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Detailed investigation of submicrometer-sized grains of chemically sprayed ($Sn_{1-x}Al_x$, O_2) ($0 \leq x \leq 0.085$) thin films

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ABSTRACT

In this study, the submicrometer-sized grains of chemically sprayed tin oxide, SnO_2, were largely investigated. The films ($Sn_{1-x}O_2$, Al_x), with x = 0–0.085 were grown by spray pyrolysis onto glass at a fixed temperature of 300 °C. Structural, optical, electrical and morphological properties were studied. These films are polycrystalline in nature with a tetragonal crystalline structure, and exhibited a preferred orientation along the (2 0 0) planes. Atomic force microscope (AFM) analysis demonstrated a nano-grain structure. Our nanostructured films revealed high transparency in the visible and infra-red spectra and an electrical resistivity that ranged from 1 to1000 Ω cm.

1. Introduction

Tin oxide (SnO_2) has recently become one of the most studied materials in technology research, due to its various properties such as high transparency in visible range, high reflectivity in the infrared [1], direct band gap around 3.5 eV, and high exciton binding energy at room temperature (130 meV) [2]. It is well known that SnO_2 is a semiconductor that crystallizes in a tetragonal rutile structure [3]. SnO_2 films were grown by various processes like chemical precipitation route [4], chemical vapor deposition (CVD) [5], sputtering [6,7], sol–gel [8], pulsed laser deposition (PLD) [9], and spray pyrolysis deposition (SPD) [2,10,11]. This latter is a chemical deposition technique in which fine droplets of a solution containing desired species are sprayed on a preheated substrate. SPD is a facile technique that is low cost and permits easy doping [12]. With SPD, large and uniform SnO_2 films can be deposited at low temperature. This technique consists in a thermal decomposition that occurs on the hot substrate, giving rise to a continuous film as reported in literature [13]. SnO_2 is extensively used for a variety of applications including architectural windows, flat panel displays, smart windows, and film photovoltaic and polymer-based electronics [14]. Elements such as F, Cl, Sb, Br, Ni, Cu, Fe [12], Al [1], Co [15], and In [2], have been used as dopants for SnO_2. Tin oxide was grown on different substrates such as indium tin oxide (ITO) and silicon [16,17]. In this paper, we report on submicrometer-sized grains of ($Sn_{1-x}Al_x$, O_2) thin films chemically sprayed with different Al contents in the starting solution. Furthermore, we exhibit the characterizations and the role of Al concentration levels on chemically sprayed SnO_2 films properties.

2. Experimental procedures

2.1. Precursor preparation and deposition parameters

The deposition of the films was carried out by a homemade SPD technique, as sketched in Fig. 1. First, pure and Al-doped SnO_2 films were sprayed onto a corning glass 7059, near-zero alkali baria alumina borosilicate. The starting material was ($SnCl_4 \cdot 5H_2O$) and the doping source was aluminum (3+) chloride ($AlCl_3$). Both precursor and doping compounds were dissolved in methanol. The starting material concentration was 0.2 M and the concentration of the dopants Al/Sn in the solution were 1, 1.5, 3 and 8.5%. Spray rate and substrate to nozzle distance were maintained respectively at 20 ml/min and 25 cm. The glass substrate was heated at 300 °C which was controlled by a digital thermometer connected to the heater. Finally, the film thicknesses ranged between 150 and 270 nm.

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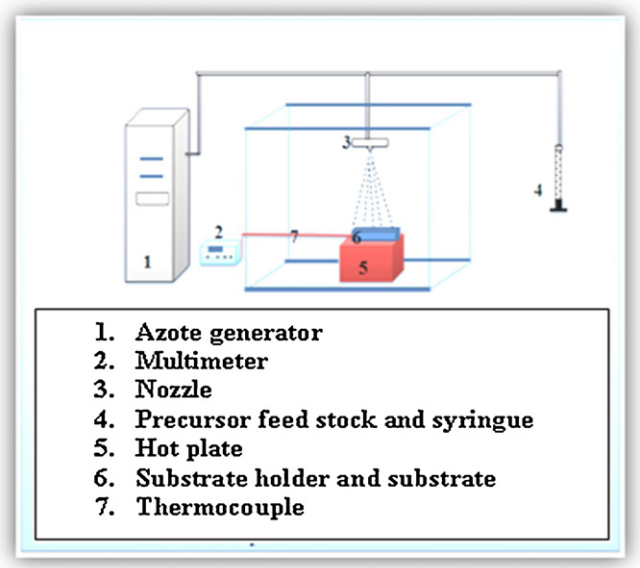

Fig. 1. Schematic diagram of spray pyrolysis deposition set-up.

2.2. Films characterization

X-rays diffraction patterns of the SnO_2 films were analyzed at room temperature using a Rigaku X-ray diffractometer, model DMAX 2200, having a copper anticathode (Cu Kα, 1.54 Å). The Bragg angle (2θ) ranged from 30° to 70°. The UV–VIS-NIR transmittance spectra of the SnO_2 films prepared at different concentrations of Al were recorded via a Shimadzu UV-3600 PC double beam spectrometer. The electrical resistivity measurement of the films was carried out by a Keithley 6517A electrometer at room temperature by two metal probes put in contact with the film, having a radius of 0.5 mm each and separated by 3–4 mm. The samples' morphology was investigated using a Park system XE-100 E atomic force microscope. Data measurements were taken at room temperature. Scans were made over areas ranging from 5 μm × 5 μm to 1 μm × 1 μm, and the scan rate ranged from 0.25 to 0.50 Hz. All AFM measurements described here were achieved with taping mode, non-contact silicon cantilever. AFM parameters details, such as section analysis, grain size distribution histogram, power spectral density (PSD) were deduced from XEI version 1.7.1 data processing and analysis software.

3. Results and discussion

3.1. Crystalline structure by XRD pattern analysis

The X-rays pattern spectra of pure and Al-doped SnO_2 were displayed in Fig. 2A. The as-grown films were identified as polycrystalline SnO_2 with a tetragonal crystal structure and preferred orientation along the (2 0 0) plane. Ours samples only exhibited the SnO_2 structure and no other was detected, as reported in the JCPDS card (No. 72-1147) data of SnO_2. Pure SnO_2 films revealed intense peak at $2\theta \sim 37.8°$ (see Fig. 2B). The main strong peaks were (2 0 0), (2 1 1) and (1 0 1) as evidenced in Fig. 2A which identifies the tetragonal structure (closed squares); the weak peaks (closed circles) demonstrated the presence of SnO_2 orthorhombic structure.

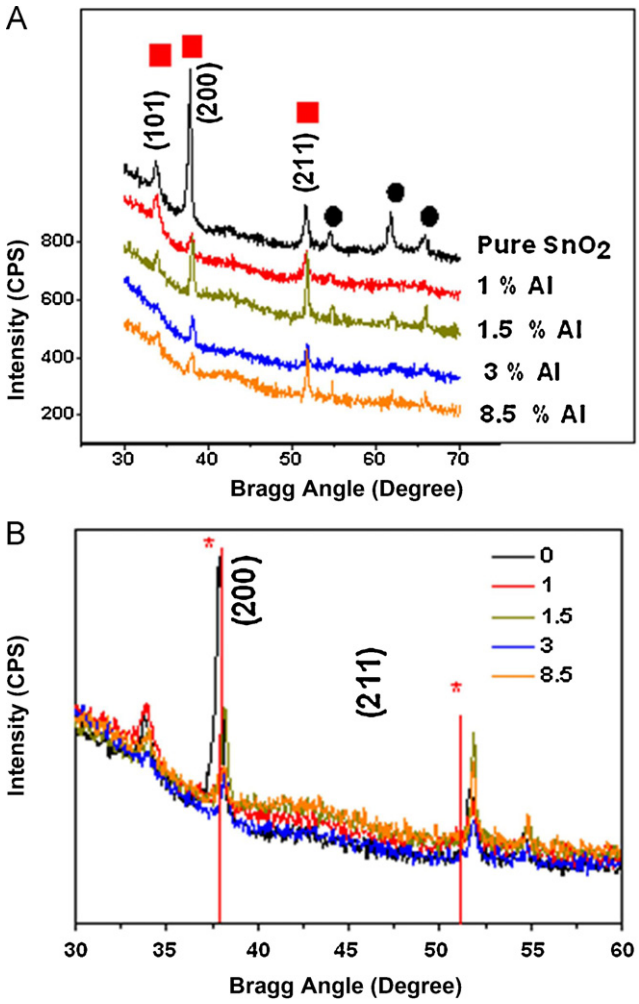

Fig. 2. (A) X-rays patterns of pure and Al doped SnO_2 grown by SPD: pure, 1%, 1.5%, 3% and 8.5% Al doped SnO_2. Peaks of SnO_2: red closed squares show tetragonal phase, while closed black circles show orthorhombic phase. (B) (2 0 0) and (2 1 1) orientations of pure and Al doped SnO_2 are evidenced, red lines of JCPDS 72-1147 card were signed by star. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The peak (2 0 0) was very intense in the case of pure SnO_2, while Al doping levels reduced it. On the other hand, the (2 1 1) orientation of the films became more pronounced with Al content; mainly for doping levels of 1.5% and 8.5% sprayed films. Furthermore, the (1 0 1) direction diminished with the increase of Al content, whereas the peaks of orthorhombic SnO_2 became insignificant in the doped samples. Overall, these peaks presented a slight broadening (FWMH increases) which led us to report on nanostructures formation. This statement was confirmed by the small grain sizes of our samples (see Table 1). The increase of Al content led to a decrease in crystalline structure of the films, a result that was

Table 1
Structural (grain size according to (2 0 0) plane, lattice parameters a, Δa, c, Δc, ε_{zz}, V, $\Delta V/V$), optical (T at 550 nm), morphological (RMS, grain size by AFM analysis) parameters of pure and Al doped tin oxide.

Al level (%)	Grain size (XRD)(nm)	Lattice constants (Å)				ε_{zz} (%)	V (Å^3)	$\Delta V/V$ (%)	T (550 nm)	RMS (nm)	Grain size (AFM) (nm)
		A	Δa	c	Δc						
0	20.98	4.745	0.008	3.201	0.016	0.502	72.104	90.28	88.252	10.41	90.28
1	26.81	4.718	−0.019	3.218	0.033	1.036	71.660	149.31	75.475	19.09	149.31
1.5	21.61	4.712	−0.024	3.212	0.027	0.848	71.342	41.67	80.701	15.82	41.67
3	19.83	4.707	−0.030	3.219	0.034	1.067	71.343	27.78	77.439	10.84	27.78
8.5	21.57	4.715	−0.022	3.211	0.026	0.816	71.394	101.56	77.435	11.52	101.56