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SPIN COATED ITO FILMS PREPARED WITH A SOLUTION OF METHANOL: N-PROPYL ALCOHOL (1:1)

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Abstract

A sol-gel method for the synthesis of Indium Tin Oxide films on glass substrate and their structural, electrical and optical characterization is presented in this paper. ITO films were deposited at room temperature by spin coating technique using a solution of ITO nano-powder in methanol (CH_3OH) n-propyl alcohol ($CH_3(CH_2)_2OH$) (1:1) solution. The surface morphology of the films was investigated by Fluoroscence Microscope (FM) and the surface smoothness of the films improved after annealing. The electrical resistivity of the films was measured using Van Der Pauw method and the resistivity is found in 10^{-1} Ω.cm range. The conductivity as well as smoothness of the films was increased with increasing number of layers and heat treatment. Optical transmittance and absorbance of the films were measured by Ultra Violet (UV) spectrophotometer in the wavelength range of 300nm - 800nm. In the visible and infrared range, the films exhibit low absorbance and high optical transmittance. The direct optical band gap (E_g) of the films was calculated using absorption coefficient (α) and the values of E_g is found in the range 3.5 ~ 3.7 eV. The optical band gap is slightly increased after annealing for lower thickness samples due to increased carrier concentration.

Keywords*: ITO, spin coating, TCO, sol-gel, solar cell, band gap.*

Introduction

Transparent conducting oxides (TCOs) deposited on glass substrates are important materials in the field of optoelectronic devices such as solar cells, electroluminescence, liquid crystal displays, etc. [1]. In modern times, TCOs are being used in various technological applications such as flat panel displays, touch panels, energy efficient windows, photovoltaic devices, light emitting diodes, gas sensors etc. because of their identical properties i.e., remarkable combination of near-metallic conductivity, high transmittance in the visible region and high reflectivity in the infrared region of light [2]. TCOs are typically wide band gap n-type semiconductors, for example, tin doped indium oxide (ITO), antimony doped tin oxide (ATO), aluminium doped zinc oxide (AZO), etc. One of the most popular materials in the TCO group is ITO and they are good candidates for many applications for example infrared reflectors, antireflection coatings, and thin film resistors [3]. Nowadays, ITO thin films are being extensively studied both in research and industrial purpose due to their impressive properties such as low resistivity, transparency in the visible region of the electromagnetic spectrum and high infrared reflectivity [4].

The fabrication of ITO thin films has already been demonstrated by many researchers using various methods such as chemical vapor deposition (CVD) [5], chemical solution deposition (CSD) [6,7], vacuum deposition and electron beam deposition [8], rf and dc sputtering [9,10], spray pyrolysis [11] and last but not the least sol-gel method [2]. Among the wet chemical processes to fabricate thin films, sol-gel method is potentially advantageous, relatively simple and less expensive compared to these physical methods. Precursor solutions

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for wet chemical deposition of thin films can be categorized into two types depending on whether an organic solvent or water is used as the solvent. Although, for the deposition of ITO films sol-gel process based on aqueous solution [2] has been studied, there are a variety of researches based on organic solvents like ethylene glycol, ethanol or acetyl-acetone, etc. [12-15]. Recently, spin coated ITO films prepared with ethanol and methanol based solutions have also been studied in our lab [16, 17].

In this paper, we report the synthesis and characterization of ITO transparent conducting films in a sol-gel process on glass substrate by spin coating technique using an eminent solution prepared with ITO nano powder (99.9%) in methanol (CH_3OH):n-propyl alcohol ($CH_3(CH_2)_2OH$) (1:1) solution. The subject of this work is to introduce a new sol-gel fabrication process of spin coated ITO films and analyze the effect of heat treatment structural, electrical and optical properties.

Preparation of Films

Solution preparation

The solution for the spin coating of ITO films can be synthesized using various methods. In this work, 0.45 gm Indium Tin Oxide (In_2O_3: Sn) nano powder (99.9%) has been dissolved in a mixture of 15 ml methanol and 15ml n-propyl alcohol using magnetic stirrer at 50°C temperature. Then for a better incorporation of nanoparticles into the solvents, the solution was carried through an ultrasonic vibrator for 10 minutes. Finally, a colloidal solution of ITO has been prepared.

ITO film deposition

Spin coating technique has been adopted in this work. Using a vacuum spin coater (VTC-100), ITO films of different number of layers have been deposited on glass substrates with the resultant solution. For coating of each layer, the vacuum spin coater was preset with 40 seconds time & 500 rpm speed coating condition.

Annealing

The spin coated ITO films were heated in a rapid thermal annealing system (Carbolite Eurotherm CMF-1200) for 10 minutes at 400°C temperature.

Characterization

Surface Morphology

The surface morphology of the prepared samples was investigated by Fluroscence Microscope (FM) with a magnified view of 50μm surface area of the films. Fig. 1 shows the Fluroscence Microscopic (FM) images of the surface of ITO spin coated samples for different layers before and after annealing. It can be observed from the figure that the films contain micro-grains and cracks which results some discontinuity throughout the films.

The reason for this might be the ITO powder was not completely soluble into the solvent and the solution was rather colloidal in nature. It is also noticed that the grains and defects of the films are reduced after annealing. As a result, the surface smoothness as well as the continuity of the films is improved with heat treatment.

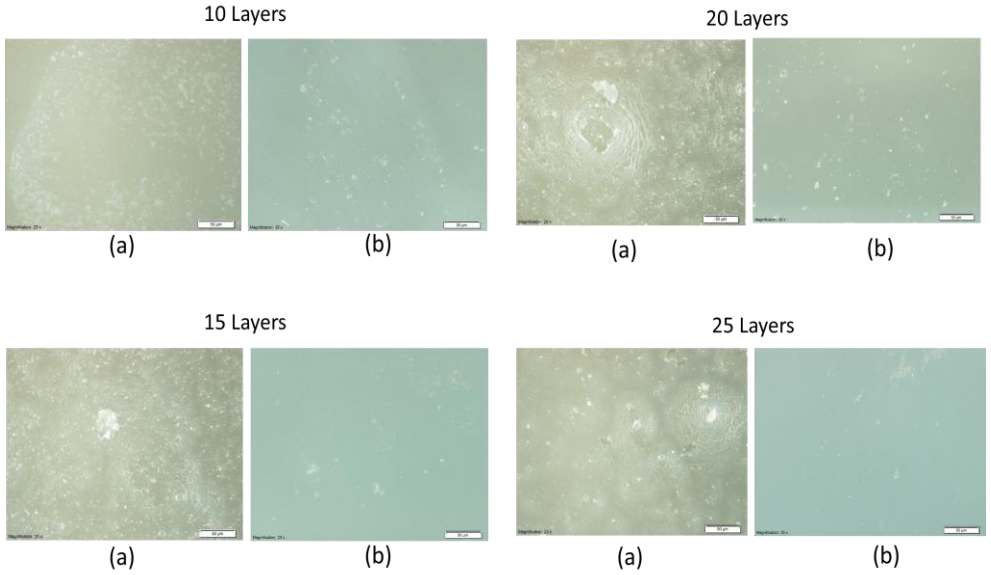


Fig. 1. Fluroscence Microscopy of 50 μm surface of ITO spin coated films with different number of layers: (a) before and (b) after annealing

Electrical Properties

The four probes Van Der Pauw method has been used in this work for measuring the electrical resistivity (ρ) of the samples of different thickness. Silver (Ag) paste was used for making contacts on the four corners of the films sins it is a good conductor and sticks firmly to the glass substrate.

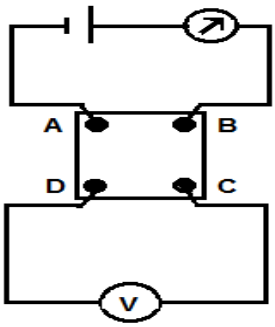


Fig. 2. Circuit arrangement for measurement of resistivity in Van Der pauw's Method

The following equation was used for the calculation of electrical resistivity (ρ) [18]:

$$\rho = \frac{\pi t}{\ln 2}\left(\frac{R_{AB,CD}+R_{BC,AD}}{2}\right) f(\mathrm{R_{AB,CD}/R_{BC,AD}}) \quad (1)$$

Where $R_{AB,CD}$ and $R_{BC,AD}$ are measured as shown in Fig. 2, and t is the sample thickness. The function $f(x)$ is defined by the equation [18]:

$$\cosh\left(\left[\frac{x-1}{x+1}\right]\frac{\ln 2}{f}\right) = \frac{1}{2}exp\left(\frac{\ln 2}{f}\right) \quad (2)$$

Under favorable conditions f may become approximately unity and thus the resistivity values obtained for different samples are shown in table 1.

Table 1. Electrical resistivity (ρ) of the ITO films of different number of layers before and after annealing

No. of Layers	Electrical Resistivity (ρ) [Ω.cm]	
	Before Annealing	After Annealing
10	25.3	3.41
15	4.64	4.31
20	4.59	4.27
25	1.39	0.99

It is observed from Table 1 that the resistivity of the spin coated films is found in Ω.cm range. Therefore, the films are more resistive in nature as compared to the other ITO films, e.g. prepared with methanol and ethanol solutions [16, 17]. This could happen because of the presence of micro-grains and discontinuity in the film. One possible reason of this might be that the used ITO powder was exposed to air for a long time which caused the degradation of the conductivity. Also the preparing solution was colloidal in nature which increases the presence of micro-grains and interrupts the flow of current throughout the films resulting low conductivity of the films. However, the resistivity of the films is decreased with increasing the number of layers i.e. thickness of the film. Table 1 and Fig. 3 also show that the annealing treatment improved the conductivity of the ITO films.

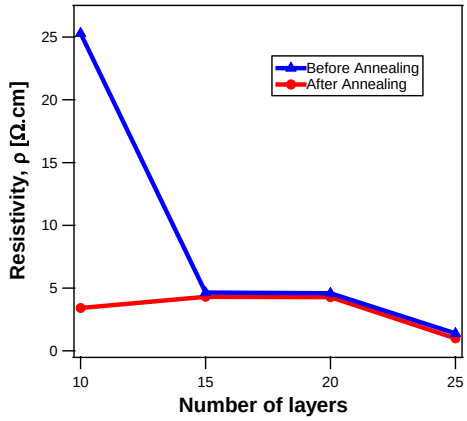


Fig. 3. Variation of resistivity with thickness and annealing

Optical Properties

The optical absorbance (a) and transmittance (T) of the films have been measured by Ultra Violet spectrophotometer (UV-1650PC) in the wavelength range of 300 nm to 800 nm for different thickness of the films.

The optical band gap (E_g) values for the prepared films are calculated from the plot of $(\alpha h\nu)^2$ versus ($h\nu$). The values of absorption coefficient (α) have been calculated from the following equation [19, 20]:

$$\alpha = \frac{1}{t}\ln\frac{1}{T} \tag{3}$$

where: t is thickness of the films and T is transmittance. The absorption coefficient (α) and incident photon energy (hν) is defined by the following equation [20]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (4)$$

where: A is a constant, hν is photon energy and E_g is optical band gap.

i) Absorbance, a: The absorbance curves of different layered samples with and without annealing are shown in Fig. 4 and the curves indicate that, the absorbance of the films, although high initially in the wavelength range (300 nm ~ 350 nm), decreased drastically in the visible and infrared range (400nm ~ 800nm). This proves the good optical transparency of the films in the visible range.

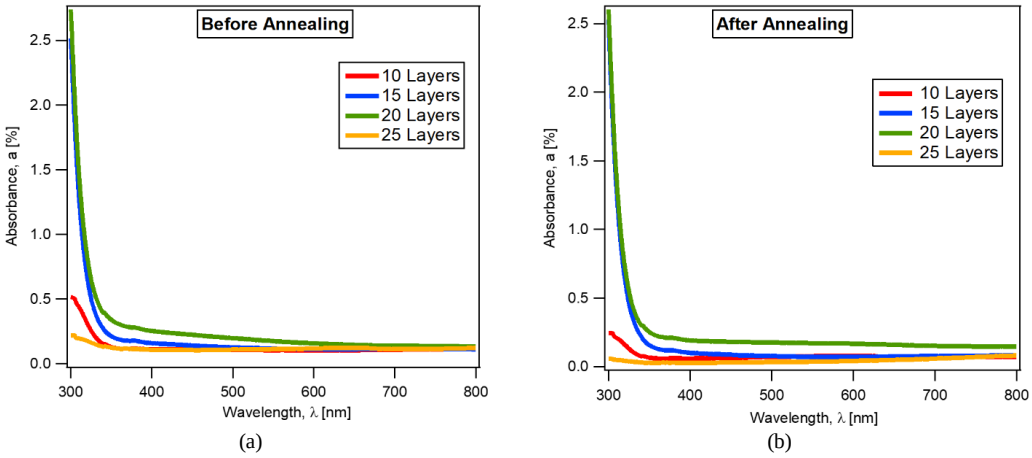


Fig. 4. Wavelength spectra for absorbance of different layered spin coated samples (a) before and (b) after annealing

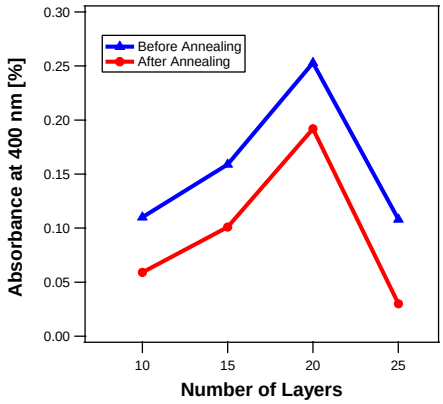


Fig. 5. Variation of absorbance with thickness and annealing at 400 nm wavelength

Fig. 5 shows the variation of absorbance of the films with thickness and annealing at 400 nm wavelength. It is observed that the absorbance is quite decreased with heat treatment of the films. It is also noticeable that although initially the absorbance increases with increasing thickness, at 25 layers it is again decreased and hence the transparency is improved.

ii) Transmittance, T: Fig. 6 shows the transmittance curves of different layered samples before and after annealing. Just in support of the absorbance curves, the transmittance of the films is highly increased in the visible and infrared range (400nm ~ 800nm) which again shows the high optical transparency of the ITO films.

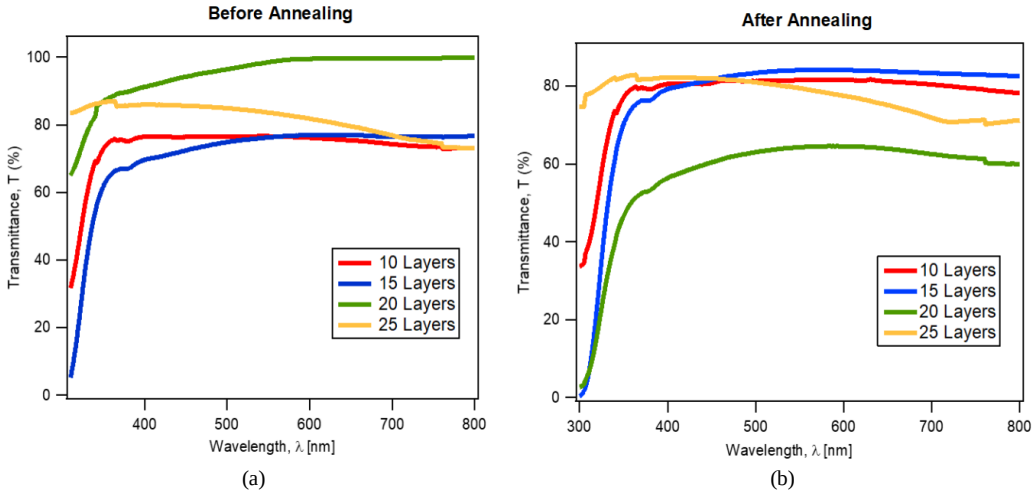


Fig. 6. Wavelength spectra for transmittance of different layered spin coated samples (a) before and (b) after annealing

The graph in Fig. 7 shows the variation of transmittance with thickness and annealing. Here we have considered the peak values for transmittance for each sample. For the samples with lower thickness (10 and 15 layers) the transmittance is increased with annealing, although at higher thickness (20 and 25 layers) the transmittance is slightly decreased. Hence, it could be said that the films showed better transparency for an optimum thickness.

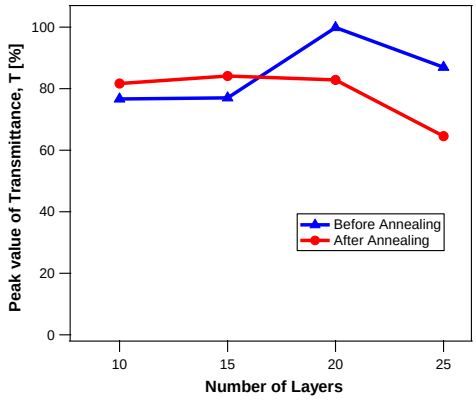
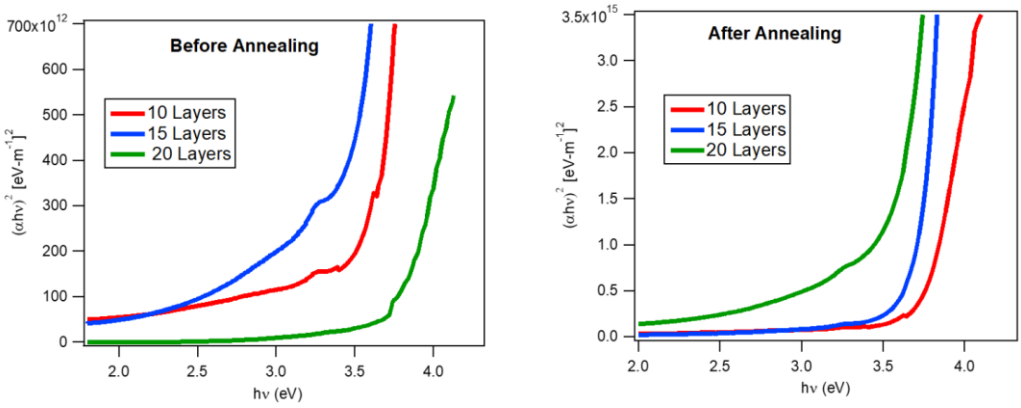


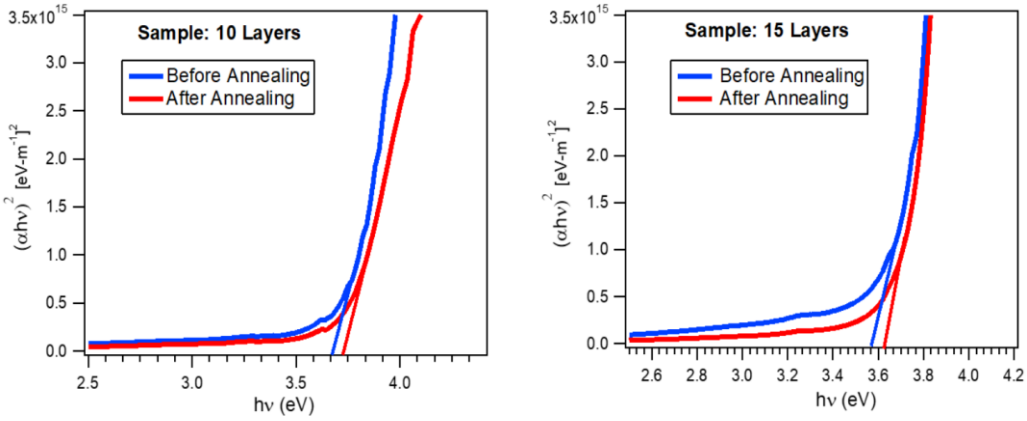
Fig. 7. Variation of transmittance with thickness and annealing

iii) Optical Band Gap, E_g: Obtained band gaps for the prepared films are plotted as a function of thickness in fig. 8. The ITO films are known to be direct allowed band gap semiconductors [21], and hence the plots are made with $(\alpha h\nu)^2$ versus $h\nu$ (Fig. 8 and Fig. 9) and the band gap (E_g) values of the samples are obtained between 3.5 eV ~ 3.7 eV. It is observed that the as prepared sample with higher thickness has the highest band gap (E_g) ~ 3.7 eV. But after annealing the band gap of 10 and 15 layered samples has been increased.



(a) (b)

Fig. 8. Optical bang gap (E_g) of the ITO samples before and after annealing



(a) (b)

ig. 9. Increase of band gap (E_g) after annealing for (a) 10 and (b) 15 layered samples.

The effect of annealing is more clearly shown in fig. 9 for the 10 and 15 layered samples. It is observed that, for both samples, the optical band gap is increased after annealing. The widening of the optical band gap might be due to increased carrier concentration and which is explained by Moss–Burstein effect [19, 22].

Conclusions

In this work, ITO thin films with methanol:n-propyl alcohol (1:1) solution has been synthesized using spin coating technique and various characteristics of the prepared films have been investigated.

The as deposited films were containing grains and defects due to the colloidal nature of the solution. But the surface smoothness was improved after annealing. The electrical resistivity of the films measured was in 10^{-1} Ω.cm range which indicates the resistive nature of the films. Therefore, the films somewhat possess low conductivity. However, the conductivity of the films has been increased with higher thickness and heat treatment. The films show a very low absorbance and high transmittance in the visible and infrared range. This suggests that the ITO films have great application prospect as anti-reflection coatings. The films contain a direct

optical band gap in the range 3.5 eV ~ 3.7 eV. The band gaps are widened after annealing which indicates increasing of carrier concentration with heat treatment.

Although the conductivity of the films is quite increased using heat treatment, the resistivity and consequently the sheet resistance is still higher compared to the ITO films prepared with other alcohol solutions [16, 17], which limits their electrical characteristics. On the other hand, the films exhibit great optical transparency. It is observed that the spin coated films with an optimum thickness of slightly above 15 layers demonstrate the suitable combination of conductivity and transmittance for antistatic application or devices requiring quite higher sheet resistance.

Therefore, it can be concluded that, this work paves the way of learning ITO thin films fabrication in a sol-gel process and analyzes the performance of the transparent conducting films which will help us proceed for the utilization of TCO coated films in various technological applications such as touch panel, photovoltaic devices, sensors, etc. by modifying and maintaining proper synthesis and post-treatment conditions in future.

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