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Structural, electrical, and optical properties of F-doped SnO or SnO_2 films prepared by RF reactive magnetron sputtering at different substrate temperatures and O_2 fluxes

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ABSTRACT

The effects of substrate temperature and O_2 flux on structural, electrical, and optical properties of the films prepared by RF reactive magnetron sputtering with SnF_2-Sn target have been investigated by X-ray diffraction (XRD), Hall effect measurements, optical transmission spectra, and photoluminescence (PL) spectra. It is found that F-doped SnO films are produced and exhibit amorphous structure at lower O_2 fluxes for substrate temperature of RT-300 °C, and window of O_2 flux for depositing the films is reduced as substrate temperature increases. F-doped SnO_2 (FTO) films are formed at higher O_2 fluxes, and they exhibit amorphous state at substrate temperature of RT but crystalline state at substrate temperature of 150 and 300 °C. Furthermore, increasing O_2 flux or substrate temperature can promote crystallinity and affect growth orientation for crystalline FTO films. Highly conductive FTO films can be obtained only at suitable O_2 fluxes and higher substrate temperatures (150 and 300 °C), at which the films keep crystalline SnO_2 structure along with high amount of oxygen vacancy (V_O). Increasing substrate temperature from 150 to 300 °C, the resistivity of FTO films cannot be further decreased due to the out-diffusion of *F* although the film crystallinity improves. Compared with F-doped SnO films, the average transmittance in visible light range and band gap (E_g) of FTO films obviously increase. The FTO films show similar shaped PL spectra that can be attributed to substitutional fluorine (F_O) and V_O defects in the films, and PL emission intensity increases with increasing O_2 flux or substrate temperature due to the improvement of film crystallinity. It is observed that the PL emission characteristics (shape and intensity) of F-doped SnO film are obviously different from FTO films and they have great changes as substrate temperature from RT to 150 °C, but corresponding mechanisms need to further clarify.

1. Introduction

The oxide of metallic tin includes tin dioxide (SnO_2) and tin monoxide (SnO). SnO_2 is a n-type semiconductor with a rutile-like tetragonal crystal structure and a wide band gap (E_g). It is of great interest in many technological applications [1,2], particularly in the field of gas sensors, transparent conducting electrodes, and oxidation catalyst. As transparent conducting electrodes, SnO_2 thin films with non-stoichiometry and/or impurities incorporation [3–8], such as SnO_{2-x}, SnO_2:Sb (ATO), and SnO_2:F (FTO), are usually used. Among impurity doped SnO_2 films, FTO films exhibit reasonable low-cost, superior stability in atmospheric conditions, outstanding chemical inertness, larger mechanical hardness, and better heat resistance. Thus, FTO films is a good alternative to In_2O_3:Sn (ITO) films which have been widely used as transparent conductive films in industry but have crisis of deficiency in supply of rare and expensive indium.

Several methods have been used for deposition of the FTO films, which include chemical vapour deposition (CVD) [9,10], sputtering [7,8], pulsed laser deposition (PLD) [11], spray pyrolysis [12,13] and sol-gel [14]. Sputtering method has several advantages over other methods such as low growth temperature, high deposition rate, and large area preparation in different growth ambiences.

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However, there are some problems in realizing fluorine doping into SnO_2 films by magnetron sputtering. For example, it has been found that preparation of highly dense SnF_2-SnO_2 target is difficult because of low melting point and boiling points as well as easily oxidization and hydrolyzation in damp air atmosphere for SnF_2 powders [15–17]; fluorine-contained gases will cause the greenhouse effect as for sputtering Sn target in an atmosphere containing fluorine (such as Ar/O_2/CF_4, Ar/O_2/CHF_3 or Ar/O_2/Freon) [7,8,18,19].

In this paper, FTO films were prepared by RF reactive magnetron sputtering. RF reactive sputtering can be defined as RF sputtering targets in the presence of chemically reactive gases. During RF reactive sputtering, pure metal, alloy or compound can be taken as the target, and O_2 or N_2 can be taken as the reactive gas. By varying the target composition and reactive gas, oxide (such as ZnO [20] and SnO_2 [21]), nitride (such as Zn_3N_2 [22]), or doped oxide (such as Al-doped ZnO [23] and Sn-doped In_2O_3 [24]) films have been synthesized with this technology. In order to realize fluorine doping into SnO_2 films in present study, the target of SnF_2-filled Sn-matrix composite was prepared and the target was sputtered in Ar+O_2 atmosphere. Because metallic Sn has high ductility and low melting point, SnF_2-Sn target with high density is easily prepared by pressing at high pressure and then sintering at low temperatures. Furthermore, this method also avoids the use of fluorine-contained gases.

On basis of the preparation of SnF_2-Sn target, the films were prepared by RF magnetron sputtering in Ar+O_2 atmosphere at substrate temperature of RT-300 °C, and their structure and transparent conductive properties were investigated as function of O_2 flux. In addition to transparent conductive properties, photoluminescence (PL) properties of the films were also investigated due to the fact that relatively little attention has been paid to the studies on PL properties of FTO films as compared to the ZnO-based films [12]. The results show that FTO film can be obtained only at higher O_2 fluxes for each substrate temperature although it is expected to prepare FTO films. Furthermore, highly transparent conductive FTO films can be obtained at suitable substrate temperatures and O_2 fluxes, and study on PL properties of FTO films will provide the reference for their further applications.

At lower O_2 fluxes, F-doped SnO films can be obtained. SnO is a promising p-type oxide semiconductor with a litharge crystal structure. Thin-film transistors (TFTs) based on p-type SnO films are highly desired for realizing low-power and high-performance complementary circuits and better compatibility with circuits of active-matrix organic light-emitting diode displays [25–27]. Although SnO film has received more attention recently due to its p-type conductivity, the physical properties of SnO films have not been investigated in detail. In present study, some interesting results are found in F-doped SnO films, which will give some enlightenment for further researches and applications on SnO-based films.

2. Experimental procedures

The SnF_2-Sn target was fabricated according to the following steps: (i) 90 g of Sn (Aldrich, 99.99%) and 10 g of SnF_2 (Aldrich, 99.99%) powders were uniformly mixed; (ii) the mixed powders were uniaxially pressed into a pellets with about 6 mm in thickness and 60 mm in diameter using a steel die; and (iii) the SnF_2-Sn pellet was sintered at 100 °C for 24 h in vacuum drying oven. The relative density of the target obtained is about 96%.

Using SnF_2-Sn target, the films were deposited on a thin plate of soda-lime-silica glass in a conventional RF magnetron sputtering system. Before deposition, the substrates were cleaned successively in alcohol, acetone, and distilled water with an ultrasonic cleaner for 15 min. The vacuum chamber was evacuated to 3.5×10^{-3} Pa, after which O_2 and Ar were introduced into the chamber as sputtering gas. To investigate the influence of different substrate temperatures and O_2 fluxes on the structure and properties of the film, the substrate temperature was set as RT, 150 and 300 °C, and O_2 flux was varied in the range of 0.3–1.7 sccm (standard cubic centimeter per minute) using mass flow controllers at each substrate temperature. RF magnetron sputtering power, sputtering pressure, Ar flux, sputtering time, and substrate-target distance were fixed at 75 W, 0.8 Pa, 20 sccm, 20 min, and 70 mm, respectively.

An interference microscope (SC57-6JA) was used to determine the thickness of the films. The crystalline structure of the films was identified by X-ray diffraction (XRD; Xpertpro, Philips) using Cu $K\alpha_1$ radiation in θ-2θ Bragg-Brentano geometry. The electrical properties of the films were determined by Hall effect measurement using Van der Pauw method at RT. The transmission spectra of the films were obtained from an UV–visible spectrophotometer (UV-2102PC, Unico) in the wavelength range of 300–800 nm. The RT photoluminescence (PL) spectra of the samples were recorded using a LabRam HR800 (Jobin-Yvon, France) spectrometer with a He-Cd laser ($\lambda = 325$ nm) as an excitation source.

3. Experimental results and discussion

3.1. Structural characterization

Fig. 1 shows the film thickness as a function of O_2 flux at substrate temperature of RT, 150 and 300 °C. As a whole, the film thickness shows a decreased trend with increasing O_2 flux at three substrate temperatures. In previous studies, Luo et al. [28] found that the film thickness increased monotonously but most researchers [29–31] observed that the film thickness decreased with increasing O_2 flux for SnO_2 or doped SnO_2 films prepared by reactive magnetron sputtering using metal or alloy target. The increase of film thickness could be attributed to more O_2-induced weight and volume variation, but its decrease was related to the decrease of Ar ions concentration during sputtering because the target could be sputtered more effectively by Ar ions. It is possible that film thickness is affected by these two factors simultaneously, but ultimately dominative factor is decrease of Ar ions concentration in present study.

Fig. 2 shows the XRD patterns of the films grown with different O_2 fluxes at three substrate temperatures. As shown in Fig. 2(a), no diffraction peak is observed at all O_2 fluxes when the substrate temperature is RT. As substrate temperature increases to 150 °C, no

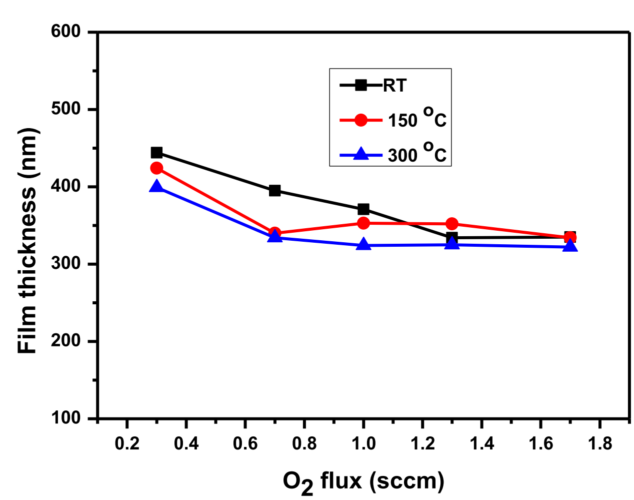

Fig. 1. The film thickness as a function of O_2 flux at three substrate temperatures.