Superlattices and Microstructures
Volume 70, June 2014, Pages 61-69

Effect of fluorine doping on the structural, optical and electrical properties of SnO_2 thin films prepared by spray ultrasonic

Atmane Benhaoua [a] [b], Achour Rahal [a] [c], Boubaker Benhaoua [a], Mohamed Jlassi [d]

Show more

Share Cite

https://doi.org/10.1016/j.spmi.2014.02.005
Get rights and content

Abstract

The undoped and fluorine doped tin oxide (SnO_2) thin films are synthesized by using cost-effective spray ultrasonic technique; the films are sprayed on heated glass substrates at 480°C. The dependence of structural, optical and electrical properties of SnO_2 films on the concentration of fluorine is investigated. X-ray diffraction, Optical absorption, four-point probe and Hall Effect studies have been performed on undoped and fluorine doped SnO_2 (FTO) films. X-ray diffraction pattern reveals the presence of cassiterite structure with (200) as preferential orientation for FTO films. The crystallite size varies from 10.3 to 27.12 nm and was affected by F concentration which was lying between 0 and 12 wt.%. All films exhibit optical transmission $T(\lambda)$ more than 83.9% in visible region; the optically estimated film thickness varies from 700 to 975 nm for the same given time (3 min deposition) and band gap (E_g) varies from 3.651 to 3.902 eV. The electrical study reveals that the films have n-type electrical conductivity and depend upon fluorine concentration too. The sprayed FTO film doped at 6 wt.% has the minimum resistivity of $1.47 \times 10^{-3}\,\Omega$cm and minimum resistance sheet (R_{sh}) of $21\,\Omega/\text{cm}^2$ whereas the carrier concentration and mobility were about $2.04 \times 10^{19}\,\text{cm}^{-3}$ and $208.4\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively.

Introduction

Transparent conducting oxides (TCO), such as tin doped indium oxide, In_2O_3:Sn (ITO), fluorine doped tin oxide, SnO_2:F (FTO), antimony doped tin oxide, SnO_2:Sb (ATO), aluminum doped zinc oxide, ZnO:Al (AZO) and gallium doped zinc oxide ZnO:Ga (GZO), are particularly attractive because of their high optical transparency in the visible region, good electrical conductivity and high infrared reflectivity. They find numerous applications, some of which includes liquid crystal displays [1], wave guide electron devices [2], light emitted diode [3], dye-sensitized solar cells [4], thick-film sensor [5], transparent electrodes in solar cells [6], flat panel displays [7], organic light emitting diodes [8] and heat mirrors [9].

The undoped stoichiometric SnO_2 films have very high electrical resistivity because of their low intrinsic carrier density and mobility. Therefore the challenge is to prepare non-stoichiometric doped thin films. The conductivity of weakly non-stoichiometric tin oxide films is supposed to be due to doubly ionized vacancies serving as donors [10]. Dopants as antimony, Sb, indium, In and fluorine, F, are frequently used [11]. Recently Li has been used as dopant with SnO_2 [12] Fluorine, due to its similar ionic radii, fluorine may substitute for the anion (O^{-2}) in SnO_2 and acts as a donor in SnO_x:F [13].

A large variety of techniques have been developed for TCOs thin film deposition. The screen printing technique [14], chemical vapor deposition [15], reactive evaporation [16] dc and rf sputtering, sol–gel [17], [18] and pulsed laser ablation [19] are some deposition methods currently used for preparation of ITO and FTO thin films. Among these, spray pyrolysis is the most convenient method because of its simple and inexpensive experimental arrangement, and spray ultra sonic [20], [21] high growth rates and wide possibility of varying the film properties by changing composition of the starting solution. It has been successfully used to synthesize many transparent conducting oxide films [22], [23], [24], [25].

The properties of spray deposited SnO_2 thin films are found to be dependent on the processing conditions, solvents and the nature of used precursors [25], [26]. The effects of precursor concentration, solvents and solvent ratio on the FTO thin films have reported in literatures [27], [28], [29]. The effect of gas sensing of F doped tin oxide has also been reported [30].

For practical application in solid-state optoelectronic devices, thin films with high transmission and low resistance are the prime requisite. In order to obtain device quality FTO thin films with different level fluorine doped tin oxide (SnO_2:F); thin films have been deposited by spray ultrasonic technique. The aim of this work is to investigate the structural, optical and electrical properties of highly conducting SnO_2:F thin films in the average of fluorine doping level lying between 0 and 12 wt.%.

Section snippets

Preparation of spray solution

The undoped and fluorine doped tin oxide thin films were prepared using a chemical spray ultrasonic technique as shown in (Fig. 1). Stannous chloride ($SnCl_2 \cdot 2H_2O$) was used as a precursor for tin. This tin precursor dissolved in double distilled water and methanol (volume ratio 1:1) with adding few drops of (HCl). The precursor concentration was (0.1 M), served as a starting solution. For fluorine doping, ammonium fluoride (NH_4F) was dissolved in doubly distilled water and added, with an…

Crystalline structure

The X-ray diffraction pattern of F (0–12 wt.%) doped SnO_2 thin films are shown in (Fig. 2). as it can be seen the diffraction peaks were observed at 2θ=26.68°, 33.97°, 37.8°, 51.79°, 61.72° and 65.95° which are related to the following plans (1 1 0), (1 0 1), (2 0 0), (2 1 1), (3 1 0) and (3 0 1) respectively. The obtained XRD spectra matched well with the space group $P4_2mnm$ according to JCPDS (No. 41-1445) of the tetragonal, rutile SnO_2 structure [31]. The peaks of the undoped SnO_2 were indexed to the…

Conclusions

In this paper, we have reported the preparation and characterization of the SnO_2:F thin films by spray ultrasonic technique. The XRD of sprayed samples with thicknesses ≈700 nm have shown polycrystalline structure with clear characteristic peak of SnO_2 cassiterite phase. The average optical transparency (T%) of the films in visible spectra decreases from 93% for the undoped to 81.3% for the doped one at 6wt.%. The Hall Effect has shown n-type conductivity in those films with F-doping. The…

Acknowledgments

This work was supported in part by the National Project Research (PNR) and VTRS laboratory of El-Oued University. X-ray diffraction data in this work were acquired with an instrument supported by the University of Biskra. We thank Prof. S. Rahmane and B. Gasmi (Biskra University) for the assistance in XRD data acquisition.…

References (46)

N. Yamamoto *et al.*
Thin Solid Films (2012)

Y.Q. Chen *et al.*
Chem. Phys. Lett. (2003)

V. Palenskis *et al.*
Solid-State Electron. (2010)

J.L. Kwo *et al.*
Diam. Relat. Mater. (2000)

M.F. Al-Kuhaili *et al.*
Sol. Energy (2009)

P.V. Bhuvaneswari *et al.*
Mater. Sci. Semicond. Process. (2013)

A.V. Moholkar *et al.*
Appl. Surf. Sci. (2009)

A.N. Banerjee *et al.*
Thin Solid Films (2005)

S. Benramache *et al.*
Superlattices Microstruct. (2012)

S. Benramache *et al.*
Superlattices Microstruct. (2012)

View more references

Cited by (60)

Crystal growth of fluorine-doped tin oxide structures with extraordinary morphology by the hydrothermal method and their electrical conductivity

2023, Journal of Crystal Growth

Show abstract

Design of experiments optimization of fluorine-doped tin oxide films prepared by spray pyrolysis for photovoltaic applications

2023, Ceramics International

Show abstract

Elaboration and characterization of Ni and Al co-doped SnO<inf>2</inf> thin films prepared by spray pyrolysis technique for photovoltaic applications

2022, Materials Science and Engineering B: Solid-State Materials for Advanced Technology

Show abstract

Elaboration, characterization and applications of SnO<inf>2</inf>, 2 %Gd-SnO<inf>2</inf> and 2 %Gd-9 %F-SnO<inf>2</inf> thin films for the photocatalytic degradation of MB by USP method

2022, Inorganic Chemistry Communications

Show abstract

Achievements of high figure of merit and infra-red reflectivity in SnO<inf>2</inf>:F thin films using spray pyrolysis technique

2021, Superlattices and Microstructures

> *Citation Excerpt :*
> …As it is shown in Fig. 9 (d) with increasing the doping concentration the band gap of the films are increased. In degenerate samples Burstein-Moss (B.M.) effect [37,43,44] could be the possible reason for the observed incremental variations of the band gap. Based on this theory, the incremental changes of the band gap could be due to accumulation of free carriers in an energy interval (ΔEg) at the bottom of the CB, which obeys the relation: ΔEg α n2/3, where n is the free electron density.…

Show abstract

Rapid Open-Air Fabrication of Perovskite Solar Modules

2020, Joule

> *Citation Excerpt :*
> …There is a significant opportunity for extending the open-air spray-based capabilities discussed in this work to develop fully open-air manufactured perovskite modules with scalable methods that eliminate the remaining vacuum-based processes. One specific example could include replacing the sputtered ITO bottom electrode with an open-air, solution-processed TCO using either conventional spray pyrolysis38,39 or RSPP to supplement or replace the thermal curing requirement and introduce a tunable chemical environment (reductive, oxidative, or neutral) to yield high quality TCOs. These processes can also be extended or combined with atmospheric chemical vapor deposition (CVD) processes for fabricating the ETL13 and top electrode.…

Show abstract

View all citing articles on Scopus

Recommended articles (6)

Research article

The effect of Mo and F double doping on structural, morphological, electrical and optical properties of spray deposited SnO_2 thin films

Ceramics International, Volume 40, Issue 8, Part B, 2014, pp. 12891-12898

Show abstract

Research article

Study of structural, electrical and photoconductive properties of F and P co-doped SnO_2 transparent semiconducting thin film deposited by spray pyrolysis

Materials Science in Semiconductor Processing, Volume 30, 2015, pp. 400-405

Show abstract

Research article

Improved mechanical properties of SnO_2:F thin film by structural modification

Ceramics International, Volume 40, Issue 2, 2014, pp. 2557-2564

Show abstract

Research article

Effect of F doping on physical properties of (211) oriented SnO_2 thin films prepared by jet nebulizer spray pyrolysis technique

Superlattices and Microstructures, Volume 89, 2016, pp. 378-389

Show abstract

Research article

Sheet resistance dependence of fluorine-doped tin oxide films for high-performance electrochromic devices

Ceramics International, Volume 44, Issue 8, 2018, pp. 9408-9413

Show abstract

Research article

Spray solution flow rate effect on growth, optoelectronic characteristics and photoluminescence of SnO_2:F thin films for photovoltaic application

Optik, Volume 126, Issues 7–8, 2015, pp. 708-714

Show abstract

View full text