Optical Properties of Thermally-Annealed Tin-Doped Indium Oxide Thin Films

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In this work, results of thermal annealing of tin-doped indium oxide thin films were presented. The effect of thermal annealing of the optical characteristics of such films was introduced. These characteristics include transmission, absorption coefficient, absorption depth, type of band gap and the dominant absorption processes. Thermal annealing may improve the diffusion of Sn dopants in the In_2O_3 structure and hence affect the optical properties of the resulted structure. The Sn-doped In_2O_3 thin films are widely used in the optoelectronics and integrated optics architecture.

Keywords: In_2O_3, Thermal evaporation, Annealing conditions, Optical properties
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1. Introduction

Thin films made of metal oxides have some distinct characteristics such as good electrical conductivity, high optical transmission in the visible wavelengths region, good adhesion on crystalline and amorphous substrates, chemical stability and excellent photochemical properties. These characteristics are originated from the behavior of such materials as n-type semiconductors with wide energy bandgap. Examples of such films are indium oxide (In_2O_3) deposited on glass substrate and tin-doped indium oxide (Sn-doped In_2O_3). These films are widely used in solar conversion devices, photovoltaic devices and flat displays [1-3].

Too many recent and advanced applications impose using of In_2O_3 films with low electrical resistance and high transmission in the visible region. So, in order to optimize such properties, several parameters, such as films thickness, doping type and concentration, and deposition conditions, should be controlled. Accordingly, a figure of merit should be determined to introduce the quality of the transparent conducting oxides (TCOs) [4,5].

The electrical and optical properties of the semiconducting oxides, like In_2O_3, highly depend on the density of defects resulted from the external doping as well as their preparation and growth conditions [6]. Tin (Sn) is the much suitable materials to perform the external doping in indium oxide other than fluorine (F), chlorine (Cl) and antimony (Sb) [7]. It is important to control the concentration of tin dopants those replace In_2O_3 molecules in the lattice in order to obtain low-resistance films. When a tin atom replaces indium atom, it releases a free electron inside the lattice, hence, the electrical conductivity is increased. However, this atom will also act as a scattering center since it is neutral; hence, the electrical conductivity is decreased [8].

Indium oxide films can be prepared by several techniques, such as DC sputtering, RF sputtering, chemical vapor deposition (CVD), thermal evaporation and spray pyrolysis [9-13].

In this work, tin thin films were deposited on In_2O_3 layer then thermal annealing was performed to obtain Sn-doped In_2O_3 films and enhance their optical properties.

2. Experiment

High purity (99.999) indium oxide was used to deposit thin films on glass substrates using vacuum evaporation system (Balzer-80) at vacuum pressure of 10^{-6}torr. The deposited films were about 500nm in thickness, which was determined by the weighing method. The optical measurements were carried out on the prepared In_2O_3 films then thin films of tin were deposited over the In_2O_3 films with different thicknesses. The optimum results were found at 30nm Sn film. An electronically-controlled furnace was used for thermal annealing of the Sn/In_2O_3 structures. The transmission measurements were performed within the wavelength range of 300-90nm using GECIL GE-720 spectrophotometer.

3. Results and Discussion

Figure (1) shows the transmission spectrum of the prepared samples of Sn-doped In_2O_3 for three different cases (without thermal annealing, 600K annealing and 800K annealing). The transmittance is continuously increased with the incident wavelength. The transmission in this case is mainly determined by absorption coefficient and thickness of the sample as tin atoms are not stimulated to diffuse inside the In_2O_3 structure. Therefore, the optical properties of the sample are fundamentally belonging to the under-layer material (In_2O_3) as the thickness of tin layer is too small to affect the transmission.

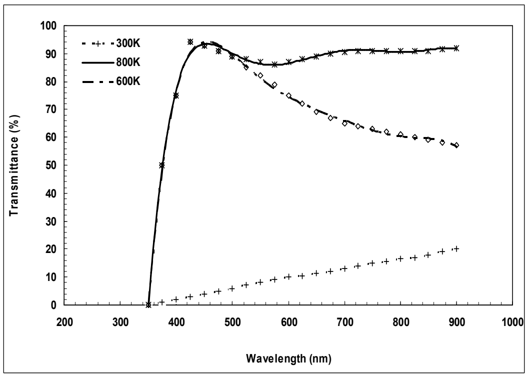

Fig. (1) Transmittance of the prepared samples in both cases (without annealing, at different annealing temperatures)

In case of thermal annealing at 600K, tin atoms are stimulated to diffuse inside In_2O_3 structure according to Fick's law [14]:

$$D = D_0 \exp(-\frac{E_a}{K_B T}) \quad (1)$$

where E_a is the activation energy of the dopants (tin atoms), D is the temperature-dependent diffusion coefficient and D_0 is the diffusion coefficient at 0K

As shown in Fig. (1), in cases of annealing at 600K and 800K, the transmittance is rapidly increased for wavelengths shorter than 450nm, where the transmittance is slightly decreased. The rapid increase is attributed to the effect of tin atoms diffusion and formation of a Sn-doped In_2O_3 layer. Indium oxide has too high sensitivity to doping as its optical and electrical properties are highly changed with the doping type and concentration.

The transmission spectrum at annealing temperature of 800K is clearly distinguished from that at 600K above 480nm as the latter (600K) is decreased to reach 57% at 900nm while the former (800K) is slightly decreased then slowly increased over 600nm to reach about 92% at 900nm.due to Fick's law, the diffusion coefficient of tin atoms inside indium oxide structure at 600K is smaller than that at 800K. Therefore, the electrical and optical characteristics may differ depending on the diffusion depth of dopants as well as their distribution profile inside the substrate (In_2O_3).

At the beginning, the Sn films did not affect the transmission of In_2O_3 because tin atoms were not yet stimulated by annealing to diffuse inside the In_2O_3 structure. After annealing of In_2O_3 films, the effect of tin atoms diffusion and formation of a Sn-doped In_2O_3 layer made In_2O_3 films to be high sensitive for doping.

Figure (2) represents the variation of absorption coefficient with incident photon energy. The absorption coefficient was determined from the following relation:

$$\alpha = -\frac{1}{t}\ln(T) \quad (2)$$

where t is the thickness of sample (in cm) and T is the transmittance (%)

The different behavior of the function with incident photon energy is attributed to the diffusion of tin atoms those act as dopants inside In_2O_3 structure [15]. As shown, there several regions can be distinguished. In the first region (>828nm), the absorption coefficient is increased with photon energy to its peak at 1.5eV corresponding to wavelength of 828nm. In this region, the absorption by impurities is the dominant absorption process as the incident photon energy is higher than impurity ionization energy (0.025eV) but lower than the energy bandgap of the semiconductor. So, the absorption coefficient is given by:

$$\alpha_{imp} = N_T . \sigma \quad (3)$$

where N_T is the concentration of unionized impurities and σ is the absorption cross section, which is dependent of temperature, concentration of impurities and their ionization energy

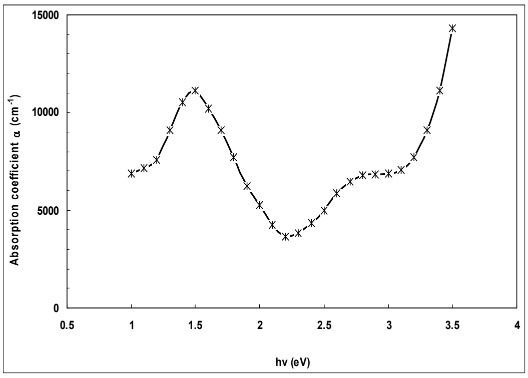

Fig. (2) Variation of absorption coefficient with incident photon energy for the sample annealed at 800K

In the second region (566-828) nm, the absorption coefficient is decreased with increasing photon energy because the absorption is achieved by the substrate material (In_2O_3) and the dopants have no more effect on absorption process since the incident photon passes the region through which tin atoms diffuse to reach indium oxide layer. This behavior is a general feature of semiconductors with varying incident photon energy below the cutoff wavelength. The absorption coefficient has a minimum at 566nm.

In the third region (<566nm), the absorption coefficient is increased with incident photon energy as the fundamental absorption processes are the dominant since the incident photon energy is higher than or equal to the direct energy bandgap of the semiconductor (~2.6eV). This increase is continued within the ultraviolet (UV) region of wavelengths and a small region of approximately constant absorption coefficient appears within 415-434nm.

The behavior in the third region may support the assumption that direct and indirect transitions occur at these values of incident photon energy with a probability depending on selection rules those governing inter-level transitions between valence and conduction bands as well as the effect of tin atoms on the type of bandgap in the semiconductor [16].

In order to determine either the direct or the indirect transitions are the dominant, the adsorption depth was sketched with incident photon energy. The value of adsorption depth for the fundamental direct absorption processes is ranging within 100-1000nm while it is expected to be 10m, for the indirect processes. As shown in Fig. (3), the fundamental indirect absorption processes are the dominant with a small occurrence probability for the direct ones. Thermal annealing of the prepared samples lead to increase the adsorption depth to its maximum (5um), after which it rapidly decreases at high energy regions (short wavelengths).

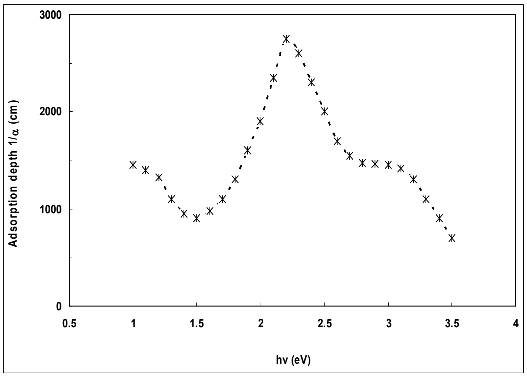

Fig. (3) Variation of adsorption coefficient with incident photon energy for the sample annealed at 800K

Figure (4) shows the relation between the function $(\alpha hv)^{1/2}$ and the incident photon energy (hv) and the linear function confirms that the fundamental indirect absorption processes are the dominant, i.e., the semiconductor has an indirect energy bandgap. Such semiconductors are widely used for manufacturing semiconductor lasers, narrow-response quantum detectors, multi-quantum wells structures and their devices.

However, there is a probability for the forbidden fundamental direct absorption processes to occur since indium oxide has a direct bandgap of about 3.75eV and an indirect bandgap of about 2.6eV. Therefore, controlling the doping of such materials make possible to control their optical properties to serve some required applications. Accordingly, the doped indium oxide is currently one of the most important materials used for building integrated optics those moving dramatically fast to replace the integrated circuits together with the enormous developments of optical communications and their wide applications [17].

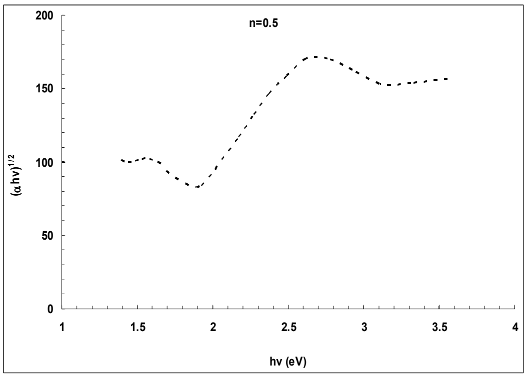

Fig. (4) Variation of $(\alpha hv)^{1/2}$ with incident photon energy for the sample annealed at 800K

4. Conclusion

Due to the results obtained from this work, thermal annealing lead to change the optical properties of tin-doped indium oxide samples as their transmission in the visible and near-infrared regions was increased. Accordingly, the absorption characteristics in these regions was changed too leading to obtain an extrinsic semiconductor in which the fundamental indirect absorption processes dominate with lesser probability for the direct processes to occur. As a consequence of annealing, this material became a candidate to serve different applications of optoelectronics in several spectral regions. As well, the semiconductor having different types of absorption processes is very important in the architecture of advanced optical communications systems.

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