) \) film by vapor deposition with increase of the Cu coverage at room temperature followed measurements of surface geometric and electronic structure. Fig. 2 presents a sharp LEED pattern with superstructure of Cu on \( \text{Cr}_2\text{O}_3(0001) \), indicating a geometric structure of Cu with (111) orientation rotated 30° related to substrate, \( \text{Cu}(111)R30^\circ/\text{Cr}_2\text{O}_3(0001) \). This surface structure is the same as the results of Cu on \( \text{V}_2\text{O}_3(0001) \) film [8], as well as on the single crystal oxides of \( \alpha\text{-Al}_2\text{O}_3(0001) \) and \( \text{Cr}_2\text{O}_3(0001) \) [21–23], but with different orientation on \( \alpha\text{-Fe}_2\text{O}_3(0001) \) due to reconstructive composite formed on the substrate of hematite [24]. One interesting result is that the epitaxial growth of Cu on the corundum (0001) surfaces is not lattice match dependent. The lattice constants of \( \alpha\text{-Al}_2\text{O}_3(0001) \) and \( \text{V}_2\text{O}_3(0001) \), for instance, are 0.476 and 0.510 nm, respectively, which are much larger than that of Cu (111) lattice constant of 0.256 nm. It seems certain that, in general, a very large lattice mismatch of 46.2 and 49.8% for Cu(111)/\( \text{Al}_2\text{O}_3(0001) \) and Cu(111)/\( \text{V}_2\text{O}_3(0001) \) makes it impossible to have an epitaxial growth of Cu. Observably, there must be one kind of drive force for the Cu growth oriented as (111)30° on the \( \text{M}_2\text{O}_3(0001) \) surfaces.

It is well known that the growth modes are many parameters dependent, such as crystal symmetry and lattice constant mismatch, surface free energy, substrate surface step density as well as overall substrate morphology and so on [3,4]. For metal and semiconductor systems, the three fundamental growth modes, namely layer-by-layer growth, layer-by-layer growth followed by three-dimensional islands and three islands growth, have been observed and well discussed. Apparently, the lattice constant mismatch is exception in our case, and a rather different situation appears due to a largely ionic oxide of corundum.

The XPS, UPS, HREELS and Auger parameter \( \alpha \) (the sum of the kinetic energy of the X-ray induced Auger peak of Cu_{LMM} and the binding energy of the Cu 2p_{3/2}) measurements were used for further investigation. As one example, the Auger parameter change as a function of Cu coverage on \( \text{Cr}_2\text{O}_3(0001) \) film is shown in Fig. 3, indicating a formation of Cu(I) state at the initial Cu coverage [7]. In fact, this conclusion is particularly obvious when the Cu is grown on corundum (0001) surfaces. The Cu(I) state is caused by chemical bonding between Cu and surface O since the Al atoms lies above O layer, and Al–O bonds are partially covalent. Experimentally, the Cu(I) state caused by Cu–O bonding at interface has been detected at the initial Cu growth on the \( \text{V}_2\text{O}_3(0001) \) film [8], \( \text{Al}_2\text{O}_3 \) film [25], bulk single crystal \( \text{Cr}_2\text{O}_3(0001) \) [23], \( \alpha\text{-Al}_2\text{O}_3(0001) \) [26] and \( \alpha\text{-Fe}_2\text{O}_3(0001) \) [27]. The similar spectra of chemical bonding at the interface with initial coverage strongly

Fig. 1. XPS (Mg Kα) spectrum and LEED pattern from a prepared \( \text{Cr}_2\text{O}_3(0001) \) film with \( \sim 20 \) MLE thickness on \( \text{Re}(0001) \) at room temperature.

Fig. 2. The LEED pattern and schematic of Cu deposited on \( \text{Cr}_2\text{O}_3(0001) \) film. The dash lines represents the reciprocal lattice vectors from \( \text{Cr}_2\text{O}_3(0001) \), and bold lines from Cu(111).
suggests a similar electronic structure of Cu on the surfaces of M2O3(0001).

Fig. 4 gives an ideal atomic arrangement from a (0001) corundum surface with a hexagonal unit cell. Assuming that, in spite of a complicated structure from real surface, the outermost layer consists of Al atoms (Al\(^{+3}\) ions, in fact), the second layer of oxygen and the third layer is again Al, but in a position off from that of the outermost Al atoms [28–33]. In this idealized surface, we can simply choose a unit cell consisting of outermost aluminum atoms, and the direction of lattice constant \(a_0\) in the unit cell is pointed as bold line in Fig. 4. At the R30° direction, the direction of the unit cell of Cu(111) aligned 30° off with respect (0001) corundum surface, it is oxygen atoms in lines as indicated by dash line in Fig. 4. The oxygen atoms beneath first-layer Al atoms are equidistant from each other forming a close packed structure with a hexagonal symmetry, each first-layer Al atom is bonded to only three second-layer O atoms, i.e. the octahedral environment is destroyed. In the relaxed surface, the nearly coplanar configuration with O allows rehybridization to a near-sp\(^2\) bonding environment [28,31], which opens a way to react with the atomic Cu at interface. Thus, the initial deposited Cu can be ‘held’ along the direction of the O lines, the dash line direction in Fig. 4. The Cu is nucleated with an increase of coverage due to release of the surface strain and grown epitaxially as Cu(111)R30° finally.

Studies over many systems have shown that the interface energy from surface strain caused from lattice mismatch and the surface free energies from prepared film on the substrate also influence the growth mode. The spectra intensity ratio between deposit and substrate can give some useful information on the growth mode. Thus, the XPS intensity ratio of Cu 2p\(_{3/2}\) signal to the metal signal of M2O3 versus the Cu coverage in Cu/M2O3(0001) system was measured [7,8]. The results demonstrate that at submonolayer coverage the initially deposited Cu is highly dispersed, most likely forming two-dimensional patches or quasi-two-dimensional patches. With increasing Cu coverage, above 1 MLE coverage of Cu, three-dimensional clusters form since the signal from substrate still can be detected by XPS even after about 20 MLE Cu deposition. Since no LEED pattern can be observed at the lower coverage of Cu, the deposited Cu clusters must be smaller than 10 nm in size based on that the incident energies normally used in LEED have a coherence length of about 10 nm. Due to a big lattice mismatch, a surface strain should be existed at interface, which blocks the formation of layered Cu in large area. At higher coverage, the Cu become bigger resulting in a release of the surface strain. Thus, a clear LEED pattern is observed as shown in Fig. 2. This can be proved by a calibration from LEED pattern using the lattice constant. From Fig. 2, for instance, assuming that the lattice constant of the prepared Cr\(_2\)O\(_3\)(0001) film is 0.51 nm as the value of bulk Cr\(_2\)O\(_3\), we calculate the distance between Cu atoms (a* = b* = 2/√3a\(_0\), where a*
and \( b^* \) are reciprocal lattice vectors and \( a_0 \) is the lattice constant) in Cu(111) to be 0.26 nm, which agrees well with the bulk Cu value of 0.256 nm.

4. Conclusions

The surface geometric and electronic structure of Cu grown on corundum (0001) has been studied. The results show a formation of Cu(I) at the interface for the initial Cu deposition. An epitaxial growth of Cu as Cu(111)R30° grown on corundum (0001) has been studied. The results in case of Cu growth on the ionic oxide surface of M₃O₃(0001) the chemical bonding strength caused by Cu and substrate oxygen and surface symmetry play an important role in the alignment of Cu growth and epitaxy.

Acknowledgements

We acknowledge with pleasure the support of this work by the National Science Foundation of China (90206036 and 60021403).

References

[1] D.W. Goodman, Model catalysts: from imaging to imaging a working surface, Journal of Catalysis 216 (2003) 213–222.
[2] H.J. Freund, Clusters and islands on oxides: from catalysis via electronics and magnetism to optics, Surface Science 500 (2002) 271–299.
[3] S.A. Chambers, Epitaxial growth and properties of thin film oxides, Surface Science Reports 39 (2000) 105–180.
[4] R. Franchy, Growth of thin, crystalline oxide, nitride and oxynitride films on metal and metal alloy surfaces, Surface Science Reports 38 (2000) 195–294.
[5] C.R. Henry, Surface studies of supported model catalysts, Surface Science Reports 31 (1998) 231–325.
[6] M.S. Chen, D.W. Goodman, The structure of catalytically active gold on titania, Science 306 (2004) 252–255.
[7] W. Xiao, K. Xie, Q. Guo, E.G. Wang, Growth and electronic structure of Cu on Cr₂O₃(0001), Journal of Physics-Condensed Matter 15 (2003) 1155–1163.
[8] W. Xiao, K. Xie, Q. Guo, E.G. Wang, Cu on V₂O₃(0001) films: Growth and interaction, Journal of Physical Chemistry B 106 (2002) 4721–4724.
[9] Q. Guo, D.W. Goodman, Surface plasmon of Ag clusters on alumina films, Chinese Physics, Supplement 10 (2001) S80–S84.
[10] Q. Guo, Kai Luo, Kent A. Davis, D.W. Goodman, Initial growth of Au on oxides, Surface and Interface Analysis 32 (2001) 161–165.
[11] W. Xiao, K. Xie, Q. Guo, E.G. Wang, Interaction of metal with oxide films: V on Cr₂O₃(0001)/Re(0001) and Cr on V₂O₃(0001)/Re(0001), Journal of Physics-Condensed Matter 14 (2002) 6321–6328.
[12] W.Y. Howng, R.J. Thorn, Investigation of the electronic structure of La₇₋₈(M₂⁺)₂Cr₂O₇, Cr₂O₃, La₂O₃ and La₃O₃ by X-ray photoelectron spectroscopy, Journal of Physics and Chemiristy of Solids 41 (1980) 75–81.
[13] J.C. Carver, G.K. Schweitzer, T.A. Carlson, Use of X-ray photoelectron spectroscopy to study bonding in Cr, Mn, Fe, and Co compounds, Journal of Chemical Physics 57 (1972) 973–982.
[14] H. Ma, Y. Berthier, AES, XPS, and TDS study of the adsorption and desorption of NH₃ on ultra-thin chromium oxide films formed on chromium single, Applied Surface Science 153 (1999) 40–46.
[15] C. Xu, M. Hassel, H. Kuhlenbeck, H.J. Freund, Adsorption and reaction on oxide surfaces: NO, NO₂ on Cr₂O₃(111)/Cr(110), Surface Science 258 (1991) 23–34.
[16] V. Maurice, S. Cadot, X.P.S. Marcus, XPS, LEED and STM study of thin oxide films formed on Cr(110), Surface Science 458 (2000) 195–215.
[17] L. Zhang, M. Kuhn, U. Diebold, Growth of ultrathin films of chromium and its oxides on Pt(111), Journal of Vacuum Science and Technology A 15 (1997) 1576–1580.
[18] L. Zhang, M. Kuhn, U. Diebold, Growth, structure and thermal properties of chromium oxide films on Pt(111), Surface Science 375 (1997) 1–12.
[19] A. Maetaki, K. Kishi, Preparation of ultrathin chromium oxide films on Cu(110) investigated by XPS and LEED, Surface Science 411 (1998) 35–45.
[20] A. Maetaki, M. Yamamoto, H. Matsumoto, K. Kishi, The preparation of ultra-thin chromium–vanadium oxides on Cu(100) studied by XPS and LEED, Surface Science 445 (2000) 80–88.
[21] P.J. Møller, Q. Guo, Growth of ultrathin films of coper onto \( \alpha \)-Al₂O₃(0001): mechanism and epitaxy, Thin Solid Films 201 (1991) 267–279.
[22] Q. Guo, P.J. Møller, L. Gui, Surface geometric structures of Cu deposited upon \( \alpha \)-Al₂O₃(0001), Acta Physica Polonica A 81 (1998) 647–651.
[23] Q. Guo, L. Gui, P.J. Møller, K. Binau, AES and LEED studies of Cu deposited on Cr₂O₃(0001) surfaces, Applied Surface Science 92 (1996) 513–518.
[24] Q. Guo, P.J. Møller, HREELS and LEED studies on Cu deposited on \( \mathrm{CrO}_3 \), \( \mathrm{Cr}_2 \mathrm{O}_3 \), and \( \mathrm{Cr}_3 \mathrm{O}_4 \) surfaces, Surface Science Letters 340 (1995) L999–L1004.
[25] Q. Guo, P.J. Møller, On the thermal stability of copper deposits on a \( \mathrm{Al}_2 \mathrm{O}_3(0001) \) sapphire surface, Surface Science 244 (1991) 228–236.
[26] Q. Guo, P.J. Møller, On the electronic structure of Cu ultra-thin film on \( \alpha \)-Al₂O₃(0001) surfaces, Vacuum 41 (1990) 1114–1117.
[27] P.J. Møller, Q. Guo, L. Gui, Ultrathin film of Cu on \( \alpha \)-Fe₂O₃(0001), Thin Solid Films 281–282 (1996) 76–79.
[28] J. Ahn, J.W. Rabalais, Composition and structure of the \( \alpha \)-Al₂O₃(0001) \( \times 1 \) surface, Surface Science 388 (1997) 121–131.
[29] J. Toofan, P.R. Watson, The termination of the \( \alpha \)-Al₂O₃(0001) surface: a LEED crystallography determination, Surface Science 401 (1998) 162–172.
[30] I. Manassidis, A. De Vita, M.J. Gillan, Structure of the \( \alpha \)-Al₂O₃ surface from first principles calculations, Surface Science 285 (1993) L517–L521.
[31] T.J. Godin, John.P. LaFemina, Atomic and electronic structure of the corundum (\( \alpha \)-alumina) (0001) surface, Physical Review B 49 (1994) 7691–7696.
[32] X.G. Wang, A. Chaka, M. Scheffler, Effect of the environment on \( \alpha \)-Al₂O₃(0001) surface structures, Physical Review Letters 86 (2000) 3650–3653.
[33] G. Renaud, Oxide surfaces and metal/oxide interfaces studied by grazing incidence X-ray scattering, Surface Science Reports 32 (1998) 1–90.