

Surface Morphology and Electrical Properties of FTO (Fluorine Doped Tin Oxide) with Different Precursor Solution for Transparent Conducting Oxide

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Abstract. Fluorine doped tin oxide (FTO) thin film was prepared by using two different precursor solutions which are tin (ii) chloride dihydrate and tin (iv) chloride pentahydrate. These two precursors are used in spray pyrolysis method to compare which one can give the best performance to be applied as transparent conducting oxide. In order to clarify the characteristic of FTO thin film, surface morphology of the thin film was characterized using field emission scanning electron microscope (FE-SEM). FESEM image shows the particle distribution and the morphology of fluorine doped tin oxide thin film. Two point probe I-V measurement and UV-Vis spectroscopy were used to study the electrical and optical properties of both films. Both precursors produced different particles distribution, electrical properties and also optical properties. The results show that the sheet resistance (R_s) of fluorine doped SnO_2 is about $49.24 \times 10^6 \Omega$ for tin (iv) chloride pentahydrate compared to $43.03 \times 10^{12} \Omega$ for tin (ii) chloride dehydrate. It was decided that SnCl_4 was chosen because it nearly fulfill the characteristics of transparent conducting oxide

Introduction

Fluorine Doped Tin Oxide (FTO), is one of transparent conducting oxide (TCO) thin film, is widely used in various fields of device making technologies such as window layers in solar cells, gas sensor devices, substrates for electrodeposition and transparent contact in optoelectronic devices and etc. There are several of methods to prepare FTO thin film that have been reported which include sol-gel, SPD, CVD and also sputtering deposition method. FTO thin film is developed for a low cost with optimized performance of solar thin film usage. Spray pyrolysis deposition (SPD) is a process in which thin film is deposited, on a hot surface, by spraying method. By using SPD method, a low cost and high performance FTO thin film can be produced. To improve characteristic of the FTO thin film, several tin compounds, such as tin(ii) chloride dihydrate [1], tin(iv) chloride pentahydrate, tetra(n-butyl)tin and di(n-butyl) tin(iv) diacetate (DBTDA) [2], have been used as a tin element in the precursor solution for preparing FTO films by using the SPD technique. Their preferred crystal growth orientation and crystal size differ with the nature of the compounds used which in turn affect the optical and electrical properties of resulting thin films of FTO.

The undoped SnO_2 films have very high electrical resistivity because of their low intrinsic carrier density and mobility. Therefore the doping process is needed to improve conductivity [3]. The doped SnO_2 , due to its wide band gap (approximate to 3.67 eV), high optical transmittance in the visible light range and good substrate adherence, has many potential applications such as gas sensors, solar energy conversion [4], infrared-reflecting glass [5], antistatic coatings [6] and transparent electrode preparation [7, 8]. Fluorine (F) [9], has been used as dopant for SnO_2 . Fluorine-doped tin oxide (FTO), in which fluorine atoms replace the oxygen sites in the lattice creating free electrons to promote higher conductivity in the samples [10], is an n-type transparent conducting oxide (TCO). Compared with the widely used indium tin oxide (ITO) and antimony-doped tin oxide (ATO), fluorine doped SnO_2 has higher transparency in visible light range and possesses extraordinary high temperature resistance, strong adhesion to glass and excellent chemical stability. Numerous techniques have been used to obtain fluorine doped SnO_2 materials.

In order to investigate the effect of precursor on the properties of FTO thin film two precursors are used for spray pyrolysis deposition method. Furthermore, the influences of the different precursors on the surface morphology, electrical properties and optical properties of SnO_2 were investigated by FE-SEM, UV-Vis spectroscopy, and two point probe I-V measurement

Experimental

Tin(II) Chloride Dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$)

Tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) at 0.5M of concentration was dissolved in 5 ml of concentrated hydrochloric acid (HCl). The solution was stirred with magnetic stirrer at 100 °C. After $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ fully dissolved in HCl, 10 ml of deionized water was added into the solution and stirred until it turns into an almost clear solution. The fluorine doping was achieved by using ammonium fluoride (NH_4F). A concentration of 1.5 M of NH_4F salt which are soluble in water was added into 15 ml of deionized water and stirred. A clear solution will be formed after a few seconds of stirring. Two solutions ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and NH_4F) are then mixed together. Glass substrates were cleaned by using deionized water, acetone and ethanol with volume ratio of 1:1:1 in an ultrasonic cleaner. After that, the substrates were placed inside an oven for drying. Substrate temperature was fixed at 400 °C on a hot plate before the spray pyrolysis process start. A volume of 10 ml of the stock solution was adopted by using pipette and was put into the spray glass jar. Another 10 ml of isopropanol was added and a little shake was needed to mix both solutions. The glass jar was then connected to the air brush and then the nozzle was set at 15cm from the glass substrate. The solution was then fully sprayed on the substrate for a period of 5 minutes and 30 seconds interval.

Tin(IV) Chloride Pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$)

The precursor solutions were prepared by using 2.63g of tin(IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) which was fully dissolved in 15 ml of deionized water. Ammonium fluoride (NH_4F) salt with mass of 0.833g was then placed into a beaker and 15 ml of deionized water was then poured into the beaker. The solution was then stirred. Both of the starting solution was then mixed together. Glass substrates were cleaned by using deionized water, acetone and ethanol with volume ratio of 1:1:1 in an ultrasonic cleaner. Substrates were then sent into oven for drying process. Temperature of substrate was then fixed at 400 °C on a hot plate for spray pyrolysis deposition. A volume of 10 ml of the stock solution was extracted and put into glass jar. Another 10 ml of isopropanol was added into the glass jar. The mixture was then stirred with glass rod and the glass jar is then connected to the airbrush. The nozzle was set to a distance of 15 cm from the substrate. The deposition process was carried on with a period of 5 minutes spraying and 30 second resting.

Result and Discussion

Surface Morphology

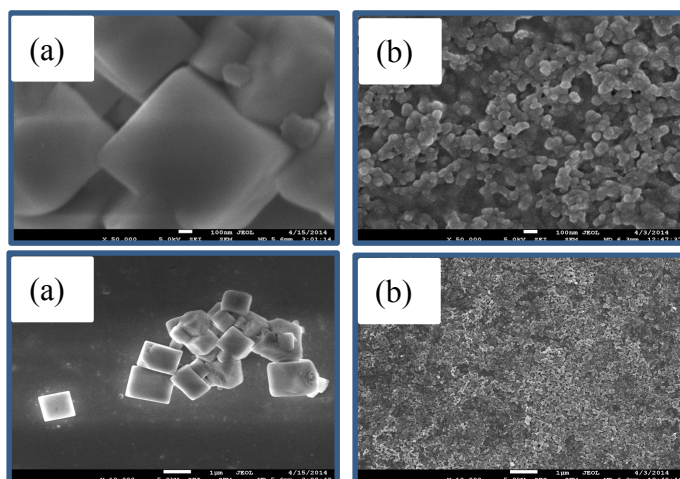


Figure 1: FESEM of FTO with different precursor top view at 50k magnification: a) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ b) $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$

Figure 2: FESEM of FTO with different precursor top view at 10k magnification: a) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ b) $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$

Figure 1 and 2 shows the surface morphology of fluorine-doped tin oxide (FTO) by using two different precursors which were tin (ii) chloride dihydrate and tin (iv) chloride pentahydrate. According to the pictures shown, tin (ii) chloride produced quite a big particle size on the substrate. It formed cubes by spray pyrolysis deposition on glass substrate. On the other hand, tin (iv) chloride pentahydrate deposition showed a huge number of small particles that deposited on the glass substrate. Tin (iv) pentahydrate precursor deposited completely and successfully on the substrate while tin (ii) dihydrate failed to do that. Only a few portion of glass substrate was deposited with tin (ii) dihydrate precursor. Highest surface area (small grains) gives highest electron density and the lowest surface area (larger grains) gives lowest electron density and to produce a complete solar cell, tin (iv) pentahydrate will be taken into consideration compared to tin (ii) dihydrate because of its high surface area of FTO particles deposited by using tin (iv) pentahydrate precursor.

Electrical and Optical Properties

Table 1. Resistance of FTO deposited by using different precursor

Material	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$
Resistance (Ω)	101.125M	1058.64
Resistivity ($\Omega \text{ cm}$)	202.25M	2117.28
Thickness (cm)	4.7×10^{-6}	4.3×10^{-5}
Sheet Resistance (Ω/cm^2)	43.03×10^{12}	49.24×10^6

By comparing both of the FTO formed by both precursor solutions, it was found that tin (iv) chloride pentahydrate has lower sheet resistance compared to tin (ii) chloride dihydrate. Larger grains size makes SnCl_2 thicker than SnCl_4 . The increase of thickness leads to the increase of resistance. Grain size and thickness directly affects to the electron mobility due to the variation of no of grain boundaries with the grain size of FTO film. SnCl_4 has larger surface area than SnCl_2 thus more possible to have maximum conductivity as well as the lowest grain boundaries for higher mobility. The grain size and its distribution are very important in a FTO film since they affect not only to the sheet resistance but also transmittance [11]. TCO layer of solar cell need a low sheet resistance material for transferring electron.

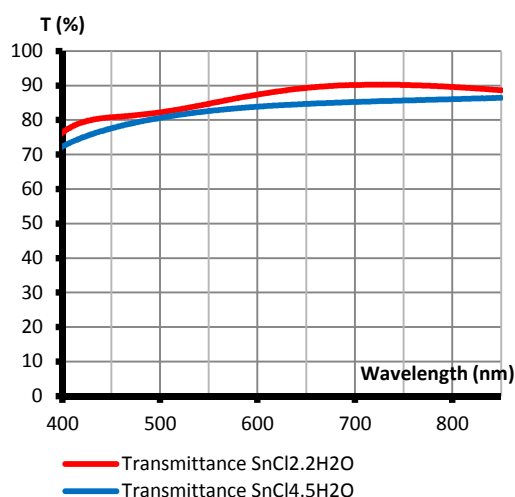


Figure 3: Transmittance of FTO with different precursors

Transmittance of FTO deposition by using different precursor solution was shown in Figure 3. These data show that at normal transmittance (T_n 400 nm – 800 nm) both of the precursor solutions which are tin (ii) chloride dihydrate and tin (iv) chloride pentahydrate can be used to produce a high transparency transparent conductive oxide (TCO). Although the transmittance for SnCl_2 is higher than SnCl_4 , it may be caused by the uneven distribution of grains on the soda lime glass. SnCl_4 has

lowest value of transmittance because it has arrangement crystallite particles with fully densely packed resulting most of the visible light unable to pass through rather than SnCl_2 . Both of the FTO achieved transmittance more than 80 % which showed high transparency. As a TCO layer for a solar cell, high transparency is needed for the window layer to allow light to pass through to the absorbance layer. In this context both of these FTO precursors can be considered.

Conclusion

The FTO films were prepared from the SnCl_2 and SnCl_4 precursors by the spray pyrolysis technique. Structural, electrical and optical properties have been studied. Tin (iv) chloride pentahydrate is a suitable precursor solution for producing a good transparent conductive oxide (TCO). With small particle size and large area particle deposition, tin (iv) chloride pentahydrate is more suitable for TCO layer of solar cell compared to tin (ii) chloride dihydrate. This is because FTO with tin (iv) chloride pentahydrate have high surface area compared to tin (ii) chloride dihydrate.

Acknowledgments

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