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Preparation of $CuAlO_2$ Thin Films on Si or Sapphire Substrate by Sol-Gel Method Using Metal Acetate or Nitrate

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***Abstract*—**$CuAlO_2$ thin films are prepared on Si or sapphire substrate by sol-gel method using two kinds of sols. One is combination of Cu acetate and Al acetate basic, and the other is Cu nitrate and Al nitrate. In the case of acetate sol, XRD peaks of $CuAlO_2$ observed at annealing temperature of 800-950 ºC on both Si and sapphire substrates. In contrast, in the case of the films prepared using nitrate on Si substrate, XRD peaks of $CuAlO_2$ have been observed only at the annealing temperature of 800-850 ºC. At annealing temperature of 850ºC, peaks of other species have been observed beside the $CuAlO_2$ peaks, then, the $CuAlO_2$ peaks disappeared at annealing temperature of 900 ºC with increasing in intensity of the other peaks. Intensity of the other peaks decreased at annealing temperature of 950 ºC with appearance of broad SiO_2 peak. In the present, we ascribe these peaks as metal silicide.

***Keywords*—**$CuAlO_2$, silicide, thin films, transparent conducting oxide, sol-gel.

I. Introduction

TRANSPARENT conductive oxides (TCOs) have been recognized as important materials because their preferable characteristics as electrode materials for some optical devices. It is well known that the most of TCOs have n-type conductivity, for example, indium tin oxide [1] or Al-doped or Ga-doped zinc oxide [2], [3]. Absence of the p-type TCOs has prevented the development of transparent semiconductor science because the formation of transparent p-n junction that can be applied to various kinds of optical devices has been impossible. In 1997, Kawazoe and co-workers have reported the p-type conductivity of Delafossite structured ternary wide bandgap metal oxide, $CuAlO_2$ [4]. $CuAlO_2$ shows conductivity of 10^0 Ωcm and optical bandgap of more than 3.1 eV, those characteristics are preferable as p-type TCOs.

$CuAlO_2$ thin films have been prepared by various methods, for example, pulsed laser deposition [4], [5], sputtering [6]-[8], and sol-gel method [9]-[11]. Among those methods, sol-gel method has been recognized as a relatively simple and low-cost method, because it does not require high-cost vacuum system. Up to now, various metal precursor materials have used in sol-gel preparations of $CuAlO_2$. For example, thin film preparation using combination of copper acetate and aluminum alkoxide [9], copper acetate and alumatrane [10], or combination of copper nitrate and aluminum nitrate [11] have been reported.

In the present work, $CuAlO_2$ thin films are prepared on Si substrate by sol-gel method using acetate or nitrate as metal sources. We observed not only the formation of $CuAlO_2$ but also solid phase reaction of the nitrate-gel films and Si substrate after the heat treatment at high temperature range.

II. Experimental Procedure

We used two kinds of metal precursor material combinations. One is acetate precursors combination that was consist of Cu(II) acetate monohydrate and Al acetate basic. The other is nitrate precursors combination that was Cu(II) nitrate trihydrate and Al nitrate enneahydrate. All the reagents used in the present work have been supplied by Wako. Cu and Al source solution were prepared separately by dissolving Cu precursor material or Al precursor material in a 2-methoxyethanol by stirring for 12-72 h at room temperature with concentration of 0.4 M. In the case of acetate solution, 2-aminoethanol was used as a stabilizer. Moller ratio of 2-aminoethanol to Cu(II) acetate and Al acetate basic were 4 and 12, respectively. Then, 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 (100)-oriented Si substrate with thickness of 525 μm and *c*-plane sapphire substrate with thickness of 500 μm by the dip-coating of the sol. Prior to preparation of the gel films, the substrates were degreased by ultrasonication in EtOH for 10 min. The sol was dip-coated with a lifting up speed of 1 mm/s. The coated films were heat treated first at 200 ºC for 10 min and then heated again at a higher temperature of 500 ºC 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 0.2 μm. The prepared gel films were finally annealed at temperatures in the range of 800–950 ºC 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. Thickness of the films prepared from acetate precursors were 0.4 μm, and thickness of the films prepared from nitrate precursors were 0.1-0.2 mm. Difference in thickness was thought to be caused not only by difference in substrate but also by difference in viscosity of sol used in dip-coating.

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Structural properties of the films were studied by X-ray diffraction (XRD) measurement which were performed on a D8 discover (Bruker) operating with Cu-Kα radiation.

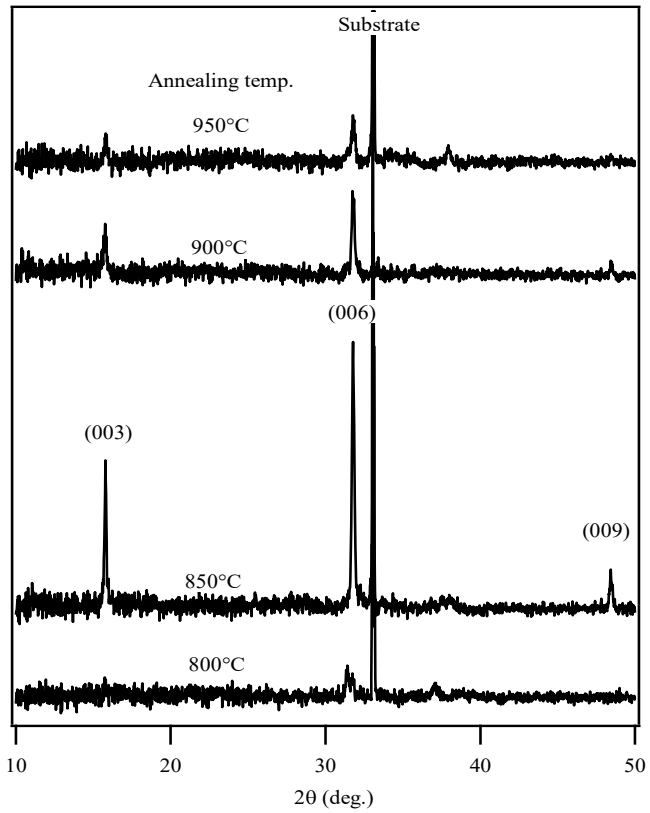

Fig. 1 XRD patterns of the films prepared on Si substrate using acetate precursors Peaks indexed with *hkl* numbers are due to $CuAlO_2$

III. Results and Discussion

In Fig. 1, the XRD pattern of the films prepared on Si substrate using acetate precursor combination are given as a function of annealing temperature. A strong peak at 33° is due to the substrate, Si (200). At annealing temperature of 800 °C, a peak of $CuAlO_2$ with orientation of (006) is observed at 31.7° (JCPDS 75-1988). At higher temperature than 850 °C, other peaks of $CuAlO_2$ have also been observed at 15.8° (003) and 48.4° (009), respectively. Intensity of the peaks becomes the highest at annealing temperature of 850 °C, and then decreased at higher temperature than 900 °C. In addition, the peaks of other orientation have not been observed. The results mean $CuAlO_2$ thin films prepared by sol-gel method using acetate precursors are highly *c*-axis oriented. In the previous reports, relatively *c*-axis oriented $CuAlO_2$ thin films have been reported [9]-[10]. However, the films in those works also show the peaks of other orientations. A weak peak at 38.0 °C observed at annealing temperature of 950 °C is thought to be due to CuO (111) (JCPDS 45-937).

Fig. 2 depicts the XRD patterns of the films prepared on sapphire (Al_2O_3) substrate prepared using acetate precursors using same annealing conditions as samples shown in Fig. 1. The *c*-axis oriented $CuAlO_2$ peaks have been observed as well as in the case of Si substrate films. The peak intensity of the $CuAlO_2$ is higher than that of the films on Si substrate. As the thicknesses of the films are almost same, the difference in the peak intensity is thought to be caused by difference in characteristics of substrates. In addition, the temperature dependence of the structural properties of the films is different from that in the films prepared on Si substrate. The intensity of the peak becomes the highest at annealing temperature of 900°C that is higher than in the case of Si substrate. In addition, the $CuAlO_2$ peaks with orientation of (003) and (009) have been observed at 800°C that is lower temperature than that in the case of Si substrate. The results suggest that the sapphire substrate is adequate to form the $CuAlO_2$ thin films on it with high crystallinity. Here, we have to note that all the films become $CuAlO_2$ after the annealing as far as the acetate precursors are used at the annealing temperature range used in the present work.

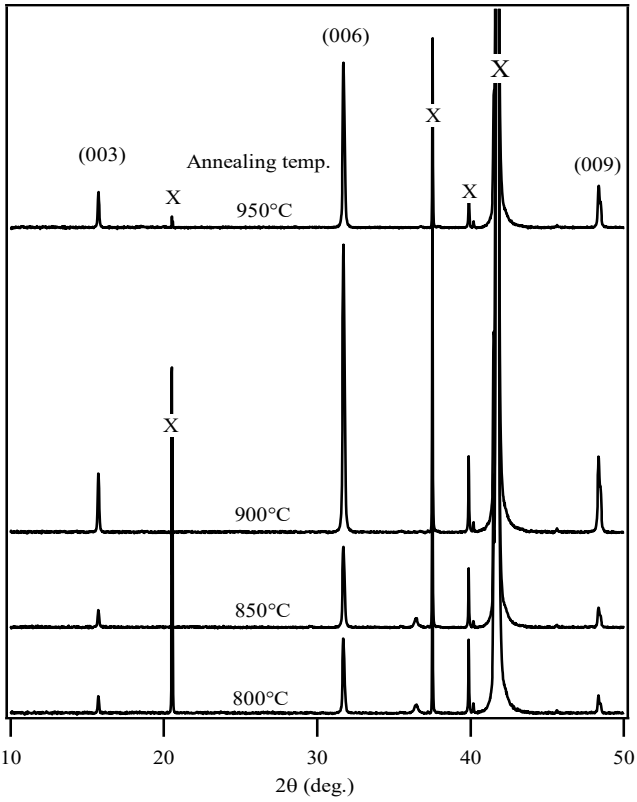

Fig. 2 XRD patterns of the films prepared on sapphire substrate using acetate precursor material. Peaks marked X are due to substrate.

Fig. 3 shows the XRD patterns of the films prepared on Si substrate using nitrate precursor combination. At the annealing temperature of 800 °C, the film shows XRD peaks of $CuAlO_2$, as well as in the film prepared using acetate precursors. However, there are some differences in the structural properties of the films. At first, XRD signal intensity of the films is weaker than that of films using acetate. In addition, crystalline orientation is different from that shown in Fig. 1. As shown in Fig. 4, peaks of $CuAlO_2$ with various orientations, including non-*c*-axis oriented peaks, (109), (012), and (104) have been

observed at 36.6°, 37.8°, and 42.5°, respectively. It means the $CuAlO_2$ film prepared by nitrate precursor annealed at 800°C has relatively random oriented crystalline characteristics compared with the films prepared using acetate precursors.

The XRD patterns of the film prepared using nitrate become different significantly from that of the films prepared using acetate at higher annealing temperature. At the annealing temperature of 850 °C, the peak of $CuAlO_2$ (006) at 31.7° has been observed, however, intensity of the peak has been decreased. Instead, peaks of other species have been observed at 25.4° and 45.2°. Intensity of those peaks increased at annealing temperature of 900 °C. At the same time, the peaks of $CuAlO_2$ disappeared. In addition, a peak of another species is observed at 31.4°. Then, peaks at 25.4° and 45.2° disappeared, and the peak at 31.4° decreased significantly at annealing temperature of 950 ºC with appearance of a broad peak at 22° that is due to SiO_2. Those results indicate that the films prepared on Si substrate using nitrate precursors have significantly different structural properties from that of the films prepared using acetate precursors.

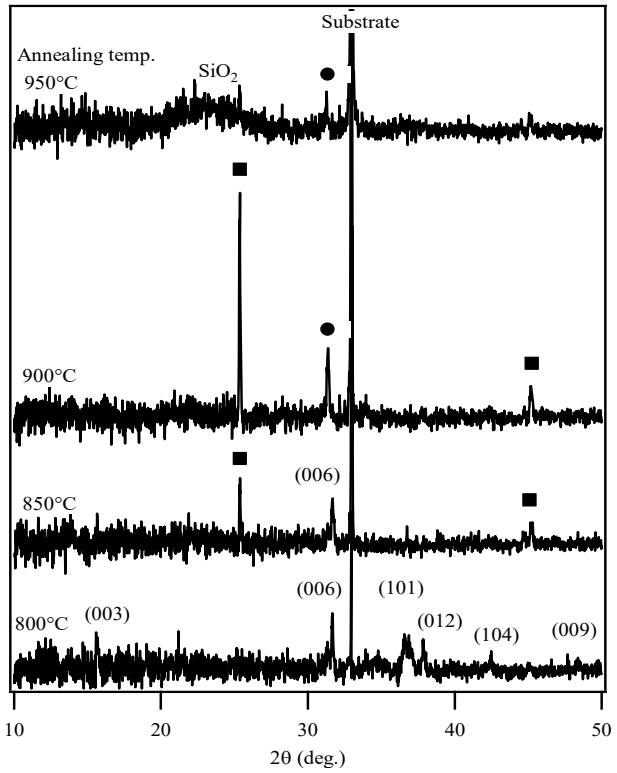

Fig. 3 XRD patterns of the films prepared on Si substrate using nitrate precursor material. Peaks indexed with *hkl* numbers are due to $CuAlO_2$. Peaks with marker ■ and ● are thought to be due to copper silicide and aluminum silicide, respectively

In Fig. 4, the XRD pattern of the films prepared on sapphire substrate using nitrate precursors are given as a function of annealing temperature. The peaks at marked by X in the figure are due to the sapphire substrate. The peak of $CuAlO_2$ is observed at annealing temperature of 800 °C at 31.7° (006). However, other peaks of $CuAlO_2$ observed in the film prepared on Si substrate have not been observed. The result indicates that the structural characteristics of the film are different from the film prepared on Si substrate. Intensity of the peak increases with annealing temperature gradually until 900 °C. Then, the peaks of $CuAlO_2$ increased significantly at annealing temperature of 950 °C. In addition, the other *c*-axis oriented $CuAlO_2$ peaks of 15.8° (003) and 48.4° (009) have also been observed at 950°C. These results suggest that the larger thermal energy is needed to form $CuAlO_2$ from nitrate precursors than from the acetate precursors. Decrease in XRD signal intensity at high temperature that observed in the case of acetate precursors has not been observed. In the case of nitrate precursors, the structure of the films on sapphire substrate is different from that on Si substrate and $CuAlO_2$ is dominant species at all annealing temperature in the present work.

On the other hand, at annealing temperature of 950 °C, peak of CuO (002)(-111) is observed at 35.5º (JCPDS 45-937). The CuO is thought to be synthesized because copper becomes excessive in the film. The CuO have been observed in the previous works on $CuAlO_2$ thin films preparation [9].

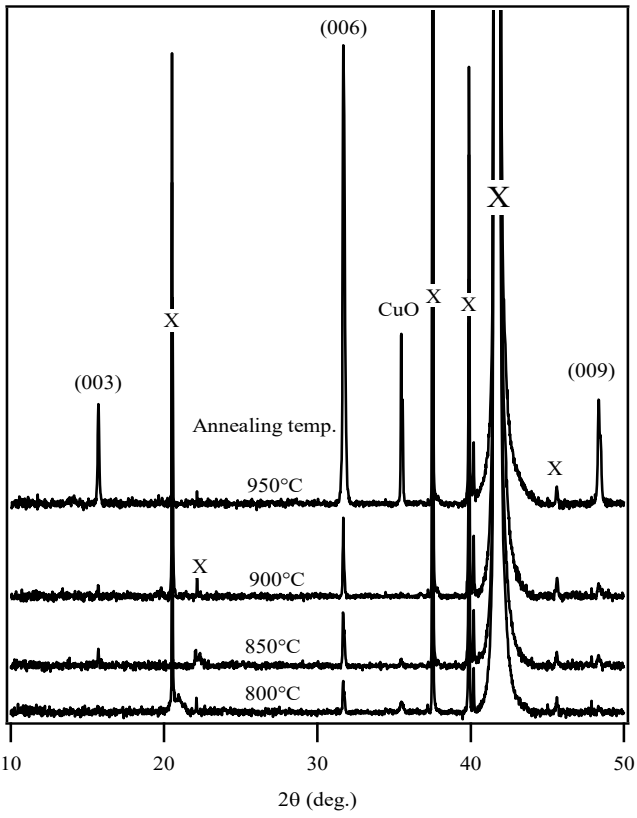

Fig. 4 XRD patterns of the films prepared on sapphire substrate using nitrate precursor material. Peaks marked X are due to substrate

The peaks observed in the films prepared using nitrate on Si substrate at 25.4°, 45.2° and 31.4° have not been observed in any acetate precursor films or sapphire substrate films. In addition, we have shown previously that $CuAlO_2$ thin films are formed without peaks at 25.4°, 45.2° or 31.4° when the nitrate precursors and the SiO_2 substrate are used [12]. These results suggest that both the nitrate precursors and Si substrate are

needed to form the species corresponding to the peaks. The origin of the peaks observed in Fig. 3 beside $CuAlO_2$ peaks at higher temperature than 850°C are thought to be due to the silicon including species. In addition, the peaks at 25.4° and 45.2° appeared at annealing temperature of 850 °C and disappeared at 950 °C simultaneously. It means these two peaks are thought to be due to same species. On the other hand, the peak at 31.4° appeared at 900 °C and still be observed at 950 °C. This result suggests that the peak at 31.4° is due to the different species from origin of the peaks at 25.4° and 45.2°. In the present, author thinks that the peaks at 25.4° and 45.2° are ascribed to copper silicide, Cu_3Si (JCPDS 59-0263). On the other hand, the peak at 31.4° is thought to be due to Aluminum silicide, Al_4Si (JCPDS 24-0035). However, author does not deny the possibility of other origins.

IV. Conclusion

$CuAlO_2$ thin films are prepared on Si and sapphire substrate by sol-gel method using copper and aluminum acetate as precursor materials. Although the XRD peak intensity show dependency on annealing temperature, all the films have $CuAlO_2$ structure at annealing temperature 800-950°C. In contrast, the films using copper and aluminum nitrate show significant dependence on substrate. At higher temperature than 850°C, different structure from that of $CuAlO_2$ is observed in the films prepared on Si substrate. We found that two conditions are required to form those species, one is using nitrate as precursors and the other is using Si substrate. In the present, we ascribed the peaks to copper and aluminum silicide.

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