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Preparation of $CuYO_2$ 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, $CuYO_2$ thin films were prepared on SiO_2 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 $(\alpha h\nu)^2$ 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

$CuYO_2$, 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 ban gap semiconductor materials have recently attracted much attention because the discovery of p-type conductivity of $CuAlO_2$ [3].

$CuYO_2$ is one of p-type TCO having delafossite structure, which has been prepared by some methods. For example, solid phase reaction of CuO and Y_2O_3 though $Cu_2Y_2O_5$ [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 $CuYO_2$ films have displayed green PL properties that have a peak at 540 nm (2.3 eV). The result suggests that the $CuYO_2$ have a possibility to be a material for transparent light emitting devices.

In the present work, we describe the preparation of delafossite type $CuYO_2$ 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

$CuYO_2$ thin films were prepared on SiO_2 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 SiO_2 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 SiO_2 substrate. The

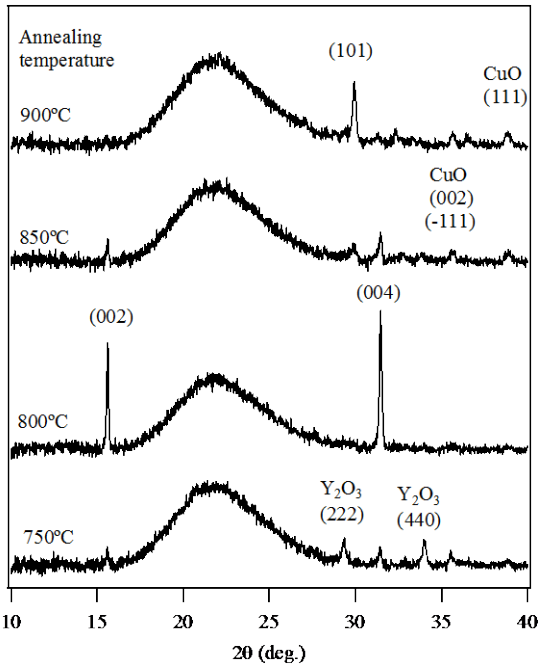


Figure 1. XRD patterns for thin films annealed at temperatures in the range of 750˚C - 900˚C.

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_2O_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_2O_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_2O_3 and CuO. Due to the XRD peak intensity, it is considered that the fraction volume of Y_2O_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 $Cu_2Y_2O_5$ 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 $(\alpha h\nu)^2$ 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

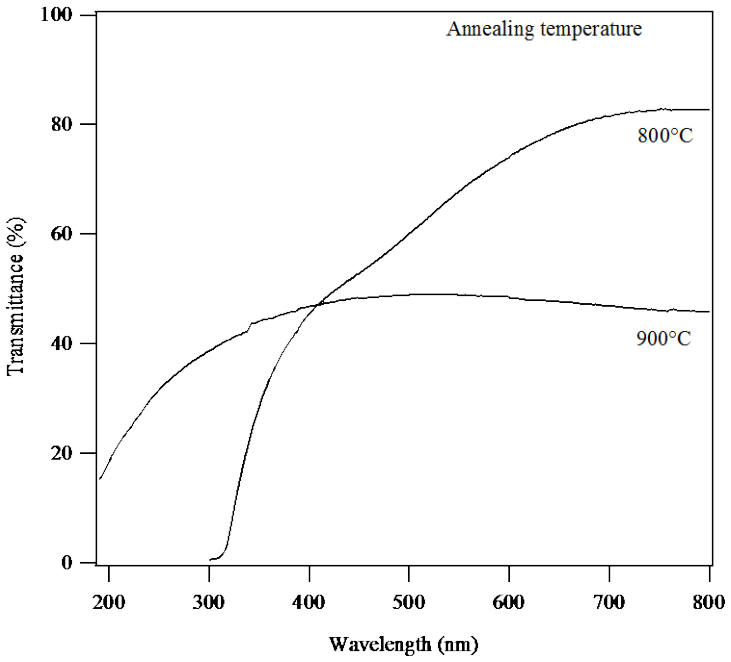
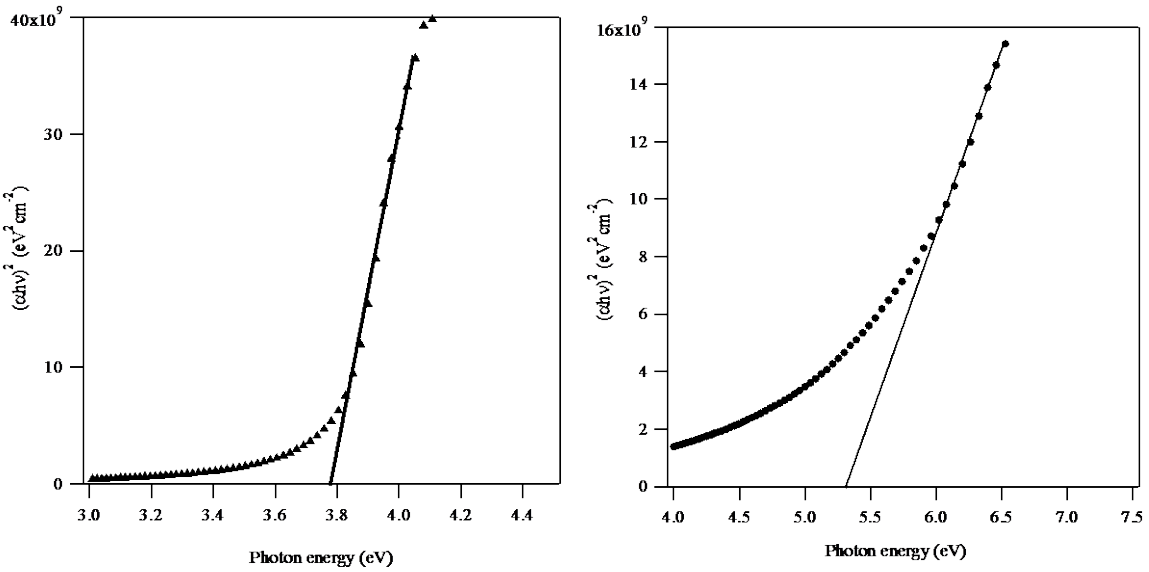


Figure 2. Absorption spectra of thin films annealed at 800˚C and 900˚C.



(a) (b)

Figure 3. A plot of $(\alpha hv)^2$ against the photon energy of the film annealed at (a) 800˚C shown above; and (b) 900˚C shown below.

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 $CuYO_2$ crystalline. It is considered that the film is consist of $CuYO_2$ crystalline fraction and amorphous Y_2O_3 fraction that has bandgap of 5.6 eV [7]. As mentioned previously, the fraction volume ratio of $CuYO_2$ crystalline is thought to be low, thus, the optical bandgap of the film is thought to be determined by properties of the amorphous Y_2O_3 fraction that have significantly higher fraction volume ratio than $CuYO_2$ 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 $CuYO_2$ films [5]. It is because the synthesis of $CuYO_2$ is directly from Cu-Y-gel, not from the $Cu_2Y_2O_5$ 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 $CuYO_2$ and Y_2O_3 at temperature of 750˚C, then becomes highly *c*-axis oriented $CuYO_2$ at 800˚C, then finally, becomes mixture of non-*c*-axis oriented $CuYO_2$, CuO and amorphous Y_2O_3 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 Y_2O_3 to $CuYO_2$, decomposition reaction of $CuYO_2$ to amorphous Y_2O_3 and CuO, and crystalline orientation changing of $CuYO_2$ 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 $CuYO_2$ 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 $CuYO_2$ films [5]. Although the preparation details are different, the $CuYO_2$ 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 $3d^94s^1$ to $3d^{10}$ with Stokes shift [8].

4. Conclusion

Delafossite material, $CuYO_2$ 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, $CuYO_2$ is successfully synthesized without synthesize $Cu_2Y_2O_5$. XRD patterns reveal that the film annealed at lower temperature shows the patterns of Y_2O_3 crystalline rather than $CuYO_2$. At annealing temperature of 800˚C, the film shows highly *c*-axis oriented $CuYO_2$ 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

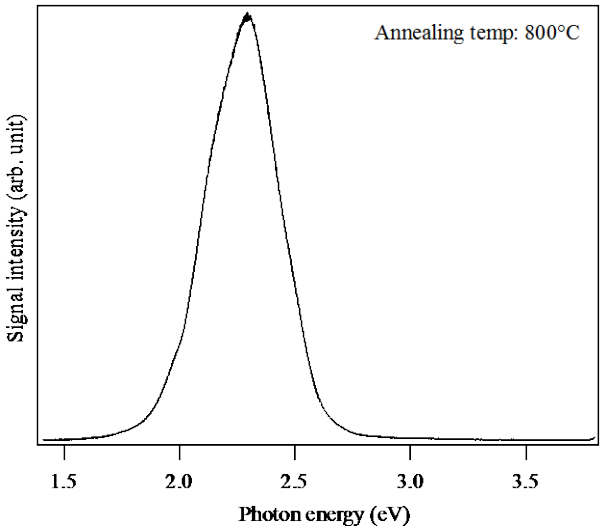


Figure 4. PL spectrum of thin films annealed at 800˚C, measured at room temperature.

becomes mixture of (101) oriented $CuYO_2$ and amorphous Y_2O_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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References

[1] Kim, H., Gilmore, C.M., Pique, A., Horwitz, J.S., Mattoussi, H., Murata, H., Kafafi, Z.H. and Chrisey, D.B. (1999) Electrical, Optical, and Structural Properties of Indium-Tin-Oxide Thin Films for Organic Light-Emitting Devices. *Journal of Applied Physics*, **86**, 6451-6461. http://dx.doi.org/10.1063/1.371708

[2] Minami, T., Nanto, H. and Tanaka, S. (1984) Highly Conductive and Transparent Aluminum Doped Zinc Oxide Thin Films Prepared by rf Magnetron Sputtering. *Japanese Journal of Applied Physics*, **23**, L280-L282. http://dx.doi.org/10.1143/JJAP.23.L280

[3] Kawazoe, H., Yasukawa, H., Hyodo, H., Kurita, M., Yanagi, H. and Hosono, H. (1997) P-Type Electrical Conduction in Transparent Thin Films of $CuAlO_2$. *Nature*, **389**, 939-942. http://dx.doi.org/10.1038/40087

[4] Ishiguro, T., Ishizawa, N., Mizutani, N. and Kato, M. (1983) A New Delafossite-Type Compound $CuYO_2$. *Journal of Solid State Chemistry*, **49**, 232-236. http://dx.doi.org/10.1016/0022-4596(83)90117-2

[5] Tsuboi, N., Tosaka, K., Kobayashi, S., Kato, K. and Kaneko, F. (2008) Preparation of Delafossite-Type $CuYO_2$ Films by Solution Method. *Japanese Journal of Applied Physics*, **47**, 588-591. http://dx.doi.org/10.1143/JJAP.47.588

[6] Tarari, M., Bouguelia, A. and Bessekhouad, Y. (2006) P-type $CuYO_2$ as Hydrogen Photocathode. *Solar Energy Materials and Solar Cells*, **90**, 190-202. http://dx.doi.org/10.1016/j.solmat.2005.03.003

[7] Wang, W.C., Badylevich, M., Afanas'ev, V.V., Stesmans, A., Adelmann, C., Van Elshocht, S., Kittl, J.A., Lukosius, M., Walczyk, Ch. and Eenger, Ch. (2009) Bnd Alignment and Electron Traps in Y_2O_3 Layers on (100)Si. *Applied Physics Letters*, **95**, 132903. http://dx.doi.org/10.1063/1.3236536

[8] Jacob, A., Parent, C., Boutinaud, P., Le Flem, G., Doumerc, J.P., Armer, A., Elazharic, M. and Elaatmeni, M. (1997) Luminescent Properties of Delafossite-Type Oxides $LaCuO_2$ and $YCuO_2$. *Solid State Communications*, **103**, 529-532. http://dx.doi.org/10.1016/S0038-1098(97)00224-X