

# Electrical Characterization of Iodine Post-Doped Amorphous Carbon Thin Films By Natural Precursor

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**Abstract**—Carbon based solar cell has attracted researcher attention as a replacement of silicon for use in solar cell material in the future. The amorphous carbon thin films doped with p-type iodine have been prepared by using a thermal CVD system. In this work, the effect of doping time for the electrical properties of nanostructured iodine doped amorphous carbon thin films was investigated. The thin films were characterized and analyzed using current-voltage (I-V) measurement, UV-VIS-NIR spectroscopy, Raman spectroscopy and FESEM. The current-voltage results shows that the doping time of 10 minutes has the highest electrical conductivity of a-C:I thin film. Raman and FESEM results indicate the amorphous structural in a-C:I thin films and consists of sp<sup>2</sup> and sp<sup>3</sup> bonded carbon atoms. The electrical properties were affected by the existence of iodine atoms in amorphous carbon thin films.

**Index Terms**— Amorphous Carbon; Camphor; Iodine Doping.

## I. INTRODUCTION

Since the invention of solar cell, continues efforts have been done to investigate any materials to replace silicon that having high stability, high efficiency, low cost and environmentally production process. The drawback of silicon based solar cell is lifetime degradation under using light illumination. Amorphous carbon (a-C) material has captured researcher attention in a variety possible application such as hard-coating, gas sensor and other optical or electronic devices [1, 2]. The a-C based material has a tunable band gaps by varying sp<sup>2</sup> and sp<sup>3</sup> bonded carbon content which are useful for photovoltaic application [3]. Other than that, a-C based material has outstanding properties such as unresponsive to any aggressive chemical, high hardness, high electrical resistivity and optical transparency [4, 5]. In this work, camphor oil which is one of the natural carbon precursor has been use to deposit the a-C thin film. The camphor is a fossil based carbon precursor, cheap, eco-friendly and no fear of depletion [6]. Camphor also

can be purified to requiring quantity by a thermal chemical vapor deposition (CVD) in order to bring down the low cost of fabrication. However, a-C thin film is revealed as a weakly p-type and has complicated structure due to the presence of both  $\sigma$  and  $\pi$  states thus leading to high density of defects. Because of this reason, the effectiveness of using this material for carbon based solar cell application is limited. Thus, a doping process with p-type material has been reported could show an improvement in the electrical conductivity. Therefore, the main motivation of this work is the fabrication of a-C thin film with iodine doping in order to assess its performance with a view to future use towards carbon material for solar cell applications.

## II. METHODOLOGY

The deposition of a-C thin films has double tubular furnaces, a quartz tube and water bubbling system. First, the corning glass substrates (1mm) were thoroughly cleaned using the common organic cleaning technique. The quartz tube (deposition container) was placed inside the tubular furnaces. An unreactive Argon gas is utilized as a carrier gas to transfer the vapor particles between two furnaces. Besides, camphor oil as a carbon source to deposit a-C thin film was used in this work. The camphor oil (3ml) filled into combustion boat was placed at first furnace inside the quartz tube by heating at 200°C. The substrate was placed at the second furnace and set the temperature at 550°C for the deposition of a-C thin films. Then, the deposition container was purged with the carrier gas for approximately 10 minutes in order to remove the air inside the quartz tube before the deposition process was started. The deposition of a-C thin film took 30 minutes with carrier gas flow rate at 20 sccm.

Once the deposition process completed, the iodine doping procedure was conducted. The p-type dopant (Iodine) was

doped onto the deposited a-C thin film through thermal CVD method. Argon gas flow rate was set at 20 sccm. In this process, iodine was heated at 100°C in the first furnace while deposited thin film in second furnace was heated at 400°C. The doping time ranged from 10 minutes to 40 minutes. The optimization of doping time parameter is crucial for the effectiveness use of a-C:I thin films. Characterization of the thin films were conducted using two probe current-voltage (I-V) measurement system in dark and under light illumination using a standard solar irradiation for electrical properties. Then, measurement for optical and structural properties was characterized and analyzed by UV-VIS-NIR spectroscopy, Raman spectroscopy and FESEM.

### III. RESULTS AND DISCUSSION

The electrical conductivity of the a-C:I thin films were characterized and analyzed using the I-V characteristics of the thin films deposited on glass substrates. Prior to measurement, the gold (Au) metal contact grids (thickness = 60 nm) were deposited on top of the a-C:I thin film by electron beam thermal evaporator to achieve the ohmic contacts between the a-C:I thin film and the electrodes. Two probes were then attached to adjacent metal contacts which supply the voltage and the current between metal contacts was measured. Figure 1 shows the deposited a-C:I thin films' I-V characteristic at 400°C at different doping time. The I-V characteristic illustrates the linear current-voltage relation for both a-C and a-C:I thin films. This characteristic indicates the ohmic behavior achieved between the thin films and electrodes. As presents in Figure 2, the a-C:I thin films' electrical conductivity was initially increased from  $4.45 \times 10^{-4}$  S.cm<sup>-1</sup> to maximum value of  $1.35 \times 10^{-3}$  S.cm<sup>-1</sup> when doping time reached 10 minutes in dark condition. This electrical conductivity improvement occurs due to the increasing of mobile holes after 10 minutes iodine doping period. This finding also indicates that the iodine dopant could assists dangling bonds neutralization, hence improves the electrical conductivity. It is also suggested that 10 minutes doping time would help to stabilize the sp<sup>3</sup> bonded carbon content in doped sample. Thus, it would lead to highest electrical conductivity due to an increase of sp<sup>2</sup> bonding in a-C thin film. However, as the doping time increased from 10 minutes to 40 minutes, the conductivity was decreased to  $7.02 \times 10^{-4}$  S.cm<sup>-1</sup>. This is could be caused by the microstructural change of a-C thin film which longer reaction exposure on deposited a-C thin film. At 10 min of doping time, the iodine atoms assist the carbon atoms to increase sp<sup>2</sup> bonding and to generate the graphitization [7, 8]. The electrical conductivity of the a-C:I thin films theoretically occurs based on the electrical transport in the valence band [9]. The conductivity under illumination are higher than conductivity in dark for a-C:I thin film doped at 10 minutes indicates a photo-response occurred which is due to the generation of excess carriers. The excess carries are possible due to the presence of sp<sup>2</sup> bonded carbon atoms in the a-C:I thin film [10].

The absorption coefficient,  $\alpha$  value of a-C:I thin film doped at 10 min suggests the highest  $\alpha$  value ( $10^4 \sim 10^5$  cm<sup>-1</sup>) in the visible wavelength region as shown in Figure 3. The high  $\alpha$  value indicated that the a-C:I thin film doped at 10 minutes

has the highest photon absorbance in the visible region. The optical band gap of a-C:I thin films was calculated from the extrapolation of the linear part of the curve at  $\alpha = 0$ , by using the Tauc equation which defined as amorphous semiconducting materials [11]. Figure 4 shows the optical band gap for a-C:I thin films with different doping time. Interestingly, the optical band gap value shows that the decrease of the optical band gap from 0.54 eV (as-deposited) to 0.23 eV (doping time at 10 minutes) that can be supported by highest  $\alpha$  value of a-C:I thin film doped at 10 minutes. This can be explained caused by the increasing of sp<sup>2</sup> content during doping process and has a minimum dangling bonds in the carbon bonding due to the existence between carbon and iodine bonding [12, 1].

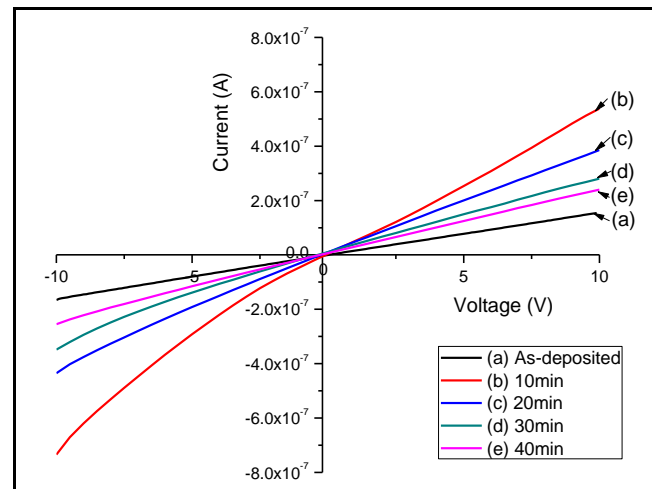


Figure 1: I-V characteristics of a-C:I thin films at different doping time

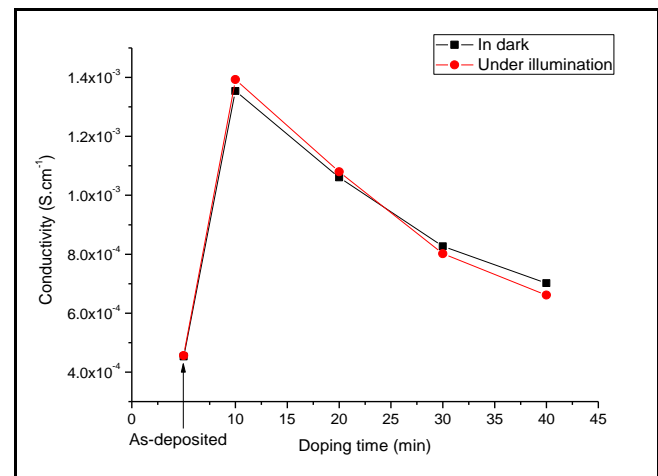


Figure 2: Conductivity of a-C:I thin films with different doping time

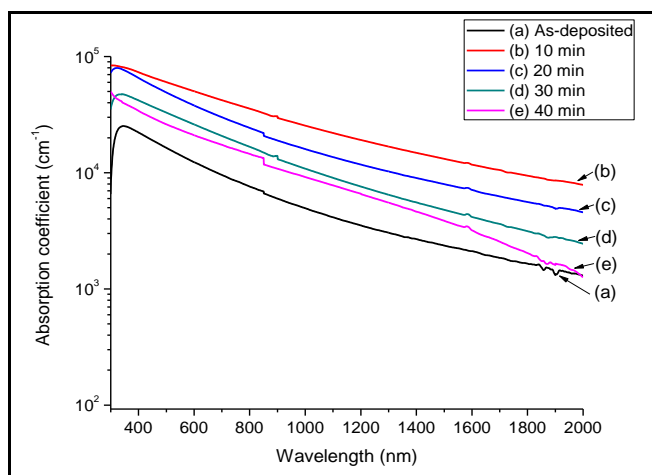


Figure 3: Absorption coefficient of a-C:I thin films with different doping time

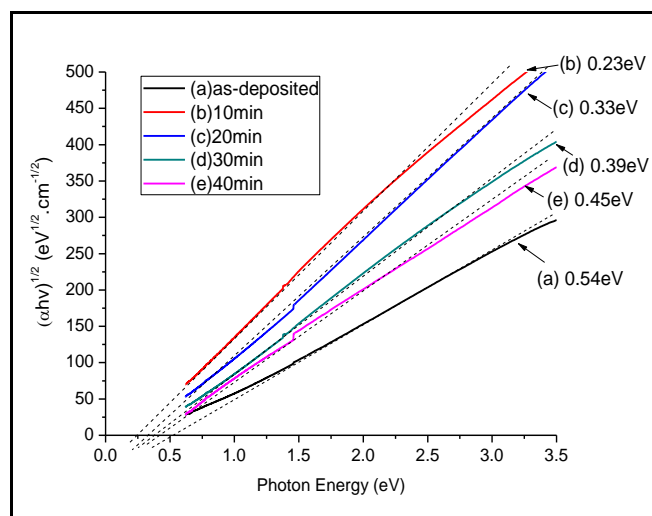


Figure 4: Optical band gap of a-C:I thin films with different doping time

This effect could be caused by the graphitization occurred in the a-C structure and then leads to the optical band gap become less. Our result is in agreement with that reported by Omer et.al. [13], the iodine in the a-C deposited thin film induced graphitization of the structure and assists the decrease of  $sp^3$  content in the a-C:I thin films. However, the value of optical band gap increases as the doping time increase. This may be due to the increase of  $sp^3$  content in the a-C:I thin films caused by longer exposure to the iodine doping and leads to the defect generation.

For the investigation of iodine doping process into the deposited a-C thin film, the Raman analysis was performed at room temperature. Figure 5 shows the Raman spectra analysis of the a-C:I thin films in the region from 1000 to 2000  $cm^{-1}$  wavelength at different doping time. The D peak positions of the thin films are at about 1340  $cm^{-1}$  while the G peak positions are in the range of 1590-1595  $cm^{-1}$ .

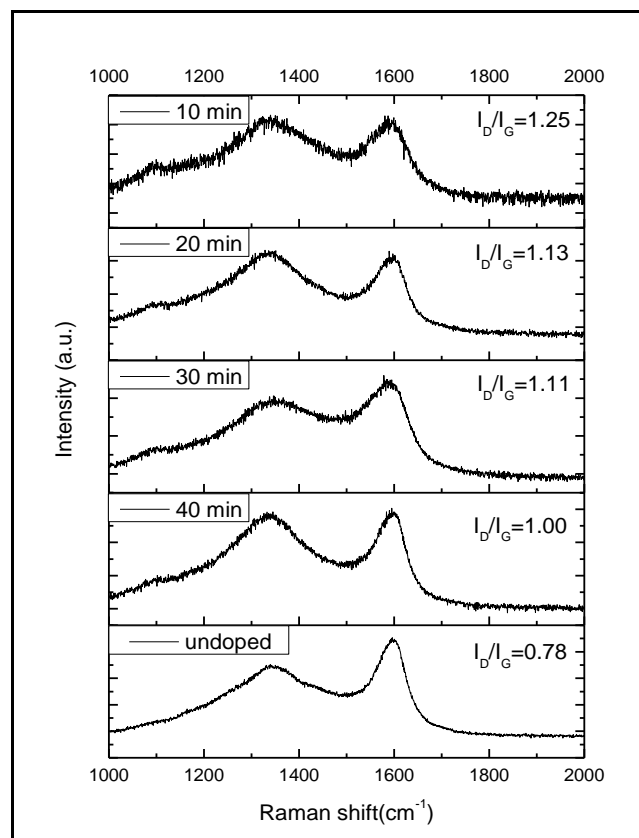


Figure 5: Raman spectra of a-C:I thin films with different doping time

This result shows that the shifting of G peak positions to higher wavenumber side was observed between deposited a-C thin film (1593  $cm^{-1}$ ) and a-C:I thin film doped at 10 minutes (1595  $cm^{-1}$ ). The G peak shifting is because of the effect of the  $sp^2$  cluster size [14]. The downshift of G peak of a-C:I thin films has been noticed when doping time increasing up to 40 minutes from 1595 to 1590  $cm^{-1}$ . This behavior was due to the size of the  $sp^2$  clusters decreases [15,16]. Ratio of  $I_D/I_G$  shows an increase from 0.78 (as-deposited) to 1.25 at doping time of 10 minutes. However,  $I_D/I_G$  ratio decreases with further increase in doping time. It has been stated that the  $I_D/I_G$  ratio can determine the  $sp^3$  contents. A low value of intensity ratio  $I_D/I_G$  will correspond to the increasing of  $sp^3$  content [16-18]. Thus, it suggests that the a-C:I thin film doped at 10 minutes has a major effect of iodine introduction which responsible in increasing the cluster of the  $sp^2$  phase. Therefore, the increase of  $sp^2$  content in the thin film leads to contain more delocalized electrons which contribute to an increase in conductivity and a narrow optical band gap of a-C:I thin films [19]. This phenomenon supported electrical and optical analysis described previously.

The a-C:I thin films are shown to have an irregularly scattered tiny ball-like particles after doping process as shown in Figure 6. The structural properties of a-C:I thin film are related with the amorphous nature having diameter ranging from 40 - 60 nm.

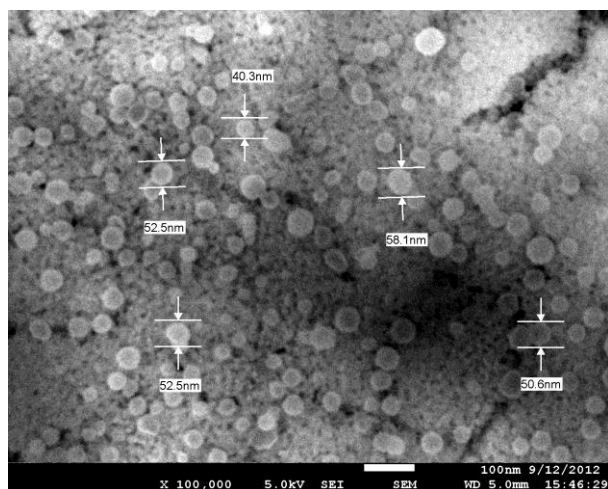


Figure 6: FESEM image of a-C:I thin film

#### IV. CONCLUSION

This work is intended to prepare a-C:I thin film from naturalness carbon precursor (camphor oil) by thermal CVD method to explore the possibility of this material for carbon based solar cell application. For the doping time setting parameter, it reveals that the a-C:I thin film doped at 10 minutes can be identified as best preparation parameters. The longer doping time will decrease the electrical conductivity and the optical band gap of the thin films will increase. An increase in doping time allows the defect generation, creating more  $sp^3$  bonded carbon atoms due to the longer exposure of doping process. The nanostructured of a-C:I thin film proved that amorphous nature of the samples was noticed.

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