Current Applied Physics 14 (2014) 850–855

Contents lists available at ScienceDirect

Current Applied Physics

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

Structural and electrical properties of fluorine-doped zinc tin oxide thin films prepared by radio-frequency magnetron sputtering

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ARTICLE INFO

Article history:
Received 30 December 2013
Received in revised form
6 March 2014
Accepted 24 March 2014
Available online 29 March 2014

Keywords:
Transparent conductive oxide
F doped ZTO
RF magnetron sputtering

ABSTRACT

Transparent and conductive thin films of fluorine doped zinc tin oxide (FZTO) were deposited on glass substrates by radio-frequency (RF) magnetron sputtering using a 30 wt% ZnO with 70 wt% SnO_2 ceramic targets. The F-doping was carried out by introducing a mixed gas of pure Ar, CF_4, and O_2 forming gas into the sputtering chamber while sputtering ZTO target. The effect of annealing temperature on the structural, electrical and optical performances of FZTO thin films has been studied. FZTO thin film annealed at 600 °C shows the decrease in resistivity 5.47×10^{-3} Ω cm, carrier concentration $\sim 10^{19}$ cm^{-3}, mobility ~ 20 cm^2 V^{-1} s^{-1} and an increase in optical band gap from 3.41 to 3.60 eV with increasing the annealing temperatures which is well explained by Burstein–Moss effect. The optical transmittance of FZTO films was higher than 80% in all specimens. Work function (ϕ) of the FZTO films increase from 3.80 eV to 4.10 eV through annealing and are largely dependent on the amounts of incorporated F. FZTO is a possible potential transparent conducting oxide (TCO) alternative for application in optoelectronics.

1. Introduction

Transparent conducting oxide (TCO) thin films, an important optoelectronic material, have been widely studied and applied for transparent and flexible device applications such as solar cells, flat panel displays, plasma display panels, touch panels, organic light emitting diode, and gas sensors due to their unique combined electrical and optical properties [1]. Different metal oxide semiconductors such as In_2O_3, SnO_2, ZnO, and TiO_2 have been extensively employed to fabricate TCO thin films [2]. The most common TCO consists of large band gap semiconducting metal oxides such as indium, tin, cadmium and zinc oxide doped with group III (Al [3–7], B [8], Ga [9–11]) or group VII (F [12], Cl [13]) elements to reduce their resistivity while retaining high transparency in the visible range ($\lambda = 380$–770 nm). Among these candidates indium tin oxide (ITO) is one of the most employed TCO because of its high conductivity, transparency, and the possibility to generate very flat films with good reproducibility [14]. However, due to the high cost of indium and its increasing demand in TCO, it is more important to identify an alternative material with low cost and similar properties [2]. ZnO is one of the best alternatives for indium tin oxide with its low cost and comparable photoelectric properties. But because of its low conductivity (energy band gap 3.3 eV) suitable dopants which can improve the electrical conductivity are needed. Zinc tin oxide (ZTO) thin film is one of the most promising materials due to the low cost of ZnO and SnO_2, low resistivity and high transparency. They have both the advantages of good thermal stability and mechanical strength of SnO_2 and good stability of ZnO under the reducing atmosphere [15]. Amorphous ZTO (a-ZTO) film has a smoother surface morphology and cleaner etched profile than those of the crystalline ITO films [16]. Fluorine can be a promising anion doping candidate with its ionic radius similar to that of oxygen ($F^- = 1.31$ Å, $O_2^- = 1.38$ Å) [17]. When fluorine substitutes zinc, a strong local perturbation to the conduction band leads to strong scattering of electrons and reduce their mobility. On the other hand, when fluorine substitutes for oxygen, the electronic perturbation is largely confined to the filled valence band and the scattering of conduction electrons is reduced leading to high electron mobility as well as low absorption. RF magnetron sputtering method is widely adopted because of its high deposition rate, good adhesion, low growth temperature, large area preparations and availability in different ambient. To the best of our knowledge, there

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http://dx.doi.org/10.1016/j.cap.2014.03.020
1567-1739/

is no report about fluorine doped zinc tin oxide (FZTO) thin films using RF sputtering which have been used for fabrication of TCO films.

In this study we report the deposition of highly transparent and conducting FZTO thin films on glass substrates by RF magnetron sputtering of ZTO ceramics target in gas mixtures contacting CF_4 and investigate the doping effect of F anion on the structural, electrical, and optical properties of FZTO films with the variations of annealing temperature.

2. Experimental

200 nm-thick FZTO thin films were prepared on glass substrates (Corning Eagle 2000) by radio frequency sputtering (rf, 13.56 MHz) of 2-in ZTO ceramic target composited with 30 wt% ZnO and 70 wt% SnO_2. All FZTO films were sputtered on to a 25 × 25 mm^2 glass substrate at a constant power of 100 W and a working pressure of 0.27 Pa. The F-doping was carried out by introducing a mixed gas of pure Ar, CF_4, and O_2 forming gas into the sputtering chamber while sputtering ZTO target. The substrate was ultrasonically precleaned in acetone, methanol and deionized water for 10 min in order to remove impurities on the substrate surface. For the uniformity of the FZTO films, the substrate was constantly rotated at a constant rate of 7 rpm during sputtering process. After deposition of FZTO films at room temperature, the FZTO films were annealed in vacuum for 10 min with the variations of temperature from 300 to 600 °C. Thickness of the films was measured using scanning electron microscopy (HR-LV NOVA-SEM, FEI). X-ray diffraction (XRD) analysis (Rigaku Dmax 2500/server) with CuKα radiation (wavelength = 1.5418 Å) was performed to investigate the crystallographic structure of FZTO thin films. Electrical resistivity, carrier concentration, and Hall mobility were characterized using Hall-effect measurement. Work functions of FZTO thin films were determined by the positions of the Fermi level measured from the tangent line extrapolation of the onset from the secondary electron cutoff peak in the ultraviolet photoelectron spectroscopy (UPS) (UPS, Kratos AXIS-NOVA) spectra. Photon energy of the UPS light source (He (I) resonance line) was $h\nu = 21.2$ eV and the energy of the band pass filter in the analyzer was fixed at 20 eV. Surface morphology of the FZTO films were examined using atomic force microscopy (Dimension 3100) as a function of annealing temperature. Optical transmittance of the films was measured using a UV–Visible spectrometer (Perkin Elmer UV/Vis spectrometer Lambda 18) in the wavelength range from 200 to 900 nm.

3. Results and discussion

3.1. Crystalline structural characterizations

Fig. 1(a) shows XRD spectra of the as-deposited FZTO thin films along with the samples annealed at four different temperatures of 300 °C, 400 °C, 500 °C, and 600 °C. Even after the as-deposited FZTO films were annealed from 300 to 500 °C, they still exhibit broad peaks indicating amorphous structure. However, it is noticeable that two new diffraction peaks for the FZTO annealed at 600 °C appear in XRD spectra at $2\Theta = 34.0°$ and 52.02° respectively corresponding to the (101) and (211) planes of SnO_2 [18]. This means the amorphous FZTO films are converted into polycrystalline rutile structure through vacuum annealing at 600 °C. Fig. 1(b) shows the XRD patterns of FZTO thin films with different fluorine contents (0–2 at.%) are plotted in 2Θ ranges 20°–80°. All the as-deposited FZTO films grown at room temperature are found to be amorphous because of the immiscibility of SnO_2 and ZnO.

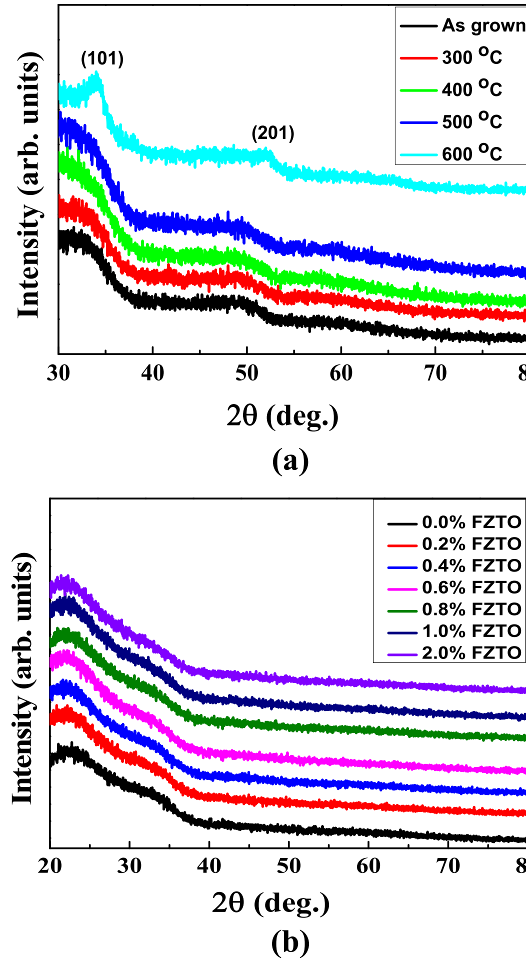

Fig. 1. (a) XRD patterns of FZTO thin films as deposited and annealed at various temperatures. (b) XRD patterns of fluorine contents (0–2.0 at.%) FZTO thin films deposited at room temperatures.

3.2. Electrical properties

Fig. 2 shows the electrical properties of FZTO thin films as deposited and annealed at various temperatures. The as-deposited thin film shows high sheet resistance $R_s = 2.26 \times 10^4$ Ω/sq and thus meaningful Hall data could not be obtained. However, it is clearly shown that the sheet resistance and resistivity (ρ) of the FZTO thin films were significantly reduced with increasing vacuum annealing

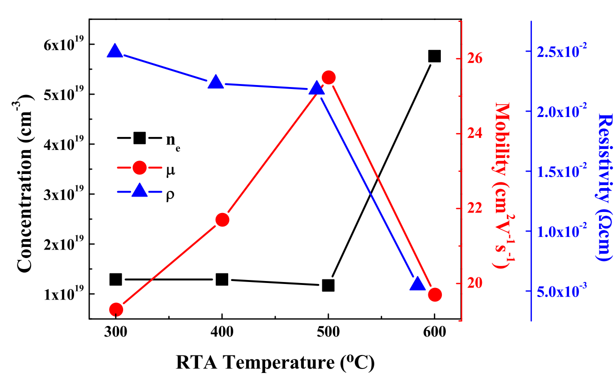

Fig. 2. Electrical properties of FZTO thin films as deposited and annealed at various temperatures.