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Physicochemistry of point defects in fluorine doped zinc tin oxide thin films

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ABSTRACT

Zinc tin oxide (ZTO) and F-doped zinc tin oxide (FZTO) films with Zn concentration up to 35 at.% were prepared by chemical spray pyrolysis technique. The X-ray diffraction results showed an expansion in the lattice of tin oxide by either doping with fluorine or adding Zn due to the incorporation of fluorine into oxygen vacancies or the replacement of the host Sn atoms by Zn, respectively. The X-ray photoelectron spectroscopy results of the FZTO films yield oxygen vacancy concentration [V_O] in the range 10^{21}–10^{22} cm^{-3} and substitutional fluorine concentration [F_O] in the range (1.71–9.66) × 10^{20} cm^{-3}. For relatively low Zn concentration the electron concentration measured using Hall effect is close to [F_O] but lower than [V_O] by two orders of magnitude. The results suggested neutral oxygen vacancies. The overall results showed that tin is in tetravalent oxidation state in the whole range of studied Zn concentrations. All films under investigation show high transparency in the visible range (T ≥ 82%). In addition, the optical transmittance shows a tail in the near IR region due to free carrier absorption. The optical energy gap of the FZTO films falls in the range 3.86 eV–4.45 eV and exhibits a UV shift with the increase in free carrier concentration due to the Burstein-Moss effect.

1. Introduction

Due to their combined high optical transparency in the visible region and their good electrical conductivity, transparent conducting oxides (TCO) have numerous technological applications such as transparent electrodes in photovoltaic cells, liquid crystal displays, light emitting diodes, heat reflecting mirrors and gas sensors [1–3]. In the last decades, different metal oxide semiconductors like SnO_2, ZnO, In_2O_3 and TiO_2 have been extensively used as TCO thin films [4,5]. Doping these oxides with specific elements like F, Al, B and Cl could increase the electrical conductivity while maintaining the high optical transparency in the visible range [6,7]. Therefore they could be more attractive for many optoelectronic applications. Among the different transparent conducting oxides, zinc tin oxide (ZTO) and fluorine doped zinc tin oxide (FZTO) films are promising candidates for many applications. They have low electrical resistivity, high optical transmittance, good thermal stability, high mechanical strength and low processing cost [8,9].

Several techniques have been used for preparing ZTO films including pulsed laser deposition [10], sputtering [11], atomic laser deposition [12] and spray pyrolysis [13,14] among others. The latter technique is known to be simple, reproducible, cheap, and adaptable to large-scale production. Yet only few reports were devoted to study spray deposited ZTO films and even fewer were dedicated to their electrical and optical properties [13,14]. Moreover, the question of physicochemistry of point defects in ZTO and FZTO films has not been investigated previously. In a recent work, El Akkad et al. [15,16] have obtained experimental evidence that oxygen vacancies are neutral in SnO_2 films at room temperature. Their results are in good agreement with recent theoretical predictions [17], but in contrary to what had long been believed to be the case [18]. Additionally, detailed analysis of the optical properties revealed the presence of optical transitions involving un-identified defects in F:SnO_2 thin films [16]. This calls for a close investigation of the role of point defects and their influence on the physical properties of hybrid systems involving SnO_2 such as ZTO. Radheshyam Rai [19] reported that doping SnO_2 with transition metal oxides influences dramatically the defect chemistry behavior of SnO_2. In addition, they found that the substitution of tin ions by zinc ions create more oxygen vacancies. Concerning FZTO films, only three reports were found in the literature that is devoted to study this TCO. Pandey et al. [9] investigated the effect of annealing temperature on the structural, electrical and optical performance of amorphous FZTO thin films prepared by radio-frequency magnetron sputtering technique. Jun-Hyuck et al. [20] described in details the preparation procedure of FZTO from aqueous solution and provided a brief description of their properties. Park et al. [21] studied the

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electrochemical characteristics of the FZTO films prepared using MOCVD. Yet, no investigations were reported on the physical properties of spray deposited FZTO films.

In this paper, a comprehensive study of the structural, electrical, optical and chemical properties of ZTO and FZTO films prepared by the spray pyrolysis method is introduced. The overall results are correlated to the preparation conditions in an attempt to throw more light on the role of point defects and to provide information that may help in optimizing the properties of this transparent conducting oxide for different device applications.

2. Experimental procedures

ZTO and FZTO films were prepared by chemical spray pyrolysis technique. The starting solution was a mixture of $SnCl_4$: propanol: H_2O with molar ratio 1:9:2. Solutions containing up to 50% Zn were prepared by adding the desired amount of Zn in the form of $ZnCl_2$. Doping with F was accomplished by adding the required amount of F in the form of NH_4F to the spray solution. The thin films were prepared by spraying the solution on well cleaned borosilicate glass substrates which were maintained at temperatures in the range of 430–500 °C using IR heater and temperature controller. Spraying was performed using N_2 as carrier gas with a pressure of 2.5 psi in pulses of duration ~1 s and time interval ~40 s in order to allow the substrate to be reheated to the preparation temperature. The distance between the spray bottle and the substrate was maintained at approximately 25 cm.

The structural properties of ZTO and FZTO films were carried out using X-ray diffractometer type Siemens D5000 with Cu Kα radiation ($\lambda = 1.5406$ Å) with Bragg-Brentano geometry. The compositional analysis of the films were carried out using X-ray photoelectron spectroscopy (XPS) model Thermo ESCALAB 250Xi spectrometer using monochromator with Al K_α radiation (1486.6 eV) with X-ray spot size 380 μm. The spectral acquisition and processing were carried out using Avantage V 4.74 data system. The parameters used in the XPS analyses are: Analysis chamber pressure 10^{-9} Torr, step size 0.1 eV, dwell time 100 ms, and pass energy of 20 eV. All binding energy (BE) values were determined using the C 1s peak at 284.6 eV which originates from adventitious carbon as the binding energy calibration reference. Etching was performed using an argon ion gun with voltage of 2 kV, current of 2 μA, and raster size of 2 mm^2.

Room temperature electrical resistivity and Hall measurements were carried out using the Van Der Pau method in MMR technologies type system. For this, four Al contacts each of area 2 mm^2 and thickness 50 nm were deposited on the sample surface by thermal evaporation. Leads to the external circuit were made by soldering gold wires to the Al contacts using indium. Currents in the range 0.5–5.0 mA and a magnetic field of 0.3 Tesla were used.

Transmission spectra were recorded in the wavelength range from 200 to 2500 nm using a double beam spectrophotometer type Cary 5000 UV–Vis-NIR and a Shimadzu Solid Spec-3700 UV- Vis-NIR Spectrophotometer where a borosilicate glass substrate was used as a reference.

3. Results and analysis

The fluorine and zinc concentrations in the starting solution were varied in a wide range. The concentration of the fluorine and zinc in the thin films were determined by analyzing the XPS spectra as will be discussed in Section 3.2. The investigated thin films were divided into four categories TO, ZTO, FTO and FZTO, and they were labeled as given in Tables 1 and 2.

3.1. Structural characterization

The crystal structure of ZTO and FZTO films with variable concentrations of Zn and F was investigated using XRD measurements. Fig. 1(a) shows the XRD spectra for ZTO films with Zn concentration in the range 0–31 at.%. The spectra show that below 31 at.% the films possess a single phase polycrystalline behavior with tetragonal rutile structure. The crystallites in the TO films exhibit mixed preferential orientation along the (110) and (200) planes. Upon increasing the zinc concentration, the intensity of the (110) peak decreases, while that of the (200) peak increases. This indicates a change in the preferential orientation of the grains. It is also observed that the crystalline quality decreases by increasing Zn concentration. These results agree with the observations reported on ZTO films prepared by spray pyrolysis [13,22].

Fig. 1(b) shows the XRD spectra for the FZTO films. The spectra show that the films with low Zn concentration (0–13 at.%) possess a single phase polycrystalline feature with tetragonal rutile structure. The zinc free film (FTO) exhibits mixed preferential orientation of crystallites along the (110) and (200) planes similar to the case of undoped TO films (Fig. 1(a)). Upon increasing the zinc concentration, a change in the preferential orientation occurs which is associated with the emergence of the (211) and (301) peaks. This is to be compared with the orientation along the (200) plane in absence of fluorine (i.e. in ZTO films). Therefore, it seems that the presence of fluorine in ZTO films has a role in determining the orientation of the crystallites. This may be due to the local distortion of the lattice associated with the incorporation of F into oxygen sites.

It is also noticed that by increasing Zn concentration a decrease in the crystalline quality occurs. It appears from Fig. 1(a) and (b) that ZTO and FZTO films have amorphous structure for Zn concentration above about 30%.

The XRD peaks were shifted toward lower Bragg angles after adding F or Zn to tin oxide indicating an expansion of the lattice. An example of this shift is shown in Fig. 2(a) for the (200) peak. Similar shift in the XRD peaks after F-doping has been reported previously for TO [15]. The expansion of the lattice following F doping cannot be attributed to the replacement of the host oxygen atoms by fluorine since fluorine has ionic radius (1.33 Å) which is smaller than that of oxygen ion (1.4 Å). Previous investigations have shown that non-intentionally doped TO thin films grown by chemical spray pyrolysis technique contains high

Table 1
The crystallite size (D) calculated from the XRD measurements and the atomic percentage of C, Sn, Zn, F, O for the investigated ZTO and FZTO films obtained from the XPS measurements at an etching time of 60 s.

Sample	D (nm)	C	Sn	Zn	F	O
TO	20	36.1	18.5	0.0	0.00	45.4
ZTO1	15	73.1	4.6	1.9	0.00	20.5
ZTO2	–	35.0	19.7	8.9	0.00	36.4
ZTO3	–	75.1	6.5	3.1	0.00	15.4
FTO	20	39.0	18.1	0.0	0.70	42.2
FZTO1	26	46.8	16.0	0.9	0.37	35.9
FZTO2	28	21.2	25.0	3.1	0.31	50.4
FZTO3	30	66.5	9.7	1.5	0.53	21.8
FZTO4	–	71.7	4.2	2.3	0.29	21.6

Table 2
Concentration of Zn ([Zn]), substitutional fluorine ([F]) and electrons (n). Carriers mobility (μ) and, optical energy gap (E_g), of the investigated ZTO and FZTO films.

Sample	[Zn]	[F]		n	μ	E_g
	(at.%)	(at.%)	(cm^{-3})	(cm^{-3})	(cm^2/Vs)	(eV)
TO	0	0.00	0.00	7.21×10^{19}	6.3	3.97
ZTO1	28.8	0.00	0.00	3.13×10^{17}	28	3.77
ZTO2	31.1	0.00	0.00	1.12×10^{17}	32	3.63
ZTO3	32.3	0.00	0.00	9.84×10^{16}	35	3.53
FTO	0.0	1.93	5.35×10^{20}	5.62×10^{20}	14	4.42
FZTO1	5.5	1.15	3.20×10^{20}	3.69×10^{20}	7.0	4.40
FZTO2	11.1	0.62	1.71×10^{20}	1.60×10^{20}	8.0	4.45
FZTO3	13.4	2.74	7.59×10^{20}	4.25×10^{19}	23	4.13
FZTO4	35.6	3.49	9.66×10^{20}	9.90×10^{18}	6.0	3.86