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EFFECT OF ANNEALING TIME ON ALUMINIUM DOPED TIN OXIDE (SNO_2) AS A TRANSPARENT CONDUCTIVE OXIDE

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ABSTRACT

Tin oxide (SnO_2) is one of the semiconductor that has unique optical and electrical properties and high chemical stability so it is suitable to be deposited onto glass, ceramics, oxides, and other substrate materials. However, it has a very high electrical resistivity due to its low intrinsic carrier density and mobility. Intrinsic tin oxide is an insulator, yet upon doping with other elements such as antimony, fluorine, indium and etc., electrical conductivity can be enhanced extensively. Currently, tin doped indium oxide is the most extensively used electrodes due to its low resistivity and highly transmittance. However, indium is a rare material, expensive and has high toxicity. A good TCO must have low resistivity, high transmittance in the visible region, and high chemical stability. These properties can be changed by doping process with aluminum. Aluminum doped tin oxide is prepared by spray pyrolysis deposition method using a mixture of aluminum nitrate 9-nitrate with tin (iv) chloride pentahydrate as precursor and sprayed on a glass substrate. Five samples with different annealing time were analyzed. The annealing time was from 1 hour to 5 hour with an hour of interval for each group of samples. Optical and electrical parameters were measured and calculated. Surface morphology were being observed and analyzed. The percentage of atomic element is analyzed by using an energy dispersive x-ray spectroscopy (EDS). For application on window layer of solar cells, high transmittance archived on the samples deposited. Thin films thickness was obtained by using a thickness profiler for the use of resistivity and sheet resistance. A mechanism condition of thin film is proposed and discussed; initially the visual yellow color of some samples, related with a preparation of precursor solution, is associated to the amount of aluminum nitrate with tin chloride. The comparison of all characterization result shows sample that have been annealed for about 4 hours give the best conditions of TCO properties.

Keywords: spray pyrolysis, time annealed, and characterization.

INTRODUCTION

Transparent conducting oxide (TCO) is a compound semiconductor made up of metal oxide which is high in both conductivity and transmittance. The combination of different metal with oxygen lead result in a compound semiconductor with different optical and electrical properties. These properties can be changed by doping process with either metals or nonmetal (Stadler, 2012). TCO are generally n-type semiconductor with a wide band gap which is around 3.0 eV. TCO has a relatively high electron concentration on conduction band and this property has contributed to its high conductivity (Minami, 2005). TCO films have been intensively investigated for optical and electrical applications such as flat-panel displays, liquid crystal displays, organic light-emitting diodes, thin-film transistors, and thin-film solar cells A good TCO must have low resistivity, high transmittance in the visible region (400 to 800 nm), and high chemical stability. TCO films have high optical transmittance and low electrical resistivity which are the key elements for transparent electrodes in solar cell (Gordillo, 2001). TCO is practically used for transparent electrodes are polycrystalline or amorphous and have a resistivity in the order of 10^{-4} Ω cm and an average transmittance of 80% and above in visible light spectrum range. A front TCO thin films electrode performed as a window layer for light to pass through and also electrons transporter to complete the whole cell. Therefore a very low absorbance, high transmittance with ideal light scattering properties is needed for contact electrode which has high electrical conductivity.

Materials that for production of TCO are very efficient in reflecting infrared heat radiation in a manner similar to highly conducting metal-like materials and in transmitting the light visible region. Tin doped indium oxide, (In_2O_3: Sn), fluorine doped tin oxide, (SnO_2: F), aluminum doped zinc oxide: (ZnO: Al), and gallium doped zinc oxide, (ZnO: Ga), are used for manufacturing of TCO because of their high optical transparency in the visible region, good electrical conductivity and the high infrared reflectivity. Tin oxide (SnO_2) is one of the semiconductor that has unique optical and electrical properties and high chemical stability so it is suitable to be deposited onto glass, ceramics, oxides, and other substrate materials. However, tin oxide has a very high electrical resistivity due to its low intrinsic carrier density and mobility (Moholkar, Pawar, Rajpure, Bhosale, and Kim, 2009). Intrinsic tin oxide is an insulator, yet upon doping with other elements such as antimony, fluorine, indium and etc., electrical conductivity can be enhanced extensively (Icli, Yavuz, and Ozenbas, 2014). Currently, tin doped indium oxide is the most extensively used electrodes due

to its low resistivity (~ 10-4 Ω cm) and highly transmittance (80-90 % T) (Optik, Nipis, Oksida, and Florin, 2011). However, indium is a rare material, expensive and has high toxicity (Gordillo, 2001). Thus, alternative material is suggested in order to develop new TCO (Chen *et al*., 2001). Aluminum and gallium are used as dopant for zinc oxide to improving conductivity and transparency. Aluminum play an important role along with tin oxide because of their high transmittance in visible light (Sriram & Thayumanavan, 2013).

Tin oxide thin film can be deposited by quite a number of methods such as electron beam evaporation, spray pyrolysis, chemical vapor deposition, magnetron RF sputtering (Sriram and Thayumanavan, 2013). Among all of these methods, spray pyrolysis deposition is the most suitable for deposition of tin oxide. Spray pyrolysis deposition (SPD) is a chemical technique which uses a liquid source for thin film coating (Filipovic *et al*., 2013). The advantage of using this technique is because it has a less complex process to be performed compared to sputtering method (Filipovic *et al*., 2013) but the main benefit of spray pyrolysis over other similar techniques are cost effectiveness, substrates with complex geometries can be coated, relatively uniform and high quality coatings and no high temperatures are required during processing.

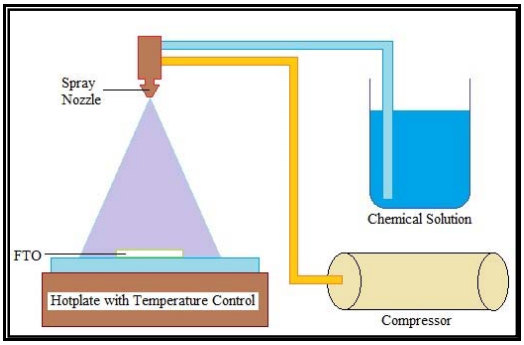

Figure-1. General schematic of a spray pyrolysis deposition process (Filipovic *et al*., 2013).

Therefore, in this study, aluminum will be used and doped with tin oxide to produce transparent conductive oxide and it will be fabricated using the spray pyrolysis deposition technique.

Post deposition annealing reduced the defects and impurities present in the thin films that has been deposited. This step improved the dielectric constant of the thin films during structural modification. Yet, the excess oxygen or other gasses formed an unpredicted interfacial layer on the thin films due to oxidation process. Therefore during post deposition annealing, oxygen level should be controlled carefully (Khairnar and Mahajan, 2012).

EXPERIMENTAL DETAIL

Phase 1: Substrate preparation

The micro slide glasses have been cut into a size of 2 cm x 2 cm by using a diamond cutter to produce the substrate for deposition. Cleaning steps are very important to prevent any contamination on the sample substrate which may affect the sample characteristic. Ethanol and acetone are used to clean the glass. Glass substrates were clean by using ultrasonic cleaner with volume ratio 1:1:1 of acetone, DI water and ethanol. The beaker will be then placed inside the ultrasonic to eliminate contaminates. The cleaner will be set for 10 minutes at a temperature of 50 °C. After the cleaning process is completed, the glass substrate will be taken out for drying process.

Phase 2: Precursor preparation

The precursor solutions were prepared by using aluminum nitrate nonahydrate with mass 0.6333g and fully dissolved it in 10 ml of deionized water. Next, 2.6333g of tin (IV) chloride pentahydrate are dissolved in a beaker of 10 ml of deionized water. Both solutions were stirred separately for about 5 minutes.

Phase 3: Spray pyrolysis deposition

Both of the solutions were mixed together and an additional solvent of 7 ml propan-2-ol were poured into the spray solution. The mixed solution was stirred using a magnetic stirrer and poured into spray cartridge before starting the spray pyrolysis deposition. The glass substrates are placed onto the hot plate with a temperature of 150 °C. After the spray solution is well prepared, thin films will be formed using spray pyrolysis deposition method by applying a constant temperature. A total of 27 ml of solution was sprayed on the glass substrate in order to produce the thin films. It takes about 30 minutes to spray the solution onto the substrates. Then, the process is continued by annealing all samples at different time using a furnace. The temperature set for the furnace is 300 ˚C and time taken for each parameter was set at 1 hour, 2 hours, 3 hours, 4 hours and 5 hours using an electronic timer.

Phase 4: Characterization

There are different physical properties that can be studied in a known material in order to obtain a possible new behavior. In this study, the electrical and optical of thin film is characterized using Field Emission-Scanning Electron Microscopy (FE-SEM), four point probes, Ultraviolet-Visible (UV-Vis) spectrometry and Energy-Dispersive X-ray Spectroscopy (EDS). A good TCO should have high transparency in the visible light range, low resistivity and high work function.

RESULT AND DISCUSSIONS

Formation of aluminum doped tin oxide (Al: SnO_2)

The formation of SnO_2 films from a tin (IV) chloride solution may take place as follows:

$$SnCl_4 + 2H_2O \rightarrow SnO_2 + 4HCl \quad (1)$$

The decomposition of aluminum nitrate takes places simultaneously according to the equation:

$$Al(NO_3)_3 \rightarrow Al^{+3} + 3NO_3^- \quad (2)$$

Aluminum nitrate is made up of an Al atom with three extra electrons borrowed from the nitrate molecule. The Al atom is represented with this extra charge as +3 and the 3 nitrate molecules collectively balanced the charges by all donating an electron in the pairing and are represented by the $3NO_3^-$. Water always exists as a combination of H^+ and OH^-, which balance as H_2O, but always exists as all three, H_2O, H^+ and OH^-. The balance of the H^+ and OH^- is the pH. The salt dissociates in the water so it isn't necessary to write H_2O in this reaction.

Surface morphology (FE-SEM)

Figure-2 shows the surface topography of the sample annealed at different hours. In this study, as the annealing time rises, the particles become more active and no obvious interfaces of the Al and SnO_2 were found in the film, indicating that the Al ions were well diffused into the SnO_2 film. When the annealing time is between 4 and 5 hour, the acceptor effect of aluminum substituting tin is activated. Generally, long period of annealing commonly leads to good crystallization and topography of all samples show that it has the same surface morphology as reported in previous study.

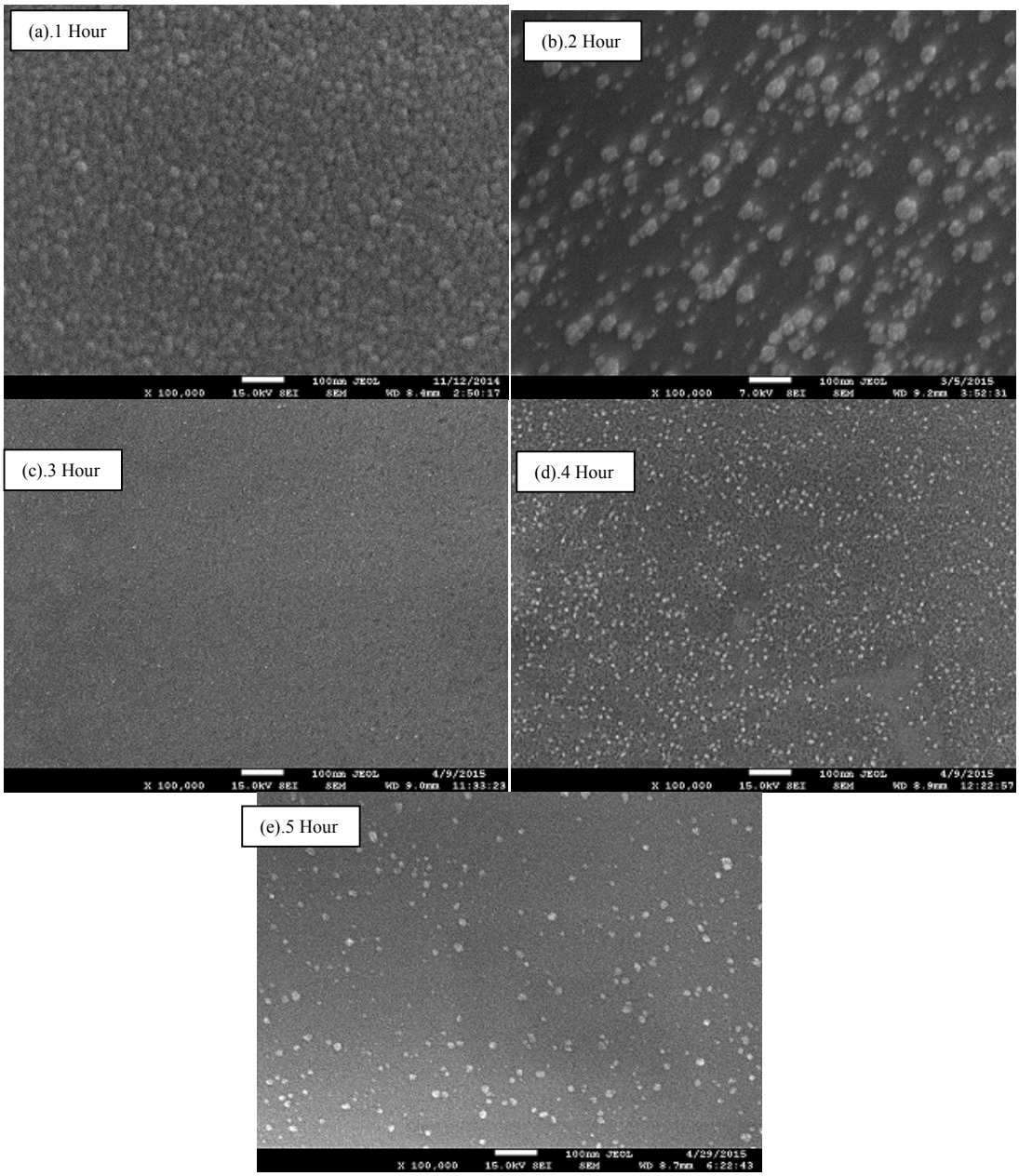

Figure-2. The surface morphology of samples that annealed with annealing time of (a) 1h, (b) 2h, (c) 3h, (d) 4h and (e) 5h.

Table-1. Atomic and weight percentages obtained with EDS of the sample.

Annealing time (Hour)	Oxide (%)		Aluminum (%)		Tin (%)	
	Weight	Atomic	Weight	Atomic	Weight	Atomic
1	66.21	92.24	3.83	2.13	30.05	5.56
2	69.80	93.43	2.39	2.49	27.81	4.07
3	70.60	93.96	3.63	2.44	25.77	3.60
4	65.28	91.88	2.82	2.55	31.90	5.57
5	73.69	94.22	2.12	1.61	24.19	4.17

Elemental analysis (EDS)

Table-2 shows the chemical composition of all samples. The analysis was taken from the whole area of the micrograph at a magnification of 100,000 times. Previous study states that as the temperature increased, more pronounced changes in chemical composition are produced (Janssen, n.d.). In general, the oxygen atomic percentage increases as the temperature rises. However, for this study it was observed that the aluminum to oxygen ratio increased with the increase of the aluminum content in the thin film. The atomic percentage of aluminum that acts as dopant has the highest value when annealed for 4 hour. This indicates that aluminum was successfully incorporated into the tin oxide and makes the thin film more conductive.

Electrical properties (Four Point Probe)

The effect of annealing time on the electrical properties of the thin film is listed in Table-3. The pattern of the resistivity seems to decrease as the annealing time rises and starts to increase back when annealed at 5 hour, indicating that thermal diffusion occurred. Sample that has been annealed for 4 hours has the lowest resistivity compared to others. In order to get the resistivity, the thickness of the thin film is obtained using a surface profiler. Scan length for the surface profiler is set from 0 to 300 um and the average value of the thickness is about 0.313 µm. Based on that, the sheet resistance, R_s can be calculated using equation (1). As seen, the optimum annealing time for a conducting thin film is approximately 4 hours, while the sheet resistance and resistivity reaches the minimum value of $6.7757 \times 10^{+6}$ (Ohm/sq) and 0.212k (Ohm-cm).

$$\rho = R\frac{A}{L} \tag{3}$$

Table-2. Electrical properties of the TCO.

Annealing time (Hr)	Resistivity (Ohm-cm)	Sheet resistance (Ohm/sq)
1	9.203 k	$2.9405 \times 10^{+8}$
2	5.322 k	$1.7001 \times 10^{+8}$
3	1.560 k	$4.9871 \times 10^{+7}$
4	0.212 k	$6.7757 \times 10^{+6}$
5	4.250 k	$1.3580 \times 10^{+8}$

Optical properties (UV-Vis)

Figure-3 shows a variation of transmittance with wavelength for spray deposited Al: SnO_2 thin films deposited by differentiating through time annealing. It is seen that the frequency of the visible light is between the range 300-800 nm. This data shows that the sample that has been annealed for one hour can be used for producing a high transparency transparent conductive oxide. The sample achieved transmittance more than 90% which showed a high transparency. Generally, TCO layer of solar cell needed high transparency for the window layer so that light can pass through the window layer and reach absorbance layer. Results show that, the sample annealed for one hour is enough for this requirement. The result also approved that there is no need to prolong the annealing time in order to get a high transmittance TCO by using the precursor solution. The transmittance variation is attributed to the variation in free-carrier concentration.

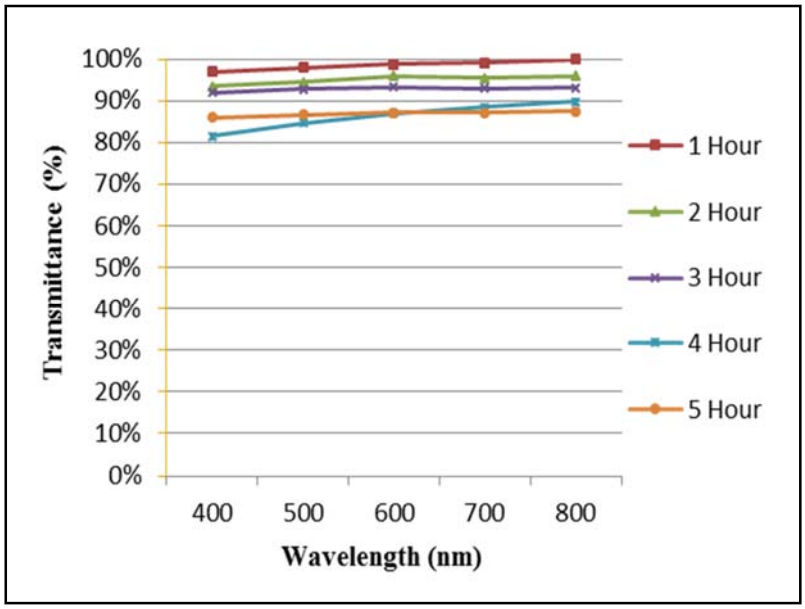

Figure-3. The percentage of transmittance of sample versus wavelength.

CONCLUSIONS

In conclusion, TCO has been fabricated by spray pyrolysis deposition method annealing with different hours by varying the time range between 1-5 hours (1 hour time interval). The surface morphology and element analysis of all samples has been checked using FE-SEM and EDS. The result shows that all samples have uniform particle on a substrate after being sprayed. All samples that have been annealed at 300 °C have small grain size which is good for TCO application because it gives a higher surface area. The thickness of the sample after being sprayed with the precursor solution has been determined by the surface profiler. The electrical properties of the samples have been conducted using two and four point probes and the optical properties have been identified by scanning using UV-Vis. The result shows the sample that has been annealed for 1 hour give a higher transmittance percentage. However, the range of percentage with the other four samples is not quite far and about 90% and above. Therefore, in this study it is proven that annealing time of about 4 hours can be the optimum condition of this thin film as it has the highest atomic percentage of aluminum as doping agent and low resistivity in electrical properties.

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