

Cu on V₂O₃(0001) Films: Growth and Interaction

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The deposition of Cu at room temperature on a V₂O₃(0001) surface, which was prepared on a Re(0001) substrate at first, is studied by XPS (X-ray photoelectron spectroscopy), UPS (ultraviolet photoelectron spectroscopy), and LEED (low-energy-electron diffraction). The XPS results indicate that the growth of Cu follows the patch-wise Stranski-Krastanov mode. Auger parameter and UPS show that at low coverages the deposited Cu has the Cu(I) state due to the interaction of Cu with V₂O₃ substrate; Cu becomes metallic at Cu coverage > 2 MLE (monolayer equivalent). The epitaxial Cu films on the V₂O₃(0001) have Cu(111)R30° superstructures observed by LEED.

1. Introduction

Considerable interest in ultrathin metal layers on metal oxide surfaces increased in recent years¹ owing to the technological relevance of these interfaces, e.g., in applications to catalysis, gas sensors, and microelectronic devices. In these applications the interaction between the metal and the substrate is often of crucial importance. Among metal/oxide systems, the Cu/oxide interface is one of the more interesting systems, because Cu is an active component in many catalytic reactions, such as CO oxidation and NO_x reduction. To aid in the understanding of mechanisms in catalysis, model oxide films have been prepared in ultrahigh vacuum (UHV) by depositing the metal of interest and oxygen onto single-crystal metal substrates followed annealing treatments. This method of preparation offers advantages over the use of oxide bulk crystals: uncontaminated surfaces can be obtained more readily; metallic substrates are easier to mount and manipulate in UHV, and can be heated resistively; specially, the surface charging can be overcome while using various electron spectroscopies. In recent years, V₂O₃(0001) on Au(111),² Pd(111),^{3,4} and Al₂O₃(0001)/Mo(110),⁵ and disordered V₂O₃^{6,7} and VO(111)⁸ on Cu(100) have been reported. Epitaxial growth of Cu on MgO(100),⁹ MgO(111),⁹ CaO(100),¹⁰ TiO₂(110),¹¹ ZnO(0001),¹² α-Fe₂O₃(0001),^{13,14} and α-Al₂O₃(0001)¹⁵ also has been investigated. The previous experiments^{9,13–27} and theoretical studies^{27–30} have shown that Cu atoms interact with some oxide substrates. However, very few studies on the interaction between Cu and single-crystal V₂O₃ have been reported.

In the present work, we use X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and low-energy electron diffraction (LEED) to study the growth of Cu on ordered V₂O₃ ultrathin film synthesized on a Re(0001) substrate and investigate the interaction of Cu atoms with the V₂O₃(0001) surface.

2. Experimental Section

The experiments were carried out in an ESCALAB-5 system made by VG Scientific Ltd, which has two UHV chambers,

both having a base pressure of 2×10^{-9} mbar. One of the chambers (the analysis chamber) is equipped with reverse view optics for LEED, dual-anode X-ray sources (Mg and Al), and a hemispherical analyzer for XPS and UPS. In the other chamber (the preparation chamber), there is an Ar⁺ sputtering gun. The sample was prepared in the preparation chamber and analyzed in the analysis chamber.

The Re(0001) sample, 10 mm in diameter, ~1.0 mm thickness, was spot welded to a Mo holder with Ta slivers, allowing electron bombardment heating to 2500 K. A W-5%Re/W-26%Re thermocouple was spot welded near to the sample for temperature monitoring. The surface was prepared by Ar⁺ bombardment at 5 keV, followed by annealing in $\sim 10^{-7}$ mbar O₂ above 1200 K, with a subsequent flash to 2000 K. After several treatments, no impurities were detected by XPS and a sharp hexagonal LEED pattern appeared.

The V doser consists of a vanadium wire wrapped tightly around a W filament, and the Cu doser is made in the same way. Both the V and Cu sources were above 99.9% purity. Before evaporation, the V and Cu sources were thoroughly degassed. The V₂O₃ film was grown on the Re(0001) substrate by evaporation of V in 5×10^{-7} mbar O₂ ambience at 700–800 K followed by about 900 K annealing in $\sim 10^{-7}$ mbar O₂ to fully enhance oxidation. Then the film was annealed by about 900 K without O₂ in a vacuum for surface ordering. The V₂O₃ films with about 20 MLE thickness were used for Cu deposition at room temperature. The deposition rates of V and Cu were 0.4 ML (monolayer)/min and 0.3 ML/min, respectively, calibrated via XPS of V 2p and Cu 2p deposited onto the Re(0001) surface as a function of deposition time. Since Cu is not necessarily grown on V₂O₃ film layer-by-layer, we prefer to use the monolayer equivalent (MLE) as a measurement for Cu coverage. The V₂O₃ film with about 20 ML thickness were used for Cu deposition at room temperature.

In XPS, Al Kα radiation (1486.6 eV) was used. Binding energies (BE) were calibrated using the Au 4f_{7/2} (BE = 84.0 eV) and Cu 2p_{3/2} (BE = 932.7 eV) features of metallic Au and Cu, respectively. All data were collected using a pass energy of 50 eV at room temperature. Helium of 99.999% purity was used for He(I) UPS (21.2 eV).

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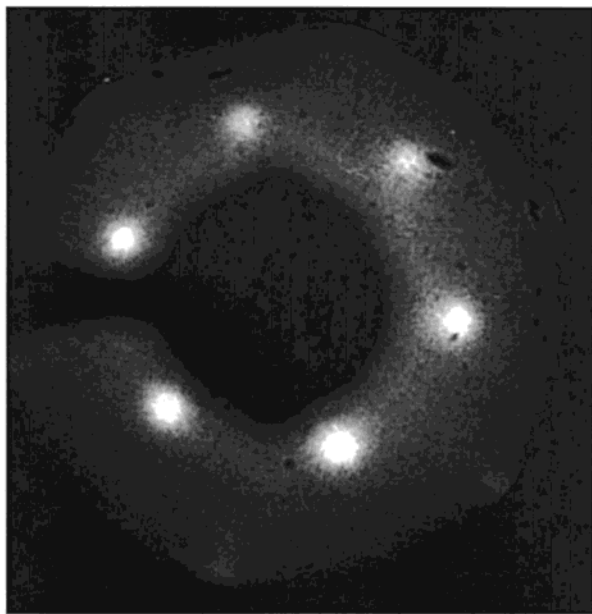


Figure 1. LEED pattern from a 20 ML $\text{V}_2\text{O}_3(0001)$ film on the $\text{Re}(0001)$. $E_p = 50$ eV.

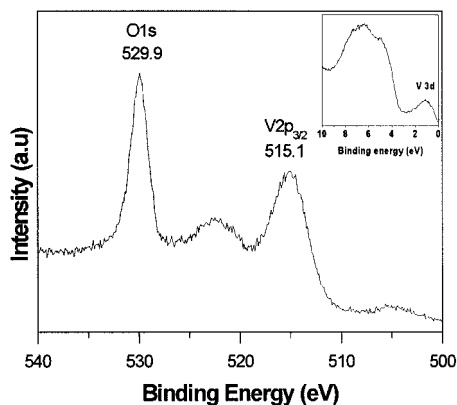


Figure 2. XPS ($\text{Al K}\alpha$, $h\nu = 1486.6$ eV) and He (I) UPS of V_2O_3 film with 20 ML thickness on $\text{Re}(0001)$.

3. Results and Discussion

3.1. Preparation of Ultrathin V_2O_3 Films. After Ar^+ bombardment and subsequent annealing and flash, a clean $\text{Re}(0001)$ substrate was checked by XPS, and from LEED it shows a sharp hexagonal pattern. Then V was deposited on the $\text{Re}(0001)$ substrate in O_2 . Figure 1 demonstrates a hexagonal LEED pattern after a ~ 20 ML vanadia film was grown on the $\text{Re}(0001)$ surface. On this surface, no Re signal was detected by XPS. Due to the variable valence of vanadium, several compounds may form in the vanadium–oxygen system with different structures and stoichiometries, such as VO , VO_2 , V_2O_3 , V_2O_5 , and some mixed-valence vanadia. Among them, VO has the rock salt structure; VO_2 , the rutile structure; V_2O_3 , the corundum structure with hexagonal symmetry; and V_2O_5 , the layered orthorhombic structure. Comparing our vanadia films grown on the $\text{Re}(0001)$, only $\text{VO}(111)$ and $\text{V}_2\text{O}_3(0001)$ exhibit a hexagonal LEED pattern, which excludes the formation of VO_2 or V_2O_5 .

The XPS data for the vanadia film on $\text{Re}(0001)$ are shown in Figure 2. Various vanadium oxides have been characterized by XPS. The V $2p_{3/2}$ core-level binding energies for bulk V_2O_5 , VO_2 , and V_2O_3 are 516.9, 516.2, and 515.7 eV, respectively.^{31–32} In our measurements, the binding energy of the V $2p_{3/2}$ feature

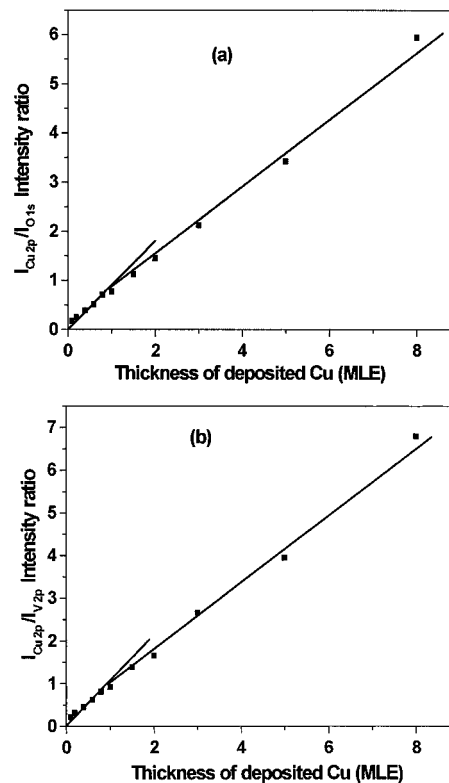


Figure 3. Growth mode of Cu on $\text{V}_2\text{O}_3(0001)$. The XPS intensity ratio $I_{\text{Cu}2p}/I_{\text{O}1s}$ (a) and $I_{\text{Cu}2p}/I_{\text{V}2p}$ (b) from $\text{V}_2\text{O}_3(0001)$ as a function of Cu deposition at room temperature.

is 515.1 eV and the O $1s$ 529.9 eV. These values agree well with previous XPS studies on the V_2O_3 surface,^{3,5–7,31–35} and suggest the prepared film being V_2O_3 .

The vanadium oxide films were also characterized by UPS shown as an insert in Figure 2. V_2O_5 has an empty 3d shell and has no V 3d peak in UPS. At room temperature, the V 3d band for VO_2 is a simple band of 1.5 eV width and is centered at 0.9 eV.^{36–37} For V_2O_3 , the 3d band ranges between BE = 0 and 3 eV with the peak position around 1.3 eV.^{37–38} The binding energy of 1.15 eV for V 3d by UPS and with a 3d bandwidth of about 3 eV, further prove our vanadium oxide films to be $\text{V}_2\text{O}_3(0001)$.

3.2. Growth of Cu on $\text{V}_2\text{O}_3(0001)/\text{Re}(0001)$. The growth of Cu was analyzed by monitoring the Cu-to-O and Cu-to-V intensity ratio by XPS as function of Cu coverage. As seen in Figure 3, straight lines can be fitted to the data for the initial growth of Cu on V_2O_3 film, with clear breakpoints for both curves of Cu-to-O and Cu-to-V at a Cu layer thickness of 1.0 MLE. This may suggest the growth of patch-wise Stranski-Krastanov type: Cu grows initially in two-dimensional (2D) patches at submonolayer coverages, and then gradually forms three-dimensional (3D) islands on top of the patches, as was also found for Cu on $\text{TiO}_2(110)$,¹¹ $\text{MgO}(100)$,¹⁷ $\text{ZnO}(0001)$,¹⁶ $\alpha\text{-Al}_2\text{O}_3(0001)$,^{15,24} and $\text{Cr}_2\text{O}_3(0001)$.²⁶ For thicker layers of Cu, the V and O intensity is larger than expected from pure layer-by-layer (2D) growth. And even at the Cu coverage of over 20 MLE, strong signals of the V and O still can be detected by XPS. That means 3D growth occurs. The lack in the LEED patterns of a structure until a Cu coverage of at least 8 MLE—combined with our application of incident energy having a coherence length of about 10 nm—indicates that Cu clusters are small. Since the XPS intensity ratio of V-to-O keeps basically constant, it can be excluded that Cu diffuses into V_2O_3 film. For revealing more detail of the surface structure a careful

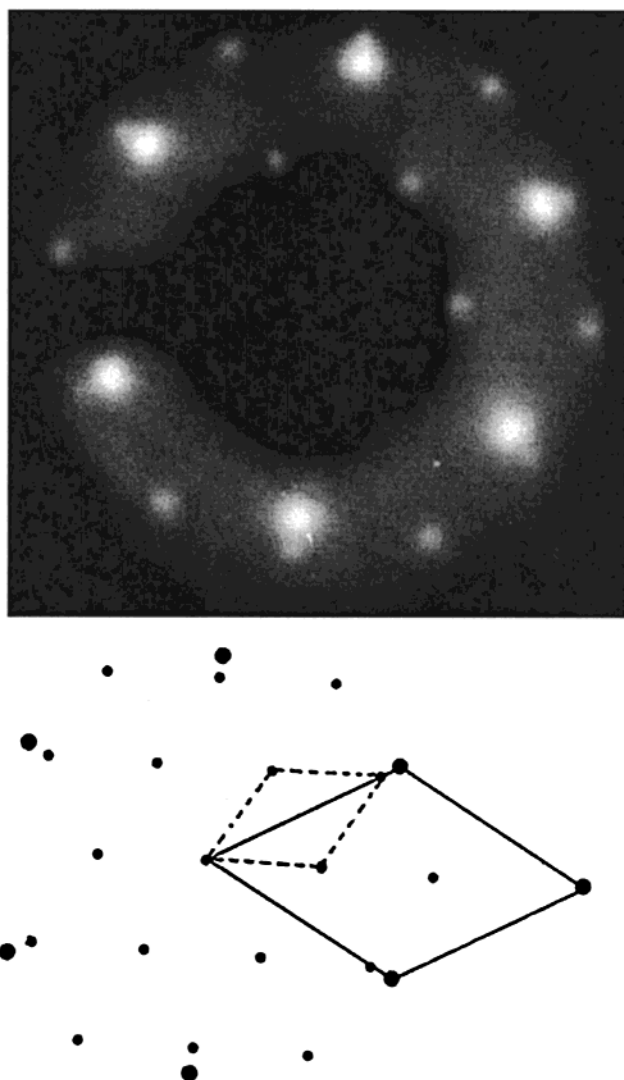


Figure 4. Top, LEED pattern from epitaxial copper superstructure, Cu(111)/V₂O₃(0001)/Re(0001). $E_p = 90$ eV. The respective unit cells are indicated in the bottom. The large (full line) unit cell corresponds to Cu(111) and the small (broken line) unit cell to the V₂O₃(0001) surface.

measurement by scanning tunneling microscopy is expected, which will be reported separately in a future study.

Figure 4 shows the LEED pattern from Cu(111) on V₂O₃(0001) with a thickness of about 20 MLE. A LEED pattern of Cu(111)R30° superstructure on V₂O₃(0001) surface was observed. This agrees with the previous results of Cu on the single-crystal oxides with corundum structure, such as Cu on Al₂O₃(0001)¹⁵ and Cr₂O₃(0001).²⁶ From a calibration using the hexagonal V₂O₃ LEED pattern spot distances (supposing the lattice constant of V₂O₃(0001) film is 0.5 nm, a value of bulk V₂O₃), we calculate the distance between Cu atoms ($a^* = b^* = 2/\sqrt{3}a_0$, 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.

3.3. Interaction of Cu with V₂O₃. Previous XPS studies have shown that the XPS spectra of CuO has a characteristic shake-up satellite,³⁹ and because the peak shapes of Cu 2p are similar and the binding energy values are very close (for Cu(0) the BE value of Cu 2p_{3/2} is 932.7 eV and for Cu(I) it is 932.6 eV),³⁹ it is difficult to further distinguish between the Cu(0) state and the Cu(I) state on the basis of the XPS data alone, but it can be achieved by considering the corresponding X-ray induced Auger

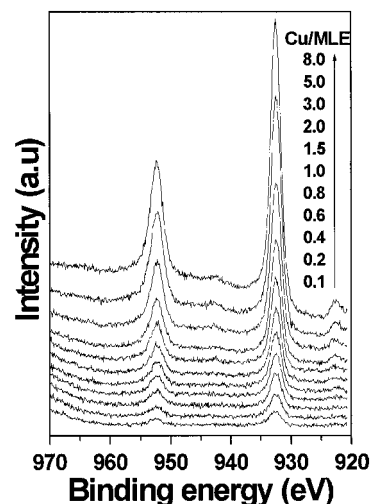


Figure 5. XPS of deposited Cu as a function of coverage. Al K α , $h\nu = 1486.6$ eV.

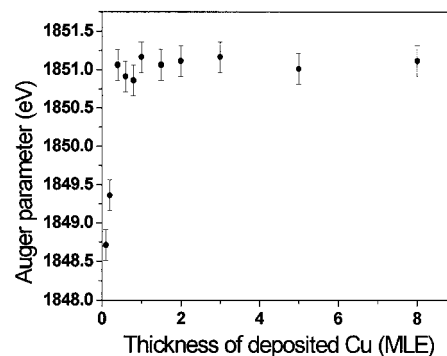


Figure 6. Auger parameter changes with increasing Cu on the V₂O₃(0001) surface.

Cu(LMM) spectra and the Auger parameter α (the sum of the X-ray induced Auger peak and the binding energy value of the highest photoemission peak, i.e., Cu 2p_{3/2}). Figure 5 shows the XPS results of Cu 2p spectra as a function of Cu deposition on V₂O₃(0001) surface. Since no characteristic shake-up satellite of CuO are observed, the chemical state of Cu should not be Cu(II). To further distinguish the Cu(0) state and the Cu(I) state, we therefore use the Auger parameter α as a function of Cu coverage showed in Figure 6. Initially α is within the range reported for Cu₂O, then a gradual approach of α to the bulk Cu value of 1851.3 eV appears.³⁹ This suggests the existent of Cu(I) state at the beginning of Cu growth on vanadia films (less than 0.2 MLE), as the similar results reported for Cu on MgO,¹⁷ ZnO,¹⁶ TiO₂,²⁵ Fe₂O₃,^{13–14} Al₂O₃,^{15,18–19,22–23} and Cr₂O₃.²⁶ The Cu(I) chemical state may origin from the charge transfer from Cu to V₂O₃ substrate. At a coverage of higher than 2 MLE, Cu becomes neutral. The peaks marked a and b are induced by Al K α ,^{3,4} as shown in Figure 5.

To further investigate the content of the different phases in the composite surface after Cu deposition, we have carried out simultaneous in situ UPS on the Cu/V₂O₃(0001)/Re(0001) samples. Figure 7 shows He(I) UPS spectra for Cu on the V₂O₃(0001)/Re(0001) surface. Clean V₂O₃ has two peaks at 4.9 and 6.9 eV below E_F , respectively, assigned to the O 2p orbital and the V(3d)-O(2p) hybridized orbital.^{37–38} For Cu/V₂O₃(0001), a very weak peak located at 2.9 eV below E_F for thickness of 0.1 MLE Cu deposition is assigned to the Cu(3d) band emission, which is slightly higher than that of metallic Cu(2.5 eV).^{18–21} As shown in Figure 7, the binding energy of Cu 3d shifts to lower energies, below E_F , approaching the bulk Cu characteristic

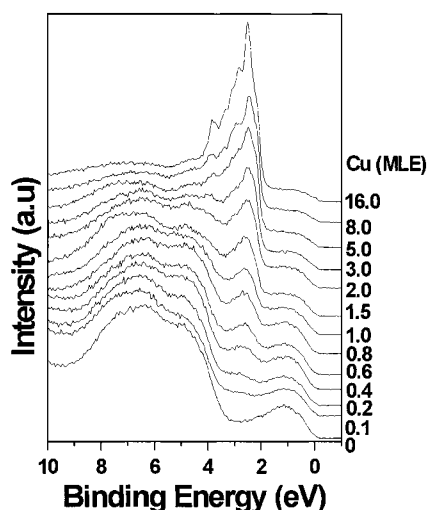


Figure 7. He(I) UPS spectra as a function of Cu thickness on V_2O_3 -(0001)/Re(0001) at room temperature.

with further Cu deposition on V_2O_3 /Re(0001). This shift of the binding energy of Cu 3d reveals an interaction of Cu atoms with the substrate. As we know that the binding energy of Cu (I) is about 2.9 eV,⁴⁰ the chemical state of Cu at low coverages (lower than 0.2 MLE) is an indication of Cu (I), consistent with our former argument. This strongly suggests the formation of Cu–O bonding during the initial Cu deposition. The Cu–O bonding orbital may form by hybridization of the partially filled Cu 3d orbital with the nonbonding O 2p orbital of V_2O_3 surface. We also note that the binding energy of V(3d)–O(2p) hybridizing orbital shifts to higher binding energy and broadens with Cu deposition. This is a signal of the formation of Cu(3d)–O(2p) bonding orbital near the bottom of the V_2O_3 valence band, which is very similar to the case of Cu deposited on Al_2O_3 .^{18–19}

4. Conclusions

On conclusion, ordered V_2O_3 (0001) films were prepared on Re(0001) substrate before Cu deposition. XPS studies indicate that at room-temperature Cu grows in a patch-wise Stranski-Krastanov mode on V_2O_3 (0001) surface: from the initial 2D Cu patches to the later 3D Cu islands. At low coverages, the Cu(I) state is found due to the interaction with V_2O_3 substrate. With further deposition at Cu coverages >2 MLE, Cu becomes metallic. A Cu(111)R30° superstructure on V_2O_3 (0001) surface was observed by LEED.

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