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W doped SnO_2 growth via sol–gel routes and characterization: Nanocubes

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ABSTRACT

The effects of W doping on the characteristical properties of SnO_2 thin films prepared by sol–gel spin coating method were investigated. The SnO_2 thin films were deposited at various W doping ratios and characterized by various measurements. XRD studies indicated that the undoped and W doped SnO_2 films had cubic and tetragonal phases. The SEM images of WTO thin films showed cubic shaped nanocubes corresponding to cubic phase and the smaller particles corresponding to tetragonal phase were formed on the film surfaces, and their distributions and sizes were dependent on the W doping ratio. EDX spectroscopy analyses showed that the calculated and participated atomic ratios of W/(W + Sn) (at.%) in the starting solution and in the WTO thin films were almost close. It was found that the sheet resistance depended on W doping ratio and 2.0 at.% W doped SnO_2 (WTO) exhibited lowest value of sheet resistance ($7.11 \times 10^3\ \Omega/cm^2$).

1. Introduction

Tin oxide (SnO_2) has various application areas [1] due to its unique properties such as low electrical resistivity, high optical transmittance in the visible region, high infrared reflectivity, chemically inert and mechanically hard [2–5]. Some properties of SnO_2 thin films can be improved by suitable dopant elements such as antimony (Sb), fluorine (F), vanadium (V), and tungsten (W). Among these dopants, tungsten has oxidation states apt to W^{6+} ion state, and the radius of W^{6+} is close to that of Sn^{4+} (W^{6+}: 67 pm, Sn^{4+}: 71 pm), which make it easy to replace the Sn^{4+} ions. Therefore, tungsten-doped tin oxide may be expected to have a potential prospect [6].

Undoped and doped SnO_2 thin films have been prepared by various experimental techniques such as electrochemical deposition [7], hydrothermal method [8], polymerizing-complexing and sol–gel [9] techniques. However, to the best of our knowledge, the fabrication of W doped SnO_2 thin films have not been reported up to now by sol–gel spin coating method. Therefore, in this study, we aimed to investigate the effect of W doping on structural, morphological, optical and electrical properties of SnO_2 thin films prepared by sol–gel spin coating method.

2. Experimental

In the present study, W-doped tin oxide (WTO) thin films were prepared by sol–gel spin coating method on glass substrate using a sol prepared with stannous chloride dihydrate ($SnCl_2{\cdot}2H_2O$), tungsten hexachloride (WCl_6), monoethanolamine (C_2H_7NO, MEA) and 2-methoxyethanol ($C_3H_8O_2$, 2-MTE), as starting material, dopant source, stabilizer, and solvent, respectively. The molar ratio of MEA to metal salts was maintained at 1:1 in all solutions. Various amounts of the stannous chloride dihydrate and tugsten hexachloride were combined to achieve different W/W + Sn atomic ratios changing from 1.0 at.% to 4.0 at.% with 1.0 at.% step. The precursor sol was stirred at 80 °C for 24 h in a tightly closed flask to obtain a clear and homogenous solution. The glass substrates firstly were kept in boiling chromic acid solution and then they were rinsed with deionized water. Finally, they were cleaned with acetone, methanol and deionized water by using an ultrasonic cleaner and dried with nitrogen. The resultant solution being dropped on glass substrate was rotated at a speed of 3000 rpm for 30 s by using a spin-coater. After the glass substrates were coated, they were sintered at 200 °C for 5 min to evaporate solvent and remove the organic sediments and then spontaneously cooled to room temperature. This procedure was repeated for 4 times and finally, the samples were annealed in air at 450 °C for 30 min.

The structural characterization of the WTO thin films was carried out by X-ray diffraction (XRD) measurements using a Rigaku Miniflex II diffractometer with Cu Kα radiation (λ = 1.5418 Å). The diffractometer reflections were taken at room temperature and the values of 2θ were altered between 15° and 80°. Morphological properties of the W-doped SnO_2 thin films were determined

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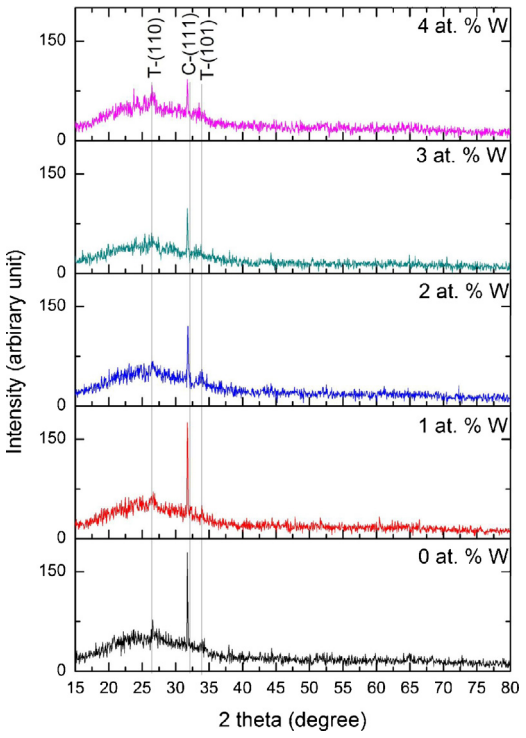

Fig. 1. XRD spectra for undoped and W doped SnO_2 thin films.

with Jeol Nano-SEM. The optical transmittance of the samples was recorded in spectral region of 300–1000 nm at 300 K using a UV-Vis spectrophotometer (Perkin-Elmer, Lambda 40) which works in the range of 200–1100 nm. The sheet resistance values of films were measured by means of four point probe technique.

3. Results and discussion

3.1. X-ray diffraction results

The crystal structure of WTO thin films was investigated by X-ray diffraction (XRD) patterns. Fig. 1 shows XRD spectra of WTO thin films. These spectra indicate that the samples have (1 1 1) plane corresponding to SnO_2 cubic phase (JPDS 50-1429) and (1 1 0), (1 0 1) planes corresponding to SnO_2 tetragonal rutile phase (JPDS 41-1445). No additional peak which implies oxides of tungsten were not observed. As seen in Fig. 1, the strongest orientation is (1 1 1) line of cubic structure and (1 1 1) peak intensity value of undoped sample has decreased continuously with increasing W dopant content. It can easily be concluded that the crystalline of WTO thin films are being deteriorated by increased W content.

Although SnO_2 crystallize in the tetragonal rutile crystal system, there are also orthorhombic and cubic phases of SnO_2. As a mineral, SnO_2 being formed at tetragonal rutile phase is also called Cassiterite [10]. Suito et al. [11] reported the phase transition from tetragonal to orthrombic structure. Shieh [12], Haines and Legér [13] observed SnO_2 cubic phase. Phase transformations of SnO_2 have usually been studied under high pressure. Jiang et al. [14] have found fluorite cubic phase with Fm3m space group above 18 GPa pressure, and Ono et al. [15] have observed peaks of (1 1 1), (2 0 0), (2 2 0), (2 2 2) belonging to the cubic structure under high pressure and temperature (about 23 GPa and 1000 K). In recent years, cubic and other phases have been reported from the experiments studies based on the solutions performed at atmospheric pressure [16–18]. Cubic phase for SnO_2 thin films prepared by reactive radio frequency magnetron sputtering with different sputtering power (about >100 W) have been reported by the Song et al. [19].

In this study, SnO_2 cubic structure has been obtained at atmospheric pressure, and to the best our knowledge, this is the first result obtained for SnO_2 films grown by the sol gel technique. In the literature, ethanole [20,21], 1-propyl alcohol [22], mixture of water and alcohol [23,24] are generally used as a solvent for preparation of SnO_2 films via sol–gel route. Huang et al. [25] have synthesized W doped SnO_2 thin film from sol–gel solution prepared by mixing a weighed quantity of $SnCl_2{\cdot}2H_2O$ with an ethanol/water, WCl_6 soluted in mixture. The reason for obtaining the cubic structure in this study may, at first, be the usage of a sol prepared with stannous chloride dihydrate ($SnCl_2{\cdot}2H_2O$), tungsten hexachloride (WCl_6), monoethanolamine (C_2H_7NO, MEA) and 2-methoxyethanol ($C_3H_8O_2$), as starting material, dopant source, stabilizer and solvent, respectively.

For the samples, the observed '*d*' values which are the interplaner distances are presented in Table 1 and these values are compared with the standard ones from the JPDS 50-1429 data files. The lattice constant '*a*' for cubic structure is determined by relation [26].

$$\frac{1}{d^2} = \left(\frac{h^2 + k^2 + l^2}{a^2}\right) \quad (1)$$

where ($h\,k\,l$) is miller indices. The calculated and standard lattice constants are also given in Table 1. The calculated '*a*' values agree with JPCDS card no: 50-1429 (a = 4.87 Å). As can be seen in Table 1, the lattice constant value for undoped sample is 4.8745 Å. This value decreases with W doping up to 2.0 at.%, and then it increases continuously with the W doping concentration in the films. This can be explained if it is considered that: W has many oxidation states such as +6, +5, +4, +3, +2 [27,28] and with decreasing the oxidation number of W, its ionic radii increases [28,29]. At the low doping levels, W^{6+} presumably substitutes with the Sn^{4+} and causes lattice constant decrease. With the increasing of W doping level in SnO_2 lattice, $W^{5,4,3,2+}$ oxidation states also substitute to Sn^{4+} and having increase in lattice constant. Similarly, in earlier studies, it was found that some of the Sn^{4+} ions in the lattice were replaced by Sb^{5+} at low doping level, however Sb^{3+} substituted to Sn^{4+} at high doping level [20].

3.2. SEM and EDX results

The composition of WTO thin films was determined by energy dispersive X-ray spectroscopy (EDX). EDX spectra of WTO thin films and the composition of elements in SnO_2 structure are together given in Fig. 2. These spectra clearly confirm the existence of Sn and W elements in the WTO thin films. The Si, Na, Mg and Ca ele-

Table 1
The structural, electrical and optical values of undoped and WTO thin films.

Sample	Cubic ($h\,k\,l$)	Cubic-d st. (Å)	Cubic-d obs. (Å)	Cubic-a (Å)	R_s ($\times 10^3$ Ω/cm^2)	E_g (eV)
Undoped SnO_2	(1 1 1)	2.8120	2.8143	4.8745	48.22	4.105
1.0 at.% W doped SnO_2	(1 1 1)	2.8120	2.8140	4.8739	12.96	4.112
2.0 at.% W doped SnO_2	(1 1 1)	2.8120	2.8236	4. 8626	7.11	4.115
3.0 at.% W doped SnO_2	(1 1 1)	2.8120	2.8146	4.8750	8.24	4.099
4.0 at.% W doped SnO_2	(1 1 1)	2.8120	2.8222	4.8852	9.60	4.097