

Optical and electrical properties of F doped SnO₂ thin films

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A wide variety of commercial devices needs conducting/semiconducting metal oxide materials due to their unique combination of high optical transparency and high electrical conductivity. Moreover, induced defects within the host atomic arrangement are fairly responsible for their desirable optical and electrical properties. Therefore, studying the effect of doped ion is essential for better understanding of the behaviour of conducting/semiconducting metal oxides. In this context, influence of fluorine doping on optical and electrical properties of polycrystalline SnO₂ thin films synthesized using sol-gel assisted spin coating method have been investigated in this work. The structural, optical and electronic analysis of pure and F doped SnO₂ thin film indicates major effect of F doping concentration. Based on the electrical measurement these films show semiconducting nature with optical band gap in the range from 2.88 to 3.11 eV with increasing F concentration. These results suggest that F doped SnO₂ thin films are suitable in field of advance electronic or nano-electronic device technology.

Keywords: Semiconductors, Thin films, Defects, Electrical properties

1 Introduction

Electronics market today is facing a massive disruptive evolution from heavy, bulky and rigid devices to light-weight, soft and flexible devices/gadgets¹. Promising new applications like smart phones, wearable and textile integrated systems^{2,3}, embedded patch-like electronics⁴, epidermal devices⁵, etc., are arriving to revolutionize our daily life. To enable all these applications, electronic devices have to become thinner, lighter, transparent, etc. Metal oxide based semiconductor thin films are particularly attractive due to their application in device technology including above all¹. Moreover, there are many applications of metal oxide thin films, in solar cells devices⁶, liquid crystal displays⁷ and light emitted diode⁸, etc., synthesized via variety of techniques.

Tin oxide, SnO₂ is particularly attractive due to its wide band-gap semiconductor nature ($E_g > 3$ eV), high optical transparency ($T \geq 85\%$) and *n*-type semiconducting character⁹. SnO₂ is mechanically, chemically and electrochemically stable. The undoped stoichiometric SnO₂ films have very low electrical

conductivity because of its low intrinsic carrier density and mobility¹⁰, whereas, the electrical conductivity can largely enhanced via doping with foreign impurities. The most favored dopant is antimony which substitutes the tin cation or by fluorine (F) via substituting the oxygen atoms¹⁰. In the present work, we report influence of fluorine (F) doping on structural, optical and electrical characteristics of SnO₂ thin film synthesized via sol-gel assisted spin coating technique.

2 Experimental Details

For deposition of films, F doped SnO₂ solution was prepared by dissolving 0.4 M Stannous chloride and (0, 10, 20 and 30 wt %) Ammonium fluoride in ethylene glycol (EG) solution under rigorous stirred at room temperature. Few drops of this solution were placed on cleaned glass slide and spined at 2000 RPM for 15 s using spin coating system. Above procedure was repeated 10 times for all F concentration mentioned above and samples were annealed at 400 °C for one hour. The thickness of the film estimated was found to be ~ 400 nm ± 10 nm. These films were then characterized using X-ray diffraction (XRD); UV-Vis spectroscopy; four probe method and I-V measurement techniques.

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3 Results and Discussion

3.1 XRD analysis

Figure 1 show XRD spectra collected on F doped SnO₂ samples and analysis confirms polycrystalline nature of SnO₂ with peaks corresponding to (110), (101), (200), (211), (301), (202) and (321) crystalline planes of rutile tetragonal SnO₂¹¹. From figure it is clear that dopants does not create additional parasitic phase, whereas, it affects the peak position and width. This shift in peak position results in increase in 'd' with increasing F concentration, which eventually increases the lattice parameters 'a' and 'c' from 4.73 to 4.77 Å and 3.18 to 3.22 Å, respectively.

In general, if the dopant with lesser ionic radius (F⁻, ionic radius 42 pm) than the host atoms (O²⁻, ionic radius 48 pm) is introduced in the matrix at substitutional site, the lattice constant decreases and vice-versa¹². Moreover, for a crystal whose lattice reacts as an elastic medium, the Vegard law is obeyed, i.e., change of the lattice constant is proportional to the concentration of the dopant and to the difference between ionic radii of the dopant and substituted host atom¹². In this case, no change in lattice constants was observed in 10 wt % F doped SnO₂, which signifies that the doped F atoms occupies substitutional site (oxygen atom site). Whereas, an increase in the lattice constants above 10 wt % F doped SnO₂ sample implies that the excess F doped in SnO₂ starts occupying interstitial positions (since up to 10 wt % F doping all oxygen vacancy positions or substitutional site in SnO₂ are occupied by F ions, while above this concentration as no substitutional

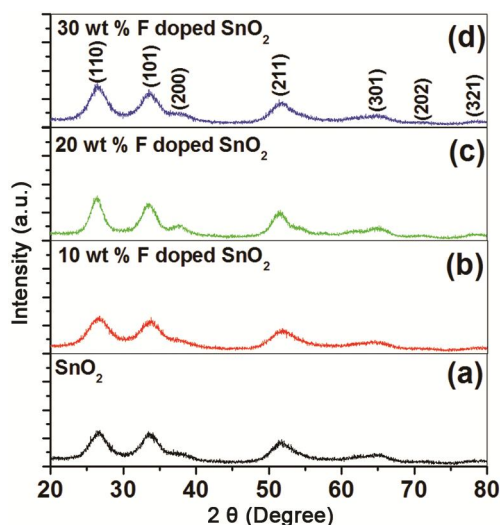


Fig. 1 – XRD patterns of (a) SnO₂, (b) 10 wt % F doped SnO₂, (c) 20 wt % F doped SnO₂ and (d) 30 wt % F doped SnO₂ samples.

site is free the excess F ions have to get accommodate in the free space (interstitial) in the crystal), which enlarges the lattice resulting in an increase in the lattice constant¹³⁻¹⁷.

3.2 UV-Vis analysis

Figure 2 shows UV-Vis optical absorption spectra of F doped SnO₂ thin film as a function of F concentrations. Each of these films possesses an average absorption in ultraviolet region. Doping at 10 wt % show increase in the absorption of the film, whereas, the absorption decreases at higher F concentration (20 and 30 wt %, respectively). In order to find the band gap (E_g) of F doped SnO₂ films at various F concentrations, the obtained absorption data was fitted with Taue's equation. From the plot of $(\alpha h\nu)^2$ versus $h\nu$ for F doped SnO₂ thin films (not shown here), the E_g value of the undoped SnO₂ thin film was found to be 2.88 eV and found to increase to 3.11 eV with increasing F concentration up to 30 wt % in SnO₂. It is clear that the optical band gap is smaller than the value of 3.62 eV for bulk SnO₂¹⁸.

3.3 Electrical properties

Electrical properties of F doped SnO₂ thin film samples were estimated using four probe resistivity and hall measurement techniques. The obtained resistivity data is shown in Fig. 3(a). For undoped SnO₂ thin film the estimated values of resistivity, carrier concentration and mobility are found to be $\sim 1.01 \times 10^5 \Omega\text{-cm}$, $\sim 7 \times 10^{16} \text{ cm}^{-3}$ and $\sim 0.0052 \text{ cm}^2/\text{V-s}$. As the F concentration increases, major decrease in the resistivity is observed with increase in carrier concentration and mobility values. For 30 wt % F doped SnO₂, the resistivity drops down to $\sim 7.3 \times 10^3 \Omega\text{-cm}$, whereas, carrier concentration and mobility increased to $\sim 1.29 \times 10^{18} \text{ cm}^{-3}$ and $0.015 \text{ cm}^2/\text{V-s}$.

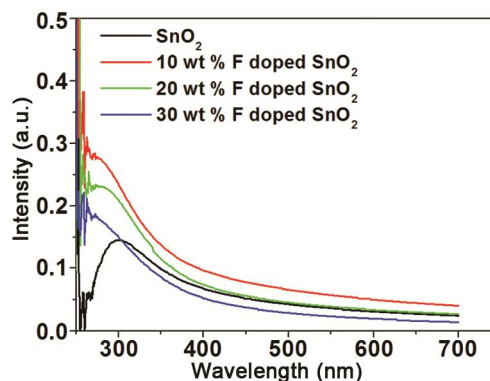


Fig. 2 – UV-Vis absorption spectra for F doped SnO₂ films with different F concentration from 0 to 30 wt % showing decrement of absorption peak.

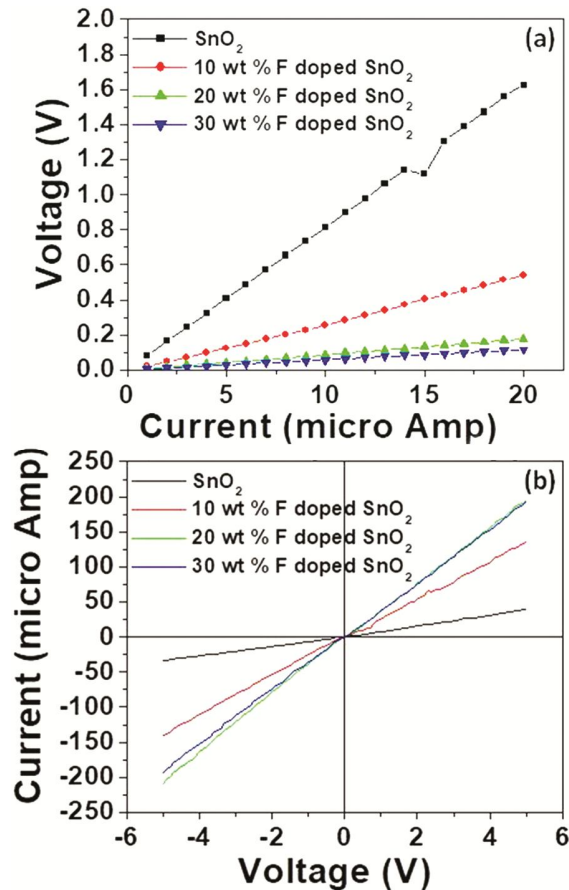


Fig. 3 – (a) The change in resistivity of F doped SnO₂ thin film with increasing F concentration and (b) *I-V* measurement on the F doped SnO₂ samples using Pt as top and bottom electrode.

It is observed that resistivity of SnO₂ thin film is dependent on the F concentration level, in particular, on the position occupied by F ions in the matrix¹². If F ion occupies the oxygen sites in the SnO₂ lattice, it creates additional donor site, which give rise to a major decrease in resistivity and increase in the free carrier concentration, as found in 10 wt % F doped SnO₂. At higher F concentration (20 and 30 wt %), slow decrement in resistivity suggests that excess F atoms do not occupy the proper lattice positions to donate excess free charge carriers, whereas, it increases disorder at interstitial position. These interstitially occupied F ion acts like compensating acceptors or potential traps for the free electrons^{17,18} resulting in not much decrease in resistivity of the film at room temperature. It is found that as the concentration of doped F increases in SnO₂ thin films the resistivity decreases and carrier concentration increases.

To confirm the above results, *I-V* measurements were carried out on the thin film samples using Pt

electrodes. Figure 3(b) shows a linear increase in transient current with voltage, moreover, the current increases with increasing F doping concentration in SnO₂ up to 20 wt %. Interestingly, a minor decrease in transient current is observed for 30 wt % F doped SnO₂ thin film. This is attributed to the induced compensating acceptors in SnO₂ lattice by excess F concentration. The obtained result resembles with the above results of four probe resistivity measurement, as shown in Fig. 3(a). Conductivity of the sample found to increase with increasing F concentration in SnO₂ thin film and the film show semiconductor nature.

4 Conclusions

In this work, F doped SnO₂ thin films have been synthesized successfully via sol-gel assisted spin coating technique. The post annealing of the films incurred rutile tetragonal phase in SnO₂ thin films at 400 °C. A red shift in the lattice constants with increasing F concentration in SnO₂ reveals lattice expansion due to excess F ion occupied at interstitial position in SnO₂ matrix. An increase in the band gap of SnO₂ with F concentration has also been observed. Moreover, influence of F doping on the electrical properties of SnO₂ thin films suggest synthesis of a semiconductor material with tailored electrical properties, which are important in field of advance electronic or nano-electronic device technology.

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