Applied Surface Science 273 (2013) 324–329

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Characterization of transparent conductive delafossite-$CuCr_{1-x}O_2$ films

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ARTICLE INFO

Article history:
Received 16 August 2012
Received in revised form 22 January 2013
Accepted 11 February 2013
Available online 18 February 2013

Keywords:
Delafossite
$CuCrO_2$
p-type
Sol–gel processes
Thin films
Stoichiometry

ABSTRACT

In this study, the $CuCr_{1-x}O_2$ films with $x = 0.00–0.25$ were prepared on a quartz substrate by sol–gel processing. The films were first deposited onto a quartz substrate by spin-coating. The specimens were annealed at 500 °C in air for 1 h and post-annealed in N_2 at 700 °C for 2 h. As the films were post-annealed in N_2, a pure delafossite-$CuCrO_2$ phase appeared in the $CuCr_{1-x}O_2$ films below $x = 0.20$. However, an additional CuO phase appeared at $x = 0.25$. The pure delafossite-$CuCrO_2$ phase can exist within $x \leq 0.20$ in $CuCr_{1-x}O_2$ films. The binding energies of Cu-$2p_{3/2}$ and Cr-$2p_{3/2}$ in the $CuCr_{1-x}O_2$ films with the pure delafossite-$CuCrO_2$ phase were 932.1 ± 0.2 eV and 576.0 ± 0.2 eV, respectively. The surface exhibited elongated grain features when the pure delafossite-$CuCrO_2$ phase was present in the $CuCr_{1-x}O_2$ films. The maximum transmittance of the $CuCr_{1-x}O_2$ films with the pure delafossite-$CuCrO_2$ phase was approximately 80%, which moved toward the visible region with the increasing x-value. The film absorption edges were observed at 400 nm, which were sharper with the increasing x-value. The optical bandgaps of $CuCr_{1-x}O_2$ films with the pure delafossite-$CuCrO_2$ phase were approximately 3.0 eV. The electrical conductivity of $CuCr_{1-x}O_2$ films with the pure delafossite-$CuCrO_2$ phase was 1.1×10^{-3} S cm^{-1} ($x = 0.00$), and increased to 0.16 S cm^{-1} ($x = 0.20$). The corresponding carrier concentration of $CuCr_{1-x}O_2$ films with the pure delafossite-$CuCrO_2$ phase was 2.8×10^{14} cm^{-3} ($x = 0.00$), and markedly increased to 1.8×10^{16} cm^{-3} ($x = 0.20$). The Cr-deficient condition in delafossite-$CuCrO_2$ films enhances film electrical conductivity and carrier concentration, but retains the film's high-visible transparency.

1. Introduction

Delafossites are p-type wide-bandgap oxide semiconductors that have recently become attractive because of their optoelectronic applications [1–3]. Wide-bandgap oxide semiconductors can be used for transparent conducting oxides (TCOs) that possess electrical conductivity and optical transparency in a single material [1]. TCOs have numerous potential applications, including solar cells, flat panel displays, electromagnetic shielding devices, light-emitting diodes, and transparent heat sources. Currently, the most popular wide-bandgap TCOs, such as ZnO, In_2O_3, and SnO_2, exhibit n-type characteristics; other p-type wide-bandgap TCOs are not well established, and have not been examined until recently [1–3]. Among the Cu-based delafossites, $CuCrO_2$ has higher electrical conductivity than the others [1].

Different thin-film deposition techniques have been employed for delafossite materials deposition since the successful preparation of p-type $CuAlO_2$ films [3]. $CuCrO_2$ films can be deposited using thin-film deposition techniques such as pulsed laser deposition [4–8], sputtering [9,10], chemical vapor deposition [11–13], and the sol–gel method [14–16]. However, the vacuum-based processes are complex and time consuming. By contrast, the chemical solution method of preparing the TCOs films has numerous advantages, including low-cost, easy set-up, large-area coating, and mass production. Previous research has shown the sol–gel method to be a powerful technique for growing delafossite thin films [14–16]. In particular, sol–gel processing can easily manipulate film stoichiometry.

A major concern issue in p-type wide-bandgap delafossite films is their much lower electrical conductivities compared to the n-type. Therefore, improving film electrical conductivity is necessary. Cation doping has been documented to improve delafossite conductivity [8,9,12,17,18], but it reduces optical transparency. Mg-doped $CuCrO_2$ films have a conductivity of 220 S cm^{-1}, but film optical transparency has a transmittance of 30% in the visual region [8]. Varying film stoichiometry enhances p-type conductivity because delafossite stoichiometry may change the defect chemistry that plays an important role in the conductivity of the structure [18–21]. Ingram et al. [18,19] showed the significant effect of Cu/Al stoichiometry on $CuAlO_2$ conductivity. Ashmore and Cann [20] prepared non-stoichiometric Cu_xGaO_2 ($x = 1.05–0.96$) polycrystalline ceramics using solid-state reaction methods, and

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http://dx.doi.org/10.1016/j.apsusc.2013.02.038

found that both the conductivity and the activation energy do not vary with the Cu content of Cu_xGaO_2.

No research has focused on Cr-stoichiometry in delafossite-$CuCrO_2$ films. This study reports on $CuCrO_2$ films with a Cr-deficient condition prepared by sol–gel processing. The $CuCr_{1-x}O_2$ film microstructure was characterized by grazing-incidence X-ray diffraction (GIXRD), X-ray photoelectron spectroscopy (XPS), and field-emission scanning electron microscope (FE-SEM). The optical properties of $CuCr_{1-x}O_2$ films were measured using an ultraviolet-visible (UV-Vis) spectrometer, and film electrical properties were investigated using the Hall-effect measurement. We also discuss the possible conductivity mechanism of $CuCr_{1-x}O_2$ films related to defect.

2. Experimental details

The $CuCr_{1-x}O_2$ films on a quartz substrate were prepared by spin-coating and two-step annealing. Copper(II) acetate (0.02 mol, purity 98%, Showa, Japan) and chromium(III) acetate (0.012–0.02 mol, EP grade, Showa, Japan) were first dissolved in 80 mL ethanol, and 0.03 mol triethanolamine (purity 95%+, Tedia, USA) was then added to the solution. This precursor, with the desired stoichiometric ratio, was then spin coated onto quartz substrates at 1000 rpm for 15 s. The specimens were then annealed at 500 °C in air for 1 h at a ramp rate of 5 °C/min before the next cycle. Three cycles were performed in this study. The specimens were post-annealed at 700 °C in flowing nitrogen gas (purity 99.9%) for 2 h at a ramp rate of 5 °C/min.

A Bruker D8 Discover SSS X-ray diffractometer operating with Cu-Kα radiation (λ = 0.154 nm) at 40 kV and 40 mA was used to determine changes in the crystal structure. The operating mode was a grazing-incidence with an incidence angle of 1° and a sample step size of 0.01° within the range of 2θ = 10–70°. XPS was performed using a Physical Electronics ESCA PHI 1600 spectrometer equipped with an Omni Focus III lens. The exciting X-ray source for XPS was Mg K_α ($h\nu$ = 1253.6 eV). Prior to the measurement, the surface was sputter-cleaned using an Ar ion gun operated at 3 keV for 2 min. The Cu-2p, Cr-2p, and O-1s spectra were obtained at an energy interval of 0.2 eV per step. All spectra were calibrated according to the C-1s peak at 284.6 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 film's surface morphology was analyzed using FE-SEM (JEOL JSM-6700F). Optical properties were measured using a Perkin-Elmer Lambda 35 UV-Vis spectrometer. The electrical conductivity, carrier type, and carrier concentration of the $CuCr_{1-x}O_2$ films were measured using a standard Hall-effect measurement.

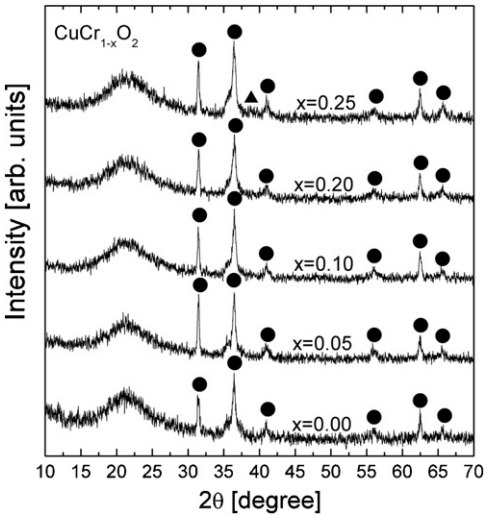

Fig. 1. X-ray diffraction patterns of $CuCr_{1-x}O_2$ films with x = 0.00–0.25 (▲:CuO and •:$CuCrO_2$).

3. Results and discussion

3.1. GIXRD analysis

GIXRD analysis was performed on the $CuCr_{1-x}O_2$ films with $x \leq 0.25$, as shown in Fig. 1. Strong delafossite-$CuCrO_2$ (R3m, JCPDS #89-6744) diffraction peaks are observable in the pattern, which are (0 0 6), (0 1 2), (1 0 4), (0 1 8), (1 1 0), and (0 0 2), respectively. The pure $CuCrO_2$ phase is observable in the $CuCr_{1-x}O_2$ films below x = 0.2. An additional CuO phase exist at x > 0.2 in the $CuCr_{1-x}O_2$ films. The values of the full width at half-maximum (FWHM) of the diffraction peaks are narrow, indicating good crystallinity in the $CuCr_{1-x}O_2$ films. This suggests that the pure delafossite-$CuCrO_2$ phase can be stabilized between x = 0.00 and x = 0.20 in the $CuCr_{1-x}O_2$ films. Hence, we used the (1 0 4) diffraction peak to calculate the film's crystallinity. The crystallinity of $CuCr_{1-x}O_2$ films was 18 nm (x = 0.00), 20 nm (x = 0.05), 18 nm (x = 0.10), and 19 nm

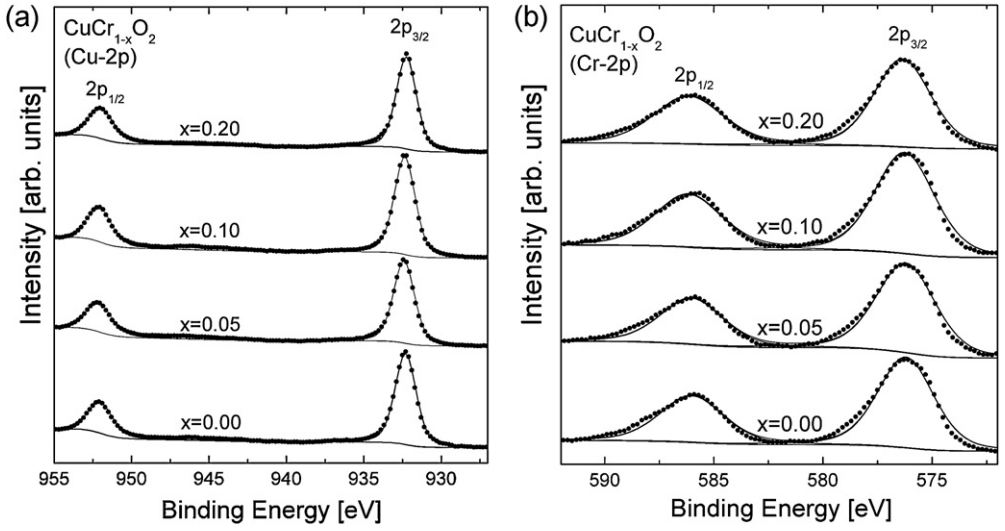

Fig. 2. X-ray photoelectron spectra of $CuCr_{1-x}O_2$ films with x = 0.00–0.20: (a) Cu-2p and (b) Cr-2p.