The Electrical and Optical Properties of Iodine Doped Amorphous Carbon Thin Films

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***Abstract*- In this work, the amorphous carbon (a-C) thin films have been deposited and doped by using Thermal Chemical Vapor Deposition (TCVD) techniques. The deposited a-C thin films have been doped at different amount of iodine in the fixed conditions. The effect of iodine amounts on the electrical and optical properties of iodine doped a-C thin films have been investigated using Current-Voltage (I-V) measurement, UV-Vis-NIR spectroscopy and Raman spectroscopy. As the amount of iodine increase, the conductivity increase while the optical bandgap decrease from 0.21 eV to 0.15 eV with iodine doping from 0 g to 2 g. Then the optical bandgap increase from 0.15 eV to 0.28 eV as the amount of iodine increase from 2 g to 5 g. This is due to increase of sp^2 bonded carbon configuration. The conductivity of the sample increases as the iodine doping increase from 0 g to 2 g. It also shows that iodine doped with 2 g were having the highest photoresponse that may due to neutralization of the dangling bonds. The raman properties proved that the presences of sp^2 and sp^3 bonding in the samples.**

***Keyword* – Amorphous carbon; TCVD; Thin film; Camphor oil; Iodine**

I. INTRODUCTION

In recent years, a-C have been considered for a wide variety of electronic devices , immediate applications as hard coating materials for magnetic disc drives or as antireflective coatings for infrared windows [1]. The previous researcher has reported that a-C thin film also shows has attracted as semiconducting carbon film. Much work has been focused on conductivity of a-C for its great potential in optoelectronic devices and photovoltaic application. A-C has outstanding properties such as chemical inertness, high electrical resistivity, high thermal conductivity and high dielectric strength, high electrical resistivity and tunable band gap by adjusting sp^2 and sp^3 carbon bonding ratio for semiconductor technology [2]. In other hand, the undoped a-C was theoretically has weak conductivity and has the high defects of intrinsic density that will restrict the ability to dope efficiently. Therefore in this work, iodine was used as the dopant for a-C thin films as it has possibility to recover the problems that occurred by un-doped a-C thin film. As reported the doping of impurities such as nitrogen (N), phosphorus (P) and iodine (I) can modify optoelectronic properties. It is by increasing either the electron or hole concentration in the semiconducting device [3]. In this work, a-C thin films were prepared by TCVD technique using natural precursor 'camphor oil' on glass substrate and proceed with the post-deposition iodine doping method. The aim of this work is to investigate the effect of amount iodine doping on the electrical conductivity and the structural and optical properties of a-C thin films.

II. EXPERIMENTAL DETAILS

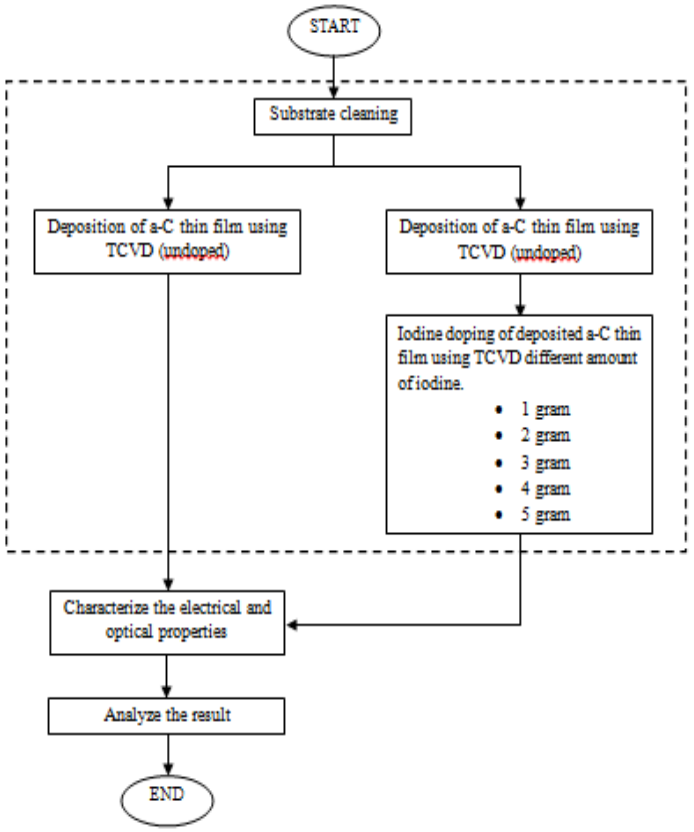

Fig.1: Flow chart for overall process

A) Cleaning substrate

The glass substrates were cleaned by a standard cleaning process. The cleaning process starts with immerging the glass substrate in acetone and was sonicated in ultrasonic cleaner for 10 minutes. The process was repeated by using

methanol and followed by Deionized (DI) water. Finally, the substrates were blow with Nitrogen gas (N_2).

B) Deposition of a-C thin film using TCVD

A-C thin films were deposited by TCVD with camphor oil as a precursor Fig. 1 shows the schematic diagram of TCVD system which is consist of two furnaces, a quartz tube and a water bubbling system. Argon gas (Ar) was supplied from furnace 1 (F1) to furnace 2 (F2) through the quartz tube as the carrier gas. Meanwhile the gas flow rates were maintained at the proper ratio of 30-40 bubbles per minute in the water bubbling system. Ar is the most extensively used inert gas that would not affect the deposition process. The F1 was placed with camphor oil (2 ml) as precursor and heat at 550 °C while the glass substrate was placed at the second furnace. F1 which contain camphor oil was set at 200 °C and vaporized the camphor the deposition process was happen in F2 as the Ar gas was carried the camphoric carbon atoms to be pyrolysis on the substrate surface. Therefore, the a-C thin film was deposited. The deposition of a-C thin film was took about 30 min. The process continues with the cooling for approximately 1 hour.

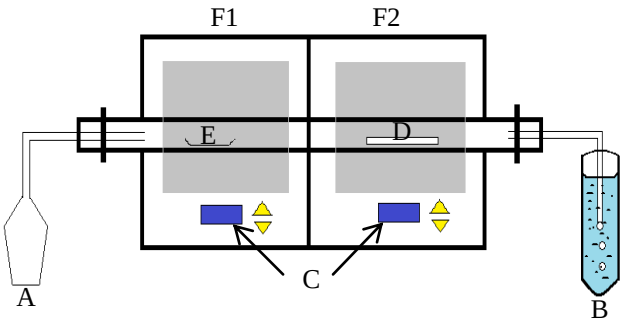

Fig. 2: The deposition of a-C thin film using TCVD (A) Ar gas (B) Water bubbling system (C) Temperature controller (D) Substrate (E) camphor oil

C) Iodine doping of deposited a-C thin film using TCVD

The process of iodine doping a-C thin film was employed using TCVD technique. For iodine doping process, the F1 was kept with the desired amount of iodine and heated at 100 °C while the F2 was placed the deposited a-C (undoped) thin film and fixed the temperature at 300 °C for 30 min. The iodine doped a-C thin films were prepared by TCVD with varying the amount of iodine (1 g ~ 5 g).The argon gas was flowed towards the quartz tube from furnace1 to furnace 2 with the gas flow rate maintained at 30-40 bubbles per minute. Characterization of the deposited a-C thin films and iodine doped thin films were conducted for electrical properties using current-voltage (I-V) measurement system. Then, measurement for optical and structural properties was conducted by UV-VIS-NIR spectroscopy and Raman spectroscopy.

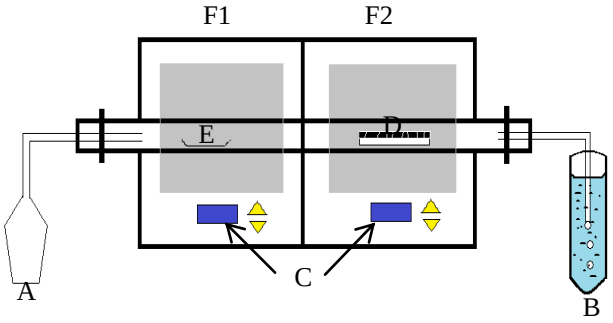

Fig. 3: The iodine doping of a-C thin film using TCVD (A) Ar gas (B) Water bubbling system (C) Temperature controller (D) a-C thin film (E) iodine dopant

III. Result And Discussion

A) Electrical properties

The electrical properties measurement of undoped and iodine doped a-C thin films were carried out by Bukoh Keiki (EP-2000) Solar Simulator System (I-V measurement). The gold (Au) electrodes (thickness = 60 nm) which is a known conductor material were sputtered on top of the thin films deposited on glass substrate by electron beam thermal evaporator to achieve the ohmic contacts between the thin film and the top contact. The I-V measurement was measured in the range of -10 V to 10 V in order to obtain the I-V graph. This is important in order to measure the electronic structure and properties of the a-C thin films [4]. The resistivity (ρ) and conductivity (σ) were calculated from the data obtained by I-V measurement. The resistivity and conductivity of a-C thin films can be defined as in equation (1) and (2).Where R is resistance obtains from I-V graph, w is the width of the electrode, t is the thickness of the sample and L is the length between electrodes.

Equation:

$$Resistivity, \rho = \frac{Rwt}{L} \quad \text{in unit } \Omega \text{ .m} \quad .....(1)$$

$$Conductivity, \sigma = \frac{1}{\rho} \quad \text{in unit S. } m^{-1} .....(2)$$

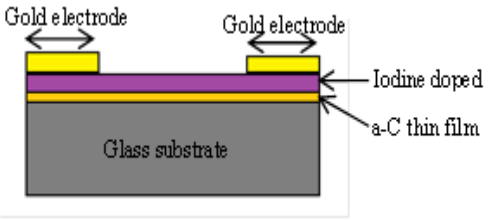

Fig. 4: Cross section of a-C thin film doped with iodine on glass substrate.

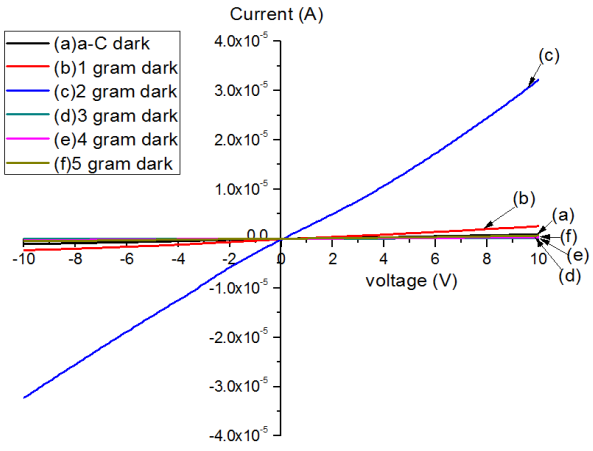

Fig. 5: The I-V curves of a-C thin films doped with iodine in various weight in dark condition

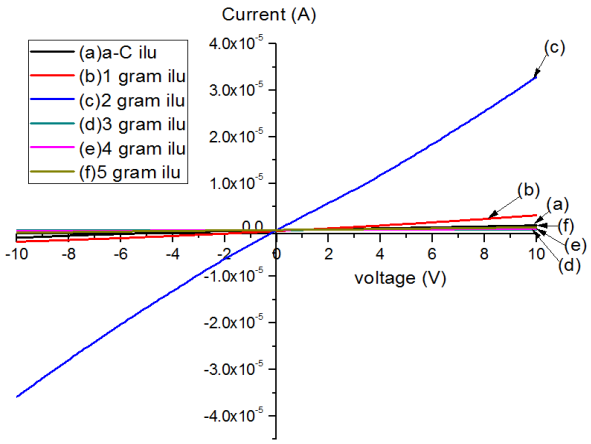

Fig. 6: The I-V curves of a-C thin films doped with iodine in various weight under illumination condition.

Fig. 5 and 6 show the result of I-V characteristics of undoped and iodine doped a-C thin films in different amount of iodine in dark and under illumination conditions. The linear curves indicate ohmic behavior was achieved for the undoped and iodine doped a-C thin films. In addition, the electrical conductivity was plotted in Figure 7 and the result was summarized as shown in Table 1. The effect of the conductivity of the different amount of iodine was investigated in this study. It has been discovered that the conductivity of iodine doped a-C thin films in dark increased from 0.02288 $S.m^{-1}$ to 0.95501 $S.m^{-1}$ as amount of iodine increase from 0g to 2g. Then, the conductivity was decreased from 0.95501 $S.m^{-1}$ to 0.00711 $S.m^{-1}$ as amount of iodine increase from 2 g to 5 g. It has been clearly observed that the appearance of high conductivity indicates at the sample doped with 2 g iodine. This pattern also has been observed on conductivity measured under illumination condition. This revealed that while the conductivity increase, the ratio of sp^2 towards sp^3 also changed. As the conductivity gets higher, the more sp^2 bonding inside the thin film was increased [5]. For under illumination condition, the conductivity increase from 0.02619 $S.m^{-1}$ to 1.03719 $S.m^{-1}$ as amount of iodine increases from 0 g to 2 g. In addition, the conductivity decrease from 1.03719 $S.m^{-1}$ to 0.00773 $S.m^{-1}$ as amount of iodine increases from 2 g to 5 g. This might due to the increase of sp^2 bonding in the thin films and can be related to graphitization [4]. The effect of different amount of iodine to the photoresponse was defined as the ratio of conductivity under illumination over in dark. Table 1 shows that the conductivity and resistivity measured under illumination were higher than the conductivity measured in dark condition. The increment in conductivity value under illumination indicate photoresponse characteristic for the thin films. The result found that the a-C thin films doped with 2 g were having the highest photoresponse. The result indicated that iodine doping at 2 g increased the electrical conductivity and photoresponse may due to iodine dopant could help in neutralization of the dangling bonds thus leading to increase of sp^2 content [6]. It has been discovered that the resistivity decreased as the amount of iodine increased from 2 g to 0 g and vice versa for the value of the conductivity (fig.7). The trend shows that the increasing conductivity and decreasing of resistivity proved that the material is a semiconductor material [7].

TABLE 1.

THE CONDUCTIVITY AND RESISTIVITY OF A-C THIN FILMS DOPEDWITH IODINEIN VARIOUS WEIGHTIN DARKAND ILUMINATION CONDITION.

Weight (gram)	Resistivity (ohm m)		Conductivity ($S.m^{-1}$)	
	Dark	Illumination	Dark	Illumination
0	43.70109	38.18129	0.02288	0.02619
1	15.83397	14.73121	0.06316	0.06788
2	1.04711	0.96415	0.95501	1.03719
3	22.92061	21.55743	0.04363	0.04639
4	63.83669	63.13104	0.01566	0.01584
5	129.36502	140.66379	0.00711	0.00773

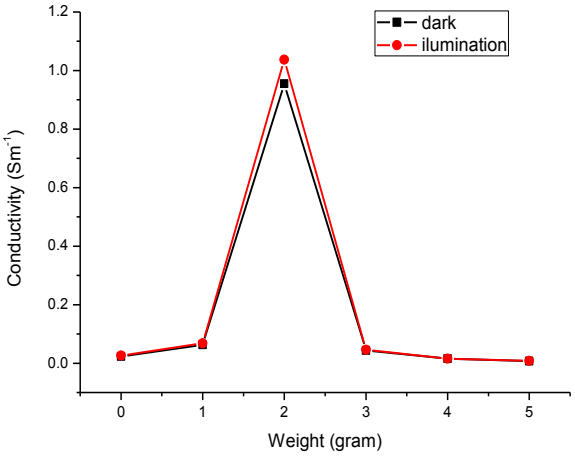

Fig. 7 : The conductivity of a-C thin films doped with iodine in various weight in dark and illumination condition.

B) Optical properties

In this work, the characteristic of the optical properties is been analyzed. The optical properties been studied in range of 200 to 2000 nm. The measurement had been done using Optical Spectrometer JASCO/V-670EX. In addition, the thickness of the sample been measured using Surface Profiler VEECO/D 150+. The graph obtained is the transmittance spectra of the undoped and iodine doped a-C thin film in various amount of iodine versus wavelength in nanometer. Both transmittance and thickness are very important in calculation of absorption coefficient (α) in equation (3) as shown below where t is the thickness of the thin film and T is the transmittance.

Equation:

$$absorption\ coefficient, \alpha = \frac{1}{t}\ln\frac{1}{T} \text{..... (3)}$$

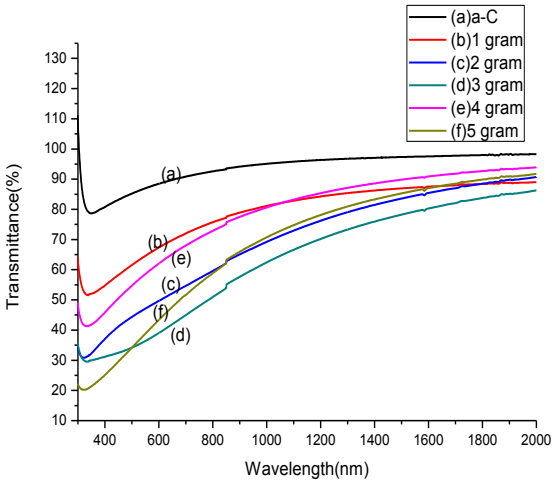

Fig. 8: Transmittance spectra of a-C thin films doped with iodine in various weight

Fig. 8 shows the transmittance spectra of a-C thin films doped with iodine in various amount of iodine. The transmittance of undoped a-C thin film has the highest transmittance compared to the other sample. As the equation (3), the transmittance and thickness of thin films affected the value of absorption coefficient. Therefore, when the transmittance spectra is higher, the absorption distance of light that can be penetrated inside the thin film is decreased [8].The result shows the optical transmittance decreased with the iodine doping which can be explained to be related to the presence of iodine atoms in the film. The transmittance results indicates that there is an optimal condition of the iodine dopant to be maintained during the doping process of a-C thin films for the higher efficiency carbon based solar cell fabrication.Fig.9 shows the absorption coefficient of a-C thin films doped with different amount of iodine. Absorption coefficients indicate the measurement on how far the light can be penetrated inside the thin film before it is absorbed by thin film [5].Therefore, the higher the absorption coefficient value will have the better light absorbed by the thin films. This means that the higher the transmittance, the lower the absorption coefficient [8].

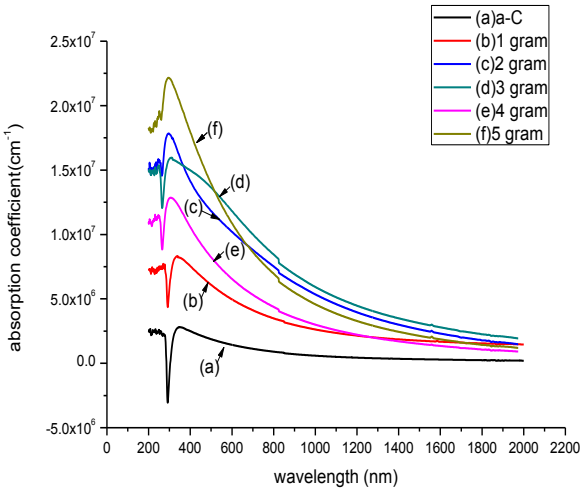

Fig. 9: The absorption coefficient of a-C thin films doped with iodine in various weight

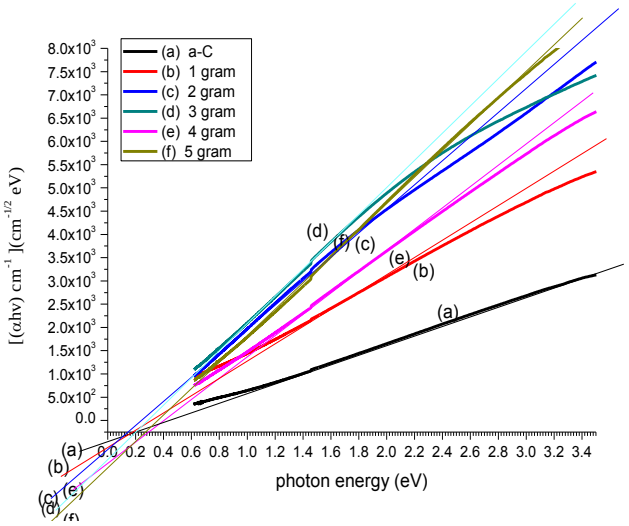

Fig. 10: The plot of $(\alpha hv)^{1/2}$ as a function of photon (hv) of a-C thin films doped with iodine in various weight

TABLE 2.

THE OPTICAL BANDGAP OF A-C THIN FILMS DOPED WITH IODINE IN VARIOUS WEIGHT

Weight (gram)	Optical bandgap (eV)
0 (undoped)	0.21
1	0.18
2	0.15
3	0.20
4	0.30
5	0.28

Fig. 10 shows the optical bandgap versus photon energy of a-C thin films doped with iodine in various weights. The results shows the decrement in the optical band gap from 0.21 eV to 0.15 eV with iodine doping between 0 g and 2 g.The optical bandgap of a-C thin films doped with iodine in various weight is obtained and match the result for conductivity which is when conductivity increase, the optical bandgap is decrease. For 2 g iodine doping condition which can be explained caused by the sp^2content in the a-C thin films increases and has less dangling bonds in the random carbon network due to the presence of the C-I bonding [6]. This effect could be due to the induced graphitization in the a-C structure and thus leading to the narrow optical band gap. Thus the results could be concluded that the optical bandgaps decrease as the conductivity increase. The narrow bandgap been obtained when achieve the optimum weight which is 2 g of iodine. This effect could be due to the induced graphitization in the a-C structure and thus leading to the narrow optical band gap [10]. The small gap between the valence and conduction band for 2 g of iodine may due to its small Eg result. Therefore, the interaction between the lattice phonons and the free electrons and holes will affect the bandgap to be smaller [3-10]. Consequently, the iodine induced graphitization helps to improve optoelectronic properties of a-C films applicable for photovoltaic devices [11].

C) Raman properties

Raman spectroscopy has been frequently used to characterize composite films of crystalline diamond, noncrystalline diamond and graphitic structures [4].Raman spectra were recorded for a-C thin films doped with iodine in various weight such as 0 g, 1 g, 2 g, 3 g, 4 g and 5 g obtained by thermal CVD. Raman spectra obtained are plotted by Gaussian peak-fitting. These peaks are also observed in microcrystalline-graphite and glassy carbon [12]. As shown in fig.11, two prominent broad peaks observed is D-peak and G-peak that is 1342 to 1360 cm^{-1} and 1549 to 1603 cm^{-1} respectively. These peaks are commonly used to characterized the disordered of carbon and been observed in the a-C thin films. The D band peak and G band peak of the a-C thin films before and after iodine doping were observed in the Raman spectrum, indicating the presence of mixed sp^2 and sp^3 bonding. For 2 g iodine doped, it also shows the presence of sp^2 and sp^3 that gives the high conductivity

IV. Conclusion

The effect of a-C thin film doped iodine at different amount (0 g ~ 5 g) using thermal CVD technique has been investigated. The electrical, optical properties of the a-C thin film with iodine doped were measured and compared. The electrical properties of the iodine doped a-C thin films were found increasing and more conductive as the iodine doped from 0 g to 2 g. The conductivity increases from 0.02288 S $.m^{-1}$to 0.95501 $S.m^{-1}$in dark condition. This pattern also has been observed on conductivity measured under illumination

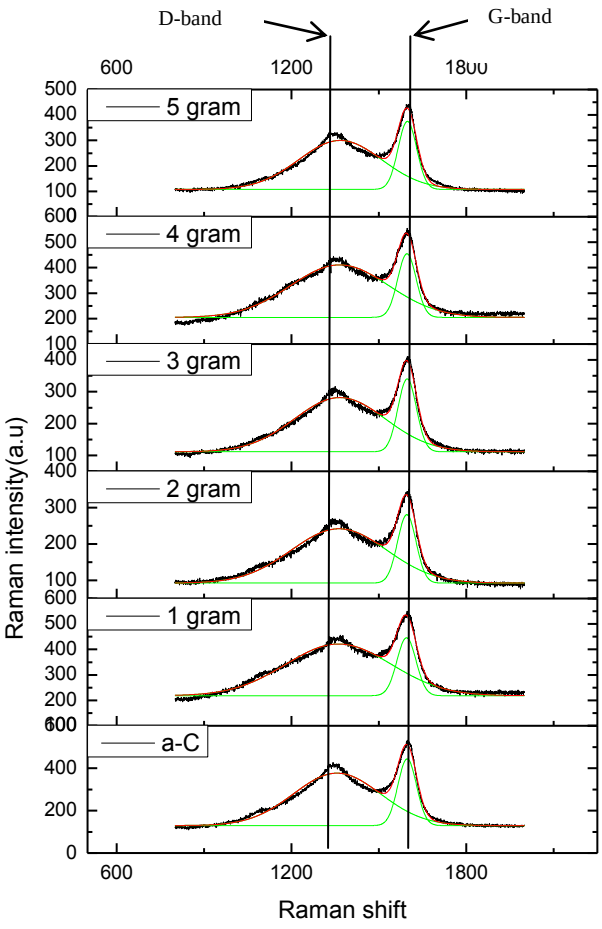

Fig.8: Raman spectra of a-C thin films doped with iodine in various weight

condition. For under illumination condition, the conductivity increase from 0.02619 S. m^{-1} to 1.03719 S. m^{-1} as amount of iodine increases from 0g to 2g. This might due to the increase of sp^2bonding in the thin films and can be related to graphitization of a-C thin films. The optical properties shows that the optical bandgap decrease as the amount of iodine increase from 0.21 eV to 0.15 eV. The 2 g iodine doping condition can be explained by the increase of sp^2 and less of dangling bond due to the presence of carbon iodine bonding that leading to the narrow optical bandgap. The raman properties proved that the presences of sp^2 and sp^3 bonding in the samples. In order to improve and to upgrade this project, there are some recommendations that are suitable to be done next time. Recommendation for future work that could be done is to optimize the deposition parameter such as by varies the deposition temperature and the Ar gas flow rate. These might lead to the higher performance of carbon based solar cell. The improved optimizing value could make the better solar cell thus would encourage the future prospect of clean, low cost and high efficiency carbon solar cell.

ACKNOWLEDGMENT

The authors would like thank the NANO- ElecTronic Center (NET), Faculty of Electrical Engineering (FKE) UiTM, lecturers and friends.

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