Structural and Electrical Properties of Fluorine Doped Nanocrystalline Tin Oxide Thin Film

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Abstract

The application of thin film technology is entirely entered into all branches of science and technology. Fluorine doped tin oxide thin films belong to a special class of metal oxide thin film, nanostructure thin film solar cell. Fluorine doped tin oxide thin films prepared on glass substrate by sol-gel dip-coating method. The effect of dopant concentration of ammonium fluoride and heat treatment temperature of SnO_2:F films on structural, surface morphology and electrical properties were investigated. The X-ray diffraction analysis of all SnO_2:F films indicated the tetragonal structure of tin oxide with polycrystalline nature. The SEM micrographs of the SnO_2:F films showed tetragonal crystal structure (flower like shape) and uniform surface pattern, at the optimized heat treated temperature 400 ºC. The best results were obtained the doping concentration of 7.5 % w/w ammonium fluoride at the heat treated temperature 400 ºC with the electrical resistance of 3.71 Ωsq^{-1} .
Key words: SnO_2:F thin film, dip-coating, tetragonal, polycrystalline

Introduction

Transparent conducting oxides (TCOs) have a wide variety of uses. Their ability to reflect thermal infrared heat is exploited to make energy conserving windows. These low-emissivity windows are the largest current use for TCOs. Oven windows employ TCOs to maintain an outside temperature which is safe to touch, and also to conserve energy. TCO's electrical conductivity is exploited in front-surface electrodes for solar cells and flat-panel displays. Automatically dimming rear-view mirrors for automobiles and electrically-controlled "smart" windows incorporate a pair of TCOs with an electrochromic material between them. Electric current is passed through TCOs to defrost windows in vehicles, and to keep freezer display cases free of frost. TCOs dissipate static electricity from the windows on Xerographic copiers. Glass touch-controls panels are etched from TCO layers. Transparent electromagnetic shields can be formed from TCOs. Invisible security circuits can be placed on windows. Transparent radio antennas can be built into automobile windows. Abrasion-resistant tin oxide coatings are used to protect the covers over optical bar-code readers. Acid-resistant tin oxide coatings are protecting windows from graffiti etched by acids sold for putting identifying marks on car windows (Stadler, 2012).

Tin (IV) oxide is a degenerate n-type wide band gap semiconductor that has a direct optical band gap of 8.37-4.3 eV. The transmittance of the tin (IV) oxide at near IR and visible wavelengths is high, typically over 80 % for thicknesses of a few hundred of nanometers, with plasma edge at a few hundred of nanometers, with plasma edge of about 3.2 mm. Tin (IV) oxide cassiterite, has a tetragonal rutile type of crystal structure. Tin (IV) oxide thin films fabricated with different deposition techniques are typically polycrystalline, retaining the crystal structure of the bulk material. The preferred orientation of the crystalline as well as the crystal size was dependent on the precursor, deposition techniques and conditions. The conductivity of undoped tin IV oxide is determined by oxygen vacancies, the concentration of which is difficult to control. Furthermore, reducing or oxidizing atmospheres have been found to strongly affect the conductivity of pure tin (IV) oxide. Changes are attributed to the electron mobility (m) rather than to the concentration of the change carries (N). This is caused by the chemisorptions and desorption of oxygen from the grain boundary. Chemisorbed oxygen at the grain boundary forms a space of positively charged layer just below the surface of the tin IV oxide and a potential barrier between the particles increases, leading to the decreased mobility of the electrons and hence to the reduced conductivity. Desorption of the oxygen from the grain boundary has an opposite effect on the electron mobility and electric conductivity. Due to these reason, undoped tin IV oxide thin film lack the thermal stability, and the doping of tin (IV) oxide in order to introduce electron degeneracy and environmental stability in preferred (Kololuoma, 2003).

The stability and conductivity of modern TCO materials, including doped tin oxide and doped zinc oxide, relies on the doping of the transparent metal oxides to yield a highly conductive thin film. The basis for selection of an appropriate dopant species relies on knowledge of the band structure for the metal oxide host. The relative energy levels associated with the valence electrons, the unoccupied conductance energy levels, and the energy levels created by dopant

atoms in the host matrix, must be considered. The structures and properties of metals are characterized by their delocalized valance electrons which give such materials high electrical conductivity. Whereas, in ionic and covalent structures the electrons are usually localized on particular ions or atoms (Solymer and Walsh, 2010).

Materials and Methods

Fluorine-doped tin oxide (SnO_2:F) thin film was prepared by using a sol-gel dip coating method on glass substrate. The precursor solution used was tin IV chloride pentahydrate ($SnCl_4.5H_2O$) prepared in ethanol. The fluorine doping was achieved using ammonium fluoride (NH_4F). The dopant concentration of the precursor (as weight percent of NH_4F to $SnCl_4.5H_2O$) was varied from 0 to 10 wt %. The layer-by-layer deposition cycle was done by alternating between dip-coating a thin layer and drying in air after each new layer. Then the film was annealed at different temperature (100 °C, 200 °C, 300 °C, 400 °C and 500 °C).

The surface morphology, structural characterization and electrical properties of the films with various doping percent concentration of ammonium fluoride and different heat-treated temperature were carried out.

Results and Discussion

XRD diffractograms were observed that well defined sharp diffraction peaks, which indicates that the film is polycrystalline nature. The undoped SnO_2 film eight peaks located at 26.636º, 33.898°, 51.747°, 54.742°, 61.863°, 64.691° and 65.965° correspond to the tetragonal phase at SnO_2 and the diffraction planes are (110), (101), (200), (211), (220), (301) and (310), respectively. The peaks were indexed using the powder diffraction files 41-1445 (SnO_2 tetragonal).

The X-ray diffraction spectra of SnO_2:F films for different fluorine doping levels in the precursor solution showed that the diffraction patterns are very similar in the target between 1 to 10 %w/w NH_4F. The X-ray diffraction studies showed that the prepared SnO_2:F thin films were polycrystalline in nature having nano scale with a tetragonal crystal structure. It can be observed that the films exhibited XRD patterns with diffraction peaks (110), (200), (211), and (222) correspond to the fluorine doped in SnO_2 crystal structure. The presence of these peaks indicates that all the films were found to be of the cassiterite type with a polycrystalline structure. All the films exhibit the preferred orientation along (110) plane which is also observed by other groups with SnO_2: F grown by dip coating technique. It is also observed that as the doping concentration increase, the intensity of peaks decreases which is because at higher doping concentration, the crystal structure starts to deteriorate. As described previously, it is mainly composed of nanocrystals with a very small amorphous portion.

A broad size distribution ranging from 43.66 nm to 75.30 nm was found for undoped film, however addition of NH_4F into the precursor decreased the crystalline size and the size distribution narrower (the calculated sizes were in the range of 42.05 nm to 51.35 nm respectively). The films are polycrystalline with (110) as a preferred growth orientation. The (110) peak is the strongest peak observed in all the films, the presence of other peaks as (021), (220), (310) and (- 201) had also been detected but with substantially lower intensities. The introduction of fluorine does not affect the structural properties of the films, however the decrease in the intensities of the main XRD peaks with increase fluorine doping levels were shown in Figure 1.

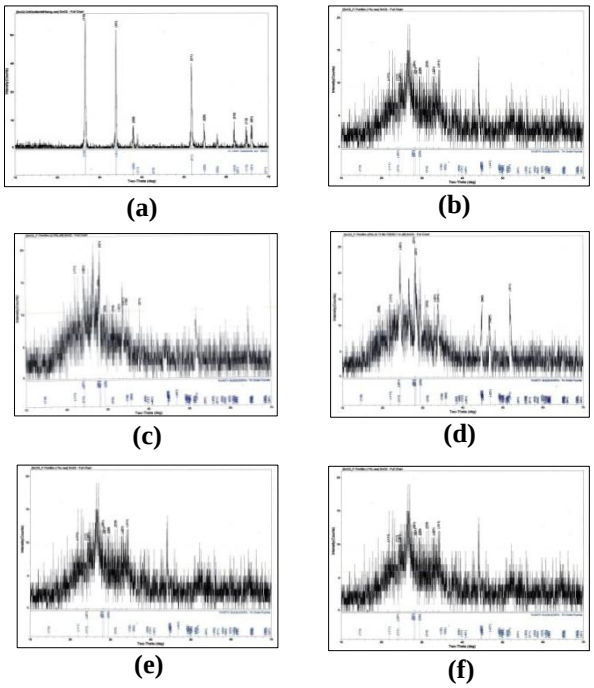
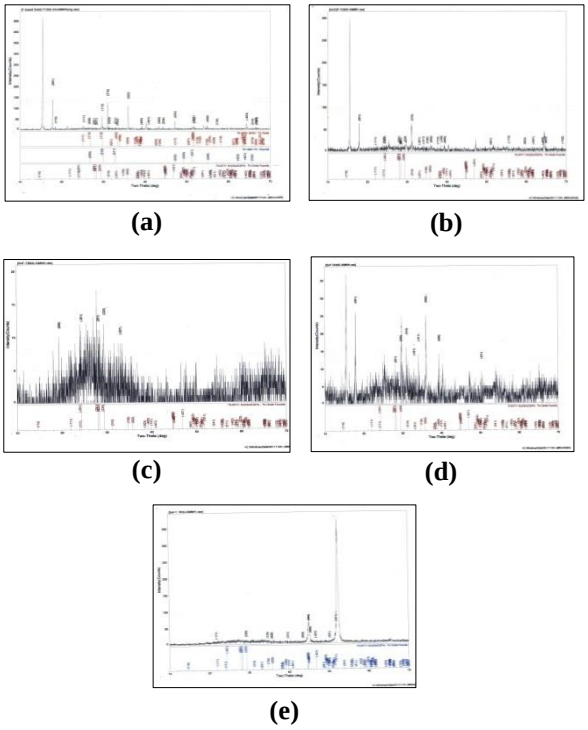


Figure 1. XRD diffraction pattern of prepared (a) un-doped SnO_2 thin film and SnO_2:F thin film with various doping concentration of ammonium fluoride (b) 1.0 % w/w NH_4 F SnO_2 (c) 2.5 % w/w NH_4 F SnO_2 (d) 5.0 % w/w NH_4 F SnO_2 (e) 7.5 % w/w NH_4 F SnO_2 (f) 10.0 % w/w NH_4 F SnO_2

The XRD diffractogram of prepared SnO_2: F thin films (7.5% w/w NH_4F) deposited by the dipping technique as a function of substrate temperatures (100 °C, 200 °C, 300 °C, 400 °C and 500 °C) are shown in Figures 2. The films deposited at 100 °C showed six peaks namely (110, (023), (113), (222) and (400) whereas the films deposited at higher temperatures showed as many as eight [(001), (201), (310), (400), (-221), (220), (-311) and (111)] peaks. Since all the peaks are sharp it is evident that the films deposited at 100, 200, 300, 400 and 500 °C are

polycrystalline in nature and are of tetragonal structure. Especially, the peaks (001), (201), (310) and (220) dominantly increased with increasing temperature. It has been found that the preferred orientation of SnO_2:F films on glass substrate is affected by heat treatment temperature.



(a) **(b)** **(c)** **(d)** **(e)**

Figure 2. XRD diffraction pattern of prepared SnO_2:F thin film at different heat treatment temperature (a) 100 °C (b) 200°C (c) 300°C (d) 400°C (e) 500°C

Lattice parameter

The average lattice constant (a) and (c) for the tetragonal phase structure of the (SnO_2:F) thin films for different fluorine doping and various temperature were determined and presented in Table 1 and Table 2. It was also found that the lattice constant (a) decrease slightly with increasing fluorine doping in the films and increase after 7.5 % w/w NH_4F of fluorine doping due to effect of doping process, while there are an arbitrary changed in the lattice constant (c) with increasing fluorine doping. At the optimum doping fluorine concentration 7.5 % w/w, the lattice constant a, c and c/a ratio are evaluated as 8.0288 Å, 5.7623 Å and 0.7177 Å, which is well in agreement with the standard values of JCPDS-PDF data (No. 41-1445) for SnO_2 powder specimen (Subramanian *et al.,* 2011). The lattice parameters a and c respectively are found to vary from 7.3389 Å to 9.4564 Å and 4.4289 Å to 6.2991 Å. Fluorine doped tin oxide is known to have fluorine incorporated by substitution of oxygen because of the similarities of the ionic radii (F-: 1.17 Å, O^{2-}: 1.22 Å), this results in free electrons which populate the conduction band. The change in lattice constant for the dipping techniques thin film over the bulk clearly suggests that the film grains are strained, which may be due to the change in nature and concentration of the imperfections. At the optimum heat treatment temperature 400 °C, the lattice constant a, c and c/a ratio are evaluated as 8.0483 Å, 5.9345 Å and 0.7374, which is well in agreement with the standard values (0.6746) of JCPDS-PDF data (No. 41-1445) for SnO_2 powder specimen (Subramanian *et al.,* 2011).

Crystalline Size

The average crystalline sizes of (SnO_2 : F) films for different fluorine doping levels were calculated by Debye Scherrer equation. It was found that the crystalline size increases initially with an increase in fluorine doping in the films reaches the maximum (51.35) nm at 7.5% w/w NH_4F, and thereafter it decrease with increasing in fluorine content in the films. This indicated that the crystalline size of the films depends on the concentration of dopant. The increase of fluorine doping will lead to smaller grain size up to 7.5 % w/w of fluoride. XRD spectra were analyzed with Gausian function where FWHM was determined. The ionic radices of F^-(1.33 Å) is close to that of O^{2-} (1.32 Å), so that doping process can take place easily. The crystalline size of SnO_2:F films deposited at temperature (100 °C, 200 °C, 300 °C, 400 °C and 500 °C) are calculated using Debye Scherrer's equation. It was found that the crystalline size of SnO_2:F film at 400 °C is (61.05) nm, and the crystalline size become larger with the substrate temperature.

Table 1. Values of lattice constant, unit cell volume, crystallite sizes and dislocation density for SnO_2:F thin films with different fluorine doping concentration

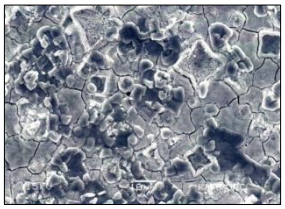
Weight of NH_4F (%w/w)	a (Å)	c (Å)	Unit cell volume ($Å^3$)	c/a	D (nm)	δ ($\times 10^{14}$ lines/m^2)
1.0	8.6004	5.4633	404.10	0.6353	42.05	5.66
2.5	8.4070	4.5809	323.76	0.5449	42.32	5.58
5.0	8.3099	4.4434	306.84	0.5347	50.78	3.88
7.5	8.0288	5.7623	371.44	0.7177	51.35	3.79
10.0	8.5690	4.3214	317.31	0.5043	50.16	3.97

Dislocation Density

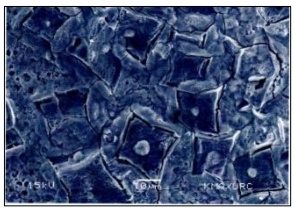
The dislocation density (δ) is defined as the length of dislocation lines per unit volume, δ is the measure of the amount of defects in a crystal. Dislocation density (d) was determined by the relations, $\delta = \frac{1}{D^2}$ (D = crystalline grain size). It was found that the dislocation density decreased with increasing grain size. Therefore, the growth mechanism involving dislocation is a matter of importance. Dislocations are imperfect in a crystal associated with the mis-registry of the lattice in one part of the crystal with respect to the other parts. Unlike vacancies and interstitial atoms, dislocations are insufficient to account for their existence in the observed dislocation densities (Tatar *et al*., 2011).

SEM Analysis

The surface morphology of the films was studied by Scanning Electron Micrograph (SEM). SEM micrographs of prepared fluorine doped tin oxide films with different heat treatment temperature (100 °C to 500 °C) and undoped tin oxide film deposited by dip coating technique are shown in Figures 3. All of the images were found to be polycrystalline with various surface grain shapes and sizes. It was observed that the grain size become larger and the crystallinity was improved with the increase in the heat treatment temperature. The SnO_2:F thin film using heat treatment 500°C contained the largest average grain size and the highest crystallinity highest peak intensity in XRD chromatogram.



(a)



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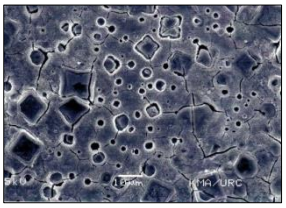

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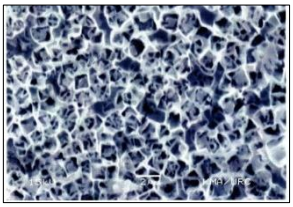
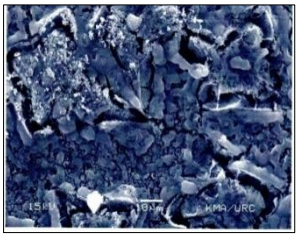


(d)



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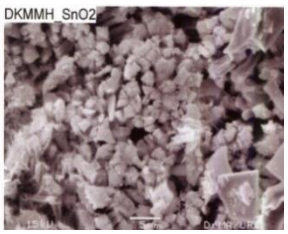

(f)

Figure 3. SEM micrographs of SnO_2:F thin films at (a) 100°C (b) 200 °C (c) 300 °C (d) 400 °C (e) 500 °C temperatures and (f) undoped SnO_2 film

Besides that, there are some crystal shapes structures like as mostly tetragonal shape. This observation was approved to the XRD results as tetragonal shape. Therefore, SEM results were corroborating the XRD findings. Although being the most crystallized, surface porous microstructure was observed on the surface of the films. The films deposited at higher temperature had developed much better-defined facets than lower temperature and this indicated that higher temperature can caused better crystallinity. The film deposited by dip-coating showed clear flowerlike crystal shape on the surface and the presence of uniform and dense microstructure apparently devoid of any cracks and voids, although it was possible that some microscale porosity was present in the film. The SnO_2:F film deposited at different temperature was found to be polycrystalline with various surface grain and sizes. The fluorine doped tin oxide films characterized by uniform size grains with cubical shape at the substrate temperature 400 °C, which is on the average smaller than grains in the high temperature region. Consequently, the results were good agreement with XRD observations.

Table 2. Values of Lattice constant, unit cell volume, crystalline sizes and dislocation density for SnO_2:F thin films with different temperatures

Temperature (°C)	a (Å)	c (Å)	Unit cell volume ($Å^3$)	c/a	D (nm)	δ ($\times 10^{14}$ lines/m^2)
100	9.1600	4.6394	389.27	0.5065	65.03	2.36
200	9.5464	4.9654	452.52	0.5201	77.51	1.66
300	9.2596	4.9507	424.47	0.5347	65.04	2.36
400	8.0483	5.9345	384.41	0.7374	61.05	2.68
500	8.8469	6.0673	474.87	0.6858	87.88	1.29

Electrical Properties of Prepared Fluorine Doped Tin Oxide Thin Film

Sheet resistance measurements were recorded using a linear four point probe (Olopade *et al.,* 2012) method. The minimum sheet resistance value of 9.06 Ωsq^{-1} was found for 7.5 % w/w NH_4F and at the point of 10.0 % w/w NH_4F, the sheet resistance observed the higher value of 14.35 Ω sq^{-1}. It can be suggested that additional fluorine atom as oxygen substitute or at the interstitial into the SnO_2 structure causes a decreased in resistivity and give rise to n-type conductivity, which may be depends on stoichiometric deviation and heat treatment temperature. This is due to the fact that at higher concentration, fluorine atoms incorporates at the interstitial sites and crystal structure of the films start to deteriorate hence decrease the mobility of the free electrons and increase the electrical restitutes for an O^{2-} anion in the lattice, creates more free electrons and decreases the value of sheet resistance. The improvement of optical and mechanical properties of thin film from sol-gel deposition method, the sample should be heat treated to remove water and organic materials. The sheet resistance value of SnO_2:F thin films at 250 °C was (9.85 Ωsq^{-1}) and its gradually decrease to 3.71 Ωsq^{-1} with the heat treated temperature of 400 °C. And then, the resistance value increased with the heat treated temperature of 450 °C and 500 °C. According the previous reports, the substrate temperature was over 400 °C, the amorphous structure transformed into crystal structure, and then the narrowing of grain boundaries which result in a decreased in the conductivity (Adelkhani *et al.,* 2007). The sheet resistance does not change more with the temperature increase from 400 °C to 500 °C, due to the slight change of the crystal structure. Therefore, the sheet resistance was slightly varied with the substrate temperature in the range of 400-500 °C. Therefore, the sheet resistance value and polycrystalline nature depends directly on the heat treated temperature. Thus, the sheet resistance of prepared SnO_2:F thin films at 400 °C was observed lowest value and this temperature is optimal temperature for that treatment process.

Conclusion

The fluorine doped tin oxide transparent thin film was fabricated by sol-gel dip coating method. The X-ray diffraction studies confirmed the tetragonal structure with polycrystalline nature. The preferred directions of crystal growth in the diffractogram of SnO_2: F films correspond to the reflection from the (110), (200), (220) and (310) planes. The matching of the observed and standard d-values confirmed that the deposited films are of tin oxide with tetragonal structure. The mean grain size varies between 51.99 nm and 87.88 nm and the increase in grain size beyond the temperature 400 °C may be due to the increase in grain growth rate and crystalline size. The SEM micrographs showed that the variation of substrate temperature results in different grain size and shapes for different orientations while the SnO_2:F film heat treated at 400 °C shows uniform surface pattern with evenly distributed fine grains. However there was some crystal shapes structures like as mostly tetragonal shape were found in other heated temperature of SnO_2:F thin films. This observation was approved to the XRD results as tetragonal structure of prepared SnO_2:F thin films. The minimum sheet resistance was obtained with the dopant concentration of 7.5 % w/w NH_4F and heat treated temperature at 400 °C. It can be explained that the incorporation of fluorine is well known to enhance the conductivity of SnO_2. Thus, the sheet resistance of prepared SnO_2:F thin films at 400 °C was observed lowest value and this temperature is optimal temperature for that treatment process. Thus this studied indicated that the prepared SnO_2:F thin films were used as low coast transparent conducting electrodes in the fabrication of Dye Sensitized Solar Cell.

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