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Characterization of crednerite-$Cu_{1.1}Mn_{0.9}O_2$ films prepared using sol–gel processing

Hong-Ying Chen*, Da-Je Hsu

Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, 415 Chien Kung Road, Kaohsiung 807, Taiwan, ROC

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ABSTRACT

In this study, pure crednerite-$Cu_{1.1}Mn_{0.9}O_2$ films were deposited onto quartz substrates using a sol–gel processing and a two-step annealing process. The sol–gel-derived films were annealed at 500 °C for 1 h in air and post-annealed at 600–700 °C for 2 h in N_2. X-ray diffraction patterns showed that the films were CuO and $Cu_xMn_{3-x}O_4$ phases in air annealing. When the films were post-annealed above 600 °C in N_2, a pure $CuMnO_2$ phase with the monoclinic crednerite structure (space group: C2/m) was obtained. The lattice parameters of the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ films where a = 0.5579–0.5587 nm, b = 0.2878–0.2881 nm, c = 0.5880–0.5891 nm, and β = 104.16–104.34° and were agreement with the literature reports. The binding energies of Cu-2p of the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ films were 932.3 ± 0.2 eV and 952.3 ± 0.2 eV to represent the monovalent Cu in the films. Additionally, the binding energies of Mn-3p of the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ films were 47.5 ± 0.2 eV, 48.2 ± 0.2 eV, and 50.0 ± 0.2 eV and revealed coexistence of +2, +3, and +4 valences in the films. The cation distributions of the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ films prepared using post-annealing at 650 °C and 700 °C were $Cu^{+}{}_{1.1}[Mn^{4+}{}_{0.25}Mn^{3+}{}_{0.51}Mn^{2+}{}_{0.24}]_{0.9}O_2$ and $Cu^{+}{}_{1.1}[Mn^{4+}{}_{0.24}Mn^{3+}{}_{0.52}Mn^{2+}{}_{0.24}]_{0.9}O_2$, respectively. Two optical bandgaps of the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ films at 4.5–4.0 eV and 3.5–3.0 eV were observed. The electrical conductivities of the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ films were 1.20×10^{-5}–2.50×10^{-5} S cm^{-1}. Moreover, the activation energies for the carrier conduction were 0.20–0.30 eV. Hence, our results demonstrate that sol–gel processing is a feasible preparation method for crednerite-$CuMnO_2$ films.

1. Introduction

The crednerite-$CuMnO_2$ is a member of ternary Cu-based oxides family. Crednerite-$CuMnO_2$ exhibits the $R\bar{3}m$ symmetry above 950 °C [1], in which Mn^{3+} ions occupy octahedral sites. However, the crednerite-$CuMnO_2$ becomes a monoclinic distortion (space group: C2/m) due to the Jahn–Teller effect, which decreases cell symmetry at room temperature [2]. The potential application of the crednerite-$CuMnO_2$ is served as a novel hydrogen photoevolution catalyst [3]. Moreover, the crednerite-$CuMnO_2$ is also used as a three-way catalyst and is proposed for the removal of air pollutants, such as carbon monoxide and nitrous oxide from exhaust gas [4].

However, the reported crednerite-$CuMnO_2$ phase exists in a narrow composition range [2,5] that leads to challengeable preparations for the pure crednerite-$CuMnO_2$ phase. Moreover, investigations in the physical properties of the crednerite-$CuMnO_2$ films are little examined. Few reports have addressed the preparation of pure crednerite-$CuMnO_2$ powder or thin films [2–4,6–8]. Crednerite-$CuMnO_2$ powder is synthesized from solid-state reaction [2] and ionic-exchange reaction [6]. However, the deposition of crednerite-$CuMnO_2$ films is little reported [7,8]. Hiraga et al. [7,8] have used pulsed laser deposition (PLD) to prepare crednerite-$CuMnO_2$ films on $MgAl_2O_4$ substrates because of a small lattice distortion between substrate and thin film. They found that optical absorption curve for crednerite-$CuMnO_2$ films at 4.5 eV, 3.7 eV, and 3.0 eV, respectively. The peak was at 4.5 eV and was assigned to an excitation from the valence band to the conduction band. Conversely, the peaks at 3.7 eV and 3.0 eV are attributed to the charge transfer excitation from valence band to Mn-3d orbital as caused by the Jahn–Teller effect.

Nevertheless, other deposition techniques have not been reported for the preparation of the crednerite-$CuMnO_2$ films. Hence, this paper attempts to deposit crednerite-$CuMnO_2$ films on quartz substrate using sol–gel processing from our preparation of $CuCrO_2$ and $CuFeO_2$ films with delafossite structure using sol–gel processing with two-step annealing [9–11].

2. Experimental details

According to a previously published Cu–Mn–O phase diagram [2,5], the pure crednerite-$CuMnO_2$ phase is stabilized in

* Corresponding author. Tel.: +886 7 3814526x5130; fax: +886 7 3830674.
E-mail address: hychen@cc.kuas.edu.tw (H.-Y. Chen).

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$Cu_{1+x}Mn_{1-x}O_2$ with $0.1 \le x \le 0.13$ [2]. Therefore, the stoichiometry of Cu:Mn = 1.1:0.9 was selected for this study and is in the stable phase range of the crednerite-$CuMnO_2$ phase. This stoichiometry corresponds to the chemical composition of the films with the $Cu_{1.1}Mn_{0.9}O_2$. Copper acetate (0.011 mol, $Cu(CH_3COO)_2{\cdot}H_2O$, purity 98%+, Showa, Japan) and manganese acetate (0.009 mol, $Mn(CH_3COO)_3{\cdot}4H_2O$, purity 99%+, Showa, Japan) were dissolved in 30 mL of ethanol before 5.0 g of triethanolamine (purity 99%+, Tedia, USA) was added to the solution. This precursor was then spin-coated onto quartz substrates at 2000 rpm for 15 s using a spin coater (WS-400A-6NPP/LITE, Laurell Technology Corporation). Next, these specimens were annealed at 500 °C in air for 1 h at a ramp rate of 5 °C/min and cooled to room temperature at a cooling rate of 5 °C/min in a muffle furnace. After air annealing, the specimens were post-annealed between 600 °C and 700 °C in flowing nitrogen (purity 99.995%) for 2 h at a ramp rate of 5 °C/min and cooled to room temperature at a cooling rate of 5 °C/min in a tube furnace to obtain the pure crednerite-$CuMnO_2$ phase. The flow rate of the nitrogen was 200 sccm throughout this study.

The crystal structures of the films were examined using a GIXRD (Bruker D8 Discover) with a Cu K_α (λ = 0.154 nm) excitation source by an incidence angle of 1°. The operating voltage and current were 40 kV and 40 mA, respectively. The scan rate was 4°/min, and the collected interval was 0.01° (2θ). The lattice parameters of the films were refined using the TOPAS software. XPS was performed using an ULVAC PHI-5000 spectrometer with the Al K_α ($h\nu$ = 1486.6 eV) exciting X-ray source. The surface was sputter-cleaned using an Ar ion gun operated at 3 keV for 2 min before the measurement. The spectra of Cu-2p, Mn-3p, and O-1s were obtained at an energy interval of 0.2 eV per step. All spectra were calibrated according to the C-1s peak at 284.8 eV. The XPS spectra were fitted using a nonlinear least squares fit with a Gaussian/Lorentzian peak shape (G/L mixing ratio = 0.3) and the background was subtracted prior to each fitting routine. The morphology and thickness of the films were examined using an FE-SEM (JEOL JSM-6700F) operated at 3 kV. Optical properties, such as the transmission and absorption of films, were measured using an UV–vis spectrometer (Perkin Elmer Lambda 35) at a range of 190–1100 nm. The electrical resistivities of the films were measured using a standard four-point probe station with a power supply (PSP-603, GW Instek, Taiwan) and an electrometer (R8340, Advantest, Japan).

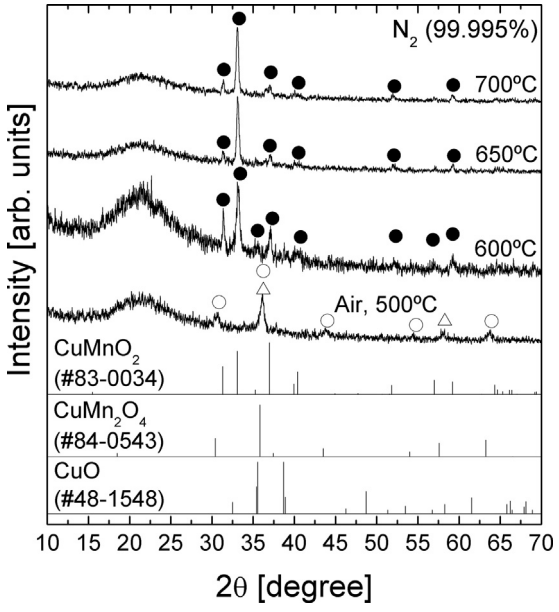

Fig. 1. GIXRD pattern of sol–gel-derived specimens annealed in air at 500 °C and post-annealed in N_2 between 600 °C and 700 °C. (●: $CuMnO_2$, △: CuO, ○: $Cu_xMn_{3-x}O_4$). The broadening peak observed at $2\theta \sim 20°$ is attributed to the quartz substrate.

3. Results and discussion

3.1. GIXRD analysis

Fig. 1 shows the GIXRD results of sol–gel-derived Cu–Mn–O films as a function of the annealing temperature. This figure shows that the diffraction peaks match $CuMn_2O_4$ (JCPDS #84-0543) and CuO (JCPDS #48-1548) in specimens annealed at 500 °C in air. However, the diffracted peaks have slightly deviated from the $CuMn_2O_4$ (JCPDS #84-0543), which were ascribed as $Cu_xMn_{3-x}O_4$ phase as caused by the Jahn–Teller distortion of Mn^{3+} [2,12] and the mass conservation of Mn cation (Cu: Mn = 1.1:0.9). When the films were post-annealed in the N_2 at 600–700 °C, the single $CuMnO_2$ phase (JCPDS #83-0034) with the crednerite crystal structure (space

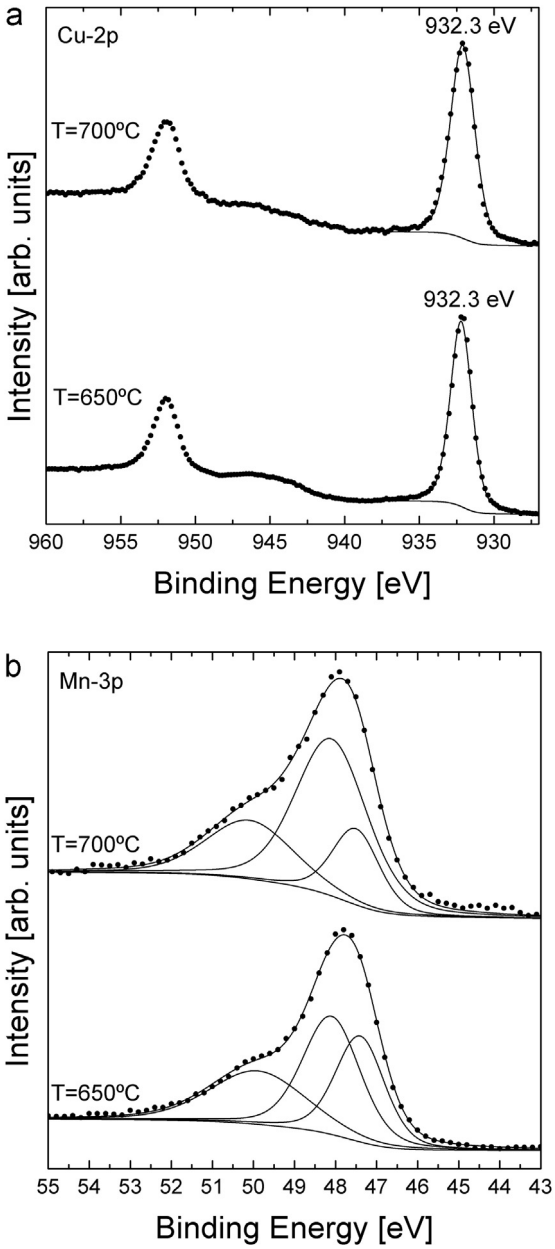

Fig. 2. XPS spectrum of (a) Cu-2p and (b) Mn-3p for the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ films prepared use of the post-annealing at 650 °C and 700 °C.