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PROPERTIES OF IODINE DOPED AMORPHOUS CARBON THIN FILMS GROWN BY THERMAL CVD

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ABSTRACT

Thin film of undoped and doped amorphous carbon has been achieved using the simple thermal CVD system in an ambient gas of Ar and Ar with I_2, respectively. The electrical and optical properties of the iodine doped amorphous carbon (a-C:I) thin films were studied. The incorporation of iodine into the amorphous carbon thin film results in increase of electrical conductivity as doping temperature increase up to 400°C, which indicates that doping effect of iodine. Heterojuction is confirmed by rectifying current-voltage characteristics of a-C:I/n-Si junction. The decreasing of optical band gap from 0.54 to 0.25 eV after iodine doping was determined which contribute to induce graphitization in the films. Raman result indicates that sp^2 and sp^3 bonded carbon atoms were dominated in the both with and without iodine doped thin films.

Keywords: Amorphous carbon; Iodine doped; Chemical Vapor Deposition (CVD); Thin film

INTRODUCTION

Amorphous carbon (a-C) has a lot of attention as an environmentally benign and economically material viable a wide variety of opto-electronic devices such as hard coating materials for magnetic disc drives, antireflective coatings for infrared windows and as a semiconductor in photovoltaic solar cells [1, 2]. In recent years, there has been progress in carbon based solar cell research and a-C is reported as a remarkable element in carbon based semiconductor to replace silicon in solar cell applications. A-C thin films are attractive materials because they has the unique 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 [3].Furthermore, like other amorphous semiconducting material, it can be doped and made n-type or p-type. However, the a-C

was theoretically has weak conductivity and has the high defects of intrinsic density that will restrict the ability to dope efficiently. This is because carbon possess both π and σ bonds while silicon only has σ states [4]. Therefore, this gives a complicated doping in carbon compared doping in silicon. 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.
In this paper, 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. The a-C thin films were prepared by thermal chemical vapor deposition (CVD) technique using natural precursor 'camphor oil' and proceed with the post-deposition iodine doping method. The aim of this work is to study the effect of iodine doping on the electrical properties of a-C thin film grown on silicon and glass substrates by Thermal CVD. The structural and optical properties of both a-C and a-C:I thin films are also discussed.

EXPERIMENTAL

Amorphous carbon (a-C) and iodine doped amorphous carbon (a-C:I) thin films were grown on glass substrate and n-type silicon by a simple thermal CVD system. This system has a horizontal double furnace, a quartz tube and a water bubbler system. The well cleaned glass substrates were used for the deposition of these thin films. Ar gas is used as a carrier gas while camphor oil used as a carbon source precursor. The camphor oil was put inside the quartz tube at first furnace and heated at 200°C for the deposition of a-C thin films. At the second furnace, the substrate was placed and heated at 550°C for 30 min. Then, the a-C thin films were doped by incorporation of iodine by post deposition process. Iodine in solid form was kept at first furnace and heated in the temperature of 100°C while second furnace for controlling temperature of the deposited a-C thin films, was varied between 300 to 400°C during the doping process. Characterization of the deposited a-C thin films and a-C:I thin films were carried out by using current-voltage (I-V) measurement system for electrical properties. Top metal contacts were sputtered through a mask by sputter coated. The UV-VIS-NIR spectroscopy, Raman spectroscopy were also conducted to analyze the optical and structural properties of a-C and a-C:I thin films.

RESULTS AND DISCUSSIONS

Raman measurements were performed at room temperature to characterize the microstructure of all kinds of amorphous carbons. The most common chemical bonds in amorphous carbon is reported has sp^2 and sp^3 bonding [5]. Figure 1 shows the Raman spectra examined for a-C thin film and a-C:I thin film at different doping temperature. The G and D peaks were located roughly at ~1590 and ~1350 cm^{-1} [6]. Generally, the D peak represents disordered sp^2-hybridized carbon with an amount of sp^3-hybridized carbon in the films due to bond angle disorder [7]. The G peak indicates the existence of sp^2 clustering or π electron delocalization in the samples [8]. Both the G and D peaks intensity were observed in the Raman spectrum of both thin films, indicating the coexistence of sp^2 and sp^3 bonding which reveals the amorphous nature in the samples.

Raman G peaks shift towards higher wavenumber and become narrower with the doping temperature increase up to 400°C indicates the increase sp^2 carbon atoms and growth of graphite domains [9].

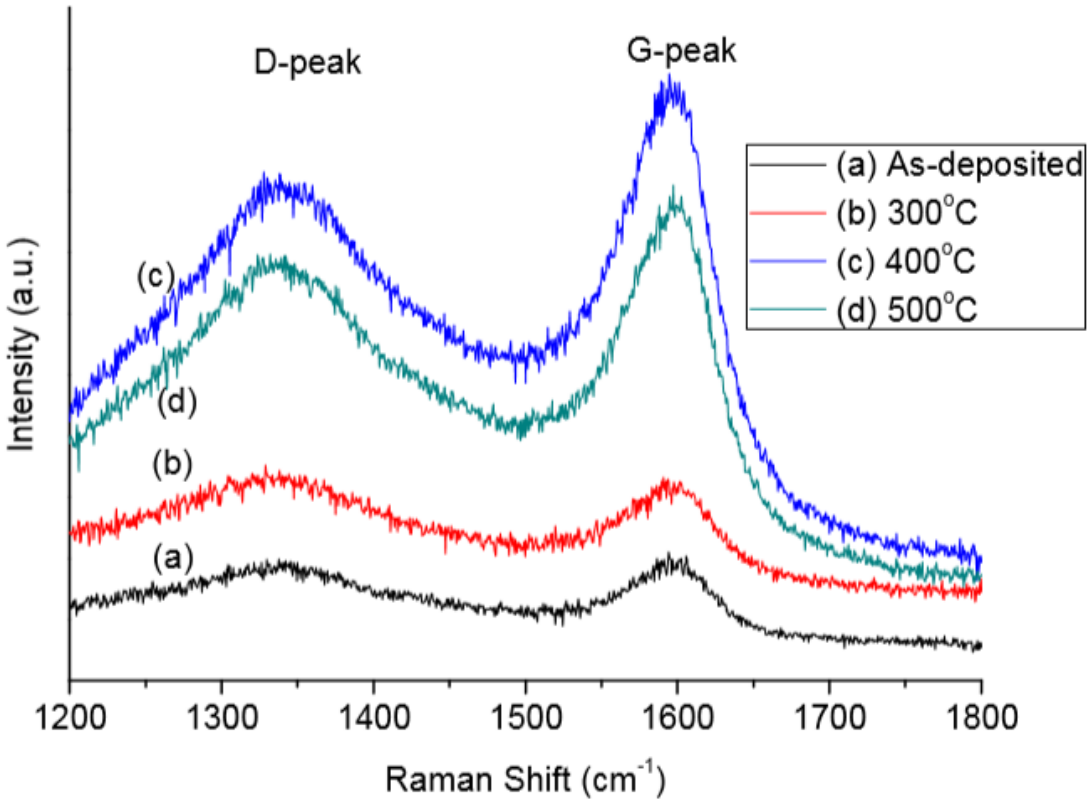

Figure 1: Raman spectra of as-deposited a-C and iodine doped a-C thin films

The UV-Vis-NIR measurement was performed to measure the optical properties. Figure 2 shows the transmittance of a-C and a-C:I thin films. It can be observed that the transmittance decreased after iodine doping which can be related to the existence of iodine atoms in the film [10]. The transmittance of a-C:I thin film doped at 400°C shows the lowest transmittance in the visible region and this result indicates it has the maximum photon absorbance. Optical band gap was obtained from the extrapolation of the linear part of the curve by using the Tauc relation: $(\alpha h\nu)^{1/2} = B(Eg - h\nu)$ [11], conventionally defined for amorphous semiconducting materials. Where α is the absorption coefficient, $h\nu$ is the photon energy, B is the Tauc parameter and E_g is the band gap energy of the material under investigation.

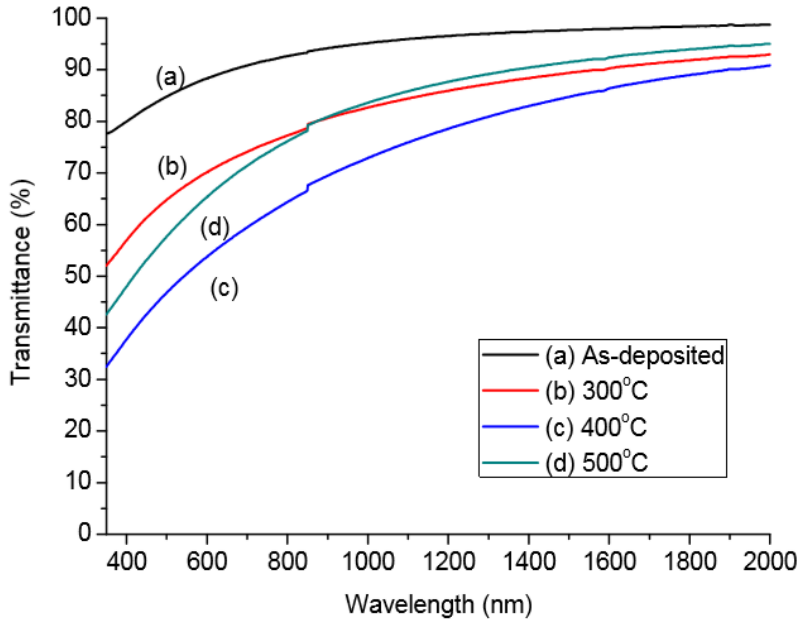

Figure 2: Transmittance of a-C:I thin films at different doping temperature

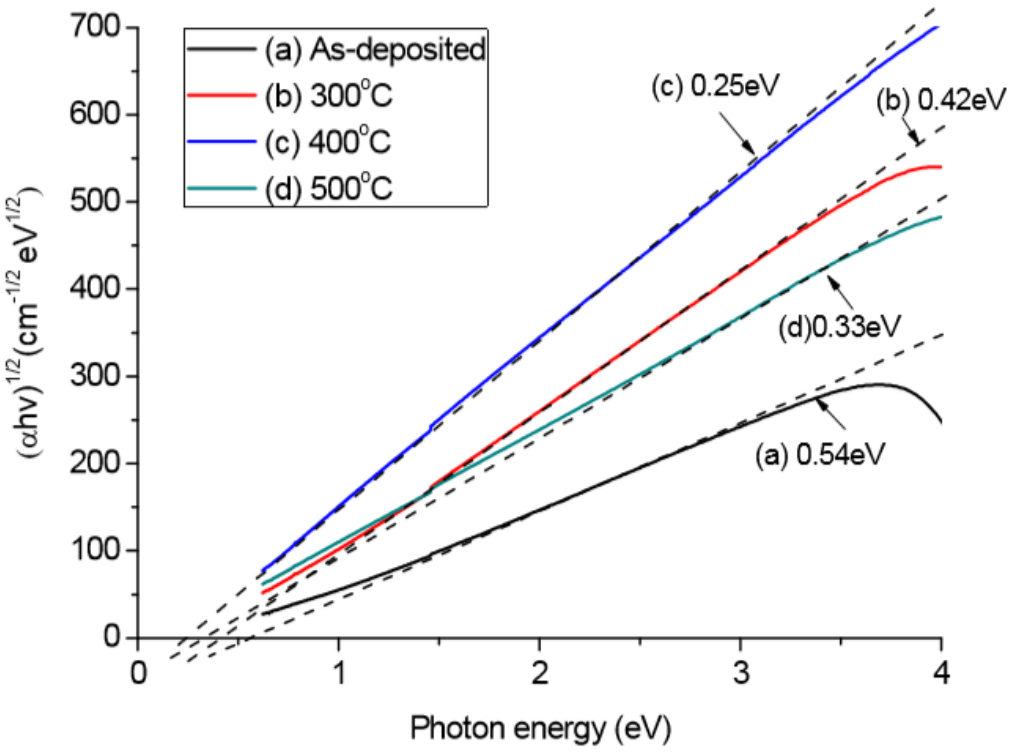

Figure 3: The Tauc plot of $(\alpha h\nu)^{1/2}$ as a function of photon energy for a-C:I thin films

The optical band gap gradually reduces from 0.54 to 0.25 eV as the doping temperature is

increased up to 400°C, then increase to 0.33 eV at 500°C as shown in Figure 3. This result indicates that the optical band gap of a-C:I thin film is narrower with the increasing of doping temperature up to 400°C can be related to the tendency of a-C:I thin film towards an increasing of sp^2 bonding inside the film, which contains delocalized electrons [12]. These free electrons give rise to an increase in conductivity of the films. While sligth increase of optical band gap at 500°C may due to the defect generation inside the thin film.
The electrical properties of the a-C:I thin films were tested by using two point probe current- voltage (I-V) measurement in the dark and under illumination. Figure 4 illustrates the I-V characteristics of both a-C and a-C:I thin films. As shown in the Figure 4, the ohmic behavior exhibits between the top contact (Au) and the both a-C and a-C:I thin films. This behavior indicate a relatively low barrier between the semiconductor and the metal to allow electrons to flow in and out of the interface freely when the voltage is applied [13]. The electrical conductivity of the a-C thin film and a-C:I thin film was carried out by I-V measurement data and the film thickness data at room temperature. The electrical conductivity of the both a-C and a-C:I thin films is shown in Figure 5. It can be observed that the electrical conductivity increase after iodine doping process. This could be explained due to the C-I bonds replace the C-C bonds due to the formation of a C-I network [14].

The electrical conductivity was found to be increased from 1.55×10^{-4} (as-deposited) to 1.64×10^{-3} $\Omega^{-1}cm^{-1}$ doped at 400°C and then decreased to 3.65×10^{-4} $\Omega^{-1}cm^{-1}$ as doping temperature increase up to 500°C. The electrical conductivity value obtained by using this simple thermal CVD technique is higher in comparison with the electrical conductivity value of a-C thin film ($\sim10^{-7}$ Ω^{-1} cm^{-1}) reported by B. Kleinsorge et al.[15] and O.S. Panwar et al.[16].The result indicated that iodine doping increased the electrical conductivity and showed that iodine dopant could help in neutralization of the dangling bonds. Therefore, this may be ascribed to that the role of iodine atoms in assisting carbon atoms to form sp^2 bonding and to facilitate graphitization which decreased the optical band gap in a-C thin film [17, 18]. However, the electrical conductivity decreases at 500°C may be due to the degradation of the conductive film thus give rise the optical band gap. Furthermore, it was found that electrical conductivity value under illumination shows low photo response characteristic in the thin film.

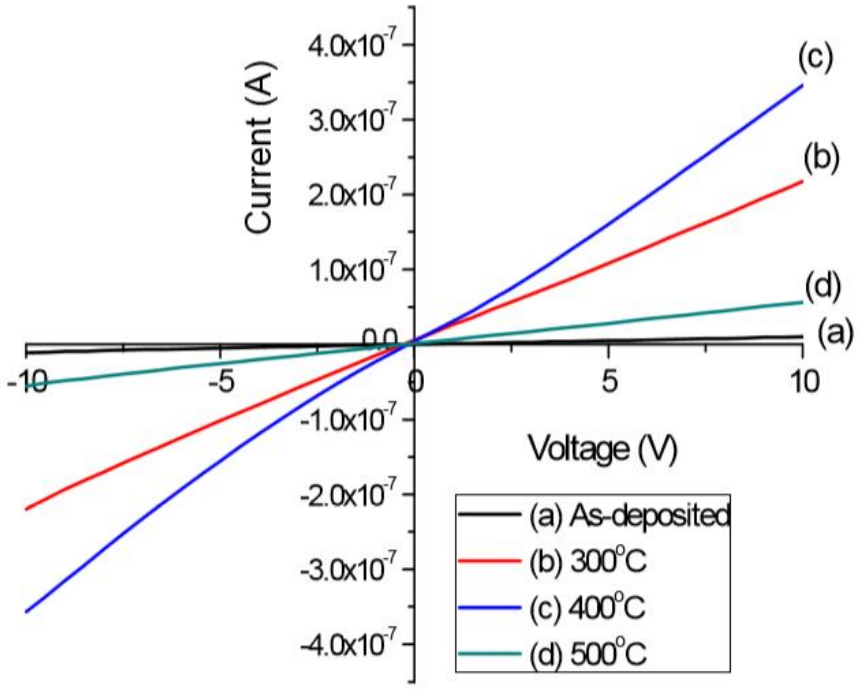

Figure 4: Current-Voltage (I-V) characteristics of both a-C and a-C:I thin films

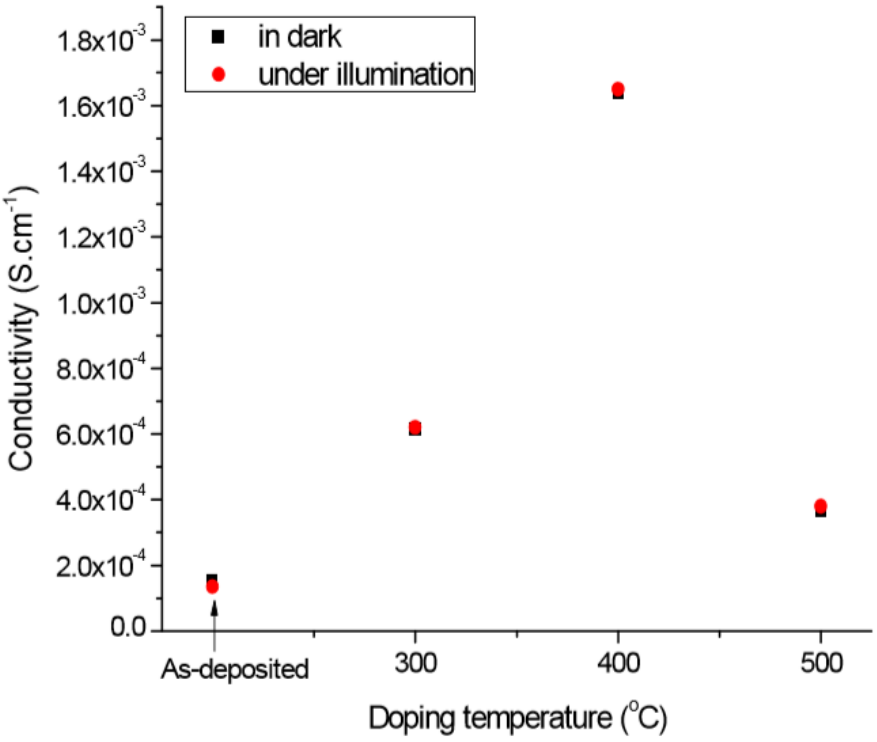

Figure 5: The conductivity of a-C:I thin films at different doping temperature

The current-voltage characteristics of the a-C/n-Si cell without and with Iodine doped in dark condition is shown in Figure 6. It can be seen that both cells displayed rectifying characteristics which indicates the formation of heterojunction. This result may lead to conclude that the ohmic characteristic of the metal contacts gives the rectifying behavior to the interface of the p-n junction between a-C thin films and silicon. Iodine doping proved that the iodine dopant can help to reduce the defects and improve the conductivity [19]. Thus, the improvement of the performance of the junction between a-C/n-Si cell and a-C:I/n-Si cell.

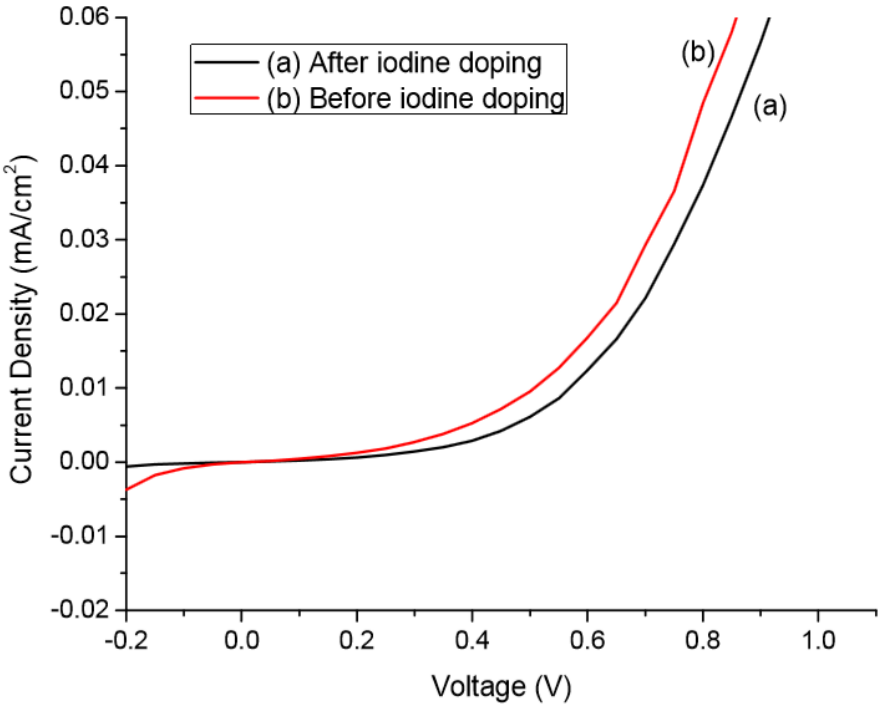

Figure 6: The current-voltage characteristics of a-C/n-Si heterojunction diode in the dark (a) a-C/n-Si cell (as-deposited) and (b) a-C:I/n-Si cell (doping temperature at 400°C)

CONCLUSION

We have investigated the effect of iodine doping on the properties of a-C thin films deposited by a simple Thermal CVD. The electrical, optical and structural properties of the a-C thin films are greatly affected by the incorporation of iodine into the film. The optical band gap of a-C thin films decreased from 0.54 to 0.25 eV as doping temperature increase up to 400°C which contribute to induce graphitization in the films. The room temperature electrical conductivity increases with the presence of iodine atoms in the a-C thin films. The sample doped at 400°C is found to be a higher electrical conductivity due to contain the π delocalized electrons and has the rectifying properties. The amorphous nature of the films were examined by Raman studies which show that the sp^3/sp^2 bonding change when iodine doping was employed. It has been

observed that sp^2 content present in the films increases after iodine doping. This explains that the role of iodine dopant in assisting carbon atoms to facilitate graphitization, improved the conductivity and reducing the defects in the films. Raman studies are strongly co-related with the electrical and optical properties.

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