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Preparation of *p*-type conductive transparent $CuCrO_2$:Mg thin films by chemical solution deposition with two-step annealing

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Abstract

Mg-doped copper–chromium oxide ($CuCrO_2$:Mg) thin films are prepared on glass substrate by chemical solution deposition. Metal acetate salts are examined as metal sources in the precursor solution for the preparation of $CuCrO_2$:Mg thin films. Annealing conditions, such as ambient gas and temperature, are investigated in order to produce pure $CuCrO_2$ phase *p*-type conductive thin films at a relatively lower process temperature. Single-phase delafossite $CuCrO_2$ structures are obtained by subsequent two-step annealing at 400 °C in 5% forming gas ambient, followed by a rise to sintering temperature in a nitrogen atmosphere. Annealing in forming gas reduces Cu(II) ion to Cu(I) and inhibits the formation of spinel-type $CuCr_2O_4$, thus allowing $CuCrO_2$ to form at 500 °C. The transmittance of the $CuCrO_2$ thin films is above 50% in the visible region and increases with increases in the sintering temperature. The highest conductivity is obtained with sintering at 600 °C, and a resistivity of 0.31 Ω cm is achieved.

Keywords: A. Films; C. Electrical conductivity; C. Optical properties; Delafossite

1. Introduction

Transparent conducting oxides (TCOs) are attracting more and more attention. They are widely used in flat panel displays, touch panels, light-emitting diodes, low-e glass, defroster glass and solar cells [1]. In general, most of the known TCOs, such as indium-doped tin oxide (ITO) and aluminum- or gallium-doped zinc oxide (AZO, GZO), are *n*-type materials. The fabrication of a *p–n* junction is the most fundamental step in developing electronic devices, such as transparent diodes, transistors, UV-LEDs, and applications in photovoltaic cells [2,3]. However, acceptable *p*-type transparent conducting oxides have yet to be realized, as past attempts have resulted in low electrical conductivity or low optical transmittance. Since Kawazoe et al. reported on *p*-type conductivity transparent $CuAlO_2$ thin films [4], delafossite films, such as $CuYO_2$ [5], $CuCrO_2$ [6], and $CuScO_2$ [7], etc., have attracted considerable scientific and technological attention. Of these *p*-type materials, Mg-doped $CuCrO_2$ reportedly has the highest conductivity, 220 S/cm [6]. Up to now, most delafossite films have been prepared by vacuum-based methods, such as pulsed laser deposition (PLD) [8] and sputtering [6]. There have only been a few reports on the wet-chemical approach [9–11], which can be partially ascribed to the fact that the chemical solution-derived films are transformed to the delafossite phase via a rather complex sequence of solid-state reactions during the thermal treatment.

Cu ion in a delafossite structure is Cu(I); however, typically wet chemical-derived Cu ion is Cu(II), which will react with B site ions, such as Al and Cr, to form stable spinel-type AB_2O_4 [9,12].

According to the isobaric phase diagram of the bulk Cu_2O–Cr_2O_3–CuO ternary system, reported by Jacob et al. [13], when CuO and Cr_2O_3 react in air, CuO and Cr_2O_3 favorably react to form spinel-type $CuCr_2O_4$ at 700 °C. Pure delafossite-type $CuCrO_2$ is converted from spinel-type $CuCr_2O_4$ with residual CuO above 1000 °C. Its chemical formula is shown in (1) and (2):

$$2CuO + Cr_2O_3 \rightarrow CuCr_2O_4 + CuO \quad (1)$$

$$CuCr_2O_4 + CuO \rightarrow 2CuCrO_2 + 1/2O_2 \quad (2)$$

According to formula (2), the reduced ambient helps obtain the $CuCrO_2$ phase thermodynamically. Götzendörfer et al. prepared $CuCrO_2$:Mg thin films by the sol–gel route with annealing in argon at 700 °C [10]. In this work, two-step

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annealing using forming gas and nitrogen gas were investigated in order to obtain pure delafossite-type $CuCrO_2$:Mg thin films.

2. Experimental

Copper acetate (798.2 mg, 4.0 mmol), ethanolamine (976.0 mg, 16.0 mmol) and magnesium acetate (42.8 mg, 0.20 mmol) were dissolved in 2-ethoxyethanol (15.0 ml). The solution was stirred on a hotplate for 2 h, after which chromium acetate (939.0 mg, 3.8 mmol) was added and the mixture was stirred for another 12 h to obtain a deep emerald precursor solution. This solution was diluted by adding 2-ethoxyethanol to adjust the concentration of the precursor solution to 0.2 M. The precursor solution was then applied for 25 s onto a 30 mm square-shaped Corning 1737 glass substrate surface spinning at 4000 rpm. The spin-coated films were dried on a hotplate at 150 °C for 4 min and pre-annealed in the tube furnace at 400 °C in air for 5 min. This process was repeated five times to obtain a suitable film thickness. In order to compare the effects of the annealing conditions on the properties of $CuCrO_2$ thin films, the pristine coated 30 mm square glass substrate was cut into four pieces.

In order to obtain pure delafossite-type $CuCrO_2$:Mg thin films, the combination of forming gas (mixture of 5% hydrogen in nitrogen gas) and two-step annealing was investigated. In the first stage of this two-step annealing method, all samples were annealed under forming gas at 400 °C for 15 min. During the second stage, the annealing atmosphere was switched to pure N_2 and the temperature was raised to various sintering temperatures for 1 h.

The film samples were evaluated in terms of structural, electrical and optical properties. Crystalline phases in the films were identified using grazing-incidence X-ray diffraction (GIXRD) (incident angle of X-ray = 0.5°) (X'pert MPD, Panalytical). A scanning electronic microscope (SEM, Hitachi S-4700) was used to observe the film thickness. The current–voltage response and carrier transport properties of the samples were determined at RT by the Hall measurement method (Ecopia HMS-3000) and the four-point probe method (Mitsubishi Chemical LORESTA-GP MC CP-T610). The optical transmission of the films was obtained using a UV–vis spectrometer (Jasco V-630).

3. Results and discussion

3.1. Forming gas annealing

In order to inhibit the formation of spinel-type $CuCr_2O_4$, during heat treatment, the Cu(II) ion in the precursor needed its oxidation state reduced to Cu(I). For this purpose, the effect of the forming gas annealing was examined. GIXRD studies were carried out to evaluate the crystalline structure of the chemical solution-derived thin films. In Fig. 1, the GIXRD patterns of $CuCrO_2$:Mg thin films are given as a function of annealing temperatures under forming gas ambient. The XRD chart revealed that, for the films annealed in forming gas at 400 °C, the broad peaks seemed to belong to Cu_2O crystalline. When

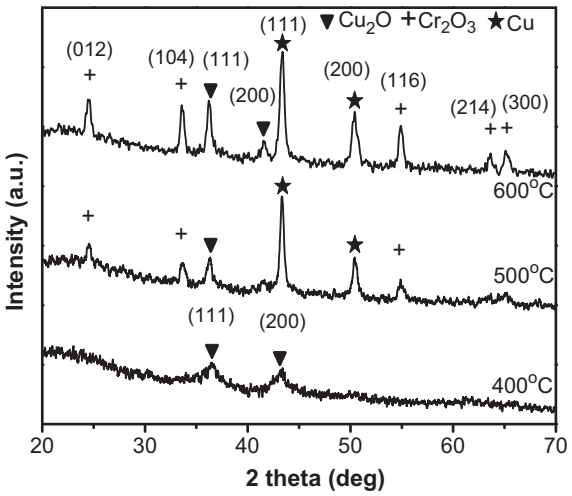

Fig. 1. GIXRD pattern of Cu–Cr–O thin films annealed at various temperatures under forming gas ambient.

the annealing temperature was raised to 500 and 600 °C, peaks belonging to Cu_2O also appeared, as well as peaks belonging to Cu metal and residual Cr_2O_3. However, peaks belonging to spinel-type $CuCr_2O_4$ were not observed. These results indicated that annealing in forming gas at 400 °C reduced Cu(II) to Cu_2O. Due to the reduction of Cu(II) to Cu(I), the formation of spinel-type $CuCr_2O_4$ was inhibited. However, with forming gas annealing at higher than 500 °C, some Cu ion was reduced to Cu metal phase. The Cr_2O_3 maintained its oxidation state in these conditions. Therefore, the two-step annealing process was designed.

3.2. Two-step annealing

The two-step annealing process consisted of a forming gas annealing step at 400 °C to reduce Cu(II) ion to Cu(I), and an inert gas annealing step at sintering temperature to form $CuCrO_2$:Mg and improve its crystallinity.

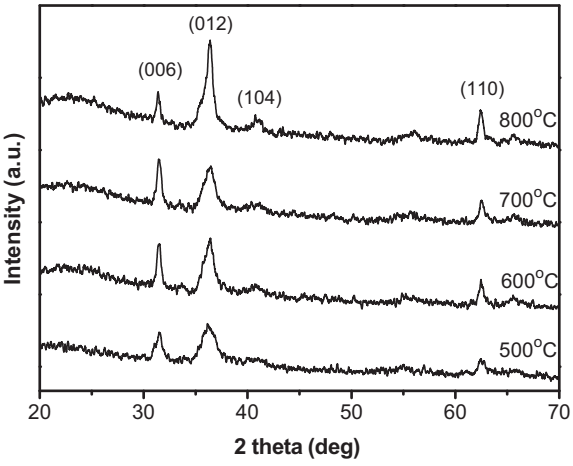

Fig. 2. GIXRD patterns of $CuCrO_2$:Mg thin films prepared with two-step annealing, annealing at 400 °C in forming gas for 15 min and then sintering at various temperatures in nitrogen for 1 h.

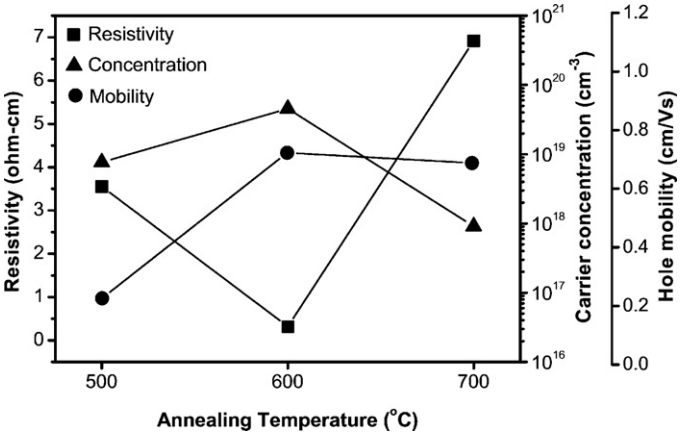

Fig. 3. Resistivity, Hall mobility, and carrier concentration of $CuCrO_2$:Mg thin films prepared with two-step annealing, annealing.

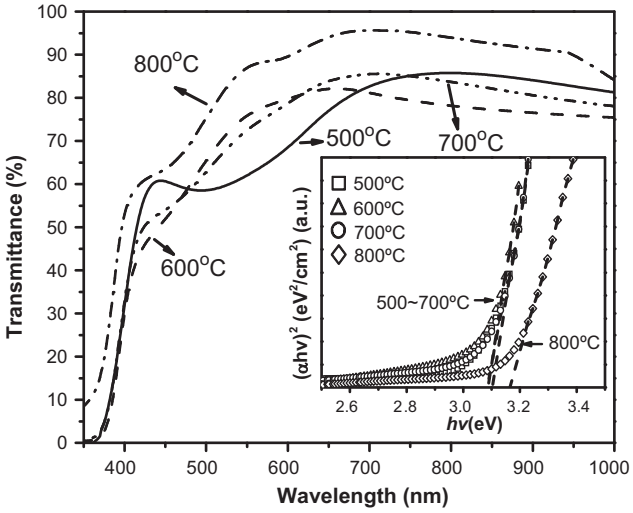

Fig. 4. Optical transmittance spectra of $CuCrO_2$:Mg thin films prepared with two-step annealing. The inset shows the absorption edge of $CuCrO_2$:Mg thin films.

Fig. 2 presents the X-ray diffraction pattern of $CuCrO_2$:Mg thin films prepared with the two-step annealing method as a function of the sintering temperature. As shown in Fig. 2, only peaks belonging to $CuCrO_2$ (0 0 6), (0 1 2), (1 0 4) and (1 1 0) can be observed. The intensity of the peak signal increased with increases in sintering temperature. In this process, the solid-state reaction was assumed as Cu_2O reacted with Cr_2O_3 to form $CuCrO_2$ without the formation of spinel-type $CuCr_2O_4$, which appears in single-step annealing in argon or air [10]:

$$Cu_2O + Cr_2O_3 \rightarrow 2CuCrO_2 \quad (3)$$

3.3. Electrical properties of films

The four-point probe method and Hall measurement were carried out to determine the electrical measurements. Fig. 3 shows the resistivity, carrier concentration, and mobility of the films with two-step annealing corresponding to the samples in Fig. 2.

The Hall measurement confirmed that the $CuCrO_2$:Mg thin films prepared by chemical solution deposition with two-step annealing were *p*-type. The highest conductivity was obtained with sintering at 600 °C, and a resistivity of 0.31 Ω cm was achieved. This was lower than the $CuCrO_2$:Mg thin films annealed under argon at the same sintering temperature as reported by Götzendörfer et al. A possible explanation was that the thin films prepared by two-step annealing did not contain undetectable low conductive CuO and $CuCr_2O_4$. The carrier mobility increased with the sintering temperature due to phase development; however, at sintering temperatures above 600 °C, the conductivity declined because the carriers generated from copper vacancies and oxygen interstitials decreased at the higher temperatures. A similar observation was reported by Ingram et al. for $CuScO_2$ and $CuYO_2$ [14], and by Götzendörfer et al. for $CuCrO_2$ [9], at low oxygen partial pressure. The resistivity of the sample sintered at 800 °C was too high for Hall measurement. The electrical and optical properties of $CuCrO_2$:Mg thin films prepared by various methods reported in the literature have been summarized in Table 1.

3.4. Optical properties

The optical transmittance spectra of $CuCrO_2$:Mg films prepared by chemical solution deposition with two-step annealing are shown in Fig. 4. These films formed in the

Table 1
Reported electrical and optical properties of $CuCrO_2$:Mg thin films.

Composition	Method	Process temperature (°C)	Resistivity (Ω cm)	Transmittance (%)	Thickness (nm)	Ref.
$CuCr_{0.95}Mg_{0.05}O_2$	Sputtering	600	0.045	30	250	[6]
$CuCr_{0.95}Mg_{0.05}O_2$	PLD	500	0.1	60	100	[8]
		600	0.5	60	100	
$CuCr_{0.93}Mg_{0.07}O_2$	Splay Pyrolysis, Ar annealing	800	1.0	80	155	[11]
$CuCr_{0.95}Mg_{0.05}O_2$	Sol–gel, Ar annealing	600	16	21	210	[9]
		700	210	32	200	
$CuCr_{0.95}Mg_{0.05}O_2$	CSD, Two-step annealing	500	3.55	50	197	This work
		600	0.32	70	195	
		700	6.92	70	195	

same sequence have nearly identical average thicknesses, $d \sim 195$ nm. The transmittance of $CuCrO_2$:Mg thin films yielded above 50% in the visible region and increased with increases in sintering temperature due to improvement in the crystallinity. All samples showed distinct drops in the optical transmittance beyond a threshold wave length, indicating the emergence of a well-formed optical band gap due to the delafossite semiconductor phase. The inset of Fig. 4 shows the absorption edge of $CuCrO_2$:Mg thin films. The direct band gap of $CuCrO_2$:Mg thin films sintered at 500, 600 and 700 °C by two-step annealing was estimated as 3.09–3.10 eV. These values were closely matched with the reported values for undoped bulk $CuCrO_2$ [15]. The $CuCrO_2$:Mg thin films sintered at 800 °C showed a blue-shifted direct band gap, as 3.16 eV was related to an improved degree of crystallization of the films.

4. Conclusions

Transparent *p*-type $CuCrO_2$:Mg wide gap oxide semiconductor thin films with delafossite structure were successfully prepared on glass substrate by chemical solution deposition with a two-step annealing method. Single-phase delafossite $CuCrO_2$ structures were obtained by subsequent two-step annealing at 400 °C in 5% forming gas ambient, followed by a rise to sintering temperature in a nitrogen atmosphere. Two-step annealing effectively reduced Cu(II) ion to Cu(I) in the forming gas annealing step and inhibited the formation of spinel-type $CuCr_2O_4$, thus allowing pure $CuCrO_2$ to form during the subsequent nitrogen gas sintering step at 500 °C.

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