Preparation of $CuAlO_2$ Thin Films by Sol-Gel Method Using Nitrate Solution Dip-Coating

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Abstract. $CuAlO_2$ thin films are prepared by sol-gel dip-coating followed by annealing in nitrogen atmosphere using copper nitrate and aluminum nitrate as metal source materials. X-ray diffraction (XRD) patterns show (003), (006) and (009) oriented peaks of $CuAlO_2$ at annealing temperature of 800 - 1000ºC. This result indicates that the $CuAlO_2$ films prepared in the present work are *c*-axis oriented. XRD peak intensity increase with annealing temperature and becomes maximum at 850ºC. The $CuAlO_2$ XRD peak decreased at annealing temperature of 900ºC with appearance of a peak of CuO, and then increased again with annealing temperature until 1000 ºC. The films have bandgap of 3.4 eV at annealing temperature of 850ºC in which the transparency becomes the highest. At the annealing temperature of 850ºC, scanning electron microscope (SEM) observation reveals that the films are consist of amorphous fraction and microcrystalline $CuAlO_2$ fraction.

Keywords: $CuAlO_2$, Sol-gel, Transparent conductive oxide, X-ray diffraction

1 Introduction

Transparent conductive oxide (TCO) materials have been widely used in various kinds of opt-electric devices as a transparent electrode in solar cells, light emitting diodes, and liquid crystal displays. TCO materials have enough high optical bandgap more than 3.1 eV and enough high conductivity. However, most of the TCO materials have n-type conductivity, for example, indium tin oxide [1] and Al-doped ZnO [2]. In contrast, high conductive and highly transparent p-type TCO has not been fabricated. This fact has limited the application of TCO materials in devices because fabrication of pn-junction has been difficult. Although some metal oxide materials, such as NiO or Cu_2O have shown p-type conductivity, NiO have high resistivity [3] and Cu_2O has narrower bandgap to be a transparent [4]. In 1997, Kawazoe

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and co-workers reported a p-type and wide bandgap delafossite structured ternary metal oxide, $CuAlO_2$ thin films prepared by pulsed laser deposition. The $CuAlO_2$ films show optical bandgap of 3.5 eV and conductivity of 1 $^{-1}$cm^{-1} [5]. Other delafossite structured ternary p-type wide gap materials have also been reported as a candidate of p-type TCO [6,7]. However, $CuAlO_2$ is more preferable as an electric material because it is consists only of abundant elements. $CuAlO_2$ thin films have also been prepared by sol-gel method using copper acetate monohydrate and aluminum-tri-sec-butoxide as metal source materials [8] or using copper acetate monohydrate and aluminum nitrate nonahydrate [9]. The sol-gel method is more convenient and less expensive than the other methods, because the sol-gel method is non-vacuum preparation process.

In the present work, preparation of $CuAlO_2$ by the sol-gel dip-coating method using SiO_2 substrate is examined. Alcohol solution of copper nitrate and aluminum nitrate are used as metal source solutions. The dependencies of structural properties, optical properties, and morphology on annealing temperature are investigated.

2 Experimental

Cu and Al source solution were prepared by dissolving copper (II) nitrate trihydrate or Aluminum nitrate enneahydrate in a 2-methoxyethanol by stirring for 12 h at room temperature with concentration of 0.4 M. The two solutions were mixed with a Cu/Al ratio of 1:1 and stirred at room temperature for 12 h to form a thin blue sol. Copper-aluminum gel thin films were prepared on SiO_2 glass substrates with size of 25 mm ×75 mm and thickness of 0.5 mm by the dip-coating of the sol. Prior to preparation of the gel films, the SiO_2 substrates were degreased by ultrasonication in EtOH for 10 min. The sol was dip-coated onto a SiO_2 substrate with a lifting up speed of 1 mm/s. In the case of the samples prepared for transmission spectroscopy measurements, the sol adsorbed on the back side of the substrate was carefully removed after dip-coating. The coated films were heat treated first heated at 200ºC for 10 min and then heated again at a higher temperature of 500ºC for 20 min by hot-plate-type heating devices. The dip-coating and subsequent heat treatment procedures were repeated for 6 times, to obtain adequate film thickness of 0.4 m. The prepared gel films were finally annealed at temperatures in the range of 750–1000ºC for 10 h under nitrogen flow. 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 6 h.

Structural properties of the films were studied by X-ray diffraction (XRD; D8 Discover, Bruker) analysis in the mode using CuKα radiation. Transmission spectra were measured using a UV/vis spectrophotometer U-3000 (Hitachi). Scanning electron microscope observation was carried out by using JSM-6380LV (JEOL).

3 Results and Discussion

Fig. 1 shows XRD patterns for the films prepared using dip-coated gel films annealed at temperatures in the range of 750–1000ºC in nitrogen atmosphere. The XRD pattern of the film annealed at 850°C is reduced in its scale. A broad signal and a sharp peak observed at around 22º are due to the amorphous SiO_2 substrate and crystalized SiO_2, respectively. A sharp peak observed at 26º at higher annealing temperature than 900ºC is also due to the substrate, -quartz. The -quartz peak has been observed previously in the work of the $CuAlO_2$ thin films preparation [10].

The film annealed at 750°C shows a peak of $CuAlO_2$ with orientation of (006) at 31.7°. At annealing temperature of 800°C, other peaks of $CuAlO_2$ are observed at 15.8° (003),

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36.8° (101) and 48.5° (009). At the annealing temperature of 850°C, intensity of the *c*-axis oriented peaks, (003), (006) and (009) increased significantly. The intensity of the XRD peaks becomes several tens of times as that in the film annealed at 800°C. The result indicates that the film annealed at 850ºC is highly *c*-axis oriented crystalline structure. Such high *c*-axis oriented films are not consistent with previous sol-gel works [8,9]. The intensity of those *c*-axis oriented peaks decreased drastically at annealing temperature of 900°C. Then, at higher annealing temperature than 950°C, the peak intensity increased again until 1000°C. In the film annealed at 900°C, a diffraction peak of CuO (111) is observed at 35.7º with significant decreasing of intensity of the $CuAlO_2$ peaks. The formation of CuO at those annealing temperature have also been reported in the sol-gel preparation study of $CuAlO_2$ using other starting material [8]. It can be thought that the temperature 900°C is adequate for the formation reaction of CuO, rather than $CuAlO_2$. It is also considered that the use of nitrate as metal source material is the cause of the formation of CuO in the film, because the nitrate has high oxidizing power compared with other counter reagent of metal ions, such as acetate or alcohol. In addition, at annealing temperature of 900ºC or higher temperature, the peak of -SiO_2 is observed. It is considered that there are some competitive reactions against the $CuAlO_2$ formation reaction at higher temperature than 900°C, then, the yield of formation reaction of $CuAlO_2$ is decreased. Due to the result observed in fig. 1, CuO crystalline formation or reaction of substrate SiO_2 and the films are thought to be those competitive reactions. The existence of those competitive reactions can be thought as the cause of the XRD signal intensity decreasing at 900ºC.

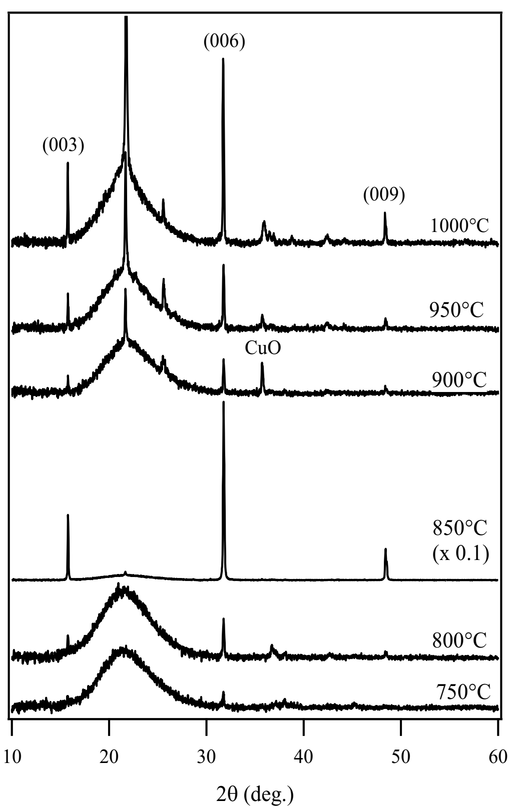

Fig. 1. XRD patterns of the films annealed at 750 -1000ºC.

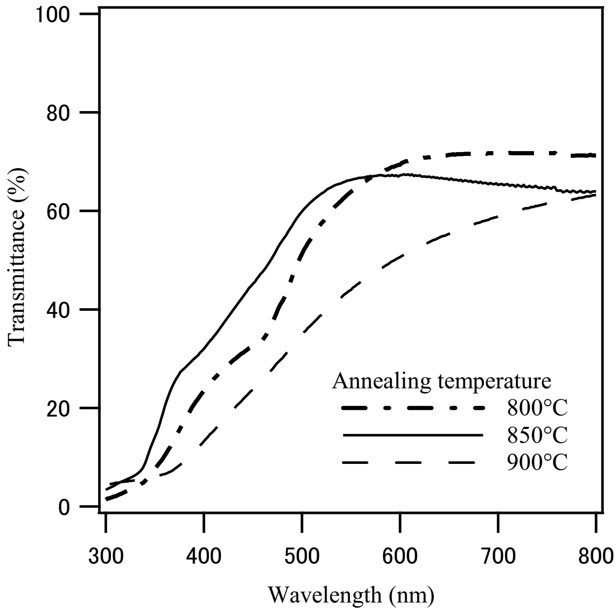

Fig. 2. Transmission spectra of the annealed films.

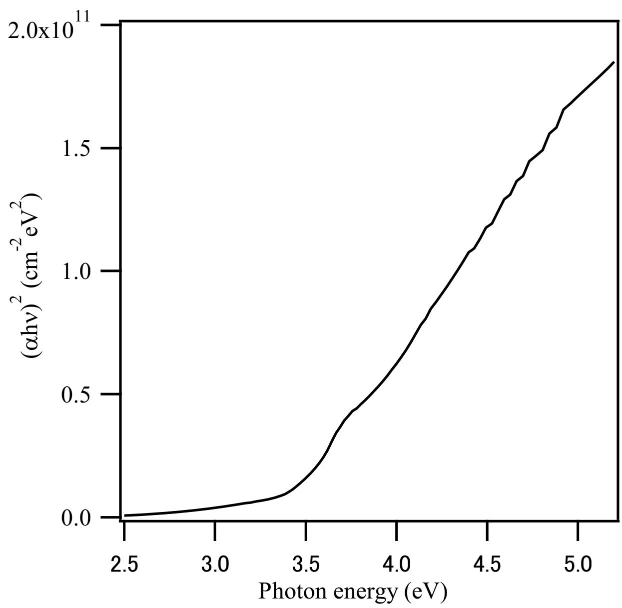

Fig. 3. Tauc plot of the film annealed at 850ºC

Fig. 2 depicts the transmission spectra of the films annealed at 800°C, 850°C and 900°C that are the films having relatively high transparency. Both of the films annealed at 800ºC and 850ºC shows transmittance of more than 60% in the wavelength from 500 to 800 nm. However, the transparency is less than 30% at the wavelength of 400 nm. The color of the films become thin brown rather than transparent or white. We think the cause of the brown color is amorphous cooper oxide fraction, CuO that has black color and Cu_2O with red color. Fig. 3 shows the Tauc plot of the film annealed at 850°C. The bandgap of the films is estimated as 3.4 eV and is almost consistent with the previous work [5].

Fig. 4 shows the SEM images of the films annealed at 850°C and 900°C. It is shown in the image that the film annealed at 850°C is consist of microcrystalline $CuAlO_2$ with the crystallite size of 0.1 - 0.2 m in diameter, and amorphous fraction which surround the microcrystalline. The films annealed at lower temperature do not show this kind of structural characteristics. Due to the results observed in the XRD, these crystalline are thought to be *c*-axis oriented, thus, it is considered that the crystalline are in the pillars structure that have are under influence of the substrate. Because, if the grains are embedded in amorphous fraction free from the influence of the substrate interface, orientation of the crystalline grain would become random. If so, the XRD of the film would not be *c*-axis oriented. As mentioned previously, thickness of the films are 0.4 m and is comparable to the crystalline diameter observed in the SEM image. Hence, the crystalline can be satisfied two conditions at the same time, being spherical and being in contact with the substrate. The assumption can explain the highly *c*-axis orientation of the film annealed at 850°C. On the other hand, the film annealed at 900°C does not have the microcrystalline-amorphous two phase structure. Instead, SEM image shows that the film has larger scaled surface texture of crystalline. However, the XRD signal intensity of the film is significantly lower than that of the films annealed 850°C. It is considered that the films annealed at higher temperature are random mixture of crystalline $CuAlO_2$, amorphous fraction, and CuO as an impurity. In such mixture, it is thought to be difficult to maintain the high $CuAlO_2$ crystalline volume ratio.

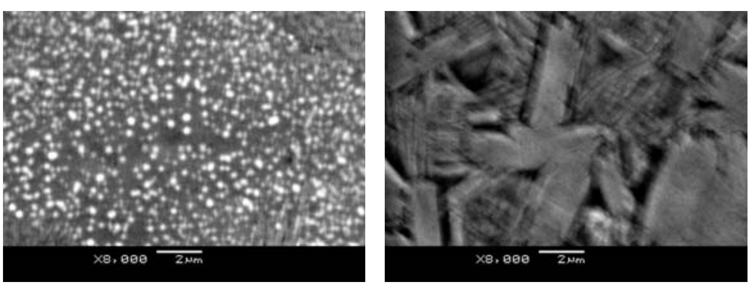

Fig. 4. Surface SEM image of the films annealed at

We have measured the conductivity of the films and obtained the conductivity of 10^{-4} or 10^{-5} $^{-1}$cm^{-1} and independent on the annealing temperature. The value is not preferable as a TCO material. Conductivity of the film annealed at 850°C that has significantly high XRD signal intensity is almost same as other films. It is thought to be due to the two phase structure of the films. The low conductivity is caused by the high resistive amorphous fraction, not by the $CuAlO_2$ crystalline fraction that is thought to have low resistivity.

4 Conclusion

Delafossite structured p-type wide bandgap material, $CuAlO_2$ thin films were prepared by sol-gel method using copper and aluminum nitrate as starting materials. XRD patterns shows that the films prepared with annealing temperature higher than 800ºC have *c*-axis oriented $CuAlO_2$ crystalline structure. XRD signal intensity become the highest at annealing temperature of 850ºC. The film is consist of two fractions, one is $CuAlO_2$ crystalline fraction and the other is amorphous fraction at the annealing temperature of 850ºC. The low conductivity is thought to be caused by the amorphous fraction with high resistivity.

Acknowledgements

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