CHAPTER 5

ELECTRICAL AND ELECTRONIC TRANSPORT BEHAVIOR IN NANOCLUSTER CARBON FILMS

5.1 Introduction

Room temperature grown Nanocluster Carbon (NC) thin films are emerging as a potential material for large area and flexible microelectronics. There is limited information on electrical, electronic and optoelectronic properties, of these room temperature grown nanocarbons. Reported in this chapter is the electrical, electronic and optoelectronic properties of these films. As it is a new material, to ascertain the feasibility of this material for the above mentioned applications, a broad range of nanocluster carbon films covering diverse process conditions has been considered in the study. The process conditions studied include deposition ion energy, throw distance (distance between the ion sources and the substrate), arc current during deposition and varying helium, nitrogen, and hydrogen partial pressures during the deposition.

5.2 Results

Electrical, electronic and optical measurements have been carried out using experimental arrangements discussed in chapter 3. All the contacts have been fabricated using thermal evaporation and found to be ohmic in nature. The measurements are repeatable in nature.

5.2.1 Semiconducting behavior of nanocluster carbon thin films

Dark conductivity $\sigma (T)$ measurements have been carried out using coplanar geometry. The conductivity measurements have been carried out under dark conditions and constant channel width of 500 um in each sample. Figure 5.1 shows the variation of dark conductivity with temperature of nanocluster carbon thin films grown using cathodic arc
process under varying deposition conditions including arc current, deposition ion energy and gas partial pressure.

![Conductivity graph](image)

**FIGURE 5.1** Variation of dark conductivity with temperature of nanocluster carbon films grown using cathodic arc process under varying deposition conditions.

It may be seen from figure 5.1 that the samples grown under diverse parameters exhibit a typical increase in conductivity with the increase temperature for all samples. This indicates that within the range of process parameters studied, all samples exhibit semiconducting behavior. This is a very significant result as this suggests the possibility of use of cathodic arc to grow semiconducting nanocluster carbon films.

### 5.2.2 Electronic behavior of the nanocluster carbon thin films grown under varying deposition ion energies

Electronic behavior of nanocluster carbon thin films grown under four different deposition ion energies has been discussed here to further understand the possibility of specific process parameters. Electrical
conductivity and transport mechanism of the nanocluster carbon thin films has been studied by observing the change in dark conductivity with respect to temperature. The temperature has been varied from room temperature to 423 K. Further, transport mechanisms of nanocluster carbon thin films will be discussed in order to understand the intrinsic behavior by varying the temperature from 123 K to room temperature.

Figure 5.2 shows variation of dark conductivity of nanocluster carbon thin films grown using cathodic arc process under four different deposition ion energies. These films typically exhibit two regions of operations and are governed by equation 5.1.

\[
\sigma = \sigma_1 \exp\left(\frac{-\Delta E_{a_1}}{kT}\right) + \sigma_2 \exp\left(\frac{-\Delta E_{a_2}}{kT}\right)
\]

where \(\sigma_1\) and \(\sigma_2\) are two conductivity pre–factors of region I and region II, \(E_{a1}\) and \(E_{a2}\) are two activation energies of these two regions.

**FIGURE 5.2** Variation of dark conductivity with respect to temperature of nanocluster carbon films grown using cathodic arc process under four different deposition ion energies.
Room temperature (RT) conductivity of the nanocluster carbon films varies from $10^{-5} \, (\Omega\text{-cm})^{-1}$ to $10^{-4} \, (\Omega\text{-cm})^{-1}$ when the deposition ion energies are varied from 20 to 80 eV. The conductivity in the high temperature range (423 K–357 K) for all samples shows limited variation. The trend appears similar to extended state conductivity observed in hydrogenated amorphous silicon (a–Si: H) or even tetrahedral amorphous carbon (ta–C) [88,165]. However, values of the RT conductivity appear to be slightly higher than the above compared materials inspite of the films being grown without any dopants. In the case of the temperature ranges from 356K–303K, conductivity follows slightly different paths. Any further explanation needs more detailed study of the defect densities.

For region I, conductivity data and activation energies extracted are governed by first part of equation 5.1. The activation energies vary from 0.55 to 0.61 eV. All these values are enumerated in Table 5.1.

### Table 5.1 Enumerated values of activation energies of Samples A, B, C and D for region I.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Ion energy (eV)</th>
<th>$Ea_1$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20</td>
<td>0.55±0.013</td>
</tr>
<tr>
<td>B</td>
<td>30</td>
<td>0.61±0.0086</td>
</tr>
<tr>
<td>C</td>
<td>70</td>
<td>0.57±0.0044</td>
</tr>
<tr>
<td>D</td>
<td>80</td>
<td>0.59±0.013</td>
</tr>
</tbody>
</table>

### Table 5.2 Enumerated values of activation energies of Samples A, B, C and D for region II.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Ion energy (eV)</th>
<th>$Ea_2$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20</td>
<td>0.31±0.0086</td>
</tr>
<tr>
<td>B</td>
<td>30</td>
<td>0.26±0.011</td>
</tr>
<tr>
<td>C</td>
<td>70</td>
<td>0.073±0.002</td>
</tr>
<tr>
<td>D</td>
<td>80</td>
<td>0.17±0.0017</td>
</tr>
</tbody>
</table>

For region II, conductivity data and activation energies extracted are governed by second part of equation 5.1. High values of the activation energies indicate thermal or activated type of transport. Low values of the
activation energy suggest that transport could be due to band tail conduction.

**Variable range hopping conduction**

Dark conductivity at very low temperature range (123 K to 300 K) for nanocluster carbon thin films needs to be understood in terms of various models available for electron transport in disordered materials like amorphous, polymeric and low dimensional nanostructures [188-191]. In these type of films, the carrier conduction at very low temperatures may be assisted by variable range hopping (VRH) conduction given by

$$\ln(\sigma_d) \propto \left( \frac{T_0}{T} \right)^m$$

(5.2)

where $T_0$ is a constant for the material. The value of $m$ depends on the microstructure and the temperature region. The exponent $m$ gives information on the type of carrier conduction mechanism. In a bulk material, $m=1/4$ is attributed to Mott’s VRH conduction where electron-electron ($e-e$) interactions are neglected [188]. On the other hand, the inclusion of long range $e-e$ leads to $m=1/2$ as suggested by Efros-Shklovskii (ES) hopping mechanism [189].

According to Mott’s equation for the three dimensional case, if the density of states (DOS) is constant in a $kT$ energy range around Fermi level, the $\sigma_d(T)$ is expressed as:

$$\ln(\sigma_d) \propto \left( \frac{T_M}{T} \right)^{0.25}$$

(5.3)

where $T_M$ is related to the DOS at the Fermi energy ($N_f$) by expression

$$T_M = \frac{\beta_M \alpha^3}{kN_f}$$

(5.4)

where $\alpha$ is the decay constant of localized wave function and $\beta_M$ is a constant. According to Mott, the value of $\beta_M$ is $\sim 16$ for a constant density of states around the Fermi level [188]. However, the variations in the value of $\beta_M$ are described by Rosenbaum *et. al.* [190] and Godet [191].
Godet et al. [191] has reported high values of $\beta_{M}\sim310$ for materials having an exponentially distributed DOS.

The hopping parameters like hopping distance ($R_{hop}$) and hopping energy ($W$) can be expressed as:

$$R_{hop} = \frac{0.4}{\alpha} \left( \frac{T_{M}}{T} \right)^{1/4} \quad (5.5)$$

and

$$W = k \left( T_{o} T \right)^{1/4} \quad (5.6)$$

Generally, the widely used percolation theory has been used to study the transport phenomena in semiconductors, in particular, to calculate the hopping parameters of Mott’s equation for the case of VRH. Many disordered or amorphous semiconductors and metal alloys follow this equation. Recently, this behavior has been reported not only in the range of low temperatures and constant DOS, as it was originally predicted by Mott [188], but also at high temperatures and for materials with a non-constant DOS around the fermi level[191]. A constant DOS model has been considered in the case of nanocluster carbon thin films.

A plot of temperature dependency as $\sigma T^{1/2}$ vs. $T^{-1/4}$ is shown in Figure 5.3. From the graph, regression statistic of the fit has been calculated for nanocluster carbon thin films. The squared regression coefficient is found to be 0.98 and the standard deviation is $3.622 \times 10^{-4}$. These two parameters confirm that the fit is very well and conduction is due to the variable range hopping. The conduction mechanisms in carbon films are closely related with the film microstructure and the $sp^2$ C–C bonding.

Various parameters have been calculated like density of states($N(E_f)$), hopping distance ($R$), and Hopping energy($W$) using Mott model. All the parameters have been extracted for temperature at 123K. For variable range hopping, the value of $W$ should be greater than $kT$ and $\alpha R$ should be greater than unity or of the order of unity, as suggested by Mott [188] and validated from Table 5.3. It is also observed that hopping distance increases with decrease in temperature while hopping energy decreases with decrease in temperature.
Figure 5.3 shows the variation of disorder parameter $T_0$ with respect to the ion energies. Disorder decreases gradually and minimum at ion energy of 30 eV and then increases. Conductivity prefactor varies from the $10^{-6}$ (Ω⋅cm)$^{-1}$ to $10^{-3}$ (Ω⋅cm)$^{-1}$. The low values of
the pre–exponential factors $\sigma_0$ suggest that hopping transport localised state dominates the conduction process. But Mott relation is contradicted by the film grown under deposition ion energy of 30 eV even though the data is fitted well with Mott equation. In this, $W$ is less than $kT$ and $\alpha R$ is less than 1 with relatively high values of defect states. Origin of high defect density in this case is a matter of future investigation.

![Graph](image)

**FIGURE 5.4** Variation of disorder parameter $T_0$ and conductivity pre–factor with respect to the different deposition ion energies. Lines are guide to the eye.

Apart from variation with respect to deposition ion energies, conductivity variation with respect to arc current and throw distance also have been discussed.

### 5.2.3 Variation of conductivity data with respect to arc current and throw distance

Figure 5.5 (a) shows the variation of room temperature conductivity of the nanocluster carbon films grown under varying arc current conditions using the cathodic arc process.
FIGURE 5.5 Variation of room temperature conductivity of nanocluster carbon thin films grown using cathodic arc process under varying (a) arc current (b) throw distance.

The maximum room temperature dark conductivity observed is found to be $1.9 \times 10^{-5} \, (\Omega \cdot \text{cm})^{-1}$ for a deposition arc current of 150 Amp. The conductivity value decreases thereafter to $1.66 \times 10^{-5} \, (\Omega \cdot \text{cm})^{-1}$ at arc current...
of 250 Amp. After that, it once again increases to $2.89 \times 10^{-5} \text{ (Ω–cm)}^{-1}$ at arc current of 360 Amp. However, these films also exhibit increase in conductivity with increase in temperature and exhibit semiconducting behavior.

Discussed next is the nanocluster carbon films grown using the cathodic arc process with the substrates placed at varying distances from the arc, also referred as the “Throw distance”. Figure 5.5 (b) shows the variation of the room temperature dark conductivity of the nanocluster carbon samples with respect to the changing throw distance during the growth using the cathodic arc process. The maximum value of conductivity is found to be $3.28 \times 10^{-5} \text{ (Ω–cm)}^{-1}$ at the throw distance of 250 mm. As the distance between target and cathode source increases, velocity of $C^+$ ion source decreases. This leads to the deposition of material that is energetically favorable for $sp^2$ bonding [63]. However, with in the range of samples studied, it is observed that both in the case of varying arc current and throw distance there is no significant variation in the room temperature conductivity in the case of nanocluster carbon thin films.

### 5.3 Conductivity measurement of nanocluster carbon thin films grown under varying condition of helium and nitrogen partial pressure

Dark conductivity measurements were carried out on helium incorporated nanocluster carbon thin films in the temperature range of $\sim 297 \text{ K}$ to $\sim 403 \text{ K}$ in the coplanar configurations with fixed nitrogen partial pressure. The basic configuration of setup is same as discussed in chapter 3. The conductivity is given by

$$\sigma = \sigma_o \exp \left( \frac{-E_a}{kT} \right) \quad (5.7)$$

where $E_a$ is the activation energy. A plot of log ($\sigma$) vs. $1/ T$ will yield a straight line, with the slope being the activation energy $E_a$, i.e. the distance between Fermi level and conduction band edge and the intercept with the ($\sigma$) axis will be $\sigma_o$. Figures 5.6 and 5.7 show variation of the
conductivity with respect to $1000/T$, for the nanocluster carbon films grown under constant nitrogen partial pressure of $10^{-4}$ Torr and $10^{-3}$ Torr and varying helium partial pressures. The conductivity varies with helium partial pressures and films are semiconducting in nature. As evident from the Figure 5.6 and 5.7, single type of conduction is prominent in these films. Activation energies are varying from 0.14 eV to 0.22 eV ($N_2=10^{-4}$ Torr) and from 0.17 eV to 0.36 eV ($10^{-3}$ Torr). These conductions for both cases could be in localized states around fermi level ($N_2=10^{-4}$ Torr) and in band tails or through extended states ($10^{-3}$ Torr). All data have been enumerated in Table 5.4 with standard deviation.

The variation of the activation energies with respect to deposition conditions (varying helium partial pressure and for fixed nitrogen partial pressure of $10^{-4}$ Torr and $10^{-3}$ Torr) is shown in Figure 5.8.

**FIGURE 5.6** Conductivity variations with respect to $1000/T$ for nanocluster carbon thin films grown under varying helium partial pressures with fixed nitrogen pressure of $10^{-4}$ Torr.
FIGURE 5.7 Conductivity variations with respect to 1000/T for nanocluster carbon thin films grown under varying helium partial pressures with fixed nitrogen pressure of $10^{-3}$ Torr.

Table 5.4 Calculated activation energy for nanocluster carbon thin films grown under varying partial pressure of helium and nitrogen

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation Energy(eV) N2=10^{-4} Torr</th>
<th>RT Conductivity ($\Omega^{-1} \text{cm}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td>0.15±0.0019</td>
<td>2 x 10^{-9}</td>
</tr>
<tr>
<td>NB</td>
<td>0.14±0.0019</td>
<td>4.5x10^{-9}</td>
</tr>
<tr>
<td>NC</td>
<td>0.16±0.0049</td>
<td>2.4x10^{-8}</td>
</tr>
<tr>
<td>ND</td>
<td>0.21±0.0037</td>
<td>3.1x10^{-7}</td>
</tr>
<tr>
<td>NE</td>
<td>0.22±0.0044</td>
<td>2.7x10^{-7}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation Energy(eV) N2=10^{-3} Torr</th>
<th>RT Conductivity ($\Omega^{-1} \text{cm}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF</td>
<td>0.17±0.0022</td>
<td>3.6x10^{-6}</td>
</tr>
<tr>
<td>NG</td>
<td>0.21±0.0132</td>
<td>1.6x10^{-6}</td>
</tr>
<tr>
<td>NH</td>
<td>0.36±0.00216</td>
<td>8x10^{-8}</td>
</tr>
</tbody>
</table>
FIGURE 5.8 Plot of the activation energy versus He/N2 ratio, for two fixed Nitrogen partial pressure of (a) $10^{-4}$ Torr and (b) $10^{-3}$ Torr.

In nanocluster carbon thin films with fixed Nitrogen partial pressure of $10^{-4}$ Torr, activation energy initially increase from 0.14 eV up to 0.22 eV at He pressure of $5 \times 10^{-3}$ Torr (He/N2=5) and then decreases to 0.16 eV at He pressure of 0.5 Torr (He/N2=5000) as shown in figure 5.8. Similarly, in the case of nanocluster carbon films with fixed Nitrogen partial pressure of $10^{-3}$ Torr, activation energy gradually increases with increase in helium partial pressure and maximum of 0.36 eV for helium
partial pressure of 0.5 Torr (He/N2=500). Lowering of activation energy could be possible due to Fermi level shift or alloying. This could be reflected from Fermi level shift and band gap lowering which is matter of future investigations.

5.4 Conductivity measurement of nanocluster carbon thin films grown under varying hydrogen and nitrogen partial pressure

In this section, electrical conductivity of the films grown under varying conditions hydrogen partial pressure and fixed nitrogen partial pressure has been discussed. The variation of conductivity with temperature has been studied in the range of 178 K to 423 K in order to determine the conduction mechanisms in different temperature regions for these films. Nanocluster carbon thin films are mixed phased material containing both sp\(^3\) and sp\(^2\) bondings. Therefore, properties of nanocluster carbon thin films are governed by localized π states over large energy range. The variation of dark conductivity (\(\sigma\)) as a function of inverse of temperature ranges from 178K to 423K is shown in figure 5.9. Activation energies have been enumerated in Table 5.5.

Dark conductivity of these films are estimated using the relation given by Eq. (5.8)

\[
\sigma = \sigma_0 \exp \left( \frac{-E_a}{kT} \right)
\]  

(5.8)

The conductivity has been found to increase with increasing temperature, revealing semiconducting behavior of the films. Most of the films show two regions for the conduction phenomenon with the exception for films H1 and H5 which shows three regions of operations. It shows kink (transition temperature) at around 399±6 K and 278±1 K for three regions of operation and 278±1 K for two regions of operations. The resultant conductivity for three regions of conduction is given by Eq. (5.9)
The resultant conductivity for 2 regions of conduction is given by Eq. (5.10)

\[
\sigma = \sigma_{o1} \exp\left(\frac{-E_{a1}}{kT}\right) + \sigma_{o2} \exp\left(\frac{-E_{a2}}{kT}\right)
\]

(5.10)

The activation energies have been enumerated in the Table 5.5.

Sample H1 and H5 only show activated type of transport (Region R1, from 423 K to 399 K) with activation energy of 0.4 and 0.32 eV. This semiconductor-like signature suggests thermal activation of electrons from valence to conduction band states separated by a band gap. Moreover in the temperature range of 399 K to 178K, all samples show two regions of operation with region divided between two temperature ranges 399 K–278 K and 278K–178K.

In the temperature range of 399 K to 278 K for all samples, the activation energy varies from 42 to 72 meV. The R² values vary from 0.98 to 0.99. At room temperature, conductivity is highest for sample H2 with the value of 30 Ω⁻¹ cm⁻¹ (H2=10⁻³ Torr) while for other samples, it varies from 3 to 5.2 Ω⁻¹ cm⁻¹. These low values of activation energy could indicate formation of interconnected sp² carbon cluster networks. Starting with the electrical conductivity data, figure 5.10 (a) shows the variation of \(\sigma_{RT}\) and activation energy as a function of the ID/IG ratio obtained for all the films.

The maximum conductivity corresponds to minimum activation energy when ID/IG ratio is maximum of 0.88. This corresponds to deposition condition of fixed N2=10⁻³ Torr and Hydrogen pressure of 10⁻⁴ Torr. Minimum conductivity and maximum activation energy corresponds to near minimum ID/IG ratio of 0.48. The increase of ID/IG ratio, explained by an increase in the clustering of the C sp² graphitic clusters which corresponds to a larger sp² content and a smaller distance between the localized π–π* states. The changes observed in \(\sigma_{RT}\) could be due to a combination of two effects, due to CN bonds and the formation of the sp² C
graphitic clusters. Also, figure 5.10 (b) shows conductivity is maximum with FWHMG of 73 cm\(^{-1}\) and G–peak position is maximum of 1568 cm\(^{-1}\). FWHM is a measure of disorder, so it indicates the formation of graphitic clusters as also evident from the G–peak positions. As disorder increases with the increase of FWHMG, conductivity decreases.

**FIGURE 5.9** Variation of dark conductivity versus inverse of temperature for nanocluster carbon thin films grown under varying H2 gas pressures and fixed N2 pressure of \(10^{-3}\) Torr.
FIGURE 5.10 (a) Variation of the room temperature conductivity $\sigma_{RT}$ and activation energy as a function of the ID/IG ratio obtained for all the films. The lines are guide for the eye. (b) Variation of the room temperature conductivity $\sigma_{RT}$ as a function of the FWHMG obtained for all the films. Lines are guide to eye.
Table 5.5 Enumerated values of activation energy of nanocluster carbon thin films grown under varying partial pressure of hydrogen and fixed nitrogen

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Activation Energy</th>
<th>Region 1</th>
<th>Region 2</th>
<th>Region 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>0.32 eV</td>
<td>49 meV</td>
<td>7.25 meV</td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td>-</td>
<td>42 meV</td>
<td>27 meV</td>
<td></td>
</tr>
<tr>
<td>H3</td>
<td>-</td>
<td>44 meV</td>
<td>22 meV</td>
<td></td>
</tr>
<tr>
<td>H4</td>
<td>-</td>
<td>55.2 meV</td>
<td>16 meV</td>
<td></td>
</tr>
<tr>
<td>H5</td>
<td>0.4 eV</td>
<td>72 meV</td>
<td>17.5 meV</td>
<td></td>
</tr>
</tbody>
</table>

**VRH conductivity**

In the very low temperature regime (region R3) varying from 178 to 278K, conductivity of the samples is governed by variable range hopping (VRH) conduction as evident from the Figure 5.11. A linear fit for \( \sigma \) vs. \( T^{-1/4} \) with \( R^2=0.99 \) confirms VRH conduction. From this plot, it is clear that the conductivity increases slowly with increasing temperature over the temperature range 178 to 278 K, which suggests that the conduction is due to variable range hopping (VRH) due to Mott [188].

![Conductivity versus T\(^{-1/4}\) plot of the nanocluster carbon thin films.](image)

**FIGURE 5.11.** Conductivity versus \( T^{-1/4} \) plot of the nanocluster carbon thin films.
We have calculated the various parameters like density of states ($N(E_f)$), hopping distance ($R_1$), Hopping energy ($W$), and $T_0$ (measure of disorder) using Mott parameters. For variable range hopping, the value of $W$ should be of the order of a few $kT$ and $\alpha R$ should be greater than unity or of the order of unity, as suggested by Mott [188] and validated from Table 5.6. It is also observed that hopping distance increases with decrease in temperature while hopping energy decreases with decrease in temperature.

**Table 5.6** Calculated value of Density of states (DOS), hopping distance and hopping energy under varying partial pressure of hydrogen and fixed nitrogen

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$N(E_f)$ (cm$^{-3}$ eV$^{-1}$)</th>
<th>$R_1$(cm), 278 K</th>
<th>$W$(meV), 278 K</th>
<th>$\alpha R_1$, 278 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>$1.4 \times 10^{20}$</td>
<td>4.3$x10^{-7}$</td>
<td>23</td>
<td>1</td>
</tr>
<tr>
<td>H2</td>
<td>$7.5 \times 10^{18}$</td>
<td>9$x10^{-7}$</td>
<td>48</td>
<td>1.9</td>
</tr>
<tr>
<td>H3</td>
<td>$2 \times 10^{17}$</td>
<td>2$x10^{-6}$</td>
<td>116</td>
<td>4.7</td>
</tr>
<tr>
<td>H4</td>
<td>$6.6 \times 10^{18}$</td>
<td>9$x10^{-7}$</td>
<td>49</td>
<td>1.8</td>
</tr>
<tr>
<td>H5</td>
<td>$3 \times 10^{18}$</td>
<td>1$x10^{-6}$</td>
<td>62</td>
<td>2.5</td>
</tr>
</tbody>
</table>

DOS is varying from $2 \times 10^{17}$ to $1.4 \times 10^{20}$ cm$^{-3}$ eV$^{-1}$. So, there are three order changes in DOS. It is evident that defect state is maximum of $1.4 \times 10^{20}$ cm$^{-3}$ eV$^{-1}$ in sample H1 (no hydrogen gas). This may be due to the fact that ionized hydrogen atom on account of its interaction with unbounded carbon, could possibly facilitate the passivation of defective bonds, and the lack it in H1 could be the cause for high defect density states in the film in the case of sample H1. So presence of hydrogen leads to decrease in defect densities with minimum density of $2 \times 10^{17}$ cm$^{-3}$ eV$^{-1}$. Conductivity is maximum for sample H4 grown under hydrogen partial pressure of $10^{-4}$ Torr due to graphitic nature of the film. The very high DOS for sample H1 could be due to non-passivation of the films by hydrogen gas.
Figure 5.12 (a), (b), (c) show the variation of the electrical conductivity of nanocluster carbon films with temperature grown under diverse process parameters including (a) ion energy, throw distance and arc current (b) fixed nitrogen with varying helium (c) fixed nitrogen with varying hydrogen. Shown in figure 5.12 (d) is the maximum and minimum conductivity data observed under the set of parameters studied. Summarizing the conductivity values of the room temperature deposited nanocluster carbon films, grown under varying process /deposition parameters, the values varies from as maximum as \(~10\) (\(\Omega\text{–cm})^{-1}\) to \(~10^{-10}\) (\(\Omega\text{–cm})^{-1}\). This indicates that, even with in the limited set of parameters studied to understand the nature of the electronic properties of the novel room temperature grown nanocluster carbon films, as a first study, the material is inherently semiconducting. Further the room temperature conductivity can be varied over \(10^{10}\) orders from near insulating to degenerate semiconductor (metallic) values, and already in the range of samples studied the density of states as low as \(10^{17}\) have been observed.
2.4 2.6 2.8 3.0 3.2 3.4
10
-11
10
-10
10
-9
10
-8
10
-7
10
-6
10
-5
Conductivity, (\( \Omega^{-1} \text{cm}^{-1} \))
N_2 = 10^{-3} \text{Torr, varying helium}

(b)

2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0
10
0
10
1
10
2
Conductivity, (\( \Omega^{-1} \text{cm}^{-1} \))
N_2 = 10^{-3} \text{Torr, varying hydrogen}

(c)
5.5 Meyer–Neldel Rule (MNR) in nanocluster carbon thin films grown under diverse deposition conditions

Semiconductors are characterized by the temperature dependence of their electrical conductivity. Most semiconductors exhibit an exponential temperature dependence of the conductivity. For many classes of materials, especially organic semi–insulators, chalcogenide glasses, amorphous silicon, fullerenes and amorphous carbon films experimental evidence suggest that a correlation exist between the activation energies and pre–exponential factors of the following form [192-194]

$$\ln \sigma_0 = bE_a + \ln \sigma_{00}$$

(5.11)

where b and $\sigma_{00}$ are constant. This relation can be written as
Here $b = 1/kT_0$. The relation, given by Equation (5.11), gives the dependence of a pre-factor $\sigma_0$ on the activation energy $E_a$ and represents Meyer–Neldel empirical rule. Equation (5.12) is often referred to as the MN rule or the compensation rule [195]. Constant $\sigma_{00}$ is often called the Meyer–Neldel pre-exponential factor and $kT_0$. $E_{MN}=kT_0$ the MN characteristic energy.

For electric conductivity of upper mentioned group of substances it holds

$$\sigma = \sigma_{00} \exp \left( \frac{E_a}{kT_0} \right) \exp \left( \frac{-E_a}{kT} \right)$$

(5.13)

This rule holds in disorder materials when $E_a$ is varied by doping, by surface absorption, light soaking or by preparing films under different conditions. This rule has also been observed for liquid semiconductors and fullerenes. The validity of the MN rule has also been reported in the case of chalcogenide glasses. Electrical conductivity in the dark is measured as a function of temperature for this purpose.

**FIGURE 5.13.** Exponential pre-factor $\sigma_0$ plotted against the activation energy $E_a$ for different nanocluster carbon thin samples.
Figure 5.13 shows a semi–logarithmic plot between $\sigma_0$ and activation energy $E_a$ obtained for various nanocluster carbon thin films including films grown under different deposition ion energies. The data plot is found to be satisfying the Meyer–Neldel (MN) rule. MNR parameters have been found to be $b \sim 3.45 \text{ eV}^{-1}$ (or $E_{MN} = 0.29 \text{ eV}$) and $\sigma_{00} \approx 7.64 \times 10^{-4} \text{ (}\Omega\text{–cm})^{-1}$. The coefficient $\sigma_{00}$ can be interpreted as the conductivity evaluated at the temperature $T_{MNR} = 1/(kb)$[195].

5.6 Space Charge Limited current (SCLC) conduction in nanocluster carbon thin films

To understand electrical, electronic and optoelectronic properties of the room temperature grown Nanocluster Carbon (NC) thin films and to consider it for possible device applications, it is very important to understand the possibilities of the presence of defects and the nature of their distribution. Hence, SCLC technique is used to determine the Density of defect States (DOS). Typically SCLC data is evaluated using current–voltage (I–V) characteristics with a n–i–n and p–i–p structure. Nespurek et al.[196] had proposed a differential method which have been used to study the defect density of states (DOS) of nanocluster carbon thin films. The density of energy states is calculated from the nonlinear I–V characteristics under the following assumptions [196]:

(i) The free and trapped carriers are in local quasi–thermal equilibrium and the presence of a moderate electric field does not affect the elementary microscopic processes of electron capture and thermal reemission. The relation between the thermal reemission rate constants and the capture rate constant follows from the principle of detailed balancing.

(ii) The localized energy states are homogeneously distributed in the material which is investigated.

(iii) Constant carrier mobility.

(iv) Carrier diffusion is not taken into account.
(v) The injection contact is an infinite reservoir of carriers, that is, the current is not electrode limited and the band bending near the contact has an only minor influence on the I–V characteristics.

(vi) Double injection does not occur. Either holes or electrons are injected.

5.6.1 Basic Current–Voltage (I–V) characteristic

Studies of I–V characteristics are very much important to investigate the nature of the nanocluster carbon films.

![Current-Voltage characteristic of nanocluster carbon thin film](image)

**FIGURE 5.14** Current-Voltage characteristic of nanocluster carbon thin film.

The I–V curve shows overall non-linear behavior within the applied bias of −2V to 2V as shown in Figure 5.14. Dielectric breakdown of the thin film occurs if voltage is more than 2V for nanocluster carbon thin films. Figure 5.15 shows the logarithmic I–V curve of nanocluster carbon thin film. In the Figure 5.15, it is evident that slope of the curve changes from low bias to high bias. A quite good fit is obtained for both ohmic and SCLC regions. I–V curve shows two regions of conduction viz. (a) nearly ohmic conduction at low bias i.e. from 0.0256 to 0.304 and (b) SCLC conduction at high bias i.e. from 0.304V to 2V. In ohmic region the slope is
1 and in SCLC region in our case, it nearly equal to 2. In the ohmic region, the current follows the relationship given by

\[ I = aV \] (5.14)

and in the SCLC region, it follows the

\[ I = aV^2 \] (5.15)

where \( I \) is the current and \( V \) is the applied voltage.

**FIGURE 5.15** Logarithmic I–V plot of the nanocluster carbon thin films showing electronic charge behavior under varying voltage.

Nanocluster carbons thin films were grown under different deposition conditions. Different values of slopes for different films are given in Table 5.7.

For lower bias the injected charge carrier density is lower than the thermally generated behavior. At higher bias, the slopes are nearly equal to two which clearly suggest that the conduction in this region is dominated by trap limited space charge limited conduction mechanism and the traps are at shallow level. The transition voltage (\( V_T \)) at which
the transition occurs from ohmic to SCLC is expected to depend on the film growth conditions.

Table 5.7 Calculated values of slope for different nanocluster carbon thin films grown under different deposition conditions.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Slope values</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1.9</td>
</tr>
<tr>
<td>S2</td>
<td>2.1</td>
</tr>
<tr>
<td>S3</td>
<td>2.1</td>
</tr>
<tr>
<td>S4</td>
<td>1.8</td>
</tr>
<tr>
<td>S5</td>
<td>1.8</td>
</tr>
</tbody>
</table>

5.6.2 Electronic transport mechanism in nanocluster carbon thin films

It has been observed from chapter 4, that these films are mixed phased materials with sp² and sp³ type bonding varying with process parameters, with varying defect density concentration. The defect states in the films, which effectively act as either trapping or recombination centers, play an important role in determination of conduction mechanism. After trapping the injected charge from electrodes, the defects become charged and thereby expected to build up a space charge. The built up of space charge by inherent native defects then play a key role in determining the SCLC process. These defects are discrete in nature. Discrete trap levels are more often associated with traps that are farther apart from each other, preventing them from strong coupling [197]. Because of the discrete nature, the I–V characteristic usually has a sharp transition region, signifying the change from empty to filled states of the traps.

For low biasing voltage i.e., from 0V to transition voltage (V_T), the injected charge carriers are negligible as compared to thermally generated carriers. It follows ohm’s law. At lower bias up to transition voltage (V_T), the current density (J) governed by thermally generated carriers (n₀), in the film can be expressed as[199]
Here \( d \) is gap between the electrodes and \( \mu \) is electron mobility. Only unipolar charge transport is considered. In the high bias region, i.e., 0.304 to 2 V a slope of two indicates shallow trapping and slope greater than two indicates exponential trap distribution. However, in present case the slope in the case of nanocluster carbon thin films are nearly equal to two indicating the presence of shallow traps. Therefore, this trap limited SCLC current density governed by Mott and Gurney law[199] is given by

\[
J = \frac{n_0 \mu V_T}{d} \tag{5.16}
\]

The total trap concentration is given by

\[
N_T = \frac{3\varepsilon_s\varepsilon_0 V_T}{2qL^2} \tag{5.17}
\]

The trapping parameter[197] \( \theta \) is given by equation 5.19.Here the \( N_c \) effective density of states considered in the conduction band=2.04x10^{19}/cm^3.

At high bias condition, the injected carrier density from electrode is more than the thermally generated carriers. At this stage SCLC conduction dominates over the ohmic conduction. At the transition voltage of \( V_T \), where the conduction changes from Ohmic to SCLC, the injected carrier density is equal to the thermally generated carrier density.

The measurement of normal volume generated free carrier density [197] in SCLC region is given by

\[
n_0 = \frac{\xi_s\varepsilon_0 V_T}{ed^3} \tag{5.19}
\]

In some cases, SCLC phenomenon is governed by the exponential trap distribution with deep traps [199]. Therefore, this trap limited SCLC current density is expressed as
Here, \( N_0 \) is the trap density per unit energy range at conduction band edge, \( \varepsilon \) the permittivity of the film and \( l \) the ratio of \( (T_l/T) \), here \( T_l \) and \( T \) are the characteristic temperature of energetic trap distribution and ambient temperature, respectively. The total trap concentration is given by

\[
N_t = N_0 kT_l
\]  

(5.21)

The injected carrier density becomes greater than the free carrier density at high bias which leads to SCL conduction in the films. At transition voltage \( (V_t) \) where conduction changes from ohmic to SCLC, the injected carrier density is equal to free carrier density. The total trap concentration is also determined as

\[
N_t = \left( \frac{N_c}{n_0} \right)^{1/2} \left( \frac{\varepsilon V_t}{ed^2} \right)
\]  

(5.22)

The trap depth, \( E_t \), is a function of \( \theta \) which can be expressed as

\[
\theta = \left( \frac{N_c}{N_t} \right) \exp \left( \frac{-E_t}{kT} \right)
\]  

(5.23)

The exponential set of traps that are created due to amorphous nature and dangling bonds in the structure. The calculated values of \( \theta \), \( N_t \), \( n_0 \) and \( E_t \) for different samples are systematically tabulated in Table 5.8.
Table 5.8 Trapping parameter, trap concentration, free carrier density and trap depth of different nanocluster carbon thin films calculated using SCLC Technique.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Trapping parameter θ</th>
<th>Total trap concentration $N_t (cm^{-3})$</th>
<th>Free carrier Density $n_0 (cm^{-3})$</th>
<th>Trap depth $E_t (eV)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.012</td>
<td>9.8x10^{16}</td>
<td>8x10^{14}</td>
<td>0.253</td>
</tr>
<tr>
<td>S2</td>
<td>0.013</td>
<td>11.2x10^{16}</td>
<td>9.84x10^{14}</td>
<td>0.248</td>
</tr>
<tr>
<td>S3</td>
<td>0.0125</td>
<td>10.8x10^{16}</td>
<td>9x10^{14}</td>
<td>0.25</td>
</tr>
<tr>
<td>S4</td>
<td>0.018</td>
<td>7.6x10^{16}</td>
<td>9x10^{14}</td>
<td>0.25</td>
</tr>
<tr>
<td>S5</td>
<td>0.015</td>
<td>7.6x10^{16}</td>
<td>7.7x10^{14}</td>
<td>0.2543</td>
</tr>
</tbody>
</table>

5.6.3 Calculation of defect density of states (DOS)

The defect Density of states (DOS) distribution ($g(E_d)$) can be obtained from differential technique proposed by Nespurek and Swarakowski [196]. In this case the traps are assumed to be discrete in nature and there is no coupling between them as evident from slope in the SCLC region is nearly equal to two shown in figure 5.18. In this technique, the DOS at the quasi–fermi level is given

$$DOS = \left( \frac{\chi \varepsilon \sigma}{ed^2 kT} \right) \left( \frac{V}{m(V) - 1} \right)$$

(5.24)

where $m(V) = d(ln I)/d(ln V)$ is slope[199,200], $\chi$ is the correction factor for non-uniformity of internal field, here its value is 0.75, $\varepsilon$ is the permittivity of the material which is taken as 4x10^{−10} C/V·m for tetrahedral amorphous carbon films is assumed [201], e is the electronic charge, d is the thickness of the films, k is the Boltzmann constant, T is the temperature in Kelvin, and V is the voltage at which SCLC sets in. This method is sensitive to the DOS at the quasi–fermi level. Calculated values of the DOS have been summarized for various nanocluster carbon samples in Table 5.9.
Table 5.9 Defect density of states (DOS) of different nanocluster carbon thin films obtained from shallow-trap I–V characteristic.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>DOS (cm$^{-3}$eV$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>8.13x10$^{17}$</td>
</tr>
<tr>
<td>S2</td>
<td>7.26x10$^{17}$</td>
</tr>
<tr>
<td>S3</td>
<td>7.47x10$^{17}$</td>
</tr>
<tr>
<td>S4</td>
<td>7.121x10$^{17}$</td>
</tr>
<tr>
<td>S5</td>
<td>5.93x10$^{17}$</td>
</tr>
</tbody>
</table>

The Density of states extracted is in the range of 6x10$^{17}$ – 8x10$^{17}$ cm$^{-3}$ eV$^{-1}$.

5.6.4 SCLC based defect density calculation of nanocluster carbon thin films grown under varying helium and nitrogen partial pressure

Figure 5.16 (a) shows the current density ($J$) vs. voltage ($V$) plot of sample NA. The very first measurement clearly shows all four regions, characteristic of a one carrier discrete set of traps. The first region (I) is ohmic, where the current density is proportional to the voltage, $j=\frac{q n_0 \mu V}{d}$, $n_0$ being the free carrier density, $d$ the thickness of the polymer layer, and $\mu$ is the carrier mobility with slope of 1.06, next region (II) is the SCLC trap–limited where the current density is directly proportional to the square of the voltage, $J=\frac{9 \varepsilon \varepsilon_0 \theta V^2}{8d^3}$, $\theta$ is the trapping fraction, $\varepsilon$ is the dielectric constant of the polymer, $\varepsilon_0$ the permittivity of free space, with observed value of ~1.6. The third region (III) is the trap–filled limit where current increases nearly vertically and the onset of the trap–filled voltage $V_{TFL}$ gives the density of traps $N_t$, slope here is ~5. Here $N_t$ is given by

$$N_t = \frac{3 \varepsilon \varepsilon_0 V_{TFL}}{2qd^2} \quad (5.25)$$
The final region (I–V) is the traps free SCLC where current is limited by the space charge and free from the influence of traps with slope ~2. The trap–limited current arises from shallow electron traps.

Similar nature has been also observed in sample NB with four regions as shown in figure 5.16 (b). The first region (I) is ohmic, where the current density is proportional to the voltage with slope 1.12, next region (II) is the SCLC trap–limited region where the current density is directly proportional to the square of the voltage with extracted value of slope ~1.8. The third region (III) is the trap–filled limit where current increases nearly vertically and the onset of the trap–filled voltage $V_{TFL}$ gives the density of traps $N_t$ with slope of ~16. The final region (I–V) is the traps free SCLC where current is limited by the space charge and free from the influence of traps with slope ~1.85. Same characteristic is observed for sample NE also as shown in figure 5.16 (c). The transition region from $V_{TFL}$ to trap–free SCLC for the sample NA,NB and NE is not perfectly vertical which could be due to the generation of additional traps. Moreover, the decrease in current at higher fields (trap–free SCLC region) suggests both emptying of traps and additional creation of defects.

In the Figure 5.16 (d) and 5.16 (e) (sample NC and ND), two regions have been observed, ohmic region with the slope of ~1.14 and SCLC region with the slope of ~2.5. At small voltage, the SCL current is not observable, and Ohm’s law dominates the current-voltage characteristics due to the presence of thermal equilibrium free carriers. When the voltage becomes large enough, the SCL current is noticeable and enters the exponential trapping field region as evident from slope value $m=2.5$.

The density of traps $N_t$ and their energy levels have been obtained from the I–V characteristics. Density of defect states has been calculated using Dan Boer technique [202]. One can extract all the relevant parameters from the two, three and four regions depending upon the characteristic of the materials. The trap densities vary from $10^{17}$ cm$^{-3}$ to $10^{18}$ cm$^{-3}$ and the average trap energy of nanocluster carbon thin film is ~ 0.25 eV.. DOS vary from $9.4 \times 10^{16}$ cm$^{-3}$ eV$^{-1}$to $9.73 \times 10^{19}$ cm$^{-3}$ eV$^{-1}$. The extracted values of DOS, trap density and trap energy for all samples are enumerated in Table 5.10.
The maximum defect density of $9.73 \times 10^{19}$ (cm$^3$ eV$^{-1}$) has been obtained for sample ND grown under nitrogen partial pressure of $10^{-4}$ Torr and helium partial pressure of $5 \times 10^{-4}$ Torr. As evident from Table 5.4, conductivity of ND sample is maximum of $3 \times 10^{-7}$ (Ω–cm)$^{-1}$ with broad G–width corresponds to disorder which is maximum for sample ND. Also sp$^2$ clustering is more for this film.

![Graphs showing experimental observation of traps of nanocluster carbon thin films](image)

**FIGURE 5.16** Experimental observation of traps of nanocluster carbon thin films. (a), (b) and (c) show discrete shallow trap and (d) and (e) shows exponential trap behavior.
Table. 5.10 Calculated value of trap density, DOS and trap energy for films grown under varying partial pressure of helium and fixed nitrogen pressure of $10^{-4}$ Torr.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Density of Traps, $x 10^{17} N_t (cm^{-3})$</th>
<th>DOS ($cm^3 eV^{-1}$)</th>
<th>Trap Energy, $Et (eV)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td>1.35</td>
<td>9.4 x $10^{16}$</td>
<td>0.247</td>
</tr>
<tr>
<td>NB</td>
<td>3.63</td>
<td>9.13 x $10^{17}$</td>
<td>0.237</td>
</tr>
<tr>
<td>NC</td>
<td>2.15</td>
<td>1.26 x $10^{18}$</td>
<td>0.235</td>
</tr>
<tr>
<td>ND</td>
<td>37.2</td>
<td>9.73 x $10^{19}$</td>
<td>0.28</td>
</tr>
<tr>
<td>NE</td>
<td>1.72</td>
<td>4.34 x $10^{18}$</td>
<td>0.242</td>
</tr>
</tbody>
</table>

NC, ND= exponential trap distribution, NA, NB and NE= discrete shallow trap distribution.

5.7 Estimation of dielectric constant and defect density using Capacitance–Voltage (CV) measurement of nanocluster carbon films grown under different ion energies

The nanocluster carbon thin films are clustered and disordered materials. Nanocluster carbon thin films contain defects which act as a trap centres capturing mobile carriers. The existence of traps affects the performance of the MIS devices. Here, we have tried to establish Capacitance–Voltage (CV) measurement to estimate the dielectric constant and defect densities.

The traps levels present in the films capture carriers and lie below the Fermi–level in semiconductor. As biasing voltage is increased, these traps level rise above the Fermi level and contribute to the depletion layer charge. In the case of a–si:H [203], nature of $1/C^2$ versus V curve changes in the presence of traps. A $p^+–n$ junction model was proposed by Senechel and Basinski [204] to address the issue of slowly responding traps which were determined by the transient variation of high frequency capacitance. However, an alternative case for abrupt $p^+–n$ junction has been considered for both deep lying and shallow impurity states and model has been
proposed for both high and low frequency C–V relationship [205]. Our work has been based on the work of Nandi et al. [206] on DOS determination of hydrogenated amorphous silicon samples obtained from rice husk.

The basic schematic of the MIS structure setup with interface states has been discussed in chapter 3. Figure 5.17 (a) shows C–V characteristics of nanocluster carbon thin film MIS diode. There are variations in C–V characteristics of nanocluster carbon thin films. In general, all these sample have three regions of operations: accumulation at negative bias, depletion at positive/negative bias and inversion at positive bias with the measured value of C corresponding either to the insulator capacitance (C_{ins}) or to the series sum of the insulator capacitance and the capacitance of the amorphous semiconductor ((C_{ins}^{-1} + C_s^{-1})^{-1}) respectively. The inversion phenomenon has been explained by the extraordinarily long generation times for minority carriers and activated at much higher bias due to presence of traps. This behaviour is same as in some of the wide–gap organic semiconductors [207]. The obtained curve fit well with standard Mott–Schottky relationship for simple Schottky barrier device. The C–V measurements have been carried out measured with voltage swept from +5 V to –5 V.

The dielectric constant $\varepsilon_s$ calculated at accumulation is given by following relation [208]

$$\varepsilon_s = \frac{C_0 d}{\varepsilon_0 A}$$

(5.26)

where $C_0$ is the accumulation capacitance, $d$ is the film thickness, $\varepsilon_0$ is the permittivity of free space ($8.854 \times 10^{-14}$ F/cm), and $A$ the area of Aluminium electrodes.

From the extrapolation of $1/C^2$ versus $V$ curves on the voltage axis gives approximately the barrier height of one film as shown in Figure 5.17 (b) for one sample and given by Eq. (5.29). The measured values for other films are enumerated in Table 5.14. The barrier height can be determined by[208]
\[ \phi_b = V_i + V_n \left( \frac{kT}{q} \right) - \Delta \phi \] 

(5.27)

Where \( V_i \) is the voltage intercept, and \( V_n \) the depth of the Fermi level below conduction band.

From slope of the \( C-V \) characteristics of nanocluster carbon thin films shown in Figure 5.17 (a), DOS was determined using relation given by Spear et.al.[205]

\[ \frac{d(1/C^2)}{dV} = \frac{2}{\left( \varepsilon_r \varepsilon_0 qN_A A^2 \right)} \] 

(5.28)

This method was described by Schroder [208] for crystalline semiconductor and used for a–Si: H MIS structure by Spear et.al. [205] and Nandi et.al. [206]. Alongwith the gradient (from the depletion region) of the \( 1/C^2-V \) curve and equation 5.28 lead to extraction of density of states. The densities so obtained near the Fermi level of undoped specimens may not represent the true value of the DOS, as the present method is normally used for crystalline semiconductors and so any deductions from these values have to be treated with some caution [205].

The dielectric constants, barrier heights and DOS are enumerated in Table 5.1. Dielectric constant is varying from 2.76 to 11.8. High dielectric constant could be due to rich sp\(^3\) content in the mixed phase nanocluster carbon thin film. The observation of the variation in the Defect density of the films from \( 5.68 \times 10^{16} \) to \( 4.9 \times 10^{19} \) cm\(^{-3}\) in the randomly studied samples clearly indicate the possibility of tailoring the materials with varying properties for electronic application, when the process is optimized. DOS of the films have been also calculated using Dan Boer Technique[202] given by

\[ g(E_{Fn}) = \frac{\chi \varepsilon_r \varepsilon_0 (V_2 - V_1)}{eL^2 (\Delta E_{Fn})} \] 

(5.29)

where all the symbols used in the expression have already been defined in the literature [202]. Values have been enumerated in Table 5.11.DOS
values calculated using Dan Boer differ with DOS values calculated using CV technique by order of 1 or 2. This typical difference is due to average density consideration in Dan Boer Technique.

![Graph A](image1.png)

(a)

![Graph B](image2.png)

(b)

**FIGURE 5.17** (a) Capacitance–Voltage characteristics of Al/Nanocluster carbon/c–Si MIS structures (b) Plot of $1/C^2$ versus V of Al/NC thin film/c-Si MIS structure in depletion region.

Nanocluster carbon thin films contain both sp$^2$ and sp$^3$ bonding. Sp$^2$ sites are embedded in the sp$^3$ bonded matrix. Variation of dielectric constant with respect to the ion energies has been studied. Dielectric
properties are controlled by $\sigma - \sigma^*$ states found only in sp$^3$ bond with wide band gap. Electronic properties are controlled by $\Pi - \Pi^*$ states found in sp$^2$ bonds. Explanation of the variation of dielectric properties is based on sub–implantation model proposed by John Robertson\[10\].

Table 5.11 Measured dielectric constant, DOS and barrier height of nanocluster carbon thin films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition Cond., Ion Energy(eV)</th>
<th>Dielectric Constant</th>
<th>DOS (cm$^3$)</th>
<th>Barrier Height(eV)</th>
<th>DOS (cm$^3$ eV$^{-1}$) By Dan Boer Tech.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100</td>
<td>6.583</td>
<td>4.9x10$^{19}$</td>
<td>-0.8141</td>
<td>7.6x10$^{17}$</td>
</tr>
<tr>
<td>B</td>
<td>200</td>
<td>2.76</td>
<td>1.4x10$^{17}$</td>
<td>0.0926</td>
<td>5.3x10$^{17}$</td>
</tr>
<tr>
<td>C</td>
<td>60</td>
<td>2.84</td>
<td>1.52x10$^{17}$</td>
<td>-1.1225</td>
<td>1.1x10$^{18}$</td>
</tr>
<tr>
<td>D</td>
<td>25</td>
<td>11.8</td>
<td>2.01x10$^{17}$</td>
<td>-0.9805</td>
<td>1.9x10$^{18}$</td>
</tr>
<tr>
<td>E</td>
<td>20</td>
<td>9.36</td>
<td>5.68x10$^{16}$</td>
<td>0.0664</td>
<td>3.8x10$^{18}$</td>
</tr>
</tbody>
</table>

So, in the end it can be concluded that it is difficult to draw any specific conclusion with this limited data (only five samples), except that the process offers the option to possibly tailor the dielectric constant varying from ~2 to 12, which is indeed a very interesting observation, in the age of wide range of meta materials and increasing use of both high and low K dielectric materials in many applications.

5.8 Photoconductivity of the nanocluster carbon thin films

In semiconductors, electronic conduction is enhanced by the generation of photo excited charge carriers due to the absorption of photons with energy greater than the band gap energy. The electron moves to the conduction band where it contributes to the conductivity, or it may be trapped in the localized states. In general, the photoconductivity is expressed as

$$\sigma_{ph} = e(n_e \mu_e + n_p \mu_p)$$  \hspace{1cm} (5.30)
where $G$ is the generation rate, that is, the number of charged carriers generated per unit time per unit volume, and $\tau$ is the average recombination lifetime. The recombination lifetime in turn is sensitive to the density of localized states, in particular dangling bond defects. Determining the suitability of nanocluster carbon films for optoelectronic applications begins by examining the conductivity of the material under illumination and comparing it to the material’s conductivity under dark conditions. This ratio of dark to photo conductivity is known as the photosensitivity of the material and is a general indication optoelectronic capability of the semiconducting material. The photo sensitivity varies from material to material, varying from $10^5 – 10^6$ in high quality a–Si:H, to $10^2$ in a–(Si, Ge): H with an $E_{g}$ gap of 1.5 eV, and ~1 in doped crystalline silicon or germanium [88].

\[
n_e = G\tau_e \quad \text{and} \quad n_p = G\tau_p
\]  

(5.31)

**FIGURE 5.18.** Photoconductivity and Dark conductivity of the C1 nanocluster carbon thin sample.

The illuminated and dark conductivity measurements are performed in an apparatus having a provision to use a tungsten iodide halogen lamp. The intensity was kept at 30 mW/cm² and the
measurements were made using coplanar configuration. Figure 5.18 and 5.19 show dark and illuminated conductivity of two different nanocluster carbon thin films. It may be seen that there is photo response though not in multiple orders. This indicates that with further optimization it would be possible to have optoelectronics response from these room temperature grown nano cluster carbon thin film samples.

FIGURE 5.19. Photoconductivity and dark conductivity of the C6 nanocluster carbon sample.

5.9. Discussions

5.9.1 Electrical and electronic properties of nanocluster carbon thin films grown under diverse deposition conditions

The electrical and electronic properties of room temperature grown nanocluster carbon films using the cathodic arc process is being reported for first time. Multiple process parameters including arc current, arc voltage, deposition ion energy, target temperature, nature of target surface, nature of excitation, magnetic field used for control of the macro
particle, deposition pressure, temperature of the substrate, throw distance, substrate bias, the surrounding gases or ambient gas environment and partial pressure influence the properties of the material. There have been enough review of amorphous carbon films, diamond-like carbon films and tetrahedral amorphous carbon grown using cathodic arc process by leading academic institutions and companies [9,74,86,87,179,185,209,210]. However, there have been no reports on systematic study of the growth of nanocluster carbon films. As this is one of the first studies, hence it is beyond the scope of this study to analyze in detail every property systematically. Rather samples grown under some key process parameters which cover a wider gamut and convey a sense of feasibility of using the room temperature grown nanocluster carbon as a possible emerging electronic material have been studied and reported. The room temperature conductivity values of the room temperature deposited nanocluster carbon films, grown under varying process deposition parameters, including varying ion energy, throw distance, arc current, varying helium and hydrogen partial pressures at fixed nitrogen partial pressure, show that the values varies from as maximum as \(30 \Omega^{-1} \text{cm}^{-1}\) to \(10^{-10} \Omega^{-1} \text{cm}^{-1}\) which is \(10\) to \(11\) order variation. Thus, it indicates the nature of electronic conduction which varies from degenerate semiconductor (metallic) to semiconducting to near insulating samples. This indicates that, the material is inherently semiconducting as the conductivity increases with temperature in all the case. The highest room temperature conductivity varying from \(3 \Omega^{-1} \text{cm}^{-1}\) to \(30 \Omega^{-1} \text{cm}^{-1}\) have been observed in nanocluster carbon films grown under varying hydrogen partial pressure conditions and constant nitrogen partial pressure. These films seem to have more uniform, smaller, \(sp^2\) graphitic clusters as observed from the Raman response and the highest ID/IG ratio among all hydrogen samples. High ID/IG ratio could mean increase in ordering of the films and could be increase in CN bonds as nitrogen is also present [10, 21]. For nanocluster carbon thin films grown under fixed nitrogen and
varying helium partial pressure, conductivity varies from $\sim 10^{-9}$ $(\Omega \text{-cm})^{-1}$ to $\sim 10^{-6}$ $(\Omega \text{-cm})^{-1}$, a variation of three order change in conductivity.

The nanocluster carbon films depending on the nature of the films grown, demonstrate multiple electronic transport mechanisms. With the diverse range of samples studied, three electronic transport mechanisms, namely, transport in extended states, band tails conduction (few samples) and variable range hopping (VRH) near the Fermi level, have been observed from the thermal activation measurements in the temperature range from 123 K to 423 K. The VRH transport parameters for nanocluster carbon thin films are studied over wide deposition parameters, and the density of states near the Fermi level extracted from the hopping transport parameters has been found in the range of $\sim 10^{16}$ to $10^{21}$ cm$^{-3}$ eV$^{-1}$. Metallic like conduction has been observed in films grown under varying hydrogen and nitrogen partial pressures along with conduction in band tail in few samples. This seems to be similar to other amorphous semiconductors and discussed above, the range of room temperature conductivity seems to be in the same range or higher compared to similar materials like hydrogenated amorphous silicon or organic semiconductors or oxide semiconductors [88,211,212].

5.9.2 Electronic behavior of the nanocluster carbon films grown under different deposition ion energies, arc currents and throw distance

Nanocluster carbon films grown under different deposition ion energies exhibit extended state and hopping conduction. But room temperature conductivity varies from $10^{-4}$ $(\Omega \text{-cm})^{-1}$ to $10^{-5}$ $(\Omega \text{-cm})^{-1}$ in nanocluster carbon films. These values are two–three order higher than ta–C films reported in the literature [195,196] and follows Arrhenius conductivity. Conductivity values for a–C and a–C:H prepared by R.F magnetron sputtering of graphite targets in an Ar atmosphere, found to be varying from $10^{-1}$ to $10^{-5}$ $(\Omega \text{-cm})^{-1}$ [213]. Total conductions have been due to sp$^2$ rich bonds, variable range conduction (VRH) and sp$^3$ rich bonds at various temperature ranges. There conductivity is explained based on
hetero–quantum–dots (HQD) model. According to theory of hetero–quantum dots (HQD), the microcrystalline grains and their amorphous counterparts have very different band gap and band structures. As a result, the electrons will first be thermal activated to the quantum wells in the hetero junctions, and then tunnel through the interface barrier. Amorphous carbon (a–C) film deposited using a filtered cathodic vacuum arc as a function of the ion energy show conductivity varying from $\sim 10^{-6}$ (Ω–cm)$^{-1}$ to $\sim 10^{-8}$ (Ω–cm)$^{-1}$ [174]. This value is minimum for 100 eV energy. Activation energy of 0.45 eV, which is less than midgap value suggests conduction near the band tail.

At very low temperature, nanocluster carbon thin films grown under deposition ion energies of 20 eV, 70 eV and 80 eV satisfies the mott conductivity conditions like $W > kT$ and $aR > 1$. Thus, dominant conduction mechanisms in this range (from 123 K to room temperature) is Mott’s variable range conduction. The calculated density of states of nanocluster carbon films is similar in order as reported in literature with respect to other carbon based materials like nitrogen doped tetrahedral amorphous carbon [214], boron implanted diamond films [215] and other diamond–like films [64, 201,202]. One of the value of DOS of $10^{23}$ states cm$^{-3}$ eV$^{-1}$ for a nanocluster carbon thin films seems very high and has to analyzed in detail as a future study. The minimum defect density of $10^{18}$ cm$^{-3}$ eV$^{-1}$ corresponds to FWHMG of 82 cm$^{-1}$ as discussed for 70 eV ion energy deposited film, which is minimum. However, uniqueness is in the cluster size.

Meyer–Neldel rule, is exhibited by nanocluster carbon films. The characteristic MNR value obtained by us is comparable with that N–doped hydrogen–free DLC films produced by PECVD ($b \approx 3.6$ eV$^{-1}$) [216]. MNR line of nanocluster carbon films with $E_{MN}=290$meV is close to hydrogenated boron–doped nanocrystalline silicon–silicon carbide alloys [217] and that of some specific porous silicon [218] with $E_{MN}=166$meV. Higher values have been reported in the case of the a–Si: H [219], nanostructured carbon produced by supersonic cluster beam deposition.
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[220], and magnetron sputtered carbon thin films \((A\approx 45 \text{ eV}^{-1})\) [213]. Conductivity pre-factor value of nanocluster carbon films \(\sigma_{00}\) yields the value of \(2.7 \times 10^{-3} \text{ (}\Omega\text{–cm})^{-1}\) magnitude which is one order higher than that of amorphous carbon films \((10^{-4}–10^{-5} \text{ (}\Omega\text{–cm})^{-1})\). The high conductivity pre-factor than amorphous carbon films is due to the presence graphitic cluster even though it contains amorphous phases and disorderness.

In the films grown under different arc current and throw distance, conductivity lies in the range of \(1.7 \times 10^{-5} \text{ (}\Omega\text{–cm})^{-1}\) to \(4 \times 10^{-5} \text{ (}\Omega\text{–cm})^{-1}\) with no variation of conductivity values.

5.9.3 Electronic behavior of the nanocluster carbon films grown under varying helium and nitrogen partial pressure

Films grown under varying conditions of helium and nitrogen partial pressure, show semiconducting behavior. Single activation energy exhibit single type of conduction mechanisms. The room temperature conductivity varies from \(1.6\times10^{-6} \text{ (}\Omega\text{–cm})^{-1}\) to \(4.5\times10^{-9} \text{ (}\Omega\text{–cm})^{-1}\). There is a variation of three orders for films grown with fixed N2 pressure of \(10^{-4}\) and \(10^{-3}\) Torr with varying helium. Conductivity is more in films grown under condition of fixed nitrogen pressure of \(10^{-3}\) Torr and varying helium partial pressure with large clustering.

As mentioned in the Table 4.1 of chapter 4, film with He/N2 ratio \((\text{N2}=10^{-4} \text{ Torr})\) of 5 has maximum FWHMG and minimum ID/IG ratio of 0.35. This is consistent with Tuinstra and Koenig [120] statement that ID/IG minimum for maximum size sp\(^2\) cluster. In this case, room temperature conductivity is maximum of \(3.6 \times 10^{-7} \text{ (}\Omega\text{–cm})^{-1}\). As reported by Satyanarayana et. al. [179] and Coll et. al. [85], nitrogen and helium helps in the clustering of the films which is sp\(^2\) in nature. Lowest conductivity of \(2 \times 10^{-9} \text{ (}\Omega\text{–cm})^{-1}\) has been found for as grown film (without helium and nitrogen). Nitrogen incorporation could lead to creation of donor levels which could increase the electrical conductivity of the films with He/N2 ratio of 5 [221,222]. Kleinsorge et.al. [223] and Hellgren et.al. [181] have also reported in nitrogen doped ta–C grown using DC filtered
cathodic arc that nitrogen helps in creation of large sp$^2$ clusters and broadening of G–peak.

Similarly, films grown under the fixed N$_2$ pressure of 10$^{-3}$ Torr has highest FWHMG of 131 cm$^{-1}$. Clustering is more prominent at this nitrogen partial pressure of 10$^{-3}$ Torr than N$_2$ partial pressure of 10$^{-4}$ Torr as reported by Satyanarayana et.al. [179]. Room temperature conductivity values vary from $\sim$8 x 10$^{-8}$ (Ω·cm)$^{-1}$ to $\sim$1 x 10$^{-6}$ (Ω·cm)$^{-1}$ which is two–three order higher than the films grown under N$_2$ partial pressure of 10$^{-4}$ Torr. In this case, Helium is used for cooling effect and induces formation of various clusters.

High field SCLC mechanism has been observed in nanocluster carbon thin films. Density of states (DOS) have been calculated using Dan–Boer technique and have been established for nanocluster carbon thin films. It is one of the first reports on nanocluster carbon thin films. For samples S1–S5, DOS values vary uniformly from 6 x 10$^{17}$ cm$^{-3}$ eV$^{-1}$ to 8 x 10$^{17}$ cm$^{-3}$ eV$^{-1}$. Considering the nanocluster carbon thin films grown under varying helium and fixed nitrogen partial pressure of 10$^{-4}$ Torr, DOS varies from $\sim$10$^{17}$ cm$^{-3}$ eV$^{-1}$ to 10$^{20}$ cm$^{-3}$ eV$^{-1}$. There is a change of three orders in the values. Silva et.al. [95] reports that the density of state in amorphous carbon deposited by plasma-enhanced chemical vapor deposition (PEVCD) is of the order of 10$^{19}$ cm$^{-3}$ eV$^{-1}$ near the center of the band gap. Wagle et.al. [224] observed this effect in a vacuum deposited Sb$_2$Pb$_1$Se$_7$ films. Ashok et.al. [225] has reported space-charge-limited current in thin–film diamond [225]. May et.al.[226] also reported the SCLC model in CVD as grown and doped diamond .

For films grown under nitrogen partial pressure of 10$^{-4}$ Torr and varying helium, films NA( as–grown), NB(only N$_2$) and NE(He=0.005 Torr) and films NC (0.5 Torr) and ND(He=0.0005 Torr) show shallow and exponential trap behaviors respectively. Shallow trap is due to the boundary defect at sp$^2$–sp$^3$ bonding which introduces disorder in structure. Exponential defects can be due to creation of additional defects at higher voltages. This may be due to disorder in rings and chains as also observed
from Raman’s spectroscopy with presence of D and G–peaks. Also, the maximum defect density of $9.73 \times 10^{19}$ (cm$^{-3}$ eV$^{-1}$) is for sample ND. As evident from Table 5.7, conductivity of ND sample is maximum of $3 \times 10^{-7}$ (Ω–cm)$^{-1}$ with maximum FWHMG corresponds to disorder, which is maximum for sample ND. Also sp$^2$ clustering is more for this film.

5.9.4 Electronic behavior of the nanocluster carbon films grown under varying condition of hydrogen and nitrogen partial pressure

Nanocluster carbon thin films grown under varying condition of hydrogen and nitrogen partial pressure show two and three different type of conduction. The room temperature conductivity lies between 3 to 30 (Ω–cm)$^{-1}$. Activation energies lie in the range of the meVs. Low value of activation energies in the range of 42 to 72 meV is in the same range of boron–doped carbon nanotubes $[227]$ (55–70 meV) where conduction is attributed to graphite along the basal plane. This type of the low activation energy has been observed at high temperature (500 °C) grown metal doped amorphous carbon films $[228]$, where nickel induces graphitization of carbon in the amorphous carbon films. In metal and carbon multilayers, fabricated by ion–bombardment or sputtering, metal and carbon clusters have formed, which was attributed to non–homogeneous structures in the films $[229]$. Due to the formation of metal clusters and nanostructures, tunneling of electrons can take place $[229]$. As reported by Coll et.al.$[85]$ and Satyanarayana et.al.$[179]$, nitrogen helps in the formation of the clusters. This clustering is more for hydrogen partial pressure of $10^{-4}$ Torr and nitrogen partial pressure of $10^{-3}$ Torr with highest room temperature conductivity due to interconnected graphitic clusters. Low temperature conductivity follows the Mott’s rule in these films. DOS is varying from $2 \times 10^{17}$ to $1.4 \times 10^{20}$ cm$^{-3}$ eV$^{-1}$ with highest DOS for more graphitic content films.
5.10 Summary

It has been shown that nanocluster carbon films grown using the cathodic arc process at room temperature are semiconducting in nature under varying deposition conditions. Conductivity of nanocluster carbon films varies with respect to deposition parameters. Maximum room temperature conductivity of \(~30\ (\Omega \text{–cm})^{-1}\) is observed for varying hydrogen and nitrogen partial pressure. Minimum conductivity of \(10^{-10}\ (\Omega \text{–cm})^{-1}\) is observed for varying helium and nitrogen partial pressure. So, within these broad parameters there is quite good variation of conductivity of order \(~10\).

It has been observed that presence of helium and nitrogen gases aid in formation of clusters of various sizes. This corresponds to highly smooth film like ta–C film (N2 partial pressure of \(10^{-4}\) Torr) and significant graphitic film (N2 partial pressure of \(10^{-3}\) Torr). Hydrogen gas also helps in clustering but cluster sizes are small.

Field dependence of the charge transport in nanocluster carbon thin films follows the mechanisms of space–charge–limited current conduction. Current varies linearly for small voltages and then follows nearly square–law for all the samples with further increase of applied voltage. Defect states of nanocluster carbon thin films, grown under various deposition parameters, have been found to vary from \(~10^{16}\ \text{cm}^{-3\text{eV}^{-1}}\) to \(~10^{21}\ \text{cm}^{-3\text{eV}^{-1}}\). So, there is a five order change in defect densities. Defect states have been found to lie at shallow level and at deep level. Low temperature conduction is possible due to conduction between this defect sites.

Photoconductivity of nanocluster carbon thin films does not vary as compared to dark conductivity. These materials are not sensitive to light.

Capacitance–voltage measurements have been carried out in nanocluster carbon thin films to find out the dielectric constant and the defect states. Dielectric constant varies from \(~2\) to \(~12\). Defect densities vary from \(5.7 \times 10^{16}\ \text{cm}^{-3}\) to \(4.9 \times 10^{19}\ \text{cm}^{-3}\). Difference in dielectric property is due to the different ion energy used for deposition which has been understood according to sub–plantation model.