Preparation of CuYO₂ Thin Films by Sol-Gel Method Using Copper Acetate and Yttrium Acetate as Metal Sources

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Abstract
Delafossite structured p-type wide bandgap semiconductor, CuYO₂ thin films were prepared on SiO₂ substrate by sol-gel method using copper (II) acetate and yttrium (III) acetate as source materials. The films preparation process was studied by varying annealing temperature after the preparation of gel films by spin coating, followed by thermal annealing at higher temperature. In the present work, one step annealing directly from Cu-Y-gel under nitrogen flow was used. X-ray diffraction (XRD) revealed that the film annealed at 800°C is significantly c-axis oriented, shows only (002) and (004) peaks at 15.6° and 31.5°, respectively. The optical bandgap of 3.7 - 3.8 eV is estimated by (αhv)² plot which is higher than previous works. In addition, the films with highly c-axis orientation showed photoluminescence (PL) at room temperature with very broad peak at 2.3 eV. The films annealed at different temperature showed different structural properties.

Keywords
CuYO₂, Delafossite, Sol-Gel, Thin Films, Photoluminescence

1. Introduction
Transparent conductive oxides (TCOs) are widely used as materials in a variety of optoelectronic applications. Although some TCOs have already been produced for applications, most of them have n-type conductivity such as indium tin oxide [1] and Al-doped ZnO [2]. Thus, p-type TCOs are required to develop a variety of optoelectronic applications employing p-n junctions. Cu-delafossite structure wide gap semiconductor materials have recently attracted much attention because the discovery of p-type conductivity of CuAlO₂ [3].

CuYO₂ is one of p-type TCO having delafossite structure, which has been prepared by some methods. For example, solid phase reaction of CuO and Y₂O₃ though Cu₂Y₂O₅ [4] and so-gel method using copper nitrate and yttrium nitrate as metal sources, employing air and nitrogen-flow two steps annealing [5] have been reported. The CuYO₂ films have displayed green PL properties that have a peak at 540 nm (2.3 eV). The result suggests that the CuYO₂ have a possibility to be a material for transparent light emitting devices.

In the present work, we describe the preparation of delafossite type CuYO₂ thin films by the sol-gel method, in which copper acetate and yttrium acetate were used as metal sources. The gel films were annealed by one step

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annealing under nitrogen flow, not by two steps as described above. The dependence of the crystal structure, especially the c-axis orientation on annealing temperature is discussed.

2. Experimental

CuYO₂ thin films were prepared on SiO₂ substrates by the sol-gel method. Prior to deposition of the thin films, the substrates were degreased by ultrasonication in EtOH. Copper (II) acetate monohydrate (Wako Chemicals) was dissolved in a mixture of 2-methoxyethanol and 2-aminoethanol by stirring for 12 h at room temperature. The molar ratio of 2-aminoethanol, chelating agent, to copper acetate was maintained at 4:1 and the color of the solution was dark blue. Yttrium acetate tetrahydrate (Wako Chemicals) was dissolved in a mixture of 2-methoxyethanol and 2-aminoethanol by stirring for 12 h at room temperature. The molar ratio of 2-aminoethanol to aluminum acetate basic was maintained at 2:1. After stirring, a colorless homogeneous solution was obtained. The two solutions were mixed with a Cu/Y ratio of 1:1 and stirred at room temperature for 12 h to form a sol. The sol was with total metal ion concentrations of 0.40 M. The sol was spin-coated onto a SiO₂ substrate with spinning speed of 3000 rpm for 5 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 spin-coating. The coated films were first heated at 200°C for 10 min, and then heated again at a higher temperature of 500°C for 20 min using hot-plate-type heating devices. The spin-coating and subsequent heat treatment procedures were repeated for 6 times to obtain the desired film thickness of 0.4 μm. The prepared gel films were finally annealed at temperatures in the range of 750°C - 900°C 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.

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). PL spectrum was measured using He-Cd laser (325 nm, 3.8 eV) for excitation.

3. Results and Discussion

Figure 1 shows XRD patterns for the films prepared using spin-coated gel films annealed at temperatures in the range of 750°C - 900°C. The broad signal observed at around 22° is due to the amorphous SiO₂ substrate. The

![Figure 1. XRD patterns for thin films annealed at temperatures in the range of 750°C - 900°C.](image)
XRD patterns changed depending on the annealing temperature significantly at every increasing of 50 K. For the film annealed at 750°C, XRD pattern has three kinds of peaks, CuYO$_2$, Y$_2$O$_3$, and CuO. The peaks of CuYO$_2$ are observed at 15.6° (002) and 31.4° (004). Both of the peaks are c-axis oriented, and no other CuYO$_2$ peaks are observed. Apart from the peaks of CuYO$_2$, peaks attributed to Y$_2$O$_3$ at 29.3° (222), 34.0° (440), and CuO at 35.7° (002)(-111), are observed. The film consists of ternary metal oxide CuYO$_2$ that is target material in the present work and binary metal oxide Y$_2$O$_3$ and CuO. Due to the XRD peak intensity, it is considered that the fraction volume of Y$_2$O$_3$ is larger than that of CuYO$_2$ at 750°C. In the sample annealed at 800°C, only the two peaks of (002) and (004) of CuYO$_2$ are observed with higher intensity than the films annealed at other temperature. This result means that the direct synthesis of pure CuYO$_2$ from Cu-Y-gel without making Cu$_2$Y$_2$O$_5$ is successfully achieved in the present work. It is considered that the direct synthesis becomes possible because the metal ions and 2-aminoethanol complexes are used as metal sources which oxidized by different mechanism from non-chelating metal ions. In the films annealed at 850°C, the film displays peaks of CuYO$_2$, not only the c-axis oriented peaks, but also a peak of (101) at 29.9°. The intensity of the (101) peak increased with annealing temperature at 900°C with decreasing of c-axis oriented peaks, (002) and (004). The c-axis peak is finally disappeared at annealing temperature of 900°C. In addition, the XRD signal intensity is decreased at higher temperature again. This result indicates that the material CuYO$_2$ is not stable at higher temperature than 850°C, thus the decomposition reaction of CuYO$_2$ occurs at higher temperature than 850°C. The results indicate that the CuYO$_2$ crystalline fraction volume ration once increased with annealing temperature and becomes the highest at 800°C, then decreased again at higher temperature. Along with the decreasing of CuYO$_2$ peaks, the peaks of CuO are observed as well as in the case of films annealed at lower temperatures.

Optical transmission spectra of the films annealed at 800°C and 900°C are shown in Figure 2. The film annealed at 800°C, which has the highest XRD peak intensity of c-axis orientated peaks, has a transparency of more than 60% at the wavelength longer than 500 nm region. In contrast, the film annealed at 900°C shows lower transparency than the film annealed at 800°C at longer wavelength than 400 nm, however, shows higher transparency at shorter wavelength. In addition, the absorption edge is blue shifted significantly compared with the film annealed 800°C. The result indicates that the band structure of the films changed drastically between the annealing temperature 800°C and 900°C. Figure 3(a) and Figure 3(b) shows a plot of $(\alpha hv)^2$ against the photon energy of the film annealed at 800°C, and 900°C, respectively. In the film annealed at 800°C, the optical bandgap determined from the plot is 3.78 eV, which is higher than that of previously reported CuYO$_2$ [6] and the value is sufficiently high for use as a TCO material. In contrast, the optical bandgap of the films annealed at

![Figure 2. Absorption spectra of thin films annealed at 800°C and 900°C.](image-url)
900°C is 5.27 eV, which is significantly higher than the film annealed at 800°C. In addition, this result is inconsistent with the assignment by XRD that the film is (101) oriented CuYO₂ crystalline. It is considered that the film is consist of CuYO₂ crystalline fraction and amorphous Y₂O₃ fraction that has bandgap of 5.6 eV [7]. As mentioned previously, the fraction volume ratio of CuYO₂ crystalline is thought to be low, thus, the optical bandgap of the film is thought to be determined by properties of the amorphous Y₂O₃ fraction that have significantly higher fraction volume ratio than CuYO₂ crystalline in the film. The structural property dependency on the annealing temperature observed in the present work is not consistent with previously reported sol-gel preparation of CuYO₂ films [5]. It is because the synthesis of CuYO₂ is directly from Cu-Y-gel, not from the Cu₂Y₂O₅ that is promptly formed by the annealing of gel films in air before the annealing under nitrogen flow.

In the present work, the film becomes crystalline CuYO₂ and Y₂O₃ at temperature of 750°C, then becomes highly c-axis oriented CuYO₂ at 800°C, then finally, becomes mixture of non-c-axis oriented CuYO₂, CuO and amorphous Y₂O₃ at higher temperature than 850°C. It is considered this complicated dependence of structure on annealing temperature is caused by existence of many synthesis and decomposition reactions occur in the films simultaneously. For example, oxidization of Cu and Y gel, solid phase reaction of CuO and Y₂O₃ to CuYO₂, decomposition reaction of CuYO₂ to amorphous Y₂O₃ and CuO, and crystalline orientation changing of CuYO₂ are thought to occur in the temperature region studied in the present work.

Figure 4 displays the PL spectrum of the film annealed at 800°C which CuYO₂ crystalline in the film is highly c-axis oriented. The film exhibited a broad emission band with a broad peak at photon energy of 2.3 eV. The spectrum is very similar to previously reported CuYO₂ films [5]. Although the preparation details are different, the CuYO₂ film prepared in the present work has similar optical properties with previous works. The origin of the PL is assigned to be due to the Cu⁺ interconfiguration transition from 3d⁹4s¹ to 3d¹⁰ with Stokes shift [8].

4. Conclusion

Delafossite material, CuYO₂ thin films are prepared by sol-gel method using Cu acetate and Y acetate as metal source materials. Spin-coated gel films were annealed under nitrogen flow without carrying out promptly annealing in air. As a result, CuYO₂ is successfully synthesized without synthesize Cu₂Y₂O₅. XRD patterns reveal that the film annealed at lower temperature shows the patterns of Y₂O₃ crystalline rather than CuYO₂. At annealing temperature of 800°C, the film shows highly c-axis oriented CuYO₂ crystalline. The PL spectrum is similar to the previous works. Due to the result of XRD and transmission spectra, it is suggested that the films
Figure 4. PL spectrum of thin films annealed at 800°C, measured at room temperature.

becomes mixture of (101) oriented CuYO$_2$ and amorphous Y$_2$O$_3$ at annealing temperature of 850°C and 900°C. These complicated dependency of structural properties of the films on the annealing temperature is caused by the existence of many reactions occur in the films simultaneously.

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