Influence of Deposition Temperature on Electrical and Optical Properties of Boron Doped Amorphous Carbon Thin Films by Positive Bias- Assisted Pyrolysis-CVD

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***Abstract*— Boron-doped amorphous carbon thin films were deposited on glass substrates by positive bias-assisted pyrolysis-CVD at various deposition temperatures in the range of 200°C-350°C and characterize the electrical properties of deposition structured a-C thin film. The electrical, optical and structural properties were characterized by using current voltage (I-V) measurement, UV-VIS/NIR spectrophotometer and Atomic Force Microscopy (AFM). The electrical conductivity of amorphous carbon thin films increased as the temperature increased. The highest and lowest photo responses were found at 300°C. The resistivity is lower and thus gives the conductivity of a-C thin films increased due to the relation between the resistivity and conductivity are inversely proportional. These results show that there is the possibility to improve the electrical for the application of solar cell.**

Keywords—chemical vapor deposition;amorphous carbon; palm oil; thin films

I. INTRODUCTION

For a decade, photovoltaic solar cells are mainly fabricated using silicon material and compound semiconductor which dominated the market share [1-3]. 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 [2-4].

Carbon is a good candidate for an alternatively materials in replacement the remarkable silicon in the future due to the abundantly in nature and suitability as a nature precursor [4-6]. Carbon is found of having a wide band gap and can be tuned from 0.5eV to 5.5eV tailoring with energy band gap of photon by using different type of parameters such as deposition temperature, argon flow rate, annealing temperature, etc [7-9].

A lot of researches have been done in a past few years in amorphous carbon (a-C), hydrogenated amorphous carbon (a-C:H) and nitrogenated amorphous carbon (a-C:N) thin films because of their popular properties such as highly stable, cheap and nontoxic which can be obtained from precursors those are sufficiently available in nature [4-6]. The Apart from that, a-C thin films can be used in device applications since it has a high hardness, high electrical resistivity, high thermal conductivity, high dielectric strength, infrared transparency and anti-reflecting films [4,5,6].

Several techniques have been employed to prepare the amorphous carbon (a-C) thin film including the PLD method [4,5,6], Pulsed Filtered Cathodic method [7-9] and Filtered Cathodic Vacuum Arc method [8-10] which are generally expensive because they involves the use of sophisticated reactors and vacuum systems. On the other hand, the Chemical Vapor Deposition (CVD) technique was also being utilized in the fabrication of a-C. However, several limitations has been experienced by researchers in utilizing the method in terms of selection and delivery of multi component products, the lack of proper volatile precursor and the difficulty in controlling the stoichiometry of the deposition [9-11]. In pursuit of producing high electrical conductivity of a-C the bias assisted pyrolysist CVD will be intoduce for deposited a-C thin film. Beside of deposition temperature, it has equipped with dc voltage parameter which does not have in conventional cvd.

Furthurmore, the dc bias voltage is widely used in many high cost deposition technique for improvement the electrical, optical and structures properties. Bias assisted has many advantages over other deposition technique including simple and in merit in term of tehcnology viewpoint since it has low cost in deposition technique, bigger space size of chamber, easy to handle the sample, and can directly deposited precursor from a vapour phase state to solid thin film onto non crytalline and ctystallinne substrate.

In this work, positive bias-assisted pyrolysis-CVD is used to deposit boron doped a-C thin films and DC bias was applied to support the deposition process. In order to deposit a-C thin films, carbon source precursor is required. Vaporized of palm oil is used as a precursor to deposit amorphous carbon thin films. Therefore, less energy is needed for break down its bonding. The aim of this work is to investigate the effect of temperature on the electrical properties, optical properties and structural properties of a-C thin films.

II. EXPERIMENTAL DETAILS

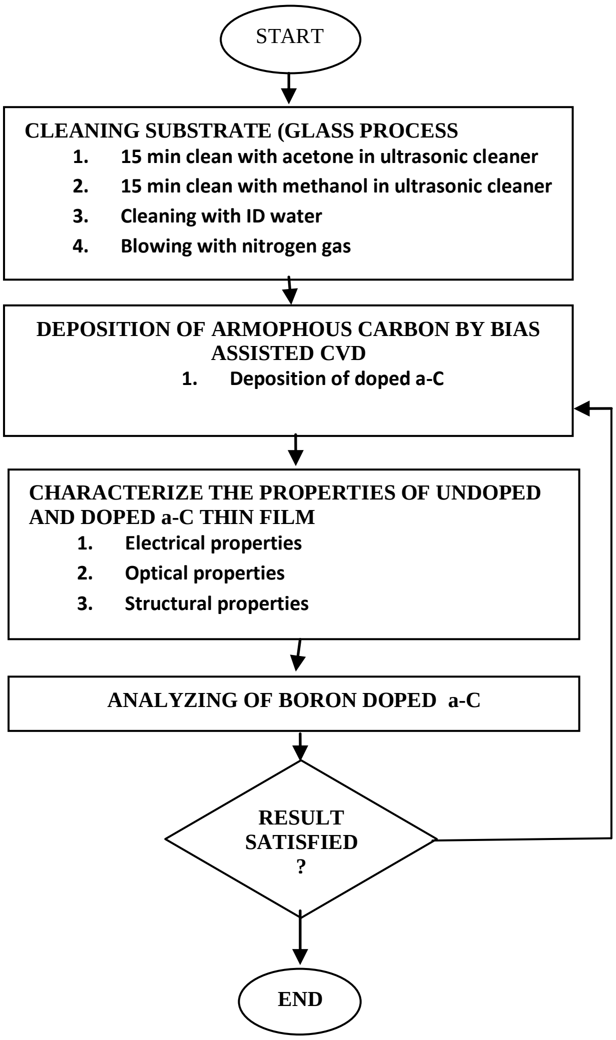

Figure 1: Main flow chart

Figure 1 shows the flowchart of all working process of boron doped amorphous carbon thin film by positive bias assisted pyrolysis cvd. Firstly, the glass substrates were cleaned with acetone (C_5H_6O) to remove the contaminated glass. The glass substrates were cleaned again with methanol (CH_3OH) to remove acetone and de-ionized water to remove methanol for 15 minutes in Ultrasonic Cleaner (power sonic 405), respectively. Finally, the glass substrates were exposing to the Nitrogen gas (N_2).

Figure 2 shows the schematic diagram of Positive bias-assisted pyrolysis-CVD for deposition of amorphous carbon thin films.

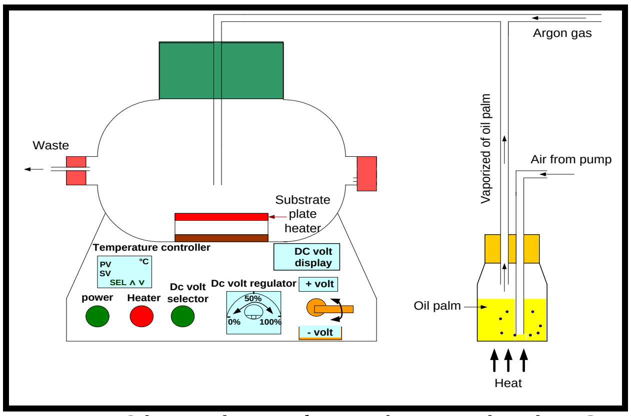

Figure 2: Schematic diagram of Positive bias-assisted pyrolysis-CVD

The cleaned of glass substrates were then placed in the chamber with 10mg of boron to dope at different temperatures. The chamber was heated with temperature starting from 200^{o}C. The palm oil was used as a precursor heated at 150^{o}C with the hot platter (Stuart CB162). A vaporized of palm oil precursor was then pushed into the chamber by two air pumps and the amount of vaporized palm oil, argon pressured into the chamber were set to be constant at 114 mL/min, 186 mL/min, respectively . The argon gas was used for carrier the deposition particles onto the substrate and also to dispose contaminated particles outside the chamber. The range of time of the deposition process is one hour. The experiment continued with temperature at 225^{o}C until 350^{o}C.

Then, all the samples were characterized by using I-V measurement to measure electrical properties, UV-VIS/NIR spectrophotometer (JASCO/V-670 EX) to measure the optical properties and Atomic Force Microscope (XE-100 Park Systems) for measuring the structural properties.

III. RESULTS AND DISCUSSION

A. Electrical Properties

In this research, electrical properties are the important data in solving many issues related to the properties of amorphous carbon thin films [12]. The electrical properties of the boron doped a-C thin films were characterized by using current-voltage (I-V) measurement whereas gold is used as a metal contact. In the I-V measurement, two probes were used as an interface for measuring a current voltage relationship between two metal contacts of a-C doped with boron thin films. There are many forms of current voltage relationships obtained in the literature [15, 16] such as linear (ohmic), slightly linear, and nonlinear forms. Besides the ohmic behavior, the low resistivity and high conductivity were also important as a semiconductor was required.

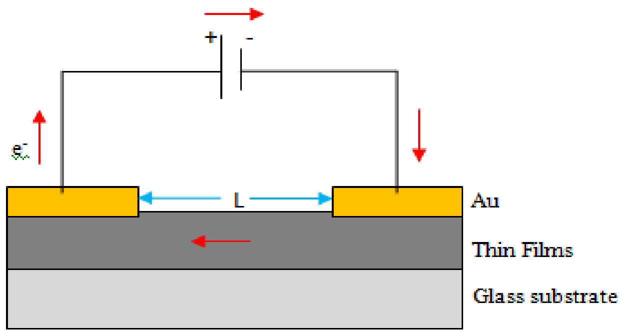

Figure 3: Cross sectional view of the a-C doped with boron thin films deposited on glass substrate

Figure 3 shows a cross sectional view of the boron doped 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 two measured metal contacts and R is resistance measured from -10V to 10V, A is area of metal contact and L is distance between two metal contacts.

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

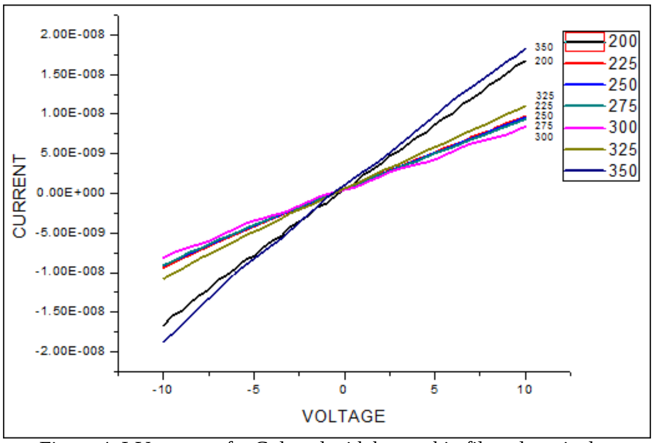

Figure 4: I-V curves of a-C doped with boron thin films deposited at different temperatures

Figure 4 shows IV curves of the boron doped amorphous carbon thin films deposited at different temperature in the range of 200°C to 350°C. The result showed that the boron doped amorphous carbon thin films were in ohmic contact behavior with different value of resistances. These show that gold is a good metal contact compared to other material. The highest slope was found for boron doped a-C thin films at 350°C while the lowest slope contact was at 300°C. The slopes contacts were then slowly decreased starting from 350°C, 200°C, 325°C, 225°C, 250°C, 275°C, and 300°C, respectively. The slope contact became smaller might be due to the additional of high resistance which come from different of thickness as shown in Table 1.

TABLE 1: THICKNESS MEASUREMENT

Temperature(°C)	Average(nm)
200	216.67
225	151.67
250	138.33
275	110.33
300	81
325	182.33
350	251.67

Table 1 shows that the average of thickness measurement of every temperature. The film thickness was measured using surface profiler. The average thickness of boron doped a-C films was calculated as the measured average film thickness.

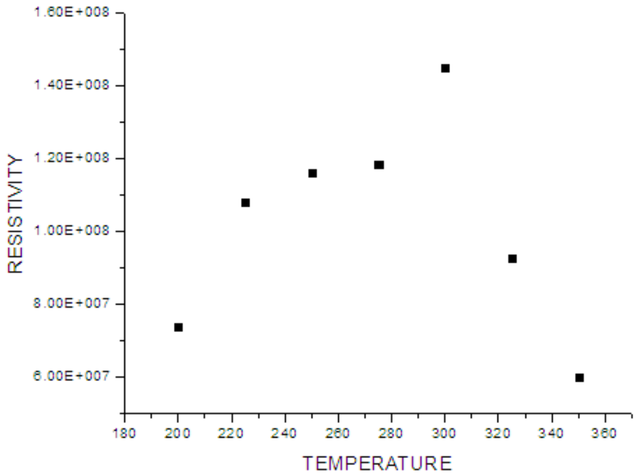

Figure 5: Resistivity curves of a-C doped with boron thin films deposited at different temperatures

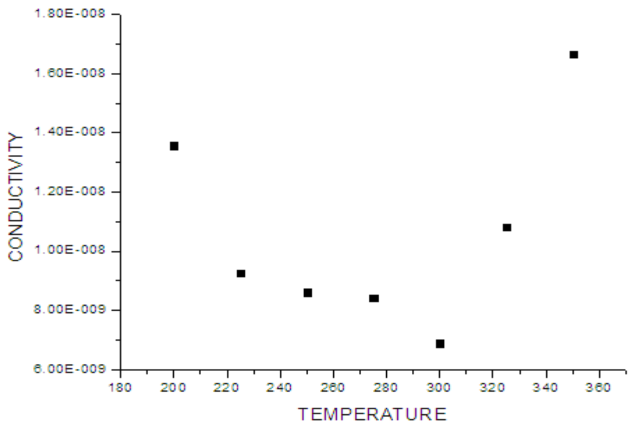

Figure 6: Conductivity curves of a-C doped with boron thin films deposited at different temperatures

Figure 5 and Figure 6 shows the effect of temperatures toward the resistivity and conductivity between two measured mask electrodes. From the Figure 4, it is observed that the resistivity is drastically increased from 200°C until 300°C and decreased starting from 325°C to 350°C. In contrast, the conductivity is drastically decreased starting from 200°C until 300°C and increased between 350°C to 350°C as shown in Figure 5.

Besides that, the density and uniformity of amorphous carbon have contributed for the increasing of the conductivity as proved by Atomic Force Microscope as shown in Figure 11. According to the Figure 5, the resistivity is varied against various deposition temperatures. The resistivity for 200°C is $7.37139x10^7$Ω.cm, increased to $1.44998x10^8$Ω.cm at 300°C and decreased until $6.00314x10^7$ Ωcm at 350°C. The conductivity decreases from 9.26553 $x10^{-9}$S.cm^{-1} to $6.89665x10^{-9}$S.cm^{-1} and increased again until $1.66579x10^{-8}$ at 350^{oC} for boron doped a-C thin films deposited from 250°C to 550°C.

TABLE 2: THE PHOTO RESPONSE OF A-C DOPED WITH BORON THIN FILMS DEPOSITED AT DIFFERENT TEMPERATURE.

TEMPERATURE		CONDUCTIVITY	PHOTORESPONSE
	ILUM	DARK	
200 celsius	1.29E-08	1.36E-08	9.49E-01
225 celsius	6.88E-09	9.27E-09	7.42E-01
250 celsius	6.51E-09	8.61E-09	7.56E-01
275 celsius	7.78E-09	8.44E-09	9.22E-01
300 celsius	2.63E-08	6.90E-09	3.81E+00
325 celsius	7.06E-09	1.08E-08	6.54E-01
350 celsius	1.33E-08	1.67E-08	7.99E-01

From Table 2, the values of photo response from temperature. The values is 200°C to 350°C were $9.49x10^{-1}$, $7.42x10^{-1}$, $7.56x10^{-1}$, $9.22x10^{-1}$, $3.81x10^0$, $6.54x10^{-1}$, and $7.99x10^{-1}$, respectively. The results showed the photo response was decreased from 200°C to 250°C, increased at 275°C and then increased dramatically at 300°C before decreased until 350°C. The highest and lowest of photo response was found at 300°C and 325°C which is $3.81x10^0$ and $6.54x10^{-1}$, respectively. By comparing with the slope variations, resistivity, conductivity, and photo response results, it was believed that at 300°C is directly interrelated with those data and concluded as the optimum temperature for positive bias condition.

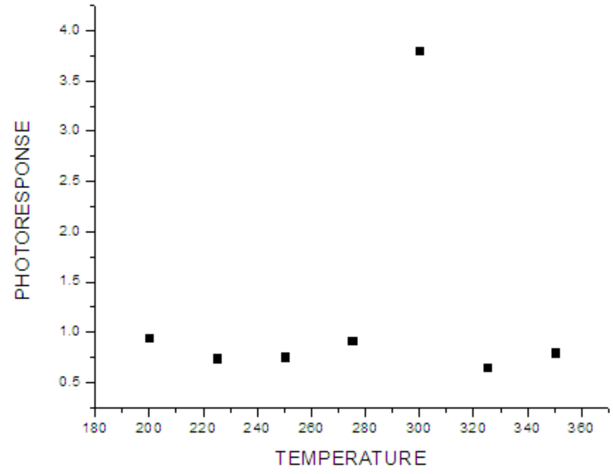

Figure 7: Photo response of a-C doped with boron thin films deposited at different temperatures

Figure 7 shows the effect of different temperatures toward the photo response. A photo response is defined as the ratio of conductivity under illumination to the conductivity under dark.

B. Optical Properties

To investigate the optical properties of amorphous carbon doped with boron thin films, transmittance measurement were carried out in the range of 200-2000nm by using UV-VIS/NIR spectrophotometer (JASCO/V-670EX). Figure 8 shows the UV-VIS transmittance spectrum of boron doped a-C thin films deposited at different temperatures.

According to the Figure 8, it is observed that all samples have high transmittance (T>90%). From this result, the optical properties of a-C doped with boron thin films vary with the composition and the thickness of the films. However, the thickness did not strongly influence the transmittance spectrum due to the smaller average thickness. It was found that in visible light, about 90% of light are transmitted to the thin films.

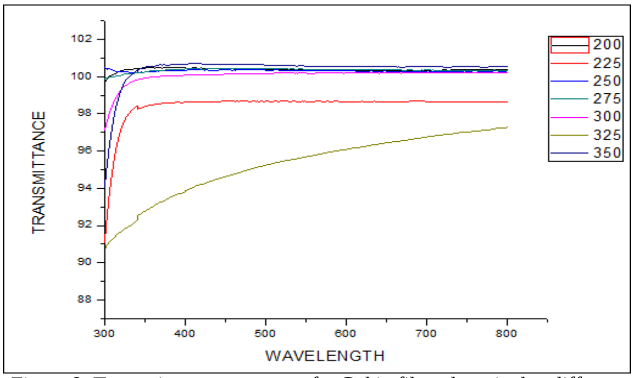

Figure 8: Transmittance spectrum of a-C thin films deposited at different temperatures

Moreover, the absorption coefficient (α) was calculated by the spectral reflectance, transmittance and the film thickness. Figure 9 shows the absorption coefficient of a-C thin films at different temperature. It was showed that thin film at 275°C is the highest absorption coefficient followed by thin films at other temperatures respectively.

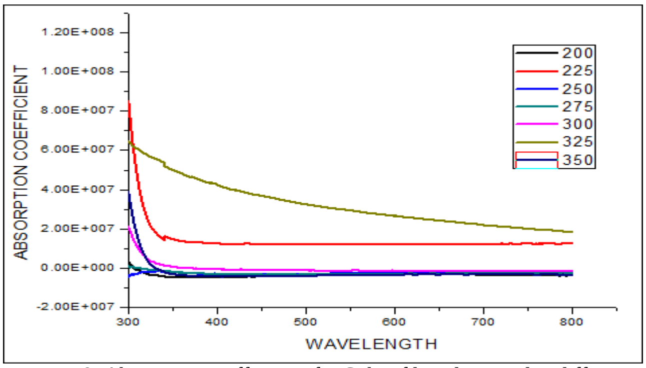

Figure 9: Absorption coefficient of a-C thin films deposited at different temperatures.

The results shown that the absorption coefficient edge where it shifts towards lower photon energy (higher wavelength) region with increasing temperature has a reduction in transparency [11]. From the Figure 9, the low absorption coefficient were found at 250^{o}C and 350^{o}C. It shows that the low absorption coefficient might be related with the inconsistently of localized electron and bonds between the electron to any other allotrope of carbon.

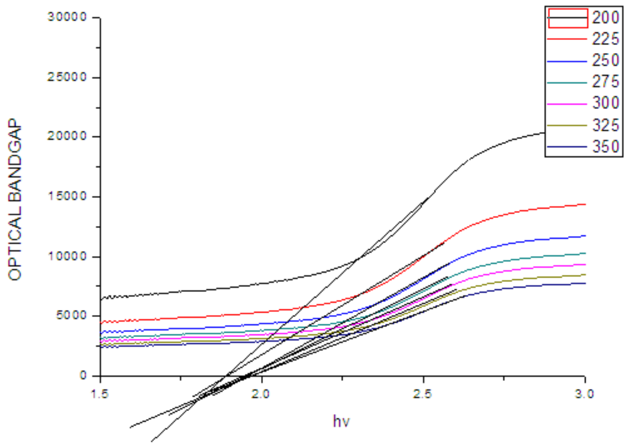

Figure 10: Optical band gap

Figure 10 shows the optical band gaps (Eg) for boron doped amorphous semiconductors were obtained by Tauc relationship as shown in equation below

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

The Eg of the a-C thin films is obtained from the extrapolation of the linear part of the curve at the $\alpha = 0$, using the Tauc relation, where α is the absorption coefficient, B is the Tauc parameter and $h\nu$ is the photon energy. Fiugure 9 shows the plot of $(\alpha h\nu)^{1/2}$ as a function of photon energy ($h\nu$) optical band gap obtained from different deposition temperature. The results show that the decrease of the optical band gaps with the increase of deposition temperature is caused by the sp2 content in the boron doped a-C thin films increases and the sp3 content decreases due to the high ionization rate of the argon gas as compared to carbon ions. This effect could be due to the induced graphitization in the a-C structure and thus leading to the narrow optical band gap [8]. Our results also agrees with the literature reported by Pradhan et.al., that the a-C thin films deposited at lower deposition temperature induced disorder of the structure and have higher sp3 content compared to carbon films deposited at higher temperature [14]. With the increase in deposition temperature, sp2 content increases whereas the defect density decrease which could lead to the narrow band gap. The change of optical properties could be explained due to the variation of sp2 and sp3 bonding content in the a-C thin films.

C. Structural Properties

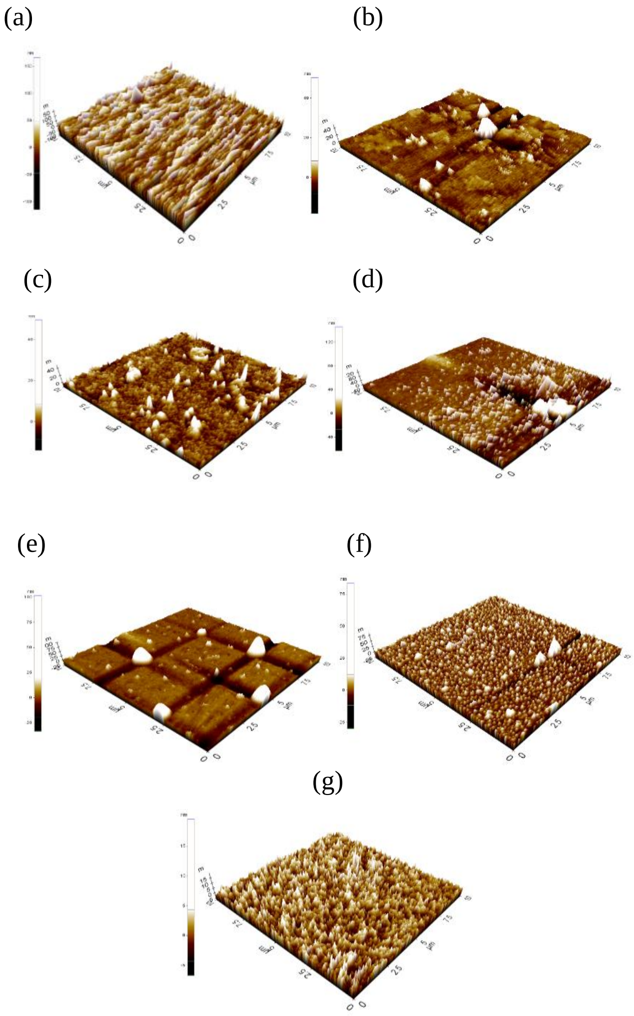

Figure 11: AFM 3-dimensional image of a-C thin films at different temperatures: (a) 200^{o}C, (b) 225^{o}C, (c) 250^{o}C, (d) 275^{o}C, (e) 300^{o}C, (f) 325^{o}C, (g) 350^{o}C.

Figure 11 shows 3-dimensional (3-D) of the a-C doped with boron thin films deposited at different temperatures with a scan rate 1 Hz and scan size of 10 µm. The results show that changing the temperature affects the uniformity and thickness of the amorphous carbon thin films. It can be seen at table below.

TABLE 3: THE SURFACE ROUGHNESS AND AVERAGE GRAIN SIZE OF AMORPHOUS CARBON THIN FILMS DEPOSITED AT DIFFERENT TEMPERATURE.

Deposition Temperatures (^oC)	Surface Roughness (nm)	Average Grain Size (μm^2)
200	0.790	1.099
225	0.435	1.031
250	0.269	0.9162
275	0.151	0.5315
300	0.148	0.5139
325	0.517	1.094
350	0.959	1.155

Table 3 shows surface roughness properties of amorphous carbon thin film and characterized by using AFM (XE-100, Park System). The surface roughness average from 200^{o}C to 350^{o}C is 0.435nm, 0.148nm, 0.151nm, 0.790nm, 0.269nm, 0.959nm, and 0.517nm, respectively. At temperature 225^{o}C and 350^{o}C, the surface roughness has the lowest is 0.148nm and highest value is 0.959nm respectively. The surface roughness of thin film is decreased from 200^{o}C until 300^{o}C and increased starting from 325^{o}C to 350^{o}C. From this result, it shows that, at temperature of 300^{o}C, it has the optimum value of the surface roughness. From Table 2, the grain sizes are 0.9162μm^2, 1.094μm^2, 1.155μm^2, 1.031μm^2, 1.099μm^2, 0.5315μm^2, and 0.5139μm^2, respectively. For the average grain size, 1.155μm^2 is the highest for the sample 350^{o}C while 0.5139μm^2 is the lowest average grain size for sample 300^{o}C. It was believed that the grain boundary and surface roughness are related with electrical properties especially carrier concentration and mobility of the electron.

IV. CONCLUSION

The doped of amorphous carbon with boron thin films were successfully deposited by Positive bias-assisted pyrolysis–CVD. The temperatures were strongly influenced the electrical, optical and structural properties of a-C thin films. All the thin films showed the ohmic contact with the different slope of current voltage relationships. The resistivity of doped a-C with boron thin films from 200^{o}C to 350^{o}C is 7.37139x10$^7\Omega$cm, 1.07927x10$^8\Omega$cm, 1.16126x10$^8\Omega$cm, 1.18451x10$^8\Omega$cm, 1.44998x10$^8\Omega$cm, 9.25203x10$^7\Omega$cm, and 6.00314x10$^7\Omega$.cm, respectively. The resistivity of all thin films increased as the temperature increased. The electrical conductivity of amorphous carbon thin films decreased from 200^{o}C to 275^{o}C but increased again at 325^{o}C to 350^{o}C when the temperature increased from 200^{o}C to 350^{o}C. All thin films at temperature 300^{o}C and 325^{o}C showed the highest and the lowest of photo response, respectively. The optical properties revealed high transmittance which is above 90% for all thin films. The highest and lowest of transmittance were at 275^{o}C and 325^{o}C. However, the highest and lowest of absorption coefficient at visible wavelength were at 250^{o}C and 350^{o}C. It has the optimum value of the surface roughness at 300^{o}C. The AFM images showed that, density and uniformity has correlated with the resistivity and conductivity of doped a-C with boron thin films at different temperatures. These results show that there is the possibility to improve the electrical for the application of solar cell.

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