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THE EFFECTS OF ANNEALING TEMPERATURE ON PROPERTIES OF ALUMINIUM-DOPED TIN OXIDE (AL/SNO$_2$) THIN FILMS DEPOSITED BY SPRAY PYROLYSIS DEPOSITION (SPD) METHOD

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ABSTRACT
The effects of annealing temperature on properties of aluminium-doped tin oxide (ATO) thin films deposited by spray pyrolysis deposition (SPD) method were studied. Transparent sandwich structure ATO multilayered thin films were deposited on glass substrates from aluminium nitrate and tin (IV) chloride solution using spray pyrolysis deposition method. The deposited films were annealed at different temperatures using a furnace from 100 ^oC to 500 ^oC. Characterization of the films for its surface morphology, elemental analysis and optical properties were done by using FE-SEM, EDS and UV-Visible spectroscopy (UV-Vis).Sample of 500 ^oC annealing temperature was the optimum annealing temperature since the sample exhibited the lowest resistivity of 493.44 Ω · cm and highest percentage of transparency .

Keywords: spray pyrolysis deposition method, aluminium doped Tin oxide, transparent conducting oxide.

INTRODUCTION
A transparent conductive oxide (TCO) is a doped metal oxide and have been used in optoelectronic devices such as flat panel displays and photovoltaic devices including inorganic devices, organic devices, and dye-sensitized solar cell (Murdoch, 2010), (S.-M. Park *et al.*, 2007). For example, TCO has been used as electrodes in solar cells which for its low resistivity and wide band gap (Minami, 2005). The band gap of a TCO can be made smaller or larger by doping. Smaller band gap can contribute to better conductivity while a larger band gap means higher transmittance and better transparency. Most of these films are fabricated with polycrystalline or amorphous microstructures. A good TCO is expected to have more than 80% transmittance and conductivity higher than 10^3 S/cm. One of the most common TCO is produced by doping Tin (Sn) into Indium Oxide (In_2O_3) to produce ITO(Terzini, Thilakan, and Minarini, 2000). Indium is selected because it has low resistivity and high transmittance in the visible rays region of the electromagnetic spectrum (380-770 nm) (McDowell, Sanderson, and Hill, 2008). However, due to the high cost and rarity of indium, other alternative materials which are low cost are needed to develop a new type of TCO (McDowell *et al.*, 2008), (K.-Y. Park *et al.,* 2012). Aluminium (Al) has been identified as the most abundant metal in the Earth's crust (Shakhashiri, 2007). Thus, it is a potential material that can be used for producing a new TCO which can be developed by doping Al into SnO_2.

Aluminium-doped tin oxide (Al/SnO_2) will be used in this study and fabricated to function as a TCO. Tin oxide (SnO_2) has been reported to behave as an n-type semiconductor (Joseph, Renugambal, Saravanan, Raja, and Venkateswaran, 2009). However, when there is a suitable dopant doped into it; such as Aluminium, the carrier conversion takes place and the material changes to a p-type semiconductor (Ji, Zhao, He, Zhou, and Chen, 2006). Aluminium has been identified as a good dopant for Tin Oxide (SnO_2) since it can produce a TCO with high transparency in the visible range(Bagheri-Mohagheghi and Shokooh-Saremi, 2004). Aluminium also has high heat and electrical conductivity which is suitable for the properties of a TCO(Agura, Suzuki, Matsushita, Aoki, and Okuda, 2003). A transparent p-type Al/SnO_2 multilayer thin film had been prepared by Spray Pyrolysis Deposition (SPD) method. SPD method is one of the most versatile methods to grow or deposit thin films as it can coat substrates with complex geometries with uniform coating and the method is low cost enough for mass producing. Thin films fabricated by SPD method also doesn't require high heat to be grown and deposited(Goto, Kawashima, and Tanabe, 2006). A solution consists of Tin Oxide (SnO_2) and Aluminium (Al) has been prepared and deposited on the glass substrate. The deposited films have been annealed at different temperatures from 100^oC to 500 ^oC in order to observe the difference in structural, electrical and optical properties using Energy-Dispersive X-Ray Spectroscopy (EDS), Field Emission Scanning Electron Microscopy (FE-SEM), IV Measurements and UV-Visible spectroscopy respectively.

METHODOLOGY
In this experiment the substrate used is microscope glass. The glass substrates were first treated

ARPN Journal of Engineering and Applied Sciences

with acetone, ethanol and distilled water of the same ratio in an ultrasonic bath for 10 minutes. By using the Spray Pyrolysis Deposition (SPD) technique, ATO thin film was fabricated. Tin (IV) chlorides mixed with deionized water in a beaker and aluminium nitrate is also mixed with deionized water but in a separate beaker. The two solutions are stirred on a magnetic stirrer before mixed together. Propanol which acts as a solvent is added into the mixture and stirred well.

The chemical equations involved are as follows:

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

$$Al\ (NO^3)^3 + H_2O \rightarrow Al\ (OH)^{2+} + H^+ + 3NO^{3-} \qquad (2)$$

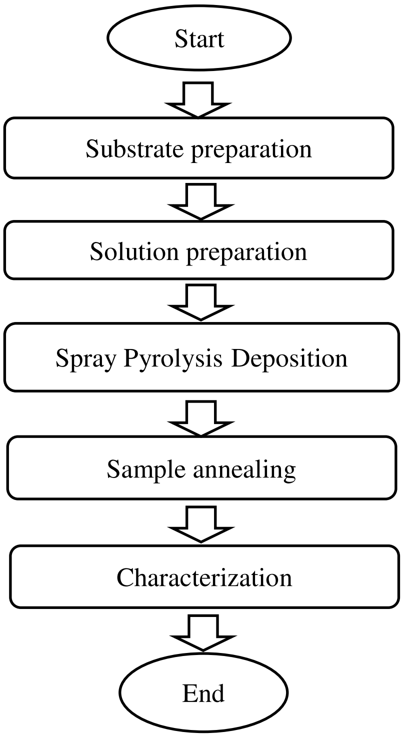

Figure-1. Flowchart of the procedures.

ATO solution was then sprayed onto substrate by using Spray Pyrolysis Deposition (SPD) technique. After that, the sample was annealed at varying temperature from 100°C to 500°C for 1 hour. The thickness of the ATO film was measured using a surface profiler (alpha-step IQ). The surface morphologies of the ATO films were characterized using a field emission scanning electron microscope (FESEM: JEOL JSM-7600F). The elemental analysis of the film was analyzed by using Energy Dispersive X-Ray Spectroscopy (EDS). The sheet resistance was measured by using the four-point probe (Lucas labs: Pro4). The optical transmittance of the film was evaluated by using a UV-spectrophotometer (Shimadzu, UV-1800) in the wavelength range from 300 to 800 nm. The summarization of the methodology is shown on the flowchart in Figure-1.

RESULTS AND DISCUSSIONS

Surface topography and elemental analysis

Figure-2 shows the surface morphology of the Aluminium doped Tin Oxide sample with different annealing time which are as deposited, 100 °C, 200 °C, 300 °C, 400 °C and 500 °C. The as deposited sample as in Figure-2(a) depicts all the samples before annealing process. There are a number of agglomerated particles deposited on the sample and they are not evenly distributed. However, the surface morphology changed when the sample is annealed. For as deposited and 200 °C samples as in Figure-2(a) and 2(c), the surface shows that the ATO layer is still not evenly distributed on the sample but the particles are less agglomerated. The particles are further apart from each other if compared to the sample in 2(a). When the ATO films are annealed at higher temperature than 300 °C as can be seen in Figure-2(d), the particles on the sample becomes more evenly distributed. There is less gap between the particles compared to samples annealed below than 300 °C.

Higher annealing temperature results in larger size of particles deposited on the substrate. For the sample in Figure-2(f), the particles of ATO deposited on the substrate are the largest and the surface is rougher compared to others. It can also be found that the sample of ATO layer of sample in 2(f) has large grains that were well defined on the substrate. Therefore, as a method of improving solar cell performance and also to produce a high efficiency solar cell, ATO annealed with 500 °C will be taken into consideration compared to the other samples with lower annealing temperature because of its more uniform deposition. ATO with lower annealing temperature such as 300 °C and 400 °C have smaller grain size compared to 500 °C. Smaller grain size presents highest concentration of electron density but lower mobility and transparency, as to be discussed later. Grain size and its distribution affect the overall surface area as well as the number of grain boundaries of the ATO film. ATO film having the largest surface area and the lowest number of grain boundaries can be obtained only through the largest distribution of grain sizes. This is because smaller grain boundaries cause higher mobility and surface area which will increase the electron density.

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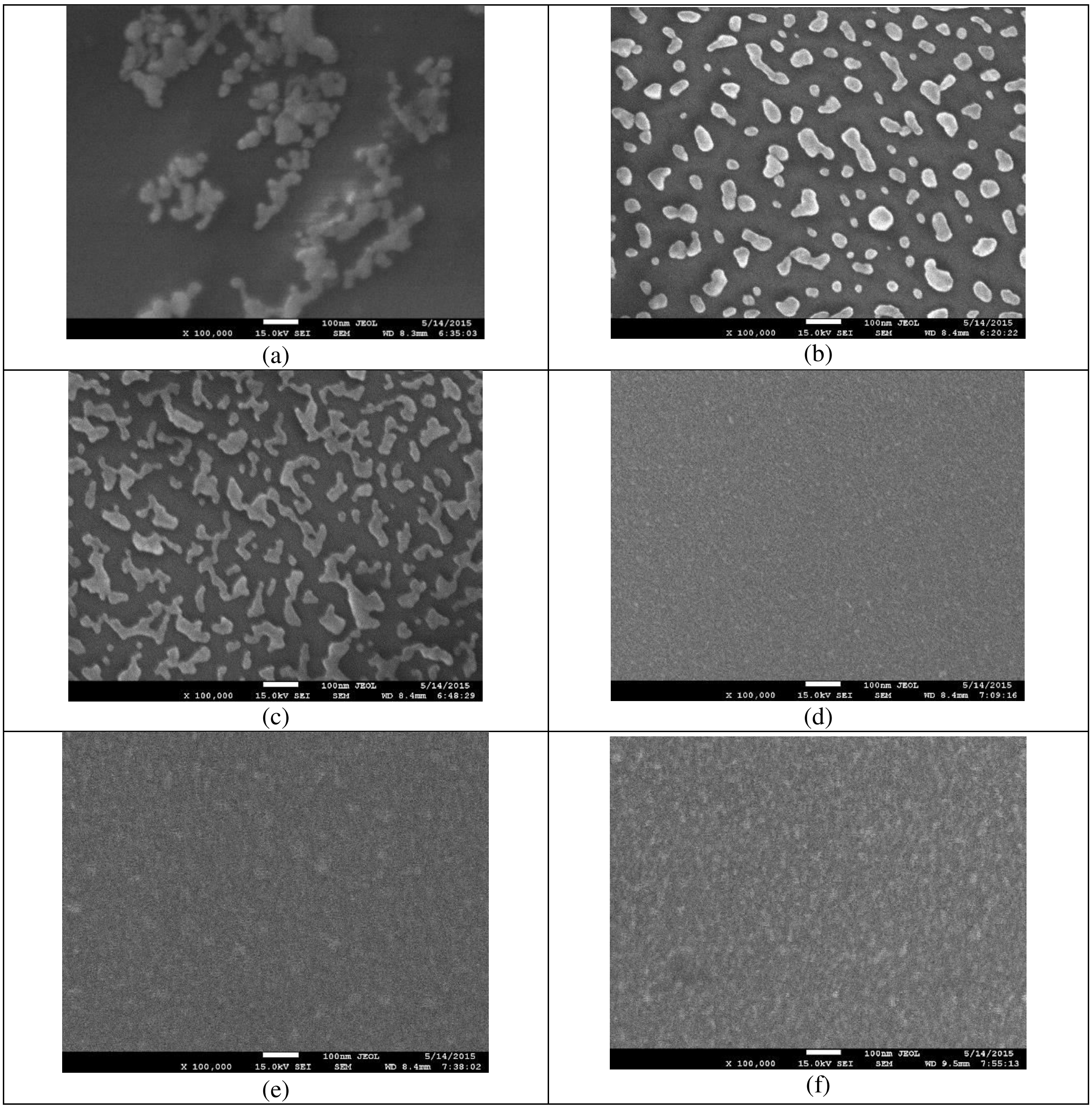

Figure-2. FE-SEM surface morphologies of samples (a) as deposited and annealed at (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C and (f) 500 °C for 1 hour.

As shown in Figure-3, the EDS results confirmed that the samples fabricated is ATO. Table-1 shows the quantity of the element growth on the sample which are Aluminium (Al), Tin (Sn), and Oxygen (O). Aluminium acts as a dopant to the Tin Oxide and will affect the transparency and sheet resistance of the sample. Oxide layer has less conductivity, so Aluminium acts as a conductive element to increase the conductivity of the sample. Tin and Oxygen element can be shown to have higher concentration on all sample. Tin oxide acts as an oxide layer and aluminium acts as dopant to change the properties of the samples. The concentration of the oxygen element on the sample is more than 70% which is the highest number of element found on the sample.

Higher annealing temperature will increase the concentration of Aluminium on the sample. The sample annealed at 500 °C shows the highest weight percentage of Aluminium growth on the sample which is about 4.9 % and the sample for 100 °C shows the lowest weight percentage which is 2.54%. This shows that with higher temperature of annealing, the weight percentage of Aluminium grown on the sample also increased. Relating Table-1 to Table-2, as the Aluminium percentage increased, the conductivity also increased which means that the resistivity of the sample will decrease accordingly.

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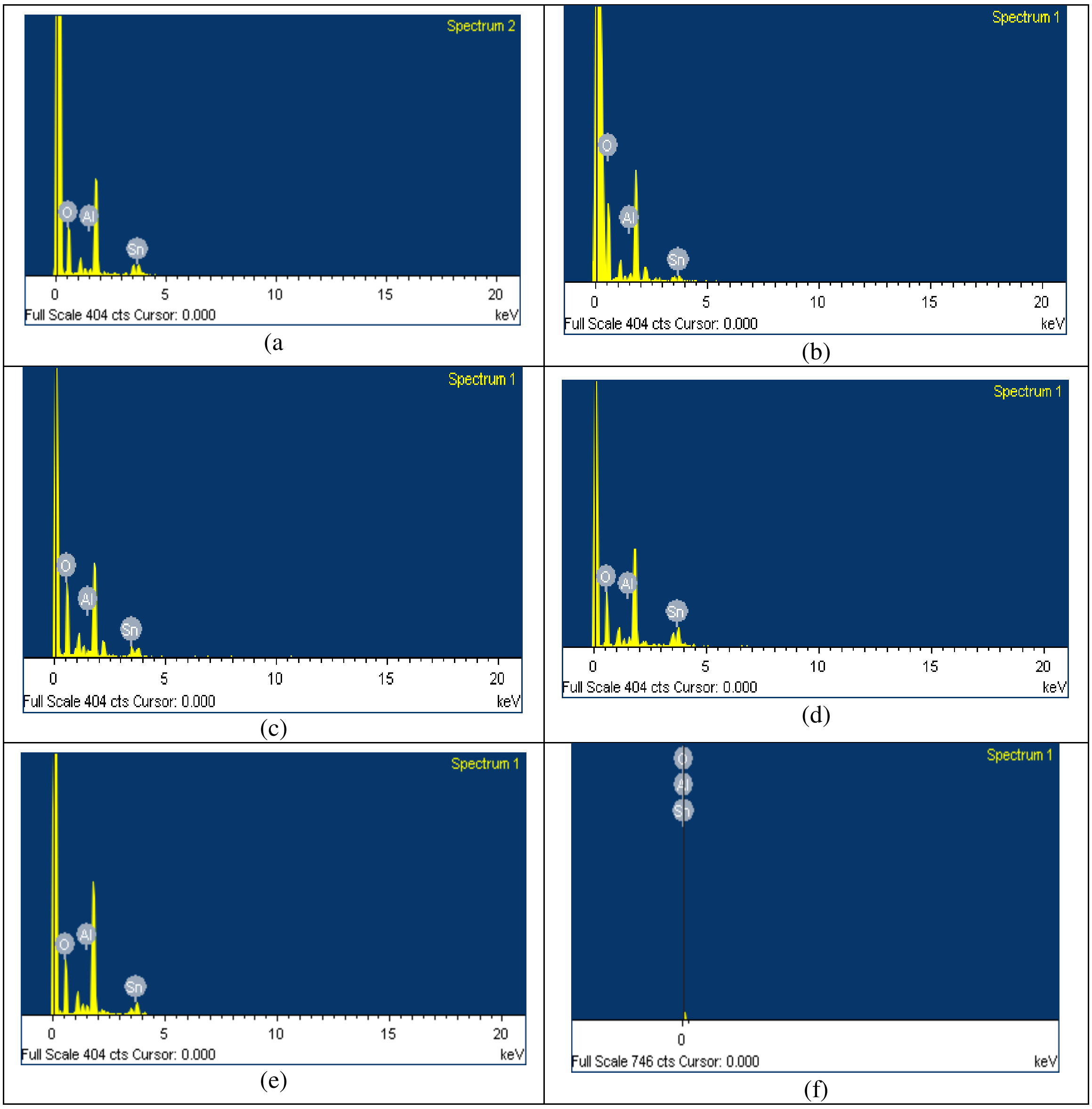

Figure-3. EDS results for samples (a) as deposited and annealed at (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C and (f) 500 °C

Table-1. Elemental analysis of sample.

Sample	Temperature (°C)	Elemental analysis - Weight (%)		
		Al	Sn	O
A	As deposited	2.94	25.77	71.30
B	100	2.54	18.09	79.36
C	200	3.48	15.56	80.96
D	300	3.66	15.40	80.94
E	400	3.83	30.06	66.12
F	500	4.90	24.26	70.83

I -V measurement

The resistivity, ρ is calculated using the formula as below:

$$\rho=2\pi s\ V/I \quad (3)$$

Where,
ρ = Resistivity
s = Gap spacing between the probe
V = Voltage
I = Current

The thickness of the sample is obtained from the Surface Profiler. The average thickness of the samples are 0.34μm. Thin layers are often characterized by their sheet resistance, R_{sh} expressed in units ohms per square. R_{sh} can be obtained using the formula as in equation (4) below:

$$R_{sh}= (\rho)/t \quad (4)$$

Where,
R_{sh} = Sheet resistance
ρ = Resistivity
t = thickness of the sample

The sheet resistance of the sample annealed at different temperature gradually decreased as the temperature increased. The sample of highest annealing temperature which is 500°C shows the lowest resistivity (493.44 Ω-cm) and sheet resistance (1.45×107 Ω/□) compared to others. This shows that it is more conductive than the samples of lower annealing temperature. TCO layer of a solar cell needs to have low sheet resistance for mobility of electron. So, the samples are not suitable to be a TCO layer because of the high resistance.

Table-2. Resistivity of the sample.

Temperature (°C)	**Sheet Resistance** R_{sh}(Ω/□)	**Resistivity, ρ** (Ω-cm)
as deposited	49.78 x 10^7	16 926.74
100	8.02 x 10^7	2 775.83
200	7.65 x 10^7	2 599.32
300	6.35 x 10^7	2 159.82
400	1.79 x 10^7	608.24
500	1.45 x 10^7	493.44

Optical performance (Ultraviolet–visible spectroscopy)

Figure-4 shows the variation of transmittance for Al/SnO_2 thin films deposited by SPD method and annealed at different temperature for 1 hour. The samples are characterized by using UV-Vis in the range of wavelength from 300 to 800 nm. These data show that all the investigated temperature can be used to produce high transparency of transparent conducting oxide (TCO). The transparency of the as deposited sample is the lowest compared to the others. On the other hand, the sample of 500 °C annealing temperature shows the highest transparency. It can be concluded that higher annealing temperature produces higher transparency for the samples. Most of samples with different temperature achieved more than 90% transmittance which is appropriate for a TCO. High transparency samples are needed for a TCO because light must be able to pass through to the absorbance layer of a DSSC. Therefore, it is proven that all samples annealed at different temperature can be considered for a TCO in the aspect of transmittance.

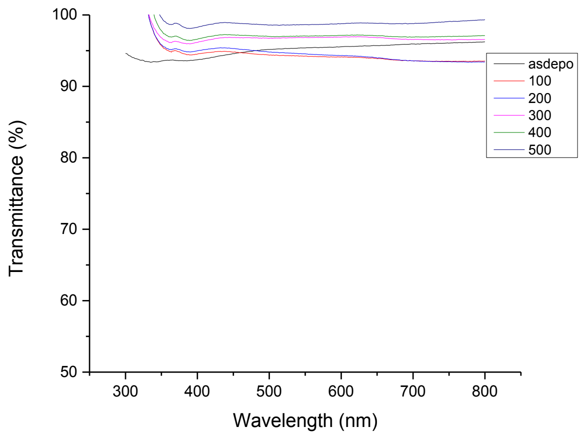

Figure-4. Transmittance of the sample with different temperature.

CONCLUSIONS

Aluminium-doped tin oxide (ATO) is fabricated using Spray Pyrolysis Deposition (SPD) method for the production of an alternative low cost transparent conducting oxide (TCO). The optimum annealing temperature for ATO is 500°C which shows larger area of particle deposition, low resistivity and high transmittance. The particle on the sample is larger and the surface is smoother when annealed at higher temperature. Higher annealing temperature gives higher transparency for the samples. Most of the annealed samples give high percentage of transparency; higher than 90%. So, ATO with higher annealing temperature is more suitable to be used as a TCO layer based on surface topography and transmittance of the sample. The resistivity of the samples also decrease when annealed at higher temperature which consequently will increase the conductivity. But, the sample is not suitable to be a TCO layer because of the high resistance.

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REFERENCES

Agura, H., Suzuki, A., Matsushita, T., Aoki T. and Okuda, M. 2003. Low resistivity transparent conducting Al-doped

ZnO films prepared by pulsed laser deposition. Thin solid films, 445(2), 263-267.

Bagheri-Mohagheghi, M.-M. and Shokooh-Saremi, M. 2004. The influence of Al doping on the electrical, optical and structural properties of SnO_2 transparent conducting films deposited by the spray pyrolysis technique. Journal of Physics D: Applied Physics, 37(8), 1248.

Goto, K., Kawashima, T. and Tanabe, N. 2006. Heat-resisting TCO films for PV cells. Solar energy materials and solar cells, 90(18), 3251-3260.

Ji, Z., Zhao, L., He, Z., Zhou, Q. and Chen, C. 2006. Transparent p-type conducting indium-doped SnO_2 thin films deposited by spray pyrolysis. Materials Letters, 60(11), 1387-1389.

Joseph, D. P., Renugambal, P., Saravanan, M., Raja, S. P. and Venkateswaran, C. 2009. Effect of Li doping on the structural, optical and electrical properties of spray deposited SnO_2 thin films. Thin Solid Films, 517(21), 6129-6136.

McDowell, M., Sanderson, R. and Hill, I. 2008. Combinatorial study of zinc tin oxide thin-film transistors. Applied Physics Letters, 92(1), 13502-13502.

Minami, T. 2005. Transparent conducting oxide semiconductors for transparent electrodes. Semiconductor Science and Technology, 20(4), S35.

Murdoch, G. B. 2010. Transparent conductive oxides for organic electronics. University of Toronto.

Park, K.-Y., Kim, G.-W., Seo, Y.-J., Heo, S.-N., Ko, H. J., Lee, S.-H., Koo, B. H. 2012. Effect of annealing temperature on properties of p-type conducting Al/SnO_2/Al multilayer thin films deposited by sputtering. Journal of Ceramic Processing Research, 13, S385-S389.

Park, S.-M., Ebihara, K., Ikegami, T., Lee, B.-J., Lim, K.-B. and Shin, P.-K. 2007. Enhanced performance of the OLED with plasma treated ITO and plasma polymerized thiophene buffer layer. Current Applied Physics. 7(5), 474-479.

Shakhashiri, B. Z. 2007. Chemical of the Week: Aluminum. Science is Fun. Retrieved on, 08-28.

Terzini, E., Thilakan, P. and Minarini, C. 2000. Properties of ITO thin films deposited by RF magnetron sputtering at elevated substrate temperature. Materials Science and Engineering: B, 77(1), 110-114.