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Cu₂O epitaxial films with domain structures prepared on Y-stabilized ZrO₂ substrates by pulsed laser deposition

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Abstract

Copper oxide films have been deposited on the Y-stabilized ZrO₂ (YSZ) (100) substrates by pulsed laser deposition and the effect of oxygen pressure (P_{O_2}) on the film properties was investigated in detail. The phase, crystallinity, and surface morphology of the films were strongly influenced by P_{O_2} and the film prepared at 0.09 Pa was pure cuprous oxide (Cu₂O) having the best film crystallinity. An out-of-plane epitaxial relationship of Cu₂O (110)//YSZ (100) with six different kinds of domain structure were observed for the 0.09 Pa-deposited sample and the corresponding in-plane epitaxial relationships were deduced. The lowest resistivity of 13.4 $\Omega\cdot\text{cm}$ and highest Hall mobility of 16.3 $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ were also obtained for the film deposited at 0.09 Pa. The optical band gap of the as-prepared copper oxide films varied from 2.37 to 2.57 eV.

Keywords: Epitaxial growth; Cuprous oxide; Electrical properties; Pulsed laser deposition

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1. Introduction

As a p-type semiconductor with a direct band gap of 2.0-2.6 eV [1-5] and a maximum hole mobility exceeding $100 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ [6], cuprous oxide (Cu_2O) has been considered as a promising candidate for applications in solar cells due to its abundance, nontoxicity and large optical absorption coefficient [1, 7]. There have been many reports on Cu_2O -based solar cells [8-10]. Until now, the highest reported conversion efficiency of Cu_2O solar cells was around 6.1% with a $\text{MgF}_2/\text{AZO}/\text{AlGaO}/\text{Cu}_2\text{O}:\text{Na}$ heterojunction structure formed on the thermally oxidized Cu sheets [10], while the maximum theoretical energy conversion efficiency of a solar cell fabricated using Cu_2O as the active layer is 20% [11]. The unsatisfactory photovoltaic performance of Cu_2O -based solar cells are mostly due to the difficulties in synthesizing high quality Cu_2O films with proper electrical properties of both low electrical resistivity and high mobility. Therefore, to further improve the performance of Cu_2O -based solar cells, it is necessary to obtain high quality Cu_2O films with well controlled orientation, microstructure and electrical properties [12].

Many methods have been used to prepare Cu_2O films such as sputtering [3], thermal oxidation [8], evaporation [5], molecular beam epitaxy [13], and electrodeposition [9]. But up to now, only a few studies were reported on the growth of Cu_2O films by pulsed laser deposition (PLD) [12, 14-18], which could deposit highly oriented crystalline films at low substrate temperatures due to the high kinetic energy of the ionized and ejected species in the laser produced plasma. Especially, the

effect of oxygen pressure (P_{O_2}) during the deposition on the film properties was rarely studied [15, 16]. In addition, various substrates such as MgO [12], ZnO [19], GaN [20], SrTiO₃ [14] and Al₂O₃ [21] have been implemented for the Cu₂O growth, among which MgO having a cubic lattice and a small lattice mismatch with Cu₂O was the most commonly used substrate to prepare high quality Cu₂O epitaxial films. However, MgO is also known to be unstable in air if exposed for a prolonged period of time which can cause huge problems with the reproducibility of the growth on such surfaces [22]. The Y-stabilized ZrO₂ (YSZ) substrate with a cubic lattice could be a candidate to grow high quality Cu₂O films for its high optical transmittance, high thermal resistivity and excellent corrosion and erosion resistance [23-25]. However, until now, there are very few reports on the growth of Cu₂O films on YSZ substrates [26], and especially the epitaxial growth of Cu₂O films on YSZ substrates has never been reported. Furthermore, the reported Cu₂O films grown by PLD usually had high electrical resistivities due to the difficulties in simultaneously achieving relatively high carrier concentration and mobility [16-18], which strongly restricts their applications in Cu₂O solar cells.

In this study, copper oxide films were deposited on YSZ (100) substrates by PLD and the influence of oxygen pressure on the structural, morphological, electrical and optical properties of the films was investigated. The Cu₂O epitaxial film having six different kinds of domain structure is reported, which exhibits a low resistivity of 13.4 $\Omega \cdot \text{cm}$ and a high Hall mobility of 16.3 $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ that are quite suitable for photovoltaic applications.

2. Experimental

Copper oxide films were grown by PLD using a KrF excimer laser (wavelength: 248 nm) and a Cu₂O ceramic target (purity: 4N). The pulse duration and frequency were 20 ns and 20 Hz, respectively. The YSZ (100) single crystals were used as the substrates after a four-step ultrasonic cleaning in 5% Decon 90 aqueous solution, deionized water, acetone and anhydrous ethanol for 5, 10, 5 and 5 min., respectively. The laser power density was $\sim 6 \text{ J/cm}^2$ at the target surface, which yielded a film growth rate of $\sim 7 \text{ nm/min}$. The substrate temperature was maintained at 600°C and the P_{O_2} during deposition varied from 0.02 to 0.12 Pa with a base pressure under 10^{-4} Pa .

The crystalline quality and epitaxial relationship were determined by the θ -2 θ and in-plane Φ -scans using the Rigaku and Philips X'Pert PRO X-ray diffractometers (XRD), respectively. High resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) were used to observe the atomic arrangements across the substrate-film interface with a Tecnai F30 transmission electron microscope operated at 300 kV. The surface morphology was observed by a FEI Nova NanoSEM 450 field emission scanning electron microscope (SEM). The room temperature micro-Raman spectroscopy (μRS) analyses were carried out employing a Renishaw inVia Reflex Raman system with a 532 nm laser. The electrical properties were measured by Van der Pauw method. The optical transmittance was measured using a TU-1901 double-beam UV-vis-NIR spectrophotometer.

3. Results and discussion

Fig. 1 XRD patterns of copper oxide films grown on YSZ (100) substrates under different oxygen pressures.

Typical XRD patterns of θ -2 θ scan for the copper oxide films prepared under different oxygen pressures are shown in Fig. 1. In addition to the substrate diffraction peaks of YSZ (200) and (400) located respectively at 34.9° and 73.6° (JCPDS No.30-1468), four other peaks can be observed at 0.02 Pa, which are identified as Cu₂O (110), Cu₂O (200), Cu (111) and Cu₂O (220) located at 29.2° , 41.7° , 43.2° and 60.6° (JCPDS No.65-3288 for Cu₂O, No.04-0836 for Cu), respectively, corresponding to a mixed phase of Cu₂O and Cu. As the P_{O_2} increases to 0.06 and 0.09 Pa, the Cu (111) and Cu₂O (200) peaks are absent, indicating that pure phase Cu₂O with a single orientation along (110) is obtained. The full widths at half maximum (FWHMs) of the Cu₂O (110) peak are 0.143° and 0.141° for the samples grown at 0.06 and 0.09 Pa, respectively, indicating a better crystalline quality of the Cu₂O film deposited at 0.09 Pa. As the P_{O_2} increases further to 0.12 Pa, the CuO (111) and CuO (200) peaks

located respectively at 35.5° and 38.9° (JCPDS No.48-1548) show up, indicating a mixed phase of Cu_2O and CuO and the degradation of film crystallinity. The XRD results reveal that the crystalline quality of copper oxide films is strongly affected by oxygen pressure and the film prepared at 0.09 Pa has the best crystallinity with an out-of-plane epitaxial relationship of Cu_2O (110) // YSZ (100).

Fig. 2. XRD patterns of off-specular Φ -scan for the (a) Cu_2O {111} and (b) YSZ {111} planes of the sample grown under P_{O_2} of 0.09 Pa. (c) Proposed in-plane epitaxial relationships between the Cu_2O film and YSZ substrate.

Fig. 2(a) shows the off-specular Φ -scan of Cu_2O {111} planes ($\Psi=35.26^\circ$) for the film deposited under P_{O_2} of 0.09 Pa. As we know, the {111} plane of Cu_2O is two-fold symmetrical along Cu_2O [110]. However, twelve diffraction peaks are clearly observed in Fig. 2(a), which indicate the existence of six different kinds of domain structure as labeled respectively by *A*, *a*, *B*, *b*, *C*, and *c* inside the film. Fig. 2(b) shows the off-specular Φ -scan of YSZ {111} planes ($\Psi=54.73^\circ$) for the substrate,

from which four diffraction peaks separated by 90° with the same Φ -angles as the Cu_2O $\{111\}$ planes could be seen. The proposed in-plane epitaxial relationships between the Cu_2O film and YSZ substrate deduced from Fig. 2(a) and (b) are schematically shown in Fig. 2(c). The commercially available YSZ substrate we used has a cubic structure with the lattice parameter of $5.14 \text{ \AA}$, and the cubic Cu_2O has a lattice parameter of $4.26 \text{ \AA}$. As shown in Fig. 2(c), two domains have the in-plane epitaxial relationships of **A**: $\text{Cu}_2\text{O} [001] // \text{YSZ} [011]$ and **a**: $\text{Cu}_2\text{O} [001] // \text{YSZ} [0\bar{1}1]$, both of which correspond to a lattice mismatch of 17.2% ($6.02 \text{ \AA}$ for Cu_2O film and $7.27 \text{ \AA}$ for YSZ substrate). The domains **B** and **b** grow in principle with their $[1\bar{1}1]$ orientation parallel to YSZ $[011]$ and $[0\bar{1}1]$, and the domains **C** and **c** grow with their $[1\bar{1}\bar{1}]$ orientation parallel to YSZ $[011]$ and $[0\bar{1}1]$, respectively. However, due to the existence of multiple domains and therefore the possible interaction and stress among them, the above-mentioned parallel relationships are not strict with a deviation of 0.9° for all the four domains as deduced from Fig. 2 (a) and (b). These four domains grow with a lattice mismatch of 1.5% between $\text{Cu}_2\text{O} \langle 111 \rangle$ ($7.38 \text{ \AA}$) and $\text{YSZ} \langle 011 \rangle$ ($7.27 \text{ \AA}$).

Fig. 3. (a) Cross-sectional HRTEM and (b) SAED micrographs of the film-substrate interface for the sample grown at 0.09 Pa.

The heterostructure of the sample grown at 0.09 Pa was further studied using the cross-sectional TEM measurements. The HRTEM and SAED micrographs of the interface between the Cu_2O film and YSZ substrate are shown in Fig. 3(a) and (b), respectively. The incident electron beam was parallel to the $[0\bar{1}1]$ direction of the YSZ substrate. From Fig. 3(a), the uniform and ordered crystal lattice arrays of both the Cu_2O film and YSZ substrate with a clean and sharp interface inbetween can be observed clearly. The as-marked spacings of the lattice planes for the Cu_2O film are about 0.155 and 0.216 nm, corresponding to Cu_2O (220) and (200) planes, respectively, with a standard angular separation of 45° . For the substrate, the as-marked interplane spacings are consistent with YSZ (111) and (200) planes, respectively. From the SAED pattern as shown in Fig. 3(b), the Cu_2O (200), Cu_2O (110), YSZ (200) and YSZ (111) diffraction spots are clearly observed, indicating the good crystallinity of this sample area. From the HRTEM and SAED analyses, the

epitaxial relationship between Cu_2O film and YSZ substrate can be deduced as Cu_2O (110)//YSZ (100) with Cu_2O [001]//YSZ $[0\bar{1}1]$, corresponding to the domain marked as **a** in Fig. 2(c).

Fig. 4. Plan view SEM micrographs of the copper oxide films grown under the oxygen pressures of (a) 0.02, (b) 0.06, (c) 0.09 and (d) 0.12 Pa.

The plan view SEM images of copper oxide films deposited under the oxygen pressures of 0.02, 0.06, 0.09 and 0.12 Pa are shown in Fig. 4(a), (b), (c) and (d), respectively. From Fig. 4(a), submicron particles can be seen on the film surface of the sample prepared at 0.02 Pa, in which metallic Cu is assumed to act as a catalyst of the growth and mainly exists at the surface of the particles [27]. In Fig. 4(b) and (c), crosswise arranged islands are observed for the films prepared at 0.06 and 0.09 Pa, which are consistent with the existence of multiple domains inside the films. A more compact surface with regularly-shaped islands and well-defined boundaries are observed for the film grown at 0.09 Pa, which is in agreement with the best

crystallinity of this sample. For the film deposited under 0.12 Pa as shown in Fig. 4(d), irregular and ill-defined grains are observed due to the mixed phase and degraded crystallinity of this film as revealed from the XRD result. The SEM results demonstrate obviously that the film morphology and crystallinity are strongly influenced by the oxygen pressure, which are in accordance with the XRD analyses.

Fig. 5. Raman spectra of copper oxide films grown under different oxygen pressures.

Raman spectra of the as-prepared copper oxide films in the range of 100-800 cm^{-1} are shown in Fig. 5. The Raman frequencies at 109, 149, 221, 416 and 629 cm^{-1} were observed for the 0.02-0.09 Pa-deposited samples. The phonon modes at 109 and 149 cm^{-1} are an inactive Raman mode Γ_{12}^- and an infrared mode $\Gamma_{15}^{-(1)}(\text{LO})$ in Cu_2O crystal [28, 29], respectively. The most intense peak at 221 cm^{-1} is the second order overtone of Cu_2O , corresponding to $2\Gamma_{12}^-$ mode [28, 29]. The other two peaks at 416 and 629 cm^{-1} are referred to one fourth order overtone $4\Gamma_{12}^-$ and one red allowed mode $\Gamma_{15}^{-(2)}(\text{TO})$ [29], respectively. For the sample grown at 0.02, the presence of Cu particles could not be ascertained from μRS due to instrumental limitations for metals

because they can exhibit surface plasmon resonance (SPR). For metals, local SPR is responsible for field enhancement and therefore leads to surface-enhanced processes, which are only visible using surface enhanced Raman spectroscopy that is helpful for characterizing metallic samples [28]. With the increase of P_{O_2} to 0.06 and 0.09 Pa, only the peaks at 109, 149, 221, 416 and 629 cm^{-1} could be detected, indicating the pure phase Cu_2O is obtained. Furthermore, the sharp defined mode $2\Gamma_{12}^-$ demonstrates the high crystal quality of the samples. As the P_{O_2} increases further to 0.12 Pa, phonon mode at 298 cm^{-1} corresponding to the A_g symmetry of CuO can be observed [30], indicating the presence of CuO . The results of μRS analyses also correspond very well with the X-ray diffraction results.

Fig. 6. Dependence of Hall mobility, carrier concentration and resistivity on the oxygen pressure of the copper oxide films.

The Hall mobility, carrier concentration and electrical resistivity of the copper oxide films as a function of oxygen pressure are shown in Fig. 6. The film prepared

under the P_{O_2} of 0.02 Pa is insulating probably due to the compensation of holes caused by the existence of metallic Cu. During the measurement, the p-type conductivity was observed for the rest of the samples as shown in Fig. 5. The carrier concentration initially increases from 2.08×10^{16} to $2.85 \times 10^{16} \text{ cm}^{-3}$ with the increase of P_{O_2} from 0.06 to 0.09 Pa and then decreases to $1.65 \times 10^{16} \text{ cm}^{-3}$ at 0.12 Pa. The Hall mobility also initially increases from 16.1 to $16.3 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ with the increase of P_{O_2} from 0.06 to 0.09 Pa and then decreases to $14.1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ under the P_{O_2} of 0.12 Pa. Correspondingly, the resistivity initially decreases and then increases as the P_{O_2} increases, with a minimum value of $13.4 \Omega \cdot \text{cm}$ obtained at 0.09 Pa. This resistivity is also the lowest value reported so far for the pulsed laser deposited Cu_2O thin films [16-18]. Cu_2O films with such low resistivity and high Hall mobility are quite suitable to be used in photovoltaic devices. It is well-known that the p-type conductivity of Cu_2O is due to the Cu vacancies [9, 15]. The initial increases of the Hall mobility and carrier concentration are mainly due to the improvement of crystallinity and increased number of Cu vacancies, respectively. With further increase of P_{O_2} to 0.12 Pa, the CuO phase is formed leading to the decrease of Cu vacancies and therefore the decrease of carrier concentration. Meanwhile, the Hall mobility also decreases probably due to the degraded film crystallinity.

Fig. 7. (a) Transmittance spectra and (b) the plots of $(\alpha h\nu)^2$ versus $h\nu$ for the copper oxide films prepared under different oxygen pressures.

Fig. 7(a) shows the optical transmittance spectra of the copper oxide films as a function of oxygen pressure in the wavelength range of 300-900 nm. The film prepared at the P_{O_2} of 0.02 Pa presents feeble transmittance due to the existence of opaque metallic copper in it. As the P_{O_2} increases to 0.06 and 0.09 Pa, benefiting from the large band gap of Cu_2O (2.0-2.6 eV) and improved crystallinity, much higher transmittance is obtained for these films. With the further increase of P_{O_2} , the transmittance of the film decreases again, which is due to the presence of CuO (1.2-2.0 eV) and degraded crystallinity [31]. A distinct difference between the optical absorption edges can also be seen. The pure Cu_2O films exhibit sharper absorption edges than the films having impurity phases. As a direct-band gap semiconductor, the optical band gap of Cu_2O can be estimated by $(\alpha h\nu)^2 = A(h\nu - E_g)$ [32], where α is the absorption coefficient, A is a constant, h is the Planck constant, ν is the frequency and E_g is the optical energy band gap. The absorption coefficient α is calculated from the transmittance (T) and thickness (d) of the film by using the

equation of $\alpha = \frac{1}{d} \ln \left(\frac{1}{T} \right)$ [33]. Therefore, the E_g could be determined by plotting $(\alpha h\nu)^2$ vs. $h\nu$ and then extrapolating the straight-line portion of this plot to the energy axis. As shown in Fig. 7(b), the optical band gaps of the copper oxide films deposited at 0.02, 0.06, 0.09 and 0.12 Pa are about 2.37, 2.57, 2.57 and 2.43 eV, respectively. Similar values and variation tendency of E_g were also observed in other reports [5, 34].

4. Conclusions

In summary, the copper oxide thin films were prepared on YSZ (100) substrates by PLD and the effect of oxygen pressure during deposition on the structural, morphological, electrical and optical properties of the films was studied. With the increase of oxygen pressure from 0.02 to 0.12 Pa, transitions from mixed phase of Cu_2O and Cu to pure Cu_2O then to mixed phase of Cu_2O and CuO were observed. The film prepared at 0.09 Pa had the best crystallinity with an out-of-plane epitaxial relationship of Cu_2O (110)//YSZ (100). Six different kinds of domain structure were observed and the corresponding in-plane epitaxial relationships were proposed for the 0.09 Pa-deposited sample. An obvious change of film surface morphology was observed with oxygen pressure. The lowest resistivity of $13.4 \Omega \cdot \text{cm}$ with a carrier concentration of $2.85 \times 10^{16} \text{ cm}^{-3}$ and a Hall mobility of $16.3 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ were obtained for the film deposited at 0.09 Pa. The transmittance of the films was strongly influenced by oxygen pressure and the optical band gap varied between 2.37 and 2.57 eV. The high quality Cu_2O epitaxial films with low resistivity and high mobility

obtained in our study may have promising applications in different fields such as photovoltaic devices and thin film transistors.

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Figure Captions:

Fig. 1 XRD patterns of copper oxide films grown on YSZ (100) substrates under different oxygen pressures.

Fig. 2. XRD patterns of off-specular Φ -scan for the (a) Cu_2O {111} and (b) YSZ {111} planes of the sample grown under P_{O_2} of 0.09 Pa. (c) Proposed in-plane epitaxial relationships between the Cu_2O film and YSZ substrate.

Fig. 3. (a) Cross-sectional HRTEM and (b) SAED micrographs of the film-substrate interface for the sample grown at 0.09 Pa.

Fig. 4. Plan view SEM micrographs of the copper oxide films grown under the oxygen pressures of (a) 0.02, (b) 0.06, (c) 0.09 and (d) 0.12 Pa.

Fig. 5. Raman spectra of copper oxide films grown under different oxygen pressures.

Fig. 6. Dependence of Hall mobility, carrier concentration and resistivity on the oxygen pressure of the copper oxide films.

Fig. 7. (a) Transmittance spectra and (b) the plots of $(\alpha h\nu)^2$ versus $h\nu$ for the copper oxide films prepared under different oxygen pressures.