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FABRICATION OF COBALT DOPED TIN OXIDE THIN FILM FOR DYE-SENSITIZED SOLAR CELL USING SPRAY PYROLYSIS DEPOSITION METHOD

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ABSTRACT
The cobalt doped tin oxide thin film was frabicated by using the mixture of cobalt (II) chloride and tin (IV) chloride. It was fabricated on microscopic glass using spray pyrolysis deposition technique. The samples were annealed with different annealing time at 300 ºC. The duration of annealing time is 1, 2, 3, 4 and 5 hours. The samples were then characterized by energy dispersive X-ray spectroscopy (EDX), field-emission scanning electron microscopy (FESEM), ultraviolet visible spectrophotometer (UV-vis) and four-point probe. The FESEM results indicate that as the annealing time duration increased, the crack pattern on the surface of the samples increased. The optical properties of the samples were studied with the UV-vis results show the transmittance of all sample were between 70% to 80%. The sheet resistance for IV-characteristic increased when annealing time increased. The lowest resistivity was achived at 2 hours annealing time.

Keywords: cobalt (II) Choloride, Tin (IV) Chloride, spray pyrolysis deposition, DSSC.

INTRODUCTION
Thin films of semiconducting compounds have been studied extensively in recent years due to their applications in solar cell. The transparent conduction oxide (TCO) is one of the semi conducting thin films. TCO films with excellent optical properties are required in the development of concentration solar collector. So, the TCO are widely used in optoelectronics and solar arrays because it has greater than 3 eV of optical band gap (Morales-Acevedo, 2006).

It is usually made of indium tin oxide (ITO) because it has low resistivity and high transmittance in the visible rays region of the electromagnetic spectrum (380-770 nm)(Morales-Acevedo, 2006). It has been used in development of light such as light emitting diodes (LED) and thin film solar cells. However, the ITO is an expensive material (Parka 2012). Therefore, it is necessary to develop a new TCO based on inexpensive material. Nowadays, Indium (In) is widely used as Transparent Conduction Oxide (TCO) material for solar cell application. However, the material is expensive due to its rarity on earth (Parka 2012). A new element with excellent properties and low cost is needed in order to replace indium. According to previous study, cobalt is suitable to be doped with tin oxide because of its high conductivity, good transparency and low cost (Benramache 2012). Cobalt has been used in various applications such as transparent conductive, semiconductors and solar cells because it has low resistivity and good optical band gap energy at low temperatures (Benramache 2012).

In this study, cobalt (II) chloride was chosen as the dopant materials. In recent years, cobalt is widely used in solar cell as a replacement to ITO due to its abundant element and has good performance when used in dye sensitized solar cell (DSSC) (Pirmoradi 2011).

For this experiment, the cobalt doped tin oxide thin film was prepared by spray pyrolysis deposition (SPD) method. Effect of different annealing time on cobalt doped tin oxide will be investigated for DSSC application.

METHODOLOGY

Substrate cleaning
At the beginning of experiment, the microscopic glass was used as a substrate for cobalt doped tin oxide thin film. The glass substrate was cut into 2.5cm x 1.5cm size. The glass substrates were then cleaned by using the mixture of acetone, ethanol and deionized water (DI water) with ratio of 1:1:1. Next, the substrates were cleaned by using an ultrasonic cleaner machine for 10 minutes and then dried in the oven at 150ºC for 10 minutes.

Preparation of cobalt doped tin oxide solution
In this preparation process, 0.1g of cobalt chloride was put in a beaker containing 15ml of DI water and the solution was stirred for 5 minutes. Then, 2.633g of Tin Chloride was put into another beaker containing the mixture of 15ml DI water and 10ml propan-2-ol. The solution was then stirred for 5 minutes .Finally, the solution from both beakers were mixed together and stirred until it was well mixed.

Deposition of cobalt doped tin oxide solution on thin film using spray pyrolysis deposition method
The spray was loaded with the cobalt doped tin oxide solution. The deposition process was done by spraying the glass substrates on the hot plate at 150 ºC. Then, the deposited cobalt doped tin oxide film were

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annealed in the furnace at 300 °C for 1, 2, 3, 4 and 5 hours.

Characterization method

The sample was characterized by using energy dispersive X-ray spectroscopy (EDX), field emission scanning electron microscopic (FESEM), UV VIS Spectrophotometer and four point probe to investigate the surface morphology, optical properties and electrical properties, respectively.

RESULTS AND DISSCUSSIONS

Elemental properties

The chemical composition and the respective percentage of each atom present in the samples were analysed by EDX. The result obtained for different annealing time was recorded in figure and table below.

Table-1. EDX detector element composition.

Annealing time (hrs) / Element	1	2	3	4	5
Oxygen (O) (atomic %)	91.07	89.21	87.23	85.44	83.64
Cobalt (Co) (atomic %)	2.41	2.55	2.69	3.55	4.10
Tin (Sn) (atomic %)	6.52	8.24	10.08	11.01	12.26

The elemental composition in this research can be analysed by using EDX as shown in Figure-1. The result proved that the cobalt doped tin oxide solution has been properly deposited and annealed as the cobalt and tin can still be detected after the sample has been fabricated.

The result for 1 hour shows the atomic percent of cobalt has the lowest percentage (2.41%). For 2 hours, the atomic percent of cobalt is 2.55 and the atomic percentage of cobalt increased when the anealling time was increased. For 3.4 and 5 hours the result were obtained at 2.69%, 3.55% and 4.1% respectively. As the annealing time increased, organic compound (referring to oxygen) dissipated into the air.

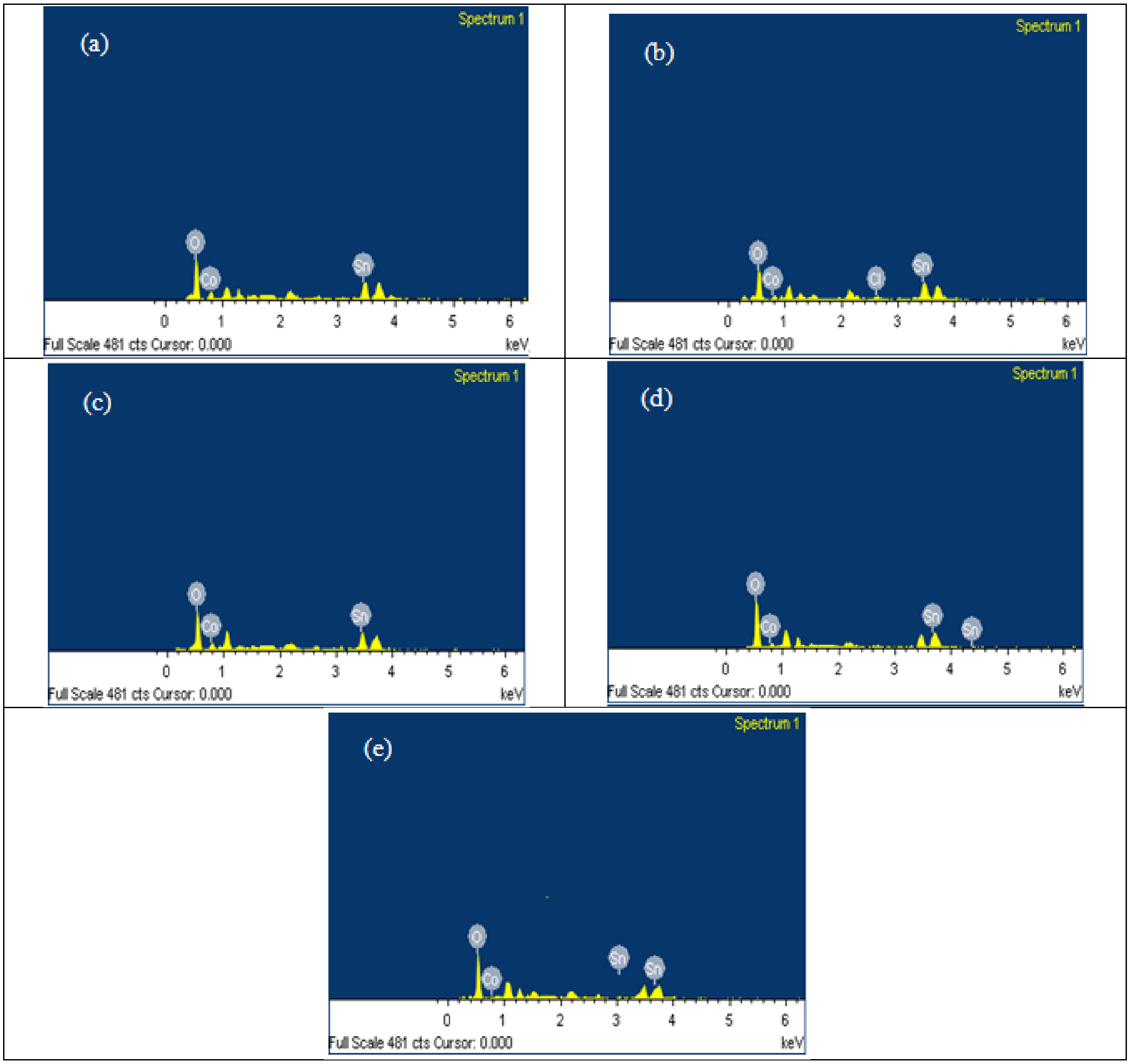

Figure-1. EDX result for different annealing time. (a) 1 hour (b) 2 hours (c) 3 hours (d) 4 hours (e) 5hours.

Surface morphology

The surface morphology of the film was analyzed using field emission scanning electron microscopy (FE-SEM).

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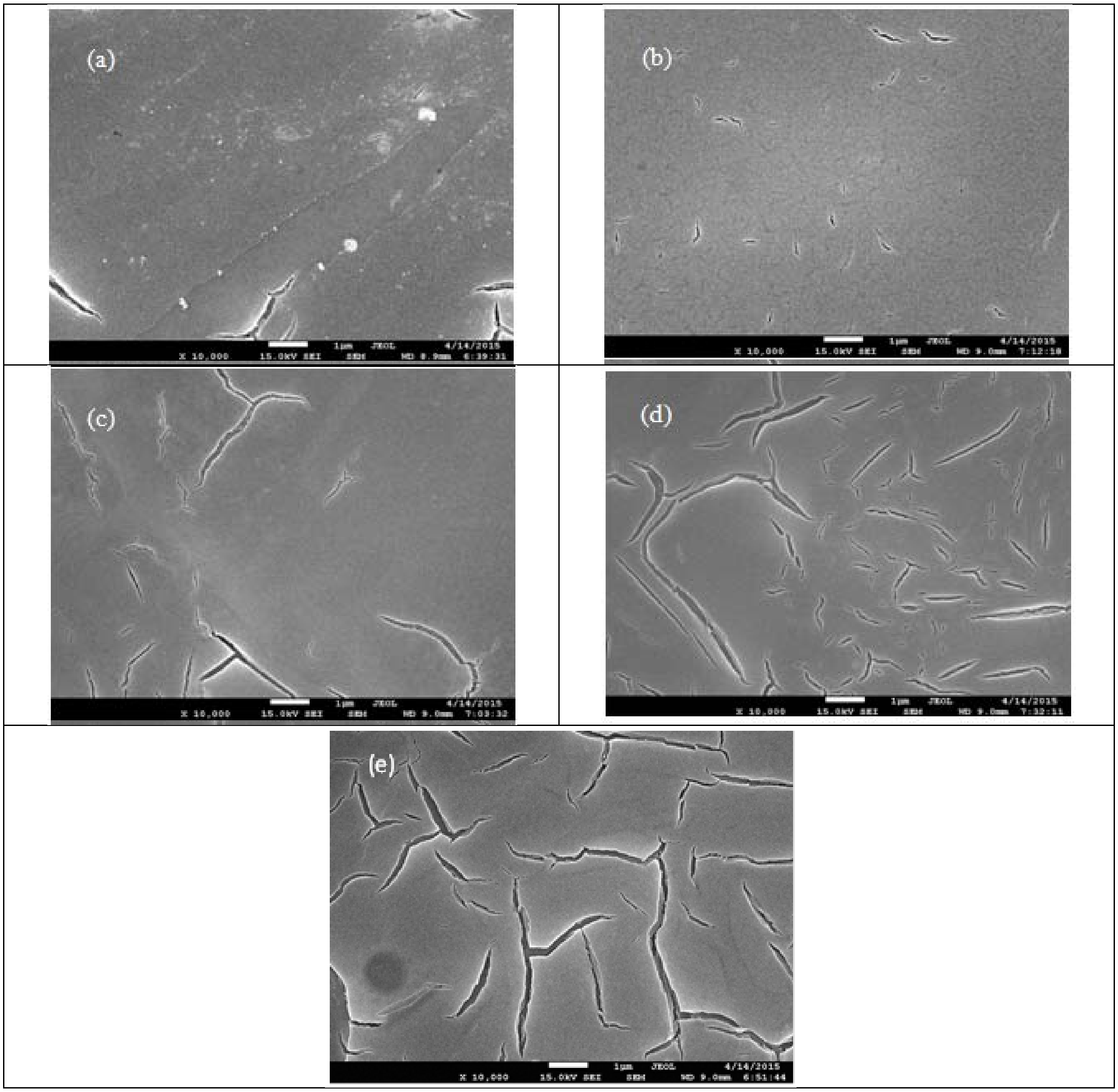

Figure-2. FESEM images of different annealing time. (a) 1 hour (b) 2 hours (c) 3 hours (d) 4 hours (e) 5hours.

Figure-2 shows the FESEM images of different annealing time for 1 hour, 2 hours, 3 hours, 4 hours and 5 hours of cobalt doped tin oxide. All samples were annealed at 300 ^{o}C. The surface morphology of cobalt doped tin oxide thin film was influenced by the duration of annealing time.

For 1 hour, the crack of the surface morphology already started and when the duration of annealing time increased for 2, 3, 4 and 5 hours, the number of crack on the surface of cobalt doped thin film increased dramatically. The crack became larger and the crack distribution was also increased when the annealing time increased.

As the cracks on the surface of the thin film increased, the electron faced the difficulties to move and hence the solar cell efficiency was decreased.

Electrical properties

The sheet resistance was measured by the equation 1 below.

$$Rs = R/t \quad (1)$$

Rs = Sheet resistance
R = Resistivity
t = thickness

Table-2. Electrical properties of cobalt doped tin oxide.

Parameter	Sheet Resistance (Ohm/cm^2)	Resistivity (Ohm-cm)	Thickness of film (nm)
1 hour	3.59×10^7	939.672	262
2 hours	3.18×10^7	1164.667	366
3 hours	3.93×10^7	1328.056	338
4 hours	4.28×10^7	1371.780	320
5 hours	4.72×10^7	1417.209	300

The Table-2 shows the electrical properties of cobalt doped tin oxide at different annealing time. 5 hours annealing time exhibited the highest sheet resistance. The sheet resistance was increased when the annealing time increased. While, 2 hours of annealing time showed the lowest value of sheet resistance.

The FESEM images show the increment of annealing time increased the distribution of crack on the cobalt doped tin oxide thin film. The crack gave an impact and caused the increment in value of the sheet resistance. The crack prevented the electron to transfer and led to poor conductivity.

For 5 hours of annealing time, the highest distribution of crack was detected. The increment of crack caused more electron prevented to transfer and increase the value of resistivity.

In DSSC, the lower sheet resistance can give a better performance. It will helps the electron to transport easily to the next level.

Optical properties

UV–vis spectrophotometer was carried out in order to characterize the optical transmittance of the cobalt doped tin oxide. Figure-3 show the transmittance of thin film fabricated in different annealing time. The transparency of all sample were within 70%- 80%.

The various annealing time from 1 hour to 5 hours seems to have effect to the transmittance of the thin film though there is no denying that the increment time duration of annealing time decrease the transparency of the thin film. This is due to the growth of the crack on the cobalt doped tin oxide thin film as the annealing time increased as shown in FESEM images. The crack on the thin film caused the light scattered and decreased the transmittance value.

This clearly shows that the duration of annealing time has a effect to the transparency of cobalt doped tin oxide.

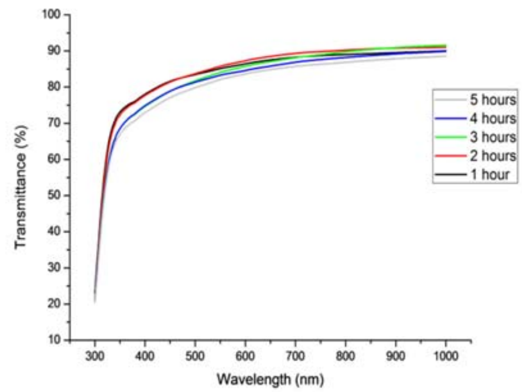

Figure-3. Transmittance of cobalt doped tin oxide for 5 different annealing time.

CONCLUSIONS

The main target for the research presented in this report was to fabricate and to analyze the performance of cobalt doped tin oxide for its optical properties, electrical properties and surface morphology. As the samples underwent the same characterization test under fixed temperature at 300°C, we can see the influence of annealing time duration towards the performance of sample under characterization tests. The results from the optical, electrical, and surface morphology test indicated that annealing time duration has a impact on optical, electrical and surface morphology properties respectively.

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REFERENCES

Benramache, S., Benhaoua, B. and Chabane, F., Effect of Substrate Temperature on The Stability Of Transparent Conducting Cobalt Doped ZnoThin Films, Semiconductors, 2012, 33 (9).

Blaise, G., and Gressus, C.L., Charging Phenomena, Dielectric Relaxation Processes and Breakdown of Oxides, Electrical Insulation and Dielectric Phenomena, 1990, pp. 231-236

Erlandsen, S.L., Macechko, P.T., and Frethem, C., High Resolution Backscatter Electron (Bse) Imaging Of Immunogold With In-Lens and Below-The-Lens Field Emission Scanning Electron Microscopes, Scanning Microscopy, 1999, 13(1), pp. 43-54.

Filipovic, L., Selberherr, S., Mutinati, G.C., Brunet, E., Steinhauer,S., Kock, A., Teva, J., Kraft, J., Siegert, J.O., and Schrank, F., Modeling Spray Pyrolysis Deposition, World Congress Engineering, 2008.

Finanda, R., Damisih., M, H.C., and Lee, H.Y., Characteristics Of P- Type Gallium Tin Oxide (GTO) Thin Films Prepared By Rf Magnetron Sputtering, Ceramic Processing Research, 2012, 13 (2), pp. 181 -185.

Frigerio, A., Grillo, G., Simulated Annealing With Time-Dependent Energy function, Mathematische Zeitschrift, 1993, 213, pp. 97-116.

Morales-Acevedo, A. 2006. Thin film CdS/CdTe solar cells: Research perspectives. Solar Energy, 80(6), 675-681. doi:10.1016/j.solener.2005.10.008

Pirmoradi, H., Malakootikhah, J., Karimipour, M., Ahmadpour, A., Shahtahmasebi, N., and Koshky, F.E., Study Of Cobalt-Doped Sno Thin Films, Scientific Research, 2011, 8 (1), pp. 253-256.

Schumann, P.A., and Gardner, E.E., Application of Multilayer Potential Distribution to Spreading Resistance Correctian Factors, Journal of the Electrochemical Society, 1969, 116, pp. 87-91.