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Properties of fluorine and tin co-doped ZnO thin films deposited by sol–gel method

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ABSTRACT

Highly transparent and conducting fluorine (F) and tin (Sn) co-doped ZnO (FTZO) thin films were deposited on glass substrates by the sol–gel processing. The structure and morphology of the films are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) with various F doping concentrations. SEM images showed that the hexagonal ZnO crystals were well-arranged on the glass substrates and the HRTEM images indicated that the individual nanocrystals are highly oriented and exhibited a perfect lattice structure. Owing to its high carrier concentration and mobility, as well as good crystal quality, a minimum resistivity of 1×10^{-3} -Ω cm was obtained from the FTZO thin film with 3% F doping, and the average optical transmittance in the entire visible wavelength region was higher than 90%. The X-ray photoelectron spectroscopy (XPS) study confirmed the substitution of Zn^{2+} by Sn ions and Room temperature photoluminescence (PL) observed for pure and FTZO thin films suggested the films exhibit a good crystallinity with a very low defect concentration.

1. Introduction

Transparent conducting oxide thin films have been widely applied as transparent electrodes for light-emitting diodes, flat-panel displays and solar cells [1–3]. In most cases, indium tin oxide (ITO) thin films deposited by direct current magnetron sputtering are in practical use. Recently, a variety of techniques have been introduced in order to improve the optical and electrical properties of ZnO based transparent conductive oxides (TCO) for its low cost, non–toxicity and high stability in H_2 plasma atmosphere [4,5].

In single-doped ZnO, F doped ZnO thin films (FZO) show comparable electrical and optical properties to those of the group III doped films and it is accepted that the low resistivity of FZO is mostly due to the high electron mobility in the material, which is attributed to the substitution of oxygen atoms by fluorine atoms and mainly perturbs the valence band, thereby leaving the conduction band relatively free from scattering [6]. Shinde et al. [7] reported a resistivity of 6.63×10^{-4} Ω cm, with mobility as high as 87.2 cm^2/V s, on films deposited at 400 °C with 15 at.% F doping and annealed in an atmospheric ambient for 2 h at 200 °C synthesized by chemical spray pyrolysis. Tsai et al. [8] reported the effects of annealing on the properties of F-doped films prepared by RF sputtered method from a ZnF_2 target and found that 500 °C vacuum annealing yielded a carrier concentration in the $10^{21}/cm^3$ range with mobility approximately 4.8 cm^2/V s and Bowen et al. [9] reported that ZnO containing 2 wt.% F, $\mu = 9.5$ cm^2/V s and $\rho = 1.3 \times 10^{-2}$ Ω cm. There are also some literatures describing the Sn doped ZnO thin films (TZO). Specially, the main reason for choosing tin as the dopant in ZnO is to enhance the electrical conductivity. When ZnO is Sn-doped, Sn^{4+} substitutes Zn^{2+} Site in the ZnO crystal structure resulting in two more free electrons to contribute to the electric conduction. Jung [10] reported that the green emission of ZnO could be enhanced by Sn doping and Tsay [11] found that Sn-doped ZnO thin films exhibited an average transmittance of 90%, and the minimum resistivity of 9.3×10^{-2} Ω cm can be achieved with 2% doping Sn concentration. Yung et al. [12] reported the effect of Sn doping on grain size, vibrational structure and optical properties of ZnO films deprived by sol–gel method. Therefore, F and Sn co-doping in ZnO thin film may further improve the conductivity or other properties of the thin films, which may be suitable for some electronic applications.

In this study, FTZO thin films have been fabricated on glass substrates by the sol–gel method and the effects of doping on the structural, morphological and optical properties of the films have been investigated.

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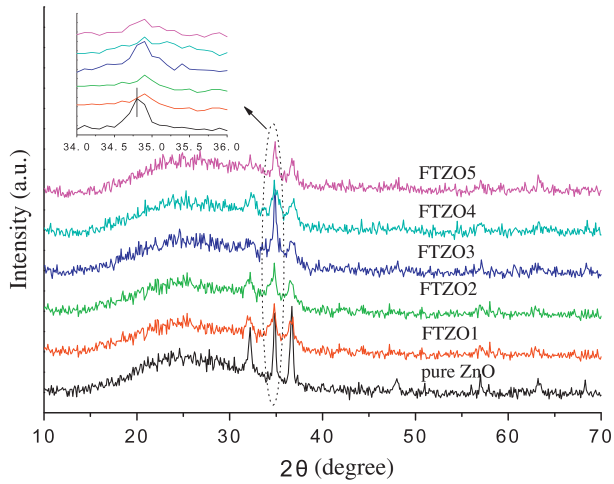

Fig. 1. XRD patterns of pure ZnO and FTZO thin films, and the enlarged image of the taken area marked by the frame with various F doping concentrations.

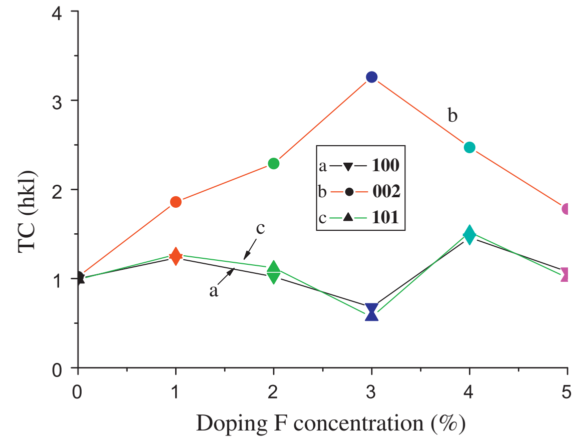

Fig. 2. *TC* values of the oriented plane of FTZO thin films with various F doping concentrations.

2. Experimental details

Pure and FTZO films were prepared by the sol–gel dip coating method. As a starting material and dopant source, Zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$], Ammonium fluoride ($NH_4F$) and tin tetrachloride pentahydrate ($SnCl_4{\cdot}5H_2O$) were used. 2-methoxyethanol ($C_3H_8O_2$) and monoethanolamine (MEA) were used as a solvent and stabilizer, respectively. The concentration of zinc acetate was 0.5 M and the ratios of MEA to [$Zn(CH_3COO)_2{\cdot}2H_2O$], ($NH_4F$) and ($SnCl_4{\cdot}5H_2O$) were maintained at 1:1. The molar ration of Sn/Zn was kept consistently at 2% and that of F/Zn was varied from 1% to 5%, and the co-doped films were named as FTZO1, FTZO2, FTZO3, FTZO4 and FTZO5, respectively, corresponding to the F doping concentration. Firstly, Zinc acetate dihydrate and tin tetrachloride pentahydrate were added to the solution which was stirred at 70 °C for 1 h and then NH_4F was added to the mixed solution. The resultant solution was stirred at 70 °C for 2 h to yield a clear and homogeneous solution. FTZO films were prepared on glass substrates by repeating dip coating, and each time after the deposition, the films were dried in air at 300 °C for 10 min. The coating procedure was repeated for six times in order to get a film thickness of approximately 400 nm, and finally the films were annealed at 500 °C for 1 h using a muffle furnace.

The crystallinity and phase purity of the films were examed by X-ray diffraction using a Rigaku–Ultima IIIXRD diffractometer (λ = 1.5405 Å). The surface morphology of the films and the cross-section film thickness were observed by using a Hitachi S-4800 field-emission scanning electron microscope (FE–SEM) and High Resolution Transmission Electron Microscopy (HRTEM) was taken out by using a JEM JEOL 2100 system. The chemical state of the dopants of co-doped thin films was investigated by X-ray photoelectron spectroscopy (XPS, ESCA LAB 220-XL). The optical properties were measured by UV–VIS spectroscopy (Hitachi U-2900), and the photoluminescence (PL) (He–Cd Laser, 325 nm). The carrier concentration (n) was determined by using a HL8800 Hall measurement system and a 4-point probe device (SZT-2A) used to measure the resistivity (ρ) of the thin films. The carrier mobility (μ) was evaluated from $\rho = 1/ne\mu$, being e the electron charge.

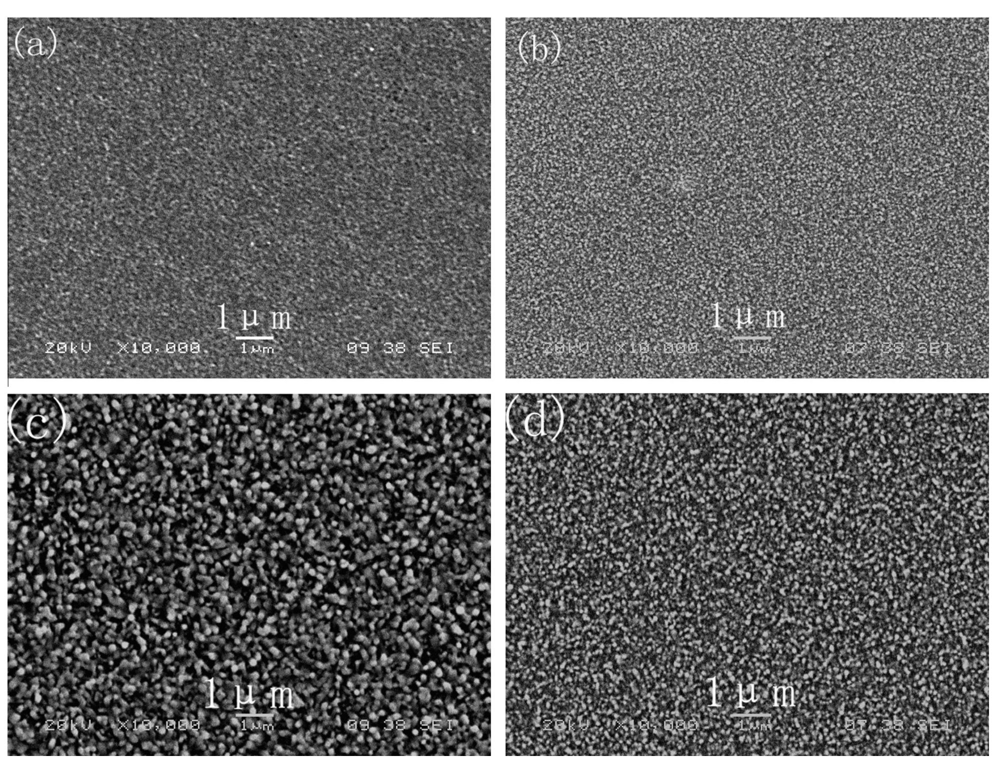

Fig. 3. SEM images of pure ZnO and FTZO thin films with various F doping concentrations: (a) pure ZnO, (b) 1% F, (c) 3% F, (d) 5% F.