

Deposition of Undoped Amorphous Carbon Thin Films on Insulator Glass Substrate by Bias Assisted Thermal-CVD System

Mohd Amirul Mohamad Sukri
2009683152
B.Eng. (Hons) in Electronic Engineering
Faculty of Electrical Engineering
Universiti Teknologi MARA, Shah Alam, Malaysia

Abstract—amorphous carbon thin films were successfully deposited by the bias assisted thermal-CVD system on insulator glass substrates at various deposition temperatures in the range of 300°C-500°C. The deposited of amorphous carbon thin films are characterized by using I-V measurement, UV-VIS-NIR spectrophotometer and Atomic Force Microscopy (AFM). The electrical properties of amorphous carbon thin films were found more conductivity when the temperature is increased. In contrast the optical band gap decreased for high deposition temperature. The AFM images show that, density and uniformity have correlated with the resistivity and conductivity for undoped amorphous carbon thin films deposited at various temperatures.

Keywords—chemical vapor deposition; amorphous carbon; dc bias; thin films; ethanol

I. INTRODUCTION

For a decade, there is a trend to adapt solar cell from an alternative material that are abundantly in nature, low cost and non-toxic instead of using remarkably prominent silicon [1, 2]. Accordingly, allotropes carbons as reported will be promised as a potential candidate for an alternative material in the future due to the abundantly in nature, suitability as a precursor, excellent photoconductivity, and high optical absorption of visible light, can be deposited on any inexpensive substrate. In addition, it is possible to form a very wide area of solar cell since it can be deposited directly from a kind of vapor phase growth onto noncrystalline substrate [3].

Carbon is found of having a wide band gap which is suitable for optical devices as well as for photovoltaic solar cells application. The band gap of some allotrope carbon such as amorphous carbon in the range of 0.1 eV to 5.5 eV could be tuned tailoring with energy band gap of photon by deposition process [4]. The unique ability to tune its energy band gap has offered a wide ability to absorb more photon energy from spectrum of light. However, there is a serious barrier to understanding of the physic of amorphous materials due to no equivalent reliable rule for theoretical analysis [5].

Unfortunately, a-C has difficulties in controlling the conduction type, carrier concentration and optical band gap [5]. Hence in order to produce good quality a-C thin films, few parameters have to be considered such as the suitable

deposition temperature, deposition time and the flow rate of the carrier gas.

Meanwhile, the undoped amorphous carbon in contrast is reported as weakly p-type, complex structure and high density of intrinsic defect [6]. Until now, various standard deposition techniques such as thermal-CVD, plasma enhanced chemical vapor deposition (PECVD), hot wire CVD, radio frequency CVD, ion beam sputtering (IBS), microwave surface-wave plasma (MW-SWP) CVD, filtered cathodic vacuum arc (FCVA) etc. are practically used [7,8]. However, the depositions were non-uniformity in conventional method. It was reported that, dc bias would improve the deposition process by acceleration deposition rate, reduce contamination or maintain repeatable process as were done in many standards CVD [9,10].

In negative DC bias, electric field developed around the substrate was significantly influences the energy with which ions impinges upon growing film. The negatively substrate repels any negatively ions in chamber from being reach the surface [11]. By this technique, contamination might reject from being reach the substrate through repulsion ion [12].

Due to those advantages, the amorphous carbon thin films were deposited by using self-fabricate bias assisted thermal CVD. A proposed to apply dc bias to support the process will be embarked. In this work, ethanol (C_2H_6O) is used as a precursor for carbon source to deposition of amorphous carbon thin films. Ethanol is a liquid that easy to vaporize because boiling point for ethanol is only at 78.37°C. Therefore, less energy is needed for break down its bonding compared with others precursor.

II. EXPERIMENTAL DETAILS

The glass substrates were cleaned with acetone (C_5H_6O) for remove the contaminated glass followed by methanol (CH_3OH) for remove acetone and deionized water for remove methanol for 15 min respectively in Ultrasonic Cleaner (power Sonic 405).

Figure 1 shows the schematic diagram of bias assisted thermal -CVD for deposition of amorphous carbon thin films.

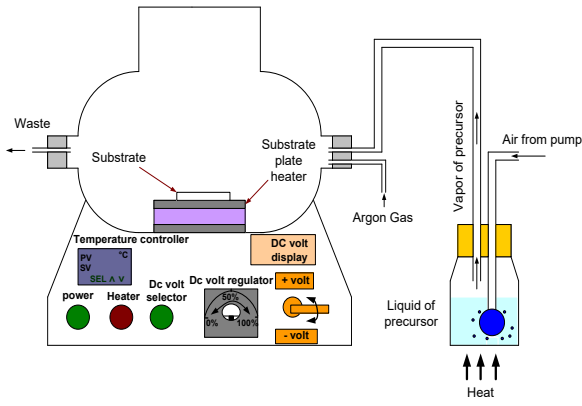


Figure 1: Schematic diagram of bias assisted thermal-CVD system

The cleaned of glass substrates are then placed in the chamber for 3 hours deposition. The chamber is heated with temperature starting from 300°C to 500°C and setup with a fixed dc bias of -40v. A vaporized of ethanol precursor is pushed into the chamber by the air pump and heated at 50°C with the hot platter (Stuart CB162). The argon gas is used for carry the deposited charge and also contaminated gas.

The samples are then characterized by using I-V measurement (Bukuh Keiki EP-200) to electrical properties, UV-VIS-NIR spectrophotometer (LAMBDA 750) to measure the optical properties, and atomic force microscope (AFM, XE-100 Park Systems) for physical properties. Band gap is calculated from the tauc plot formula.

III. RESULTS AND DISCUSSION

A. Electrical Properties

Study of electrical properties is the important way to solve many issues related to the electronics structure and properties of amorphous carbon thin films [13]. The electrical properties of the undoped amorphous carbon thin films were characterized by using current-voltage (I-V) measurement whereas gold is used as a metal contact. Figure 2 shows the amorphous carbon thin film deposited at different temperature ranging from 300 °C to 500 °C. The result showed that, amorphous carbon thin films were in ohmic contact behavior with different value of resistances.

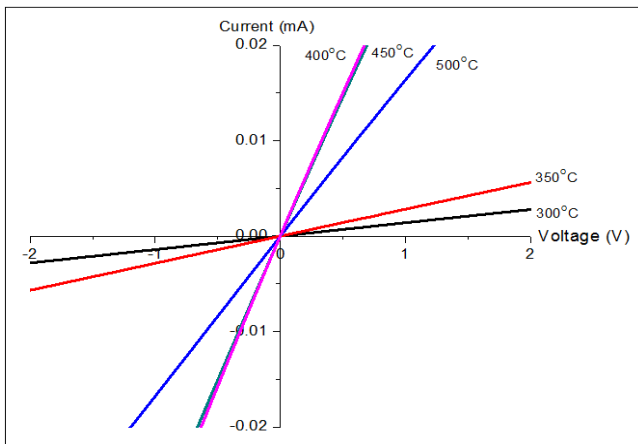


Figure 2: I-V curves of amorphous thin films deposited at different temperatures

Figure 3 shows, cross sectional view of the a-C thin films deposited on the glass substrate. Theoretically, the resistivity

and conductivity of amorphous carbon thin films can be obtained directly from the equation (1) and (2) respectively [14].

$$\rho = \frac{RA}{L} \quad (1)$$

where ρ is resistivity between 2 measured metal contact, R is resistance measured from -2v to 2 v, A is a cross sectional area ($w \times w$) and L is distance between contacts.

$$\sigma = \frac{1}{\rho} \quad (2)$$

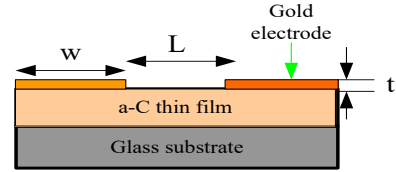


Figure 3: Cross sectional view of the a-C thin films deposited on the glass substrate

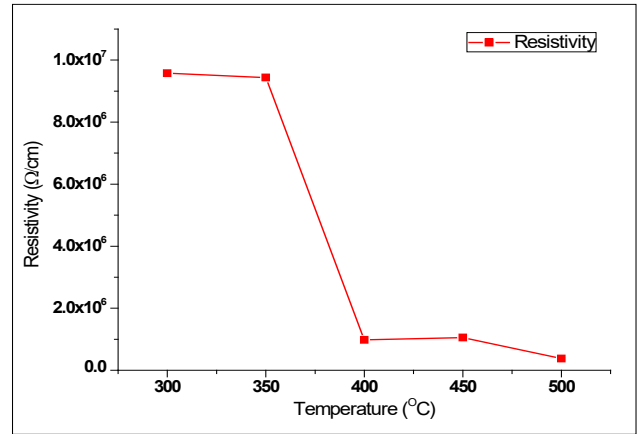


Figure 4: Resistivity curves of amorphous thin films deposited at different temperatures

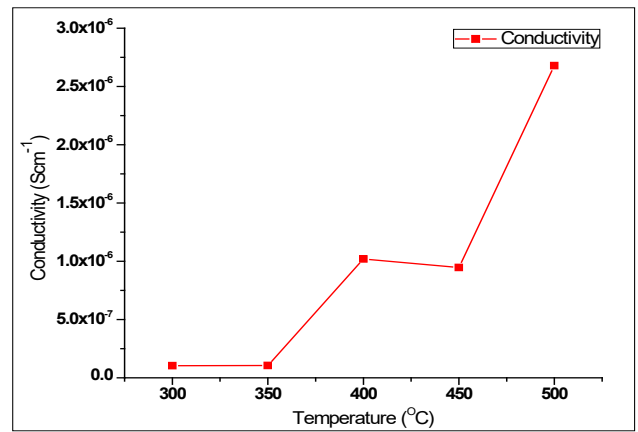


Figure 5: Conductivity curves of amorphous thin films deposited at different temperatures

Figure 4 and Figure 5 show the effect of various temperatures toward the resistivity and conductivity between two measured mask electrodes. It is observed that

from Figure 4, the resistivity is slightly decreased from 300°C until 350°C and drastically decreased starting from 400°C to 500°C. In contrast, the conductivity is flatted between 300°C and 350°C and drastically increased until 500°C but slightly decrease at 400°C as shown in Figure 5.

This might occurred due to changes in structural properties affected by deposition temperatures as proved by atomic force microscope as shown in figure 9. The conductivity increases from $1.04454 \times 10^{-7} \text{ cm}/\Omega$ to $2.67825 \times 10^{-6} \text{ cm}/\Omega$ for undoped amorphous carbon thin film deposited from 300°C to 500°C. According to the Figure 4, the resistivity is varied against various deposition temperatures. The resistivity for 350°C is $9.57 \times 10^6 \Omega/\text{cm}$ and decreased gradually to $3.734 \times 10^5 \Omega/\text{cm}$ at 500°C. This trend for resistivity and conductivity variation resembles the trend reported by Hussin et al [15] and A. N. Fadzilah et al [16].

B. Optical Properties

To investigate the optical properties of amorphous carbon thin films, transmittance measurement were carried out in the range of 300-1200nm by using JASCO UV/VIS/NIR spectrometer (LAMBDA 750). Figure 6 shows the transmittance spectrum of a-C thin films deposited at different temperatures.

According to the Figure 6, the transmittance of amorphous carbon thin film deposited at 300°C and 350°C were approximately 94% and close to the transmittance of the substrate itself. However, the transmittances of amorphous carbon thin films start to decrease gradually from 90% to 87% at 400°C to 500°C.

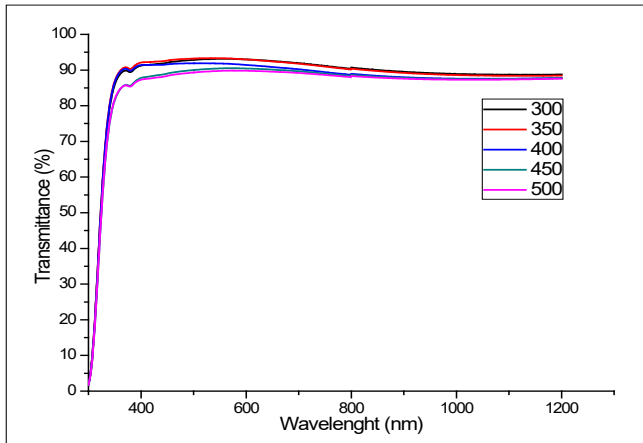


Figure 6: Transmittance spectrum of a-C thin films deposited at different temperature

Moreover, the absorption coefficient (α) was calculated by the spectral reflectance and transmittance, and the film thickness. The optical band gap was measured by using Tauc plot method. The Tauc optical band gap (E_g) was obtained from the extrapolation of the linear part of the curve at $\alpha=0$ by using the Tauc equation 3 [13].

$$(\alpha h\nu)^{1/2} = B(E_g - h\nu) \quad (3)$$

where B is the constant and $h\nu$ is photon energy.

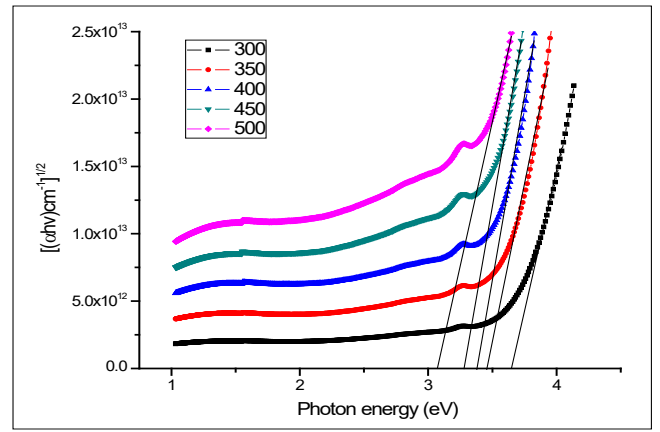


Figure 7: Graph of $(\alpha h\nu)^{1/2}$ vs photon energy of a-C thin film deposited at different temperature.

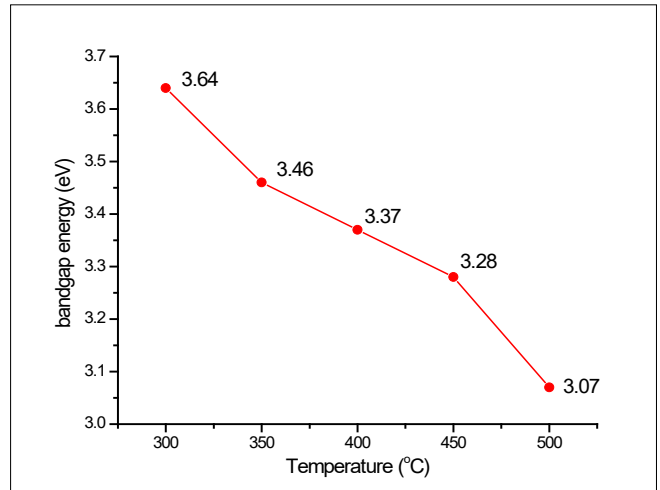


Figure 8: the optical band gap as a function of photon energy (eV) of amorphous thin films deposited at different temperatures

The optical band gap is the measurement of the gap between the extended state in the valence band and the conduction band. The optical band gap energy (E_g) of amorphous carbon thin films were plotted as shown in Figure 8. Optical band gaps of amorphous carbon thin film decrease from 3.64 to 3.07 eV.

The trend shows the energy bandgap decrease when the temperature increase. At the energy bandgap lowest, more electron can move from valence band to conduction band because electron easy to move due to a shorter distance between valence band and conduction band.

Therefore, we can see higher conductivity at lowest energy band gap. This trend for optical band gap energy (E_g) variation resembles the trend reported by F. Mohamad et al [13].

C. Physical Properties

The surface morphology of amorphous carbon thin film deposited on glass substrates were characterized by atomic force microscopy (AFM, XE-100 Park Systems), as shown in Figure 9.

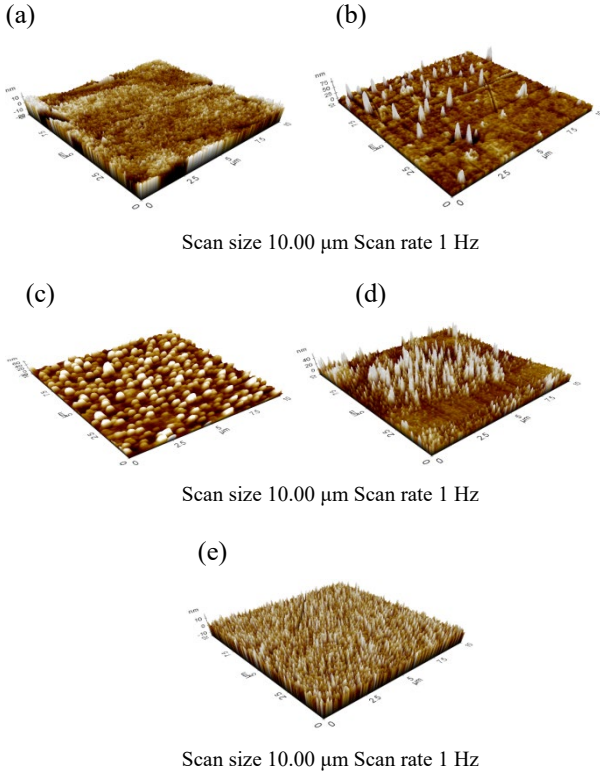


Figure 9: Representative AFM 3-dimensional image surveys of amorphous carbon thin film grown on insulator glass substrates for 3 hours using negative bias of -40V at different temperatures: (a) 300°C, (b) 350°C, (c) 400°C, (d) 450°C (e) 500°C.

Figure 9-(a) to (e) show the morphology images at which the amorphous carbon thin film deposited at different temperatures. As can be seen in AFM images, at temperature 400°C the film start to grow due to the bigger particle size on the surface of the thin film. However, the particle became smaller at 450°C and at 500°C the particle size almost growth on the each surface and became more uniformity.

This image revealed that the films at higher deposition temperature tend to be more graphite. In conclusion, the results show that changing the temperature affects the uniformity and thickness of the amorphous carbon thin film.

Table 1: AFM Surface roughness properties of amorphous carbon thin film on glass substrates.

Temperature (°C)	Root mean square Roughness, Rq (nm)	Surface Roughness Average, Ra (nm)
300 °C	2.821	1.983
350 °C	6.265	3.2963
400 °C	12.603	10.004
450 °C	8.503	5.949
500 °C	3.49	2.783

Table 1 shows surface roughness properties of amorphous carbon thin film on glass substrates and characterized by using AFM (XE-100, Park System). In Table 1, at

temperature 300 °C and 400°C, the surface has the lowest and highest roughness value of 1.983 nm 10.328 nm respectively. The surface roughness of thin film is increased from 300°C until 400 °C and slowly dropped starting from 450°C to 500°C.

The surface roughness average is 3.296 nm at 350°C, 5.949 nm at 450°C, and 2.783 nm at 500°C. From this result, we can conclude that, the surface roughness increased until reached the optimum temperature of 400°C and drastically dropped when temperature at 400°C to 500°C .

IV. CONCLUSION

The undoped of amorphous carbon thin films were successfully deposited on insulator glass substrates by using bias assisted thermal-CVD for 3 hour deposition. The effects of the temperature on electrical properties of amorphous carbon thin films were investigated by I-V Measurement. The electrical properties of amorphous carbon thin films were found more conductivity as the temperatures increased. The resistivity of undoped amorphous carbon thin film at 300°C, 350°C, 400°C, 450°C and 500°C were $9.57 \times 10^6 \Omega/\text{cm}$, $9.44 \times 10^6 \Omega/\text{cm}$, $9.81 \times 10^5 \Omega/\text{cm}$, $1.06 \times 10^6 \Omega/\text{cm}$ and $3.38 \times 10^5 \Omega/\text{cm}$ respectively. The optical band gap of amorphous carbon thin film was found to be approximately to 3.64 eV at low temperature and decreased to 3.07 eV at high temperature of 500°C. The optical band gap decreased for high deposition temperature. The AFM images showed that, uniformity has correlated with the resistivity and conductivity of undoped amorphous carbon thin films at various temperatures. The less uniformity of undoped thin films provided less conductivity and high resistivity while the more uniform contributed to the high conductivity and low resistivity.

RECOMMENDATION

Future recommendation for this project is dope amorphous carbon thin films with nitrogen. That was reported, doping process will increase the conductivity of thin films. Amorphous carbons also will deposit on silicon substrate to fabricate solar cell.

ACKNOWLEDGMENT

The author is grateful to all members of NANO-ElecTronic Center (NET) and NANO-SciTech Centre of Universiti Teknologi MARA, UiTM for their support, guidance, criticism and advices in completing this project. More importantly, special thanks to Mr Ishak Anuar as a mentor in this research and Assoc. Prof Dr Mohamad Rusop as my supervisor in completing this research. Finally, a thousand thanks to my parents for support directly and indirectly.

REFERENCES

- [1] Zheng Maxwell, Takei Kuniharu, Hsia Benjamin, Fang Hui, and Zhang Xiaobo, "Metal-catalyzed Crystallization of Amorphous Carbon to Graphene," *Applied Physics Letters*, vol. 96, pp. 63110-63110-3, 2010
- [2] S. M. Mominuzzaman, M. Rusop, T. Soga, T. Jimbo, and M. Umeno, "Photoresponse Characteristics of Nitrogen Doped Carbon/P-silicon Photovoltaic Cell," *IEEE 4th World on Conference on Photovoltaic Energy Conversion*, vol. 1, pp. 302-305, 2006.

- [3] Hongwei Zhu, Jinquan Wei, Kunlin Wang, and Dehai Wu, "Applications of Carbon Materials In Photovoltaic Solar Cells," *Solar Energy Materials & Solar Cells*, vol. 93, pp. 1461-1470, 2009.
- [4] Hiroki Akasaka, Takatoshi Yamada, and Naoto Ohtake, "Effect of Film Structure on Field Emission Properties of Nitrogen Doped Hydrogenated Amorphous Carbon Films," *Journal In Diamond & Related Materials*, vol. 18, pp. 423-425, 2009.
- [5] Sudip Adhikari, Hare Ram Aryal, Dilip Chandra Ghimire, Golap Kalita, and Masayoshi Umeno, "Optical Band Gap Of Nitrogenated Amorphous Carbon Thin Films Synthesized By Microwave Surface Wave Plasma CVD," *Journal Of Diamond & Related Materials*, vol. 17, pp. 1666-1668, 2008.
- [6] Dwivedi, Neeraj Kumar, Sushil Malik, and K. Hitendra, "Studied on Pure and Nitrogen-incorporated Hydrogenated Amorphous Carbon Thin Films and their Possible Application for Amorphous Silicon Solar Cells," *Journal Of Applied Physics*, vol. 111, pp. 14908-14916, Jan. 2012.
- [7] O. Cubero, F. J. Haug, D. Fisher, and C. Ballif, "Reduction of the Phosphorous Cross-Contamination in n-i-p solar Cells Prepared in a Single-chamber PECVD Reactor," *Journal of Solar Energy Materials & Solar Cells*, vol. 95, pp. 606-610, 2011.
- [8] C. Corbella, M. Rubio-Roy, E. Bertran, and J. L. Andujar, "Plasma Parameters of Pulsed-dc Discharge in Methane used to deposit Diamondlike Carbon Films," *Journal of Applied Physics*, vol. 106, pp. 103302-10302-11, 2009.
- [9] A. Mallikarjuna Reddy, A. Sivasankar Reddy, and P. Sreedhara Reddy, "Effect of Substrate Bias Voltage on the Physical Properties of dc Reactive Magnetron Sputtered NiO Thin Films," *Journal of Materials Chemistry and Physics*, vol. 125, pp. 434-439, 2011.
- [10] J. H. Shim, N. H. Cho, and E. H. Lee, "The Effect of Negative Direct Current Bias on the Crystallization of nc-Si:H Films Prepared by Plasma Enhanced Chemical Vapor Deposition," 4th IEEE International Conference on Group IV Photonic, 2007.
- [11] A. Mallikarjuna Reddy, A. Sivasankar Reddy, and P. Sreedhara Reddy, "Effect of Substrate Bias Voltage on the Physical Properties of dc Reactive Magnetron Sputtered NiO Thin Films," *Journal of Materials Chemistry and Physics*, vol. 125, pp. 434-439, 2011.
- [12] Jui-Yun Jao, Sheng Han, Chung-Chih Yen, Yu-Ching Liu, Li-Shin Chang, Chi-Lung Chang, and Han-C. Shih, "Bias Voltage Effect on the Structure and Property of the (Ti:Cu)-DLC," *Journal in Applied surface Science*, vol. 256, pp. 7490-7495, 2010.
- [13] F. Mohamad, A. Yusof, U.M. Noor, M. Rusop, "Effect Of Nitrogen Incorporation To Electrical And Optical Properties Of Amorphous Carbon Thin Film Prepared By Thermal CVD," *International Conference on Electronic Devices, System and Application (ICEDSA)*, pp 241-245, 2011.
- [14] I. Senain, N. Nayan, H. Saim "Structural and Electrical Properties of TiO₂ Thin Film Derived from Sol-gel Method using Titanium (IV) Butoxide," *International Journal of Integrated Engineering (Issue on Electrical and Electronic Engineering)*, pp 29-35, 2010.
- [15] H. Hussin, F. Mohamad, S. M. A. Hanapih, M. Muhammad, and M. Rusop, "Electrical properties of a-C Thin Film Deposited Using Methane Gas as Precursor," *International Conference on Electronic Devices, System and Application (ICEDSA2010)*, 2010.
- [16] A. N. Fadzilah, and M. Rusop, "Effect of Deposition Temperature of Amorphous Carbon Thin Films," *International Conference on Electronic Devices, System and Application (ICEDSA)*, 2011.
- [17] D. Pradan and M. Sharon, "Opto-electrical properties of amorphous carbon thin film deposited from natural precursor camphor" *Applied Surface Science* vol. 253, pp. 7004-7010, 2007.