Deposition and characterization of amorphous carbon thin film by thermal CVD

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Abstract. Amorphous carbon-based material has attracted a considerable attention for optoelectronic and photovoltaic applications. This remarkable element has expected to have similar properties as silicon and highly stable. This work is focused on the deposition conditions of amorphous carbon thin film for optoelectronic and photovoltaic application. However, amorphous carbon has a complicated structure and high density of defects. Due to the limited factors of the deposited amorphous carbon film, a doping process is required. The amorphous carbon and iodine doped amorphous carbon thin films were deposited on glass and silicon substrates by thermal chemical vapor deposition (CVD) technique using camphor oil as the precursor. The effect of doping temperature in the a-C and a-C:I thin films on electrical and optical properties were characterized. The conductivity of a-C:I thin films increased with the doping temperature at 450°C and it shows large photoconductivity. The photovoltaic behaviour was improved by doping the a-C with the iodine. Effective doping will encourage the future prospect of low cost, clean and high efficiency of carbon-based device.

1. Introduction
Solar energy has emerged as the most attractive and reliable source of alternative energy because it is clean and renewable. Nowadays, silicon semiconductor is dominating in solar cell technology. However, silicon has a drawback of using under illumination due to the degradation and the cost of these solar cells is very expensive. Thus, research has been conducted to replace the silicon with other suitable material for solar cell technology. Therefore, amorphous carbon (a-C) has been proposed as a replacement of silicon for use as a solar cell material. This remarkable element is a highly attractive
material and a new kind of clean and cheap energy resource. Before this material can be used for such applications, its fundamental properties must first be determined. The semiconducting properties which are a p-n junction (diode) configuration must be investigated. The electrical, optical and structural properties also should be further evaluated. Hence, this work is focusing on the deposition conditions of a-C thin film for solar cell applications by Thermal CVD. Besides, due to the limiting factors of a-C film, a doping process is a requirement to utilize carbon as an alternative material. The main objective of this work is to fabricate the iodine doped a-C thin film through in situ deposition using natural precursor. Then, the conductivity and defect density of iodine doped a-C after in-situ doping method were investigated. The optimization of a-C thin film will encourage the future prospect of clean, low-cost, and high-efficiency carbon-based solar cells. The restriction of a-C application in a solar cell is p-type nature of carbon and high defect density. Amorphous carbon has a complicated structure due to the presence of both σ and π states and high density of defects found within the optical bandgap. Thus, doping of a-C using phosphorus, nitrogen, boron, etc. has been investigated. Although a considerable amount of research works on a-C films has been conducted, the detailed doping mechanism of the films under different deposition conditions has not been fully understood because of the complex atomic structure of the films. Iodine incorporation into a-C films is expected to increase the electrical conductivity and reduce the optical bandgap of the films.

In this work, the a-C thin films were deposited on glass and silicon (Si) substrates using the Thermal Chemical Vapor Deposition (CVD). Thermal CVD is an ideal choice to deposit a-C thin film because it is a simple method and suitable for mass production of the solar cell. This method also is useful to avoid plasma-induced damages on the substrate surface [1]. To deposit a-C thin films, carbon source precursor is required. Camphor as one of the precursors available in nature is the natural source of carbon, which is a material of highly stable, cheap and non-toxic [2]. The most common chemical bonds in amorphous and nanocrystalline carbon are sp² and sp³ hybridization [3]. 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 sp³ bonded carbons and 1 sp² bonded carbon [4].

However, a-C was reported as a weakly p-type in nature due to the presence of high defect density by complex sp² and sp³ bonded carbon atom mixed structures [5, 6]. Thus, the 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 [7], boron [8] and iodine [9] to achieve different types of a-C has been reported. 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 a fixed temperature and then the a-C thin films were doped with iodine (I) using the same technique at different doping temperature. This work aims is to investigate the effect of iodine incorporation on the electrical properties, optical properties and photovoltaic properties of a-C thin film.

2. Experimental Apparatus

2.1. Material preparation

The glass substrate was cleaned using three different solutions in an ultra-sonicator machine (Power Sonic 405) for 10 minutes. The first solution is acetone (C₆H₅O) followed by methanol (CH₃OH) and lastly using deionized (D.I) water. Then, the substrates were dried with nitrogen gas (N₂) blower. The cleaning process of Si substrate is similar to the glass substrate cleaning process but needs further cleaning by etching in H₂O₂:HF (10:1) solution. Hydrofluoric acid (HF) was used to remove native silicon dioxide from the Si substrates. After that, Si substrates were rinsed with D.I water and then the substrates were dried with nitrogen gas (N₂) blower.
2.2. Thin film 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. Furnace 1 was used to vaporize the carbon source precursor which is camphor oil. Furnace 2 was used to deposit a-C thin films by controlling the temperature. The Argon gas acts as the carrier gas which flows from furnace 1 to furnace 2 through quartz tube then to the water bubbler system. The temperature at furnace 1 was set at 200°C for vaporing the camphor. The temperature at furnace 2 was set at 550°C for depositing the a-C thin film. The duration for the deposition of a-C thin film was taken about 30 minutes. After the deposition of a-C thin film was done, it was characterized and the iodine doping process was then conducted. The iodine was doped into the a-C thin films using the same technique. The temperature at furnace 1 was set at 100°C. The deposited a-C thin film was placed at furnace 2 and the doping temperature was varied in between 350°C to 550°C with an interval of 50°C. The duration of this doping process took about 10 minutes 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.

![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](image)

3. Result and discussion

3.1. Electrical properties

The studies on electrical properties are one of the most important methods to address many issues concerning the electronic structure and properties of a-C thin films [10]. The sputter coater was used to form the gold (Au) metal contact on a-C and a-C:I thin films to characterize the current-voltage (I-V). The gold metal contact was used as the conductor material. 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 Figure 2 and Figure 3. Figure 2 and Figure 3 show that at temperature 450°C, highest slope of ohmic graph occurs, followed by the temperature at 400°C, 350°C, undoped, 500°C and 550°C. The higher slope represents a lower value of resistance for the sample.

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

\[
\rho = \frac{(V/I)(w/t)}{L} \quad \text{in unit } \Omega \text{ cm} \\
\sigma = \frac{1}{\rho} \quad \text{in unit } S \text{.cm}^{-1}
\]
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.

From Figure 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 decrease of the conductivity can be seen at the temperature 500°C to 550°C while the resistivity is vice versa. The decrease of the conductivity may be due to the changed microstructural of the a-C thin film [11]. The results also show that the electrical conductivity for the sample under illumination is better than the sample in dark condition. It shows that the a-C thin film has the photo-response. The straight line of the I-V graph represents a good ohmic contact with gold.
3.2. 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 of 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 compared with the a-C:I thin films. The optical transmittance decreased for a-C:I thin films due to the presence of iodine atoms in films as reported by literatures [12-14]. The absorption coefficient ($\alpha$) of the thin films was obtained by the optical transmittance and the film thickness data. The optical band gap ($E_g$) was obtained from the Tauc relation equation as shown in equation (3).

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

The $E_g$ was obtained from the extrapolation of the linear part of the curve at the $\alpha = 0$ by using Tauc relation, where B is the density of the localized state constant and $h\nu$ is the photon energy. The graph of $(\alpha h\nu)^{1/2}$ versus $h\nu$ was plotted as in Figure 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. This might be due to the increase of the sp$^2$ in the films which causes the conductivity increase [15]. The results also agree with the findings reported by Ashraf M.M Omer et al. [16] that the iodine content in the films induced graphitization by decreasing the sp$^3$.

Table 1. The 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                        |
3.3. Photo voltaic properties

The photovoltaic properties of a-C and a-C:I doped at 450°C doping temperature a-C:I thin films were investigated by using BUKOH KEIKI (CEP-2000) Solar simulator/Spectral sensitivity Measurement. Figure 7 shows I-V characteristics for a-C and a-C:I under illumination and it shows a rectifying curve. Table 2 shows the photovoltaic behavior of the a-C and a-C:I under illumination. The results show that the photovoltaic behavior was improved by doping the a-C with the iodine.
Figure 7. 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     | 1E-5                      | 226E-3      | 0.039       | 1.61E-4      |
| a-C:I   | 5.3E-5                    | 143E-3      | 0.146       | 2.56E-3      |

4. Conclusion
In conclusion, the effect of doping temperature on the electrical properties, optical properties and photovoltaic properties of iodine doped a-C thin films has been investigated. The electrical conductivity was increased through iodine doping. At 450°C, the higher electrical conductivity was obtained. The optical properties were investigated to support electrical properties. The value of $E_g$ decreases from 0.33eV to 0.08eV with the increase of the temperature up to 450°C. The electrical conductivity, $E_g$ and photo-response of the a-C thin films are related to each other. The obtained results show that it is possible to improve the electrical properties for the application of carbon-based solar cell by optimizing the iodine doping parameter.

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