

Structural and Optoelectronic Properties of Nanostructured ITO Thin Films Deposited by Chemical Spray Pyrolysis Technique

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Abstract: In this study, the spray pyrolysis method is used to generate an indium tin oxide (ITO) thin film on a glass substrate. In_2O_3 layers were deposited and doped with tin at different doping concentration ranging from 2% to 6%. ITO thin films for application in thin-film silicon solar cells with superior structure and optical properties (grain size ranging from 44 to 84 nm; transparency of $> 87\%$) have been investigated. This investigation elucidates the properties of ITO thin films used as antireflection front electrodes in p-n junction Si solar cells. Microstructure, surface morphology, optoelectrical and optical properties of these films were then characterized and analyzed. Next, the effects of doping concentration of ITO film growth were discussed. The ITO thickness was optimized considering that the refractive index of Si emitter layer optimizes its optical characteristics and p-n junction solar cell spectral response. The best increasing in p-n junction solar cell conversion efficiency was 4% with an open circuit voltage (V_{oc}) of 0.425 V, fill factor (FF) of 0.47, and short circuit current density (J_{sc}) of 0.91 mA/cm^2 .

Key words: Indium tin oxide, spray pyrolysis, optical and structure properties, solar cell.

1. Introduction

ITO thin films are wide gap semiconductors with a relatively low resistivity and widely used as transparent in the visible range of the spectrum. Due to these characteristics, ITO continues to be the material of choice for many applications where highly conductive thin films of high transparency are required: flat panel displays, solar cells, defrosting windows, electromagnetic shielding, etc. [1-3]. It is one of the most studied transparent conducting oxides (TCOs) in terms of dependencies of its optical, electrical, morphological and structural properties on deposition conditions [4, 5].

Currently ITO is widely employed as a transparent

conductor for the fabrication of thin film solar cells. The ITO layer in thin film solar cell modules has a significant impact on the power conversion efficiency [6, 7]. In order to reduce the resistive losses and lost active area of solar cells, high resolution-patterning of ITO thin films is required in the formation of interconnect lines and assembly of thin film solar cells. Various techniques have been developed to pattern ITO electrodes with well defined edges and electrically insulated grooves between the conductor lines for thin film solar cells [8-10].

The ITO thin films commonly fabricated by different techniques such as electron beam (EB), RF and DC magnetron, spray pyrolysis and sputtering [11-14]. The spray pyrolysis method has been used frequently for the preparation of transparent conducting oxide films for many years. The conventional spray hydrolysis technique consists of spraying a dilute solution of an appropriate chloride

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from an atomizer onto a heated substrate under normal atmospheric conditions or controlled atmospheres. High pressure argon, nitrogen, or air are usually used as the spray gas. ITO films can be formed by mixing InCl_3 with a proper amount of SnCl_4 . The solutions are made usually by dissolving SnCl_4 and InCl_3 in some solvents such as ethanol, butyl acetate, propanol, HCl or H_2O . ITO films deposited by spray hydrolysis adhere strongly to various substrates and can have a very low resistivity of about $5 \times 10^{-4} \Omega\text{-cm}$ with high transparency of about 90% in the visible and near infrared parts of the spectrum. The deposition rate can be very high, ranging from 200 to 400 nm/min [14-16].

However, it is well known that the surface roughness of ITO films is an important feature in many applications, such as solar cell, and have a significant influence on device performance. A vital requirement for ITO films used in SC is an exceptionally smooth surface morphology. A strong correlation exists between the surface morphology of the ITO film and its fractal morphology, which can be fundamental parameter in determining the efficiency of the component, in such applications [17-21]. In surface studies, atomic force microscopy (AFM) techniques are now commonly employed, and have begun to be adopted for ITO film surface investigations.

In this study, ITO thin film deposited on glass and p-n junction silicon substrate at 573 K deposition temperature to prevent the substrate from damage. The different in doping concentration of ITO films deposited on substrates have been prepared by spray pyrolysis. The structural, optical and optoelectrical properties of the obtained films depending on deposition parameters, such as doping concentration have been investigated, the ITO is applied as an antireflection coating in monocrystalline silicon p-n junction solar cells.

2. Experiments

The spray pyrolysis is a simple and least expensive for the preparation of the films compared with other methods.

2.1 Sample Preparation

Aqueous and water precursor solutions, containing $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ and SnO_4 . This solved in deionized water (W). Glass and p-n junction are used as substrate for ITO thin films deposition. Slides of $25 \text{ mm} \times 25 \text{ mm} \times 0.5 \text{ mm}$ were ultrasonically cleaned by successive immersion in ethanol and dried it. A Camag nozzle, a ceramic hot plate and O_2 as carrier gas are used for the deposition of In_2O_3 thin films by chemical spray pyrolysis from precursor solutions. The films were sprayed onto pre-heated glass substrate 573 K, with the pressure of carrier gas at 1 bar. The distance between the spraying nozzle and the substrate was 25 cm used to ensure the spray cone formed was able to cover the total surface area of the substrate. The spraying time was 10 s (aqueous solutions) and the breaks between two pulses varied from 3 s to allow the substrate to attain the constant temperature; heat energy required for the evaporation water and compound formation is taken from substrate. In the spraying solutions, the average solution flow rate was 25 mL/min.

2.2 Characterization

The morphological and structural properties of the samples were characterized by atomic force microscopy AFM. The optical absorption studies were carried out by using single beam Cary Varian (Australia) UV-visible spectrophotometer in the wavelength range: 300-900 nm. The solar cell characteristics were measured by using tungsten lamp at power 100 mW/cm^2 and calculated the conversion efficiency and fill factor. The relative efficiency of the samples was then calculated for comparison to that of a calibrated reference cell.

The spectral response (SR), measurements of p-n junction solar cells were performed by using a tungsten lamp, a monochromator and optical filters to filter out the high orders, a light probe beam impinging normally on the samples.

3. Results and Discussion

Many properties of ITO thin film must be considered in p-n junction solar cell, such as structure, optical transparency and spectral response, to minimize optical losses. The key issue that should be considered is the deposition concentration of SnO_4 in the films which influences the properties of ITO and ITO/p-n Si solar cells.

3.1 AFM Studies

Fig. 1 shows AFM images of ITO thin films deposited on a glass substrate on the as-deposited film and at different doping of concentration in 2%, 4% and 6%, respectively. As can be seen, two typical morphological features are recognized readily by visual inspection of Fig. 1. The granules of various scales exist in all the films and are distributed evenly in some ranges. In addition, the granules possess different irregular shapes, sizes, and separations as shown in Fig. 1. The evolution of the interface width w (or, root mean square roughness, rms) as a function of doping concentration, where valleys, mountains, and island clusters become bigger as doping concentration was increased. In quantitative analyses on AFM images, it is known that the height roughness Ra and rms have been used to describe the surface morphology. Ra is defined as the mean value of the surface height relative to the center plane, and rms is the standard deviation of the surface height within the given area. From Fig. 1, interface width (rms) values of 1.22 nm, 3.12 nm, and 2.01 nm, respectively, were determined for the surface roughness of the as-doping 2%, 4% and 6% concentration samples. The interesting results (Ra and w) have been listed in Table 1.

It can be seen that the height roughness and interface width values increased as the doping concentration is increased. This behavior is due to the aggregation of the native grains into the larger clusters upon doping. This different cluster size influences the surface morphology of the films. The ITO thin film prepared at Cp 4%, Fig. 1, has larger clusters and becomes rougher,

as expected. The above analyses specify that height roughness Ra and w are strongly affected by the degree of aggregation and cluster size of the films.

Fig. 2 shows the granularity accumulation distribution charts of the formed films, and note the variation in grain diameter. In 2% doping concentration,

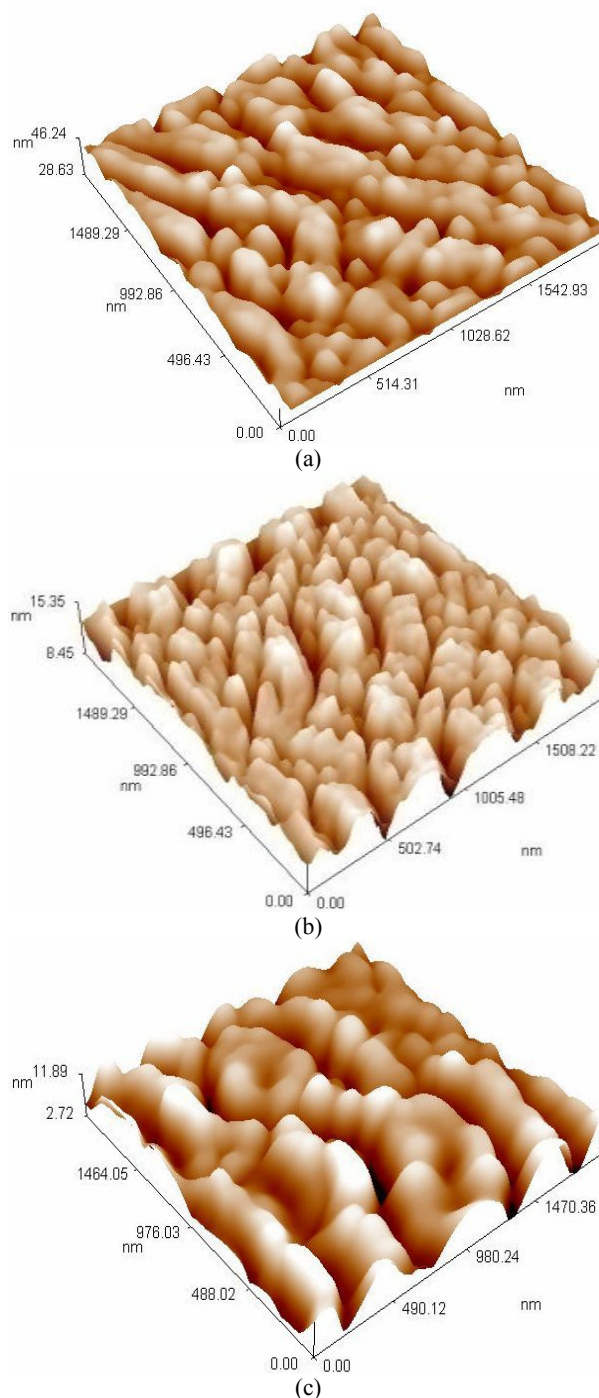


Fig. 1 AFM picture of ITO thin film deposited at different doping concentration (a) 2%; (b) 4% and (c) 6%.

Table 1 Structure and optoelectronic properties data obtained from the deposited ITO films as a function of Sn doping concentration.

Sn doping concentration	2%	4%	6%
Roughness	0.969	2.56	1.61
RMS	1.22	3.12	2.01
Peak-peak	6.9	17.2	9.09
High (<i>Ra</i>)	6.86	10.4	5.15
FF	0.41	0.43	0.37
Efficiency increasing (%)	-	4	-

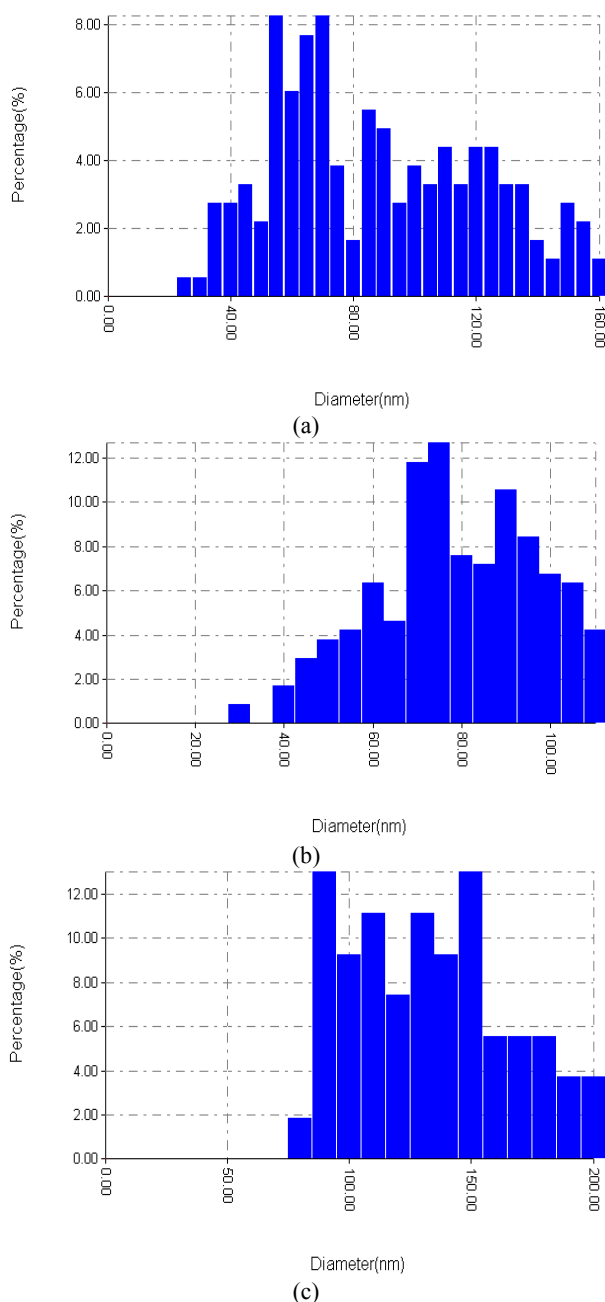


Fig. 2 Distribution charts of the formed films at different doping concentration (a) 2%; (b) 4% and (c) 6%.

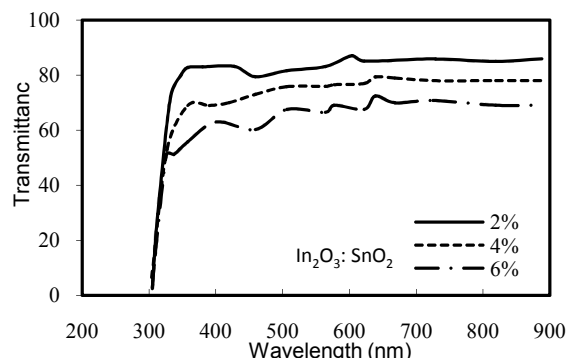


Fig. 3 Optical transmission characterizations for different doping concentration of ITO.

the grain diameter has lower value around 40-120 nm. An increase of the doping concentration up to 6%, the grain diameter have higher value around 100-200 nm.

3.2 Optical Characteristic Studies

Fig. 3 shows the variation of transmittance spectra of the ITO thin films deposited with the same conditions described in Figs. 1 and 2. The transmittance decreased with increasing the doping concentration, the optical transmission of the ITO films is greater than 87% in the visible range (400-700 nm). The results can be explained as following: when the doping concentration is higher, the particles deposited on the substrate cannot be oxidized enough so the prepared ITO thin films are anoxic and sub-oxides such as InO_x and SnO_x . The transmittance of ITO thin films was higher because sub-oxides can be oxidized with decreasing SnO rate. The redundant doping concentration can cause optical absorption and scattering. Furthermore, we calculated the optical band gap values of ITO thin films from transmittance spectra. In the strong absorption region, the absorption coefficient (α) can be calculated from Lambert's formula [7, 8]:

$$\alpha = \frac{1}{d} \ln \left(\frac{1}{T} \right) \quad (1)$$

where, T and d are transmittance and film thickness, respectively. The absorption has its minimum at low energy and increases with optical energy in a manner similar to the absorption edge of the semiconductors. The absorption coefficient for directly allowed transition for simple parabolic scheme can be ascribed

as a function of incident photon energy as Refs. [10, 12]:

$$\alpha h\nu = (h\nu - E_g)^{1/2} \quad (2)$$

where, $h\nu$ is the photon energy. The optical band gap of ITO thin films can be determined by plotting $(\alpha h\nu)^2$ versus $h\nu$, and extrapolation method. Fig. 4 indicates the variation of $(\alpha h\nu)^2$ versus $h\nu$ for ITO thin films prepared in the present study. It is observed that the optical band gap increased from 4.15 to 4.19 eV corresponding to the increase of doping concentration rates from 2% to 6% as shown in Fig. 4.

The spectral dependence of the reflectivity of $\text{In}_2\text{O}_3:\text{Sn}$ film 15 μm thickness was shown in Fig. 5. In the wavelength range 300-900 nm where the film transparency is high, direct experimental determined of the precise value of R for the film is difficult because of the existence of multiple reflections at the film-air and the film-substrate interface. Thus we determined value of R for a given wavelength range by using Eq. (3) together with experimental data for the film transmission coefficient (Fig. 3) and the film absorption coefficient (Fig. 4) [3, 9]:

$$T = (1 - R)^2 \exp(-\alpha d) \quad (3)$$

3.3 Solar Cell Characteristic Studies

Fig. 6 shows the current-voltage characteristic of the ITO/p-nSi solar cells measured under a one sun condition. After optimizing deposition parameters (ITO at doping concentration 4%) of the solar with $J_{sc} = 0.91 \text{ mA/cm}^2$, $V_{oc} = 0.425 \text{ V}$, $FF = 0.43$, and efficiency increasing of 4% was achieved.

In addition, it is well known that ITO thin film has a high refractive index, which leads to a solar-reflection of about 12%. The average reflection of approximately 4% between 400 and 1,000 nm was obtained by the ITO ARC on the p-n Si solar cell. This good result is considered to be based on the high properties of ITO film to improve efficiency of the cells.

The external quantum efficiencies (QE) of our best solar cell are shown in Fig. 7. The QE as a function of wavelength value (λ) is given by Eq. (4) [5]:

$$\eta = \frac{(1-R)(1-e^{-\alpha d})}{(1-Re^{-\alpha d})} \quad (4)$$

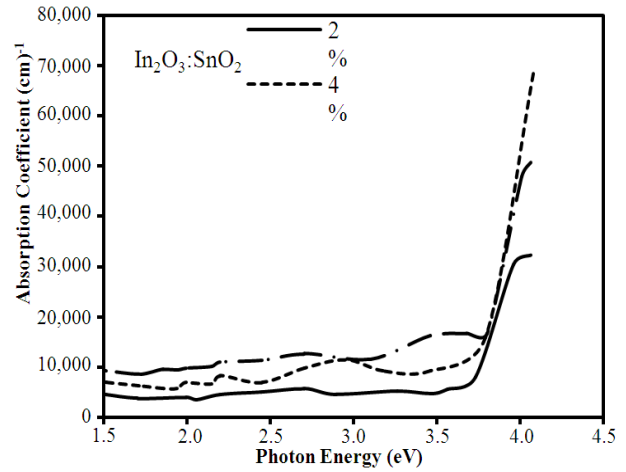


Fig. 4 The spectral of the absorption coefficient of ITO thin film.

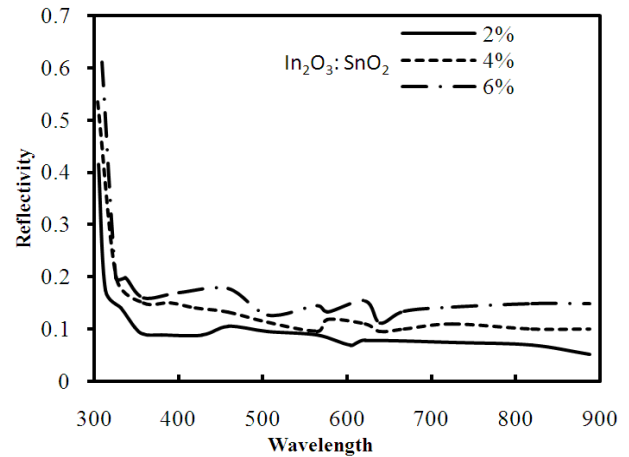


Fig. 5 Variation in reflectivity of ITO thin films as a function of doping concentration of ITO.

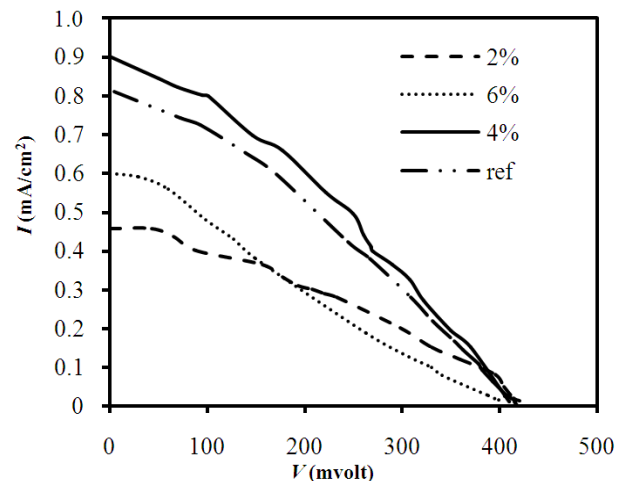


Fig. 6 I - V characterizations of ITO on silicon solar cell under simulated AM1 (100 mA/cm^2) illumination.

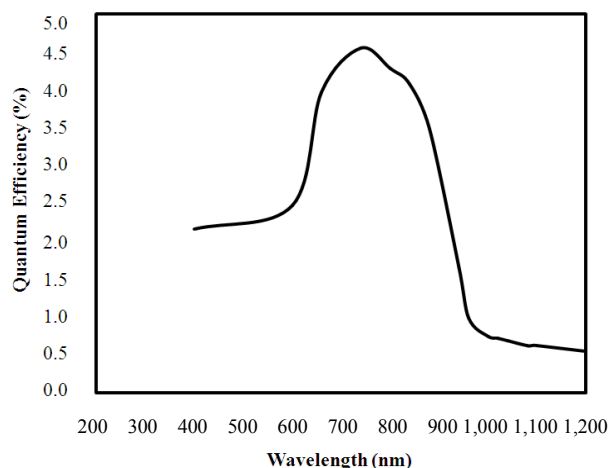


Fig. 7 The quantum efficiencies of our best solar cell as a function of wavelength.

where, R is the reflectance and QE is the quantum efficiency. QE is defined as the ratio of photo-generated electrons to the incident photon.

The QE gives access to the different loss mechanisms limiting the current density and thus the cell efficiency. We can give three regions in the quantum efficiency QE spectrum with wavelength between 300 nm and 1,200 nm. Region 1 (300-500 nm): for the short wavelength region, the QE is reduced by absorption in the ITO and the a-Si or μ c-Si emitter layer. Region 2 (500-800 nm): the EQE is also reduced by a slight absorption of 3%-5% in the ITO layer. Region 3 (800-1,200 nm): the EQE in the long wavelength region is limited by the back surface recombination. For region 1 of the spectrum, the collection efficiency is reduced by recombination process. For regions 2 and 3, high collection is obtained in the longer wavelength of spectrum due to the presence of effective back surface field.

4. Conclusions

In summery, highly reproducible ITO films can be prepared by spray pyrolysis technique within different doping concentration range. ITO films deposited at 573 K and at atmosphere pressure chamber. Doping concentration 4% exhibits good optoelectronic properties and solar cell characterizations. ITO films in this work have been used as transparent electrodes

successfully.

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