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Preparation of $CuAlO_2$ Thin Films by Radio Frequency Magnetron Sputtering and the Effect of Sputtering on the Target Surface

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Abstract

Powder, a sputtering target, and thin films of $CuAlO_2$ have been prepared by means of radio frequency (rf) magnetron sputtering and characterized. $CuAlO_2$ powder has been synthesized from a stoichiometric mixture of Cu_2O and Al_2O_3 powders by means of heat treatment at 1100 °C in N_2 for 40 h. Initially, a mixture of 3R-$CuAlO_2$ (rhombohedral) and 2H-$CuAlO_2$ (hexagonal) was obtained after the heat treatment for 30 h, then, 3R-$CuAlO_2$-dominant powder was obtained after further heat treatment as a result of the phase transformation reaction from 2H-$CuAlO_2$ to 3R-$CuAlO_2$. A $CuAlO_2$ sputtering target has been prepared by pressing the 3R-$CuAlO_2$ powder into a target form at room temperature. We have confirmed the target can be used in film preparation by means of rf magnetron sputtering. However, after film deposition, the target surface partially causes phase transformation from 3R-$CuAlO_2$ to 2H-$CuAlO_2$ owing to the effect of sputtering. Thin films prepared by means of sputtering of the target by oxygen plasma followed by thermal annealing in N_2 at a temperature higher than 800 °C for 10 h become $CuAlO_2$ thin films. The film annealed at 800 °C exhibits an optical bandgap of 3.51 eV and resistivity of 1.2×10^3; Ωcm.

Keywords: Transparent conductive oxide, sputtering, ceramic thin films, phase transformation reaction, properties

I. Introduction

Transparent conductive oxide (TCO) films are widely used as transparent electrodes in various optical devices. However, most of the TCO materials that have already been produced for applications have n-type conductivity. Development of p-type TCO is desirable to develop transparent electronics, in order to form transparent p-n junctions. In 1997 [1], Kawazoe and co-workers reported p-type conductivity of $CuAlO_2$, which is a Cu-delafossite material. In their report, a direct bandgap of about 3.5 eV and conductivity of 1 $\Omega^{-1}cm^{-1}$ were observed. Preparation of $CuAlO_2$ has been reported using various methods such as pulsed laser deposition [1,2], chemical vapor deposition [3], sol-gel method [4,5], and sputtering [6–10]. Of these methods, sputtering deposition has been recognized as a conventional method to form indium tin oxide electrodes [11], which is one of the n-type TCO materials. In the previous works on the sputtering deposition of $CuAlO_2$, various kinds of sputtering target have been used. For example, synthesized $CuAlO_2$ targets [6,7], two pairs of Cu and Al facing targets [8,9], and $Cu_{0.5}Al_{0.5}$ targets created by vacuum melting [10] have been studied. In the case of synthesized $CuAlO_2$ targets, the effect of plasma sputtering on the target surface is also interesting, because various kinds of decomposition reaction of the $CuAlO_2$ are expected, for example, reduction to metal Cu or Al, oxidation to other copper-aluminum oxides such as $CuAl_2O_4$ [12], decomposition to binary metal oxide, Cu_2O, CuO or Al_2O_3. However, to the authors' knowledge, the effect of plasma treatment on a $CuAlO_2$ target surface has not been studied.

In the present work, $CuAlO_2$ thin films are prepared by means of radio frequency (rf) magnetron sputtering using synthesized polycrystalline $CuAlO_2$ targets. Structural and optical properties of the $CuAlO_2$ thin films and the dependence of those characteristics on the preparation conditions are investigated. In addition, we have also investigated the effect of plasma sputtering on the structural properties of the sputtering target surface.

II. Experimental

(1) Target preparation

Polycrystalline $CuAlO_2$ powder target material was synthesized based on a solid-state reaction of a stoichiometric mixture of Cu_2O and Al_2O_3 at 1100 °C for 40 h under nitrogen flow. In order to study the detail of the solid-state reaction, we prepared other powders with a thermal treatment time length of 10 h and 30 h for comparison. The structural properties of the synthesized $CuAlO_2$ powder were studied by means of X-ray diffraction (XRD) using D8 Discover (Bruker) analysis in the θ-2θ mode using CuKα radiation (λ = 154.18 pm). $CuAlO_2$ sputtering tar-

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gets were prepared by pressing the $CuAlO_2$ powder under a pressure of 127 MPa into a form measuring 100 mm in diameter and 5 mm in thickness at room temperature in air.

(2) Target surface investigation

The samples of the target surface after the plasma sputtering were prepared for XRD characterization with adhesive tape. Adhesive tape was first affixed to the surface of the samples and then peeled off. After the tape had been peeled off, powder not from the target surface was carefully removed by blowing with N_2. Finally, the tapes with target surface powder were affixed to a glass substrate to enable XRD measurement. Characteristics of the surface as well as the powder samples themselves were studied with XRD.

(3) $CuAlO_2$ thin film preparation

$CuAlO_2$ thin films were prepared on ultrasonically cleaned SiO_2 substrates by rf-sputtering using pure O_2 gas with a pressure of 2.66 Pa as the sputtering gas. The depositions were performed for 2 h with an rf-power and a substrate temperature of 200 W (13.56 MHz) and 20 °C, respectively. The film thickness is about 0.9 μm determined by means of scanning electron microscope (SEM) cross-sectional observation. The films were annealed under nitrogen flow at 700 – 1000 °C for 10 h. The temperature was increased from room temperature to the specific temperature over a period of 3 h, held at the specific temperature for 10 h, and then cooled to room temperature over a period of more than 6 h. The structural properties of the films were studied with XRD analysis in the θ-2θ mode using CuKα radiation (λ = 154.18 pm). Transmission spectra of the films were measured using a U-3000 spectrophotometer (Hitachi). Surface morphology of the films was studied using SEM, JSM-6380LV (JEOL).

III. Results and Discussion

(1) Characteristics of the sputtering target material

Fig. 1 shows XRD patterns of powders synthesized by means of heat treatment of a stoichiometric mixture of Cu_2O and Al_2O_3 at 1100 °C for 10 h, 30 h and 40 h. For comparison, the powder before heat treatment is also shown. After the heat treatment lasting 10 h, the powder contains the starting materials, Cu_2O (PDF 00 – 005 – 0667) and Al_2O_3 (PDF 00 – 042 – 1468), besides the target material, $CuAlO_2$. However, after the 30-h heat treatment, the reflections of $CuAlO_2$ are dominant. In addition, symmetry of both rhombohedral (3R-$CuAlO_2$) and hexagonal (2H-$CuAlO_2$) [13–15] is observed. 2H-$CuAlO_2$ reflections have been observed at 32.0° (004), 36.7° (100), 37.5° (101), 40.0° (102), 43.6° (103), and 48.6° (006) (PDF 01 – 077 – 2494). Then, at the heat treatment time length of 40 h, the reflections of 3R-$CuAlO_2$ observed at 32.0° (006), 37.0° (101), 38.2° (012), 42.6° (104), and 48.6° (009) (PDF 00 – 035 – 1401) become dominant. The reflections at 32.0° and 48.6° have been superimposed on the reflections of 2H-$CuAlO_2$ and 3R-$CuAlO_2$. This result indicates that both 3R- and 2H-$CuAlO_2$ are synthesized based on a solid-state reaction of Cu_2O and Al_2O_3 initially, then, 2H-$CuAlO_2$ changes to 3R-$CuAlO_2$ as a result of phase transformation as shown in Fig. 1. This phase transformation reaction is consistent with previous work that shows that the 3R-$CuAlO_2$ is thermodynamically more stable than 2H-$CuAlO_2$ [13]. We have used the powder with heat treatment lasting 40 h for target preparation.

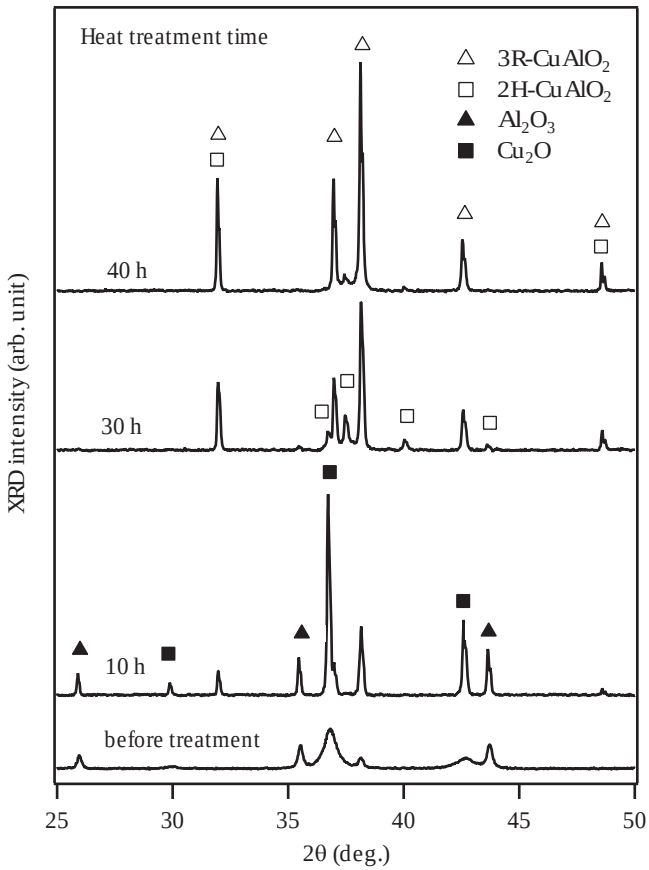

Fig. 1: XRD patterns of the powders prepared by heat treatment of Cu_2O and Al_2O_3 stoichiometric mixture at 1100 °C for 10 h, 30 h, and 40 h.

(2) Characteristics of the target surface after sputtering

Fig. 2 shows optical images of the $CuAlO_2$ sputtering target surface with (a) before sputtering, (b) after the oxygen sputtering, and (c) after the Ar sputtering. The surface of the target before sputtering is almost white. After sputtering for thin film deposition by magnetron sputtering, the color of the target surface changes to yellow after oxygen plasma sputtering. In addition, it was confirmed that the change of color occurs only at the surface of the target. In the case of the Ar sputtering, the change in the target surface color becomes more significant. The color of the surface becomes green in the central part and edge of the target and yellow in a ring-shaped area where the target has been efficiently sputtered. It may be thought that the color of the target becomes first yellow, then green as a result of the Ar sputtering, however, at the position of the target which is efficiently sputtered, a portion of the $CuAlO_2$ powder is evaporated before the color changes from yellow to green. This is thought to be the reason why the Ar sputtered target surface has the appearance shown in Fig. 2(c).

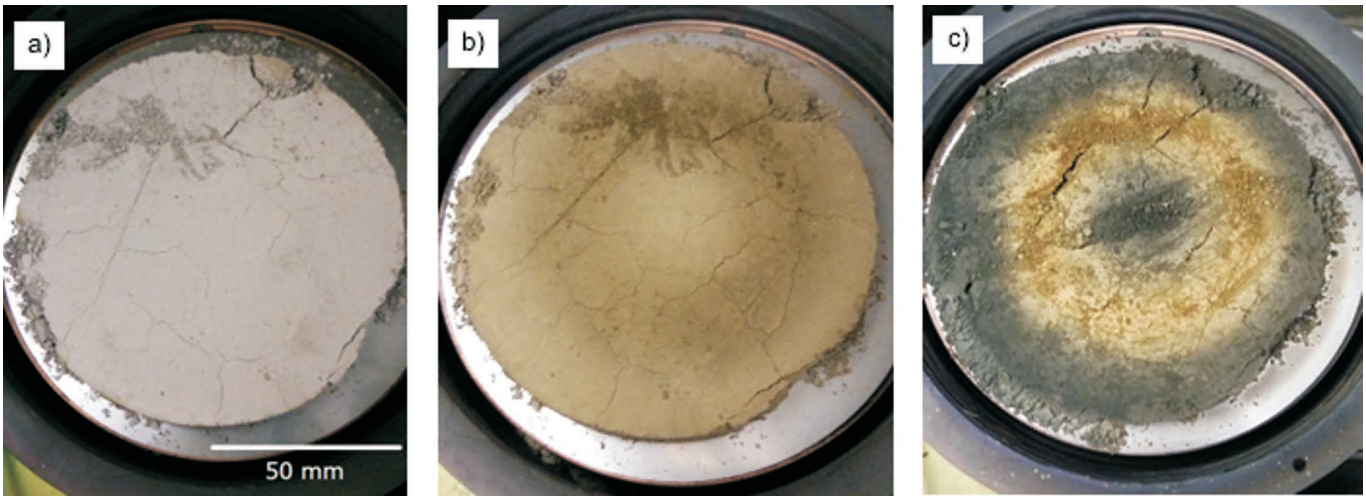

Fig. 2: Optical images of sputtering target surface (a) before sputtering, (b) after oxygen sputtering, and (c) after Ar sputtering.

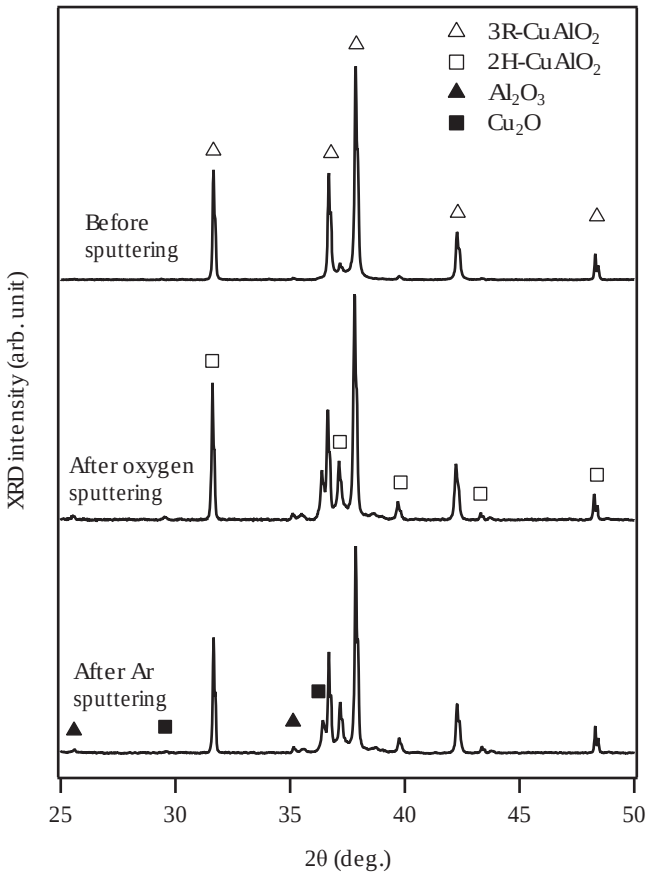

Fig. 3: XRD patterns of $CuAlO_2$ sputtering target surface, before and after oxygen or Ar plasma sputtering.

Fig. 3 shows XRD patterns of the $CuAlO_2$ sputtering target surface before and after oxygen or Ar sputtering. After oxygen sputtering, XRD reflections of 2H-$CuAlO_2$ have been observed beside the 3R-$CuAlO_2$. The reflections of 2H-$CuAlO_2$ have also been observed on the Ar-sputtered target surface. The XRD patterns observed after Ar sputtering are almost same as those after oxygen sputtering. The results mean that the phase transformation from 3R-$CuAlO_2$ to 2H-$CuAlO_2$ is not caused by oxidization or reduction of the target because it does not depend on the sputtering gas. It is thought that the phase transformation is caused by the energy provided by physical bombardment of $CuAlO_2$ and plasma, or photo reaction by emission from the plasma. However, this mechanism does not explain the change in the color of the target surface. It is thought that the change of the color is caused by oxygen elimination during sputtering, because the change in color observed is more significant after Ar sputtering than after oxygen sputtering.

(3) Characteristics of thin films

Fig. 4 shows XRD patterns of the films deposited by means of rf-sputtering using oxygen as the sputtering gas, followed by thermal annealing at 700 – 1000 °C for 10 h in N_2. A broad reflection is observed at 22°. This splits into a sharp one after annealing at high temperatures, which is due to crystallization of amorphous SiO_2 substrate. As-deposited film shows a very broad reflection at around 37° and no reflections of $CuAlO_2$. The result indicates that the structure of the film is amorphous. After the annealing at the temperature of 700 °C, reflections of CuO are observed at 35.8° (002)(-111), and 38.9° (111) (PDF 00 – 045 – 0937). In addition, weak reflections of $CuAlO_2$ are observed at around 32° and 37°. The reflections of CuO disappeared at an annealing temperature of 800 °C and reflections of $CuAlO_2$are observed at 31.8° (006), 36.9° (101), and 37.8° (012). In addition, a weak reflection at 48.4° (009) and a broad and weak reflection at 42.5° (104) of $CuAlO_2$ have also been observed. All the reflections are ascribed to 3R-$CuAlO_2$ and no unique reflections due to 2H-$CuAlO_2$ have been observed. The films become 3R-$CuAlO_2$ after annealing and the result is consistent with the previous report that the 3R-$CuAlO_2$ is thermodynamically more stable than 2H-$CuAlO_2$ [13]. The reflections of the films have shifted compared with that of the powders shown is Fig. 1, and a large reflection width is observed in the (101), (012) and (104) reflections. It is presumed that the shift and the increase of the reflection width are caused by the strain in the films. It is thought that the strain is due to the oxygen vacancy that occurs during sputtering deposition of the films. The oxygen vacancies generated by sputtering are, as we mentioned earlier, a cause of the change in the color of the target surface.

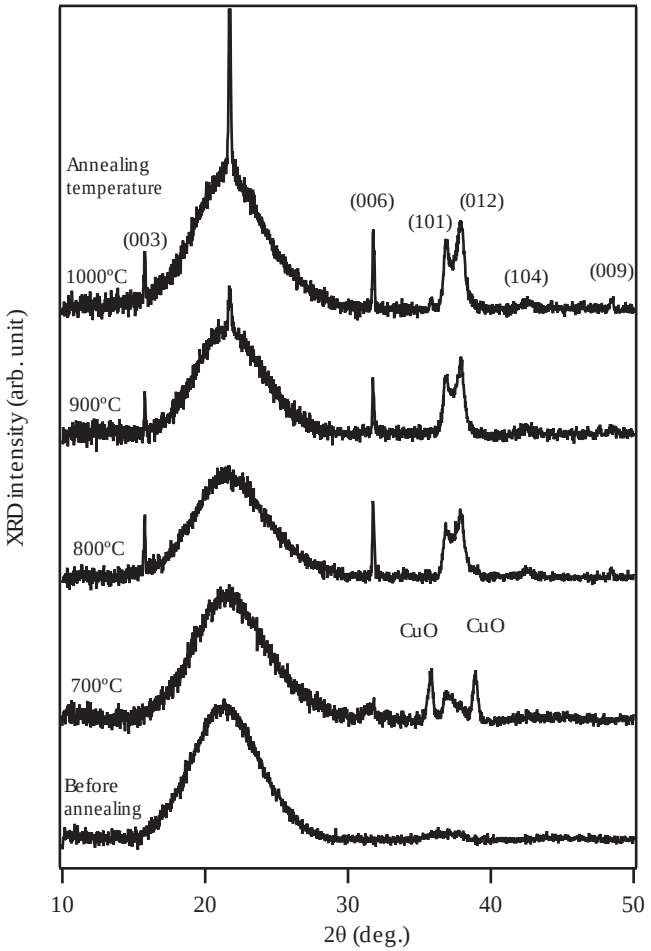

Fig. 4: XRD patterns of the thin films prepared by oxygen sputtering of a $CuAlO_2$ target followed by thermal annealing at 700–1000 °C in N_2 for 10 h.

Fig. 5 shows optical images of the films prepared by means of sputtering followed by thermal annealing at 700 °C, 800 °C and 900 °C in N_2. At an annealing temperature of 700 °C, the color of the film is brown and not transparent. It is thought that the brown color is due to the copper oxide fraction in the films as we observed in XRD. At the annealing temperature of 800 °C, the transparency of the film has been significantly improved because the $CuAlO_2$ crystalline is well formed in the film. Further improvement of the transparency was not observed at 900 °C. The result is consistent with the annealing temperature dependence of the intensity of the $CuAlO_2$ reflections in the XRD patterns. Fig. 6(a) shows the transmission spectra of the films annealed at 700 °C and 800 °C. The spectrum of the films annealed at 900 °C is almost same as that of the one annealed at 800 °C. The film annealed at 700 °C shows low transmittance, which is consistent with the appearance of the film and XRD result. The spectrum of the film annealed at 800 °C shows low transmittance in the visible light wavelength region. At a wavelength shorter than 600 nm, transmittance decreased significantly. Fig. 6(b) shows the $(\alpha h\nu)^2$ plot against photon energy of the film annealed at 800 °C for determination of the optical bandgap. The optical bandgap of the film has been estimated as 3.51 eV, which is similar to that in previous works [1–4, 8, 9]. This value is high enough for the film to be recognized as a TCO material candidate.

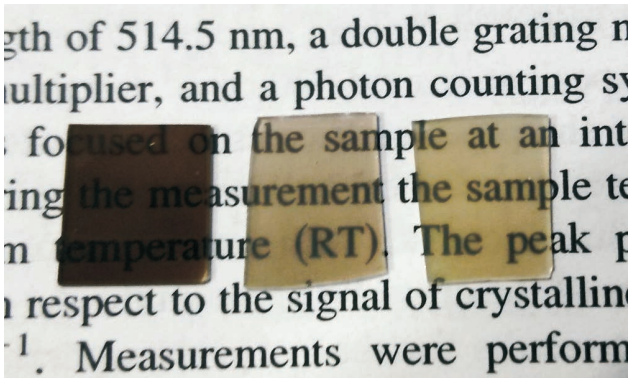

Fig. 5: Optical images of the thin films prepared by oxygen sputtering of a $CuAlO_2$ target followed by thermal annealing at 700–900 °C in N_2. Left to right, the films annealed at 700 °C, 800 °C and 900 °C.

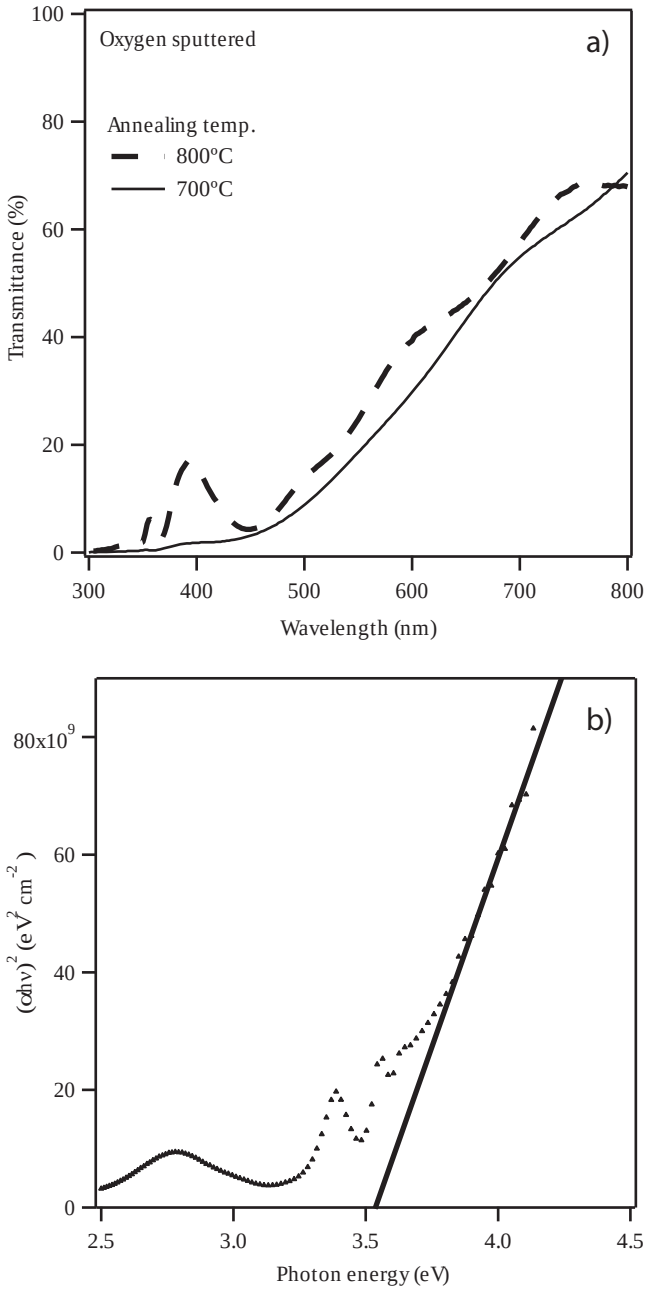

Fig. 6: (a) Transmission spectra of $CuAlO_2$ thin films annealed at 700 °C and 800 °C in N_2. (b) A plot of $(\alpha h\nu)^2$ against photon energy for the determination of the optical bandgap of the film annealed at 800 °C.

Fig. 7(a), (b) and (c) show the SEM images of the surface of the film prepared at annealing temperatures of 700 °C, 800 °C and 900 °C, respectively. The surface of the films prepared at the annealing temperatures of 800 °C and 900 °C is smoother than that of the film annealed at 700 °C. This is because the solid-state reaction of Al_2O_3 and Cu_2O to $CuAlO_2$ proceeds sufficiently at annealing temperatures higher than 800 °C. Fig. 7(d) shows a cross-sectional view of the film prepared at 800 °C. Thickness of the film is about 0.9 μm, as mentioned earlier, and the thickness of the film is relatively uniform. We have also measured the resistivity of the films using a vacuum-evaporated Au electrode. The film annealed at 800 °C show the lowest resistivity at 1.2×10^3 Ωcm. The result is more than three orders higher than that obtained in previous work [1]. The resistivity of the films annealed at 700 °C and 900 °C is 2.0×10^7 Ωcm and 5.8×10^5 Ωcm, respectively. The resistivity is higher than that of the film annealed at 800 °C by more than two orders.

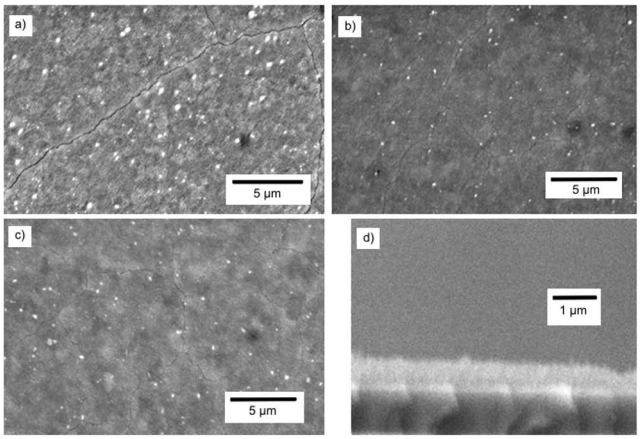

Fig. 7: SEM images of the $CuAlO_2$ thin films. Surface images of the films annealed at (a) 700 °C, (b) 800 °C and (c) 900 °C, and (d) cross-sectional image of the film annealed at 800 °C.

IV. Conclusions

In the present work, we have studied $CuAlO_2$ powder synthesis, $CuAlO_2$ target preparation and the deposition of $CuAlO_2$ thin films by means of radio frequency (rf) magnetron sputtering. $CuAlO_2$ powders have been synthesized from Cu_2O and Al_2O_3 powder based on a solid-state reaction at 1100 °C in N_2 for 40 h, then, $CuAlO_2$ sputtering targets have been successfully prepared by pressing the powder into a target form. $CuAlO_2$ thin films have been deposited by means of rf-sputtering of the target by oxygen plasma followed by annealing in N_2. The film prepared at an annealing temperature of 800 °C exhibits an optical bandgap of 3.51 eV, which is high enough to qualify it as a TCO material candidate. In contrast, the resistivity of the films is higher than 1.2×10^3 Ωcm, which is not low enough for a TCO. In addition, we have observed the phase transformation of the $CuAlO_2$ target surface from 3R-$CuAlO_2$ to 2H-$CuAlO_2$ after sputtering.

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