Epitaxial Growth Defects and Interfacial Structures of Cu Deposited on TiO₂

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Abstract. Epitaxial growth defects and the interfacial structure between vapor deposited Cu and TiO₂(110) have been studied by combined high-resolution electron microscopy (HREM) and image simulations. The Cu film was found to grow epitaxially with an orientation given by Cu(111)//TiO₂(110) and Cu(110)//TiO₂ [001]. With this relationship, there exist two equivalent domain orientations which are rotated with respect to each other by 180°. Localized misfit dislocations have not been detected, but {111} stacking faults and microtwins were observed which may occur as a result of 3-D island coalescence. HREM observations and image simulations have been used to study the interface atomic structure. The dominant interfacial structure has a stoichiometric (110) TiO₂ surface with bridging rows of O atoms and occasionally, an interfacial structure having a reduced (110) TiO₂ surface terminated by both Ti and O atoms has been observed locally.

1. Introduction

In recent years, there has been considerable interest on chemical and structural phenomena at metal/oxide interfaces [1]. For the metal/TiO₂ system, particular attention was given towards understanding the mode of metal growth on the oxide as well as their chemical reactivity. At the present time, the interaction of metals, such as Pt [2], Rh [3, 4], Cr [5], Fe [6, 7], Ni [8, 9], Cu [10, 11] and Al [12] with TiO₂ (110) have been investigated. The TiO₂ oxide is often the choice for surface and metallization studies because of its importance in catalyst systems and because well ordered stoichiometric surfaces can be produced. Another experimental advantage for selecting TiO₂ is that the bulk structure can be reduced slightly, thus minimizing charging problems, and the surface reoxidized to restore stoichiometry [13]. However, the TiO₂ surface structure and roughness are highly sensitive to annealing treatments and various surface reconstructions have been detected by STM, depending on specific surface preparation techniques [14]. Therefore, great care must be exercised to minimize surface damage and to fully characterize the surface prior to surface metallization.

Most previous metallization studies were aimed primarily at understanding the early stages of metal growth and their chemical interaction with the oxide surface. For instance, a combined reduction of TiO₂ surface and formation of a metal oxide have been observed for Al [12], while both Fe and Cr exhibit strong interaction with TiO₂ and partial reduction of the oxide but without metal oxide formation [5, 7]. In general it is observed that metal/oxide interactions, as measured by surface coverage during growth, varies with the energy of metal/oxide formation [15]. For Cu, however, contradicting results in growth mode have been reported. In one study, Möller and Wu [10] observed, using Auger-electron spectroscopy (AES), that the first monolayer of Cu on TiO₂ (110) surface formed a slightly contracted hexagonal superlattice, leading to a (111) oriented Cu layer. However, in another study,
Diebold et al. [11] found using low energy ion scattering (LEIS) and x-ray photoelectron spectroscopy (XPS) that Cu grew epitaxially as 3-D islands even at a temperatures as low as 160 K. In neither study, the Cu/TiO\textsubscript{2} atomic structure and the degree of interracial coherence were reported.

The goals of this investigation are three folds. First, to study the morphology and orientation of a thick Cu overlayer on TiO\textsubscript{2} (110), second, to understand the interracial misfit accommodation and third to obtain atomistic information on Cu/TiO\textsubscript{2} interracial structure and chemistry by combined High Resolution Electron Microscopy (HREM) and image simulations.

2. Experimental

The Cu film was grown epitaxially on a TiO\textsubscript{2} (110) substrate by vapor deposition in a UHV chamber with a base pressure of \(\sim 1 \times 10^{-10}\) torr and containing all basic probes for surface characterization, such as XPS and low energy electron diffraction (LEED) [15]. Before deposition, the TiO\textsubscript{2} (110) substrate was treated by sputtering with a 500 eV Ar ion beam and subsequent annealing for 10 minutes in an oxygen atmosphere of \(2 \times 10^{-6}\) torr and at a temperature of 1000 K, followed by cooling in oxygen. XPS, LEIS and ultraviolet photoemission spectroscopy (UPS) data indicate that TiO\textsubscript{2} (110) surfaces prepared in this way are clean, stoichiometric and stable under ultrahigh vacuum. Any residual surface defects (oxygen vacancies) have a low concentration, approximately \(10^{-2}\) monolayers [16]. The surface exhibits a (1 x 1) LEED pattern and is believed to have an ideally bulk-truncated TiO\textsubscript{2} (110) surface structure, which is terminated by rows of oxygen atoms, called “bridging oxygen”, oriented in the [001] direction [17, 18]. The Cu evaporation was performed by joule heating with a tungsten filament. The Cu layer, of about 20 nm in thickness, was deposited at rate of \(\sim 0.5\) nm/s onto the TiO\textsubscript{2} (110) substrate maintained at room temperature.

Cross-sectional HREM specimens were prepared using the following procedure. First, two pieces were glued together with the Cu film surfaces facing each other. The “sandwiched” sample was cut in strips of 1 mm in thickness with the foil normal parallel to the TiO\textsubscript{2} [001] direction. The cross-section specimens were thinned by mechanical polishing, dimpling and Ar ion beam milling at 5 keV. The last 10 minutes was thinned at 2 keV and at a sputtering angle of 12°. The samples were examined with a Topcon-002B high resolution electron microscope having a point-to-point resolution of \(\sim 0.18\) nm. HREM image simulations were performed using the EMS program [19]. The operating parameters for the microscope were as follows: coefficient of spherical aberration Cs = 0.4 mm; defocus spread \(\Delta f = 12\) nm; beam divergence angle half-width \(\alpha = 1.0\) mrad.

3. Results

3.1. Morphology and Orientation Relationship

A low magnification cross-sectional TEM micrograph of the Cu film on (110) TiO\textsubscript{2} is shown in Fig. 1 with the corresponding select area diffraction pattern shown in Fig. 2(a). The average thickness of the Cu determined from bright-field TEM micrograph was about 16 nm with a variation of about 3 nm. The electron diffraction pattern indicated that Cu grows epitaxially with an orientation relationship given by:

\[
(111)\text{Cu}//(110)\text{TiO}_2 \quad \text{and} \quad (110)\text{Cu}//[001]\text{TiO}_2
\]

This relationship is consistent with previous results obtained by LEED [10, 11]. However with this orientation, the Cu film possesses two equivalent domains which are rotated by a 180° about the [111] surface normal. A schematic diagram of the two domains, viewed along the surface normal is shown in Fig. 3. These two orientations are not distinguishable by diffraction when viewed along the [111] film normal but can be observed in cross-section as shown in the diffraction pattern of Fig. 2a. This micrograph is a superposition of the [001] pattern from the TiO\textsubscript{2} substrate and two (110) patterns from the two Cu domains, as shown schematically in Fig. 2b.

Within each domain, \{111\} stacking faults or microtwins on \{111\} planes are visible as indicated in the low magnification image shown in Fig. 1. A boundary separating two domains is also visible in Fig. 1. Two Cu domains can be identified easily from the relative orientation of