High-index Cu$_2$O (113) film on faceted MgO (110) by molecular beam epitaxy

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Abstract

We report the growth of single-oriented Cu$_2$O (113) film on faceted MgO (110) substrate by radio-frequency plasma assisted molecular beam epitaxy. A MgO (100) faceted homoepitaxial layer was introduced beforehand as a template for epitaxy of Cu$_2$O film. The epitaxial relationship is determined to be Cu$_2$O (113)//MgO (110) with a tilt angle of 4.76° and Cu$_2$O [1T0]/MgO [1T0] by the combined study of in-situ reflection high-energy electron diffraction and ex-situ X-ray diffraction and transmission electron microscopy. The film demonstrates a good p-type conductivity and excellent optical properties, indicating that this unique approach is potentially applicable for high-index film preparation and device applications.

1. Introduction

Cuprous oxide (Cu$_2$O) is a typical p-type semiconductor with a direct band gap of 2.17 eV, which is of considerable interest due to its potential applications in photocatalytic water splitting and solar-energy cells, as well as the possibility of realizing Bose–Einstein condensation (BEC) at relatively high temperature [1]. In recent decades, various substrates have been used to fabricate Cu$_2$O films, such as sapphire [2,3], SrTiO$_3$ [4–7], silicon [8–11], ZnO [12–14], and MgO [15–23]. Among them MgO has attracted most attention due to its smallest lattice mismatch (~1.3%) with Cu$_2$O. With the lowest energy [24], Cu$_2$O (110) surface was found predominantly forming on MgO (001) substrate [15], and single-oriented Cu$_2$O (110) films on MgO (110) substrate are highly reproducible and possess a much wider growth window [23]. On the other hand, Cu$_2$O (001) epitaxial films were realized on MgO (001) by using plasma-assisted molecular beam epitaxy (MBE) technique [21].

In addition to the Cu$_2$O films with low-index surface orientations, polycrystalline Cu$_2$O films with a high-index (113) surface were often observed [25–28]. The Cu$_2$O (113) surfaces exhibit a much higher catalytic activity than the low-index surfaces, considering the fact that a higher density of atomic steps, ledges, and kinks exist in high-index surfaces [29]. It is significant, therefore, to find a route for the synthesis of single-oriented Cu$_2$O (113) films and investigate its optical and electrical properties as an active layer. Interestingly, Sugawara and Mae [30] have presented their findings of (100) facets on MgO (110) homoepitaxial surface when the substrate temperature was higher than 500 °C. Although in other researches single phase Cu$_2$O films grown on MgO (110) substrate were all (110) oriented [17–19,23], Cu$_2$O films on faceted MgO (110) substrate may not definitely follow the normal cube-on-cube orientations. Herein we adopted the faceted MgO (110) surface as a template for the epitaxy of Cu$_2$O, and finally achieved a single-oriented Cu$_2$O (113) film. The epitaxial relationship was investigated by the in-situ observation of reflection high-energy electron diffraction (RHEED) and ex-situ characterization of X-ray diffraction (XRD) and transmission electron microscopy (TEM). A special epitaxial relationship of Cu$_2$O (113)//MgO (110) is revealed, with a tilt angle of 4.76°. The in-plane orientation relationship is determined as Cu$_2$O [1T0]/MgO [1T0]. Concurrently, Cu$_2$O (113)
Cu₂O (113) film demonstrates a good p-type conductivity and excellent optical properties, suggesting that high-index Cu₂O (113) film is promising for further device applications.

2. Experimental

Cu₂O (113) film was grown on MgO (110) single crystal substrate by using radio frequency plasma-assisted MBE (rf-MBE) technique. Elemental Cu (6 N) and Mg (5 N) were evaporated from commercial Knudsen cells while active oxygen radicals were produced by an rf-plasma source. After degreased in acetone and ethanol, the substrate was loaded into the MBE chamber and then thermally cleaned at 750 °C for 30 min, followed by oxygen plasma treatment (300 W/2.0 sccm) at 500 °C for 30 min. A homoepitaxial MgO buffer layer (~30 nm) was firstly deposited at 500 °C and subsequently annealed at 750 °C for 10 min. A regular two-step growth process was performed for Cu₂O synthesis, that is, a low temperature buffer layer grown at 500 °C for 20 min and a high temperature epilayer grown at 700 °C for 3 h. The growth conditions for both layers were kept the same, that is, Cu cell temperature of 1000 °C, rf-power of 230 W and oxygen flux of 1.0 sccm, respectively. The growth rate is ~100 nm/h, much larger than that of the Cu₂O (111) on sapphire (0001) (~50 nm/h) [2].

In situ RHEED was applied to monitor the whole growth process. Kinematical electron diffraction simulations were performed on the website of Web Electron Microscopy Applications Software (WebEMAPS, http://emaps.mrl.uiuc.edu/). XRD (Rigaku SmartLab, Cu Kα radiation, λ = 1.5406 Å) measurements were carried out to confirm the growth orientation and epitaxial relationship, which were further evidenced via TEM (JEOL-ARM200F). The surface morphology was characterized by scanning electron microscope (SEM, Hitachi 4800) and atomic force...
microscopy (AFM, SIINT SPA400). Hall measurements and transmittance spectroscopy characterization were also performed to study the electrical and optical properties, respectively.

3. Results and discussion

The evolution of RHEED patterns during the sample preparation process is shown in Fig. 1. Three well-defined patterns, containing distinct Kikuchi lines, are observed with incident electron beams along [110], [111] and [001] directions of the pretreated MgO substrate [Fig. 1(a)]. The patterns along [110] and [111] become brighter and more streaky after the homoepitaxy of MgO (110) buffer layer [Fig. 1(b)], indicating an improved crystal quality. Meanwhile, the pattern along [001] shows diffraction streaks parallel to [010] and [001], originating from the (100) and (010) facets which were well depicted in Ref. [30]. In our case, the formation of faceted MgO (110) buffer layer plays an important role in growth of high-index Cu₂O(113) film, which will be discussed later. The RHEED patterns, observed along MgO [110], change drastically when the growth of Cu₂O starts [Fig. 1(c)], and evolve into more distinct diffraction spots with an improved contrast against the background during the rest growth process [Fig. 1(d)]. To understand these complicated patterns, we simulated the diagram of kinematical electron diffraction with zone axis along Cu₂O [110] orientation by WebEMAPS, as shown in Fig. 1(e). Obviously, it is quite different from those patterns we observed in Fig. 1(d), indicating that the growth does not follow the commonly reported cube-on-cube orientation due to the insertion of faceted MgO (110) buffer layer.

After careful analysis, we found that the symmetric spots in present Cu₂O RHEED patterns could be divided into two groups,
corresponding to two different domains. They are proved to be 180° rotated with each other, confirmed by XRD and TEM results which will be discussed below. Each group of spots occupies a rectangular lattice with an aspect ratio of \(\sqrt{2} : 1\), which is similar to the diagram in Fig. 1(e) except for a rotation of 60°. Hence, by rotating and mirroring, the simulated diagrams of kinematical electron diffraction for the 180° rotation domains are obtained, as shown in Fig. 2(a). Note that Cu₂O [113] is inclined at 64.76° to Cu₂O [110], so that Cu₂O [113] is close to the normal direction of substrate, namely, MgO [110]. The simulated diagrams are overlapped together and the integrated diagram is shown in Fig. 2(b). The dotted box part of the integrated diagram matches very well with the observed RHEED patterns [Fig. 2(c)], while other parts cannot be seen in RHEED due to apparatus limitation. Some spots in RHEED patterns are missing in the integrated diagram because of extinction phenomenon. Therefore, we can make a conclusion that Cu₂O [110] orientations of the 180° rotation domains are inclined at 60° to MgO [110], and Cu₂O [113] is the epitaxial orientation despite of a small tilt angle of 4.76°, which has further been confirmed by XRD and TEM analysis shown below.

XRD curves of Cu₂O film on MgO [110] substrate are shown in Fig. 3. A normal \(\theta-2\theta\) scan curve [Fig. 3(a)] only presents two peaks at 62.27° (denoted by Peak 1) and 72.55° (denoted by Peak 2), corresponding to the diffractions from MgO (220) and Cu₂O (113) surfaces, respectively. Peak 2 shifts approximately 1.01° from the standard 73.56° position for bulk Cu₂O (113) (ICDD PDF no. 78-2076), which is attributed to the out-of-plane expansion of the film. Here we exclude the possibility of Peak 2 originating from CuO (113) surface despite of the close peak position (72.44°, ICDD PDF no. 80-1917), as CuO phase does not exist in this epitaxial film, which has been proved by the well-defined RHEED patterns [Fig. 1(d)] and an optical band gap of 2.54 eV (determined by the transmittance spectrum, not given here). \(x\)-dependent \(\chi\) (a left-handed rotation about a horizontal axis) \(\theta-2\theta\) scans are performed to identify the tilt angle between Cu₂O [113] and MgO [110], as shown in Fig. 3(b). The intensity of Peak 1 greatly reduces when \(x = 2.5^\circ\) and disappears when \(x = 5.2^\circ\). Concurrently, Peak 2 achieves its maximum when \(x = 4.7^\circ\) while Peak 1 is almost ignorable. Thus the tilt angle between Cu₂O [113] and MgO [110] is reasonably judged around 4.7°. Fig. 3(c) shows the \(\psi\) scan (\(\psi\) is an in-plane rotation around the center of the sample) curve of the film performed with \(\chi, \theta\) and \(2\theta\) fixed at 60°, 31.14° and 62.27°, respectively, while that of MgO substrate with same configuration is also presented as a reference. Two relatively broad Cu₂O (220) peaks with a 180° interval are observed, proving the existence of 180° rotation domains, which strongly supports the RHEED observations. The additional four sharp peaks have originated from MgO (202), (022), and (113), respectively. Additionally, Cu₂O (220) peaks are in the middle of MgO (202) and (022) or MgO (022) and (202) peaks, indicating that the two rotation domains could be simultaneously observed along MgO [110] orientation, which have already been observed in the RHEED patterns [Fig. 1].

Further evidences of the film orientation and microstructure by TEM are shown in Fig. 4. Cross-sectional TEM image of Cu₂O film viewed down the Cu₂O [110] zone axis is shown in Fig. 4(a). Two regions of different domains are selected and the corresponding 2D fast Fourier transform (FFT) patterns reveal that the orientations of the two domains are rotated around the film normal axis by 180° each other, confirming again the existence of 180° rotation domains. Domain boundary marked by dotted polygon consists of some superlattice structure. The cross-sectional high-angle annular dark-field (HAADF) images show the interface of Cu₂O film and MgO substrate in two domains [Fig. 4(b) and (c)], respectively. The zone axes are along MgO [110] orientation for both images. Primitive cells selected in the enlarged regions belong to Cu₂O [110] surfaces, which proves that Cu₂O [110] is parallel to MgO [110]. Note that Cu₂O [110] and [110] are different crystal orientations in Cu₂O [113] film, and they can equally form along MgO [110]. That is the reason why 180° rotation domains occur in the Cu₂O (113) film. The orientation relationship is demonstrated in the images as well. As we expected, unlike the normal cube-on-cube epitaxial relationship of Cu₂O [110]/MgO [110] and Cu₂O [001]/MgO [001], Cu₂O [110] orientations are inclined at 60° to MgO [110]. Although Cu₂O [112] orientation is also close to MgO [110], the angle between Cu₂O [112] and [110] is 54.74°, so Cu₂O [112] is inclined at 5.26° to MgO [110], which is bigger than that of Cu₂O [113]. Furthermore, the atoms of Cu₂O film at the interface arrange along [332], which is vertical to [113]. The lattice mismatch between Cu₂O [110] (3.016 Å) and MgO [110] (2.978 Å) is 1.3%, and 15.8% between Cu₂O [332] (5.004 Å) and MgO [001] (4.213 Å). Through 6/7 domain matching, the latter could be reduced to 1.77%. Therefore, Cu₂O [113] surface can follow an epitaxial growth on MgO [110] substrate with misfit dislocations.

Given the above results, the crystal orientation and epitaxial relationship are clearly evidenced and schematically illustrated in Fig. 5. The as-grown film is confirmed to be Cu₂O (113), which is inclined at 4.76° to MgO (110) and consists of 180° rotation domains. This special growth is most likely caused by MgO (100) faceted homoepitaxial layer. In SEM and AFM characterizations, the Cu₂O (113) film manifests a grainy surface and a relatively small root mean square roughness of 9.9 nm. The film thickness is determined as \(-350\) nm by cross-sectional SEM image. A good p-type conductivity (hole concentration of \(1.5 \times 10^{20}\) cm\(^{-3}\), mobility of 36.5 cm\(^2\)/V s and resistivity of \(12 \Omega\) cm) is attributed to the smooth and continuous film structure. The optical transmittance of the Cu₂O (113) film shows a sharp absorption edge and opacity beyond 480 nm, while the band gap \(E_g\) is deduced as 2.54 eV (not shown here). More investigations will be needed to explore the growth mechanism of high-index Cu₂O (113) film on MgO (110) substrate with (100) facets.

4. Conclusion

Single-oriented Cu₂O (113) film has been fabricated on faceted MgO (110) substrate by rf-MBE. The complicated RHEED patterns originate from the unique orientation and the existence of 180° rotation domains. XRD curves and TEM images confirm that the Cu₂O film is [113] oriented with a tilt angle of 4.76° to MgO [110], and 180° rotation domains are proved to exist in this high-index film. The smooth and continuous surface, good p-type conductivity and high transparency beyond the band gap indicate this Cu₂O (113) film can be promisingly applied in further device applications.

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