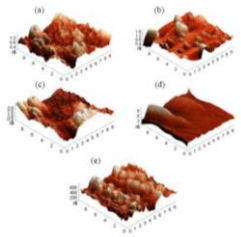
Malaysian Journal of Catalysis
http://mjcat.utm.my/
MJCat

Influence of annealing temperature on In_2O_3-SWCNTs (0.1 wt%) in DSSCs

Huda Abdullah[a*], Savisha Mahalingam[b], Masrianis Ahmad[c], Izamarlina Asshaari[d], Nowshad Amin[e], Iskandar Yahya[f], Brian Yuliarto[g]
[a]Department of Electrical, Electronics & System Engineering, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, MALAYSIA., [b]Unit Pengajian Asas Kejuruteraan UPAK, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, MALAYSIA.
[c]Engineering Physics Department, Faculty of Industrial Technology, Lab. Tek. VI Jl. Ganesha 10 Bandung, 40132 INDONESIA
Corresponding author email: huda.abdullah@ukm.edu.my

Article history :
Received 1 September 2016
Accepted 24 August 2017

GRAPICAL ABSTRACT



ABSTRACT

In_2O_3 is a n-type semiconductor material with excess indium and oxygen atoms that serve as donors by implemented a host electrode in photoanode layer. In this research, Indium oxide-single wall carbon nanotubes (In_2O_3-SWCNTs) as a photoanode in DSSCs was successfully fabricated using sol-gel spin coating method. The objective of this work is to determine the optimum annealing temperature vary at 400 °C, 450 °C, 500 °C, 550 °C, and 600 °C for SWCNTs doping 0.1 wt. % in In_2O_3-based DSSCs. The changes in the structural properties were analyzed by means of X-ray diffraction (XRD) and atomic force microscopy (AFM) analysis. X-ray diffraction analysis proved the In_2O_3 - SWCNTs have a formation of a body center cubic structure. While AFM results indicate the grain have a decrease in rough surface (RMS) from 26.21 nm to 15.17 nm as the annealing temperature increase from 400 °C to 500 °C. Above 500 °C, the grain size of In_2O_3 will back to normal size due to the loss of carbon element from CNTs compound. The optimum annealed temperature was found at 450 °C by produced the highest photovoltaic performance with power conversion efficiency (η), photocurrent density (*Jsc*), open circuit voltage (*Voc*), and fill factor (*FF*) of 0.0131 %, 0.29 mA/cm2 , 0.15 V, and 0.302, respectively. The result showed, by increasing the annealing temperature, the carbon element in the CNTs tend to burn out and consequently the thin films remain is the In2O3 nanoparticles without the presence of SWCNTs on the substrate and dropped the photovoltaic efficiency of the cell. The study shows the incorporation of SWCNTs play a role in In_2O_3 - based DSSCs by enhancing the performance and the efficiency.

Keywords: In_2O_3, single – wall carbon nanotubes (SWCNTs), DSSCs, Morphology, power conversion efficiency (PCE)

1. INTRODUCTION

A dye-sensitized solar cell (DSSCs) is green energy source which is clean, renewable and cheap. DSSCs are one of the third-generation organic photovoltaic (PV) cells. The main challenge of DSSCs is they are expected to produce high efficiency at low manufacturing cost compared to other single – crystal silicon solar cells. The PV technology is aiming to reduce material cost by introducing nanotechnology in the methodology of the solar cells. Research development of the cell's efficiency has been carried out within these 25 years since O'regan and Grätzel made the first breakthrough in 1991 by introducing dye sensitizer in TiO_2-based solar cell [1,2]. The research of DSSCs as a promising efficient PV cell made its way by using alternative nanostructure metal-oxide film, such as ZnO [3,4], In_2O_3 [2,5], and SnO_2 [6] On the other hand, hybrid metal oxide such as SiO_2-P_2O_5 [7] and Ag-SiO_2-TiO_2 [8] also have been extensively used to enhance the performance of DSSCs. Nowadays nanotechnology is rapidly sweeping in all fields especially electronic through design, synthesis, characterization, and application of material and devices on the nanometer scale to provide opportunity to develop new classes of advanced materials which meet the demands from high – tech applications.

Research on In_2O_3 as a photoanode material in DSSC is due to its direct band gap and indirect band gap of 3.6 and 2.6 eV, respectively. However, In_2O_3 is less favorable material as photoanode and still implemented as a host electrode in DSSCs even it shows low power conversion efficiency (PCE) performance due to higher electron life time of the cell in contrast to TiO_2 materials [9]. Furthermore, stability of In_2O_3 in DSSCs was seen through the change in light and dark current density-voltage photo electrochemical performance [10]. In addition, we proposed single-walled carbon nanotubes (SWCNTs) in the composition of metal oxide semiconductor. Carbon nanotubes (CNTs) act as a catalyst to improve the electrical properties of the DSSCs. In the present work, the fabrication of In_2O_3-based DSSCs were doped with concentration of 0.1 wt % SWCNTs via sol–gel spin-coating method. The aim of this study is to examine the power conversion efficiencies derived from 0.1%-SWCNTs-In_2O_3 based DSSCs and annealed at different temperature.

2. MATERIALS AND METHODS

All chemicals were used as received without further purification. Pristine SWCNTs were purchased from Sigma-Aldrich (USA) and used as received. The acid treatment process was then introduced to generate SWCNTs with carboxyl groups [2].

2.1 Preparation of In2O3 - SWCNTs

The sol-gel method via a spin-coating technique was used to prepare In_2O_3-SWCNTs thin films. The chemical reagents used in this work are indium chloride ($InCl_3$), 2-

methoyethanol, monoethanolamine (MEA) and acid-treated SWCNTs. 2-methoyethanol used as solvent to dilute InCl3 and MEA was added as a stabilizer in the solution. 0.1 wt% of SWCNTs was added in the mixture separately to form 0.1 M of starting solution. The mixture was ultrasonicated at 50 °C for 1 h and stirred at 60 °C for 24 h. The heated solution was spin-coated at 1500 rpm for 30 s and repeated for 5 times to coat 5 layers on the FTO substrate. The spin-coated FTO substrate was annealed at different temperature °C for 30 min to produce 0.1%-SWCNTs-In_2O_3.

2.2 Fabrications of DSSCs

The photoanode (PE) of the DSSC was prepared by immersing the annealed thin film in 0.5 mM ethanolic N719 dye solutions for 24 h. After the immersion period, the photoanode was rinsed in ethanol to remove any excess dye. At the same time, the counter electrode (CE) was prepared using a screen printing technique. The platinum paste was deposited on a clean FTO glass and then annealed at 400 °C for 1 h. The DSSCs were fabricated by sandwiching the CE and the dye-immersed thin films together. The cell was fixed by covering the edge of the FTO substrates with a parafilm layer and two binder clips facing each other. Lastly, an electrolyte (Idolyte MPN 100 Solaronix SA) was injected into the fabricated cell and a DSSC was formed with an active area of 1.0 cm^2.

2.3 Characterization of the thin films

The photoanode was characterized by using X-ray diffraction, atomic force microscopy (AFM) and a photocurrent density–voltage (J-V) curve for the structural, morphology and electrical properties, respectively. Crystallinity of the films was characterized by Siemens D-5000 X-ray diffractometer (XRD) to investigate the crystal structure and orientation of the thin films. An AFM analysis measured the surface roughness of the photoanode. Photocurrent density–voltage (J-V) curves were recorded by using an electrochemical impedance spectroscopy (EIS) unit (GAMRY Series G300 Potentiostat) under 1,000 Wm^{-2} illumination (1.5 AM) of OSRAM halogen lamp, 50 W.

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction Analyses

Figure 1 shows the X-ray diffraction patterns of In_2O_3 doping with 0.1 wt % SWCNTs and annealed for 30 minutes at different temperature (a) 400 °C, (b) 450 °C, (c) 500 °C, (d) 550 °C and (e) 600 °C. The pattern we observed from XRD match very well with the databases PDF No: 01-071-2194. In_2O_3 diffractions peaks were traced at 2θ of 21.3°, 30.6°, 33.2°, 35.4°, 37.9°, 41.8°, 45.6°, 48.6°, 51.1° and 55.9° attributed to hkl plane of (211), (222), (321), (400), (411), (332), (431), (521), (440) and (611), respectively.

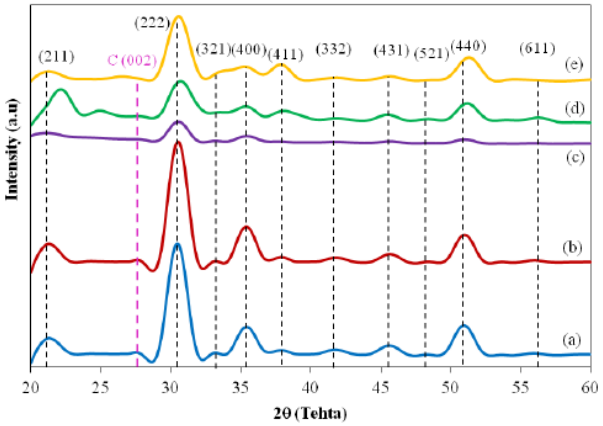


Figure 1 X-ray diffraction patterns of In_2O_3 mixed with 0.1 wt % SWCNTs and annealed at different temperature (a) 400 °C, (b) 450 °C, (c) 500 °C, (d) 550 °C and (e) 600

Table 1 XRD parameter for thin films In2O3 – SWCNTs

Annealing Temperature (°C)	2θ (°)	d_{222} (Å)	a (Å)	*Particle Size (nm)*	R_{rms}
400	29.675	3.0081	10.420	26.21	12.3
450	30.525	2.9262	10.137	18.16	24.5
500	30.600	2.9192	10.112	15.17	23.6
550	30.625	2.9169	10.104	19.45	13.8
600	30.650	2.9146	10.096	10.93	15.9

The lattice constant for bulk In_2O_3 crystal with cubic structure is a = 10.117 Å (JCPDS number 01-071-2194). XRD diffraction was confirmed that the crystallized is a body-center cubic structure. The orientation of (222) crystal plane is predominant for In_2O_3 as the annealing temperature was increased. We observed the peaks traced at 2θ = 26.6 ° with (002) plane was confirm belong to carbon [11]. While increasing the annealing temperature, the strong peak of carbon (002) is disappearing or nearly flat due to annealed temperature above 500 °C. Table 1 also shows a decrease in lattice constant of d222. It suggests that the ultimate strain is released after the annealing process. These results indicate the presence of SWCNTs in a thin film only changes the size of the crystal and not affect the In_2O_3 lattice structure. Although a greater value (10.137 Å) is obtained higher than the bulk value (10.117 Å) for thin films annealed at temperature of 450 °C. It also exhibits the highest efficiency (0.0131%) and showed it was influenced by the addition of SWCNTs. Accordingly, the peak shift also occurred subsequent to the impairment of a bulk lattice, a. In all the surveyed thin film has no stranger XRD peak or no peak attendance FTO glass itself. This indicates all sample does not suffer any fracture during sample preparation.

On the other hand, the thin film produced by spin coating method is more homogeneous and also forming a

larger surface area. CNTs provide a high surface area on the thin film and facilitate a greater loading dye on the surface photo electrode, thus improve the efficiency of the DSSCs [12]. Furthermore, the rough surface structure of thin film will improve the PCE (η) performance in DSSCs due to the decrease in the photon reflecting angle [13]. The surface roughness with larger angle on the surface texture of the thin will cause the photon indirectly bounce in the thin films and increase the photon absorption [2].

Table 2 Photovoltaic performance of In2O3 – SWCNTs

Annealing Temperature (°C)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
400	0.358	012	0.298	0.0128
450	0.290	0.15	0.302	0.0131
500	0.251	0.12	0.262	0.0079
550	0.289	0.08	0.257	0.0059
600	0.082	0.05	0.269	0.0011

3.2 AFM Analysis

Figure 2 shows the AFM images of In_2O_3-SWCNTs thin films. The rougher structure with RMS values and particle size of the annealed thin films were tabulated in Table 1. The AFM images indicate the grain have a rough surface from 12.3 nm but have a highest particle size of 26.21 nm when annealed at temperature 400 °C. At annealed temperature 450 °C, the RMS and particle size is 24.5 nm and 18.16, respectively. It shows an increase in RMS but decrease in particle size. Furthermore, continue annealing temperature above 500 °C shows a decrease in RMS and particle size. Moreover, at temperature 550 °C, the particle size of In_2O_3 is increase or back to normal size but the RMS is still decrease due to the loss of carbon element from SWCNTs compound.

3.3 Photovoltaic Performance

Figure 3 shows a graphical image of the J-V characteristics and the corresponding photovoltaic parameters of In_2O_3-SWCNTs annealed at different temperature. Table 2 lists the corresponding photovoltaic properties. The performances of each interface have been design using the parameter of open-circuit voltage (Voc), fill factor (FF), and short circuit current density (Jsc), and expressed as efficiency (η) using the equation below:

$$\eta = \frac{V_{oc} I_{sc} FF}{P_{in}} \qquad and \qquad FF = \frac{I_{max} V_{max}}{I_{sc} V_{oc}}$$

where Voc, is the maximum voltage obtained at zero current; Isc, the short circuit current is the maximum current obtained under less resistance (short circuit) conditions and Pin is the solar radiation intensity. Imax and Vmax are the maximum current and maximum voltage, respectively. Critical current density is depending on the charge injection and transport on the metal performance of oxide/dye/electrolyte interface [7].

The results show a significant increase in Jsc and open circuit voltage (Voc) when SWCNTs were incorporated in the In2O3 composition. These results signify that the incorporation of SWCNTs is also one of the reasons for PCE improvement in In_2O_3-based DSSCs. The PCE (η) and the open circuit voltage (Voc) is increase from 0.0128% to 0.0131% and 0.12 V to 0.15V for annealed temperature at 400 °C and 450 °C, respectively. Although In_2O_3-SWCNTs annealed at 400 °C exhibited the highest Jsc of 0.358 mA cm^{-2}, they showed lower PCE (η) than that of those that annealed at temperature 450 °C (0.29 mA cm^{-2}). This is because the Voc and fill factor (FF) obtained for In_2O_3-SWCNTs annealed at temperature 400 °C was much lower than that of those that annealed at temperature 450 °C. Furthermore, continue annealed above 500 °C, both efficiency and Voc dropped due to the loss of carbon from CNTs. The average roughness measured through AFM analysis showed that In_2O_3-SWCNTs possess rougher surface structure that could absorb more photo generated electrons. Consequently, better and rough surface morphologies of In_2O_3-SWCNTs have improved the dye loading inside the photoanode thin film. The high dye loading impact not just speeds up the electron transport and conduction path but also increase the power conversion efficiency, η of In_2O_3-SWCNTs based DSSC. However, the study of it requires details analysis of the electron transport parameter and impedance data.

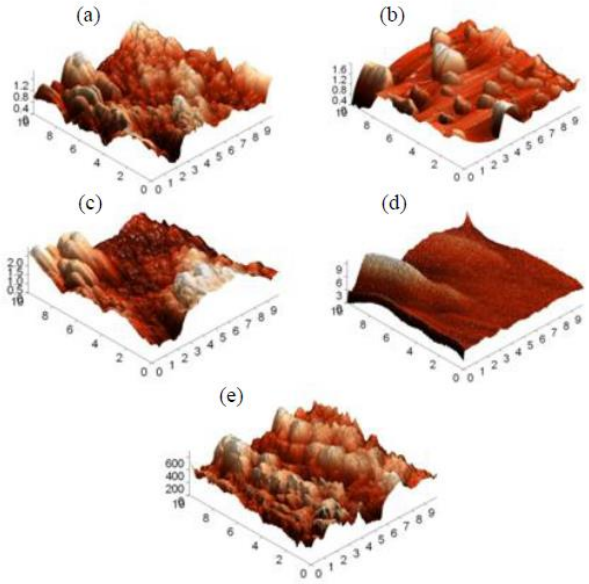


Figure 2 AFM images of thin films of In_2O_3 mixed with 0.1 wt % SWCNTs and annealed at different temperature (a) 400 °C, (b) 450 °C, (c) 500 °C, (d) 550 °C and (e) 600

4. CONCLUSION

In summary, the influence of annealed temperature in In_2O_3-SWCNTs based DSSCs was successfully studied. The

presence of SWCNTs in a thin film only changes the size of the crystal and not the structure of In_2O_3. Lattice parameter changes are insignificant because the annealing temperature change and not for the effect of SWCNTs due to the substance of the strain relief annealing. The optimum annealed temperature was found at 450 °C by produced the highest photovoltaic performance with power conversion efficiency (η), photocurrent density (*Jsc*), open circuit voltage (*Voc*), and fill factor (*FF*) of 0.0131 %, 0.29 mA/cm^2 , 0.15 V, and 0.302, respectively. Hence, the optimum annealed temperature for In_2O_3-SWCNTs was found at 450 °C due to the presence of CNTs on the substrate that can improve the overall DSSCs performance.

ACKNOWLEDGEMENTS

This work was supported by Exploratory Research Grant Scheme No.: ERGS/1/2013/TK07/UKM/03/2 and Photonic Technology Laboratory (IMEN), Department of Electrical, Electronic & Systems Engineering, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia.

REFERENCES

[1] O'Regan B., Gratzel M., Nature 353 (1991) 737.
[2] S. Mahalingam, H. Abdullah, I. Ashaari, S. Shaari, and A. Muchtar, J. Phys. D. Appl. Phys. 49(7) (2016) 075601,.
[3] A. Omar and H. Abdullah, Renew. Sustain. Energy Rev. 31 (2014) 149.
[4] H. Abdullah, A. Omar, M. A. Yarmo, S. Shaari, and M. R. Taha, J. Mater. Sci. Mater. Electron. 24(9) (2013) 3603.
[5] A. Info, Australian J. Basic and Appl. Sci. 9(12) (2015) 44.
[6] Mahalingam S, Abdullah H, Omar A, Nawi N A M, Shaari S, Muchtar A and Asshari I, Adv. Mater. Res. (2015) 1107
[7] I. Battisha, New J. Glas. Ceram. 02(01) (2012) 17.
[8] D. D. Le, T. M. D. Dang, V. T. Chau, and M. C. Dang, Adv. Nat. Sci. Nanosci. Nanotechnol. 1(1) (2010) 15007.
[9] Mori S, Asano A. J Phys Chem C, 114 (2010) 13113.
[10] Sharma R, Mane RS, Min S-K, Han S-H, J Alloy Compd. 479 (2009) 840.
[11] Lee, S.W. Sigmund, W.M, Chemical Communication 6 (2013) 780.
[12] Hara K, Horoguchi T, Kinishita T, Sayama K, Sugihara H and Arakawa H, Sol. Energy Mater. Sol. Cells 64 (2000) 11.
[13] Ariyanto, N.P., Abdullah, H., Syarif, J., Yuliarto, B. & Shaari, Functional Material Letters 3 (2010) 303.