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Carbon nanotube: An indirect ~ 0 eV band gap material

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Abstract

Thin film of carbon was synthesized from camphor ($C_{10}H_{16}O$) by CVD technique in hydrogen atmosphere. For the first time it is confirmed the presence of almost zero indirect band gap in addition to its direct band gap. Carrier concentration with intrinsic carbon is found to be in the range of $0.601x10^{21}$ to $0.077\ x10^{21}$ n/cm^3. It is suggested that unless the zero indirect band gap is increased carbon thin film cannot be used for making a p : n junction. XRD, Raman and SEM analysis are performed.

1.0 Introduction

Silicon solar cell though is available commercially, yet scientists are trying to explore some economical cheap material for harnessing solar energy. Carbon possessing almost similar properties to silicon is being considered as a possible material for solar cell development. Unfortunately there are some hurdles in using carbon nanotube as a semiconducting material. For example, unlike silicon carbon nanotubes can be synthesized as a direct band gap material in the range of 1.4 eV [1]. In spite of possessing direct band gap of even 1.4 eV, the carrier concentration is observed in the range of $0.601x10^{21}$ to $0.077\ x10^{21}$ n/cm^3. Because of such high carrier concentration it is difficult to form large depletion width to develop homojunction carbon solar cell. Perhaps due to this Au/nC/pC/nSi/Au could not be made with efficiency greater than 4% [2-12].

In this short communication we discuss the results of our effort to find out why carrier concentration for intrinsic carbon is as high as 10^{21} n/cm^3, though the band gap of carbon is around 1.4eV or more.

2.0 Experimental

2.1 Precursor: Camphor (technical grade) without any purification was used as precursor for the synthesis of carbon film by chemical vapour deposition technique. Three temperatures were tried (700,800 and 900^{o}C) using hydrogen as a carrier gas.

2.2 Carrier concentration: The Hall Effect of thin films of carbon was studied using Systronics Hall unit (max. field 1.5 Tesla); to find out the carrier concentration.

2.3 Morphology study: The morphology of carbon was assessed by SEM (S440I/Q500 (with Oxford EDS) Model).

2.4 XRD and Raman spectra were measured to find out the graphitic nature of the film.

2.5 Synthesis of carbon thin film by CVD: setup used for synthesizing carbon thin film from camphor is shown in figure 1. The unit consists of a steel tube of length 80 cm and diameter around 7 cm (A), which was inserted into the furnace (B) controlled by a PID controller (C). A quartz boat (D) was kept near the inlet of the steel tube (A) and another quartz boat (E) near the center of the tube (A). Hydrogen gas (F) was flushed into the furnace for 15 min to remove oxygen and then its flow rate was maintained as 5cc/min (G). Glass bubblers (H) were used to avoid back flow of gas. Valves (I) were attached to the steel cylinder (A).

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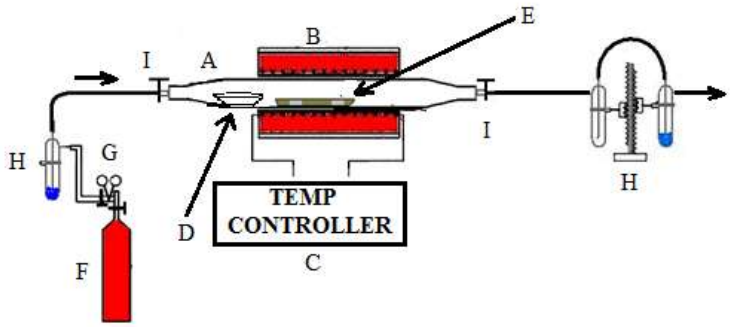

Figure - 1 Schematic set up of a chemical vapor deposition unit.

Mixture of camphor (1g) and ferrocene (0.2g) was kept in the boat (D). After flashing cylinder (A) with hydrogen gas, furnace was switched on to attain the desired temperature (700,800 and 900^{o}C). At this condition the temperature near the boat (D) was around 300^{o}C.Vapours of camphor and ferrocene were transported by hydrogen gas near the boat E where ferrocene catalyst decomposed to give iron nanoparticles [13]. In presence of Nano size iron particles, camphor vapour decomposed to produce a thin film of carbon over the quartz plate kept in the boat E. Temperature near the boat D was found to be around 300^{o}C which was suitable to vaporize camphor and ferrocene. After 2h of attaining the desired temperature, the furnace was switched off. When furnace cooled down to room temperature, thin film of carbon deposited on quartz plate was removed for the various analysis. Three sets of experiments were carried out at each temperature.

3.0 Results and Discussions

3.1 Band gap calculation: The absorption spectra of carbon films were studied by using Systronic double beam spectrophotometer-2203 in the wavelength range of 200 to 1100 nm. From the absorption graph, absorption coefficients (α) was calculated for each hυ. OD obtained at each wavelength was assumed as its absorption coefficient for the corresponding wavelength. These data were used to calculate the band gap using the Tauc relationship (equation 1):

$$\alpha h\upsilon = A\,(h\upsilon - Eg)^{n/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where, Eg = band gap energy, α = Absorption coefficient (assumed equivalent to OD), h = Planck constant, υ = Frequency of radiation absorbed, n = 1 for direct band gap, & n = 4 for indirect band gap and A= constant. Graphs of $(\alpha h\upsilon)^{2/n}$ i.e. $(\alpha h\upsilon)^{2}$ for direct band gap and $(\alpha h\upsilon)^{1/2}$ for indirect band gap were plotted versus hυ. The intercept of linear plot on X-axis at $(\alpha h\upsilon)^{2/n} = 0$, was taken as the band gap value (Figure 2). This exercise was done for both direct band (i.e. n = 1) and for indirect band gap (i.e. n = 4).This exercise was carried out with carbon film obtained with each experiment. Since the nature of all graphs were similar, a typical graph of carbon obtained at 700^{o}C is shown in Figure 2.

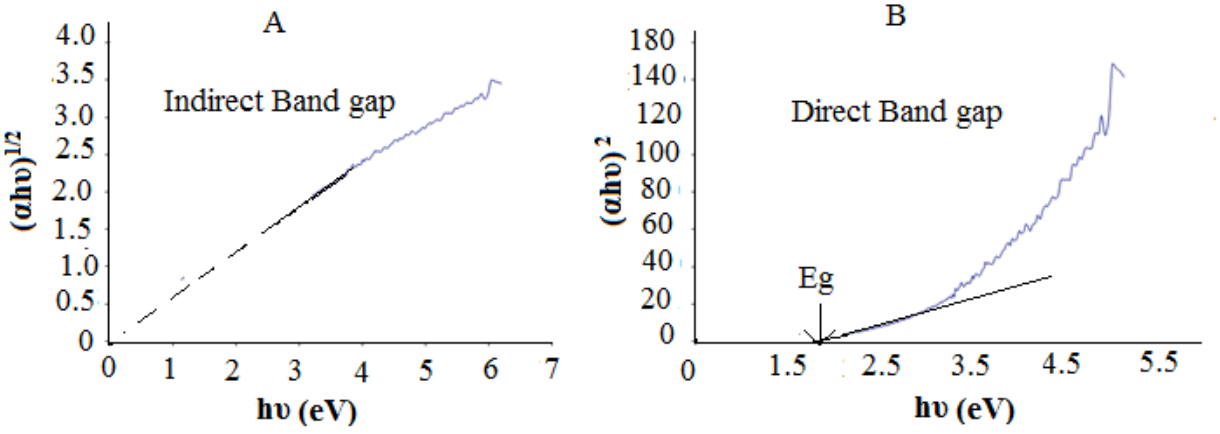

Figure 2: Graph of (A) $(\alpha h\upsilon)^{½}$ Vs hυ for indirect band and (B) $(\alpha h\upsilon)^{2}$ Vs hυ for direct band gap

Results of average band gap and the carrier concentrations (shown in bracket) obtained from three experiments carried out at three temperature (700^{o}C,800^{o}C and 900^{o}C) are shown in Table-1.The band gap of carbon thin film obtained by the pyrolysis at temperature 700^{o}C shows average value of 1.23eV (Table 1) and while at 900^{o}C it shows a low band gap of 0.95eV.It is also interesting to observe that the indirect band gap of all carbon films show band gap of almost zero eV i.e. 0.01eV, with carrier concentration in the range of 0.601x10^{21} to 0.077 x10^{21} n/cm^{3}. It can therefore concluded that the

higher carrier concentrations are due to the presence of zero indirect band gap and are not controlled by the presence of the direct band gap.

Table 1: Average of three experiments showing the band gap and Carrier concentration of thin films prepared at three temperatures 700°C, 800°C and 900°C.

Pyrolysis Temp. (°C)	Optical Band gap (eV)		Carrier concentration from Hall measurement
	Indirect (eV)	Direct (eV) (average in bracket)	$(n/cm^3)x10^{21}$ (average in bracket)
700	~0.01	1.4-1.1 (**1.23**)	0.235-0.077 (**0.125**)
800	~0.01	2.0-1.1 (**1.46**)	0.382-0.018 (**0.176**)
900	~0.01	1.0–0.90 (**0.95**)	0.601-0.271 (**0.443**)

Formation of indirect band gap in carbon could be explained by considering the π-π interaction. In carbon film, perhaps π-bond ($1C_{px}$) of one carbon with π-bond with second carbon atom ($2C_{px}$) of at (000) plane might be forming the direct band gap and the indirect band gap might be formed by π-valence band of $1C_{px}$ with π- conduction band of third carbon atom $3C_{px}$ (Figure 3).

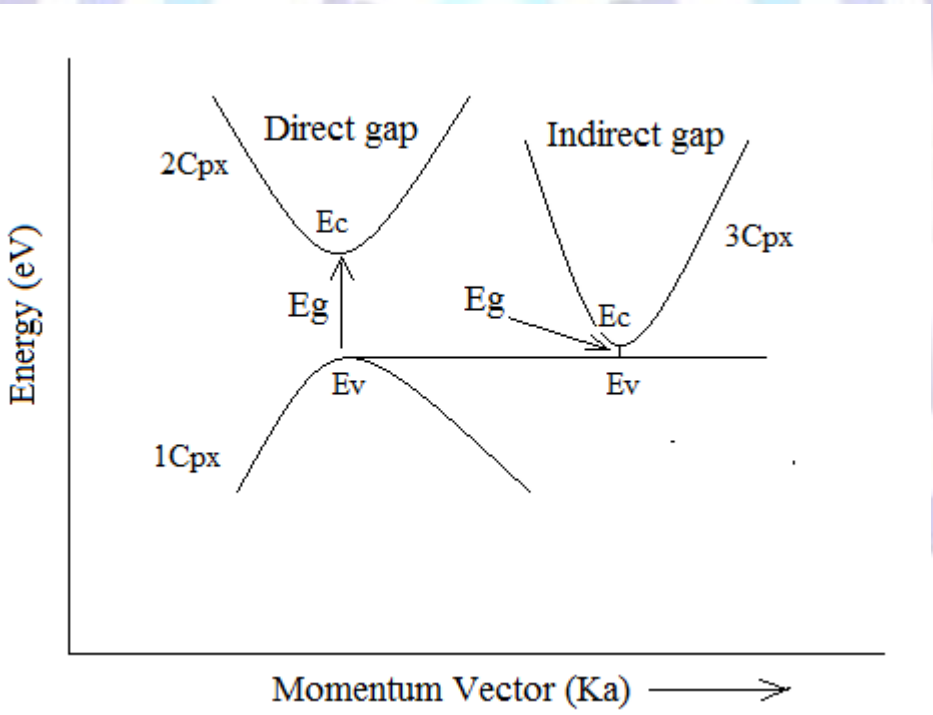

Figure 3 Schematic diagram to show the direct and indirect band gap formation.

3.2 XRD and Raman studies

It was observed that there was not much difference in XRD as well as in Raman spectra of carbon thin films obtained at 700°C, 800°C or 900°C. Hence a typical XRD and Raman spectra of carbon prepared at 700°C are shown in Figure-4. The XRD of carbon film shows a broad peak at 2 θ = 26 corresponding to (002) plane and one sharp peak at 2Θ = 44.62 corresponding to (100) plane (Figure4A).

RAMAN spectrum (Figure 4B) shows one peak at 1590 cm^{-1} due to G-band and other at 1362 cm^{-1} due to D-band. These two peaks are characteristic for graphitic material containing some disorder structure.

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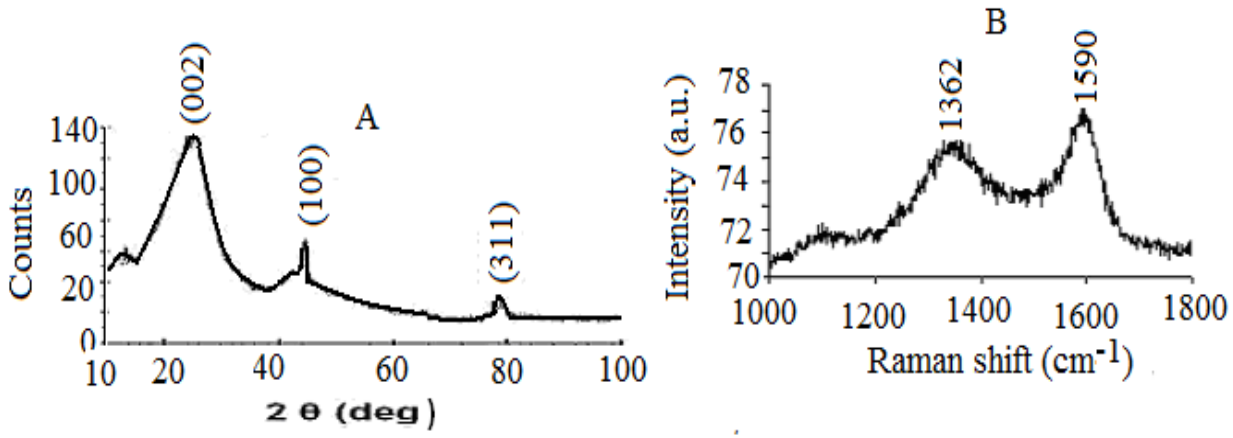
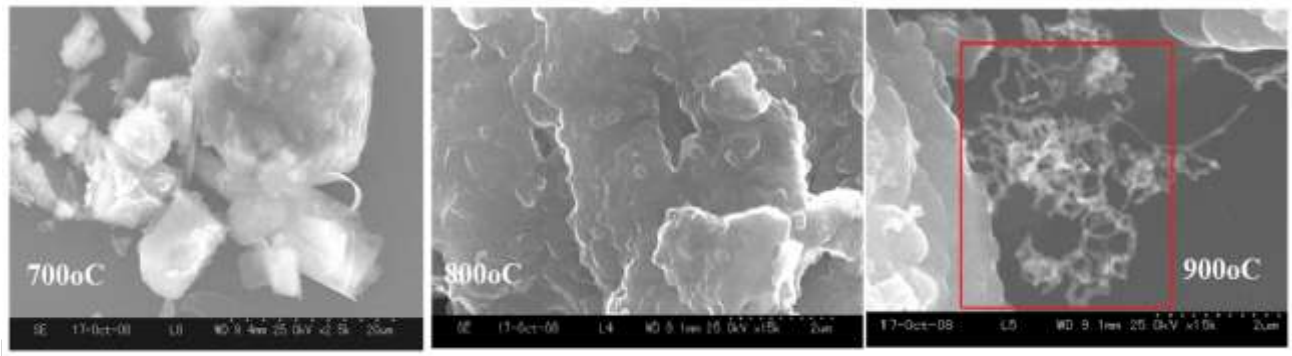


Figure 4 (A) XRD of carbon film obtained with carbon film obtained by pyrolysis at 700°C showing specific planes for graphite i.e. (002) and (100) and (B) Raman spectra of carbon film showing G-band and D-band at 1590cm^{-1} and 1362 cm^{-1} respectively.

3.3 Hall Effect study - was carried out for the carbon films obtained under the different conditions. Carrier concentrations for each film were calculated and the values are shown in Table-1. Results suggests that irrespective of conditions of synthesis the carrier concentration is more of less of the order of 10^{21}n/cm^3. It is interesting to note that though the direct band gap for all carbon materials synthesized under various condition (Table-1) are in the range of 2.0 eV to 0.90 eV and the carrier concentrations are also in the range of 0.601x10^{21} to 0.077 x10^{21} n/cm^3. Though these carbon thin films are intrinsic, and the carrier concentration instead of being low is very high, it can therefore be concluded that the carrier concentration is related to the indirect band gap and not the direct band gap of carbon film. Hence if carbon films are to be used for making p : n junction its indirect band gap should be altered so that carrier concentration falls in the range of 10^{18} to 10^{19}n/cm^3.

3.4 Morphology of Carbon as affected by Temperature

SEM images of all carbon films prepared under three different temperatures are shown in figure 5. Carbon films grown at 700°C shows cotton ball type while for 800°C it shows block type growth. However at 900°C some carbon fibrous type structures are also observed. These SEM micrographs suggests that carbon film with a band gap 1.23eV are of cotton ball type fibers whereas very low band gap carbon (0.95eV) shows carbon nano fiber type of growth.



4.0 Conclusion

It is concluded that carbon films synthesized from camphor by CVD technique possesses both type of band gaps i.e. indirect band gap of almost zero band gap value and direct band gap in the range of 2.0 eV to 0.95eV. The high carrier concentration observed by carbon films are due to presence of indirect zero band gap. If this material is to be used for developing carbon solar cell, the first requirement is to increase its indirect band gap to around 1 eV so that its carrier concentration could be in the range of 10^{18} to 10^{19} n/cm^3 as is the case with intrinsic silicon material.

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