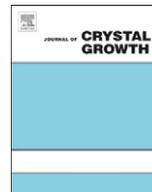




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Growth of single-crystalline Cu₂O (111) film on ultrathin MgO modified α -Al₂O₃ (0001) substrate by molecular beam epitaxy

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ABSTRACT

We report the synthesis of Cu₂O single crystalline films on the *c*-plane α -Al₂O₃ substrate by radio-frequency plasma assisted molecular beam epitaxy. An ultrathin MgO layer was adopted to modify the complex surface structure of sapphire (0001) and engineer the interfacial atomic matching between the epilayer and the substrate. The experimental results solidly proved the single crystallinity of cubic Cu₂O (111) without twin crystals. A coincident match mode was proposed to explain the unusual in-plane orientation between strained MgO (111) and Cu₂O (111). It was found that the crystal quality of Cu₂O is very sensitive to the thickness of MgO layer, which is optimized to be \sim 2 nm. The reason why MgO has a critical thickness in Cu₂O single crystal growth was also tentatively discussed.

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1. Introduction

As a p-type semiconductor with a direct band gap of about 2.1 eV, cuprous oxide (Cu₂O) has been considered as a promising candidate for applications in resistive random access memory (RRAM) [1], spintronics [2] and photovoltaic devices [3], as well as the best material for observing Bose–Einstein condensation (BEC) of excitons [4]. In recent years, special demands for renewable energy resources have stimulated intense studies of Cu₂O thin films and related heterostructures aiming for solar cell and water splitting applications [5]. However, the highest solar cell conversion efficiency ever reported is only 3.83% from a polycrystalline Cu₂O [6], still far away from the theoretical value of 20% [7]. Progress is now limited because of the difficulties in synthesizing high-quality single crystalline Cu₂O films. Similarly, BEC research on Cu₂O excitons has been restricted to natural bulk crystals so far.

Cu₂O thin films have been fabricated on various substrates such as ZnO [8–10], GaAs [11], SrTiO₃ [12–14] and MgO [14–18] etc., among which MgO seems to be the best candidate due to the small lattice mismatch. However, Cu₂O grown on MgO (100) did not

follow the cube on cube epitaxy relationship, resulting in Cu₂O films with multiple orientations [14–16]. Only those grown on MgO (110) got single oriented Cu₂O (110), but the single crystallinity was not investigated [14,17,18]. Synthesis of Cu₂O (111) on bulk MgO (111) has been rarely reported before. Considering the complex surface structure of α -Al₂O₃ (0001) and the large in-plane lattice mismatch (36.6%) between these two materials, sapphire might not be an ideal substrate for high-quality Cu₂O growth in spite of its apparent merits of high crystal quality, low cost, superior thermal and chemical stabilities, and insulating property. However, by adopting an ultrathin MgO buffer layer to engineer the interface, the surface atomic structure and the lattice matching mode can be efficiently modified. A single crystalline Cu₂O films can be therefore achieved on sapphire. In this letter, we report the epitaxial growth of single crystalline Cu₂O (111) films on α -Al₂O₃ (0001) substrates by radio-frequency plasma assisted molecular beam epitaxy (rf-MBE) technique.

2. Experimental

The growth was carried out in an rf-MBE system with a background pressure of $\sim 10^{-7}$ Pa. Elemental Cu (6N) and Mg (5N) evaporated by Knudsen cells and oxygen radicals (5N5) generated by the rf-plasma system were used as sources for the growth. Sapphire substrates were thermally cleaned at 750 °C

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for 30 min and then pretreated by O plasma (300 W/2.0 sccm) at 500 °C for 15 min to get an O-terminated clean surface. An ultrathin MgO buffer layer was then deposited at 500 °C with a delicately controlled thickness of about 2 nm, which is very critical for the accomplishment of single crystal Cu₂O. A conventional two-step growth of Cu₂O, i.e. a low-temperature buffer layer at 500 °C and a high-temperature epilayer at 700 °C, was performed with constant Cu cell temperature of 1000 °C and O₂ flux of 1.0 sccm. The growth rate was ~50 nm/h and the film thickness is ~150 nm. The whole growth process was in-situ monitored by reflection high-energy electron diffraction (RHEED), so the evolution of crystal structures and qualities can be clearly observed. The crystal structure of the epilayer was further investigated by ex-situ X-ray diffraction (XRD) measurements.

3. Results and discussion

The crystallinity of Cu₂O film is quite sensitive to the thickness of MgO buffer layer. To realize a single crystalline Cu₂O (111) film on α -Al₂O₃ (0001), the optimized thickness of MgO buffer layer was determined as ~2 nm. Fig. 1 shows the evolution of RHEED patterns during Cu₂O growth. Streaky RHEED patterns and clear Kikuchi lines indicate the achievement of a clean sapphire surface after thermal cleaning and oxygen plasma pretreating [Fig. 1(a)]. After the deposition of MgO buffer layer, some new streaky lines appeared [Fig. 1(b)], and Kikuchi lines of the substrate were still visible. This RHEED pattern was enlarged in Fig. 1(c) to clearly show the minor but important change after MgO deposition, where two new bars from MgO lattice indicated by long dashed arrows can be distinctly seen apart from those of sapphire indicated by short solid arrows. This observation suggests the MgO layer is very thin (~2 nm), very smooth, and highly strained. Moreover, a six-folded symmetry demonstrated the MgO ultrathin layer has a hexagonal in-plane atomic structure and was (111) oriented. On this MgO-modified α -Al₂O₃ substrate, the large lattice mismatch induced a large lattice strain which resulted in a three-dimensional growth of Cu₂O buffer layer, and it was reflected by the spotty RHEED patterns shown in Fig. 1(d). However, when we increased the substrate temperature after 10 min buffer deposition, the patterns

tended to be streaky and sharp. Fig. 1(e) shows the streak-like diffraction spots of Cu₂O buffer layer at 700 °C, indicating an improved surface morphology. However, when the growth of Cu₂O epilayer started at 700 °C, the streaky patterns gradually degenerated into spots again [Fig. 1(f)]. It implies that a three-dimensional growth mode is mostly favored in such a growth temperature range for this epitaxial system. The two diffraction patterns in Fig. 1(g) were recorded along two opposite incident azimuths of $\langle 1\bar{1}0 \rangle$ and $\langle \bar{1}10 \rangle$, from which we can conclude that no rotation domains or twin crystals exist and we obtain a single crystalline Cu₂O (111) film.

By tracing the evolution of RHEED patterns as shown in Fig. 1, we can deduce the in-plane orientations are Al₂O₃ [10 $\bar{1}$ 0]//MgO [1 $\bar{1}$ 0]//Cu₂O [11 $\bar{2}$], and Al₂O₃ [1 $\bar{2}$ 10]//MgO [$\bar{1}$ 12]//Cu₂O [1 $\bar{1}$ 0]. It is somehow strange that Cu₂O did not follow an overlap in-plane orientation with MgO layer in consideration of the small mismatch (1.4%) and similar cubic cells. This is the key point for the reduction of big lattice mismatch between Cu₂O (111) layer and sapphire substrate and realization of single crystalline Cu₂O, which will be discussed later.

To confirm the single phase and single crystallinity of our Cu₂O films, XRD θ - 2θ and ϕ -scan measurements were carried out. Fig. 2(a) shows the XRD θ - 2θ scan curve. Only two sharp and intense peaks at 36.4° and 41.7° were detected, corresponding to the diffraction from Cu₂O (111) and α -Al₂O₃ (006), respectively. No sign of Cu, CuO or Cu₂O with other orientations were observed. The full width at half maximum of Cu₂O (111) rocking curve is about 0.8°, which is relatively big but reasonable in terms of the large lattice mismatch between Cu₂O (111) and *c*-plane α -Al₂O₃ and the small thickness of the Cu₂O epilayer. Moreover, the lattice constant of the Cu₂O film calculated from the XRD data is very close to the bulk value with a deviation less than 0.4%, suggesting that it has been relaxed already. Fig. 2 (b) shows the ϕ -scan profiles of Cu₂O (200) and Al₂O₃ (113) planes, and only three peaks from Cu₂O (200) with 120° intervals can be clearly seen, which serves as a solid evidence of the single crystallinity without rotation domains or twin crystals and the unique orientation relationship we concluded from RHEED observations.

Note that α -Al₂O₃ (0001) and Cu₂O (111) have similar hexagonal in-plane atomic arrangements, but Cu₂O (111) is three-folded

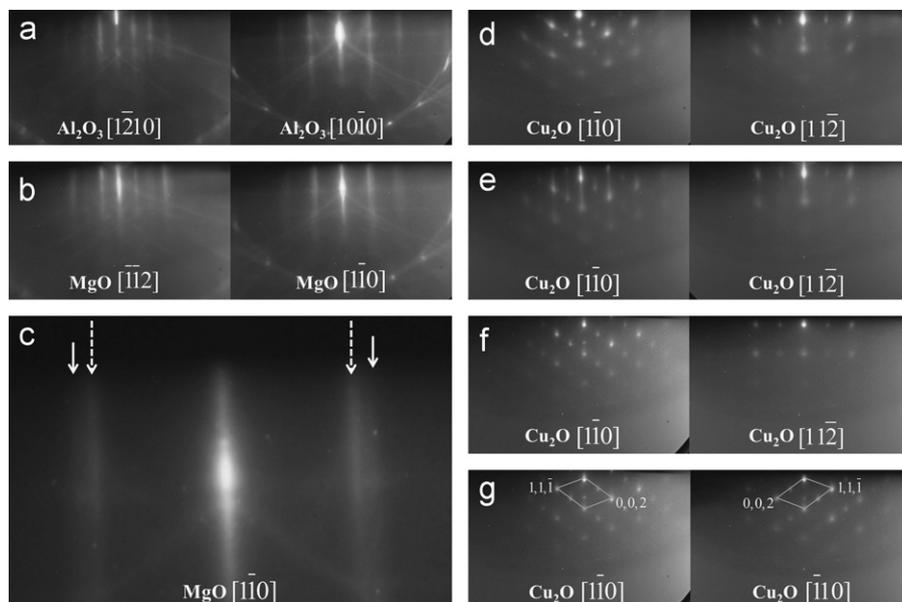


Fig. 1. RHEED patterns with incident electron beams along [11 $\bar{2}$ 0] and [10 $\bar{1}$ 0] Al₂O₃ azimuths, respectively, obtained from α -Al₂O₃(0001) surface (a); after MgO buffer deposition (b); enlarged pattern of (b), where short solid arrows and long dashed arrows indicate the diffraction lines of α -Al₂O₃ and MgO, respectively (c); after Cu₂O buffer deposition at 500 °C(d); Cu₂O buffer at 700 °C (e); after Cu₂O epitaxy at 700 °C (f), and Cu₂O with different azimuths (g).

symmetric because of the cubic crystal structure. Previous reports on a six-fold symmetry of Cu₂O (111) confirmed by ϕ -scan measurements originate from twin crystals [11], which are quite common in cubic crystals but hamper the high-quality film growth. However, our results clearly show the three-fold symmetry of Cu₂O (111) epilayer, indicating the absence of twin crystals and the possibility of further optimization of crystal qualities. We attribute

the successful suppression of twin crystals to the insertion of MgO modification layer. Though this MgO layer is very thin, it demonstrates a cubic structure, which can provide a suitable epitaxial template for Cu₂O growth.

As indicated by the RHEED patterns and XRD results, the Cu₂O (111) film did not follow an overlap epitaxial relationship on MgO (111) template, i.e., MgO [1 $\bar{1}$ 0]//Cu₂O [1 $\bar{1}$ 0]. Instead, it rotated 90° with respect to the zone axis of MgO, resulting in an in-plane orientations of Al₂O₃ [10 $\bar{1}$ 0]//MgO [1 $\bar{1}$ 0]//Cu₂O [11 $\bar{2}$], and Al₂O₃ [1 $\bar{2}$ 10]//MgO [1 $\bar{1}$ 2]//Cu₂O [1 $\bar{1}$ 0]. This epitaxial relationship is confirmed by the ϕ -scan results as shown in Fig. 2(b). As we have mentioned, it is unusual considering the small lattice mismatch (1.4%) between the (111) planes of MgO and Cu₂O using bulk parameters ($a_{\text{MgO}} = 0.2978$ nm and $a_{\text{Cu}_2\text{O}} = 0.302$ nm, here a denoted as the two-dimensional lattice constant of (111) plane). However, this rotated epitaxial relationship is very critical for the change of atomic matching mode and the decrease of large lattice mismatch which contributes to the single crystal growth. Detailed analysis of the RHEED patterns [Fig. 1(c)] revealed that the big strain in MgO ultrathin layer is the main reason for this unusual epitaxial relationship. The two-dimensional lattice constant of the strained MgO (111) layer was estimated to be ~ 0.314 nm ($a_{\text{MgO}}^{\text{est}}$) from the spacing of diffraction lines, which was considerably bigger than the bulk value and hence enlarged the lattice mismatch from 1.4% to 3.9%. However, as illustrated in Fig. 3, when Cu₂O rotates 90° (the same atomic arrangement as 30°), that is to say, the epitaxial relationship changes from MgO [1 $\bar{1}$ 0]//Cu₂O [1 $\bar{1}$ 0] to MgO [1 $\bar{1}$ 0]//Cu₂O [11 $\bar{2}$], the coincidence lattice mismatch would be notably reduced to 0.1% [$F = (3 \times \sqrt{3}a_{\text{Cu}_2\text{O}} - 5a_{\text{MgO}}^{\text{est}}) / 5a_{\text{MgO}}^{\text{est}}$] in a periodic coincidence match mode [19,20]. In that case, the domain-matched (periodic coincidence match) epitaxy would be more energetically favored, and it's quite natural that Cu₂O would choose such a rotated epitaxial relationship. One big benefit of this matching mode is that the lattice strain can be mostly relaxed at the interface of Cu₂O/MgO through the formation of periodic dislocations, which guaranteed the single crystallinity of the epitaxial films. This mechanism has been well established by a high-resolution transmission electron microscope observations in GaN and ZnO growth [19,20]. In our case, the MgO layer is high-strained and the lattice constant of Cu₂O film is very close to the bulk value, which is the natural result of the unique matching mode. It implies that this technique is promising to get thicker films with high quality for device fabrications.

As we have claimed at the beginning, the Cu₂O crystalline quality is very sensitive to the thickness of MgO buffer layer. Once MgO grows thicker, it will relax from the strained condition and the RHEED pattern correspondingly changes as shown in Fig. 4(a).

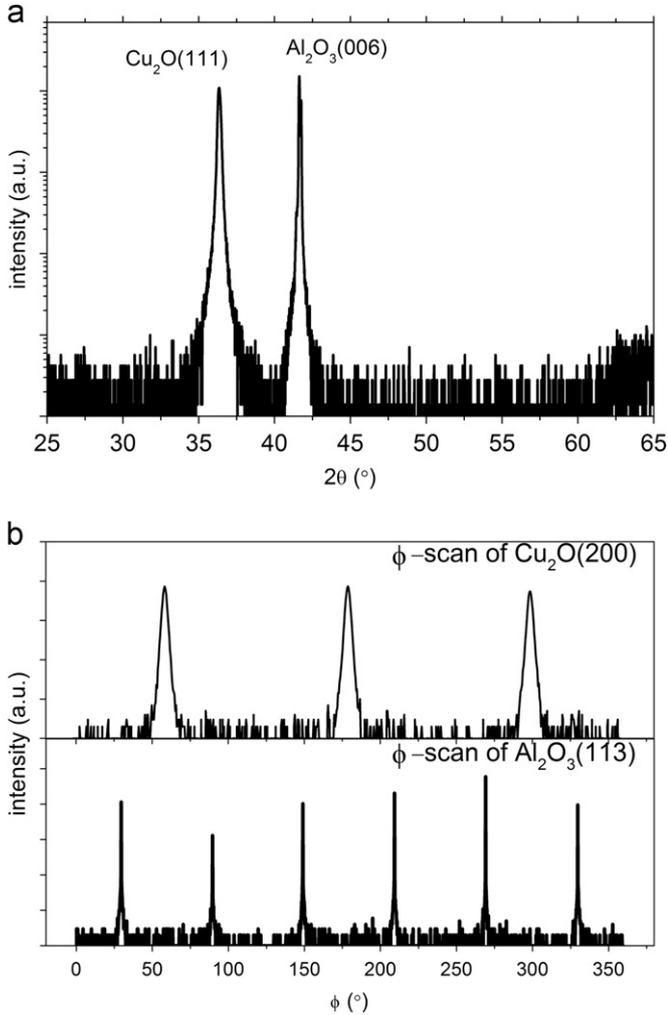


Fig. 2. XRD θ - 2θ scan of Cu₂O films on α -Al₂O₃ (a) and ϕ -scan profiles of Cu₂O (200) and Al₂O₃ (113).

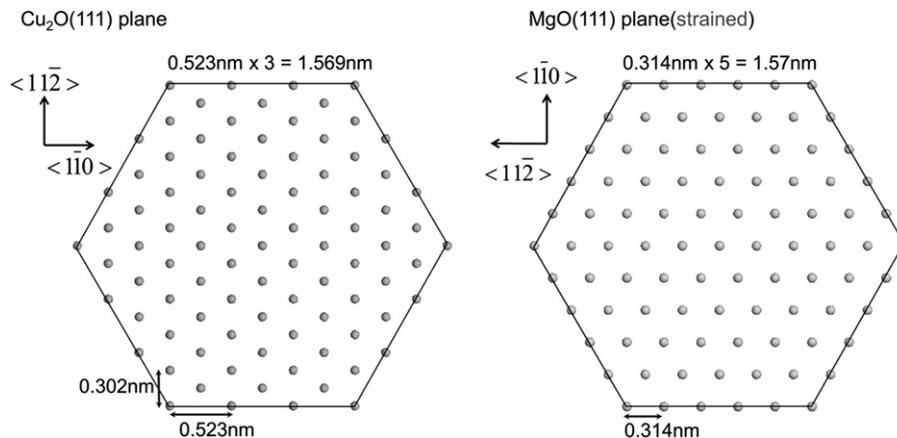


Fig. 3. Schematic illustration of the coincident periodic match mode of Cu₂O (111) epitaxial film on strained MgO (111) buffer.

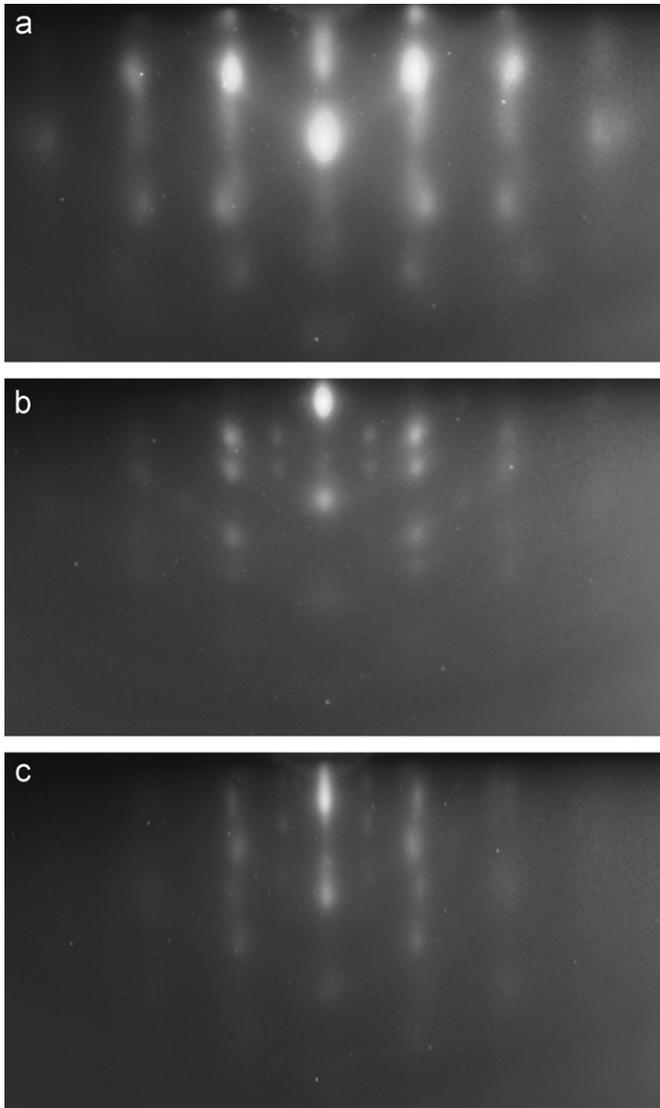


Fig. 4. RHEED patterns with incident electron beams along $[10\bar{1}0]$ α - Al_2O_3 azimuths, obtained from relaxed MgO buffer (a); after Cu_2O buffer deposition at 500 °C (b); and Cu_2O buffer at 650 °C (c).

The pattern also reflects the existence of twin crystals in thicker MgO layer, which is a common way for cubic crystals to relax the strains. The surface roughness also increased compared to the strained thin MgO buffer layer judging from the spotty pattern. It is quite understandable that Cu_2O grown on such a buffer layer will be also twin-crystalline, as clearly shown in Fig. 4(b). It should be noted that an overlap orientation occurs between Cu_2O (111) and relaxed MgO (111), that is, Cu_2O did not rotate with respect to the zone axis of MgO, yielding an in-plane overlap orientation of Al_2O_3 $[10\bar{1}0]$ //MgO $[1\bar{1}0]$ // Cu_2O $[1\bar{1}0]$ and Al_2O_3 $[10\bar{1}0]$ //MgO $[1\bar{1}0]$ // Cu_2O $[1\bar{1}0]$. The relaxed thicker MgO buffer layer owns a lattice constant very close to the bulk value, which made the overlapped epitaxy more favorable. Moreover, we noticed that this twin-crystalline Cu_2O is not stable as it would turn to CuO phase at a higher temperature as shown in Fig. 4(c), which never happened on those films growth on ultrathin MgO buffer layers. The rough MgO surface is supposed to be responsible for this undesirable growth process. As is well-known, MgO (111) is a typical polar surface with diverging surface energy, and it can be lowered to the smallest finite value and become stable when faceting into neutral faces [21]. In this case, the surface will

become rough and demonstrate complex structures, which may supply some nucleate sites for CuO or induce the transition of Cu_2O to CuO. Deposition of Cu_2O on the CuO layer is possible, and the film did show twin crystalline Cu_2O (111) pattern initially. However, it would gradually change into poly crystalline as it grows thicker and thicker, because CuO has a monoclinic structure which is not suitable for Cu_2O epitaxy at all. Generally speaking, Cu_2O deposited on thick MgO buffer are always poly crystalline because of the formation of CuO at the interface. As far as we know, there are few reports about Cu_2O growth on bulk MgO (111) substrates, and we think that would be very challenging due to the fact of MgO (111) faceting and the difficulties in surface pretreating. As we mentioned above, the achievement of an atomic smooth surface is very crucial for the growth of Cu_2O single crystals.

4. Conclusion

In summary, growth of high-quality single crystalline Cu_2O film on the *c*-plane α - Al_2O_3 substrate were demonstrated by inserting an ultrathin strained MgO buffer layer, which effectively modified the complex surface structure of sapphire (0001) and the interfacial atomic matching mode between the epilayer and the substrate. XRD and RHEED observations proved the formation of three-folded symmetrical cubic Cu_2O (111) film without twin crystals. A coincident match mode was proposed to explain the unusual rotated in-plane orientation between MgO (111) and Cu_2O (111), where the lattice mismatch reduced a lot. The single crystallinity of Cu_2O was found very sensitive to the thickness of strained MgO layer, which is optimized to be ~ 2 nm.

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