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FABRICATION OF Co/SnO_2ON GLASS SUBSTRATE USING SPRAY PYROLYSIS DEPOSITION TECHNIQUE WITH VARIATION OF ANNEALING TEMPERATURE

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ABSTRACT

Cobalt doped tin oxide thin film (Co/SnO_2) have been prepared by using spray pyrolysis method.The thin film were annealed at various temperatures ranging from 100 °C to 400 °C for one hour in a furnace. The effects of annealing temperature on the properties of thin film including structural morphology, electrical and optical properties have been characterized by the Field Emission Scanning Electron Microscope (FE-SEM), Energy Dispersive X-ray Spectrometry (EDS), Four point probe I - V measurement and Ultraviolet-spectroscopy (UV-Vis). Sample at 200 °C annealing temperature forming large grains shows the highest transmittance percentage that exceed 90% with 0.2k (Ohm-cm) of electrical resistivity.

Keywords: cobalt, Tin Oxide (SnO_2), spray pyrolysis deposition, TCO.

INTRODUCTION

Transparent conducting oxide (TCO) films with excellent optical properties are required in the development of concentration solar collector. The TCO are widely used in optoelectronics and solar arrays because it has greater than 3 eV of optical band gap(Julia E. Medvedeva, 2010).TCO is usually a naturally n-type degenerate semiconductor such as ZnO, SnO_2, ITO and FTO with high transmittance in the visible rays region of the electromagnetic spectrum (380-770 nm)(Morales-Acevedo, 2006; Sohn and Kim, 2011). It has been used in a wide range of applications, including low-e windows, transparent contacts for solar cells, optoelectronic devices, flat panel displays, liquid crystal devices, touch screens, EMI shielding and automobile window deicing and defogging(Materion, n.d.).The most important factor that makes TCO conducting and transparent is the band gap, smaller band gap could enhance conductivity, while larger band gap leads to higher transparency. Performance of TCO conductivity can be described in terms of resistivity, affected by charge transport properties as electron effective, carrier concentration, and charge carrier mobility. The enhancement of TCO conductivity can be increase by increasing carrier concentration or mobility. On the other hand, optical transparency requires large band gap due to absorption of materials, and it could be improved by doping elements to increase carrier concentration or enhance the simplicity of TCO structure(Klein *et al.*, 2010).

Tin oxide (SnO_2) has been widely used in optoelectronic devices and solar cell because it has wide band-gap semiconducting material (E_g= 3.6 - 4.0 eV). Its also have good conductivity and high optical transparency (Pirmoradi *et al.*, 2011). Without obstructing photons from traveling through the optical active area, the SnO_2 areable to be useful in many industries.

Recently, cobalt (Co) was doped with tin oxide and it is known as cobalt tin oxide (Pirmoradi *et al.*, 2011). Cobalt has been used in various applications such as transparent conductive, semiconductors and solar cells because its low resistivity and good optical band gap energy at low temperatures (Benramache, Benhaoua, and Chabane, 2012).

Spray pyrolysis deposition (SPD) method is a technique to grow the required thin film. It used a liquid source for deposition of a transparent thin film on glass substrate. In the process, heat was used to break the molecules into element source and then the spray is used to deposit the chemical onto a substrate. The SPD technique could give the uniform and high quality coatings with advantages in low cost fabrication process(Stadler, 2012).The major interest in spray pyrolysis is due to its low cost, while it is increasingly being used for some commercial processes, such as the deposition of a transparent layer on glass (Major, Banerjee, and Chopra, 1983), the deposition of a SnO_2 layer for gas sensor applications (Korotcenkov, Brinzari, Schwank, DiBattista, and Vasiliev, 2001), anodes for lithium-ion batteries (Ng, Wang, Wexler, Chew, and Liu, 2007), and optoelectronic devices (Blandenet, Court, and Lagarde, 1981).

In this study, the cobalt tin oxide thin film will be prepared by SPD method. The purpose of this study was to investigate the effect of annealing temperature on the structural, electrical and optical properties of cobalt doped tin oxide thin film.

MATERIALS AND METHODS

Solution preparation

For preparation of precursor solutions, 0.6g of cobalt (II) chloride was stirred to dissolve in 15 mL of deioinized (DI) water (A). Then, 2.6333g of tin (IV) chloride solution was mixed with 15 mL of DI water in a separate beaker (B). Both solutions were stirred separately about 5 minutes before they are combined (A+B). Then, 10 mL propan-2-ol was added into the solution (C). The final solution was stirred using magnetic stirrer for 10 minutes before starting the spray pyrolysis deposition.

Spray pyrolysis deposition

After the precursor solution was prepared, spray pyrolysis deposition method are applied to deposit conducting thin film using an airbrush. The glass substrates are placed onto the hot plate with 150 ^{o}C temperature. The 40 ml of precursor solution are used in the spray process. The distance between substrate on hot plate and airbrush spray assumed to be 20cm to make sure that only the fine spherical droplets hits on the glass substrate. The spray process consumed 40 minutes to spray the solution onto the substrates.

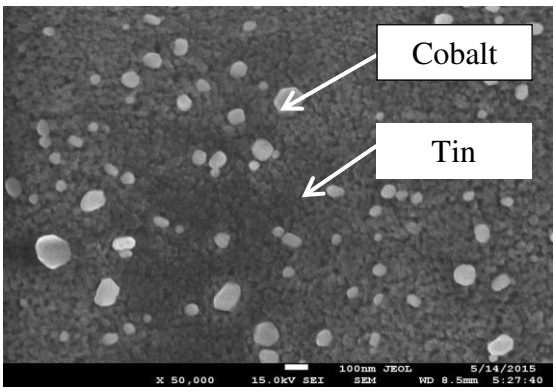
Annealing process

The Protherm Furnace was used in the annealing process. The thin film was annealed at four different temperatures of 100 °C, 200 °C, 300 °C and 400 °C to make sure that organic substances is fully evaporated and the thin film is strongly deposited to the substrate. The substrate is annealed for one hour.

RESULTS AND DISCUSSIONS

Structural properties

The surface morphology of the thin film annealed at different temperature is shown in Figure-1. Sample annealead at 100 ^{o}C shows formation of two types of grain; dark grain (SnO_2) and white grain (Co). Further increase of temperature from 100 ^{o}C to 200 ^{o}C revealed that the pores area for dark grain decreased leaving only the white grain on top of it(Ahmad *et al*., 2010). Size of the white grain increase as temperature increased to 200 ^{o}C as shown in Figure-1(b). From Figure-1(c), the morphology of sample annealed at 300 ^{o}C shows that the white grains has decreased in size but the number of grains increases. As for sample annealed at 400 ^{o}C, the morphology shows micro-size grain with further decrease in its quantity. There is also a powder-like white grain forming in this sample. Thus, it can be said that the surface morphology is greatly influenced by the annealing temperature (Pirmoradi *et al*., 2011).



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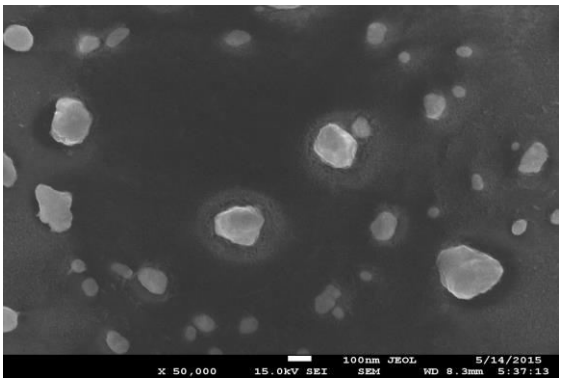

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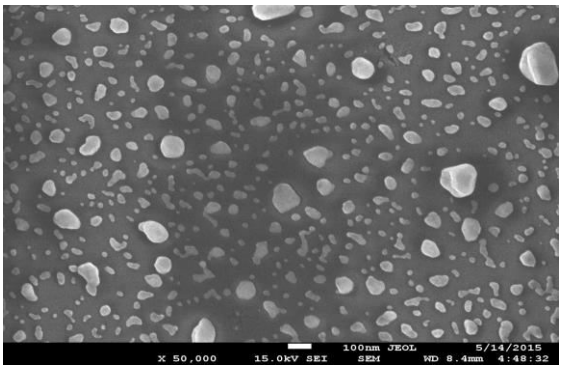

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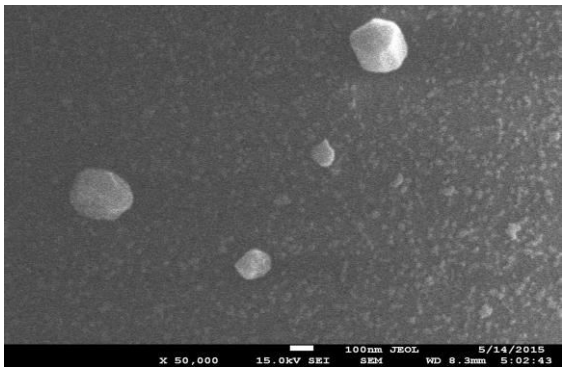


(d)

Figure-1. FE-SEM images of Co/SnO_2thin films at different temperature: (a) 100 ^{o}C, (b) 200 ^{o}C, (c) 300 ^{o}C, (d) 400 ^{o}C.

To confirm the existence of required element, EDS analysis was performed on the surface structure of the thin film. The results in Table 1 show the existences of oxide, cobalt and tin elements with its weight percentage. The results reveal that the element in spray solution was not disappeared even though the thin film was annealed at high temperature from 100 °C to 400 °C. Figure 2 shows the spectrum of the EDS results for (a) 100 °C, (b) 200 °C, (c) 300 °C, and (d) 400 °C. It can be seen that cobalt give higher atomic percentage at annealing temperature 200 °C.

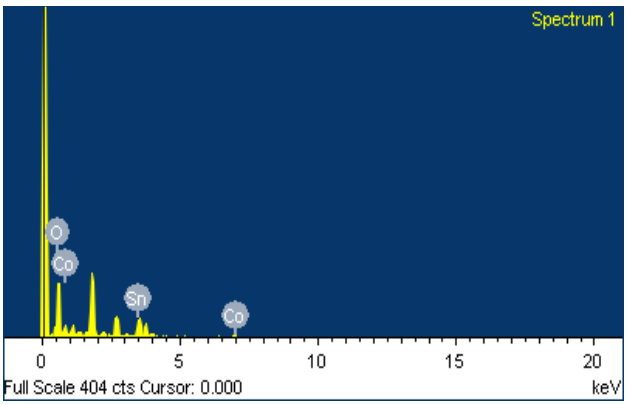
Electrical properties

The thickness of thin film must be measured to obtain the electrical properties data by using surface profiler. The average value of the thickness is 0.356 µm.A decrease in resistivity was observed in the annealing temperature range between 100 °C to 200 °C. Annealing temperature at 200 °C gives the lowest value of resistivity that is 0.2k (Ω-cm) as shown in Table-2.

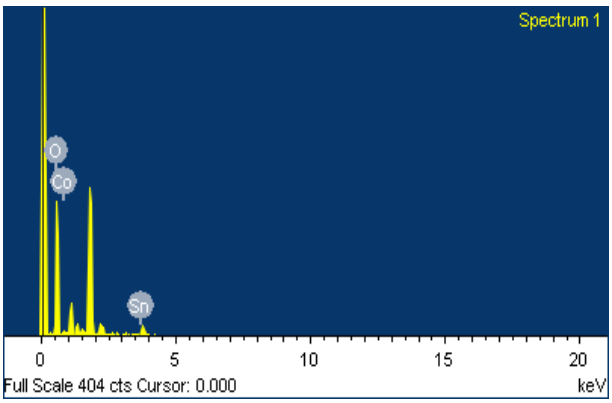
However, when the temperature increase to 300 °C, the resistivity show an increase with the highest value of resistivty that is 12.3k (Ω-cm) before decreasing again at 400 °C. Thus, there exists an optimum temperature for the thin film is at 200 °C with 0.08 $x10^{+8}(\Omega/_{\square})$ of sheet resistance. The electrical property of the films was found to be related to the surface morphology, which in turn strongly depend on the annealing temperature (Benramache *et al.*, 2012).

Table-1. Weight percentage of present element at different annealing temperature from EDX result.

Sample	Annealing temperature	Weight %		
		O	Co	Sn
A	100 °C	61.71	7.85	30.44
B	200 °C	39.81	6.04	54.15
C	300 °C	69.11	6.24	24.65
D	400 °C	68.26	8.88	22.86



(a)



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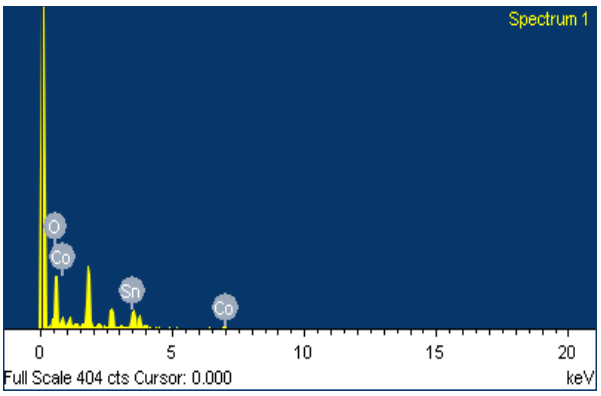

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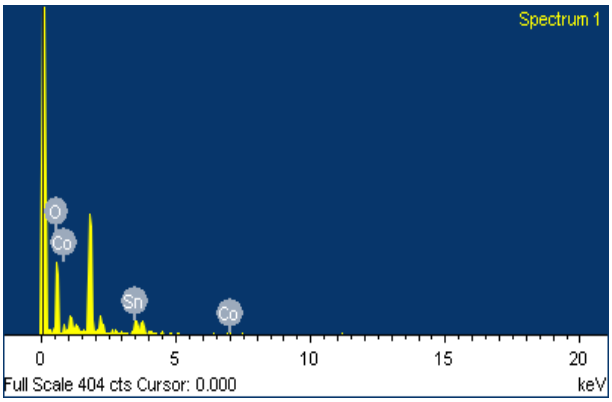

(d)

Figure-2. EDS images of Co/SnO_2thin films at different temperature: (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C.

Optical properties

From the graph in Figure-3, samples have a transmittance percentage in the visible range that is from 400 nm to 780 nm, all above 80% of transmittance percentage; which indicate a good transmittance for TCO. Overall graph shows an abnormal behavior of the transmittance percentage. The percentage increase when the temperature was increase from 100 °C to 200 °C and then gradually decrease when the temperature increased to 300 °C and 400 °C. This anomalous behavior may be due to the effect of light scattering (Abudula *et al.*, 2014). Hence, the annealing temperature is found to have a great influence on the optical properties of the thin film.

Table-2. Electrical properties of TCO with different annealing temperature from four point probe I–V measurement result.

Sample	Annealing temperature	Resistivity, R (Ω-cm)	Sheet Resistance, Rs ($\Omega/\square$)
A	100°C	11.6k	3.26 x10^{+8}
B	200°C	0.2k	0.08 x10^{+8}
C	300°C	12.3k	3.45 x10^{+8}
D	400°C	1.1k	0.31 x10^{+8}

CONCLUSIONS

In conclusion, the TCO has been successfully fabricated by using spray pyrolysis method with variation temperatures from 100 °C to 400°C. This work shows that the structural, optical and electrical properties of cobalt doped tin oxide were strongly dependent upon the annealing temperature. Annealing temperature of 200°C gives an optimum annealing temperature of the transparent conducting oxide in one hour where the result shows the minimum sheet resistances was0.08 x10^{+8}($\Omega/\square$). The thin film produced at annealing temperature 200°C also shows average transmittance in the visible range that was higher than 80%. EDS results shows that the thin films possessed the required element such cobalt, tin and oxide. Thus, this cobalt-doped TCO films can be useful in the development of concentration solar collector.

FUTURE RECOMMENDATION

In order to obtain more precise and effective result, some additional recommendation should be taken after completing this report including:

a) Modifying the precursor solution to avoid unclear image of surface morphology.
b) Parameter of volume precursor solution should be reconsidered to get high of transparency.
c) The annealing temperature and time should be smaller gapping interval such 50 °C, 100 °C, 150 °C, 200 °C and 250 °C to get more precise result.

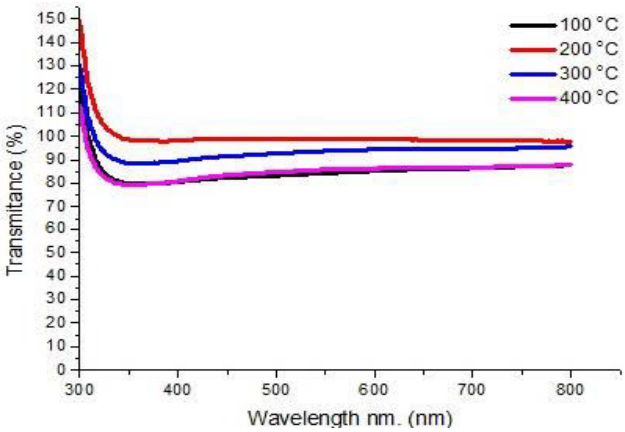

Figure-3. Graph transmittance percentage against wavelength.

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