Epitaxial Electrodeposition of Copper(I) Oxide on Single-Crystal Gold(100)

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Introduction

Single-crystal films are important for device applications, as the intrinsic properties of the material of interest can be exploited rather than its grain boundaries. The ability to simply and inexpensively prepare epitaxial films with a desired orientation allows the selection of the film orientation that most enhances the property of interest. For example, it would be desirable to select the orientation of a material that exhibits the highest ionic mobility[1] or to select the plane of a material that shows the highest degree of catalytic activity.[2] Recently, we reported that epitaxial thin films of δ-Bi_2O_3 can be electrodeposited from an alkaline tartrate solution onto single-crystal Au at a temperature of 65 °C.[3] This cubic polymorph of Bi_2O_3 has been shown to have the highest oxide ion mobility of any known material.[4] In the present work we use electrodeposition to prepare epitaxial films of copper(I) oxide (Cu_2O) on a single-crystal Au(100) substrate. Cu_2O is a p-type semiconductor that has been electrodeposited previously on a variety of substrates.[5−8] We have previously shown that the orientation of electrodeposited Cu_2O films is a function of the pH of the alkaline lactate solution and that the deposition current is limited by a Schottky-like barrier that forms between Cu_2O and the deposition solution.[9] We have also shown that, under certain galvanostatic conditions, the working electrode potential spontaneously oscillates,[10,11] forming a Cu/Cu_2O layered nanostructure that shows a negative differential resistance (NDR) feature during perpendicular transport measurements.[12] The NDR feature shifts with a $1/L^2$ dependence on the Cu_2O layer thickness, suggestive of quantum confinement of carriers in the nanoscale Cu_2O.[13] These layered nanostructures were deposited on polycrystalline substrates. However, it would be desirable for device applications to deposit these structures as epitaxial films on single-crystal substrates. In the present work, we explore the epitaxial growth of pure Cu_2O onto single-crystal gold. In subsequent work, we will study the deposition of Cu/Cu_2O layered nanostructures on single-crystal substrates.

The underpotential deposition of monolayers of metals on single-crystal substrates has been studied quite extensively.[14] Little work, however, has been done on the electrodeposition of epitaxial semiconductor films with thicknesses in the micrometer range. Electrochemical atomic layer epitaxy has been used for the formation of CdSe monolayers on Au(111).[15] Epitaxial CdTe films can be electrodeposited from aqueous solution onto InP(111) single crystals.[16] Large area epitaxial thin films of CdSe[17] and quantum dots of Cd(Se,Te) have been prepared on evaporated Au(111) films.[18] Epitaxial CdS nanocrystals have been prepared on graphite by a combined electrochemical/chemical method.[19,20]

We show in the present work that electrodeposited films of Cu_2O grow epitaxially on Au(100) single crystals. The crystal structures of Au and Cu_2O are shown in Figure 1. Cuprous oxide is primitive cubic, space group $Pn3m$, with a lattice parameter of 0.427 nm. Au is fcc, space group $Fm3m$, with a lattice parameter of 0.4079 nm. The lattice mismatch ($(a_{\mathrm{film}} - a_{\mathrm{substrate}})/a_{\mathrm{substrate}}$) between the two materials is 4.7%. The epitaxial Cu_2O film grown on Au(100) shows a high degree of structural perfection, with no rotation of the Cu_2O with respect to Au.

Experimental Section

The deposition solution was prepared by adding 450 mL of 5 M NaOH to 60 g of Cu(II) sulfate pentahydrate and 150 mL of 85+% lactic acid, resulting in a dark blue solution. The final pH of the solution was adjusted to pH 9.0 with 5 M NaOH. HPLC-grade water (Aldrich) was used to prepare the 5 M NaOH. All other chemicals were reagent grade, purchased from Aldrich. The working electrode consisted of an electropolished Au(100) single-crystal purchased from Monocrystals Co. The Au crystal had a diameter of 10 mm and a thickness of 1 mm. A gold wire was fitted around the edge of the crystal to

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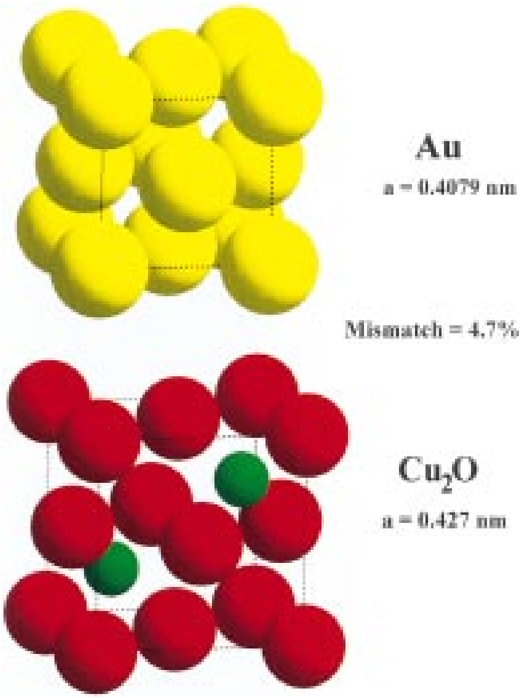

Figure 1. Crystal structures of Au and Cu_2O. Au is fcc, space group *Fm*3*m*, with a lattice parameter of 0.4079 nm. Cu_2O is primitive cubic, space group *Pn*3*m*, with a lattice parameter of 0.427 nm. In the Cu_2O structure, the large spheres are copper and the small spheres are oxygen. The lattice mismatch between the two materials is 4.7%.

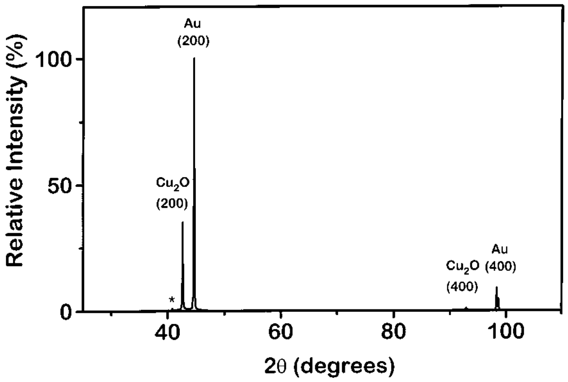

Figure 2. 2θ X-ray pattern for a 0.5 μm thick Cu_2O film electrodeposited on single-crystal Au (100). Only the (200) and (400) reflections for the film and substrate are observed. The minor peak marked with an asterisk is from the (200) Au reflection and is due to Cu Kβ radiation.

serve as the electrical contact during deposition. The counter electrode was a large area copper wire. A constant cathodic current density of 0.01 mA/cm^2 was applied to the working electrode with an EG&G Princeton Applied Research model 273A potentiostat/galvanostat for a period of 40 000 s, giving a nominal Cu_2O film thickness of 0.5 μm. This current density corresponds to a deposition rate for Cu_2O of approximately 0.12 Å/s, assuming a 100% current efficiency for deposition. Application of current densities higher than about 0.1 mA/cm^2 in this solution gives rise to oscillations in the potential coincident with the deposition of a Cu/Cu_2O layered nanostructure on the working electrode.[10-12] To deposit pure cuprous oxide, it is necessary to apply current densities below this threshold value. The stirred deposition solution was maintained at a constant temperature of 30 °C with a Fisher model 9100 circulator. X-ray diffraction (XRD) experiments were performed with a Scintag 2000 diffractometer using Cu Kα radiation. Azimuthal and tilt scans were obtained by the use of a texture goniometer accessory that had been fashioned in-house for the Scintag 2000.

Results and Discussion

Figure 2 shows the 2θ X-ray pattern for the electrodeposited Cu_2O film on single-crystal Au(100). Only the (200) and (400) peaks for the film and the substrate are observed. The (200) Cu_2O peak is greater than a thousand times more intense than any other Cu_2O reflection, indicative of a strong out-of-plane texture. Rocking curves performed on the (200) reflections of both Au and Cu_2O gave full-width at half-maximum (fwhm) values of 0.6 and 0.7°, respectively, indicating that the film had only a slightly greater mosaic spread than the substrate. An epitaxial relationship might be inferred from Figure 2, as the Cu_2O appears to follow the orientation of the Au substrate. However, there is a complicating factor. Under the presently used deposition conditions the kinetically preferred growth direction for Cu_2O is [100]. Hence, even a Cu_2O film grown on a polycrystalline substrate will show a strong (100) texture. To show that the Cu_2O film truly has grown epitaxially on the Au substrate, it is necessary to show both in-plane as well as out-of-plane orientation.

To determine the in-plane epitaxial relationship between the film and substrate, it is necessary to bring other reflections, besides the (100), into the Bragg condition. This is accomplished by tilting the sample, through the use of a goniometer, to the tilt angle (χ) between the planes of interest. Given that the angle between the (100) and (110) plane is 45° and the (100) plane is oriented parallel to the surface in our sample, χ must be 45° in order to bring the (110) reflection into the Bragg condition. Setting 2θ equal to the reflection of interest, in this case the (220) reflections of Au and Cu_2O, and rotating the sample provides an azimuthal (ϕ) scan. Azimuthal scans run at a succession of different tilt angles can be used to generate a three-dimensional pole figure for the crystal of interest. Figure 3 shows the (220) pole figures for both Au and Cu_2O. The pole figures were obtained by setting 2θ equal to the angle of maximum diffracted intensity for the material of interest ($2\theta = 64.58$ and 61.34° for Au and Cu_2O, respectively) and obtaining azimuthal scans at tilt angles from 0 to 60°. Four-fold symmetry is observed in both cases, with a maximum intensity at $\chi = 45°$, and with no rotation of the Cu_2O with respect to Au. The pole figure shows that the film has a strong in-plane orientation in addition to the out-of-plane orientation that was measured in the 2θ scan. If the film had a random in-plane orientation but a strong out-of-plane orientation (i.e., a fiber texture), the 4-fold symmetry would not be seen. Instead, a ring with maximum intensity at a tilt angle of 45° would be observed in the pole figure.

Figure 4 shows a plot of the logarithm of intensity vs azimuthal angle, ϕ, for the (220) reflections of Au and Cu_2O both obtained at a tilt angle, χ, of 45°. Consistent with the rocking curve measurements, the average fwhm values for the azimuthal scans were 1.1° and 1.4° for Au and Cu_2O, respectively. The baseline of the Cu_2O azimuthal scan is essentially identical to that of the Au, indicating a minimal presence of polycrystalline Cu_2O in the film.

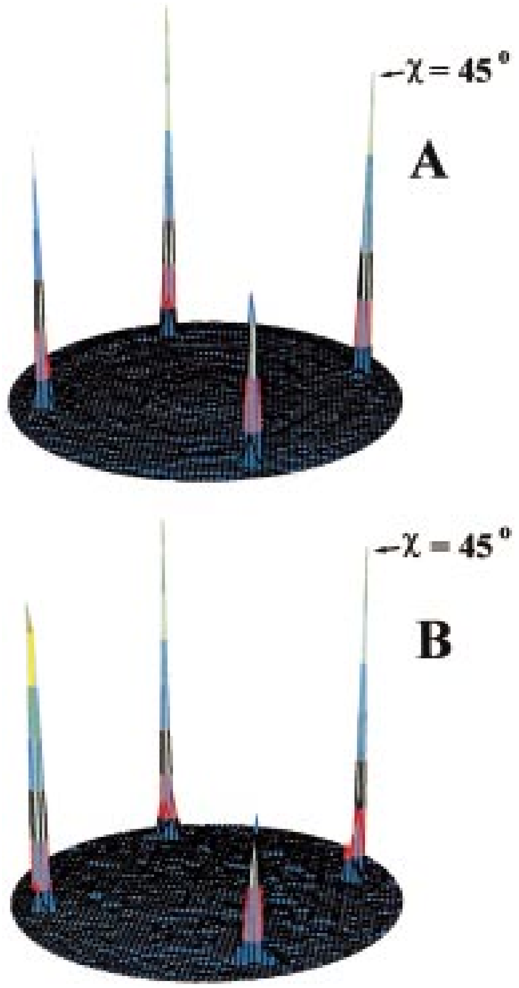

Figure 3. (220) pole figures for (A) Au ($2\theta = 64.58°$) and (B) Cu_2O ($2\theta = 61.34°$). No other maxima are observed in either pole figure except for those occurring at $\chi = 45°$. The pole figure extends to $\chi = 55°$.

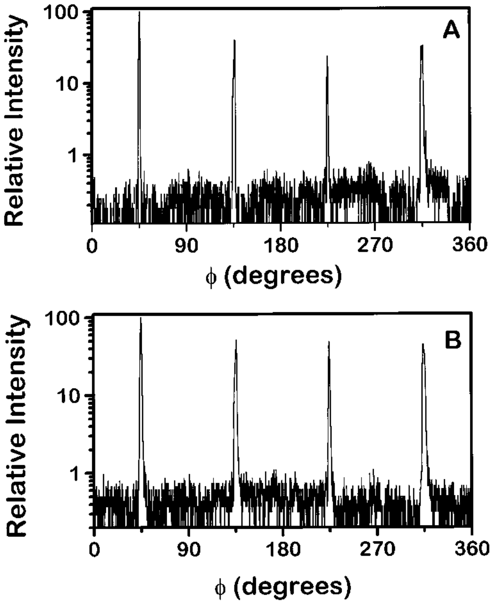

Figure 4. Azimuthal scans for the (220) reflection of (A) Au ($2\theta = 64.58°$) and (B) Cu_2O ($2\theta = 61.34°$) both obtained at $\chi = 45°$. The expected 4-fold symmetry is observed, with no rotation of the Cu_2O film with respect to the substrate. The average fwhm for the Au peaks is 1.1°, while the average for the Cu_2O peaks is 1.4°.

Another measure of the structural perfection of the epitaxial Cu_2O film is a tilt scan. These were obtained by setting the azimuthal angle, ϕ, equal to the angle of the first of the four maxima observed for Cu_2O and Au in Figures 3 and 4. Leaving ϕ fixed, χ was varied from 0 to 70° and the diffracted intensity was observed for the (220) reflections of Au and Cu_2O, independently. The fwhm values for the tilt scans were identical for Au and Cu_2O, with a value of 1.4°, indicating that, within the resolution of our instrument, the Cu_2O film and Au substrate are of comparable quality, despite the lack of strict commensurism between film and substrate.

This study has shown that epitaxial films of Cu_2O can be electrodeposited on single-crystal Au(100). The epitaxial films are of high quality and are not rotated with respect to the Au substrate. A question that remains to be answered is how the significant lattice mismatch of 4.7% is accommodated in this epitaxial system. The experimentally determined lattice parameter of the Cu_2O film (0.426 nm) is within experimental error of the literature value for Cu_2O (0.427 nm),[9] showing that the bulk of the film has not been strained into commensurism with the substrate. These results do not rule out the possibility of a strained pseudomorphic Cu_2O film growing to a very thin critical thickness before relaxing to the bulk structure. Monitoring the growth of the epitaxial film in real time with a scanning tunneling microscope and using cross-sectional transmission electron microscopy should provide important details about the interface between the two materials.

Preliminary results for the electrodeposition of Cu_2O on the other low-index faces of Au reveal that initial growth of the film is epitaxial with no rotation relative to the substrate. However, as the film becomes thicker, the kinetically preferred [100] growth direction predominates. This should provide a convenient means to study the interplay between the thermodynamics of epitaxial growth and the kinetically preferred growth direction of Cu_2O. Epitaxial electrodeposition of other oxides, such as ZnO,[22] Tl_2O_3,[23,24] PbO_2,[25] and AgO[26] should also be possible. Electrodeposition provides a simple and inexpensive means for the deposition of high-quality epitaxial films that could be used for device applications, with our specific interest being the Cu/Cu_2O layered nanostructure system.[13]

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