Optical and electrical properties of p-type transparent conducting CuAlO$_2$ thin film

D.S. Kim [a], S.J. Park [a], E.K. Jeong [a], H.K. Lee [b], S.Y. Choi [a],*

[a] Optical Information Materials Research Laboratory (OIMRL), School of New Materials Science and Engineering, Yonsei University, 134, Shinchon-dong, Sudaemoon-gu, Seoul, 120-749, Republic of Korea
[b] School of Advanced Materials and Systems Engineering, Kumoh National Institute of Technology, 1, Yangho-dong, Gumi, 730-701, Republic of Korea

Abstract

P-type transparent conducting CuAlO$_2$ thin films were prepared by e-beam evaporation and wet-oxidation technique. CuAlO$_2$ film was preferentially (006) oriented after wet-oxidation. The transmittance varied from 20 to 85% and the resistivity varied from 5×10^{-3} to 4 Ω cm with wet-oxidation conditions. The nature of p-type films was confirmed by the positive hall coefficient. Optical band gap was estimated to be in the range of 3.96–4.20 eV. These behaviors were due to the decrease of oxygen deficient state in the film as oxidation progresses. Microstructural observations of films showed smooth morphology with 23.2–29.7 Å rms roughness.
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1. Introduction

The major applications of transparent conductive oxides (TCOs) are transparent electrodes in flat panel displays, solar cells, and touch panels [1,2]. These materials are required to have high optical transparency and electrical conductivity. To be applied to transparent devices, such as transparent diodes, transistors and light-emitting diodes (LEDs), p–n junction with n-type and p-type transparent conductive materials is required [3,4]. However, most TCOs such as ZnO, In$_2$O$_3$:Sn (ITO), and SnO$_2$ are n-type materials, while few transparent p-type conductors are known. The conductivity of p-type transparent materials is due to the metal deficient or oxygen excessive defects within the crystallite site. Excess oxygen atmosphere on fabrication process can induce p-type conductivity. Subsequent improvement in the conductivity can be obtained by controlling the processing conditions. These p-type TCOs, combined with n-type transparent semiconductors, will enable to fabricate the p–n junction for transparent devices and these materials will become more effective [5,6]. Recently, Kawazoe et al. [7] reported new p-type transparent semiconductors, CuAlO$_2$ and

SrCu$_2$O$_2$ prepared by pulsed laser deposition. The essential feature for p-type TCOs is the selection of a monovalent copper, which has electronic configuration and energy level of the filled 3d orbital. Cuprous ion has an electronic configuration of $3d^{10}4s^0$ (closed shell), which is free from visible coloration arising from a d–d transition commonly seen in partially occupied transition metallic ions. The energy level of Cu $3d^{10}$ is
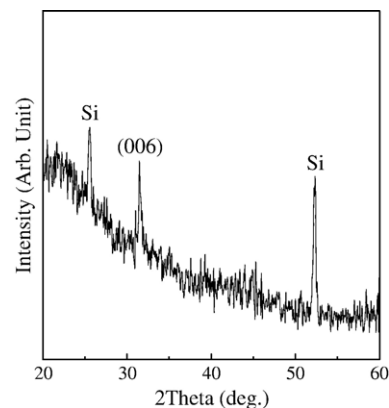

Fig. 1. XRD pattern of CuAlO$_2$ film deposited on Si substrate after oxidation at 500 °C for 5 h at water vapor pressure of 0.467 atm.

* Corresponding author. Tel.: +82 2 2123 2851; fax: +82 2 365 5882.
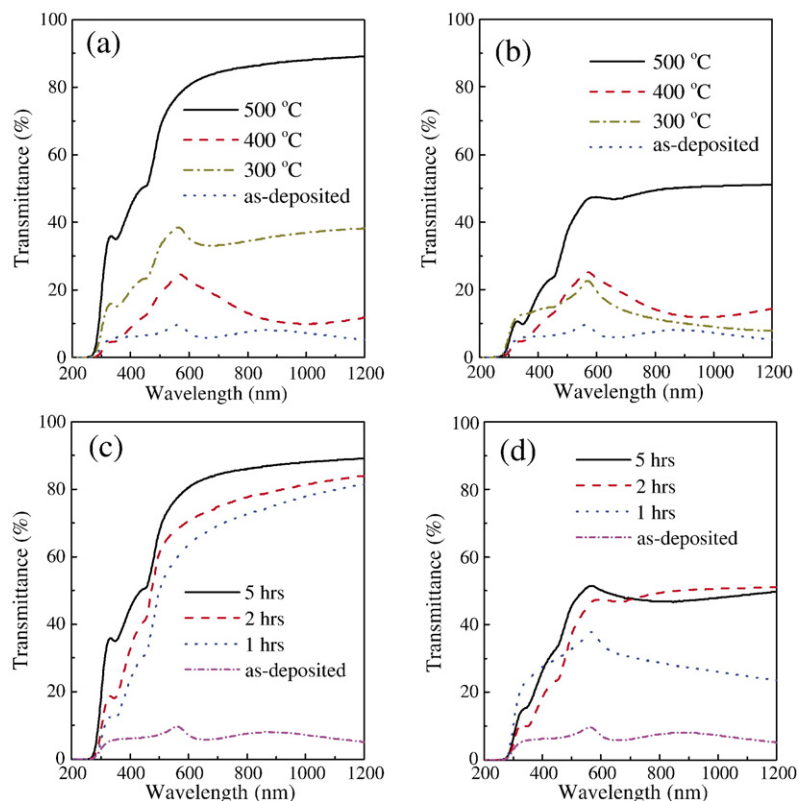 E-mail address: sychoi@yonsei.ac.kr (S.Y. Choi).

Fig. 2. Transmittance variations of the CuAlO$_2$ thin film with different wet-oxidation conditions; temperature variations for 5 h at (a) 0.467 atm, (b) 0.031 atm, and time variations at 500 °C at (c) 0.467 atm, (d) 0.031 atm.
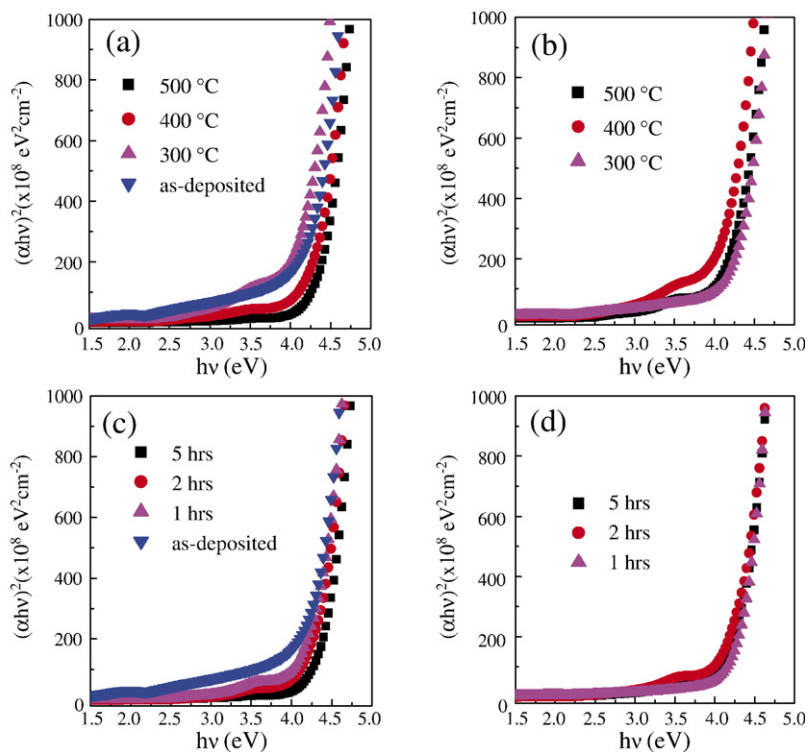

Fig. 3. Optical absorption plots of the film with different wet-oxidation conditions; temperature variations for 5 h at (a) 0.467 atm, (b) 0.031 atm, and time variations at 500 °C at (c) 0.467 atm, (d) 0.031 atm.
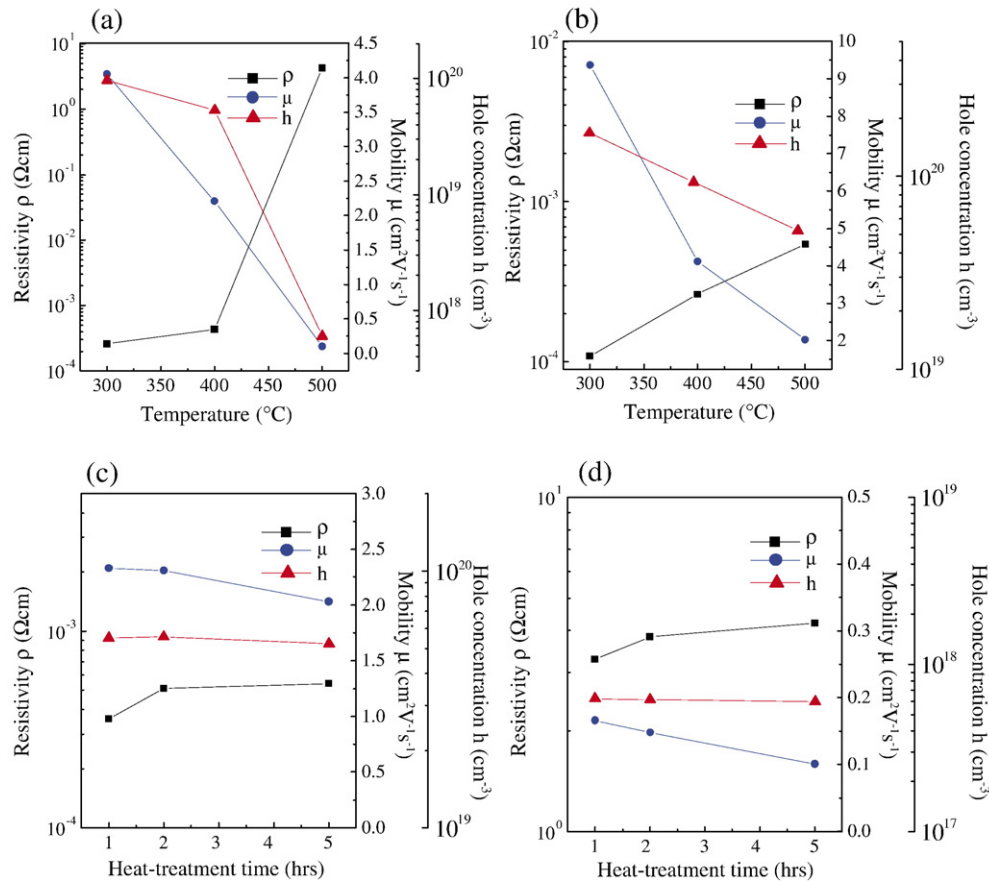
Fig. 4. Hole density, resistivity of film, and carrier mobility variations as a function of wet-oxidation conditions; temperature variations for 5 h at (a) 0.467 atm, (b) 0.031 atm, and time variations at 500 °C at (c) 0.467 atm, (d) 0.031 atm.

similar to that of O $2p^6$. As a consequence, formation of covalent bonding is possible between Cu $3d^{10}$ and O $2p^6$. By covalent bonding, there shows large dispersion in the valence band and reduction in localization of positive holes. However, the Cu_2O, the simplest oxide of Cu^+, has rather small band gap (2.1 eV), thus, it is not transparent in visible range. Yanagi et al. [8] suggested that the small band gap was due to three-dimensional interaction within $3d^{10}$ electrons of neighboring Cu^+ ions. It was expected that choice of low dimensional crystal structure suppresses the interactions. The delafossite $CuAlO_2$, composed of alternate stacking of O–Cu–O dumbbells and AlO_6 octahedral layers, was selected as one of the promising materials for p-type TCOs. Thin films of Cu^+ delafossites were prepared, and their optical transparency and p-type conductivity were experimentally evidenced [8–10].

The wet-oxidation is a general process used in semiconductor industry. Its oxidation rate is faster than that of dry oxidation, and oxide thereby has better electrical properties. The oxidation of free metal takes place via a diffusion-controlled process and the final electrical and optical properties of the films are determined by the relative rates of oxidation and diffusion of the metal [11].

In this paper, we report on $CuAlO_2$ thin films, which were initially deposited by e-beam evaporation and then oxidized by wet-oxidation process. The effects of wet-oxidation conditions such as oxidation temperature, time, and vapor pressure of water on electrical and optical properties were investigated.

2. Experiment procedure

A copper–aluminum oxide target was prepared with CuO (98.5%, Showa Chem., Japan) and Al_2O_3 (GR, Junsei Chem., Japan). The CuO and Al_2O_3 powder were mixed for 24 h by using a ball milling. The pellets was made by pressing with the mixture and sintered at 1200 °C for 4 h. The thin film was deposited on alumino-borosilicate glass and (100) Si wafer by e-beam evaporation technique (Semiconductor Nano Technology Co. Ltd., Korea). The base pressure was 5×10^{-6} Torr with 1.5 Å/s of deposition rate. The film was deposited until its thickness reached 100 nm. As-deposited films were oxidized by wet-oxidation process. N_2 carrier gas (99.99%, Samheung gas, Korea) was bubbled through the de-ionized water and the flow rate of the carrier gas was 300 ml/min. In order to study the effect of wet-oxidation conditions on the optical and electrical properties, wet-oxidation was carried out at different oxidation temperatures (300–500 °C) and for different time durations (1–5 h), and water temperatures (25–80 °C) governing vapor pressure of water.

The film structure was analyzed by X-ray diffraction (XRD, Rigaku D/Max Rint2000, Japan) with CuK_α radiation. The composition of the film was identified by electron probe micro
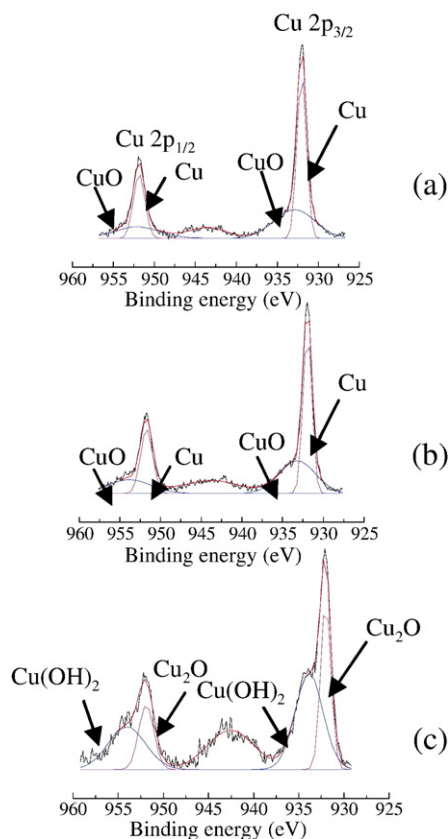
Fig. 5. XPS spectra of Cu 2p region of the film with wet-oxidation conditions; (a) as-deposited, (b) at 500 °C for 1 h at 0.031 atm, and (c) at 500 °C for 5 h at 0.467 atm.

analysis (EPMA, JXA-8900R, Jeol, Japan). The optical properties were measured at room temperature using UV/VIS/NIR spectrometer (Jasco UV-570, Jasco, Japan) and the sheet resistance of the film was measured by four-point-probe method (CMT-SR2000N, ChangMin, Korea). Hall measurement was carried out at room temperature by Hall effect method (HL5500PC, Bio-Rad, U.S.A.). The chemical binding of the film was analyzed by XPS (ESCALAB 200i-XL, VG Scientific Instrument, U.S.A.). The microstructure of thin films was observed by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4200, Japan) and surface morphology was examined by atomic force microscopy (AFM, SPM-9500J, Shimazu, Japan).

3. Results and discussion

Fig. 1 shows the XRD pattern of the CuAlO$_2$ thin film deposited on Si substrate after oxidation at 500 °C for 5 h at 0.467 atm of water vapor pressure. The XRD pattern shows the preferential (006) orientation, and this result was previously reported with our work [12]. Similar results were reported for CuAlO$_2$ film deposited by different deposition methods and on various substrates [7,13–15]. Generally, the composition of the film deposited by e-beam evaporation is different from the target composition owing to the different vapor pressure of target elements. Therefore we deposited the films with different target compositions and the film compositions were analyzed by EPMA. Stoichiometric CuAlO$_2$ film was experimentally obtained when the Cu:Al atomic ratio of the target was 1:1.5.
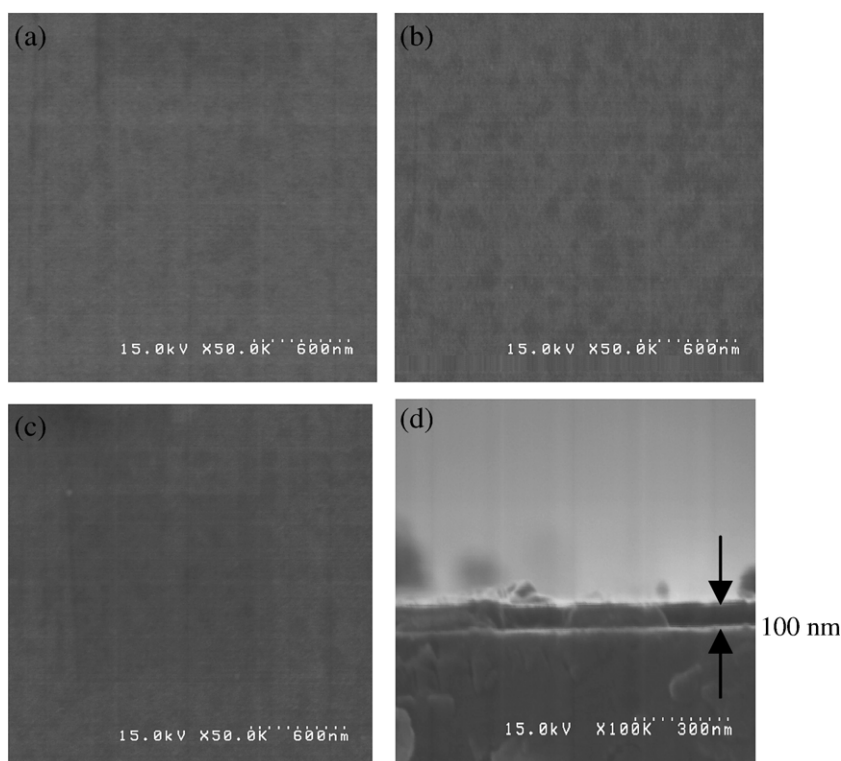

Fig. 6. Microstructures of the film with different wet-oxidation conditions; (a) as-deposited, (b) at 500 °C for 1 h at 0.031 atm, and (c) and (d) at 500 °C for 5 h at 0.467 atm.
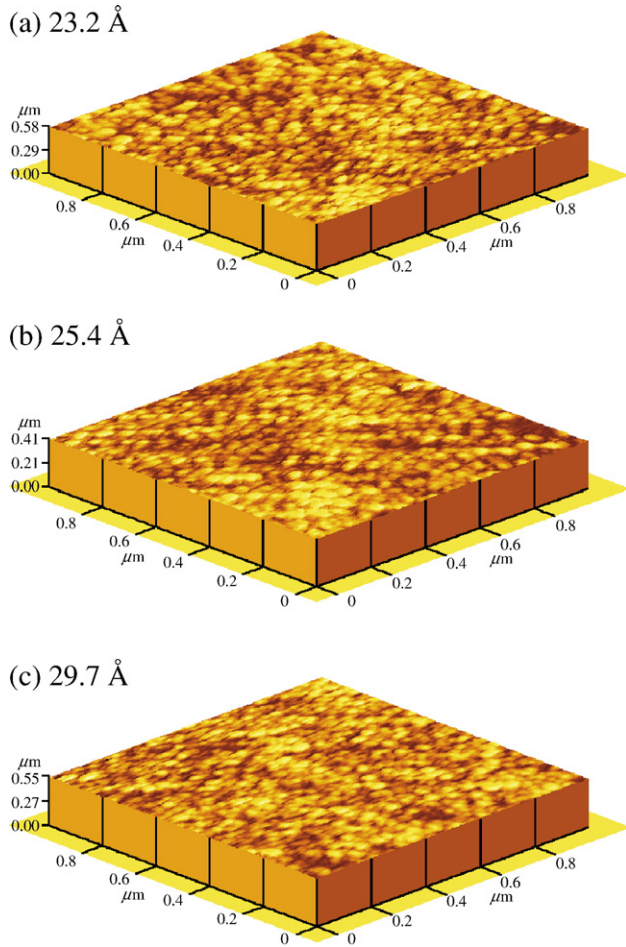
(a) 23.2 Å

(b) 25.4 Å

(c) 29.7 Å

Fig. 7. AFM images of the film with different wet-oxidation conditions; (a) as-deposited, (b) at 500 °C for 1 h at 0.031 atm, and (c) at 500 °C for 5 h at 0.467 atm.

Fig. 2 shows the optical transmittance of the thin film deposited on glass substrate and oxidized at different temperature, time, and water vapor pressure. The transmittance of as-deposited film was very low as in metallic film. However, the transmittance was increased to ∼ 85 % in the visible range with increasing oxidation temperature at water vapor pressure of 0.467 atm (Fig. 2(a)), while, at 0.031 atm, the transmittance was about 50% at the same oxidation temperature and time (Fig. 2(b)). In addition, the transmittance was a little varied according to the oxidation time. These phenomena were due to the oxidation of the as-deposited film. Generally, when oxides are evaporated, they are deposited as oxygen deficient states and formed to opaque films. The opaqueness of as-deposited films has been ascribed to the presence of free metal in the oxide matrix, resulting from the reduction of oxide species that are present in vapor phase. The film transmittance improvement may be due to the conversion of oxide deficient state to the oxide state by wet-oxidation [16]. However, transmittance was not much affected with oxidation time. This was due to the fact that most metallic copper was already oxidized at high temperature.

The absorption coefficient (α) was calculated using Mani-facier model [17]. By calculated absorption coefficient, the optical transition type and optical band gap can be determined.

The relation of absorption coefficients and incident photon energy (hν) is expressed below [18]:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

where A is a constant, E_g is the optical band gap, and the exponent n depends on the type of the transition. In case of direct allowed transition, n is 1/2. For indirect allowed transition, n is 2, and for direct forbidden transition, n is 3/2. The relation of $(\alpha h\nu)^{1/n}$ vs. hν were plotted in Fig. 3. The optical band gap varied from 3.96 to 4.20 eV with wet-oxidation conditions, and transition type was direct allowed transition. Our films showed wider optical band gap than the previously reported [7,8,15,19]. However, a curvature was changed at about 3.5 eV and this implies that another energy state exists. This phenomenon was due to the remaining deficient state oxygen, as mentioned. As the water vapor pressure increases, which means the oxygen amount at wet-oxidation atmosphere increases, and the oxidation temperature increases, oxidation rate increases. Therefore the lower oxides gradually vanish, and the curvature change is decreased.

The variations of hole density, resistivity of film, and carrier mobility with wet-oxidation conditions are shown in Fig. 4. In all cases, hall coefficient was positive, and therefore conduction nature was p-type. As shown in Fig. 4(a), the resistivity was varied from 5×10^{-3} to 4 Ω cm at water vapor pressure 0.467 atm. However, at 0.031 atm, the resistivity was much lower than that of the film oxidized at 0.467 atm. As the water vapor pressure and oxidation temperature increase, oxidation is accelerated, and thus, the hole concentration decreases and resistivity increases. These resistivity values were lower than those in the previous reports [5,7,8]. This is caused by higher defect concentration of lower oxides. The increase of resistivity upon temperature and water vapor pressure may be due to the decrease in hole mobility and its concentration upon oxidation of oxygen deficient state. As oxidation progresses, oxygen deficient species diminishes, so hole concentration decreases. Hole mobility was also a little decreased. This situation was due to the increase of scattered sites. As thin film was oxidized, even though hole concentration decreases, the number of various bonds increases, and complexity of theses bonds could act as scattered sites. The effect of oxidation time on electrical properties was similarly little as in case of optical properties. Most of metallic copper was already oxidized at high temperature, so electrical properties were not much affected by oxidation temperature at high temperature. As a result, the electrical properties could be controlled in the wide range by oxidation temperature and water vapor pressure.

Fig. 5 shows the XPS spectra of the Cu 2p with different wet-oxidation conditions. In as-deposited film, the portion of metallic Cu was similar to that of CuO. However, in wet-oxidation process, oxygen is introduced into the structure and the Cu–O bonds increase. Therefore in case of oxidation at 500 °C for 5 h at water vapor pressure of 0.467 atm, Cu_2O bonds appeared and metallic Cu disappeared. Chawla et al. [19] reported the difference in binding energies between main Cu $2p_{3/2}$ peak for Cu_2O and metallic Cu is very little (0.1 eV), while those for CuO and

Cu(OH)$_2$ are 1.6 and 2.0 eV, respectively. The satellite peak at 943 eV, which is originating from Cu^{2+} is due to Cu(OH)$_2$ in the surface, increase with water vapor pressure increase. At high vapor pressure, OH$^-$ dangling bonds increase. Defects in metallic Cu and lower oxide phase decrease, the transmittance and resistivity increase. This means that crystal defects can be controlled by wet-oxidation conditions [12].

Scanning electron micrographs of surfaces and cross-section of CuAlO$_2$ thin films according to wet-oxidation conditions are shown in Fig. 6. Thin films showed perfectly flat and uniform morphology without microcracks. It may be noted that from Fig. 6(d) that the film had uniform thickness and the thickness was about 100 nm after wet-oxidation at 500 °C for 5 h at 0.467 atm.

Fig. 7 shows AFM images of CuAlO$_2$ thin films having a thickness of 100 nm by wet-oxidation conditions. The image covered a 1.0 μm × 1.0 μm and the films had a smooth surface. Values of root mean square (rms) roughness were 23.2, 25.4 and 29.7 Å for as-deposited, wet-oxidized at 500 °C for 1 h at 0.031 atm and at 500 °C for 5 h at 0.467 atm, respectively.

4. Conclusions

The CuAlO$_2$ thin film was deposited by e-beam evaporation and then oxidized by wet-oxidation technique. The CuAlO$_2$ film, preferentially (006) oriented, was obtained after the wet-oxidation. The transmittance was increased from 20 to 85% in the visible range and the resistivity of the thin film increased from 5×10^{-3} to 4 Ω·cm with increasing the oxidation temperature and water vapor pressure. The nature of p-type film was confirmed by a positive hall coefficient. The optical band gap was estimated to be in the range of 3.96–4.20 eV. These behaviors were due to the decrease of oxygen deficient state in the film as oxidation progresses, therefore the electrical and optical properties could be controlled by the oxidation temperature and water vapor pressure. The microstructure of thin films appeared smooth with 23.2–29.7 Å rms roughness.

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