Pulsed-laser-deposited, single-crystalline Cu₂O films with low resistivity achieved through manipulating the oxygen pressure

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Xianjin Feng; Aimin Song

Dear Editor,

We would like to submit the manuscript entitled "**Pulsed-laser-deposited, single-crystalline Cu₂O films with low resistivity achieved through manipulating the oxygen pressure**" for possible publication in **Applied Surface Science**.

Cu₂O is a well-known p-type semiconductor having promising applications in the electronic and optoelectronic devices such as solar cells and thin film transistors. However, because the film crystal orientation and microstructure as well as the electrical properties could not be well controlled in most of the previously reported Cu₂O films, the Cu₂O-based functional devices have not shown good performance. In this paper, high quality pulsed-laser-deposited Cu₂O single crystalline films with low resistivity and high Hall mobility were realized through manipulating the oxygen pressure. The lowest resistivity of 6.67 $\Omega\cdot\text{cm}$ and highest mobility of 23.75 $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ were obtained for the film prepared at 0.09 Pa, which may have promising applications in solar cells and thin film transistors. This resistivity is also the lowest value reported so far for the pulsed-laser-deposited Cu₂O films.

This work is original, unpublished, and is not being considered for publication elsewhere. Submission of this work has been checked and approved by all the co-authors.

Thank you for your consideration.

Sincerely yours,

Xianjin Feng

- High quality single crystalline Cu_2O films were deposited on MgO (110) substrates by PLD.
- The influence of oxygen pressure on the film properties was studied.
- A low resistivity of $6.67 \, \Omega \cdot \text{cm}$ with a high Hall mobility of $23.75 \, \text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ were obtained.
- The optical band gap of the films varied from 2.33 to 2.57 eV.

Dear Editor and Reviewer:

Thank you very much for giving us the opportunity to revise our manuscript entitled **“Pulsed-laser-deposited, single-crystalline Cu₂O films with low resistivity achieved through manipulating the oxygen pressure”** (Ms. Ref. No.: APSUSC-D-17-07664R2). The comments and suggestions are all valuable and helpful for revising and improving our paper. We have studied the comments carefully and have made corrections which we hope will meet with approval. Our responses to the Reviewer’s comments are as follows:

Reviewer #1 Comment: In response to my first comments the Authors have satisfied the majority of my queries. However, one important, fundamental scientific point is still needed to be addressed:

It is impossible to say that Cu₂O [111]/MgO [111]. Even small strains of 1.4% will effect a distortion in-plane and, thus through Poisson's ratio also out-of-plane, in the film material. This is clear. The {111} directions in the film and substrate will be close to but not exactly parallel because of this distortion. In the response to comment 1 in the first review the authors write "As can be seen in Fig. 2, the peak positions of Cu₂O {111} and MgO {111} planes coincide very well, indicating an epitaxial relationship of Cu₂O [111]/MgO [111]". This is completely incorrect and indicates that they do not understand the measurement. The phi scan in Figure 2 is a standard method to assess epitaxy. Here the diffractometer is aligned to a reflection that has an off-axis (in this case the [111]) of both the film and substrate, a rotation about the normal of the sample is then initiated. Seeing reflections for both film and substrate in the same positions shows that the crystal lattices for both materials are aligned in-plane. In this case, this means that Cu₂O (100)/MgO (100) and Cu₂O (011)/MgO (011). However, as only one axis of the diffractometer is actioned, it is

impossible to distinguish if the out of plane component is well aligned, in fact it is probably not due to substrate imposed strain. The only way to test if the Cu_2O [111]//MgO [111] is to do a reciprocal space map around the (111) reflection. If there is only a single peak, then one can say that Cu_2O [111]//MgO [111]. Here, it would be typical to see a doublet due to substrate strain.

Our comment and action: We are sorry for our inadequate understanding of phi scan and inappropriate description of the epitaxial relationship. The inappropriate description has been corrected and the relevant text has been revised. (See the Abstract & paragraph 1, page 8 & paragraph 1, page 10 & paragraph 2, page 16)

Thanks a lot again for your kind help and such important comments. We tried our best to improve the manuscript and made some changes in the manuscript which were marked in red in the revised paper. Now we send the revised manuscript back to you, and hope it is OK now. Thank you for your reconsideration.

Yours sincerely,

Xianjin Feng

Pulsed-laser-deposited, single-crystalline Cu₂O films with low resistivity achieved through manipulating the oxygen pressure

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Abstract

Low-resistivity, single-crystalline Cu₂O films were realized on MgO (110) substrates through manipulating the oxygen pressure (P_{O₂}) of pulsed-laser deposition. X-ray diffraction and high resolution transmission electron microscopy measurements revealed that the films deposited at P_{O₂} of 0.06 and 0.09 Pa were single phase Cu₂O and the 0.09-Pa-deposited film exhibited the best crystallinity with an epitaxial relationship of Cu₂O (110)//MgO (110) with Cu₂O (001)//MgO (001). The pure phase Cu₂O films exhibited higher transmittances and larger band gaps with an optical band gap of 2.56 eV obtained for the 0.09 Pa-deposited film. Hall-effect measurements demonstrated that the Cu₂O film deposited at 0.09 Pa had the lowest resistivity of 6.67 Ω·cm and highest Hall mobility of 23.75 cm²·V⁻¹·s⁻¹.

Keyword: copper oxide; PLD; epitaxial; oxygen pressure

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1. Introduction

Depending on the crystal bonding and structure between the metal cation and oxygen, metal oxides show quite different functional properties. Metal oxides could exhibit magnetic, insulating, conducting and semiconducting properties [1]. Metal oxide semiconductors were applied to fabrication of various devices such as light emitting devices, thin film transistors (TFTs) and solar cells [2]. Cuprous oxide (Cu_2O) is a well-known p-type semiconductor. It has a direct band gap ($E_g=2.0\text{-}2.6\text{ eV}$) [3-7] and can exhibit a hole mobility exceeding $100\text{ cm}^2\cdot\text{v}^{-1}\cdot\text{s}^{-1}$ at room temperature [8]. Cu_2O is also regarded as one of the promising functional materials for its abundance, nontoxicity and large optical absorption coefficient [9]. There are many reports on Cu_2O -based solar cells and thin film transistors [10-14]. However, the highest reported energy conversion efficiency of Cu_2O solar cells was only around 6.1% with the Cu_2O active layer formed through oxidation of Cu sheets [12] even though the maximum theoretical conversion efficiency is 20% [15]. For Cu_2O thin film transistors, the performance is also unsatisfactory. Yao et al. demonstrated a p-type TFT formed by sputtered Cu_2O , showing a field effect mobility of $\sim 2.40\text{ cm}^2\cdot\text{v}^{-1}\cdot\text{s}^{-1}$ and an on/off current ratio of $\sim 3.96 \times 10^4$ [13]. Using the atomic layer deposition method, Maeng's group fabricated a p-type Cu_xO TFT with a field effect mobility of $5.64\text{ cm}^2\cdot\text{v}^{-1}\cdot\text{s}^{-1}$, an on/off current ratio of 1.79×10^5 , and a subthreshold swing of 0.75 V/decade [14]. Because the film crystal orientation and microstructure as well as the electrical properties could not be well controlled in most of the

previously reported Cu₂O films, Cu₂O-based functional devices have not shown good performance. It is therefore necessary to obtain high quality Cu₂O films with good electrical properties (high Hall mobility, proper resistivity) in order to further improve the performance of Cu₂O-based functional devices [16].

During the past years, in order to obtain high quality Cu₂O films, many methods such as sputtering [5], thermal oxidation [10], evaporation [17], molecular beam epitaxy [18], and electrodeposition [19] have been used. Due to the high kinetic energy of the ionized and ejected species in the laser produced plasma, pulsed-laser deposition (PLD) technique could deposit highly oriented crystalline films at low substrate temperatures [20, 21]. Furthermore, PLD is very suited to stoichiometric growth due to its operating far away from equilibrium [22]. However, until now, there are only a few reports on Cu₂O films prepared by PLD and the influence of oxygen pressure (P_{O_2}) during the deposition on the film properties was especially rarely studied [23, 24]. Moreover, the reported pulsed-laser deposited Cu₂O films usually had high electrical resistivities in the range of 10^2 – $10^5 \Omega \cdot \text{cm}$ [24–26], which are not suitable to be used in both solar cells and thin film transistors. It is well-known that the optimum resistivity for the absorber layer in a solar cell is around 0.1 – $1 \Omega \cdot \text{cm}$ [27]. While for high performance thin film transistors, the typical carrier concentration of the channel layer is usually in the range of 10^{16} – 10^{17} cm^{-3} [28, 29] with a Hall mobility higher than $10 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ (normally the higher the better), leading to a resistivity value lower than $10^2 \Omega \cdot \text{cm}$.

In this work, copper oxide films were prepared on MgO (110) substrates by PLD

and the structural, optical and electrical properties of the films as a function of P_{O_2} were investigated in detail. MgO (110) was chosen as substrate because the lattice mismatch between MgO and Cu_2O is very small ($\sim 1.4\%$), and the Cu_2O (110) plane has relatively lower surface free energies than other planes making it easier to be epitaxially grown [30]. High quality single-crystalline Cu_2O film with a low electrical resistivity of $6.67 \Omega \cdot cm$ and a high Hall mobility of $23.75 \text{ cm}^2 \cdot v^{-1} \cdot s^{-1}$ was obtained through manipulating the oxygen pressure, which may have promising applications in solar cells and thin film transistors.

2. Experimental

High vacuum PLD system with a KrF excimer laser (wavelength: 248 nm, pulse duration: 20 ns, pulse frequency: 20 Hz) and a ceramic Cu_2O target (4N purity) was used to deposit the copper oxide thin films. MgO (110) single crystals substrates were mounted 8 cm away from target in the PLD chamber with a base pressure under 10^{-4} Pa. The laser energy density was $\sim 6 \text{ J/cm}^2$ at the target surface. Growth condition was varied in the range of $P_{O_2}=0.02\text{--}0.12$ Pa at a fixed substrate temperature of 600°C , where Cu_2O is the stable phase in a phase equilibrium diagram [31].

The out-of-plane θ - 2θ and in-plane Φ and $2\theta\chi$ -scans were measured using respectively the Rigaku and Philips X'Pert PRO X-ray diffractometers (XRD) to determine the crystalline quality and epitaxial relationship. A FEI Nova NanoSEM 450 field emission scanning electron microscope (SEM) was used to observe the surface morphology. The atomic arrangements across the substrate-film interface were

observed using high resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) with a Tecnai F30 transmission electron microscope operated at 300 kV. The chemical composition was measured by the X-ray photoelectron spectroscopy (XPS) using an ESCALAB MK II multi-technique electron spectrometer. A TU-1901 double-beam UV-vis-NIR spectrophotometer was used to measure the optical transmittance. The electrical properties were measured by Van der Pauw method.

3. Results and discussion

Fig. 1. (a) XRD patterns of copper oxide films grown on MgO (110) substrates under typical oxygen pressures. Plan view SEM micrographs of the copper oxide films grown under the oxygen pressures of (b) 0.02, (c) 0.06, (d) 0.09 and (e) 0.12 Pa.

The crystallinity of the as-grown copper oxide films was investigated by XRD. Fig. 1(a) shows typical patterns of θ - 2θ scan for the copper oxide films deposited under representative oxygen pressures. Besides the substrate diffraction peak of MgO (220) located at 62.4° (JCPDS No.65-0476), five other peaks located respectively at 29.5° , 42.1° , 43.6° , 60.8° and 73.5° can be seen at 0.02 Pa, which are identified as Cu_2O (110), Cu_2O (200), Cu (111), Cu_2O (220) and Cu_2O (311) (JCPDS No.65-3288 for Cu_2O , No.04-0836 for Cu), indicating the presence of a mixed phase of Cu_2O and Cu. With the increase of P_{O_2} to 0.06 Pa, the Cu (111) peak disappears, indicating the existence of single phase Cu_2O . For the sample fabricated under P_{O_2} of 0.09 Pa, only the Cu_2O (110) and (220) peaks can be observed in addition to the substrate peak, indicating that a single orientation along the Cu_2O (110) direction is obtained. With

the further increase of P_{O_2} to 0.12 Pa, the CuO (020) and (310) peaks (JCPDS No.48-1548) as well as the Cu_2O (200) peaks are visible, indicating a mixed phase of Cu_2O and CuO and the degradation of film crystalline quality. It should be noticed that, due to the close 2θ values of CuO (221) and Cu_2O (311) reflections, the peak at around 73.5° is hard to distinguish for the 0.12 Pa-deposited sample and therefore it may be considered as a combined peak of these two reflections. While for the 0.02 and 0.06 Pa-deposited samples, considering the pure Cu_2O phase of the film grown at 0.09 Pa, it is reasonable to assign this peak to Cu_2O (311) rather than CuO (221) for the films prepared at such lower oxygen pressures.

It is well-known that the Cu-O phase is strongly influence by the thermodynamic conditions (substrate temperature and oxygen pressure). However, for the non-equilibrium physical vapor deposition process PLD, the increase of total chamber pressure i.e. the oxygen pressure in our study can also alter the plasma dynamics by changing the target-to-substrate transport from the ballistic to the diffuse regime, which in turn can result in the formation of different Cu-O phases [32]. Therefore, the Cu-O phase transition in our study could be attributed to the combination of pressure related kinetic and thermodynamic effects. The results of XRD measurement reveal that the film structure and crystallinity are strongly influenced by oxygen pressure and the 0.09 Pa-deposited film has the best crystalline quality.

Fig. 1(b), (c), (d) and (e) show the plan view SEM images of copper oxide films deposited under P_{O_2} of 0.02, 0.06, 0.09 and 0.12 Pa, respectively. In Fig. 1(b), submicron particles can be observed on the surface of the 0.02 Pa-deposited film, for

which metallic Cu that mainly exists at the surface of the particles is assumed to act as a catalyst of their growth [32]. Fig. 1(c) exhibits irregular grains and disordered grain edges due to the polycrystalline structure of this sample. In Fig. 1(d), a compact surface with regularly-shaped islands and well-defined boundaries could be observed, which corresponds to the best crystallization of the sample prepared at 0.09 Pa. A surface with ill-defined grain formation is observed for the film deposited under 0.12 Pa as shown in Fig. 1(e), due to the mixed phase of this sample as revealed by the XRD analyses. As mentioned above, the plasma dynamics and therefore the growth mode of the films in our study can be influenced by the different oxygen pressures. The variation of growth mode together with the Cu-O phase transition will result in the different observed film surface morphologies. The SEM analyses illustrate obviously that the oxygen pressure has a strong influence on the film morphology and crystallinity, which are consistent with the XRD results.

Fig. 2. In-plane XRD patterns of (a) and (b) Φ -scan as well as (c) 2θ -scan for the sample grown under P_{O_2} of 0.09 Pa.

The off-specular Φ -scan of Cu_2O {111} planes ($\Psi=35.26^\circ$) for the 0.09 Pa-deposited film is shown in Fig. 2(a). Two diffraction peaks separated by 180° of the Cu_2O {111} planes indicate a good in-plane alignment inside the film. The {111} plane of Cu_2O is two-fold symmetrical along Cu_2O [110], which is consistent with Fig. 2(a), indicating a complete single-crystalline structure without any domains in the obtained film. Fig. 2(b) shows the off-specular Φ -scan of MgO {111} planes ($\Psi=35.26^\circ$) for the substrate, from which two diffraction peaks separated by 180° with the same Φ -angles as the Cu_2O {111} planes could be seen, indicating that the crystal lattices for both materials are aligned in-plane with an epitaxial relationship of Cu_2O (110)// MgO (110) and Cu_2O (001)// MgO (001). To further confirm that the peaks in Fig. 2(a) are really from the film and not the tail end of the substrate peaks, we have performed the in-plane 2θ -scan of the sample at the fixed Φ and Ψ angles, as shown in Fig. 2(c). Only two distinct peaks of Cu_2O (111) and MgO (111) can be seen

obviously, confirming the (111) reflections from the substrate and film are distinguishable. These results reveal that the Cu_2O film deposited under the P_{O_2} of 0.09 Pa is epitaxial single crystal with no twins and the epitaxial relationship is Cu_2O (110)// MgO (110) with Cu_2O (001)// MgO (001).

Fig. 3. (a) Low magnification TEM and (b) HRTEM images of the film-substrate interface and (c) SAED micrographs of the film portion for the 0.09 Pa-deposited sample.

The cross-sectional TEM measurements were performed to further study the atomic arrangements and microstructure of the sample deposited under P_{O_2} of 0.09 Pa. From the low magnification TEM image as shown in Fig. 3(a), a compact film without any columnar structures inside as well as a clean and sharp interface between the film and the substrate are observed. The HRTEM image of the interface between the Cu_2O film and MgO substrate and the SAED pattern of the Cu_2O film are shown respectively in Fig. 3(b) and (c). The incident electron beam was parallel to the $[\bar{1}10]$ direction of the MgO substrate. Uniform and ordered crystal lattice arrays of both the Cu_2O film and MgO substrate can be seen clearly in Fig. 3(b). The spacings of the as-marked lattice planes in the Cu_2O film area are about 0.152 nm and 0.213 nm, corresponding respectively to the Cu_2O (220) and (002) planes with a standard angular separation of 90° inbetween. For the MgO substrate, the as-marked interplane spacings are 0.150 and 0.210 nm, which are consistent respectively with the MgO (220) and (002) planes. In the SAED pattern of the Cu_2O film shown in Fig. 3(c), the Cu_2O (110), (200) and (111) diffraction spots are clearly observed. The distinct and regular diffraction spot array implies good single crystallinity of this film. From the HRTEM analyses, the epitaxial relationship between Cu_2O film and MgO substrate can be obtained as Cu_2O (110)//MgO (110) with Cu_2O (001)//MgO (001), which is consistent with the XRD analyses, indicating the single crystalline structure of this film.

Fig. 4. XPS spectra of the Cu₂O film grown under P_{O₂} of 0.09 Pa: (a) survey, (b) Cu 2p core levels, (c) Cu LMM Auger spectrum and (d) O 1s core level.

The chemical states of different elements of the Cu₂O film prepared at P_{O₂} of 0.09 Pa were investigated by XPS. As shown in Fig. 4(a), photoelectron peaks of O 1s, O KLL Auger, Cu LMM Auger, Cu 2p, Cu 2s, Cu 3p, Cu 3s and C 1s can be observed in the survey spectrum. The C1s peak is due to the adventitious hydrocarbon contamination on the film surface. The XPS spectra of Cu 2p and O 1s core levels were numerically fitted with four and three Lorentzian-Gaussian (Lorentzian: 20%) features, corresponding to Fig.4 (b) and (d), respectively. The fitted Cu 2p core levels

displayed in Fig. 4(b), which show two main peaks at 932.8 and 952.8 eV corresponding respectively to the $2p_{3/2}$ and $2p_{1/2}$ levels of Cu^{1+} state (Cu_2O) [16]. The shoulder peaks at 935.1 and 955.2 eV together with the shake-up satellite peaks in the 940-945 and 960-965 eV regions can also be observed, indicating the presence of Cu^{2+} state (CuO) on the film surface [33], which is normally formed by exposure in humid air after the deposition of Cu_2O . Since the main peaks of Cu 2p at the same positions can also be assigned to metallic Cu, the Cu LMM Auger transition was investigated as well. As can be seen from Fig. 4(c), the Cu LMM Auger spectrum with Lorentzian peak fit has only one feature with a kinetic energy of 916.45 eV. It has been reported that the Cu^0 (metallic Cu) Auger spectrum has a distinct satellite feature at kinetic energy of ~ 2.5 eV higher than the main peak [16], the absence of which rules out the existence of metallic Cu. The fitted O 1s spectrum shown in Fig. 4(d) has three distinct peak contributions. The peak at lower binding energy (around 530.5 eV) denoted as O_{latt} represents the lattice oxygen of Cu_2O and/or CuO and the peaks at higher binding energy (531.6- 532.0 eV) denoted as O_{ads} belongs most likely to the adsorbed oxygen and/or hydroxyl group [34].

Fig. 5. Transmittance spectra of the copper oxide films prepared under typical oxygen pressures with the plots of $(\alpha h\nu)^2$ versus $h\nu$ shown in the inset.

The transmittance spectra of copper oxide films prepared under typical oxygen pressures are displayed in Fig. 5(a). It can be seen that under the P_{O_2} of 0.02 Pa, as a result of the existence of opaque metallic copper phase, the film presents feeble transmittance. For the samples deposited under 0.06 and 0.09 Pa, on the one hand, the films are pure phase Cu_2O with large band gap, without any narrow-band-gap materials that can absorb long wavelength light existent. On the other hand, the Cu_2O film crystallinity is improved with fewer structural defects present, which will subsequently decrease the light scattering and the defect level related light absorption. Both factors mentioned above may lead to the high transmittance of these two films. As the P_{O_2} increases further to 0.12 Pa, resulting from the presence of CuO ($E_g=1.2-2.0$ eV) [35] and degraded crystallinity, the transmittance of film decreases obviously. In addition, much sharper absorption edges are observed for the pure Cu_2O films than the films having impurity phases. Fig. 5(b) shows the Tauc plots of the

copper oxide films. The band gaps of copper oxide films are estimated with Tauc's equation for direct transition gaps in semiconductors given by [36]

$$(\alpha h\nu)^2 = A(h\nu - E_g), \quad (1)$$

where α is the absorption coefficient, A is a material dependent constant, h is the Planck constant, ν is the frequency and E_g is the optical energy band gap. The absorption coefficient α can be calculated from the thickness (d) and transmittance (T) of the film by using the well-known equation of [37]

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right). \quad (2)$$

Therefore, the E_g values can be derived through plotting $(\alpha h\nu)^2$ vs. $h\nu$ followed by extrapolating the straight-line portion of this plot to the energy axis as exhibited in the Fig. 5(b). The E_g values of 2.37, 2.57, 2.56 and 2.33 eV are obtained for the films deposited under oxygen pressures of 0.02, 0.06, 0.09 and 0.12 Pa, respectively. The E_g values and variation tendency in our study are similar to the results of previously reported works [7, 38].

Fig. 6. Hall mobility, carrier concentration and resistivity of the copper oxide films as a function of the oxygen pressure.

Fig. 6 shows the dependence of Hall mobility, carrier concentration and electrical resistivity on the oxygen pressure for the copper oxide thin films. The p-type conductivity was confirmed for all the samples shown in Fig.6 during the measurement. The film deposited at 0.02 Pa possesses insulating property probably due to the existence of metallic Cu and the consequent compensation of holes. With the increase of P_{O_2} to 0.06 Pa, the deposited film becomes single phase Cu_2O and the resistivity decreases. As the P_{O_2} increases further to 0.09 Pa, both of the Hall mobility and carrier concentration increase mainly due to the improvement of crystallinity and increased number of Cu vacancies, respectively, resulting in the decrease of resistivity. The Cu_2O film deposited under P_{O_2} of 0.09 Pa possesses the lowest electrical resistivity of $6.67 \Omega \cdot cm$ with the highest carrier concentration of $3.94 \times 10^{16} cm^{-3}$ and highest mobility of $23.75 cm^2 \cdot v^{-1} \cdot s^{-1}$ among all the copper oxide thin films deposited in this work. To the best our knowledge, the resistivity of $6.67 \Omega \cdot cm$ obtained in our study is also the lowest value reported thus far for the Cu_2O films deposited by PLD [24-26]. Good electrical properties of low resistivity, high Hall mobility and proper carrier concentration are essential for fabricating high performance Cu_2O -based functional devices like solar cells and thin film transistors. As the P_{O_2} increases further to 0.12 Pa, the carrier concentration decreases due to the formation of CuO phase and therefore the decrease of Cu vacancies. In the meantime, the obvious degradation of

film crystallinity leads to the decline of Hall mobility. Consequently, an increase of electrical resistivity is observed for the 0.12 Pa-deposited film.

4. Conclusions

Copper oxide thin films were deposited on MgO (110) substrates by the PLD technique and the influence of oxygen pressure on the film properties was systematically investigated. The structure, crystallinity and morphology of the films were strongly affected by the oxygen pressure. The variation of oxygen pressure in our study could not only change the thermodynamic conditions but also alter the plasma dynamics and therefore the film growth mode, which in turn could result in the formation of different Cu-O phases and film surface morphologies. The 0.09-Pa-deposited film was pure single-crystalline Cu₂O with an epitaxial relationship of Cu₂O (110)//MgO (110) with Cu₂O (001)//MgO (001). An obvious influence of oxygen pressure on the transmittance of the films was also observed and a variation of the optical band gap from 2.33 to 2.57 eV was obtained. The lowest resistivity of 6.67 $\Omega\cdot\text{cm}$ with the highest carrier concentration of $3.94 \times 10^{16} \text{ cm}^{-3}$ and highest Hall mobility of $23.75 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ were obtained for the film deposited under the oxygen pressure of 0.09 Pa. High quality Cu₂O single-crystalline films with good electrical properties may pave the way for realizing high performance Cu₂O-based functional devices such as thin film transistors and solar cells.

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Figure Captions:

Fig. 1. (a) XRD patterns of copper oxide films grown on MgO (110) substrates under typical oxygen pressures. Plan view SEM micrographs of the copper oxide films grown under the oxygen pressures of (b) 0.02, (c) 0.06, (d) 0.09 and (e) 0.12 Pa.

Fig. 2. In-plane XRD patterns of (a) and (b) Φ -scan as well as (c) 2θ -scan for the sample grown under P_{O_2} of 0.09 Pa.

Fig. 3. (a) Low magnification TEM and (b) HRTEM images of the film-substrate interface and (c) SAED micrographs of the film portion for the 0.09 Pa-deposited sample.

Fig. 4. XPS spectra of the Cu_2O film grown under P_{O_2} of 0.09 Pa: (a) survey, (b) Cu 2p core levels, (c) Cu LMM Auger spectrum and (d) O 1s core level.

Fig. 5. Transmittance spectra of the copper oxide films prepared under typical oxygen pressures with the plots of $(\alpha h\nu)^2$ versus $h\nu$ shown in the inset.

Fig. 6. Hall mobility, carrier concentration and resistivity of the copper oxide films as a function of the oxygen pressure.