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Effect of F and Nb co-doping on structural, electrical and optical properties of spray deposited tin oxide thin films

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A B S T R A C T

F and Nb co-doped tin oxide films were deposited from monobutyltin trichloride ($C_4H_9SnCl_3$) on glass substrates at 470 °C by spray pyrolysis. The evolution of the film structure and morphology was investigated by X-ray diffraction and scanning electron microscopy, respectively. All the films were a single phase with polycrystalline, exhibiting a tetragonal cassiterite structure with (200) orientation. The introduction of F and Nb contributed to the growth of the films towards (200) crystal orientation and the formation of pyramidal shape particles with (101) twin planes. Resistivity, carrier concentration, and Hall mobility values of $3.62 \times 10^{-4}\,\Omega$ cm, 7.463×10^{20} cm^{-3}, and 27.8 $cm^2\,V^{-1}\,s^{-1}$, respectively, were achieved in the films for a dopant concentration of 20 at.% F and 1 at.% Nb in the precursor solution. Also, the transmittance of all the films in the visible range reached about 80% and the infrared reflectivity was oscillated between 92 and 96%.

1. Introduction

In recent years, transparent conductive oxide (TCO) films exhibit a growing demand and play an integral role in various opto-electronic applications and energy-related technologies, such as display devices, light-emitting diodes, architectural windows and solar cells [1–5]. In particular, among the family of TCO, tin oxide (SnO_2) has become one of the most studied semiconductor materials due to its wide direct optical band gap (> 3.6 eV), excellent mechanical hardness, chemical stability, inexpensive and capability for large-area deposition. All of these properties make it to be a promising candidate for practical applications, such as gas sensors, low-e window glazing and solar cells windows [6,7].

However, the un-doped SnO_2 films present high resistivity due to the limited oxygen vacancies, low intrinsic carrier density and mobility [8,9]. Through extensive theoretical and experimental validation, researchers have found that doping can improve the film conductivity effectively. The doping of SnO_2 is mainly achieved by replacing Sn^{4+} or O^{2-} ions with dopant ions, which can provide extra carriers (free electrons or holes) in SnO_2 lattice and cause an increase in electrical conductivity. Antimony (Sb) is one of the typical cation dopants to substitute for Sn^{4+} ions in SnO_2 host lattice to obtain good quality films for device applications, but Sb-doped SnO_2 film usually involves both of Sb^{3+} and Sb^{5+} ions in SnO_2 lattice and Sb^{3+} ions is supposed to act as an electron trap which will have an opposite effect on doping efficiency in the films [10,11]. In the case of F-doped SnO_2 (FTO) films, F^- ions are use as anionic dopants to replace O^{2-} ions in SnO_2 lattice to increase the carrier concentration. However, because of its small ion radius, it is easy to enter the grain boundary and increase the grain boundary barrier as an interstitial impurity, which will decrease the Hall mobility of carriers and affect the optical properties of the film, especially when the doping concentration of F^- is relatively high [12]. Therefore, the opto-electronic properties of FTO films are constrained and there is an urgent need to find a way to further improve it.

Fortunately, there are many reports about Nb-doped SnO_2 films by Rf magnetron sputtering [13], pulsed laser deposition [7,14] and spray pyrolysis [15,16]. These researches have proved that Nb is an excellent dopant since the radius of Nb^{5+} (0.064 nm) is nearly equal to that of Sn^{4+} (0.069 nm) [17], which facilitates the substitution of Nb^{5+} for Sn^{4+} in SnO_2 crystal lattice. It can be inferred that if SnO_2 were doped with F and Nb simultaneously, the positions of O^{2-} and Sn^{4+} in SnO_2 lattice would be replaced together, and the carrier generation and Hall mobility would be further enhanced. Furthermore, the introduction of Nb^{5+}, by contrast, affects the nanostructure of the films and the

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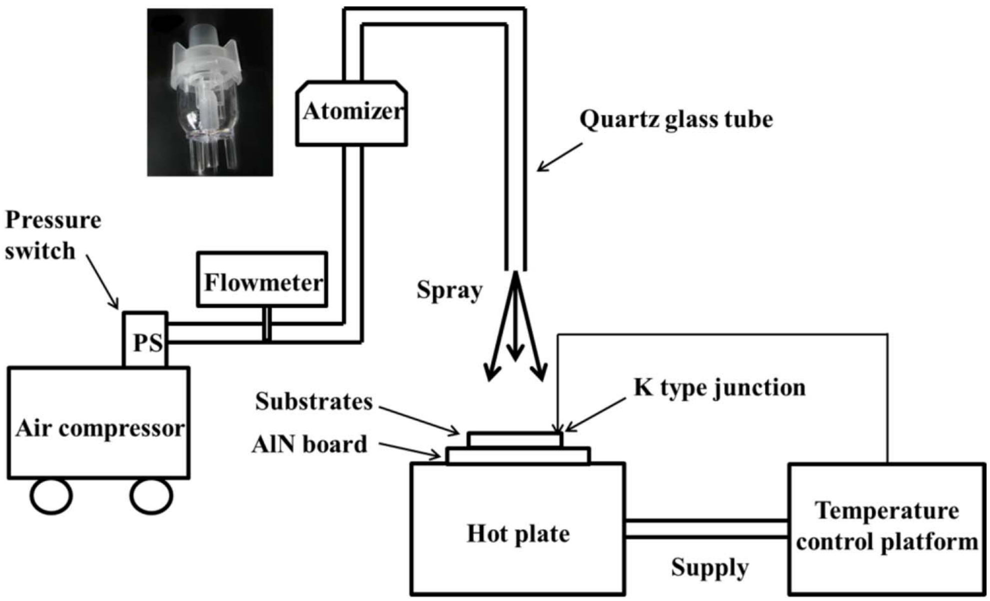

Fig. 1. The schematic of the spray pyrolysis unit of in-house design.

incorporation of F^-, which may be helpful to improve the film performance. But to date, most of the studies have focused on finding novel and effective dopants for SnO_2 [18–21], there is few report on F and Nb co-doped SnO_2 films deposited from monobutyltin trichloride ($C_4H_9SnCl_3$, MBTC) by spray pyrolysis.

In this study, F and Nb co-doped SnO_2 films with high transmittance and electrical conductivity were deposited from MBTC on glass substrates at 470 °C by spray pyrolysis, the structural, morphological, electrical and optical properties were investigated. Particularly, the evolution of microstructures was discussed by using the periodic bond chain (PBC) theory, and the mean free path was calculated to study the electrical properties in detail.

2. Experimental details

The un-doped, Nb-doped, F-doped and Nb + F co-doped SnO_2 films were deposited using a spray pyrolysis unit of in-house design. (Fig. 1). Starting solution of SnO_2 was prepared by dissolving 0.5 M MBTC in 6 ml concentrated hydrochloric acid (HCl) and diluted with methyl alcohol (CH_3OH). Necessary amounts of ammonium fluoride (NH_4F) and niobium pentachloride ($NbCl_5$) have been dissolved in deionized water and methyl alcohol, respectively. For F-doped and Nb + F co-doped SnO_2 films, the concentration of the dopant F/Sn in the solution was 20 at.%, and the concentrations of the dopants Nb/Sn in the solution were 0.5 at.%, 1 at.%, 2 at.% and 4 at.% (the films were named NFTO-0.5, NFTO-1, NFTO-2, NFTO-4, respectively). For Nb-doped SnO_2 film, the Nb/Sn was kept in 1 at.% (the film was named NTO-1). The detailed amount of chemicals used for each sample type was listed in Table 1. In order to obtain homogeneous spray solutions, all solutions were stirred at room temperature for 5 h and aged at room temperature for 24 h. The coating solutions were sprayed onto 30 × 25 × 1 mm^3 sodium silicate glass substrates, the compressed air was used as carrier gas. The substrates were fixed and the distance between the nozzle to substrate was maintained at 3 cm. The substrates were ultrasonically cleaned using acetone, distilled water and ethanol separately for 5 min, and then dried in hot oven prior to be used. The substrate surface temperature was kept at 470 (± 5) °C, measured by a k-thermocouple and controlled electronically. Each film was sprayed for 2 min and kept in hot plate for 1 min, subsequently cooled down to room temperature naturally. Each coating process was repeated at least 3 times to ensure reproducibility and one of the samples was selected for performance characterization.

The crystal structure was characterized by X-ray diffraction (Rigaku D/MAX-rB) with a Cu Kα radiation (λ = 0.15406 nm). The morphological characterization was performed on a Hitachi S4800 scanning electron microscopy (SEM). The film thickness was estimated by cross-sectional SEM images to be used for necessary calculations. The sheet resistance was evaluated by a four-point probe, the carrier concentration and mobility of the samples were confirmed by Hall effect measurement system (HMS) ECOPIA-3000 with a 0.55 T magnetic induction. UV–Vis spectroscopy was employed to investigate the optical transmission spectra and the average transmittance values in the spectral region of 380–780 nm were calculated.

Table 1
The detailed amount of chemicals used for each sample type.

Samples	NH_4F/g	$NbCl_5$/g	MBTC/g	CH_3OH/ml	H_2O/ml	HCl/ml
SnO_2	–	–	14.1	84	10	6
NTO-1	–	0.1350	14.1	84	10	6
FTO	0.37	–	14.1	84	10	6
NFTO-0.5	0.37	0.0675	14.1	84	10	6
NFTO-1	0.37	0.1350	14.1	84	10	6
NFTO-2	0.37	0.2700	14.1	84	10	6
NFTO-4	0.37	0.5400	14.1	84	10	6

3. Results and discussion

3.1. Structural properties

The typical X-ray diffraction patterns of the as-deposited films are shown in Fig. 2 (a) and (b). It can be observed that the as-deposited films are polycrystalline with SnO_2 tetragonal cassiterite structure, corresponding to the space group $D_{14}{}^{4h}$ (P42/mnm). Other phases belonging to SnF_2, SnO, Sn_2O_3, and metallic Nb are not observed in the deposited films. One interesting fact highlighted by X-ray diffraction patterns is that all the films exhibit an obviously preferred orientation with (200) plane, which is significantly increased in NTO-1, FTO and NFTO-1 films than that in un-doped SnO_2 film, while the introduction of dopants inhibits the growth of (301) plane. From Fig. 2 (b), it can be seen that the (200) orientation increases with the increase of Nb concentration in co-doped SnO_2 films, NFTO-1 film possesses the highest intensity of (200) orientation, and then decreases while Nb concentration is above 1 at.%. These results confirm that the preferred orientation and the crystallinity of the films are affected by the dopants