Materials Science in Semiconductor Processing 90 (2019) 32–40

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Improvement of structural, optical and electrical properties of iron doped indium oxide thin films by high gamma radiations for photocatalysis applications

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ARTICLE INFO

Keywords:
Iron doped indium oxide thin films
Gamma radiations
Physical properties
Photocatalytic activity

ABSTRACT

Iron doped indium oxide (In_2O_3:Fe) thin films have been deposited on glass substrates by spray pyrolysis technique and irradiated by four high gamma doses 1, 5, 10 and 100 kGy. We have investigated the influence of applied gamma radiations on structural, optical, photoluminescence and electrical properties of In_2O_3:Fe thin films using X-ray diffraction, Raman spectroscopy, spectrophotometer, Photoluminescence spectrometer and Hall Effect measurements. Structural analysis revealed that preferred orientation (400) plan depicted at $2\theta = 35.5^{\circ}$ was kept after exposure to gamma radiations with a noticeable improvement of crystallinity for all doses. Average transmission values in the transparent domain [600–2500] nm were increased from 79% to a maximum value of 88% for irradiated thin layer by 10 kGy. Band gap energy was also increased from 3.32 eV to 3.5 eV after irradiation by 10 kGy. Different optical parameters such as refractive index n(λ), extinction coefficient K(λ), lattice dielectric constant (ε_L), high frequency dielectric constant (ε_∞), plasma frequency (ω_P) and the ratio of carrier concentration to electron effective mass ($\frac{N}{m^*}$) were determined and analyzed. Single-oscillator Wemple-Didomenico model was applied to calculate the dispersion parameters E_0 and E_d after gamma irradiation. Photoluminescence spectra of thin films show an overall decrease in their peak intensities after γ-irradiation. Hall Effect measurements of In_2O_3:Fe thin films revealed that electrical resistivity have been decreased from $5.07 * 10^{-2}$ Ω cm to a minimum value of $1.75 * 10^{-2}$ Ω cm at 10 kGy. All these good experimental results can lead to a potential use of gamma irradiated iron doped indium oxide thin film for optoelectronic devices. Photocatalytic activity of γ-irradiated In_2O_3:Fe thin films to decompose methylene blue were studied under sun light. Optimum irradiated thin film shows an enhancement of photocatalytic activity under sun light with a percentage of dye decolorization equals to 87%.

1. Introduction

Many researches and development works have been done to optimize the use of oxide materials for optoelectronic devices [1–3]. In_2O_3 thin films are a part of transparent conducting oxides (TCO) family thanks to their remarkable properties; they have several applications in photovoltaic, sensor, photocatalysis and optoelectronic domains. The improved performance of indium oxide thin layers requires the optimization of their structural, optical and electrical properties. Generally, several means are used to achieve this objective such as doping in small amounts with other elements, varying the physical parameters like temperature or precursors concentrations. Iron doped indium oxide thin films have been synthesized and optimized in many previous works [4,5] in order to reduce electrical resistivity and increase optical transmission. It gives a great interest in applications like transparent conductive electrode to study ferromagnetic properties [6,7] and gas sensor applications [8,9]. A large number of studies have been investigated the effect of gamma radiations on the physical properties of thin films [10–23]. Gamma radiations have a high capacity to deeply penetrate in materials and modify their physical properties. Generally, gamma radiations produce ionization of atoms which may lead to their displacement from their sites in the crystal lattice [24] besides excitation and release of electrons. It is believed that gamma radiations produce structural modifications caused by broken bonds of oxygen atoms which create oxygen vacancies in the lattice (colors centers) and dislocations. This leads to many modifications in structural properties and their energy levels [10,24]. In this work, iron doped indium oxide thin films were firstly synthesized in our laboratory by spray pyrolysis

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https://doi.org/10.1016/j.mssp.2018.09.022
Received 16 March 2018; Received in revised form 20 September 2018; Accepted 23 September 2018

technique with optimized iron concentration at 6 at% [25]. Then, they are exposed to high energy radiations for different γ-doses 1, 5, 10 and 100 kGy with an industrial (^{60}Co) source. Photocatalytic process of waste-water is an effective mean for the deterioration of dye pollutants. Metal oxides like In_2O_3, Ag_2O, TiO_2, ZnO and WO_3 have been investigated for their photocatalytic properties [26–31]. In this work, iron doped indium oxide thin films have been tested to determine their photocatalytic properties before and after gamma irradiation by 10 kGy. Up to date, there is no work about the photocatalytic properties of gamma-irradiated thin films. Our main goal is to evaluate the photocatalytic activities of iron doped indium oxide thin films before and after gamma radiations.

2. Experimental setup

In_2O_3:Fe thin films were synthesized by spray pyrolysis technique and deposited on glass substrates as reported by Nasreddine Beji et al. [25]. The substrate temperature equals to 500 °C. Our aqueous solution contains indium chloride ($InCl_3$) and Iron chloride ($FeCl_2$) used as a doping agent. This solution is sprayed onto heated substrates as fine droplets by a conical jet nozzle. We have used compressed air as a carrier gas. Spray solution rate is fixed at 2.5 ml/min and the distance nozzle – sample is 28 cm. In_2O_3 has been synthesized by optimum indium concentration equals to 0.04 mol l^{-1} as reported by Ref. [25]. The films have been doped by optimum iron atomic concentration with $y = \frac{[Fe2+]}{[In3+]} = 6\%$. An industrial gamma irradiator composed by a Cobalt source (Co^{60}) was used to irradiate thin films at various doses of 1, 5, 10 and 100 kGy in ambient air and at room temperature. Structural characterization was carried out by X-ray diffraction (XRD) using a monochromatic PANalytical diffractometer type X'pert PRO containing a cobalt source whose designation Kα line at a wavelength λ = 1.789 Å. From the diffraction scan, we have calculated the gain size D for the preferred orientation using the Scherrer's formula [31]:

$$D_{crystallite} = \frac{K.\lambda}{\sqrt{(\beta^2 - \beta_0^2)}\cos\theta} \quad (1)$$

where λ is the wavelength of incident X-ray beam, β is the full width at half maximum (FWHM), β_0 is the width of the corresponding peak due to the instrumental expansion which is about 0.125°, θ is the Bragg angle and k = 0.9.

The dislocation density (δ_{dis}) and the number of crystallites (Nc) per unit area are given by the following relations [32,33]:

$$\delta_{dis} = \frac{1}{D^2} \text{ and } N_c = \frac{e}{D^3} \quad (2)$$

where e is the film thickness.

Raman analysis was recorded by Jobin Yvon technology T 64000 with 488 nm argon in laser like excitation source at room temperature.

Optical transmittance T (λ) and reflectance R (λ) spectra were measured using UV–vis–NIR spectra with Perkin–Elmer Lambda 950 spectrophotometer at normal incidence and room temperature in the wavelength range 250–2500 nm.

The absorption coefficient (α) was calculated at different wavelength from the following equations [14]:

$$\alpha = \frac{-1}{e}\text{Ln}\left[\frac{T}{(1-R)^2}\right] \quad (3)$$

Optical band gap values were calculated using the following relation between absorption coefficient α and the photon energy (hν) [34]:

$$(\alpha h\nu) = B(h\nu - Eg)^n \quad (4)$$

where B is a parameter depending on the transition probability, E_g is the band gap and n is the constant characterizing the transition type.

In the exponential edge region, the variation of optical absorption coefficient with photon energy is governed by Urbach's relation [34]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \quad (5)$$

where α_0 is a constant, E_u is interpreted as the width of the tail localized states in the band gap.

Refractive index was obtained from envelope method by the following expressions [35,36].

$$n = \left[N + (N^2 - n_0^2 n_s^2)^{\frac{1}{2}}\right] \quad (6)$$

and

$$N = 2n_0 n_s \left[\frac{T_{max} - T_{min}}{T_{max} + T_{min}}\right] + \frac{n_0^2 + n_s^2}{2} \quad (7)$$

where n_0 and n_s are respectively the refractive index of air and the irradiated substrate at the same wavelength, T_{max} and T_{min} are respectively the maximum and minimum transmission beyond transmittance envelope.

Extinction coefficient (K_{ex}) was calculated using the following formula [37]:

$$K_{ex} = \frac{\lambda\alpha}{4\pi} \quad (8)$$

where α is the absorption coefficient.

The real (ε_1) and imaginary (ε_2) parts of the dielectric constant can be calculated using the following formulas [34]:

$$\varepsilon_1 = n^2 - K^2 \quad (9)$$

$$\varepsilon_2 = 2nk \quad (10)$$

The lattice dielectric constant (ε_L), the high frequency dielectric constant (ε_∞) and the ratio of carrier concentration to the electron effective mass ($\frac{N}{m^*}$) were determined from the plot of (n^2) versus (λ^2) by the relation [13,38]:

$$\varepsilon_\infty = n^2 = \varepsilon_L - \frac{e^2}{\pi c^2}\frac{N}{m^*}\lambda^2 \quad (11)$$

where c is the light velocity, e is the electronic charge and m^* is the electron effective mass.

According to Drude model, the free charge carrier density ($\frac{N}{m^*}$), the electronic charge (e) and the velocity of light (c) can be used to deduce the plasma frequency (ω_P) from the relation [38] below:

$$\omega_P = \sqrt{\frac{N e^2}{\pi m^* c^2}}\ (\text{cm}^{-1}) \quad (12)$$

In order to study the dispersion of refractive index in transparent region, the well known Wemple and DiDomenico model [39] proposed the single-oscillator model which expressed by the following form:

$$\frac{1}{(n^2 - 1)} = \frac{E_0}{E_d} - \frac{(h\nu)^2}{E_0 E_d} \quad (13)$$

where n is the refractive index, hν the photon energy, E_0 the single oscillator energy and E_d is the dispersion energy or oscillator strength. The dispersion parameters E_0 and E_d obtained by plotting of $(n-1)^{-1}$ against $(h\nu)^2$. With these results, we can determine the optical susceptibility of the third order non-linear according to miller's generalized rule [38]:

$$\chi^{(3)} = \frac{A}{(4\pi)^4}\left(\frac{E_d}{E_0}\right)^4 \quad (14)$$

where A is a quantity that is assumed to be independent from frequency, $A = 1.7 * 10^{-10}$ esu,

The constant S_0 and λ_0 can be defined from the equations as [25]:

$$\lambda 0 = \frac{hc}{E_0} \text{ and } S0 = \frac{E_0 E_d}{hc} \quad (15)$$