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# FTO Thin Films: Outcome of Substrate Temperature on the Structural and Optical Properties

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**Abstract:** In this work, Fluorine doped Tin Oxide (FTO) thin films are effectively deposited by JNSP technique using ammonium fluoride and tin chloride as solution composition. The influence of Substrate Temperature (ST) on the structural and optical properties of FTO thin films is investigated. XRD pattern authenticates the presence of single phase polycrystalline orthorhombic structure with favored orientation along (230) and (200) directions. The sharp band obtained between 475 and 700 $cm^{-1}$ originated from asymmetric stretching vibrations of metal oxide ($SnO_2$:F). The highest band gap energy was obtained as 3.57 eV at 425°C and lowest band gap energy was obtained as 3.49 eV at 450°C obtained from UV-Vis spectra.

**Keywords:** FTO, Ammonium Fluoride, UV-Vis, FT-IR

## 1. Introduction

Nowadays research work has been focused on the preparation, optimal utilization and developments of Transparent conducting oxides (TCO). TCOs are electrical conductive materials with comparable low absorption of light. They are usually prepared with thin film technologies and used in optoelectronic devices such as photodiodes, TFT, solar cells, LEDs, and opto-electrical interfaces [1-3]. Glass fibers are nearly lossless conductors of light, but electrical insulators; silicon and compound semiconductors are wavelength dependent optical resistors (generating mobile electrons), but dopant dependent electrical conductors [4]. TCOs are highly flexible intermediate states with both these characteristics. The conductivity of TCOs can be tuned from insulating via semiconducting to conducting as well as their transparency also altered. As they can be produced based on the mobility of electrons as n-type and p-type conductivity, they open a wide range of power saving opto-electrical circuitries and technological applications [5,6]. Doped tin oxide thin films had kindled the enormous interest of researchers to use TCOs as electrodes. The most attracted doping atoms are Indium (In), Antimony (Sb), Fluorine (F), Nickel, (Ni) and Zinc (Zn). Among these FTO has excellent transparency in the visible range, due to its ample band gap (Eg > 3 eV) and a low electrical resistivity due to the large free carriers concentration caused by oxygen vacancies and fluorine substitution. FTO thin films have several technological applications like solar cells, low emissivity coatings for windows, gas sensors, and liquid crystal displays [7-9]. Several methods were used to prepare and deposit FTO films such as chemical vapor deposition (CVD), sputtering, plasma evaporation, sol-gel method and spray pyrolysis [10-13]. Spray pyrolysis has received more attention than the other methods due to its low-cost, simplicity, mass production with ease preparative parameters and the possibility of films deposition onto large and complex shaped substrates.

## 2. Experimental Details

High purity stannous chloride ($SnCl_2$. $2H_2O$) was used as the precursor material for the preparation. The fluorine doping was achieved using ammonium fluoride ($NH_4F$). FTO thin films were prepared using a modified respiratory therapist nebulizer. 2.2563g of ($SnCl_2 \cdot 2H_2O$) was dissolved in 20 ml of de-ionized water with the addition of few drops of concentrated hydrochloric acid (HCL) to avoid insolubility of materials and continuously stirred for 24 hours. 0.044g of ammonium fluoride was dissolved in 20 ml of de-ionized water and stirred for one hour. This solution was added to the starting solution, so that the prepared spray solution was 40 ml. The spray solutions were magnetically stirred for 1 hour. The deposition time was 20 minutes for all the deposition processes. The spray flow rate was maintained at 10 ml ($NH_4F$ - 6 ml, $SnCl_2$ - 4 ml). The preparative parameters are listed in table 1.

**Table 1.** Deposition conditions

| Parameters | Values |
|---|---|
| Nozzle to substrate distance | 5 cm |
| Flow rate | 0.5 ml/min |
| Carrier gas pressure | 3.5Kg/cm$^2$ |
| Time of Spray | 10 min |
| Solution concentration | 0.1 M |

## 3. Result and Discussion

### 3.1 Structural properties

Fig. 1 shows the XRD pattern of the FTO thin films prepared at different ST 400, 425 and 450°C. XRD patterns reveals the appearance of polycrystalline orthorhombic phase with dominant orientation along (2 3 0) [JCPDS card No.82-2194]. FTO thin films prepared at 425°C explore the presence of some faint peaks with dominancy along (2 0 0) reflection. Whereas the same prepared at higher temperature (450°C) augment the crystalline growth along all possible directions also enhance the some faint peak intensities like (3 0 1), (3 5 1) and introduce some new peaks at 31 and 33°. The substrate temperature strongly induces the crystallization process along certain domain walls with high packing factor [14]. It also distresses the peak intensities of certain domains and develops the new peaks at higher temperature. The crystallite size was found to be increased with the increase of ST. This is due to the agglomeration of the grains at the surface of grain boundaries in the lattice sites of dopant. Generally, the addition of a catalyst stops isotropic agglomeration of particles; instead anisotropic agglomeration occurs resulting in growth of particles in certain direction. The lattice parameters of FTO thin films was calculated and listed in table 2.

**Table 2.** Structural parameters of FTO thin films

| ST (°C) | Crystallite size D (Å) | Dislocation density δ (x10[18]) Lines/m2 | Micro strain ε (x10[-2]) | Stacking fault (SF) |
|---|---|---|---|---|
| 400 | 3.4075 | 1.3050 | 0.1805 | 0.4801 |
| 425 | 9.8915 | 1.7275 | 0.0417 | 0.1056 |
| 450 | 9.4398 | 1.9517 | 0.04412 | 0.1102 |

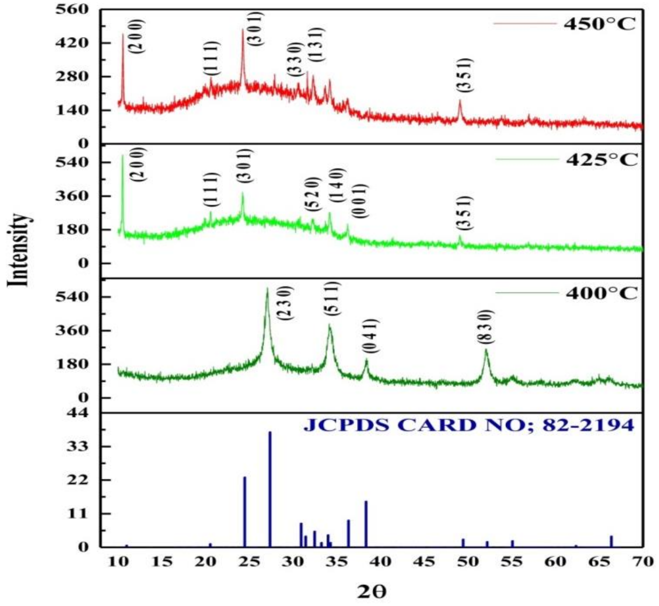


**Figure1.** XRD pattern of FTO thin films

## 3.2 Functional group Analysis

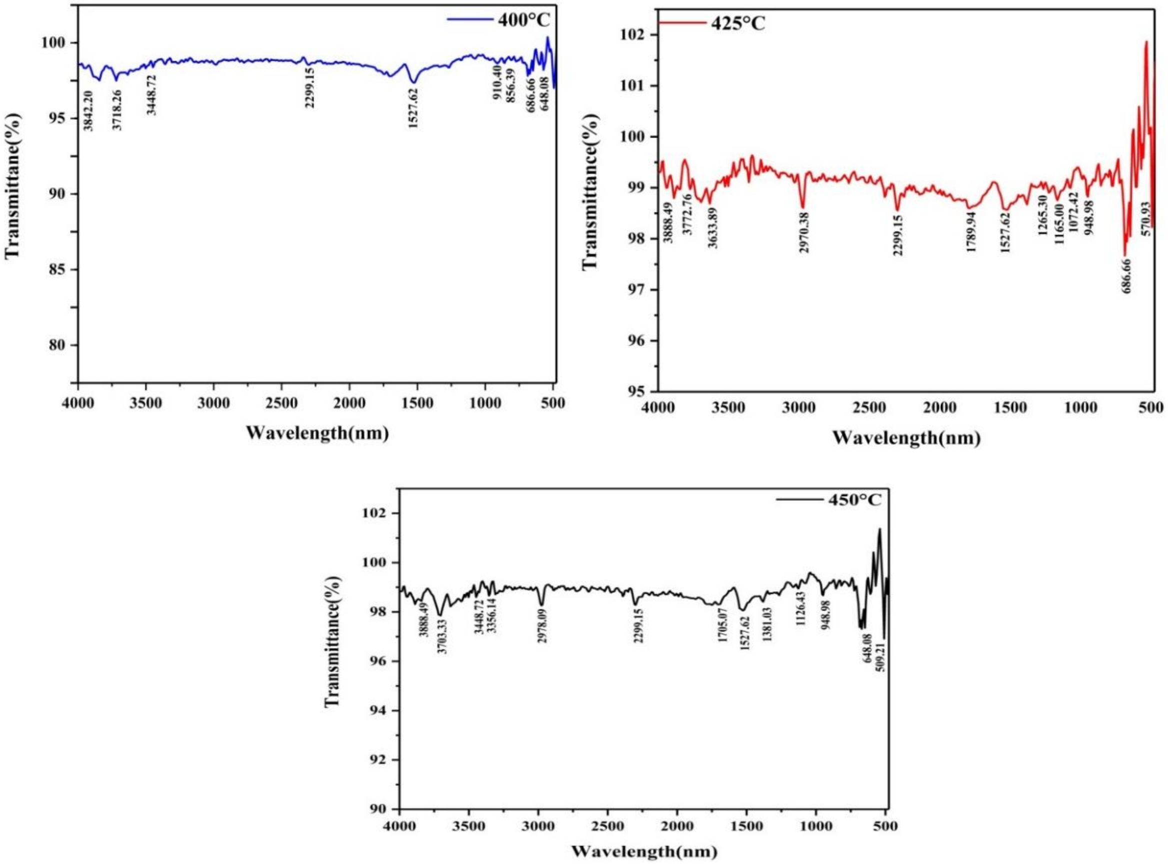


Figure2. FT-IR spectra of FTO thin films

FT-IR spectra of prepared FTO thin films on borosil glass substrate at 400 °C to 450°C are shown in Figure 2. Small peaks between 1620 $cm^{-1}$ and 1800 $cm^{-1}$ are attributed to presence of hydroxyl groups in the samples. Since the precursor solution contains water, Sn-OH vibrations mode appears in the spectrum. An absorption corresponding to the presence of adsorbed water (1630-1640 $cm^{-1}$) and hydroxide absorption bands in the range 3200-3600 $cm^{-1}$ were observed. The bands nearly 1000 $cm^{-1}$ was assigned to chloride contamination, which arises from chloride precursor. The absorption peaks between 475 and 700 $cm^{-1}$ can be assigned to asymmetric stretching vibrations of phonon band of metal oxide ($SnO_2$:F) network. At lower temperature the vibrational bands obtained from hydroxyl, carboxyl and organic species were present due to an evaporated precursor droplet reaching the substrate surface. These vibrational bands are diminished at higher temperature (450°C) due to higher crystalline property. The resemblance of fluorine to bonding hydrogen in solution is larger than to bonding tin (Sn) in films [15]. Consequently, fewer amounts of fluorine ions are incorporated in the films during spray coating deposition. Moreover, the formation of FTO depends also on the mobility of fluorine ions in the solution and its occupancy on the lattice sites of tin or oxygen at the substrate surface.

### 3.3 Optical properties

Fig. 3 represents the optical transmittance spectra of FTO thin films prepared at different temperature. ST decreases the transmittance values and shifts the absorption edge towards lower wavelength region. When metals are doped in thin films they can change the medium and the interference conditions of the films. Assuming a direct transition between valence and conduction bands, the energy band gap ($E_g$) was determined by extrapolating the straight line portion of the curve to $(\alpha h\nu)^2 = 0$.

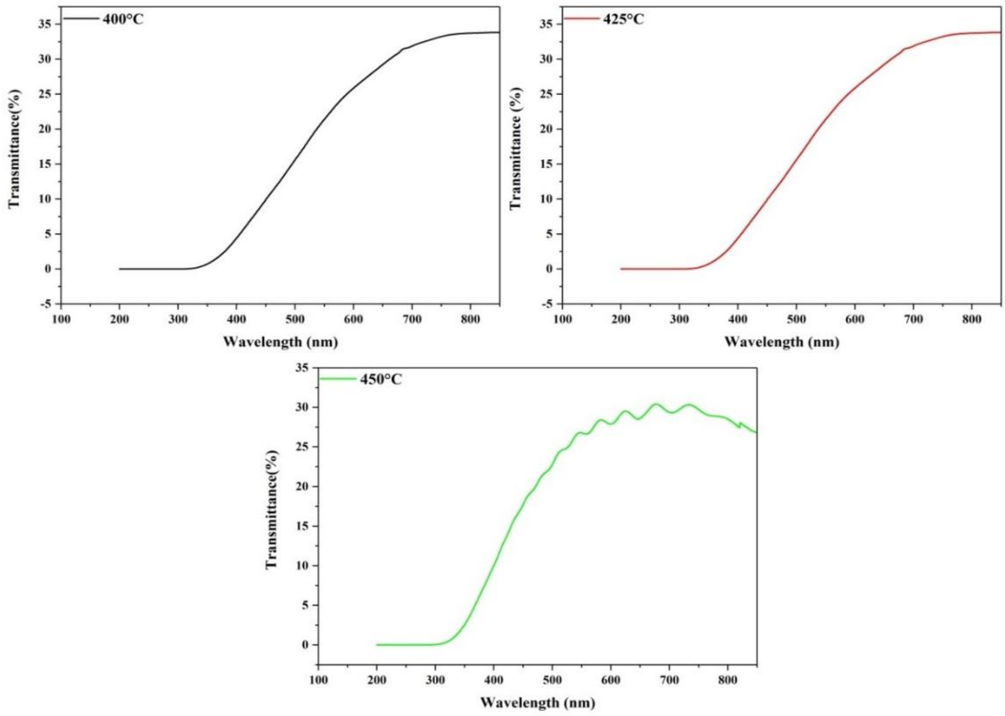


Figure 3. Optical transmittance spectra of FTO thin films

The highest band gap energy was obtained as 3.57 at 425°C and lowest band gap energy was obtained as 3.49 at 450°C. Fig. 4 illustrates the absorbance spectra of FTO thin films. It reveals the formation of two distinct intense absorption edges at 255 and 310 nm in UV region due to the anarchy in film network, restricted states appear near the band edges causing band tails formation. The states are reliable for the low energy photons absorption, a shift in the absorption edge towards the higher photon energy was observed with fluorine doping at higher temperature (450°C), and this may be attributed to the Burstein-Moss shift due to the increase in free electrons concentration [16]. The observed decrease in the energy gap may be due to the combined effect of the quantum confinement effect manifested by the increase in crystallite size with the presence of defects such as oxygen vacancies and changes in the carrier concentration.

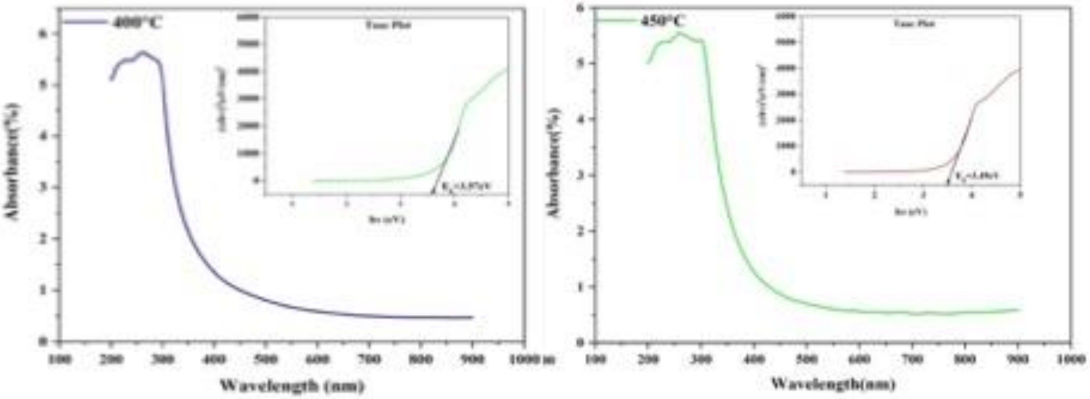


**Figure 4.** Optical absorbance spectra of FTO thin films

## 3.4 PL analysis

The photoluminescence properties of spray deposited FTO thin films were studied at room temperature in the spectral range 200-800 nm.

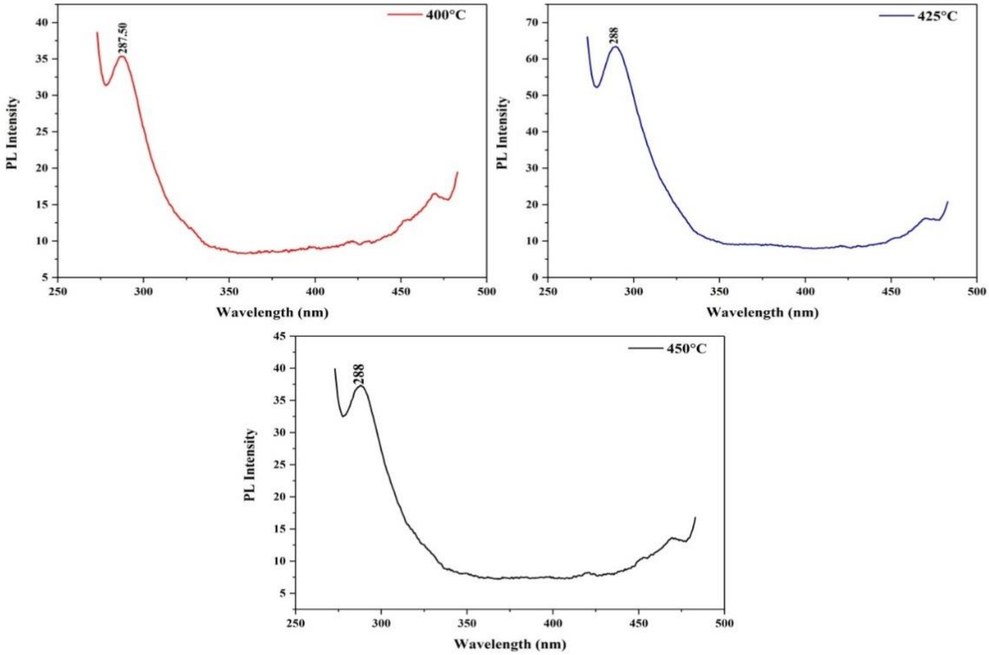


**Figure 5.** PL spectra of FTO thin films prepared at different ST

All measurements were carried out with He-Cd laser as a light source using an excitation wavelength 480 nm. The appearance of emission peak in the UV region may be owing to higher crystalline property with oxygen vacancies according to XRD results. It exhibit strong and sharp emission peak at 280 nm in the UV region may ascribed to excite the electron form 2p level to 5p level [17].

## 4. Conclusion

In this paper, we have explored the consequence of Substrate Temperature (ST) on the properties of FTO thin films. Uniform, smooth and adhesive layers of FTO thin films were deposited by JNSP technique. ST affects the properties of FTO thin films in the following aspects,

- ✓ changed the orientation of crystallites from (230) to (200) without formation of any mixed phases.
- ✓ confiscated some peaks whereas create some new peaks along possible direction and enhanced the intensity of some peaks also.
- ✓ diminished some organic, carboxyl and hydroxyl group vibrations while metal oxide network vibration are enhanced at higher temperature (450°C) due to higher crystalline properties.
- ✓ reduced the band gap energy due to the combined effect of quantum conferment manifested by the increase of crystalline size and changes in carrier concentration.
- ✓ doesn’t make any significant changes in emission properties

Moreover, substrate temperature substantially induces the structural, optical, vibrational and emission properties.

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**Conflict of interest:** The Authors have no conflicts of interest to declare that they are relevant to the content of this article.