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Effect of Sn substitution on the structure, morphology and photoelectricity properties of high *c*-axis oriented $CuFe_{1-x}Sn_xO_2$ thin film

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ABSTRACT

Epitaxial thin films of $CuFe_{1-x}Sn_xO_2$ (x = 0.00, 0.01, 0.03, 0.05, 0.07), a transparent oxide semiconductor with delafossite structure, were grow on Al_2O_3 (0001) substrate by sol–gel method, The X-ray diffraction patterns revealed that the $CuFeO_2$ film annealed at 500 °C in air was mainly composed of amorphous phase, and after post-annealed at 900 °C in N_2, single phase $CuFe_{1-x}Sn_xO_2$ films with high *c*-axis oriented were obtained. The Raman spectrum confirmed the delafossite structure of the films. The binding energy of Cu-$2p_{3/2}$, Fe-$2p_{3/2}$ and Sn-$3d_{5/2}$ were 932 eV, 711.3 eV and 486.2 eV in $CuFe_{1-x}Sn_xO_2$ films. The chemical composition of the films was close to its stoichiometry, which was determined by X-ray photoelectron spectroscopy. The films show high transmittance around 45–78% in the visible band and 78–95% in the near infrared spectral region, while the energy gaps for direct allowed transition were estimated as 3.5 ± 0.02 eV. The p-type characteristics of $CuFe_{1-x}Sn_xO_2$ thin films were determined by positive Hall coefficients. The resistivity of the film was 36.83 Ω cm for $CuFeO_2$ film at room temperature, significantly decreased to 1.043 Ω cm after substituting Sn^{2+} for Fe^{3+}. The resistivity showed a decrease at the beginning and increased with the growing of Sn ion doping ratio. These results demonstrate that the high *c*-axis oriented $CuFe_{1-x}Sn_xO_2$ films can be the very promising p-type transparent conductive thin films.

1. Introduction

In the past decades, transparent conducting oxides (TCOs) have attracted considerable attention due to their wide optoelectronic applications in industry [1–5]. Some n-type oxides, such as Sn-doped In_2O_3 (ITO), Al-doped SnO_2 [6] and Al-doped ZnO, have been practically used as transparent electrodes in optoelectronic devices. They are promising in the fields of flat panel displays, touch panels, solar cells and light emitting diode, owing to high optical transparency in the visible region (>80%) and high electrical conductivity (>1000 S/cm). However, as one of the key issues, the development of p-type TCOs limits the performance of some electronic devices, such as transparent complementary metal-oxide-semiconductor thin-film transistor and full transparent pn-junction. Thus, the preparation of high quality p-type TCO thin films becomes an urgent issue.

Since the $CuAlO_2$ film was first fabricated by Kawazoe in 1997 [7], the interest in Cu^+-based delafossite family as stable p-type wideband transparent semiconductor has been increased. After that, several p-type TCOs have been synthesized, including $CuAlO_2$ [8–12], $CuCrO_2$ [13–16], $CuGaO_2$ [17] and $CuMnO_2$ [18]. Delafossite oxides $CuAO_2$ (A is trivalent cations) are known as one of the most important wide-bandgap p-type semiconductors. They have high transmittance in the visible region compared to n-type transparent conductive oxides, and they can generate electricity by the absorption of ultraviolet part of radiation. However, the resistivity of delafossite oxide thin films is much higher than that of n-type TCOs. Thus, several approaches have been proposed to reduce the resistance of the p-type TCO thin films, including metal ions doping and the post-annealing process.

$CuFeO_2$ is a kind of delafossite oxides, and it has relatively high conductivity compared to other delafossite materials. Up to now, several methods have been reported to prepare $CuFeO_2$ thin films, such as pulsed laser deposition (PLD) [19], four mirror optical floating zone furnace (Crystal Systems Corp) [20], and chemical solution method [21,22]. $CuFeO_2$ thin film has indeed become a multi-functional p-type semiconductor. However, the transmittance and resistivity of the reported polycrystalline $CuFeO_2$ thin films are still much lower than those of n-type TCOs. Therefore, for the first time, we report the synthesis of high *c*-axis orientated Sn-doped $CuFeO_2$ thin films by sol–gel method and post-annealing

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technique. Meantime, the crystal structure, morphology and photoelectricity properties of the films are investigated systematically.

2. Experimental details

Single phase with *c*-axis oriented delafossite-oxide $CuFe_{1-x}Sn_xO_2$ (x = 0.00, 0.01, 0.03, 0.05, 0.07) thin films were prepared by a simple sol–gel method. Specifically, copper acetate (1.997 g, 0.01 mol) and iron nitrate (4.03 g, 0.01 mol) were dissolved in 30 ml of anhydrous ethanol, and 5 ml of triethanolamine was added to the solution as the thickening agent. The solution stirred on a magnetic stirrer for 3 h at first, and then stannous chloride with the desired stoichiometric ratio was dissolved in the precursor solution. This solution was stirred for another 10 h at 45 °C in order to get a fully mixed precursor. The precursor solution, with different doping ratio, was spin-coated onto the Al_2O_3 (0001) substrates at spin speed of 4000 rpm for 15 s. The obtained films were dried in a vacuum oven at 200 °C for 20 min in order to remove the organic solvent. This process was repeated for six times to get a reasonable film thickness. The $CuFeO_2$ films were annealed at 500 °C in air at first, then post-annealed in N_2 at 700, 800 and 900 °C, respectively. The $CuFe_{1-x}Sn_xO_2$ specimens were annealed at 500 °C in air and post-annealed in a tube type annealing furnace at 900 °C in flowing N_2 gas (100 ml/min) for 1 h at a ramp rate of 10 °C/min.

The crystal structure was analyzed using conventional X-ray diffractometer (XRD) technique with a Bruker D8 Advance X, Pert diffractometer (Cu-Ka: λ = 1.540 Å). The scanning speed was 4°/min from 10° to 70°. The Raman spectra was recorded at room temperature with the 514.5 nm line of an Ar^+ laser, excited from a Spectra Physics krypton ion laser. X-ray photoelectron spectroscopy (XPS, ESCALAB 250) was used to determine the chemical composition of thin films and valences of the elements. The surface morphology of the films was examined by a JSM-7500F field emission scanning electron microscope (FE-SEM). The optical transmission spectra were recorded at room temperature by using a UV–VIS–NIR spectrophotometer (Shimazu UV-3600PC) in the wavelength range of 250–2500 nm. The electrical properties of the thin films were determined using a Hall-effect measurement system (ACCENT HL55OOPC) at room temperature.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the XRD results of annealed sol–gel-derived $CuFe_{1-x}Sn_xO_2$ thin films as a function of the annealing temperature and the doping concentration. As shown in Fig. 1(a), the film annealed at 500 °C in air exhibits no significant peak in the XRD pattern, the film is amorphous. Then, after post-annealed at 700, 800 and 900 °C in N_2 for 1 h, the $CuFeO_2$ peaks gradually appear. As the sintering temperature growing, the diffraction intensities of the $CuFeO_2$ peaks increase. The diffraction peaks are indexed as (003), (006), (012), (009) and (0012) which are *c*-axis oriented belong to delafossite-$CuFeO_2$ phase (JCPDS#75-2146). The full width at half-maximum is measured from the rocking curve through the (006) peak, approximately equal to 0.199°, suggests the $CuFeO_2$ film to be good epitaxial quality. The result indicates that the annealing ambience greatly influences the crystallinity degree and phase composition of the film. The d-spacing of the (006) and (009) diffraction peaks indicate that lattice parameters of a = 3.036 Å and c = 17.158 Å for $CuFeO_2$ film in this study are in accordance with bulk ceramic $CuFeO_2$ which has lattice parameters of a = 3.035 Å and c = 17.166 Å (JCPDS# 75-2146). Fig. 1(b) shows the XRD results of the $CuFe_{1-x}Sn_xO_2$ (x = 0.00, 0.01, 0.03, 0.05, 0.07) thin films post-annealed at 900 °C in N_2. Only peaks including (003), (006), (012), (009) and (0012) belonging to $CuFeO_2$ can be observed. This *c*-axis oriented growth of the films suggests that the surface energy of the (001) plane could be the lowest in the delafossite-structured crystal [23]. However, the selection of crystallite orientation for $CuFeO_2$ is complex, which depends heavily on the fabrication method and annealing treatment. In the $CuAO_2$ ('A' is the monovalent cations) phase diagram, the structure of $CuAO_2$ is stable at lower O_2 partial pressure with temperature lower than 1000 °C [24]. Too much oxygen could make partial $CuFeO_2$ decompose into $CuFe_2O_4$ and CuO. To avoid the oxidation, the reaction of $CuAO_2$ and O_2 can be inhibited by using a protective atmosphere,

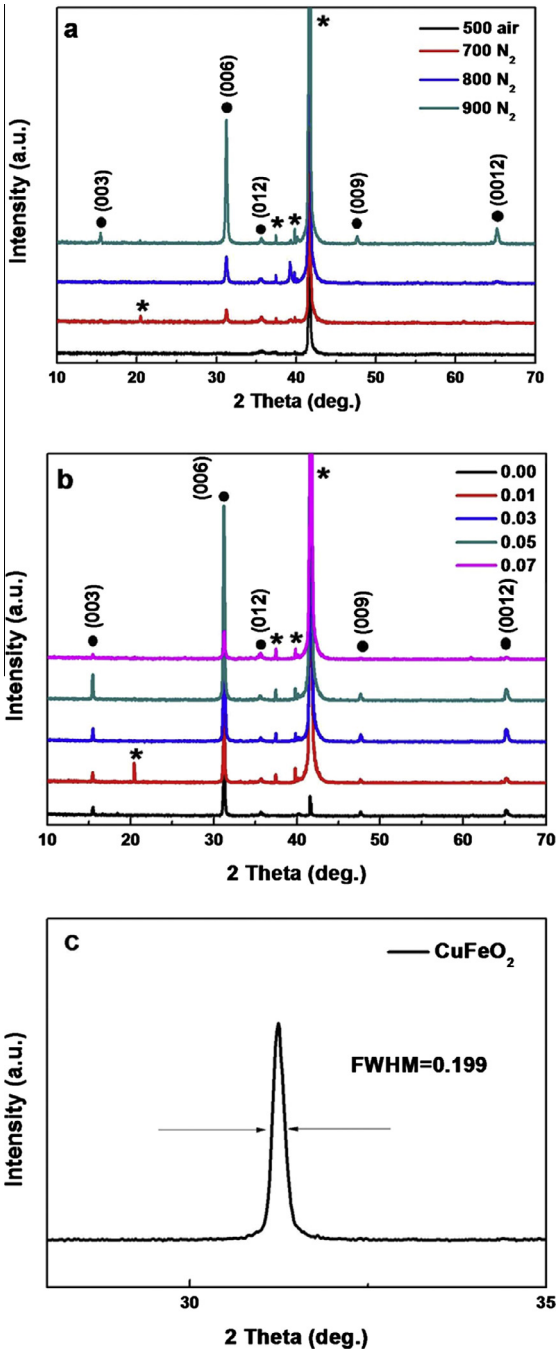

Fig. 1. XRD pattern of sol–gel derived films: (a) $CuFeO_2$ film annealed at 500 °C in air, post-annealed at 700, 800 and 900 °C in N_2, (b) $CuFe_{1-x}Sn_xO_2$ (x = 0.00, 0.01, 0.03, 0.05, 0.07) films post-annealed at 900 °C in N_2, (c) Enlarged XRD patterns of $CuFe_{1-x}Sn_xO_2$ (x = 0.00, 0.01, 0.03, 0.05, 0.07) films at (006) peaks. (●: $CuFeO_2$(R-3 m) and ∗: sapphire substrate (0001)).

such as N_2, similar results have been reported by other researchers [25,26]. The intensity of (003) and (006) peaks decreases with the increasing of Sn content. It means that the *c*-oriented becomes weaker with increasing Sn content. No impurity phase is observed even when the doping ratio rises to 0.07. The average crystalline size of the films can be calculated using the Scherrer formula [27]

$$Dhkl = k\lambda/B\cos\theta \quad (1)$$

where k is a constant (~0.9), $Dhkl$ is the average crystalline size, B is the full width at half maximum (FWHM), λ is the wavelength of