Effect of Iodine Incorporation to the Electrical Properties of Amorphous Carbon Thin Films

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***Abstract*—Amorphous carbon (a-C) thin films were deposited on glass and silicon substrates by thermal chemical vapor deposition (CVD) technique using camphor oil as the precursor. After deposited the a-C thin films, the iodine was doped on the a-C thin films using the same technique of deposition of a-C thin film. All the samples were grown in fixed conditions except the doping temperature parameter was varied. The effect of doping temperature in the a-C and a-C:I thin films on electrical, structural and optical properties was characterized by using a standard two-probe method using BUKOH KEIKI (CEP-2000) Solar simulator/Spectral sensitivity Measurement, RAMAN spectroscopy and UV-Vis-NIR spectroscopy respectively. The conductivity of a-C:I thin films increased with the doping temperature up to 450°C and it shows photoresponse under illumination condition. The UV-Vis-NIR analysis was used to obtain the optical absorption coefficient and optical band gap. The RAMAN scattering analysis was used to prove the amorphous structure of a-C and a-C:I thin films.**

I. Introduction

Carbon is the first element in group 14. Carbon is an attractive material existing in a variety of stable forms such as graphite, diamond, nanotubes and fullerenes [1]. Amorphous carbon (a-C) is one of well-known allotrope of carbon. This element has unique properties such as inertness to aggressive chemical, very hard hardness like sapphire, high thermal conductivity, low electrical resistivity and ability to tune its band gap from graphite to diamond [2, 3]. The a-C has received a lot of attention for the possible technological applications such as optoelectronic devices, field emission, hard coating and solar cell. Nowadays, a-C has attracted a great deal of interest as an alternative material for solar cell application because a-C based materials have many advantages over the silicon based material.

In semiconductor industry, silicon was widely used in manufacturing of solar cell applications. Solar cell (mostly silicon-based) fabricated to date are very expensive compared to cost of electricity obtained by conventional process [4]. The a-C is a potential candidate to replace silicon material in the solar cell applications. This is due to its semiconducting nature which shows photoconductivity [5], able to accept dopant [6], tunable band gap ranging from 0.0eV to 5.5eV [5] by adjusting the sp^2 and sp^3 of carbon bonding ratio [7]. Carbon is highly attractive because of its possible application in photovoltaic (PV) solar cells and abundance in natural [8, 9].

In this work, the a-C thin films were deposited on glass and silicon (Si) substrates using the Thermal Chemical Vapor Deposition (CVD) [10]. Thermal CVD is ideal choice to deposit a-C thin film because it is a simple method and suitable for mass production of solar cell. This method also is useful to avoid plasma induced damages on substrate surface. In order to deposit a-C thin films, carbon source precursor is required. Camphor as one of the sufficient precursors available in nature is the natural source of carbon, which is a material of highly stable, cheap and non-toxic [11]. The most common chemical bonds in amorphous and nanocrystalline carbon are sp^2 and sp^3 hybridization [12]. Carbon film deposition by using camphor as precursors could be better than any other carbon sources such as diamond and graphite because a single camphor molecule has 9 sp^3 bonded carbons [13] and 1 sp^2 bonded carbon [14].

However a-C was reported as a weakly p-type in nature and presence of high defect density by complex sp^2 and sp^3 bonded carbon atom mixed structures [15, 16]. So that doping process is required to improve the electrical properties of a-C. Effective doping can modify the properties of a-C and remodel the conduction type. Doping with phosphorus, nitrogen [17], boron [18] and iodine [19] to achieve different types of a-C has been reported. In the other hand, p-type doping in a-C is difficult and few elements has been reported as p-type dopant in a-C materials. P-type doping in a-C is suggested to increase its acceptor thus make it a strong p-type semiconductor and improve the conductivity of a-C.

In this work, a-C thin films were deposited using natural precursor which is camphor oil by thermal chemical vapor deposition (CVD) technique at fixed temperature and then the a-C thin films were doped with iodine (I) using the same technique of deposition of a-C thin films at different doping temperature. The aim of this work is to investigate the effect of iodine incorporation on the electrical properties, optical properties and structural properties of a-C thin film.

II. Experimental Details

A. Material Preparation

The glass substrate was cleaned using three different solutions in ultrasonicator machine (Power Sonic 405) for 10 minutes. The first solution is acetone (C_3H_6O) followed by methanol (CH_3OH) and lastly using deionized (D.I) water. Then, the substrates were dried with nitrogen gas (N_2) blower.

The cleaning process of Si substrate also same with the glass substrate cleaning process but need the further cleaning by etching in H_2O:HF (10:1) solution. Hydrofluoric acid (HF) was used to remove native silicon dioxide from the Si substrates. After that, Si substrates were rinse with D.I water and then the substrates were dried with nitrogen gas (N_2) blower.

B. Thermal CVD Preparation

The a-C thin films were deposited onto the glass and Si substrates using thermal chemical vapor deposition (CVD) method. Figure 1 shows the thermal CVD system's schematic drawing. The thermal CVD system consists of two furnaces, quartz tube and water bubbler system. The furnace 1 was used to vaporize the carbon source precursor which is camphor oil. The furnace 2 was used to deposited a-C thin films by controlling the temperature. The Argon gas acts as the carrier gas which flow from furnace 1 to furnace 2 through quartz tube then to the water bubbler system. The temperature at the furnace 1 was set at 200^{o}C for vaporing the camphor. The temperature at the furnace 2 was set at 550^{o}C for deposited the a-C thin film. The duration for the deposition of a-C thin film was took about 30 minute to complete it. After the deposition of a-C thin film was done, it was characterized and was proceed to the iodine doping process. The iodine was doped into the a-C thin films using the same technique of deposition of a-C thin films. The temperature at furnace 1 was set at 100^{o}C. The deposited a-C thin film was placed at furnace 2 and the doping temperature was varied in between 350^{o}C to 550^{o}C with an interval of 50^{o}C. The duration for this doping process was took about 10 minute for each set of experiments.

The current-voltage (*I-V*) characteristics were measured by using a standard two-probe method and Solar simulator measurement, UV-Vis-NIR spectroscopy was used to investigate the optical properties of thin film and RAMAN scattering analysis was used to measure the structural properties of a-C and a-C:I thin film.

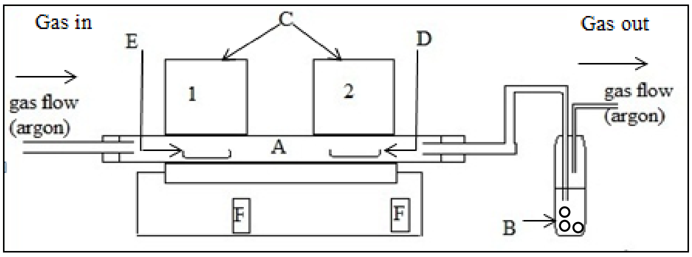

Figure 1: The schematic of CVD (A) Quartz tube (B) Water Bubbler system (C) Double furnace setup (D) Substrate (E) Combustion boat with camphor oil or iodine (F) Temperature controller

III. Result and Discussion

A. *Electrical properties*

The studies on the electrical properties is one of the most important methods to address many issues concerning the electronic structure and properties of a-C thin films [14]. The sputter coater was used to formed the gold (Au) metal contact on a-C and a-C:I thin films to characterize the *I-V*. The gold metal contact was used as the conductor material. The straight line of the *I-V* graph represents a good ohmic contact with gold [13].

The *I-V* measurements of iodine-doped a-C (a-C:I) thin films were measured in dark and under illumination in the voltage range from -10V to 10V. The *I-V* curves were plotted as shown in Fig. 2 and Fig. 3. From Fig. 2 and Fig. 3, it shows that at temperature 450^{o}C has highest slope of ohmic graph followed by temperature at 400^{o}C, 350^{o}C, undoped, 500^{o}C and 550^{o}C. The higher slope represents lower value of resistance for the sample.

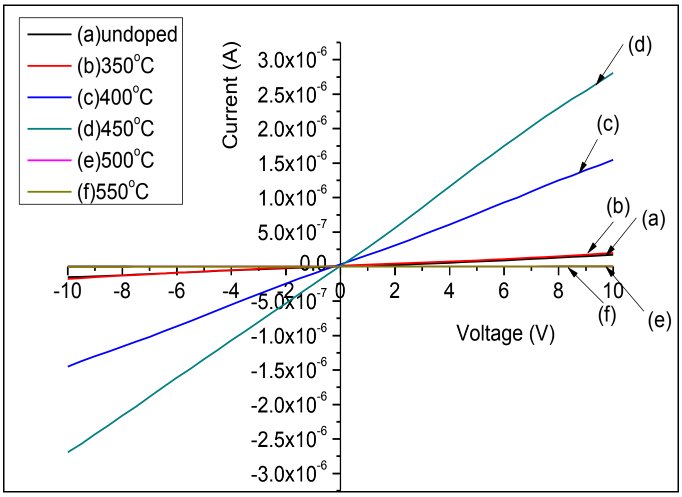

Figure 2: I-V curves of a-C:I thin films doped at different doping temperature in dark condition.

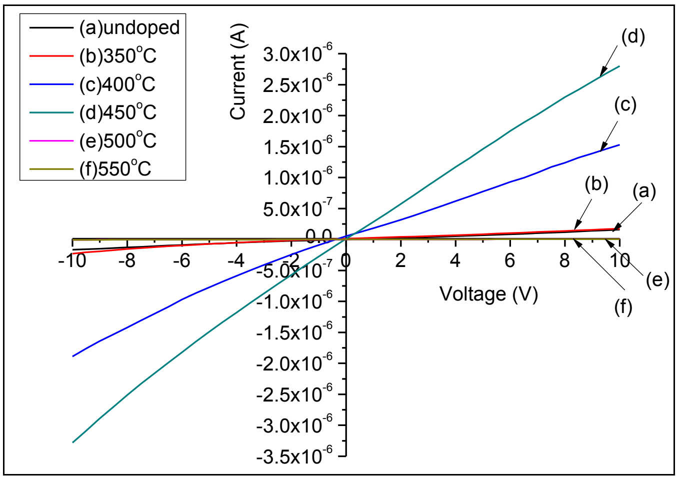

Figure 3: I-V curves of a-C:I thin films doped at different doping temperature under illumination condition.

The value of resistivity (ρ) and conductivity (σ) was calculated from the value of resistance which obtained from *I-V* data using equation (1) and (2) respectively. The value of resistance (R) obtained from *I-V* curve, *w* is the width of electrode, *t* is the thickness of the a-C:I thin films and L is the length of the electrodes.

$$\rho = \left(\frac{V}{I}\right)\left(\frac{wt}{L}\right) \quad \text{in unit } \Omega \text{ cm} \qquad (1)$$

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

From Fig. 4, the results show that the conductivity of a-C:I thin films is increased with doping temperature up to 450°C and the rapid decreased of the conductivity can be seen at the temperature 500°C to 550°C while the resistivity is vice versa. The decreasing of the conductivity maybe the microstructural of the a-C thin film was changed [20]. The result also shows that the electrical conductivity for the sample under illumination is better with the sample in dark. It shows that the a-C thin film has the photoresponse.

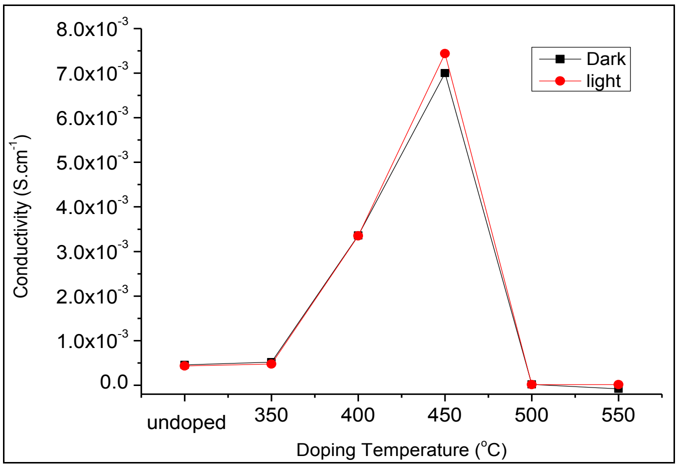

Figure 4: Conductivity of a-C:I thin films doped at different doping temperature

B. Optical properties

The optical properties were investigated by using UV Vis-NIR spectrometer (Jasco/V-670Ex) in the range of 200-2000nm for the a-C (undoped) and a-C:I on the glass substrates while the surface profiler was used to measure the film thickness. The thickness of the a-C:I thin film was in range 103.73nm to 139.53nm. Figure 5 shows the optical transmittance versus wavelength of the a-C and a-C:I thin films doped at different doping temperature. It can be seen that a-C thin film gives high transmission (T %) compared with the a-C:I thin films. The optical transmittance decreased for a-C:I thin films because the presence of iodine atoms in films as reported by literatures [20].

The absorption coefficient (α) of the thin films was obtained by the optical transmittance and the film thickness data. The absorption coefficient is to determines how far into a material light of a particular wavelength can penetrate before it absorbed [21]. The optical band gap (E_g) was obtained from the Tauc relation equation as shown in equation (3).

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

The E_g was obtained from the extrapolation of the linear part of the curve at the α = 0 by using Tauc relation, where B is the density of the localized state constant and hν is the photon energy [2, 21]. To obtained the E_g, the graph of $(\alpha h\nu)^{1/2}$ versus hν was plotted as in Fig. 6 and the values of E_g from different doping temperature was summarized in Table 1. It shows that the optical band gap was found to be in the range of 0.08eV to 0.39eV. The E_g decreased gradually up to 450°C from 0.33eV to 0.08eV. Based on electrical conductivity findings, where the conductivity is high, the E_g become narrow, this might due to the increases of the sp^2 in the films [20]. The results also agree with the reported by Ashraf M.M Omer et al. [22] that the iodine content in the films induced graphitization by decreasing the sp^3.

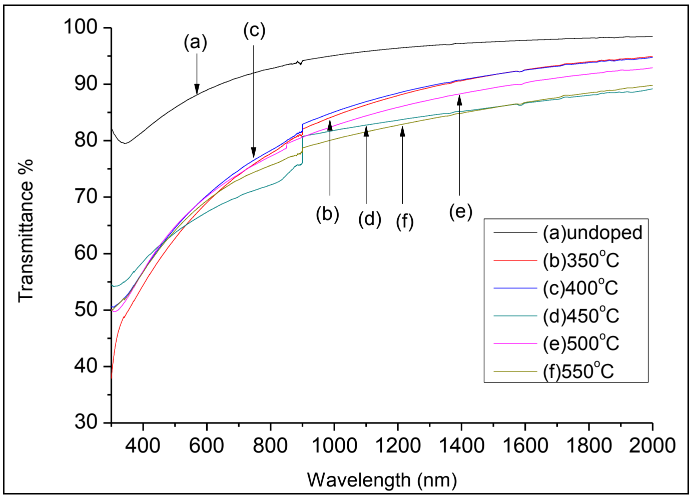

Figure 5: The optical transmittance versus wavelength of the a-C and a-C:I thin films doped at different doping temperature

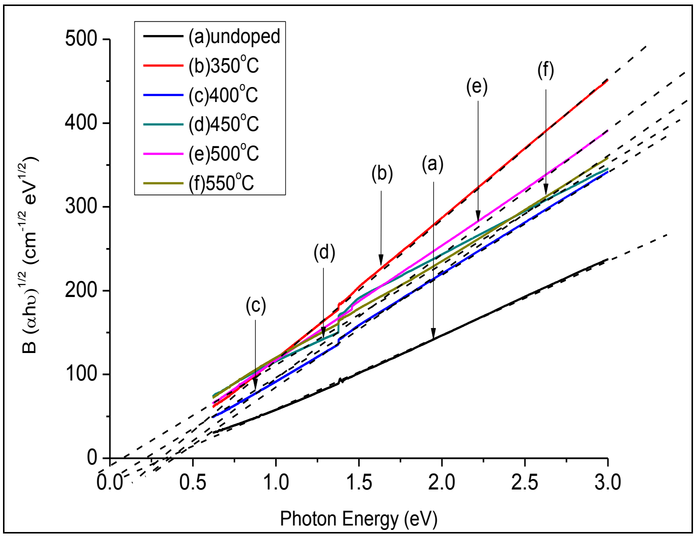

Figure 6: The Tauc plot as a function of photon energy (hν) of the a-C and a-C:I thin films doped at different doping temperature.

TABLE 1: OPTICAL BAND GAP OF A-C AND A-C:I THIN FILMS DOPED AT DIFFERENT DOPING TEMPERATURE.

Sample	Doping Temperature(°C)	Optical Band gap, E_g (eV)
1	0	0.33
2	350	0.30
3	400	0.21
4	450	0.08
5	500	0.36
6	550	0.39

C. Structural properties

Raman spectroscopy has been used to investigate that the amorphous structure has existed on the a-C and a-C:I thin film. Figure 7 shows the result of Raman spectra of a-C and a-C:I thin films doped at different doping temperature. It can be seen that the peak was shows around 1340cm^{-1} and 1590cm^{-1}. The results also agree with the reported by Caihua Wan et al. [16] that the Raman spectra of a-C consists of two broad bands which are graphite peak (G peak) at about 1580 cm^{-1} and disorder peak (D peak) at about 1350 cm^{-1}. It was proved that the a-C (undoped) and a-C:I consists a mixture of sp^2 and sp^3 bonding in the thin films. Therefore, it reveals amorphous nature of the thin films.

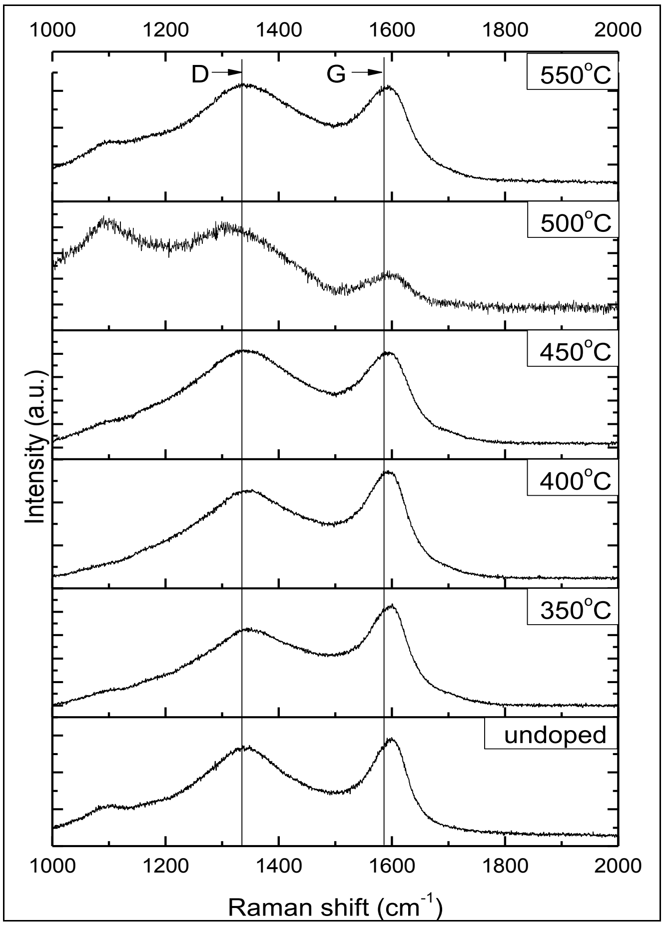

Figure 7: Raman spectra of a-C and a-C:I thin films doped at different doping temperature.

D. Photovoltaic properties

The photovoltaic properties of a-C and a-C:I doped at 450°C doping temperature prepared on n-type Si substrates were investigated by using BUKOH KEIKI (CEP-2000) Solar simulator/Spectral sensitivity Measurement. Figure 8 shows *I-V* characteristics for a-C and a-C:I under illumination while Fig. 9 shows the *I-V* characteristics in dark. It shows a rectifying curve in the dark which proved the formation of heterojunction between a-C:I thin film and n-Si [23]. Table 2 shows the photovoltaic behavior of the a-C and a-C:I under illumination. The result shows that the photovoltaic behavior was improved by doping the a-C with the iodine.

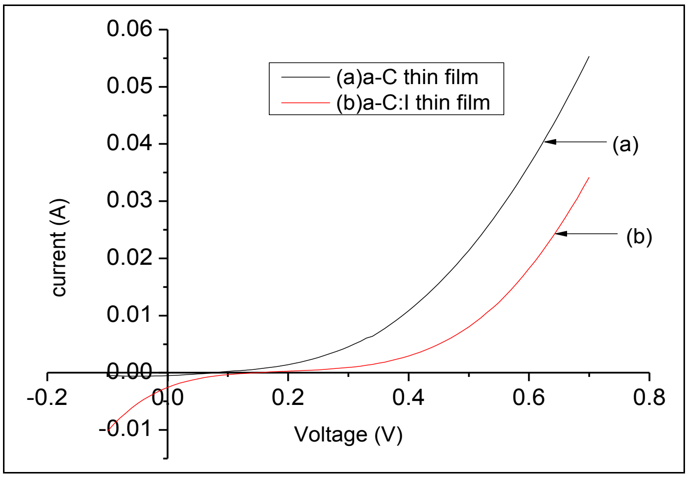

Figure 8: Solar cell graph of a-C and a-C:I doped at 450°C under illumination.

TABLE 2: PHOTOVOLTAIC BEHAVIOR OF A-C AND A-C:I DOPED AT 450°C UNDER ILLUMINATION

Sample	Conversion Efficiency (%)	Fill Factor	Voc (V)	Jsc (mA/cm2)
a-C	1×10^{-5}	226×10^{-3}	0.039	1.61×10^{-4}
a-C:I	5.3×10^{-5}	143×10^{-3}	0.146	2.56×10^{-3}

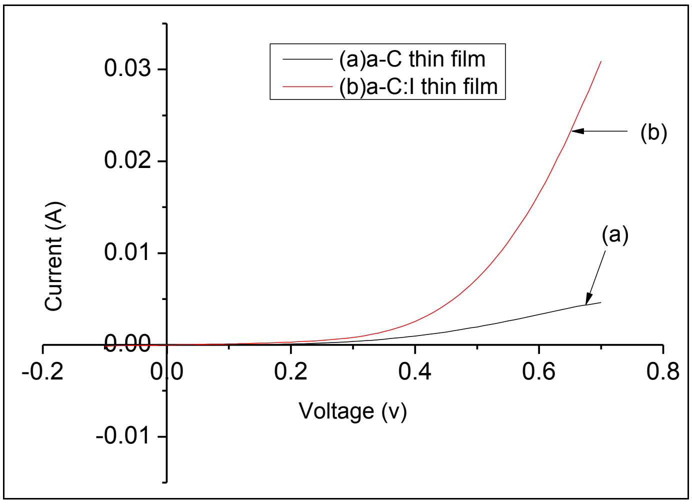

Figure 9: Solar cell graph of a-C and a-C:I doped at 450°C in dark

IV. Conclusion

In conclusion, the effect of doping temperature on the electrical properties, optical properties, structural properties and photovoltaic properties of iodine doped a-C thin films has been investigated. The electrical conductivity was increase by iodine doping. At the doping temperature of 450°C, the higher electrical conductivity 7.44×10^{-3} was obtained. The optical and structural properties were investigated to support the electrical properties. From the optical properties, the E_g decrease from 0.33eV to 0.08eV with the increase of the doping temperature up to 450°C. From the structural properties, the amorphous nature of the both thin films was revealed from RAMAN studies. The electrical conductivity, E_g, photo response and RAMAN spectra of the a-C thin films has related with each other. These result shows that there is the possibility to improve the electrical properties for the application of solar cell by iodine doping.

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