Effect of heat treatment temperature on the spin coated fluorine doped tin oxide thin films for solar cell applications

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ABSTRACT

Flourine doped tin oxide thin films have been prepared on glass substrate by spin coating method via sol-gel route. The rheological behavior of the prepared sol solution has been studied by viscosity measurement and from this, the optimum coating period has been investigated and reported. The films have been developed with fixed dopant concentration (F/Sn ratio 7.5 at %), under optimized operating condition viz., turntable spin rate (3000 rpm), spin time (10 Seconds) and number of coatings (10). The spin coated film has been heat treated at temperatures 325 °C, 350 °C, 375 °C, 400 °C, 425 °C and 450 °C. The X-ray diffraction studies of FTO films indicate the tetragonal rutile structure of tin oxide. All films show polycrystalline nature with preferred orientation along the (110) plane and the lattice constant a and c have been evaluated as 4.7324 Å and 3.1924 Å. The variation of average grain size with different heat treatment temperature have been investigated and presented. All the FTO films show good transmittance in the visible region and the fundamental absorption edge lies in the UV region. The direct band gap energy evaluated from the optical absorption data lies between 3.25 eV and 3.85 eV. The minimum value of sheet resistance and electrical resistivity come to 40 Ω/ and 7.4 x 10⁻³ Ω-cm for the FTO film heat treated at 375 °C. The effect of heat treatment temperature on resistivity, carrier concentration and mobility of the as coated FTO films have been investigated and the results are discussed. The AFM micrographs of the FTO film shows uniform surface pattern, at the optimized heat treatment temperature 400 °C. Studies indicate that the sol gel spin coated FTO films prepared under the optimized operating conditions could be the potential candidates for the solar cell technology.

Key words: Transparent Conducting Oxide (TCO) – Spin coating – Flourine doped tin oxide thin films – Heat treatment – Rheological properties – Optical properties – Structural properties – Electrical properties – Surface properties

1. INTRODUCTION

TCO thin films of semiconducting materials, such as TO (SnO₂), FTO (SnO₂:F) and ATO (SnO₂:Sb) are finding wide range of device applications, owing to their specific, combined electrical, optical and chemical properties. The FTO is an n-type and wide band gap semiconductor and has special properties viz., high transmittance in the visible and high reflectivity in the infrared region [1], excellent electrical conductivity [2], [3], greater carrier mobility [4], [5] and good mechanical stability [4], [5]. Due to these interesting Characteristics it is used in solar cells [6] as transparent and protective electrodes [1], [7], [8], flat plate collectors as Spectral selective windows [1],[8], sensors for gas detection [9],[10], photo thermal converters [11], providing thermal insulation for houses [11]. Since the properties of the FTO films strongly depend on the method of preparation and growth parameters [5], [11], several techniques such as Chemical Vapour Deposition [12], Photo CVD and Thermal CVD [13], APCVD [28], Sputtering and related methods [5],[11],[14], Spray Pyrolysis [1 – 11] and [15 – 23] and thermal evaporation [11] have been successfully tried to produce device quality films. Recently [24 - 26], an increasing interest towards sol-gel synthesis of the SnO₂ based thin films has been observed due to the method advantages such as increased capability to tailor complex compositions, simple and economical technological equipment, low thermal budget necessary for film consolidation and specific controlled porosity properties [27]. It has been found that the sol-gel spin coating method has not been widely tried for the preparation of the FTO films. In the spin coating technique, heat treatment temperature influences the stoichiometry, stability, physical, structural and surface properties of the developed film. Hence, in the present work, an attempt has been made to prepare and study, the effect of heat treatment temperature on the properties of the sol-gel spin coated FTO thin films.
2. EXPERIMENTAL

The sol was prepared by dissolving 13 grams (0.037 mole) of Tin chloride (SnCl₄·5H₂O) in 100 ml of ethyl alcohol. Ammonium fluoride (NH₄F) was then added into the solution for fluorine doping. The amounts of NH₄F added were 0.0037, 0.00925, 0.0185, 0.02275, 0.037 and 0.044625 moles, which corresponds to the [F] / [Sn] ratios of 1.0, 2.5, 5.0, 7.5, 10.0 and 12.5 at %. To increase the solubility of the solute and to induce the simultaneous condensation and gelation, 5 ml of .1N concentrated Hydrochloric acid was then added into the solution as a catalyst [32]. The mixed solutions were well stirred and refluxed for one hour at 60 °C. The solutions were cooled in the ambient and then aged in open beakers at room temperature, for gelation. The rheological behavior of the prepared sol solution is studied by viscosity measurement.

FTO thin film of [F] / [Sn] ratio 7.5 at % (in the solution) was developed by dispensing about 3 ml of the as prepared gel on the glass substrate mounted over the turn table, which was spinned at 3000 rpm for 10 sec. The number of coatings was optimized to 10, in order to get films of good electrical and optical properties. The as coated films were then heat treated in a furnace at temperatures 325 °C, 350 °C, 375 °C, 400 °C, 425 °C and 450 °C, for about 30 minutes. The transmittance of the films was measured in the UV – Visible region, using Perkin and Elmer spectrophotometer, from which the other optical constants were arrived. X-ray diffraction measurements were carried out using Philips Analytical Diffractometer. Sheet resistance, resistivity and carrier concentration, mobility were evaluated using the standard four probe and Hall- effect method. The surface of the films was investigated using atomic force microscope.

3. RESULTS AND DISCUSSION

3.1 Rheological Properties of the sol solution

The viscosity variation of the sol solution with aging time, for the sol prepared with the dopant concentration [F]/[Sn] ratio 7.5 at %, at room temperature is shown in the fig.(1), which indicates a little increase in viscosity up to the aging period of first three days. After three days, the viscosity breaks off the base line termed as break off point and saturated on the sixth day called as the saturation point. From the fig.(1), it is evident that viscosity abruptly increase between the third and sixth day of aging (i.e., between the break off point and saturation point) and this rise is apparently due to the occurrence of polymerization, i.e., condensation, among the hydroxo ligands attached to the tin ions [36]. The saturation behavior indicates the colloidal nature of the gelatinous suspension, which is devoid of strong cross-linking among the clusters in the solution [36]. The physical observation of the solution during the entire period shows increasing cloudy nature of the solution. Flow curves of the solution also show the shear thinning behavior, regardless of the aging time.

If the films were developed by using the gel aged lower than its break-off point, then the spreading and thinning mechanism of the sol becomes strong and as a result the evaporation process was also rapid, which causes non-uniformity in film thickness and striations. In contrast, if the films were coated with the solution above the saturation point, most quantity of the sol gel is thrown away from the substrate due to high viscosity, leading to poor adherence and also causes comet formation on the as-coated film. Between 3 1/2 and 5 1/2 days of aging, good and uniform coating could be obtained. So it can be inferred that the optimum coating period of the sol solution, so as to obtain good quality films, a time “ t1/2 ” can be adopted, at which the viscosity reaches one – half of the sum of the break off and saturation viscosities. From the fig.(1), t1/2 value is found to be 4 1/2 days and this is regarded as the optimum coating time for the sol solution. But experimental observations reveal that sol solution coated between the period 3 1/2 and 5 1/2 days provide good quality films. Hence in the present work the optimum coating period of the sol solution is fixed between 3 1/2 and 5 1/2 days.

3.2 Structural Properties

The XRD patterns of FTO thin films heat treated at different temperatures 325 °C, 350 °C, 375 °C, 400 °C, 425 °C and 450 °C are shown in the fig.(2). All the films show polycrystalline, tetragonal rutile structure of tin oxide with preferred orientation along (110) plane. Other orientations such as (101) and (211) are also observed for the films heat treated between 350 °C and 450 °C, with comparatively lower intensities. Apart from these planes, film heat treated at 400 °C shows two additional orientations viz., (200) and (301) whilst (301) is the additional peak noticed for the film heat treated at 425°C and 450°C.
The (110) peak is the strongest observed peak for all the films, which may be attributed to the oriented overgrowth as a result of preferred nucleation on the growing surface. K.H. Kim [34] has reported a similar observation for the undoped SnO$_2$ thin film prepared by CVD method. The sharpness and intensity count of the orientations viz., (110), (101) and (211) increases from 350 °C and reaches a maximum at 375 °C and then decreases gradually with the increase in temperature (above 375 °C). An additional plane (200) is seen only for the film heat treated at 400 °C and this plane is found missing for the films heat treated at all the other temperature. Sharpness and intensity of the additional orientation (301) increases between 400 °C and 425 °C, which may be due to the increase in grain growth and falls between 425 °C and 450 °C may be attributed to the decrease in grain growth at the plane (301) caused by the deterioration effects. The reason for the appearance of additional peaks viz., (200) and (301) beyond the heat treatment temperature 375 °C could be attributed to the unoriented growth due to homogeneous nucleation. At the optimum heat treatment temperature 375 °C, the lattice constant a, c and c/a ratio are evaluated as 4.7324 Å, 3.1924 Å and 0.6746 , which is well in agreement with the standard values of JCPDS – PDF data (No. 41 – 1445) for SnO$_2$ powder specimen.

The grain size of the films has been evaluated using the Debye Sherrer’s formula and the variation of average grain size with heat treatment temperature is shown in fig.(3). The increase in grain size beyond the temperature 375 °C may be attributed to the increase in grain growth rate and crystallite size due to the rapid increase in adsorption and diffusion rate of atoms with temperature, which significantly increases the grain size. The mean grain size varies between 143.76 nm and 414.8 nm. James Proscia [28] illustrated a similar observation for the FTO films prepared by APCVD technique. Geetha Sanon [31] has also reported an analogous observation for the undoped tin oxide thin film prepared by CVD method. These observations are also quite comparable with the results and conclusions arrived by James Proscia [28], Geetha Sanon [31], N. Srinivasa murthy [39], G.N. Advani [35], J.C.Manifacier [8] and R.Pommier [16].

3.3 Electrical Properties

Addition of fluorine atom as oxygen substitute or at the interstitial into the SnO$_2$ structure causes a decrease in resistivity and give rise to n-type conductivity, which mainly depends on stoichiometric deviation and heat treatment temperature. Variation of sheet resistance ($R_s$) and resistivity (?) with different heat treatment temperatures, is shown in the fig.(4), which clearly illustrate that the $R_s$ and ? value decreases with the increase in baking temperature up to an optimum temperature 375 °C and increases sharply above 375 °C. The as-spin coated films contain relatively low concentrations of oxygen. Therefore the initial heat treatment of these films at lower temperature (325 °C to 375 °C) leads to the chemisorption of oxygen from the atmosphere into the films, which subsequently reduces the film resistivity. Heat treating at higher temperature (above 375 °C) leads to the oxygen desorption of the films, owing to the relatively high concentration of oxygen in the film, which consequently raises the resistivity. This observation is well in agreement with the results illustrated by J.C. Manifacier [1], [8], R.Pommier [16], M.Fantini[17], E.Shanthi [29], and A.L.Dawar [38].

The sheet resistance and resistivity is found to be minimum with the value 40 O/ and 7.4 x 10$^{-3}$ Ω-cm respectively, for the FTO thin film heat treated at 375 °C. These results are well in agreement with the observations of J.C.Manifacier [1], reported a minimum value of $R_s = 10.6$ Ω / and $? = 4$ to 6 X $10^{-3}$ Ω-cm, for the spray deposited FTO thin films, M.Fantini[17] reported a low value of $? = 1.1$ x $10^{-3}$ Ω-cm for the spray deposited FTO thin films, developed with the substrate temperature 350 °C, H.De Waal [4], reported a low value of $R_s = 10$ Ω / and $? = 5.5$ x $10^4$ Ω-m, for the spray deposited FTO thin films and O.P. Agnihotri [7] reported a low sheet resistance of 3 Ω / for the spray deposited FTO thin film at the optimized substrate temperature between 400 and 450 °C.
The variation of carrier concentration ($n$) and carrier mobility ($\mu$) with different heat treatment temperature is shown in the fig. (5), which indicates a sudden increase in $n$ and $\mu$ values up to the optimum temperature $375^\circ C$ and then a drastic fall in $n$ and $\mu$ above $375^\circ C$. The films heat treated at lower annealing temperature in ambient leads to the chemisorption of the oxygen from the atmosphere into the films and also contributes very low grain boundary scattering, as a result $n$ and $\mu$ values increase rapidly up to $375^\circ C$. At higher heat treatment temperatures (above $375^\circ C$), the desorption process dominates irrespective of the amount of oxygen present in the films. Also the grain boundary scattering mechanism dominates at a higher baking temperature because of the increase in grain and crystallite size at higher temperatures due to which $n$ and $\mu$ values increases above the optimum temperature $375^\circ C$. These interpretations are well in agreement with the results of M. Fantini [17], R. Pommier [16], E. Shanthi [40].
3.4 Optical Properties

Transmission spectra of FTO thin film spin coated at different heat treatment temperatures, in the wavelength region 300 nm to 700 nm is shown in fig.(6). The plot depicts high optical transmittance for the film heat treated at the temperature 375 °C. Highest value of transmittance is observed to be 94.4 % (at 550 nm) for the film heat treated at 375 °C and this is attributed to the low scattering effect and uniform film thickness caused by smooth and good surface texture of the film. The average transmittance is found to increase sharply in the temperature range 350 °C to 375 °C and then to decrease steeply above the optimum heat treatment temperature (between 375 °C and 400 °C). The average transmission value is observed to vary between a high of 94.4 % (at 375 °C) and a low of 67.77 % (at 400 °C) and these results are well in agreement with the results reported by E.Shanthi [30], [37], S.Shanthi [3], [41], J.C.Manifacier [1], O.P. Agnihotri [7]. The increase in optical transmittance with the increase in heat treatment temperature between 350 °C and 375 °C may be attributed to the decrease in absorption, diffuse and multiple reflection caused by the fall in grain size, increase in surface smoothness, and uniformity in film thickness. The decrease in transmittance with the increase in heat treatment temperature between 375 °C and 400 °C could be attributed to the increase in scattering and perturbation effect due to large grain size and crystal aggregate, caused by the increase in film thickness with temperature and the presence of large number oxygen vacancy, which act as the scattering center. These interpretations are well in agreement with the observations reported by Y.J. Lin [33], E. Shanthi [37], S.Shanthi [41] and M.Fantini [17].
The variation of square of the absorption coefficient ($a^2$) with photon energy for FTO thin film heat treated at different temperature is shown in fig.(7). The plot yields the value for allowed direct transition, which lies between 3.25 and 3.85 eV for different heat treatment temperatures. The figure depicts a gradual decline in the band gap energy with the increase in heat treatment temperature. The band gap energy is found to be very wide with the value of 3.85 eV at 375 °C and narrow with the value of 3.25 eV at 400 °C. The smooth variation of refractive index ($n_f$) with wavelength for the FTO thin films heat treated at different temperature is shown in fig.(8). The refractive index values varies between 1.422 and 2.011 in the wavelength range of 325 to 700 nm and the lowest value of $n_f$ (1.422) is noticed for the film heat treated at the temperature 375 °C at the wavelength 550 nm. These results are good in agreement with the reported values of J.C.Manifacier [1], E.Shanthi [30], [37], and S.Shanthi [41]. The low refractive index value observed at the temperature 375 °C may be attributed to the higher optical transmittance due to low crystallite size, low extinction coefficient, regular and smooth film surface and lower absorption contributed by low absorption coefficient of the film.

All the above investigations and the interpretations depict that FTO thin films of good reproducibility and excellent opto electronic properties can be obtained by sol-gel spin coating method at the optimum heat treatment temperature 375 °C, which can be used as a potential N-type material for solar cell applications.
3.5 Surface Properties

The two and three dimensional AFM image of the FTO thin film heat treated at 375 °C is shown in fig.(9) and fig.(10) respectively. The AFM micrographs show a smooth and uniform surface pattern without any dark pits, strains and pinholes. Further the image indicates evenly distributed fine grains over the entire area of analysis.
Figure 9: 2D AFM Image of FTO thin film heat treated at 375 °C

Figure 10: 3D AFM Image of FTO thin film heat treated at 375 °C
4. CONCLUSION

Flourine doped tin oxide thin films of excellent reproducibility, adherence and device quality can be prepared by spin coating method via sol-gel route under optimized conditions viz., dopant concentration (F/Sn ratio 7.5 at %), heat treatment temperature (375 °C), turntable spin rate (3000 rpm), spin time (10 Seconds) and number of coatings (10). The rheological studies indicate that the optimum coating period for the sol solution lies between 3 1/2 and 5 1/2 days. The XRD studies indicate the polycrystalline tetragonal rutile structure of tin oxide, with preferred orientation along the (110) plane and the lattice constant a and c have been evaluated as 4.7324 Å and 3.1924 Å. The mean grain size varies between 143.76 nm and 414.8 nm and the increase in grain size beyond the temperature 375 °C may be due to the increase in grain growth rate and crystallite size. All the FTO films show good transmittance in the visible region and the fundamental absorption edge lies in the UV region. Highest value of transmittance is found to be 94.4 % (at 550 nm) for the film heat treated at 375 °C and the average transmission value of the films vary between 92.4 % (at 375 °C) and 67.77 % (at 400 °C). The direct band gap energy evaluated from the optical absorption data lies between 3.25 eV and 3.85 eV. The refractive index values varies between 1.422 and 2.011 in the wavelength range of 325 to 700 nm and the lowest value of η (1.422) is noticed for the film heat treated at the temperature 375 °C at the wavelength 550 nm. The minimum value of sheet resistance and electrical resistivity come to 40 Ω/ and 7.4 x 10^-3 Ω-cm for the film heat treated at 375 °C. Studies indicate that at lower temperatures (325 °C to 375 °C), chemisorption mechanism predominates and the grain boundary scattering becomes low, which subsequently reduces the film resistivity and increases carrier concentration and mobility. At higher temperatures (above 375 °C) oxygen desorption phenomena becomes predominant with higher grain boundary scattering, which causes an increase in resistivity and decrease in carrier concentration and mobility of the films. The AFM micrographs of the FTO film heat treated at 375 °C shows uniform surface pattern with evenly distributed fine grains. Studies indicate that the sol gel spin coated FTO films prepared under the optimized operating conditions could be the potential N-type material for the solar cell fabrication.

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