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BAND-GAP MEASUREMENT OF ROOM TEMPERATURE GROWN CLUSTERED CARBON FILMS FOR LARGE AREA MICROELECTRONICS

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ABSTRACT

The optical characteristic of the room temperature grown clustered carbon films using cathodic arc process has been investigated by spectroscopy technique. The optical band gap and localized state E_0 of the films have been determined using transmittance and absorbance at normal incidence in the spectral range of 200 nm-800 nm. The absorption edge of the films show exponential characteristic which is attributed to the electronic transition in tail states and due to disorder in the structure of the clustered carbon films. Values of the band gap were found to be 3.62 eV and 3.77 eV with breadths of 269.12 meV and 309 meV.
***Keywords*:** clustered carbon films, optical band gap, Tauc gap.

I. INTRODUCTION

Carbon based nanomaterials finds wide applicability in various fields like field assisted electron emission [1], thin-film transistors (TFT) [2,3], antifuses [4] , low dielectric films for ULSI [5] and Field-Effect Transistor [6-8]. All these possible by the three different bond hybridizations that are available to carbon: sp^1, sp^2 and sp^3. One of the nanocarbon clustered carbon films have been investigated for electrical and optical properties. Initial study shows that the clustered carbon films are semiconducting in nature [9-12] This material has great potential to be used in solid state devices, Thin-Film Transistors (TFT) and optoelectronic devices.

The study of the optical absorption particularly the optical gap and absorption edge is very useful to probe in-depth the electronic structure of the materials. Since these materials contain clusters of various dimensions and disordered in nature, absorption edge gives the width of the localized states which is measure of the disorder. It is possible to determine the band gap from the optical absorption spectra [13]. The transmittance and absorbance data are analyzed to calculate the band gap and the characteristic energy E_0 [14].

II. EXPERIMENTAL

Clustered carbon films have been deposited in a cathodic vacuum arc system [15].In cathodic arc process, an arc is initiated by touching the graphite cathode with a small carbon striker electrode and withdrawing the striker. This produces energetic plasma of carbon with high ion density. The clustered carbon films in this work have been grown using cathodic arc process at room temperature on the glass substrates and in the presence of background gas like helium, which may facilitate clustering process. The chamber is first evacuated to a 10^{-7} Torr. vacuum, before initiating the deposition process. Typically films of thickness about 100 nm have been deposited on glass and silicon substrates. The thickness of the films has been measured using a thickness profiler. The Raman measurements have been carried out using a Renishaw micro Raman system and an excitation wavelength of 514.5 nm. The SEM images of the films have been taken using JEOL field emission microscope.

Optical absorption measurements have been carried out using a conventional double beam spectrometer (Shimadzu model UV-VIS-1601) [16]. A basic set-up is shown in figure 1.

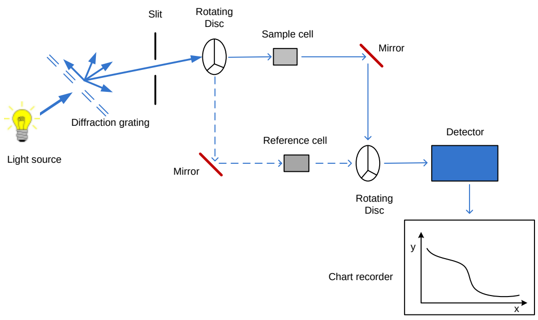

Fig. 1: Schematic of UV-visible spectrophotometer .

Ample optical energy is available for various measurements over a wide wavelength of 190 nm (ultraviolet) to 900 nm (near-infrared) with detector of photomultiplier or PbS cell. A glass substrate is used as reference to compensate the difference of light path passing through the film.

III. RESULTS AND DISCUSSION

III.1 Morphological studies of clustered carbon films

Figure 2 shows the Scanning Electron Microscope (SEM) images of the clustered carbon films grown using cathodic arc process. It may be seen from the SEM that these thin films contain clusters of varying dimension ranging from 20 nm to 200 nm. Helium gas atom as mentioned earlier helps in clustering process by taking away excess energy from carbon ions upon interacting with them [17]. For any plasma based process i.e. cathodic arc and laser produced plasma, carbon dimers (C_2) aid in formation of bigger cluster as also observed in the growth of other nanocarbons like nanotubes, nanowires and grapheme [18, 19]. This dimer are formed in the plasma plume by recombination process. Typically, helium gas is feed to the deposition chamber to aid in enhancement of carbon dimers apart from slowing down the energetic particles. This enhances the residence time and growth of bigger clusters [15, 20, 21].

Raman spectroscopy is a useful technique to identify the bonding nature (sp^2 and sp^3) and also to determine the degree of mixed phase nature of the clustered carbon films [22-24]. Raman spectra, as shown in Fig. 3 clearly indicates the presence of clustered material with the presence of the G and D peaks [25, 26].

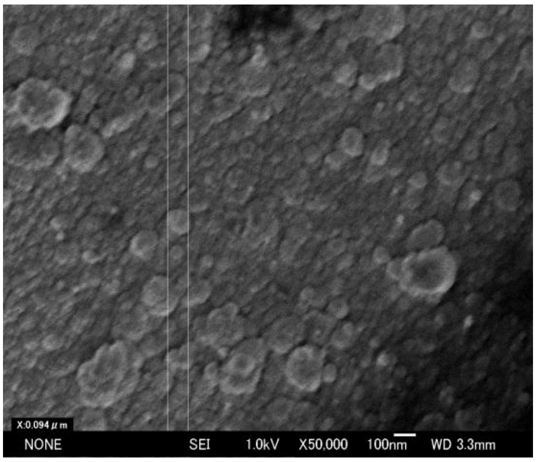

Fig. 2: SEM image of a clustered carbon film grown using cathodic arc process.

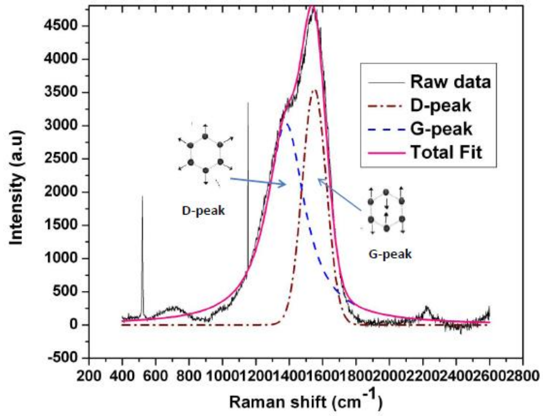

Fig. 3: Raman response of a clustered carbon film.

The Graphitic (G) peak at 1580 cm^{-1} indicates the existence of sp^2 clustering or π electron delocalization in the samples. The presence disorder (D) peak at 1332 cm^{-1} peak indicates the disorderness in the film. The D peak is due to the breathing modes of sp^2 atoms in aromatic rings due to bond angle disorder. The enhanced disordered peak at 1332 cm^{-1} as also a small hump around 1100 cm^{-1} (silicon second order peak) when measured on silicon substrates clearly indicate the of presence of some sp^3 bonded carbons.

III.2 Optical characteristic of clustered carbon film

The thin film under consideration is clustered, disordered and mixed phased material containing both sp^2 and sp^3 bonding. Optical constants are characterized by the Tauc's relations. The optical absorption curves, according to the Tauc's model [27], the spectrum can be divided into three different regions: the high absorption region (optical coefficients: $\alpha > 10^3$ cm^{-1}) , the exponential edge ($10^1 < \alpha < 10^3$ (cm^{-1}) and the weak absorption tail ($\alpha < 10^1$ cm^{-1}).

In the high absorption region, where $\alpha \geq 10^3$ cm^{-1}, the spectral behavior follows the law given by Eq. (1)

$$\alpha h\nu = Const.(h\nu - E_g)^n \quad (1)$$

where hν is the photon energy, 1 < n < 3 for indirect band gap material and 1/2 < n < 3/2 for direct band gap material and E_g, is the optical gap. Optical transitions between the valence and conduction bands are responsible for the optical absorption in this region. For determination of the optical gap, we employ the above "Tauc" approach. That is, we fit, in a least-squares sense, given by Eq. (2)

$$\sqrt{\alpha h\nu} = Const.(h\nu - E_g) \quad . \quad (2)$$

In the sub-gap region, the optical gap and the optical-absorption tail breadth are quantified. In order to determine the breadth of the optical-absorption tail, we follow the usual procedure in this analysis and fit an exponential functional dependence [14, 28-29] given by Eq. (3)

$$\alpha(h\nu) = \alpha_0 \exp\left(\frac{h\nu}{E_0}\right) \quad (3)$$

to our optical-absorption experimental data, where α_0 is a pre-exponential constant and E_0 denotes the breadth of the optical-absorption tail. The exponential rise reflects the tailing of states into the gap due to fluctuations of bond lengths and bond angles [14, 28-30]. From the above equation, Urbach energy can be obtained from the plot of the absorption coefficient versus photon energy in the vicinity of the band gap energy.

The weak absorption tail ($\alpha < 10^2$ cm^{-1}) can be attributed to impurities, charged or neutral defects, or extrinsic dopants. Investigation of the absorption profile in this region is very important, because it gives information on states in the energy gap.

III.3. Optical band-gap calculation of clustered carbon films

Optical absorption measurements have been carried out using a conventional two beam spectrometer (Shimadzu model UV-VIS-1601). For these measurements, films deposited on plain quartz substrates were used along with the reference substrate. The spectrometer actually measures the absorbance, A, which is given by Eq. (4)

$$A = \log \frac{I_0}{I} \quad . \quad (4)$$

where I_0 and I are the incident light intensity and the light intensity transmitted through the sample, respectively. The light intensity transmitted through the film follows the Beer-Lambert's law, which is given by Eq. (5)

$$I = I_0 e^{-\alpha t} \qquad (5)$$

where t is the film thickness. The absorption coefficient, α, of the film can be obtained from the equation given by Eq. (6)

$$\alpha = \frac{A \ln 10}{t} \ . \qquad (6)$$

A typical transmission spectrum of the clustered carbon films is shown in Fig. 4. Typical plot of $(\alpha h\nu)^{1/2}$ vs hν of the film is shown in Figure 5. The optical band gap is found to be 3.62±0.010 eV. In the exponential-edge region, the absorption coefficient is expressed by the Urbach relationship given by Eq.(2). α_0 is constant and E_0 characterize by slope of the exponential edge region.

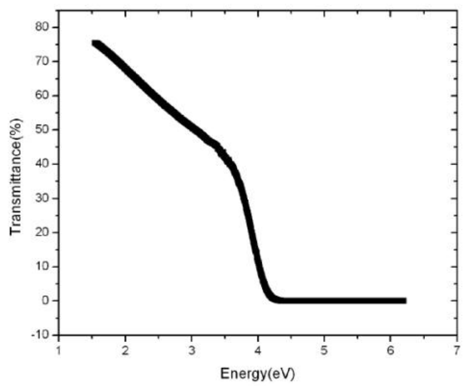

Fig. 4: Transmission spectra of the clustered carbon films.

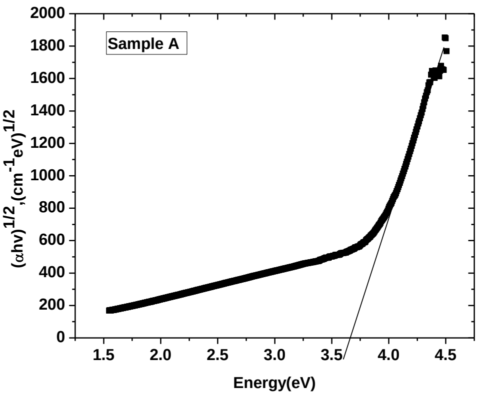

Fig. 5: The $(\alpha h\nu)^{1/2}$ vs hν plot of the clustered carbon films.

Figure 6. is the plot of the ln(α) vs energy of the clustered carbon films and E_0 is found to be 269.12±0.001meV.The inverse of the slope gives the width of the localized states. The plot is linear for the absorption region near the fundamental absorption edge. Thus absorption coefficient near the fundamental edge is exponentially dependent on the photon energy and obeys the Urbach's principle. The interaction between lattice vibrations and localized states in tail of the band gap of the clustered carbon films has significant effect on the optical property of the thin film. Optical band gap and Urbach energy of the clustered carbon films are summarized in Table 1.

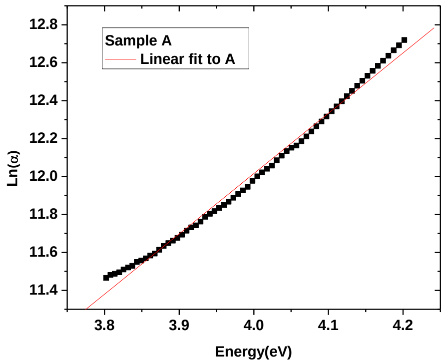

Fig. 6: ln(α) vs E plot of clustered carbon film.

Table 1: Optical band gap and Urbach energy of the Nanocluster carbon thin films.

Sample No.	E_g(eV)	Urbach Energy (meV)
S86	3.77	309
S113	3.62	269

IV. CONCLUSIONS

The optical band gap and the width of the localized states of clustered carbon films were investigated. The absorption edge follows the exponential behavior indicating the electronic transition in the localized tail state. Tail state in the band-gap of the material is due to the disorder in the structure of the clustered carbon films. Values of the optical band gap and of widths of the localized states were respectively obtained as 3.62 eV or 3.77 eV and 269.12 meV or 309meV.

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