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Preparation of $CuGaO_2$ Thin Film by a Sol-Gel Method Using Two Kinds of Metal Source Combination

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Abstract

We prepare $CuGaO_2$ thin films on SiO_2 substrates by using the sol-gel spin-coating method with two combinations of Cu and a Ga source, Cu and Ga nitrate, or acetylacetonate. X-ray diffraction analysis reveals that the thin films prepared using nitrate sol that are annealed at a temperature of 850˚C - 950˚C show both *c*-axis-orientated peaks, (006) and a non-*c*-axis-oriented peak (012) with similar intensity; little dependence of signal intensity on annealing temperature is also shown. The films are opaque in appearance at these annealing temperatures. Scanning electron microscope observation reveals that the opaque appearance is due to the texture or cracks on the surface of the films. In contrast, the films prepared using acetylacetonate show a (006) peak with higher signal intensity than the (012) peaks. The films show more transparent appearance than that of the films by nitrate. The highest conductivity of the film is 5.7×10^{-4} $\Omega^{-1}\cdot cm^{-1}$, obtained in the films by nitrate annealed at 850˚C.

Keywords

Transparent Conductive Oxide, Delafossite, $CuGaO_2$, Sol-Gel, Thin Films

1. Introduction

Transparent conductive oxide (TCO) thin films are widely used as a transparent electrode in opt-electric devices [1] [2]. However, most of the TCO thin films that have already been used in electric devices, such as indium tin oxide [3] or aluminum-doped zinc oxide [4], have n-type conductivity. Research on TCO with p-type conductivity is required for developing transparent electronics in order to form transparent pn-junctions. Cu-delafossite materials that are com-

posed of copper and trivalent metal elements are known as p-type TCO candidates. One of the Cu-delafossite materials, $CuAlO_2$ shows intrinsic p-type conductivity because its valence band maximums are dominated by hybridization of oxygen orbitals with $3d^{10}$ electrons in Cu^+. The hybridization reduces contributions of oxygen orbitals to the valence band and makes the valence band dispersive, and p-type conductivity becomes available [5] [6]. Other Cu-delafossite materials, $CuGaO_2$ has also been studied and recognized as a p-type TCO material with high transparency in thin-film form. $CuGaO_2$ thin films have been prepared by various methods, such as pulsed laser deposition [7] [8], sputtering [9] [10], and the sol-gel method [11] [12] [13]. Among these methods, the sol-gel method is more convenient and less expensive than the other methods, and has a general advantage of superior uniformity. In the sol-gel preparation of Cu-delafossite, two difficulties have been identified. One is the difficulty of the thermal treatment condition control required to form Cu-delafossite, which contains Cu^+, not Cu^{2+}. The other is difficulty in the choice of metal source materials. Use of an inadequate combination of two metal source materials can be the expected course of the formation of binary ceramics by-product because of segregation of binary by-products due to the difference between copper and gallium in the film-formation process. The difference in the film-formation process can be thought to be suppressed by using metal source materials with the same anion or same complex ligand.

In the present work, $CuGaO_2$ thin films were prepared by the sol-gel method using two combinations of a copper and gallium metal source that consist of the same counter anion or same complex ligand. One combination is copper nitrate and gallium nitrate that have the same anion, and the other is a combination of copper acetylacetonate and gallium acetylacetonate that have the same complex ligand.

2. Experimental

The raw materials for metal nitrate, copper nitrate and gallium nitrate were of analytical grade and purchased from Wako chemicals. Gallium nitrate was supplied as gallium nitrate n-hydrate (n = 7 - 9), with 8 adopted as the n value for calculating molecular weight in the present work. Both copper nitrate trihydrate (2.42 g, 0.01 mol) and gallium nitrate n-hydrate (4.00 g, 0.01 mol) were separately dissolved into 2-methoxyethanol (25 mL) by stirring for 12 hours at room temperature in air. Then, the nitrate sol was obtained by mixing two solutions and stirring for 12 hours at room temperature in air. The reagents for metal acetylacetonate, copper acetylacetonate and gallium acetylacetonate were of analytical grade and purchased from Aldrich. Copper acetylacetonate (2.62 g, 0.01 mol) and gallium acetylacetonate (3.67 g, 0.01 mol) were dissolved separately into a mixture of 2-methoxyethanol (25 mL) and 2-aminoethanol (24.0 g) by stirring for 72 hours at room temperature in air. The acetylacetonate sol was obtained by mixing two solutions and stirring for 12 hours at room temperature in

air.

The sols were spin-coated onto SiO_2 substrate at a spinning speed of 3000 rpm. The coated films were first heated at 200˚C for 10 min, then, heated again at a higher temperature of 500˚C for 20 min using hot-plate-type heating devices. We used high temperature, 500˚C, in the post-coating heat treatment under strictly temperature control in order to form Cu-delafossite crystalline without Cu^{2+} [14]. The spin-coating and subsequent heat-treatment procedures were repeated six times to obtain a film thickness of 0.2 - 0.3 μm. The prepared gel films were finally annealed at temperatures in the range of 750˚C - 1000˚C for 10 h under nitrogen flow.

The structural properties of the films were studied by X-ray diffraction (XRD; D8 Discover, Bruker) analysis in the θ - 2θ mode using CuKα radiation. Transmission spectra were measured using a UV/Vis spectrophotometer (U-3000, Hitachi). The surface morphologies of the films were observed using scanning electron microscopy (SEM; JSN76380LV, JEOL). Conductivity of the films was measured using evaporated Au interdigital electrode with a gap of 0.5 mm.

3. Results and Discussion

3.1. Structural Properties

Figure 1(a) shows the XRD patterns of the films prepared using the nitrate sol annealed at various temperatures. A broad signal at approximately 22˚ and a peak at 21.6˚ observed in the films annealed at 950˚C - 1000˚C were ascribed to SiO_2 glass and SiO_2 crystalline, respectively. In the film annealed at 750˚C, a broad signal was observed at approximately 35.5˚ - 36.3˚. It can be thought to be overlapping of three peaks, consisting of two $CuGaO_2$ signals with orientations of (101) and (012) (PDF 00-041-0255) and a signal of CuO (200)(−111) (PDF 00-045-0937). The shape of the peak changed with increase in annealing temperature. At an annealing temperature of 800˚C, intensity of the CuO signal at 35.6˚ decreased and a signal of $CuGaO_2$ of (101) at 36.1˚ and (012) at 36.5 increased. The intensity of the (101) signal decreased at an annealing temperature of 850˚C, then, it became a shoulder of the (012) peak. At annealing temperatures of 900˚C and 950˚C, the signal became one peak of (012) without a shoulder. However, the film annealed at 1000˚C showed both (101) and (012) peaks again. At an annealing temperature of 850˚C - 950˚C, a *c*-axis-oriented peak, (006), was also observed at 31.3˚ in addition to (101) and (012). The relative intensity of these peaks, (006), (101) and (102), showed little dependency on annealing temperature at the annealing temperature region of 850˚C - 950˚C, and the (006) peak became weak at 1000˚C. Aside from these peaks, weak signals of (003), (104) and (105) have been observed at 15.5˚, 41.0˚, and 44.2˚, respectively.

Figure 1(b) shows the XRD patterns of the films prepared using the acetylacetonate sol annealed at various temperatures. The film annealed at 750˚C displays no peaks, and the films annealed at 800˚C - 900˚C show three peaks of (006), (101) and (012). Peak positions of (006) and (012) are consistent with that

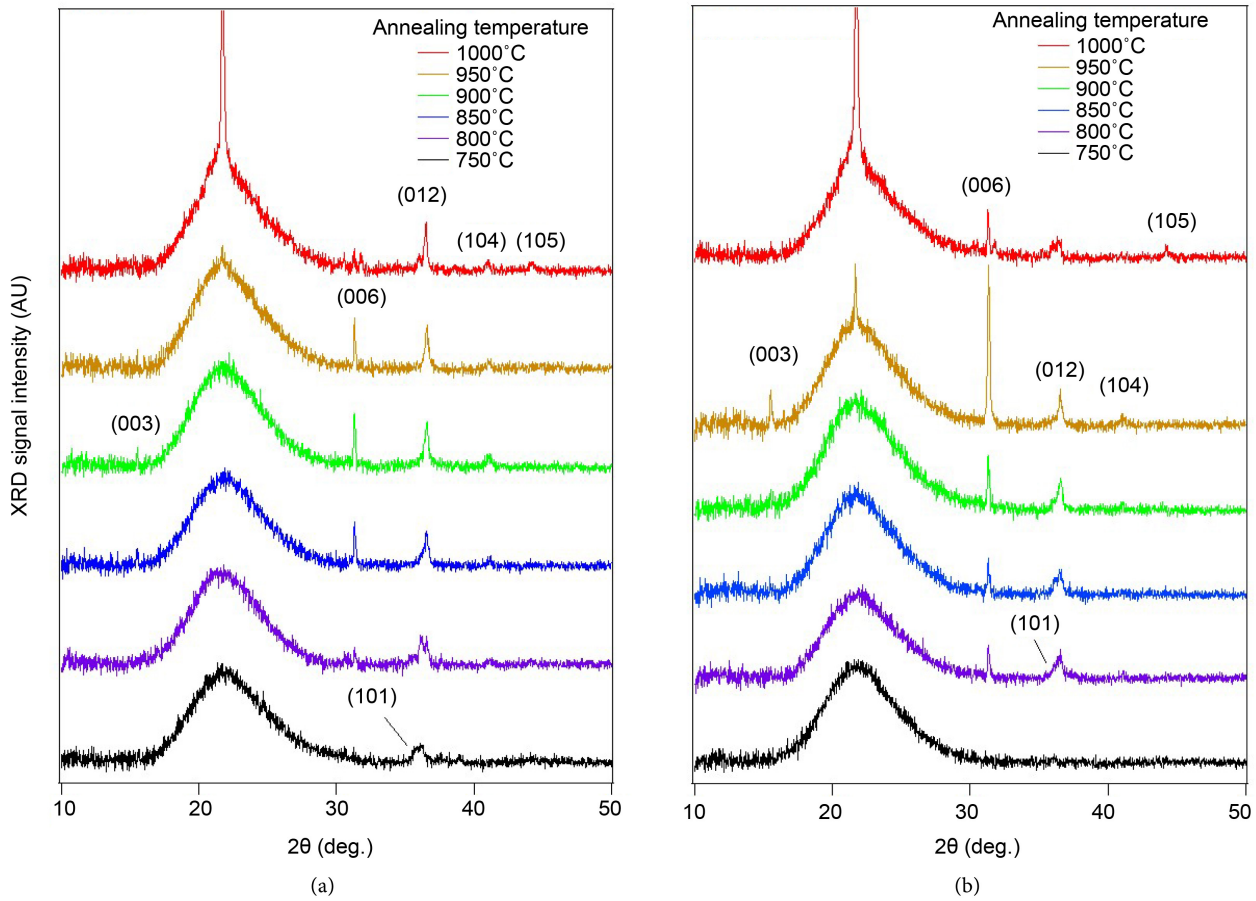


Figure 1. X-ray diffraction patterns of the thin films prepared by the sol-gel method using (a) metal nitrate and (b) metal acetylacetonate as a metal source. The films were annealed at 750˚C - 1000˚C in N_2 for 10 h.

in the film prepared using nitrate sol shown in **Figure 1(a)**. However, the signal of (101) was observed as a shoulder of the (012) peak in all films, while the signal of CuO was not observed. Unlike the films prepared using nitrate sol, the films annealed at temperatures higher than 800˚C showed a (006) peak and the signal intensity of the peak showed dependency on annealing temperature. The signal intensity increased with annealing temperature from 800˚C and the intensity became the highest at 950˚C, then decreased at 1000˚C. At 950˚C, a peak with orientation of (003), that is another *c*-axis-oriented peak, was observed at 15.5˚. This result indicates that the film annealed at 950˚C has a *c*-axis-oriented crystalline structure compared with other films in the present work. Other weak peaks, (104) and (105), were also observed, as well as in films prepared using nitrate sol.

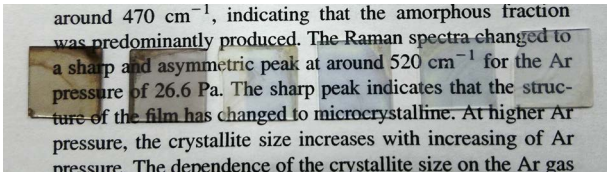
In all the XRD patterns, signals of Ga_2O_3 were not observed and only a weak signal of CuO was observed as a shoulder of peaks in some of the films. The use of sols containing only the same anion or some complex ligand can be thought to have prevented the formation of by-products. As also observed by XRD measurements, the films with different raw materials had different structures. As a trend, structural properties of the films prepared using acetylacetonate had

more significant annealing temperature dependence and more significant *c*-axis-oriented structure than the films prepared using nitrate sol.

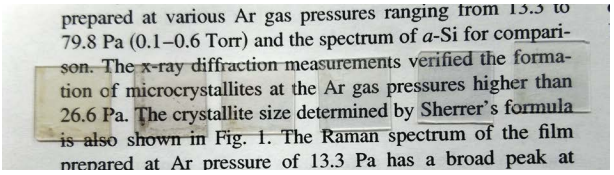
3.2. Transparency of the Films

Figure 2(a) and Figure 2(b) shows an optical image of the $CuGaO_2$ thin films prepared by the sol-gel method using nitrate sol and acetylacetonate sol, respectively. Each picture corresponds to annealing temperatures, 750˚C, 800˚C, 850˚C, 900˚C, 950˚C and 1000˚C, from left to right. As seen in the figure, films prepared from acetylacetonate show higher transparency than the films prepared using nitrate. In addition, the transparency of the films was preferable compared with that of $CuAlO_2$ used in our previous works not only for the films prepared by the sol-gel method [14] [15] but also by sputtering [16]. The films prepared from nitrate sol showed relatively higher transparency at temperatures of 900˚C or 950˚C; however, these films showed opaque appearance compared with the films prepared by acetylacetonate. Films prepared using acetylacetonate sol showed preferable transmittance at an annealing temperature range of 850˚C - 950˚C.

Transmission spectra of $CuGaO_2$ thin films prepared using nitrate sol followed by annealing at 800˚C, 900˚C and 1000˚C are shown in Figure 3(a). However, the figure does not display how the films annealed at 850˚C and 950˚C showed similar spectra as the film annealed at 900˚C. At a wavelength of 400 nm, the films annealed at 800˚C, 900˚C and 1000˚C showed transmissions of 36%, 67% and 56%, respectively. Figure 3(b) depicts the transmission spectra of $CuGaO_2$ thin films prepared using acetylacetonate sol annealed at 800˚C, 900˚C and 1000˚C. The films show higher transparency than the films prepared by nitrate. At a wavelength of 400 nm, the films annealed at 800˚C, 900˚C and 1000˚C showed transmissions of 75%, 75% and 62%, respectively. In addition, the films showed transmittance of more than 20% at a wavelength of 200 nm. These results indicate that the origin of the metal affects the optical properties of the films. Similar transmittance spectra to that observed in the sample annealed at



(a)



(b)

Figure 2. Optical images of the $CuGaO_2$ thin films prepared using (a) metal nitrate, (b) metal acetylacetonate, annealed in N_2. Left to right, the films were annealed at 750˚C, 800˚C, 850˚C, 900˚C, 950˚C and 1000˚C.

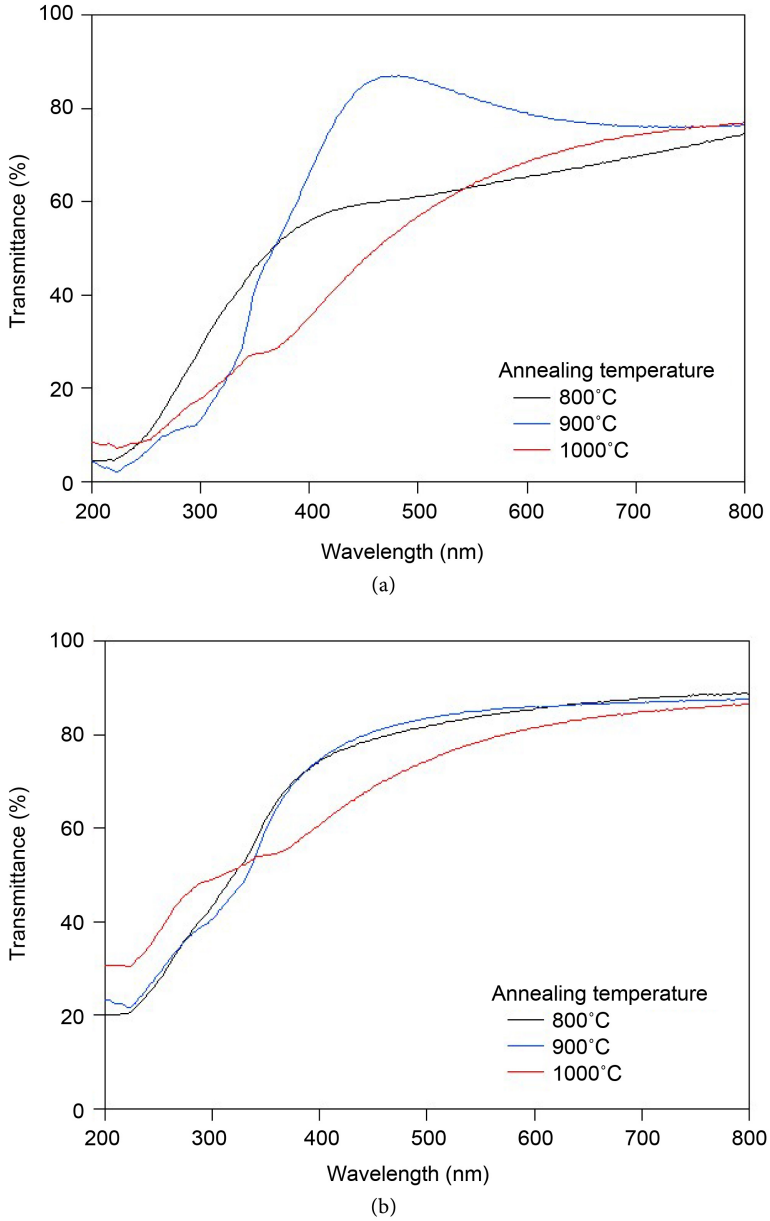
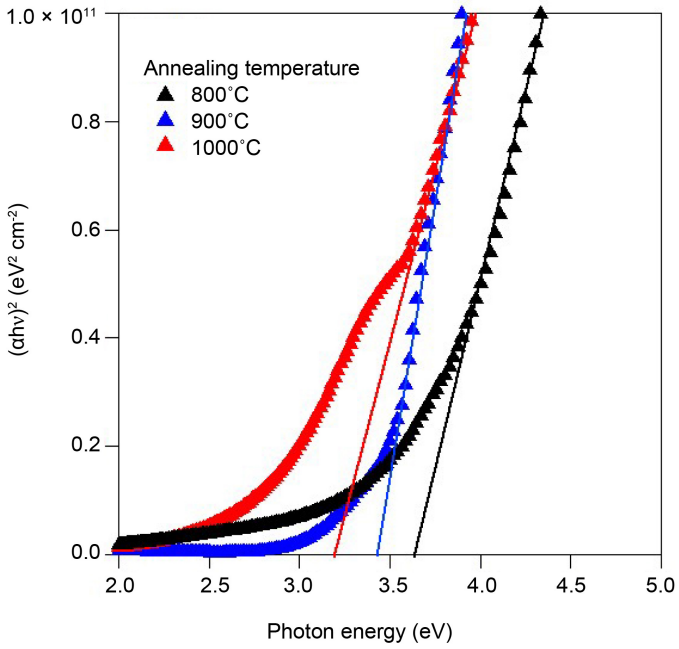


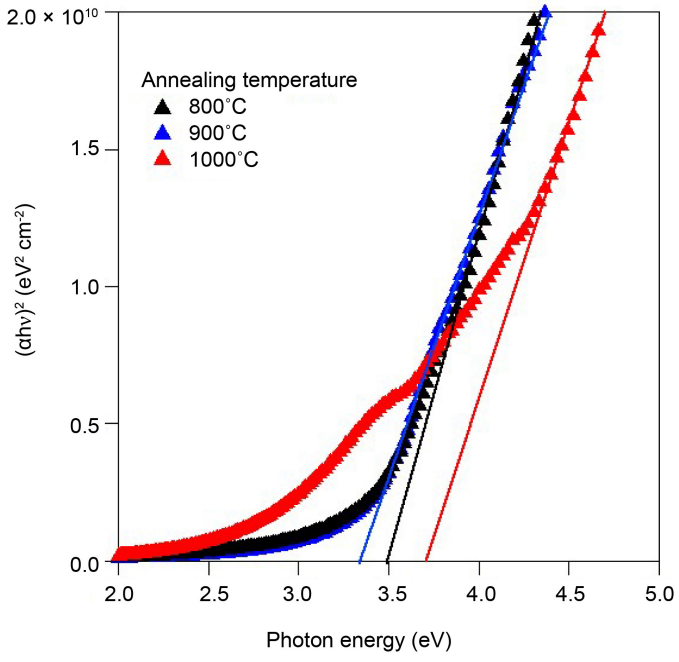
Figure 3. Transmission spectra of the $CuGaO_2$ thin films prepared using (a) metal nitrate and (b) metal acetylacetonate.

900˚C was also observed in the films annealed at 850˚C and 950˚C, although the structural properties changed depending on the annealing temperature, as observed in XRD.

Figure 4(a) and **Figure 4(b)** show Tauc plots (plot of $(\alpha h\nu)^2$ against photon energy) of the films prepared from nitrate and acetylacetonate annealed at 800˚C, 900˚C, and 1000˚C, respectively. In all the films, an optical bandgap of greater than 3.1 eV was obtained. In the films prepared using both the nitrate and the acetylacetonate sols annealed at 1000˚C, absorption at 2.5 - 3.5 eV was observed. The absorption is thought to be due to the localized state that was caused by destruction of crystalline.



(a)



(b)

Figure 4. Tauc plots (plot of $(ah\nu)^2$ against photon energy) for determining the optical bandgap of the film prepared using (a) nitrate and (b) acetylacetonate annealed at 800˚C, 900˚C and 1000˚C.

3.3. Surface Morphology

Figures 5(a)-(c) shows SEM images of $CuGaO_2$ thin films prepared using metal nitrate annealed at 800˚C, 900˚C and 1000˚C, respectively. The film annealed at 800˚C shows formation of crystalline grains with approximately 0.5 μm diameters

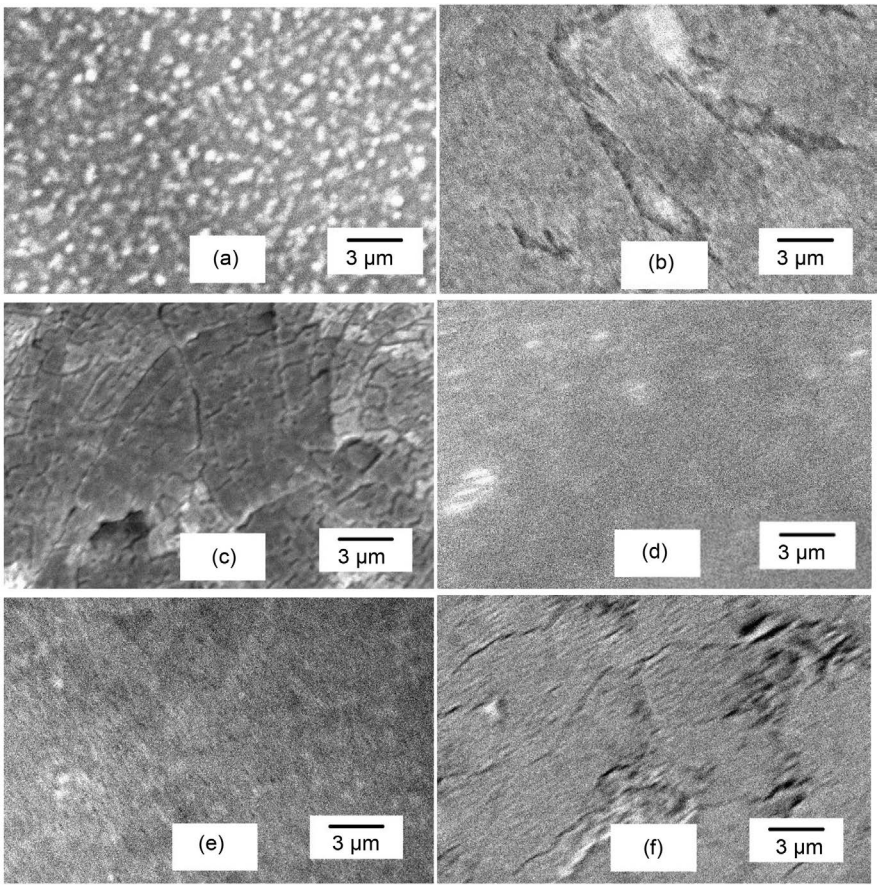


Figure 5. Scanning electron microscope images of $CuGaO_2$ thin films prepared using nitrate (a) annealed at 800˚C, (b) 900˚C and (c) 1000˚C, or acetylacetonate annealed at (d) 800˚C, (e) 900˚C and (f) 1000˚C.

on the surface. At an annealing temperature of 900˚C, textures with a scale of 5 - 10 μm were observed and crystalline grains were not observed. For the film annealed at 1000˚C, 1 - 2 μm square-structured grains were observed with cracks in the boundary of these grains. These results indicate that the surface morphology of the $CuGaO_2$ films prepared using nitrate sol changes drastically depending on the annealing temperature. The crystalline grains observed at an annealing temperature of 800˚C can be thought to become larger with increase in annealing temperature. Then, the surface becomes one with the texture or larger crystalline grains.

Figures 5(d)-(e) shows SEM images of $CuGaO_2$ thin films prepared using metal acetylacetonate annealed at 800˚C, 900˚C and 1000˚C, respectively. The films prepared using acetylacetonate show a relatively smooth surface compared with that in the films prepared by nitrate. At annealing temperatures of 800˚C - 900˚C, formation of crystalline grain is not well observed at the surface of the films. As shown in **Figure 2**, the films prepared using nitrate showed more opaque appearance compared with the films prepared by acetylacetonate. The difference in the surface morphology can be the cause of the difference in the appearance of the films depending on the metal source materials.

3.4. Conductivity of the Films

Figure 6 depicts the annealing temperature variation of conductivity of the $CuGaO_2$ thin films prepared by the nitrate sol and acetylacetonate sol. The films show p-type conductivity confirmed by Seebeck measurement. Conductivity of the films prepared at an annealing temperature of 1000˚C and the film prepared by nitrate annealed at 950˚C were too low to be measured. For the films prepared using nitrate sol, the film annealed at 750˚C showed conductivity of 1.4×10^{-7} $\Omega^{-1}\cdot cm^{-1}$ and increase with annealing temperature until 850˚C, with the highest conductivity being 5.7×10^{-4} $\Omega^{-1}\cdot cm^{-1}$. The conductivity was increased by more than three orders of magnitude. At higher temperature than 950˚C, the conductivity decreased by more than six orders of magnitude compared with that in 850˚C.

In the films prepared using the acetylacetonate sol, the film showed conductivity of 3.8×10^{-6} $\Omega^{-1}\cdot cm^{-1}$ at an annealing temperature of 750˚C, which was higher than that in the film prepared by the nitrate sol at the same annealing temperature. The conductivity of the film increased with annealing temperature as well as in the films prepared by the nitrate sol; however, the highest conductivity obtained by acetylacetonate film was 1.6×10^{-5} $\Omega^{-1}\cdot cm^{-1}$ at the annealing temperature of 850˚C, which is a lower value than that in the film prepared using nitrate. The conductivity increased by less than one order from the annealing temperatures of 750˚C - 850˚C. In addition, decreasing conductivity at higher temperature was less than two orders from 850˚C to 950˚C.

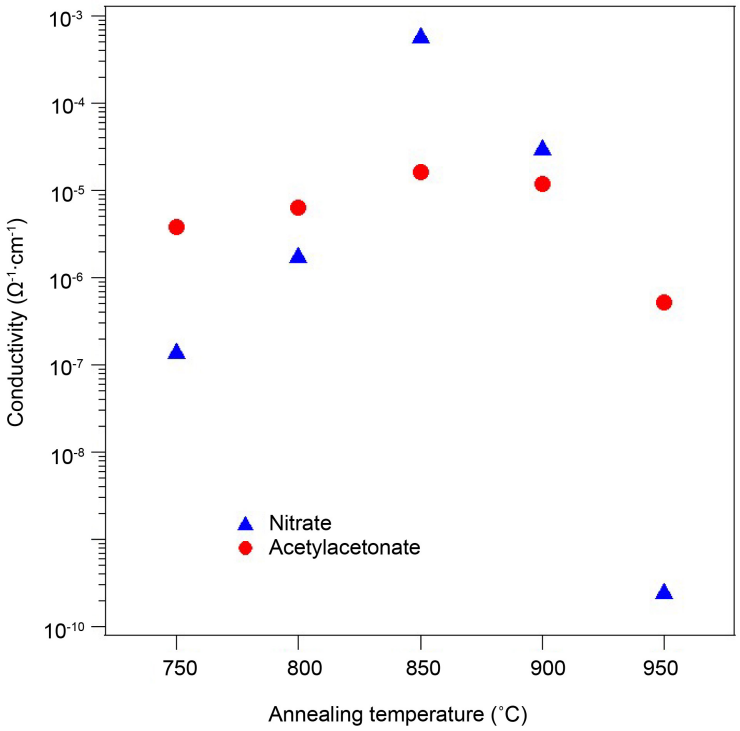


Figure 6. Conductivity of the $CuGaO_2$ thin films prepared by the sol-gel method.

4. Conclusion

$CuGaO_2$ thin films were prepared by the sol-gel method using two kinds of combination of metal source materials, Cu and Al nitrate, and acetylacetonate. The films showed dependence of the structural, optical and electrical properties not only on the annealing temperature, but also on the metal source materials. In the case of the films prepared by the nitrate sol, XRD signal intensity did not show significant dependency on annealing temperature; however, surface morphology and conductivity showed significant dependency on annealing temperature. In contrast, in the case of the films prepared using the acetylacetonate sol, XRD signal intensity showed dependence on the annealing temperature. However, surface morphology and conductivity showed independency on the annealing temperature. The films prepared using acetylacetonate showed preferable transparency compared with the films prepared using nitrate. Transmittance of the films at wavelengths longer than 400 nm was more than 75% at annealing temperatures of 800˚C - 900˚C. The highest conductivity of 5.7×10^{-4} $\Omega^{-1}\cdot cm^{-1}$ was obtained by the film prepared by the nitrate sol followed by annealing at 850˚C. Because of the use of metal source materials with the same anion or same complex ligand and strict control of heat treatment, by-products were not observed at an annealing temperature higher than 850˚C.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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