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A comparative study of dip coating and spray pyrolysis methods for synthesizing ITO nanolayers by using Ag colloidal sol

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Indium tin oxide (ITO) films were deposited on glass substrates by dip-coating and thermal pyrolysis methods. Sn (IV) is often used in the spray method as a precursor salt, but in this research we have employed a new procedure that uses Sn (II) and $In(NO_3)_3$ for preparation of transparent conductive thin films. Then, colloidal Ag was deposited on the ITO layers in order to compare the two synthesis methods, and the structural and electrical properties of the resultant films were investigated by FESEM, XRD, and four-terminal resistometry. The obtained films are polycrystalline with a preferred orientation of (200). The XRD patterns of the films indicate that in both films, the Sn phase is crystallized separately from In_2O_3. The presence of a Sn peak and the overall low intensity of XRD peaks suggest relative crystallization of ITO structure. For this reason, Ag films were deposited by dip coating method using a colloidal sol. By analyzing the XRD patterns of Ag-ITO films after eliminating the Sn peak, the increased intensity of the peaks confirmed the relatively good crystallization of the ITO films. The results show that the films with a sheet resistance as low as 2×10^{-2} Ω·cm, which is beneficial for solar cells, were achieved.

Keywords: *dip-coating; spray pyrolysis; crystallization; Ag colloid*

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1. Introduction

Today, transparent conductive oxide films are extensively used in solar cells, displays and photovoltaic devices [1, 2]. Despite the recent dramatic indium shortage that caused serious doubt over the viability of future scientific investigation in this field, tin-doped indium oxide (ITO) layers in TCO applications remain widely known and profitable due to their opto-electrical parameters. ITO is one of the transparent conductive oxides that have the unique characteristics of optical transmission higher than 80 % in the visible region, good electrical conductivity, and excellent adhesion to different substrates [3, 4]. In recent years various methods have been employed to prepare TCO films showing high transparency and low resistivity. A resistivity of $\sim 1 \times 10^{-4}$ Ω·cm and a transparency of about 90 % are often claimed as the parameters characterizing an optimized ITO film [5]. The methods such as sol-gel [6–9], spray pyrolysis [10–12], electron beam evaporation [13], laser ablation [14] and chemical vapor deposition [15, 16] have been used to synthesize ITO films. In this study, we compare dip-coating and spray pyrolysis methods using new precursor materials. Also, with both methods thin films can easily be produced in a short time. Using dip-coating method to synthesize ITO films has many advantages, such as the possibility of deposition on various surfaces, facile

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control of the final characteristics, and low preparation cost. In both dip coating and spray methods, the final temperature and also the rates of temperature change have an effect on the layer homogeneity [17–19]. ITO films prepared by spray pyrolysis generally have high electrical conductivity and homogenous distribution of grains on the surface of the films [20]. The film thickness [21] and substrate temperature [22] are two factors that influence homogeneity of the films prepared by spray pyrolysis.

In order to improve the characteristics of ITO films, we have proposed a method in which Ag nanoparticles can be doped to the ITO film [23]. Using Ag as an oxidative material to improve ITO characteristics with cheaper salt of Sn(II) results in reduced costs for both synthesis methods. In addition, we have found that the presence of Ag lowers the electrical resistivity of the films.

This study compares two methods of synthesizing ITO films with a new initial sol, which is easily affordable. The initial sol includes Sn(II) salt and indium nitrate which have been used as the precursor materials to deposit thin films. The structural and electrical characteristics of the films synthesized by two methods were investigated and compared. Then, an Ag sol was deposited on the substrates by dip coating method. The deposition process included oxidation of Sn(II) to Sn(IV) and its substitution in the locations of indium ions followed by the formation of ITO. Optical, morphological and electrical properties of the films prepared by both methods were investigated by UV/Vis transmission spectroscopy (Cary-500). The crystallization of ITO was investigated by X-ray diffraction technique (XRD, Philips PW 1400, CuKa), and the morphology and grains size were studied by field emission scanning electron microscopy (FESEM, Hitachi S-4160). Resistivity was measured by the four-terminal resistometry.

2. Experimental

2.1. Preparation of sol

As demonstrated in Fig. 1, we prepared the initial sol from an inexpensive salt of Sn(II), i.e. $SnCl_2{\cdot}2H_2O$, as the initial tin material together with indium III nitrate ($In(NO_3)_3{\cdot}5H_2O$) and ethanol (C_2H_5OH) as solvent. The secondary sol included 0.018 g Ag nitrate ($AgNO_3$) which was dissolved in water and then boiled at 250 °C. Next, sodium citrate tribasic dehydrate ($C_6H_5Na_3{\cdot}2H_2O$) was added and heated until the color of the solution changed to dark green, which indicated that silver ions successfully complexed with sodium citrate. The deposition of ITO ([Sn]/[In] = 10 wt. % or 1:9) films was performed by two methods.

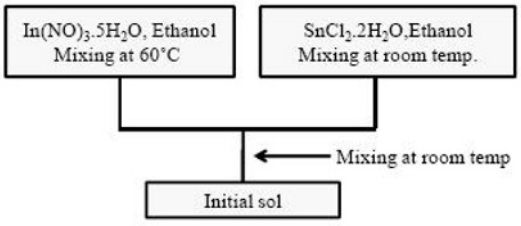

Fig. 1. Flow chart of the initial sol preparation.

2.2. Films preparation

In this report, normal transparent microscope glass slides with 1 mm thickness were used as substrates. Glass substrates were cleaned two times by using ultrasonic technique. The substrates were first immersed in ethanol and then in distilled water each for 10 minutes in an ultrasonic bath. In the sol-gel method, the initial sol was deposited by dip coating technique whereas in the spray pyrolysis method, the initial sol was poured into spray machine and deposited on a glass substrate at 520 °C. Initial ITO films prepared by both methods were dip-coated in silver solution and then annealed at 520 °C.

3. Results and discussion

3.1. The crystalline structure of the films

Fig. 2 (a, b) shows XRD patterns of the synthesized ITO films prepared by both methods before the deposition of silver sol. In both patterns, the peaks appearing at the initial coating stage are related to the separate crystallization of Sn: (220) and In_2O_3: (222) phases in the films [24]. Comparing the XRD patterns of the films prepared by

both methods, the intensity of the peak responsible for tin compared to indium oxide in the films prepared by spray pyrolysis method are significantly lower than that in the films prepared by dip coating method. The low intensity of the peak of Sn in this film is due to the substrate heating during the spray process, which leads to partial oxidation of Sn(II) to Sn(IV) and, subsequently, a lower amount of tin is crystallized separately from the ITO structure, which leads to its relative crystallization.

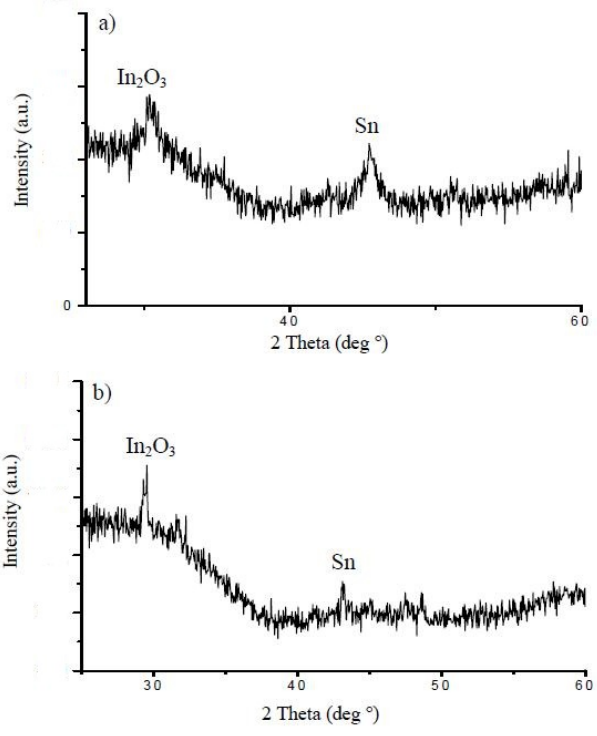

Fig. 2. The peaks related to ITO phases, (a) dip-coating method and (b) spray pyrolysis method.

Fig. 3 (a, b) shows the XRD patterns of the ITO films prepared by both methods after deposition of the Ag sol. The XRD peaks of (222), (400) and (440) at 2θ angles of 30.8°, 35.7° and 51.2° are related to the formation of bixbyite structure of indium oxide [10] (card PDF#65-3170). There is no peak indicating the presence of tin in these patterns, which suggests full oxidation of Sn(II) to Sn(IV) by silver, Sn substitution with indium in indium oxide structure and the formation of ITO structure. In addition, the existence of (111) peak indicates diffusion of Ag phase in both films. By comparing the intensity of the peaks in both patterns, it is found that the films prepared by spray pyrolysis yield sharper peaks with smaller widths, in comparison with the films prepared by dip-coating method.

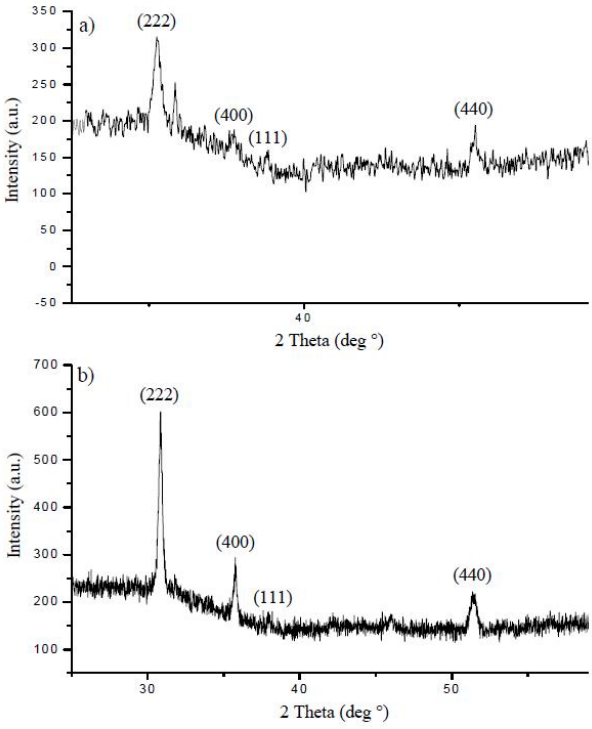

Fig. 3. The peaks related to crystalline planes of Ag-ITO phase. (a) dip-coating method and (b) spray pyrolysis method.

The diameters of crystalline domains in the synthesized grains of both films are calculated from the Debye-Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where D represents the size of crystalline domains of grains, K is the Scherrer constant, λ is wavelength, β is the half-height peak width and θ is the diffraction angle. The diameters of crystalline domains formed in the films synthesized by dip-coating and spray pyrolysis methods were calculated to be 12 nm and 18 nm, respectively, which indicates a better crystallization by spray pyrolysis.

3.2. Electrical characteristics of the films

Table 1 shows the electrical resistivity of the synthesized films. The electrical resistivity of the initial films produced by spray pyrolysis method and the sol-gel method are 2×10^{-1} Ω·cm and 4×10^{-1} Ω·cm, respectively. The high resistivity of both films indicates that ITO structure has not been formed. The electrical resistivity of the films after deposition of silver solution decreased to 7×10^{-2} Ω·cm and 1.5×10^{-1} Ω·cm, respectively. Increased electrical conductivity in the sprayed film as compared to the films synthesized by sol-gel method may be due to the crystalline growth of the ITO structure and different speeds of densification in the films. It is known that an increase in carrier concentration due to a more rapid densification process results in an increase of interaction between grains [24] and a decrease in electrical resistivity of the film.

Table 1. The electrical resistivity of the synthesized thin layers.

	Sol-gel	Spray pyrolysis
Before dip-coating in silver sol	4×10^{-1} Ω·cm	2×10^{-1} Ω·cm
After dip-coating in silver sol	1.5×10^{-1} Ω·cm	7×10^{-2} Ω·cm

3.3. Morphological characteristics of the films

Fig. 4 shows the FESEM images of the films deposited by spray pyrolysis before (mean grain size 40 nm) and after (mean grain size 80 nm) dip-coating in silver sol (a, c) and the films prepared by dip-coating method before (mean grain size 150 nm) and after (mean grain size 200 nm) silver sol deposition (b, d). As shown in Fig. 4 (a, b), despite the larger grain size related to the dip-coating method, the films do not exhibit a homogeneous morphology before addition of silver ions in both methods, and the grains are formed as separate islands. By adding silver to the structure (c, d) the films synthesized by both methods are more homogenous and have a more uniform grain size, which is due to completion of the relative crystallization of ITO in silver doped samples. Furthermore, the images confirm that the films synthesized by spray pyrolysis method have smaller grains forming a denser background in comparison with the films synthesized by the dip-coating method. The condensation of the grains during densification process leads to a more homogeneous surface of the films [24]. The lower resistivity measured for the sprayed films may be thus related to the denser morphology of the films and better crystallization behavior of these samples which has been already confirmed by XRD.

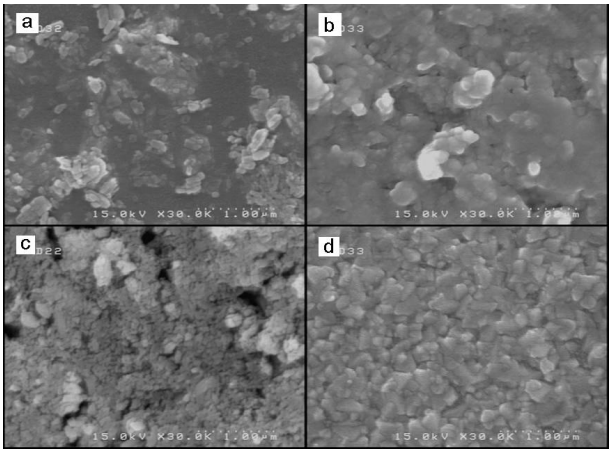

Fig. 4. (a, c) FESEM images of films deposited by spray pyrolysis before and after dip-coating in silver sol (b, d) films prepared by dip-coating method before and after silver sol deposition.

3.4. Optical characteristics of the films

Fig. 5 shows the optical transmission spectra of the films deposited by spray pyrolysis method, (a), and sol-gel method, (b). Spectra 5(a) and 5(b) show an optical transmission above 90 % and 85 %, respectively. In the transmission spectra of both films, a small drop in intensity is observed at the wavelengths of about 390 nm related to surface plasmon resonance (SPR) caused by the formation of metal Ag nanoparticles in ITO substrate. The film deposited by dip-coating method has slightly larger optical transmission in higher wavelengths than the sprayed film, which is related to the quality and properties of deposited films in terms of thickness, morphology, grain size, and

crystallization behavior of the films, but no clear understanding can be gained based on our measurements. However, the film synthesized by dip-coating method, having a higher optical transmission compared with the film synthesized by the other spray pyrolysis method, should be interesting for TCO applications.

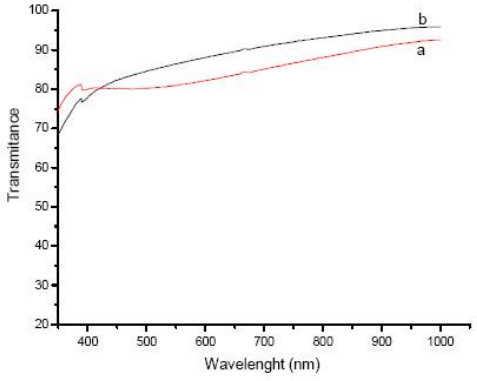

Fig. 5. The optical transmission spectra: (a) Ag-ITO sprayed thin layers, (b) Ag-ITO thin layers prepared by dip-coating method.

4. Conclusions

ITO films with adequate properties for solar cells and optoelectronic devices were deposited by dip-coating and thermal spray pyrolysis methods, and Ag colloid was coated on the initial films for oxidation of Sn(II) to Sn(IV), as a cost effective procedure. In this research, XRD measurements indicated that the ITO films grown have a cubic structure (222) after depositing the Ag layer. The peak intensity for ITO increased due to its relatively higher crystallization. Resistivity of the film synthesized by spray pyrolysis method was lower than the film synthesized by dip-coating method. The optical transmission of the films after Ag sol deposition was then 80 % for both methods. As a result, ITO films in this work have been successfully used as transparent electrodes. The procedure developed and optimized in this research is helpful for people who are interested in preparing TCO thin films by spray pyrolysis and dip-coating methods.

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