Effect of fluorine incorporation on the third-order nonlinear-optical properties of indium oxide thin films prepared by spray pyrolysis

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Undoped and Fluorine-doped indium oxide (In_2O_3:F) thin films have been prepared by spray pyrolysis technique on heated glass substrates at 450°C from the Indium chloride ($InCl_3$) and ammonium fluoride (NH_4F). The effect of fluorine doping agent on the nonlinear optical properties was investigated using X-ray diffraction, electrical resistivity, transmission, and third harmonic generation (THG). The best value of nonlinear optical susceptibility $\chi^{(3)}$ was obtained from the doped films with low electrical resistivity of 6×10^{-3} Ω cm. A strong third order nonlinear optical susceptibility $\chi^{(3)} = 1.98 \times 10^{-11}$ (esu) of the studied films was found for the 5% doped sample.

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1. Introduction

Semiconductors oxides thin films are of considerable interest for the optoelectronics applications, due to their fast response time on laser excitation and weak optical losses. In_2O_3 is an important n-type semiconductor material with wide band gap (direct band gap energy of 3.55–3.75 eV), good chemical stability, high electrical conductivity and high transmittance in the UV–Vis region [1, 2]. These characteristics are required in various applications research: solar cells [3, 4], photovoltaic devices, transparent conductive electrode [5], and gas sensors [6-8].

The In_2O_3 thin films can be prepared via many techniques such as reactive RF and DC sputtering [9], reactive evaporation [10], pulsed laser ablation [11], spray pyrolysis [3, 12] and thermal and UV-assisted sol–gel dip coating technique [13]. Tin-doped indium oxides films are more commonly prepared and used as transparent conducting oxides. Only a few publications report on fluorine-doped indium oxide thin films exist. Here we have prepared In_2O_3: F films by spray pyrolysis technique, which can be distinguished from other techniques by its simplicity, low cost and process yield. This is basically a chemical deposition technique, where the most important deposition parameters are: the precursors, the solution concentration, the deposition temperature and the spray rate. Effects of doping by Fluorine on the structural, morphological, electrical and optical properties have been investigated in detail [3, 14]. However, to our knowledge, a description concerning nonlinear optical properties has not been reported in the literature. In this paper, we analysed the effect of doping on the nonlinear optical properties.

2. Experimental details

The spray pyrolysis experimental set-up and the details on the procedure applied for the deposition of the investigated F-In_2O_3 thin films have been described elsewhere [15]. Undoped and Fluorine-doped indium oxide thin films were prepared by spraying an aqueous solution containing indium chloride ($InCl_3$) and NH_4F used as doping agent on glass substrates heated at 450°C. The solution flow rate is set to 5 ml/min. The atomic concentrations of fluorine in the solution were 3% and 5%. The structural characterizations are performed using X-ray diffraction (XRD) with Cu Kα radiation (λ = 1054A°). The optical transmission measurements were performed with a Shimadzu 3101 PC UV-Vis-NIR spectrophotometer. The electrical resistivity was measured at room temperature by the Van Der Paw method. Third order nonlinear optical susceptibility $\chi^{(3)}$ of undoped and doped In_2O_3 thin films was examined by THG method described elsewhere [16].

3. Experimental results

The structural properties of the undoped and fluorine-doped In_2O_3 grown at 450 °C with an atomic concentration of 3% and 5% are analysed by XRD patterns in Fig. 1.

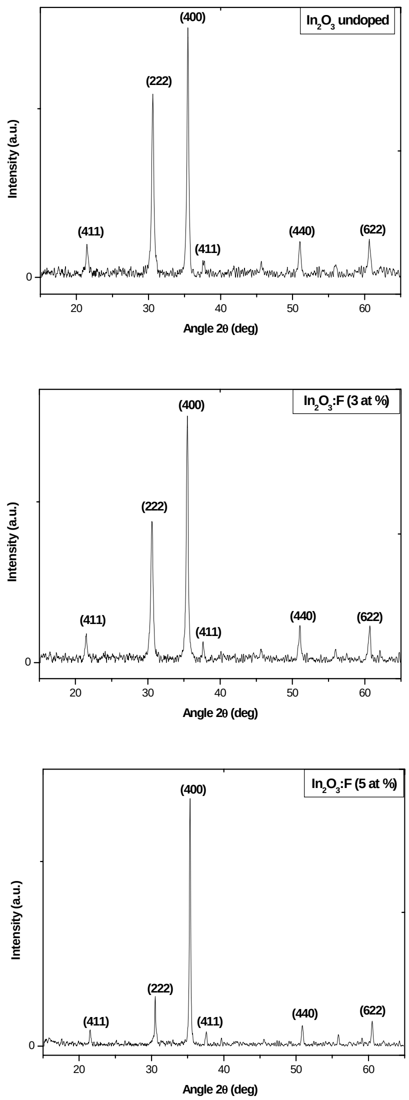

Fig. 1. X-ray diffraction spectra of undoped, 3% and 5% F doped In_2O_3 thin films at 450°C temperature.

It can be found that all the films are polycrystalline and crystallize in a cubic structure with preferential orientation along [400]. We show that the XRD intensity of preferred growth orientation of In_2O_3 thin films depends on the fluorine concentration. The intensity ratio of the (400) to (222) reflection is used to evaluate the doping effect on the film texture (Table 1).

Table 1. Integrated intensity of the (400) peak to the (222) peak I (400) /I (222), full-line width at half maximum of the (400) diffraction peaks and corresponding mean grain size calculated using Scherrer's equation as a function of atomic concentration for In_2O_3-F thin films prepared by spray pyrolysis

Fluorine rate (%)	0	3	5
I(400)/I(222)	1.36	1.74	5.23
Δ(2θ) of the (400) peak (°)	0.28	0.29	0.22
Mean grain size of the (400) peak (nm)	5.20	5.02	6.62

The ratio I(400)/I(222) increases with increasing concentration, leading at 5% F to a clear predominance of the (400) peak. The mean crystallite size *D* was calculated from the (400) diffraction peaks using Debye-Cherrer's formula [17]:

$$D_{hkl} = 0.9 \frac{\lambda}{\Delta(2\theta_{hkl})\cos(\theta_{hkl})}$$

where λ is the wavelength of incident radiation (λ = 1.542 A°), θ_{hkl} is the Bragg diffraction angle and $\Delta(2\theta_{hkl})$ is the full line-width at half maximum of the (400) peaks. The measured line-widths and the corresponding mean crystallite sizes are regrouped on Table 1. The mean size was D=6.62 nm for the sample doped 5% F which was larger as compared to the undoped and 3% doped samples. The In_2O_3: F 5% is relatively more crystallized compared to In_2O_3: F 0% and In_2O_3: F 3%. We concluded that the films which present large grain size have a good crystallinity.

The electrical resistivity of F-In_2O_3 films as a function of doping concentration is shown in Fig. 2.

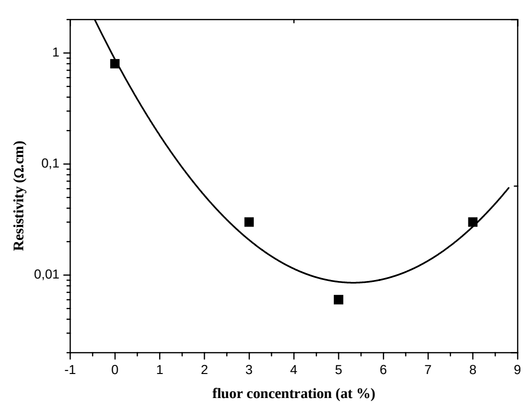

Fig. 2. Electrical resistivity versus fluorine dopant concentration of sprayed F-In_2O_3 films deposited at 450 °C

It can be seen that fluorine doping level is the most important parameter to affect the electrical properties of these films, as is evident from Fig. 2. The resistivity decreased quickly with increasing F concentration reaching a minimum of $\rho = 6 \times 10^{-3}$ Ω cm for an F atomic concentration of 5%. Note that this value is weaker compared to the values of $\rho = 2.17 \times 10^{-4}$ and 1.14×10^{-4} Ω cm, respectively, before annealing and after annealing in air at 450 °C for 1h in F-In_2O_3 deposited by reactive-ion plating [18]. Benamar et al. [19] have also observed an initial decrease in resistivity in Sn–In_2O_3 films deposited by spray pyrolysis. Afterwards, the resistivity increased with the F concentration, reaching a value of $\rho = 3 \times 10^{-2}$ Ω cm at 8 % F. The initial decrease in ρ could be due to the doping fluorine occupying oxygen vacancy sites. Whereas the oxygen vacancy denotes two electrons to the lattice, replacement of the vacancy by a fluorine atom results in the donation of only one electron. A further increase in doping concentration results in the replacement of oxygen by fluorine and thus an increase in the resistivity. The resistivity reached its minimum at 5% F, this may be due to the increase of crystallinity which can decrease grain boundary scattering of charge carriers. The decrease of resistivity is related to the improvement of crystallinity.

The optical transmission curves of fluorine-doped In_2O_3 films prepared with different doping ratios at Ts = 450°C are shown in Fig. 3.

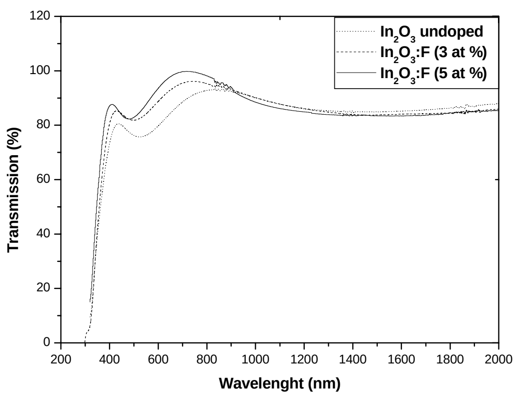

Fig. 3. Transmission spectra of undoped, 3% and 5% F doped In_2O_3 thin films at 450°C temperature

It can be observed that the optical transmittance of the films was affected by doping concentration. The average transmittance increases in the visible region and a slight decreases in the near-infrared (NIR) range. In the visible region all the films are transparent, exceeding 90% and the more important transparency is obtained for the In_2O_3: F 5%. In contrast, the observed decreases in the NIR region is due to a plasma resonance effect resulting from the high concentration of free electrons in our thin films. In the same way, transmittance in the near-infrared region is inversely related to the carrier concentration, owing to the interaction of free electrons with the incident long-wavelength radiation [20]. Thus, the In_2O_3: F 5% exhibit higher free carrier concentration comparing to the others samples. The higher transmittance observed in the films was attributed to less scattering effects, structural homogeneity and better crystallinity. In fact, the crystallinity probably affects the light scattering on the transparency of the films. The light scattering decreases with the improvement of the crystallinity of the films, resulting in better transparency. We can conclude that the crystallization enhances the transmittance and electrical properties of the IFO films, similar results observed by Han et al. [21] for ITO films.

The optical transmittance and electrical conductivity are two important parameters through which quality of the transparent conducting oxides are judged. These two parameters are inversely proportional to each other. A method of correlating the properties of TCO films by means of figure of merit (F) is given by the relation [22].

$$F = -\frac{1}{(\rho \ln T)}$$

where T is the transmittance and ρ is the resistivity of the film. The variation in the figure of merit of In_2O_3 with different doping concentration is shown in Fig. 4.

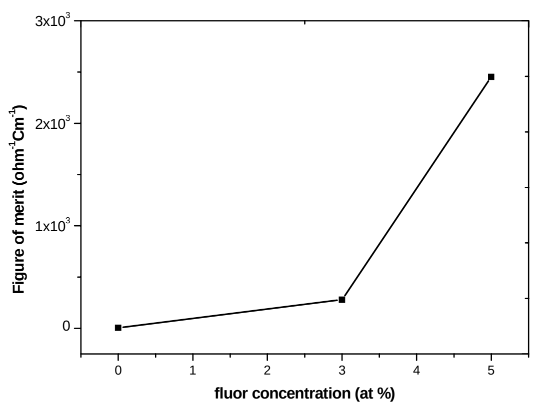

Fig. 4. Variation of figure of merit with fluorine dopant concentration of sprayed F-In_2O_3 films deposited at 450 °C

The figure of merit of the films increased from 5.52 Ω^{-1} cm^{-1} to 2.45×10^3 Ω^{-1} cm^{-1} with increasing fluorine concentration. Higher the figure of merit, better would be the performance of the films. The increase of figure of merit with doping concentration is due to the decrease in the electrical resistivity.

The transparency of In_2O_3 at 1064 nm, which is the laser excitation wavelength, makes it a good candidate for nonlinear optical applications.

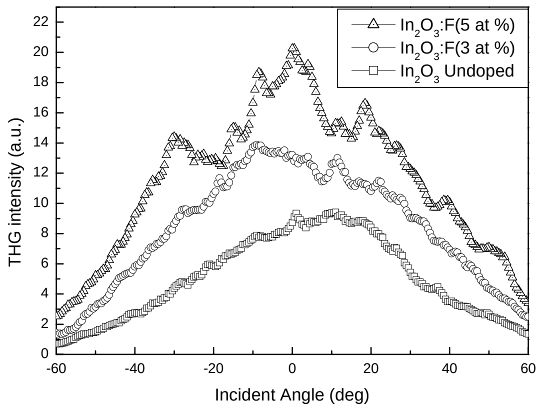

Fig. 5. Normalized third harmonic response of undoped, 3% and 5% F doped In_2O_3 thin films at 450°C temperature.

Fig. 5. Shows Maker-fringes obtained by rotating the samples through the range from ± 60° to the normal. The fringes bell shape can be explained by the fact that the layer thickness is less important than its coherence length (generally in the order of 1 μm). The aim of our investigation is to find an optimal fluorine content to get a higher value of $\chi^{(3)}$.

Table 2. Third order nonlinear susceptibility and electrical resistivity of undoped and doped In_2O_3 (3% and 5% F) thin films elaborated at 450°C.

Samples	ρ (Ω cm)	($\chi^{(3)}$ ± 0.1) x10^{-11}(esu)
In_2O_3	8 x 10^{-1}	1.29
In_2O_3:F 3%	3 x 10^{-2}	1.67
In_2O_3:F 5%	6 x 10^{-3}	1.98

The values of $\chi^{(3)}$ calculated from these spectra (Table 2) are higher than the reference material and we can notice that the doped samples have a higher TH signal compared to undoped. We can see that doping improves the nonlinear response. The highest value is found for In_2O_3: F 5%. It is not surprising because this behavior can be understood if one take into consideration that the free carrier concentration in In_2O_3: F 5% samples is higher than that in undoped In_2O_3 and In_2O_3: F 3%. The change of the value of $\chi^{(3)}$ is mainly related to the value of electrical resistivity. This result proves that there is a good correlation between optical and electrical properties. The electrical resistivity is one of the most effects acting on the nonlinear properties. In fact, when the resistivity decreases the values of nonlinear optical properties increase (Table 2). The similar results were obtained by Z. Sofiani et al [16]. It is known that the Third harmonic generation (THG) method allows determining only the purely electronic contribution to third order nonlinear optical susceptibility [23]. We can conclude that the nonlinearities of the material are strongly dependent on the electrical resistivity, which in turn strongly dependent on the doping concentration.

4. Conclusions

In this work we have studied the nonlinear optical properties using the third harmonic generation technique. Good quality of fluorine doped In_2O_3 thin films have been elaborated using spray pyrolysis technique. We found that doping by fluorine improves the nonlinear response. It is not surprising because this behavior can be understand if one take into consideration that the free carrier concentration in fluorine-doped In_2O_3 samples is higher than that in undoped In_2O_3. This result proves that there is a good correlation between optical and electrical properties. To get a high third harmonic generation we need a low electrical resistivity. This predictive capability is extremely important from the standpoint of searching for materials with large nonlinearities. The best value of $\chi^{(3)}$ = 1.98 x10^{-11} (esu) was found for the In_2O_3: F 5% samples at 450°C.

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