

# Electrical Properties Of Intrinsic Amorphous Carbon Films From Ethanol Precursor

A. Ishak, M. Rusop

**Abstract:** The intrinsic amorphous carbon (a-C) thin films were successfully prepared by via a bias assisted pyrolysis-chemical vapor deposition (CVD) using ethanol as a carbon source. The effect of deposition temperature on the electrical and structural properties was investigated. The a-C thin films were characterized by current voltage (I-V) measurement, surface profiler, and atomic force microscopy (AFM). The AFM measurements and conductivity result show the surface roughness and resistivity of a-C films decreases with increasing of deposition temperatures. Linear forms were obtained from a-C film contact. The resistivity of intrinsic a-C thin films in the range of 250°C to 550°C is  $22 \times 10^8 \Omega \cdot \text{cm}$ ,  $2.01 \times 10^8 \Omega \cdot \text{cm}$ ,  $4.44 \times 10^7 \Omega \cdot \text{cm}$ ,  $7.26 \times 10^7 \Omega \cdot \text{cm}$ ,  $6.53 \times 10^7 \Omega \cdot \text{cm}$ ,  $4.97 \times 10^7 \Omega \cdot \text{cm}$ , and  $4.32 \times 10^7 \Omega \cdot \text{cm}$ , respectively. Meanwhile, its conductivity is  $2.07 \times 10^{-8} \text{ Scm}^{-1}$ ,  $1.58 \times 10^{-8} \text{ Scm}^{-1}$ ,  $2.25 \times 10^{-8} \text{ Scm}^{-1}$ ,  $1.38 \times 10^{-8} \text{ Scm}^{-1}$ ,  $1.53 \times 10^{-8} \text{ Scm}^{-1}$ ,  $2.01 \times 10^{-8} \text{ Scm}^{-1}$ , and  $2.32 \times 10^{-8} \text{ Scm}^{-1}$ , respectively. The highest and lowest photo responses were found at 350°C, and 500°C, respectively. This electrical properties result showed the custom-made of bias assisted pyrolysis-CVD can produced the semiconducting a-C film comparably with other conventional deposition method.

**Index Terms:** Intrinsic amorphous carbon, Ethanol precursor, Negative bias, Chemical vapor deposition

## 1 INTRODUCTION

The study of electrical properties is one of the most important ways to address many issues concerning the electronic structure and properties of amorphous carbon thin film. The amorphous carbon (a-C) structure has a large variety of forms and the diversity of physical properties depending on the deposition conditions. In the consequence, different electrical properties can be obtained by different deposition method and starting material [1-4]. It was reported that, as-deposited a-C is weakly p-typed in nature with complex structure and high density of intrinsic defects [3-7], thereby contributed for high resistivity and low conductivity. In addition, there is a serious barrier to understanding of the physic of amorphous materials due to no equivalent reliable rule for theoretical analysis [8-10]. In this paper, we studied the effect of deposition temperature on electrical properties of intrinsic a-C thin films from ethanol precursor grown on glass substrates by using a custom made bias assisted pyrolysis-CVD. To the best of our knowledge, preparation and study on electrical, properties by using ethanol precursor deposited with this technique has been rarely reported by any research group. The data are important in the future as a reference.

## 2 Experimental Detail

The cleaning process of glass substrates has been previously reported [3,5,9]. A schematic diagram of bias assisted pyrolysis-CVD is shown in Fig. 1. The ethanol was heated outside the chamber at around 70°C by using the hot platter (Stuart CB162). The vapor of ethanol was pressured into the chamber by using two air pumps (not shown in Fig. 1). The vapor of ethanol, and argon were flowed at 100 mL/min, 150 mL/min, respectively. The argon gas was used as a carrier of deposition particle onto the substrate and as a medium to dispose contaminated particles outside the chamber. The samples were characterized by I-V measurement (Bukuh Keiki EP-2000), surface profiler (Veeco Dektak 150), and Park system XE-100 atomic force microscope (AFM) for electrical, thickness, atomic level properties, respectively.

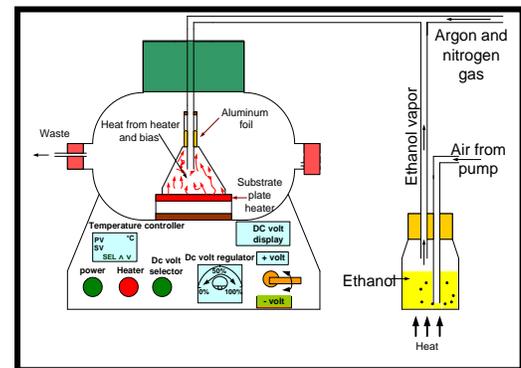


Fig. 1 A schematic diagram of bias assisted-pyrolysis-CVD

## 3 Result and Discussions

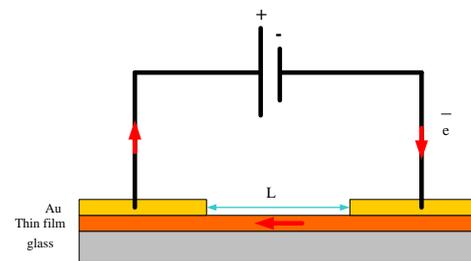


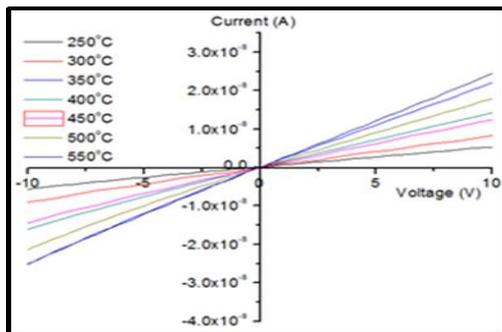
Fig. 2 Cross sectional view of a-C thin films for current-voltage measurement

Fig. 2 showed a cross sectional views of theoretically measurement of a current-voltage (I-V) relationship measured between two metal contacts with the length of L. The resistivity and conductivity of a-C film can be calculated by using equation (1) and (2) [3], respectively where R was the average of resistance; A was the area of metal contact and L was the length between metal two contacts. There were many forms of I-V relationships obtained in the literatures such as linear (ohmic), slightly linear, and nonlinear forms [10,11].

$$\rho = RA/L \quad (1)$$

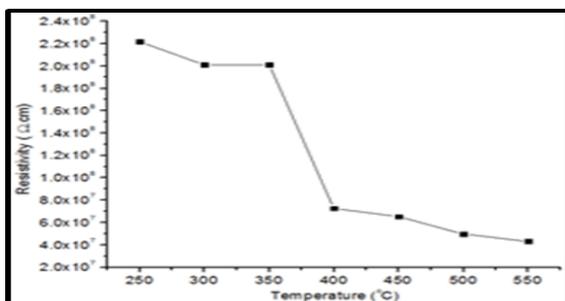
$$\sigma = 1/\rho \quad (2)$$

Metal contact has been studied by others [11,12], to search the suitable metal use with semiconducting a-C film especially from new synthesizing process. We have clearly seen that, ohmic behaviors are found for all samples when the voltage from -10V to +10V is applied as depicted in Fig. 3. The highest slopes were obtained at 550°C while the smallest slope was at 250°C. The smaller slope is attributed to the high density of intrinsic defects. The increase of deposition temperature deformed the structural of a-C thin film to form a more crystallite, thereby the resistivity decreased. The decreasing of the resistivity by the increasing of deposition temperatures was also demonstrated in the literatures [12-15]. It was observed that all deposition temperatures in the range of 250°C to 550°C is suitable to form an ohmic region for aurum and a-C film. Moreover, there was a trend of ohmic behavior for a-C thin films in the range of 250°C to 450°C. The slopes were gradually increased at 250°C until 350°C. However, the slopes were drastically decreased starting at 400°C until 450°C. The ohmic form indicated a-C thin films deposited by bias assisted pyrolysis-CVD are uniform at those applied voltage.



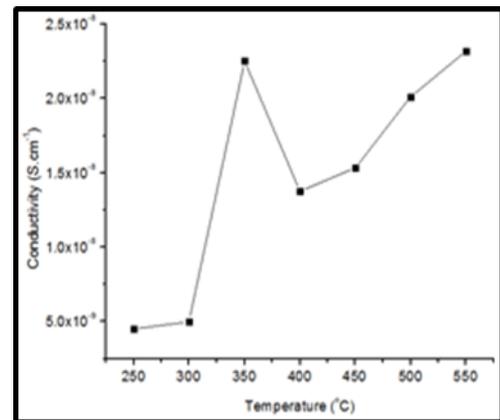
**Fig. 3** Current voltage relationships of intrinsic a-C films at various deposition temperatures

Fig. 4 shows the correlation of resistivity a-C thin films at different deposition temperature in the range of 250oC to 550oC. The resistivity of a-C thin films is calculated as 2,22x10<sup>8</sup> Ω.cm, 2,01x10<sup>8</sup> Ω.cm, 4,44x10<sup>7</sup> Ω.cm, 7,26x10<sup>7</sup> Ω.cm, 6,53x10<sup>7</sup> Ω.cm, 4,97x10<sup>7</sup>Ω.cm, and 4,32x10<sup>7</sup> Ω.cm, respectively. The resistivity of intrinsic a-C films is gradually decreased from 250oC to 550oC as shown in Fig. 4. The resistivity is drastically decreased from 350oC to 400°C, and then steadily decreased from 400°C until 550°C. We observed that, the high deposition temperature strongly influences the resistivity of a-C film. By comparing with semiconductor value [15], it was found that the resistivity of a-C film was in this range of semiconductors thin films.



**Fig. 4** Resistivity of intrinsic a-C thin films deposited on the glass substrate at different deposition temperature

Meanwhile, the conductivity of intrinsic of a-C thin films is calculated by the reciprocal of resistivity. Fig. 5 shows the correlation of conductivity with deposition temperatures. The values of conductivity in the range of 250°C to 550°C is 2.07x10<sup>-8</sup> Scm<sup>-1</sup>, 1.58x10<sup>-8</sup> Scm<sup>-1</sup>, 2.25x10<sup>-8</sup> Scm<sup>-1</sup>, 1.377x10<sup>-8</sup> Scm<sup>-1</sup>, 1.534x10<sup>-8</sup> Scm<sup>-1</sup>, 2.01x10<sup>-8</sup> Scm<sup>-1</sup>, and 2.32x10<sup>-8</sup> Scm<sup>-1</sup>, respectively. The conductivity of a-C thin films is slightly increased from 250°C to 300°C and drastically increased from 300°C to 350°C. However, the conductivity is steadily decreased at 350°C until 400°C, and gradually increased from 400°C until 550°C. This phenomenon might be due to thickness of thin films.



**Fig. 5** Conductivity of intrinsic a-C thin films deposited on the glass substrate at different deposition temperature

The influence of thickness on the conductivity were also demonstrated in literatures [16,17]. The huge numbers of intrinsic of defect are reduced as the deposition temperature increases and therefore give high mobility of electrons to flow. We estimate that the difficulty of electron to move is correlated with the average grain size. The deposition temperature below 350°C had high average grain size as compared with above 350°C. This phenomenon could explain why at above 350°C the conductivity increased. The effect of increasing temperature on the changing conductivity of thin films were also investigated and discussed by others [18-21]. A photo response is defined as the ratio of conductivity under illumination to the conductivity under dark. Table 1 shows the effect of the deposition temperature on the photo response of intrinsic a-C film deposited by bias assisted pyrolysis-CVD. The values of photo response from 250°C to 550°C are 1.07088, 1.2691, 5.9041, 5.2477, 1.1616, 0.8009, and 1.1077, respectively. The results show the photo response is slightly increased from 250°C to 300oC and gradually increased from 300°C to 350°C. A slightly increase of photo response are observed at deposition temperature of 350°C until 400°C. From 400°C until 500°C, the photo responses gradually deteriorated. The highest value of photo response is 5.9041 at 350°C while the lowest value is 0.8009 at 500°C. By comparing with the slope variations, resistivity, conductivity, and photo response results, it can conclude that at deposition temperature of 350°C is the optimum deposition temperature.

**Table1.** The photo response of intrinsic a-C thin film deposited at deposition temperatures in the range of 250°C to 550°C

Temperature	Conductivity, (S.cm <sup>-1</sup> )		Photoresponse
	Under Illumination	In dark	
250°C	4.830x10 <sup>-9</sup>	4.51028x10 <sup>-9</sup>	1.07088
300°C	6.320x10 <sup>-9</sup>	4.980x10 <sup>-9</sup>	1.2691
350°C	1.330x10 <sup>-7</sup>	2.25267x10 <sup>-8</sup>	5.9041
400°C	7.23x10 <sup>-8</sup>	1.37774x10 <sup>-8</sup>	5.2477
450°C	1.780x10 <sup>-8</sup>	1.5324x10 <sup>-8</sup>	1.1616
500°C	1.61x10 <sup>-8</sup>	2.01x10 <sup>-8</sup>	0.8009
550°C	2.570x10 <sup>-8</sup>	2.32x10 <sup>-8</sup>	1.1077

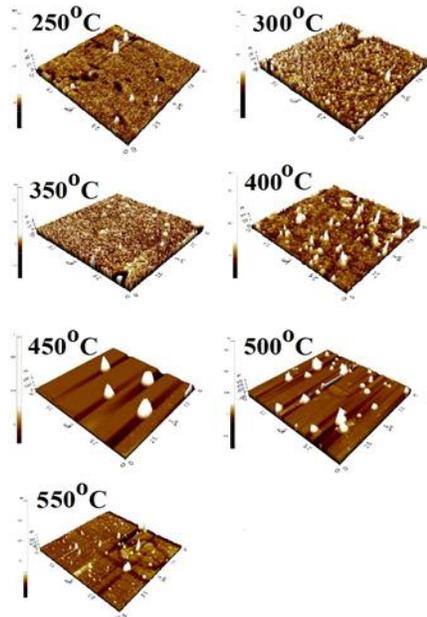
Table 2 shows the influence of deposition temperature with the thickness of a-C thin films. The average of thickness is found below 200 nm for all deposition temperatures. From Table 2, the highest thickness is found at 250oC with the value 182.5 nm and the lowest value is 120.3 nm at 350oC. In our experiment, the deposition temperatures give less significantly effect on the increasing of film thickness. We observe the average thickness is fluctuated as deposition temperature change.

**Table 2** The thickness of intrinsic a-C thin films deposited in the range of 250°C-550°C

Temperature (°C)	Average of Thickness (nm)
250	182.5
300	129.1
350	120.3
400	126.5
450	135.8
500	139.6
550	130.9

The 3-D images of intrinsic a-C thin films were characterized by atomic force microscopy (AFM, XE-100 Park Systems), as shown in Fig. 5 with a scan rate 1Hz and scan size of 10 μm. The images show different forms of particles on the surface topology. The surface roughness from 250°C to 550°C is 0.133, 0.116, 0.317, 0.194, 5.394, 6.419, and 0.417, respectively while the average grain sizes are 3.633, 1.559, 0.8059, 0.9606, 0.8325, and 7.556x10<sup>-6</sup>, respectively. Fewer particles are present for deposition temperature of 250°C, 450°C, 500°C, and 550°C, respectively compared with 300°C and 350°C. In contrast, the compact and uniform of particles are found at deposition temperatures of 300°C and 350°C. The highest surface roughness value is 6.419 nm at 500°C while the lowest surface roughness is 0.403 at 550°C. For the average grain size, 3.633 nm is the highest average grain size for sample 300°C while 7.556x10<sup>-6</sup> is the lowest average grain size for sample 550°C. It was believed that grain boundary and surface roughness are directly related with the electrical properties especially carrier concentration and mobility of the electron. From conductivity comparison, sample at 250°C has the lowest conductivity, and that could be related to the grain size of thin films even though the surface roughness is the smallest. AFM measurement reveals the average grain sizes for the sample at 250°C is the highest as compared with others temperatures and therefore restricts the ability for electron movement. Huang et al [19] reported thickness could also affect the conductivity. In our

experiment, we found the increasing of thickness can influence the average grain size.



**Fig.5.** The AFM images of intrinsic a-C thin films at difference deposition temperatures

**Table 3.** The surface roughness and average grain size of intrinsic a-C thin films at various deposition temperatures

Temperature (°C)	Surface Roughness (nm)	Average Grain Size (μm <sup>2</sup> )
250°C	0.133	3.633
300°C	0.116	1.559
350°C	0.317	1.233
400°C	0.194	0.8059
450°C	5.394	0.9606
500°C	6.419	0.8325
550°C	0.403	7.556x10 <sup>-6</sup>

**CONCLUSION**

The intrinsic semiconducting a-C thin films were successfully deposited by bias assisted pyrolysis–CVD from ethanol precursor. All thin films showed the ohmic behavior with the gold contact. The resistivity of intrinsic a-C thin films deposited in the range 250°C-550°C is 22x10<sup>8</sup> Ω.cm, 2.01x10<sup>8</sup> Ω.cm, 4.44x10<sup>7</sup> Ω.cm, 7.26x10<sup>7</sup> Ω.cm, 6.53x10<sup>7</sup> Ω.cm, 4.97x10<sup>7</sup> Ω.cm, and 4.32x10<sup>7</sup> Ω.cm, respectively. Meanwhile, the conductivity of intrinsic a-C thin films is 2.07x10<sup>-8</sup> Scm<sup>-1</sup>, 1.58x10<sup>-8</sup> Scm<sup>-1</sup>, 2.25267x10<sup>-8</sup> Scm<sup>-1</sup>, 1.3774x10<sup>-8</sup> Scm<sup>-1</sup>, 1.5324x10<sup>-8</sup> Scm<sup>-1</sup>, 2.01x10<sup>-8</sup> Scm<sup>-1</sup>, and 2.32x10<sup>-8</sup> Scm<sup>-1</sup>, respectively. The resistivity is decreased when deposition temperature increased. In contrast, the conductivity was increased as the temperature increased. All thin films had responded with the photon where the highest and the lowest photo response were at temperature 350°C, and 500°C, respectively.

## ACKNOWLEDGMENT

The authors thank to Ministry of Higher Education (MOHE) Malaysia, Universiti Teknologi MARA, Kota Samarahan Sarawak for the scholarship and Research Management Institute (RMI) Universiti Teknologi MARA (UiTM) for the facilities.

## REFERENCES

- [1] R. Gharbi, M. Fathallah, N. Alzaied, E. Tresso, and A. Tagliaferro, "Hydrogen and nitrogen effects on optical and structural properties of amorphous carbon," *Mater. Sci. Eng. C*, vol. 28, pp. 795, 2008.
- [2] C. Corbell, M. Rubio-Roy, E. Bertran, and J. L. Andujar, "Plasma parameters of pulsed-dc discharge in methane used to deposit diamondlike carbon films," *J. Applied Physics*, vol. 106, pp. 103302-10302-11, 2009.
- [3] A. Ishak, K. Dayana, M. H. Mamat, M. F. Malek, and M. Rusop, "Deposition of Amorphous Carbon Film Using Natural Palm Oil by Bias Assisted Pyrolysis-CVD For Solar Cell Applications," *Inter. J. Power and Renew. Energy Sys.* 1 (2014) 12-23.
- [4] 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.
- [5] A. Ishak, M. Rusop, "Structural Properties of Micro and Nanostructured Amorphous Carbon Films from Liquid Hydrocarbon Precursor in Photovoltaic Heterojunction Solar Cell Applications", published in *International Journal of Latest Research in Science and Technology* vol. 3 (2014) pp. 90-94.
- [6] O. Cubero, F. j. Haug, D. Fisher, and C. Ballif, "Reduction of the phosphorus cross-contamination in n-i-p solar cells prepared in a single-chamber PECVD reactor," *J. Solar Energy Materials & Solar Cells*, vol. 95, pp. 606-610 2011.
- [7] A. Mallikarjuna Reddy, A. Sivasangkar Reddy, and P. Sreedhara Reddy, "Effect of substrate bias voltage on the physical properties of dc reactive magnetron sputtered NiO thin films," *J. Material Chemistry and Physics* vol. 125, pp. 434-439, 2011.
- [8] A. Ishak, M. Rusop, "Structural Properties of P-Type Boron Doped Carbon Film from Hydrocarbon Palm Oil for Photovoltaic Heterojunction Solar Cell Device", published in *International Journal of Engineering Invention* vol. 3 (2014) pp. 35-41.
- [9] J. Podder, M. Rusop, T. Soga, T. Jimbo, Boron doped amorphous carbon films grown by r.f. PECVD under different partial pressure, *Diamond and Related Materials* 14 (2005) 1799-1804.
- [10] J. Krauser, A. K. Nix, H. G. Gehrke, H. Hofsaess, C. Trautmann, and A. Weidinger, "Conductivity enhancement of ion tracks tetrahedral amorphous carbon by doping with N, B, Cu and Fe," *Nuclear Instruments and Methods in Physics Research B*, vol.272, pp. 280-283, 2012.
- [11] F.M. Wang, M.W. Chen, and Q.B. Lai, "Metallic contacts to nitrogen and boron doped diamond-like carbon films," *Thin Solid Films*, vol. 518, pp. 3332-3336, 2010.
- [12] A.P. Zeng, Y.B. Yin, M. Bilek, and D. McKenzie, "Ohmic contact to nitrogen doped amorphous carbons films," *Surface Coating Technology* 198 (2005) 202.
- [13] A. Bubenzer, B. Dischler, G. Brandt, P. Koids, rf-plasma deposited amorphous hydrogenated hard carbon thin films: preparation, properties, and applications, *Journal of applied Physics* 54 (1983) 4590.
- [14] Peng Wang, Xia Wang, Youming Chen, Guangan Zhang, Weimin Liu, Junyan Zhang, The effect of applied negative bias voltage on the structure of Ti-doped a-C:h films deposited by FCVA, *Applied Surface Science* 253 (2007) 3722-3726.
- [15] S.M. Sze, *Semiconductor devices physics and technology*, Wiley 1985.
- [16] M. Sakaki, T. Sakakibara, Ionization and reaction mechanism of a reactive cathodic arc deposition of TiN. *IEEE Trans Plasma Science* (1994) 22.
- [17] M. S. Leu, S. Y. Chen, J. J. Chang,, et al. Diamond-like coatings prepared by the filtered cathodic arc technique for minting application, *Surface Coating Technology* 177-178 (2004) 566.
- [18] 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.
- [19] L. Y. Huang, L. Meng, "Effects of films thickness on microstructure and electrical properties of the pyrite films," *Mater. Sci. Eng. B*, vol. 137, pp. 310, 2007.
- [20] E. Liu, L. Li, B. Blainpain, Residual stresses of diamond and diamondlike carbon films, *Journal of Applied Physics*, 98 (2005) 073515.
- [21] 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.A.B. Suriani, A.A. Azira, S.F. Nik, Roslan Md Nor, and M. Rusop, Synthesis of vertically aligned carbon nanotubes using natural palm oil as carbon precursor, *Material Letters* 63 (2009) 2704-2706.