

Electrical Characterization of Fluorine Doped Tin Oxide Deposited by Spray Pyrolysis Technique and Annealed in Open Air

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Abstract: Transparent conducting Fluorine tin oxide (FTO) thin films with the thickness of 100nm were deposited on glass substrates via spray pyrolysis technique, and three samples were post-annealed in open air atmosphere for one hour at 423K, 573K and 723K selected temperature points respectively. A four-point probe measurement system was adopted to characterize the FTO thin films. Influence of thermal annealing in air atmosphere on electrical properties was investigated in detail. The sheet resistance reached the minimum of $1.53 \times 10^4 \Omega/\text{cm}^2$ for the sample annealed at 423K. It increased dramatically at even higher annealing temperature.

Keywords: Fluorine Doped Tin Oxide (FTO), Annealing Temperature, Electrical Properties, annealing condition.

1. Introduction

Doping has been widely studied to alter the properties of nanocrystals in desirable and controllable ways. Dopants can strongly influence electronic behavior of bulk semiconductors. The addition of impurity with one more valence electron than the host atom donates its extra electron to the semiconductor (n-type doping) greatly increasing the conductivity of the intrinsic semiconductor. In this sense, the development of doped nanocrystalline materials is critical for many materials [1].

During the last decade, large attention has been paid to tuning of oxygen vacancies by doping various metallic elements, changing the deposition technique and annealing under certain atmospheres [2].

Fluorine-doped tin dioxide (FTO), in which fluorine atoms replace the oxygen sites in the lattice creating free electrons to promote higher conductivity in the samples, is an n-type transparent conducting oxide (TCO). Compared with the widely used indium tin oxide (ITO) and antimony-doped tin oxide (ATO), fluorine doped SnO₂ has higher transparency in visible range and possesses extraordinary high temperature resistance, strong adhesion to glass and excellent chemical stability [1].

Several reliable approaches to fabricate high performance FTO thin films have been developed successfully. For example, RF (i.e. radio frequency) magnetron sputtering or DC (i.e. direct current) magnetron sputtering [3], [4], sol-gel or dip-coating [5], spray pyrolysis [2], [6], [7], chemical vapor deposition (CVD) [8], electron beam evaporation [9], thermal evaporation [10] and so on.

Among the various deposition techniques, the spray pyrolysis is the most suitable method for the preparation of doped tin oxide thin films because of its simple and inexpensive experimental arrangement, ease of adding various doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings, which are desirable for industrial solar cell applications. However, large area film production is economical and this is the essential characteristic of the simple spray pyrolysis technique. Usually, the chemical spray pyrolysis route is used to deposit FTOs at optimized substrate temperatures of around 723–748 K. Tin oxide is a wide band gap (~4 eV) and indirect band gap (of about 2.6 eV) nonstoichiometric semiconductor. It has low n-type resistivity (10⁻³ cm) and high transparency (90%) in the visible region [11].

In the present work, SnO₂: F thin films were prepared by spray pyrolysis (SP) technique at substrate temperature of 723K using dehydrate stannous chloride (SnCl₄·5H₂O) (98% purity, Merck) and ammonium fluoride (NH₄F) (99% purity, Merck) as precursors. The aim of this work is to study the relationship between the annealing temperatures, annealing condition and electrical properties of SnO₂: F thin films. The results obtained are compared and discussed with the specified results by several researchers.

2. Materials and Methods

Fluorine doped tin oxide (FTO) films were prepared on glass substrate at a substrate temperature of 723K for fluorine doped (0.05) by a spray pyrolysis technique using KM – 150 spray machine under ambient atmosphere. The spray solution prepared from tin tetrachloride penthydrate (SnCl₄·5H₂O) dissolved in distilled water at concentration of 0.1M and ammonium fluoride (NH₄F)

was added into the solution for fluorine doping. The deposition parameters were the same for the series of films.

The deposition temperature and solution flow rate were maintained at 723K and 1.5ml/min respectively. Other parameters were kept constant. Film thickness of 100nm was deposited on the glass substrate at a nozzle – substrate distance of 11.0cm. The growth rate was approximately 25nm/min. The film thickness was measured using a Taly step profilometer (roughness detector with a stylus Taylor Hobson model).

Before the deposition, substrates were decreased in acetone first, and then rinsed in absolute ethanol and deionised water several times, finally dried in 4N Nitrogen gas.

Four samples were prepared and labeled as F₁: as deposited sample, F₂: sample-annealed at 423K, F₃: sample annealed at 573K, and F₄: sample annealed at 723K, all in open air. Three samples designated as F₂, F₃, and F₄ were taken to a furnace one after the other and heated at temperatures 423 K, 573 K and 723 K respectively for one hour in open air. Sheet resistances of FTO thin films were measured by the standard four-probe method using a SDY-5 four-point probe meter.

3. Results and Discussion

It is known that electrical resistivity of thin films of SnO₂ depends on concentration of oxygen vacancies within their rutile crystal structure (S.G. P4/nmm²) [2]. The electrical measurements were carried out by four-point probe method at room temperature. Figures 1 and 2 show the effect of thermal annealing in air atmosphere on the resistivity and sheet resistance of FTO thin films. The resistivity of FTO thin films initially was 3.623Ω cm. It initially decreased for sample F₁, and reached the minimum of 1.53x10⁻¹Ω cm for sample F₂. It indicated that the resistivity of FTO thin films might decrease under thermal annealing at relatively low temperature. This result is consistent with that reported by [9]. After reaching the minimum, the resistivity increased significantly with further increase of annealing temperature. It reached 44.3Ω cm for sample F₄. The decrease in resistivity of the film with increase in temperature indicates the semiconducting nature of the films. [8], [12]. According to [13], Fluorine atoms incorporate at the interstitial sites and crystal structure of the films start to deteriorate, hence decreases the mobility of the free electrons and increases the electrical resistivity. The corresponding sheet resistance was 4.43 × 10⁶ Ω/cm².

Table 1 shows the values of resistance, sheet resistance, and resistivity for as-deposited FTO films, FTO films annealed at 423K and FTO films annealed at 723K.

Table 1. Values of sheet resistance and resistivity of FTO films

Temperature	Sheet Resistance	Resistivity
303K	3.623 Ω/cm^2	3.623 Ωcm
423K	15.3 Ω/cm^2	$1.53 \times 10^{-1} \Omega\text{cm}$
573K	2.28 Ω/cm^2	$22.81 \times 10^{-1} \Omega\text{cm}$
723K	0.44 Ω/cm^2	44.3 Ωcm

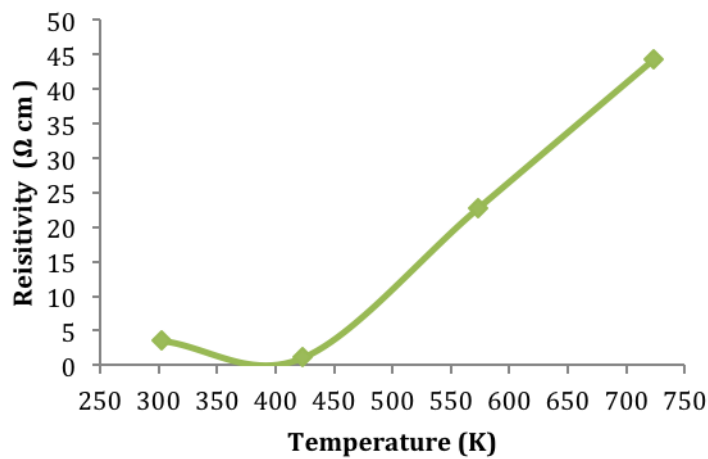


Figure 1. Resistivity of FTO thin films (F1, F2, F3 and F4) annealed at different temperatures

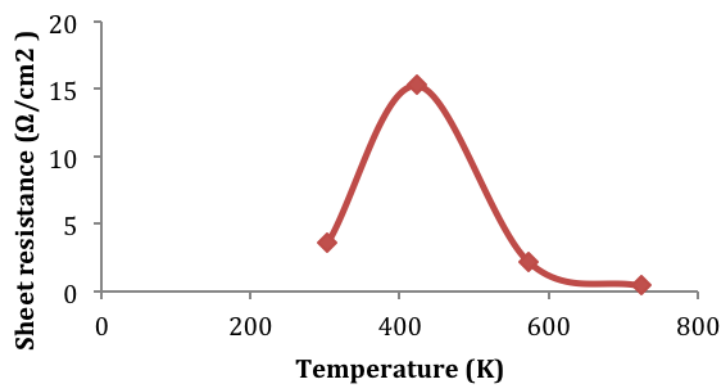


Figure 2. Sheet resistance of FTO thin films (F1, F2, F3 and F4) annealed at different temperatures

4. Conclusions

This work reports the preparation and electrical characterization of fluorine doped tin oxide thin films annealed in open-air atmosphere at different annealing temperatures. The thin films were

successfully deposited by spray pyrolysis technique. The annealing temperatures and annealing conditions influence the electrical properties of fluorine thin films.

References

- [1] Shanshan W, Yuan S, Shi L, Zhao Y, and Fang J. Preparation, Characterization, and Electrical Properties of fluorine tin dioxide nanocrystals. *Journal of colloid and Interface Science*, 2010, 346: 12–16.
- [2] Gholizadeh A, and Tajabor N. Influence of N₂- and Ar-ambient annealing on the physical properties of SnO₂: Co transparent conducting films. *Materials Science in Semiconductor Processing*, 2014, 13:162–166.
- [3] Chandra S. V. J, Chel-Jong C, Uthann S and Mohan G. R. Structural and electrical properties of radio frequency magnetron sputtered tantalum oxide films: Influence of post-deposition annealing. *Materials Science in Semiconductor Processing*, 2010, 13: 245–251.
- [4] Liu J, Shih-chin L and Y. Chih-hao. Effects of Annealing Temperature on the Properties of Strontium Copper Oxide Prepared by Radio Frequency Reactive Magnetron Sputtering Method. *Materials Transactions*, 2008, 49: 1694 –1697.
- [5] Wang Q, Xuegang W, D. Jianfeng, J. Jinlong and H. Xiaodi. Influence of annealing procession ferromagnetism of undoped TiO₂ nanoparticles prepared by sol–gel method. *Materials Science in Semiconductor Processing*, 2014, 21:111–115.
- [6] Sanchez-Juarez A, Tiburcio-Silverb A, E.P. Ortizc, J. Zironid Rickards. Electrical and optical properties of fluorine-doped ZnO thin films prepared by spray pyrolysis. *Thin Solid Films*, 1998, 333:196–202.
- [7] Ikhmayies S. J and Riyad N. A. Using I–V characteristics to investigate selected contacts for SnO₂:F thin films. *Journal of Semiconductors*. 2012, 33:1–6.
- [8] Ubale A, Weleka N. R and Amruta V. M. Effect of annealing on physical properties of CBD synthesized nanocrystalline FeSe thin films. *Materials Science in Semiconductor Processing*. 2012, 27: 280–287.
- [9] Xu Z, Peng C, Zhenlong W, X. Feng, Y. Guofeng, L. Bin, T. Chongbin, Z. Lin, Z. Rong and Z. Youdou. Influence of thermal annealing on electrical and optical properties of indium tin oxide thin films. *Materials Science in Semiconductor Processing*. 2014, 26: 588–592.
- [10] Iwan A, Igor T, S. Maciej B. Bartosz, P. Grzegorz, E. Schab-Balcerzak. Optical, electrical and mechanical properties of indium tin oxide on polyethylene terephthalate substrates: Application in bulk-heterojunction polymer solar cells. *Materials Science in Semiconductor Processing*. 2014, 24: 110–116.

- [11] Demet T and Duzgun B. The relationship between the doping levels and some physical properties of SnO₂: F thin films spray- deposited on optical glass. *Pramana journal of physics*. 2012, 79: 137–150.
- [12] Balu A. R, Manyula N, K. Usharani, V.S Nagarethinam. Studies on the Physical Properties of three Potentially important TCO Thin Films fabricated by a Simplified Spray Technique under same Deposition conditions. *International Journal of chem. Tech Research*. 2014, 6: 705–718.
- [13] Yousaf S.A and Ali S. The effect of fluorine doping on optoelectronic properties of tin dioxide films. *Coden. Jnsmac*. 2009, 48: 43–50.