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Journal of the European Ceramic Society 30 (2010) 509–512

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Phase development and crystallization of $CuAlO_2$ thin films prepared by pulsed laser deposition

Jong-Chul Lee, Se-Young Um, Young-Woo Heo, Joon-Hyung Lee *, Jeong-Joo Kim

School of Materials Science and Engineering, Kyungpook National University, Daegu 702-701, Republic of Korea

Available online 18 June 2009

Abstract

A polycrystalline $CuAlO_2$ single-phase target was fabricated by the conventional solid-state reaction route using Cu_2O and Al_2O_3. Thin films of $CuAlO_2$ were deposited by a pulsed laser deposition process on sapphire substrates at different temperatures. Then, post-annealing was followed at different conditions, and the phase development process of the films was examined. As grown thin films in the temperature range of 450–650 °C were amorphous. The *c*-axis oriented single phase of $CuAlO_2$ thin films were obtained when the films were post-annealed at 1100 °C in air after growing at 650 °C. Phi-scan of the film clearly showed 12 peaks, each of which are positioned at intervals of 30°. This is thought to be caused by the rhombohedral structured $CuAlO_2$ thin film growing in the states of 30° tilt during the annealing process. Hall effect analysis of the film was carried out.

Keywords: Films; $CuAlO_2$; Delafossite structure; Pulsed laser deposition; Transparent conducting oxide

1. Introduction

Transparent conducting oxides (TCOs) simultaneously exhibit high transparency through the visible light wavelength and high electrical conductivity. Because of the electro-optic characteristics, there has been a considerable technological interest in developing TCO, given their direct applications in solar cells or touch panels, or their use as transparent electrodes in flat panel displays. Other applications in which TCOs act as active devices require TCOs with p-type conductivity. Many efforts have been devoted so far to fabricate p-type TCOs.

A number of delafossite structured p-type TCOs having the general formula $A^{1+}B^{3+}O_2$ and containing Cu as a major cationic species such as $CuAlO_2$, $CuInO_2$ and $CuGaO_2$ have been developed. Among them, $CuAlO_2$ ceramics is known to satisfy the conditions facilitating p-type conduction without any intentional doping, and it is a potential material to apply for an efficient photovoltaic solar cell by using a p–n junction combined with an n-type TCO.

It is known that many of the delafossite structured p-type TCOs are not synthesized easily, and the densification is hardly achieved. It is because the A-site cation in the ABO_2-delafossite structure is composed of noble metals and is found to have lower formation energies which results in decomposition rather than reaction/formation to a single phase. The p-type $CuInO_2$ is a good example, which has a low formation energy about $\Delta H = 0.056$ eV.[1] Therefore, the manufacturing of pure-phase $CuInO_2$ targets is still challenging process. In the case of p-type $CuAlO_2$, it is known that the solid-state reaction is easier than $CuInO_2$ when the reacted or sintered sample is cooled down quickly before decomposition, unless $CuAlO_2$ will decompose into CuO and $CuAl_2O_4$ during cooling.[2] Preparation of the p-type TCO films has been mainly carried out by pulse laser deposition and rf sputtering using sintered bulk polycrystal targets.[3–5]

In this study, a single phase of the $CuAlO_2$ target was manufactured by the general solid-state reaction process through the sintering and quenching in air. p-Type $CuAlO_2$ thin films were grown by using the pulsed laser deposition (PLD) method under different growing and post-annealing parameters. The phase evolution, texture, structure and electrical characteristics of the film were examined.

2. Experimental procedure

A single-phase $CuAlO_2$ target was prepared by the general solid-state reaction method. High purity chemicals of Cu_2O

* Corresponding author. Tel.: +82 53 950 7512; fax: +82 53 950 5645.
E-mail address: Joonlee@knu.ac.kr (J.-H. Lee).

0955-2219/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2009.05.025

(High Purity Chemicals, 99%, Japan) and Al_2O_3 (Sumitomo, 99.99%, Japan) were used as raw materials. Cu_2O and Al_2O_3 were weighed at the 1:1 molar ratio. The weighed powders were wet-mixed for 24 h in a polyethylene jar with zirconia balls and ethanol. Then the slurries were fully dried in an oven. The dried powders were formed into 1 in. diameter disk by a sequential process of uniaxial pressing followed by cold isostatic pressing (CIP) at 200 MPa. Sintering was conducted at 1200 °C for 4 h in air at a heating rate of 3 °C/min. After sintering, for air-quenching, the disk was taken out from the furnace immediately. The density of the sintered samples was determined by the Archimedes method and the crystal structure and phase evolution were identified by an X-ray diffractometer (M03XHF, Mac Science, Japan) using Cu-Kα radiation.

Using the disk target, $CuAlO_2$ thin films were grown on sapphire substrates by the pulsed laser deposition (PLD) process. The films were deposited in the temperature range of 450–650 °C for 30 min in an ambient with the oxygen partial pressure of 10 mTorr. The films were post-annealed in different conditions; annealing temperatures at 1000 and 1100 °C and in different ambients of air, N_2 (99.99%) and O_2 (99.99%) for 30 min. The phase identification of the films was carried out by a Mulit-Purpose X-ray diffraction (X'pert PRO MRD). $CuAlO_2$ thin films were annealed at different temperatures and oxygen partial pressures.

3. Results and discussion

Fig. 1 shows a comparison of the X-ray diffraction patterns for the $CuAlO_2$ disk targets with a different thermal history after sintering: (a) air-quenched after sintering at 1200 °C for 4 h and (b) furnace cooled after sintering at 1200 °C for 4 h. Furnace cooling was carried out by turning off the electric power after sintering as the sample is kept in the furnace until the temperature of the furnace reaches room temperature. In the case of the furnace-cooled sample, CuO and $CuAl_2O_4$ phases coexist, which are produced from the decomposition of $CuAlO_2$. A single phase of $CuAlO_2$ was obtained only after quenching as observed in Fig. 1(a).

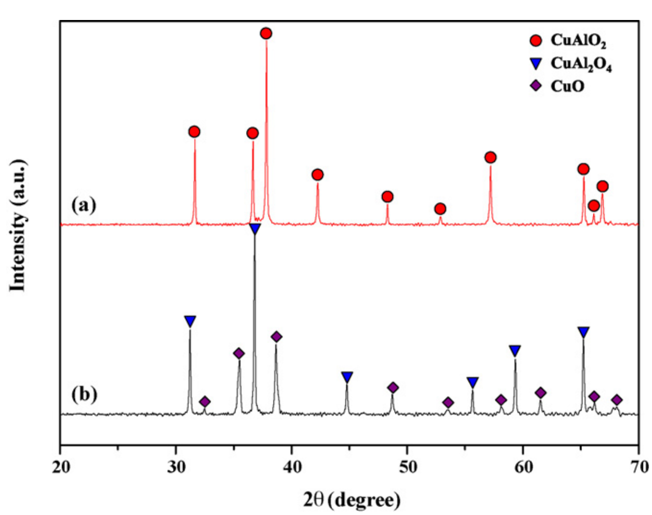

Fig. 1. X-ray diffraction patterns of the $CuAlO_2$ disk target which was (a) quenched after sintering and (b) furnace cooled after sintering at 1200 °C for 4 h in air.

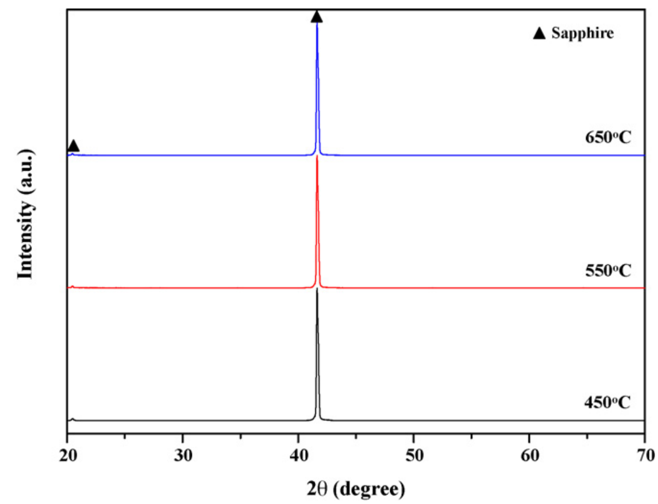

Fig. 2. X-ray diffraction patterns of the $CuAlO_2$ thin films as a function of growing temperature at 450–650 °C.

X-ray diffraction patterns of the $CuAlO_2$ thin films which were grown at 450–650 °C using the single-phase $CuAlO_2$ target are presented in Fig. 2. Since the X-ray diffraction intensity in the figure is a normal scale plot, the diffraction peaks from the thin films are hardly identified. The magnified view of the X-ray diffraction which is not presented here revealed amorphous characteristics with broad spread low intensities regardless of the growing temperature when the oxygen partial pressure was fixed to 10 mTorr.

Fig. 3 shows the X-ray diffraction patterns of the thin films post-annealed at (a) 1000 °C and (b) 1100 °C in air as a function of deposition temperature. It should be noted that the diffraction intensity is in log scale. When the films were post-annealed at 1000 °C in air, only CuO and $CuAl_2O_4$ phases appeared regardless of the deposition temperatures. Even though the annealing temperature is increased to 1100 °C as shown in Fig. 3(b), CuO and $CuAl_2O_4$ phases still remained when the films were deposited at 450 and 550 °C. While single-phase $CuAlO_2$ thin film was formed only in the case when the film was deposited at 650 °C and post-annealed at 1100 °C. Development of the (0 0 3) (0 0 6) (0 0 9) and (0 0 1 2) planes of the film indicates that the film is *c*-axis oriented.

In most cases as seen in Fig. 3(a) and (b), the second phases of CuO (as a major phase) and $CuAl_2O_4$ (as a minor phase) were observed consistently. This result evokes to have a question if Al or Cu has different deposition and/or adhesion rates comparatively or one component has higher vapor pressure than the other and resulted in the compositional inhomogeneity in the films, i.e., Al- or Cu-deficient $CuAlO_2$ films. For a confirmation, $CuAlO_2$ targets with 5 at% excess Al and Cu were prepared.

Fig. 4 shows the X-ray diffraction patterns of the thin films which were annealed at 1100 °C in air after deposition with the targets containing (a) 5 at% of excess Al and (b) 5 at% of excess

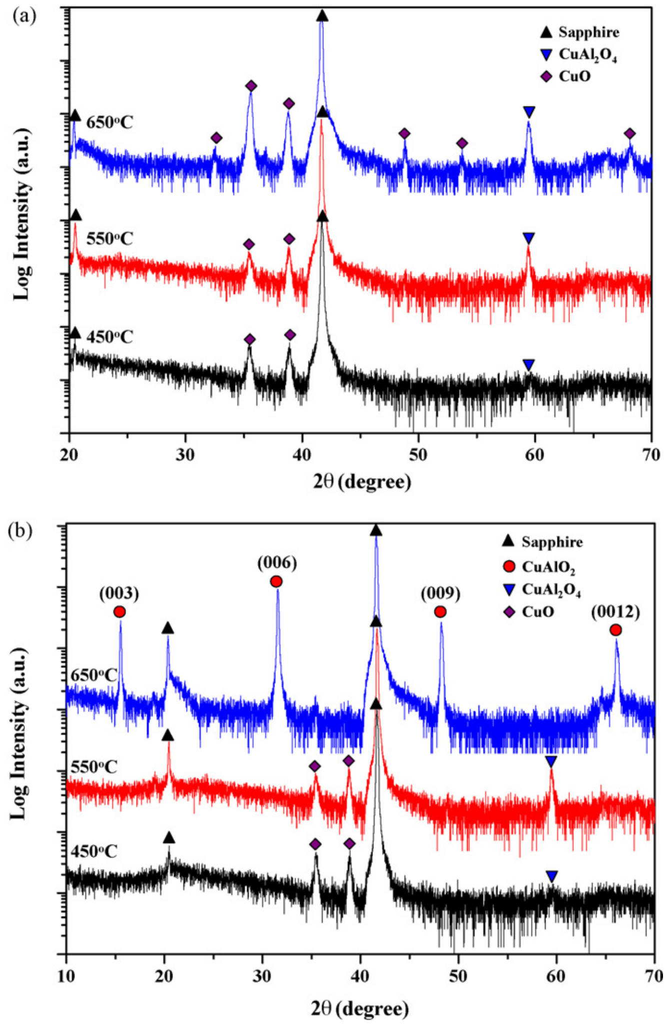

Fig. 3. X-ray diffraction patterns of the thin films post-annealed at (a) 1000 °C and (b) 1100 °C in air as a function of growing temperature.

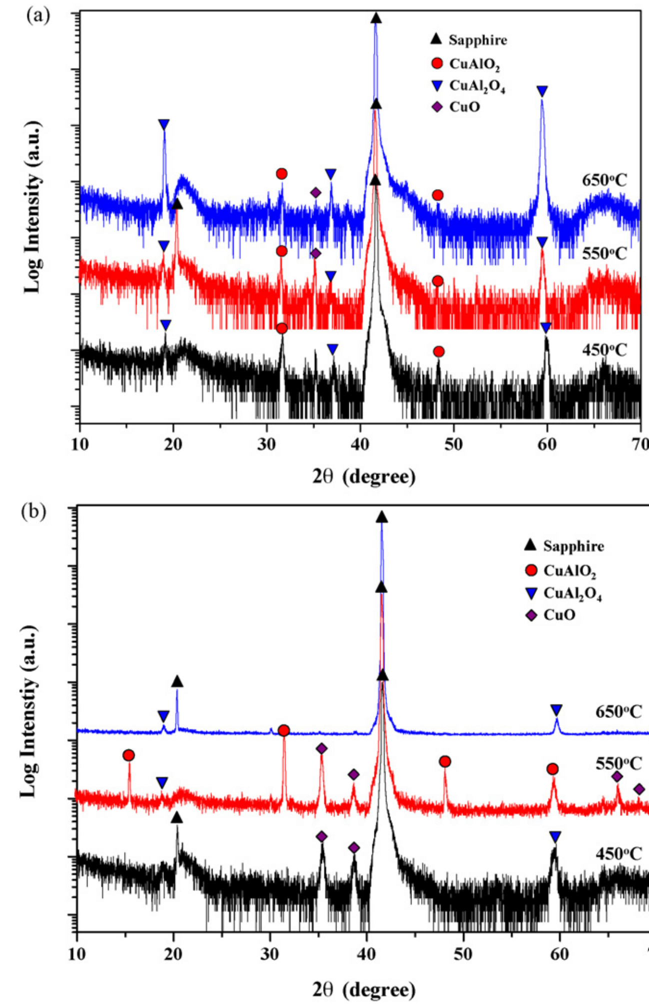

Fig. 4. X-ray diffraction patterns of the thin films annealed at 1100 °C in air after deposition with the targets containing (a) 5 at% of excess Al and (b) 5 at% of excess Cu.

Cu. As seen in the Fig. 4, change in the Cu/Al cationic ratios did not seem to contribute to the formation of $CuAlO_2$, and the second phases of CuO and $CuAl_2O_4$ still remained regardless of the different deposition temperatures. From the experimental results shown in Figs. 3 and 4, the optimum condition for the growing of single-phase $CuAlO_2$ film can be deduced; deposition at 650 °C using the target composed of Cu/Al ratio = 1 and annealing at 1100 °C. On the other hand, the thin films deposited at 650 °C were annealed at 1100 °C in different ambients of air, N_2 and O_2. The X-ray diffractions for the films are presented in Fig. 5. The *c*-axis oriented single phase of delafossite structured $CuAlO_2$ was formed only when it was annealed in the air.

Fig. 6 shows the results of HR-XRD analysis of (a) phi-scan and (b) pole-figure for the $CuAlO_2$ thin film annealed at 1100 °C for 30 min in air after deposition at 650 °C for 30 min in the oxygen pressure of 10 mTorr. In the phi-scan, 12 peaks are clearly apparent and the peaks are positioned at every 30° interval. Here, two groups of peaks can be originated from the $CuAlO_2$ thin films, each of which is positioned at every 60° interval. This is thought to be caused by the rhombohedral structured $CuAlO_2$[6] thin film is grown on the sapphire substrate in the state of a 30°

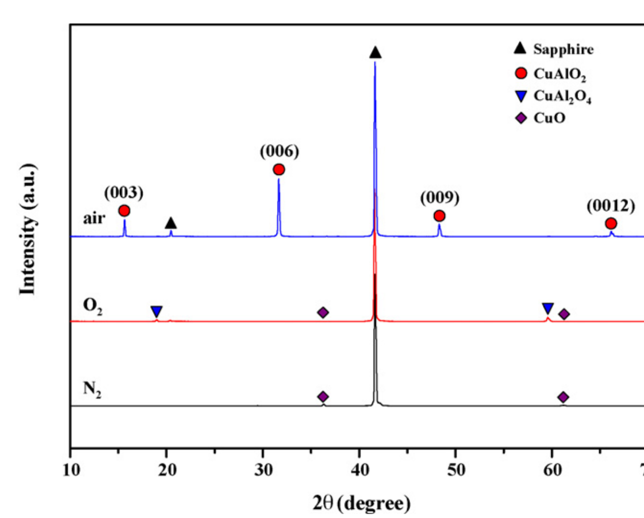

Fig. 5. X-ray diffraction patterns of the thin films deposited at 650 °C and annealed at 1100 °C in different ambient of air, N_2 and O_2.

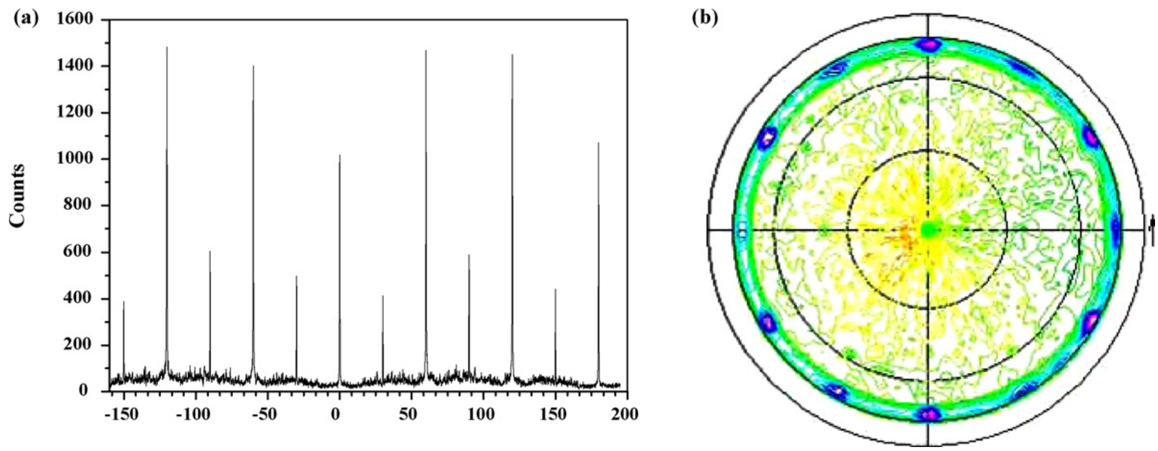

Fig. 6. HR-XRD analysis of (a) phi-scan and (b) pole-figure of the *c*-axis oriented $CuAlO_2$ thin film annealed at 1100 °C for 30 min in air after deposition at 650 °C for 30 min in the oxygen pressure of 10 mTorr.

tilt during the annealing process. This has probably happened due to the formation of stacking faults or thermal strains in the films during the annealing process.

The Hall effect measurement was carried out for the *c*-axis oriented $CuAlO_2$ thin film. It shows p-type behavior. The electrical conductivity, carrier concentration and mobility were 4.4×10^{-2} S/cm, 3.75×10^{17} cm^{-3} and 0.79 cm^2/V s, respectively.

4. Conclusions

A single-phase $CuAlO_2$ target was manufactured when the sample was quenched after sintering at 1200 °C for 4 h, and the phase evolution of the thin films grown by the PLD process was examined. As obtained the $CuAlO_2$ thin films were amorphous regardless of the growing temperature. A *c*-axis oriented single-phase $CuAlO_2$ thin film was formed when the film was grown at 650 °C and annealed at 1100 °C in air. The electrical conductivity, carrier concentration and mobility of the *c*-axis oriented $CuAlO_2$ thin film were 4.4×10^{-2} S/cm, 3.75×10^{17} cm^{-3} and 0.79 cm^2/V s, respectively.

Acknowledgement

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2007-521-D00220).

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