Chapter 6

Fabricating Graphene by Chemical Vapor Deposition Directly on Dielectric Substrates and Its Diode Characteristic and Field Electron Emission Study

In this chapter, horizontally and vertically oriented few-layer graphenes have been synthesized directly on dielectric substrates by thermal and hot-filament chemical vapor deposition, respectively without any catalyst or special substrate treatment. The effect of the direction of mass flow on the fabrication of graphene film has been analysed and a plausible mechanism is proposed. The fabricated horizontally and vertically oriented graphenes are shown to grow according to Volmer-Weber (VW) and Stranski-Krastnov (SK) growth mechanisms, respectively. Typical dark current-voltage characteristic of graphene-on-Si (p-type) heterojunction is investigated at room temperature for both types of graphene and an effort has been made to correlate the structure-property relationship. Considering the fact that, field-emission from flat graphene sheets is a challenge due to less number of emission sites. Herein, we have also shown the enhanced field emission characteristics of the free-standing vertically-oriented FLG films. The ease of large area preparation and the low turn-on field of 22 V/µm in addition to the large field enhancement factor of ≈6520 for electron field emission suggest that the vertically-oriented FLGs could be used as a potential edge emitter.

6.1 Introduction

In order to implement graphene into technology, an appropriate method must be taken to integrate into desired device structures. Chemical vapor deposition (CVD) of graphene has shown substantial promise for large area deposition with reasonably high quality and low process time on transition metal substrates such as copper (Cu), nickel (Ni), cobalt (Co), platinum (Pt), iridium (Ir) and ruthenium (Ru) [10]. However, for electrical characterization and electronic applications, graphene on insulating substrates is required, and thus as-grown graphene has to be transferred from metallic surfaces onto desired insulating substrates. This transfer process poses challenges for large area and large volume commercialization. Therefore, it becomes essential to develop direct growth techniques of graphene on insulating substrates including SiO$_2$/Si wafers, glasses or plastic foils.

Graphene, due to its high transparency and larger electrical conductivity, is a suitable candidate for optoelectronic applications including solar cells, light emitting diodes, sensors etc. In photovoltaic science, graphene has demonstrated promising applications in dye-sensitized solar cells and organic solar cells. A very limited number of experimental works have been done to explore graphene in semiconductor devices due to lack of insufficient experimental studies of graphene-on-semiconductor junctions. However, graphene is advantageous over other carbon nanostructures for its two dimensional planar structure. Even though the CVD graphene-based solar cells has already shown photo conversion efficiency of about 8-9%, but a thorough study on the diode characteristics of graphene/p-Si junction is still lacking for the improvement of the device. Herein, we report on the direct fabrication of few-layer graphene (FLG) on a SiO$_2$/Si substrate using thermal chemical vapor deposition (TCVD) and hot-filament chemical vapor deposition (HFCVD). TCVD and HFCVD rely on the horizontal and vertical mass flow with respect to the substrate, respectively. The horizontally and vertically oriented graphenes are shown to grow according to Volmer-Weber (VW) and Stranski-Krastnov (SK) growth mechanisms, respectively. Typical dark current-voltage characteristic of graphene-on-Si (p-type) heterojunction is investigated at room temperature for both types of graphene and an effort is made to correlate the structure-property relationship.

Most electron emitters such as X-ray sources utilize thermionic emission to generate high-current electron beams but are problematic because they are unstable and bulky and
cause heating of the surrounding device housing. Therefore cold cathode emitters that remain at room temperature and provide high emission current density at low electric fields are desirable. High aspect ratio materials such as carbon nanotubes and metallic tips exhibit excellent electron emission characteristics due to local field enhancement at the tip, which decreases the barrier width, allowing electrons to tunnel into vacuum at low electric fields. Due to atomic thickness, high aspect ratio and better electrical conductivity, graphene is an ideal material for field electron emission (FEE) applications [89, 90]. However, for better FEE performance, controlled growth of graphene sheets in different orientations and geometries with respect to the substrate is required. Limited work has been done to realize free-standing graphene films [91, 119], but direct growth of free-standing vertically oriented few-layer graphene has been rarely reported. Finally, field emission characteristics and current stability were also studied at room temperature.

6.2 Experimental Methodology

A thermally grown SiO$_2$ of thickness ca. 300 nm on Si [p-type Si (1 0 0) wafer] was used as the substrate for graphene growth. The growth experiments were carried out using a TCVD reactor consisting of a horizontal quartz tube and mounted inside a high temperature furnace, [Barnstead Thermolyne, Model Number: F21135] which was connected to a mechanical pump with mass flow controllers. Vertically oriented graphene films were developed by a custom designed HFCVD reactor [104] with methane (CH$_4$), hydrogen (H$_2$) and argon (Ar) gases as the precursors. Both the CVD systems are represented in Figure 6.1.

![Figure 6.1: (a) Thermal and (b) Hot-Filament Chemical Vapor Deposition System.](image-url)
6.2.1 Synthesis of Graphene by TCVD: The synthesis of graphene film using TCVD reactor was carried out following the procedures reported by Chen et al. [120]. First, the SiO$_2$/Si substrate was heated to 500 °C in air and held for half an hour for the removal of organic residue and activation of oxygen sites in the SiO$_2$ surface. Then the reactor was cooled to nearly 100 °C at slow rate, followed by evacuation to a base pressure of 40 mTorr. Next, the SiO$_2$/Si was heated to 1100 °C at 40 °C/min with the flow of hydrogen at 200 sccm. At 1100 °C, the gas with a composition of CH$_4$:H$_2$:Ar=50:150:200 sccm was introduced into the reaction chamber maintaining a pressure of 75 mTorr, for the growth of graphene. After an hour of growth, the chamber was cooled at a rate of 25 °C/min with a simultaneous flow of H$_2$ and Ar gas at a rate of 150 sccm and 200 sccm, respectively.

6.2.2 Synthesis of Graphene by HFCVD: Unlike the TCVD experiment, the chamber was first evacuated to 0.1 mTorr and the SiO$_2$/Si substrate was heated to 1000 °C with a flow of hydrogen at 10 sccm. At 1000 °C, the gas with a composition of CH$_4$:H$_2$=1:50 sccm was introduced into the reaction chamber maintaining a pressure of 400 mTorr, for growth of graphene. The chamber was cooled down at a rate of 25 °C/min under the flow of hydrogen at 10 sccm after a typical growth period of half an hour. The detailed compositions of the reactive gas mixture used for synthesizing FLG by TCVD and HFCVD are given in Table 6.1.

Table 6.1: FLG samples synthesized on a SiO$_2$/Si substrate at various gas flow compositions using TCVD and HFCVD.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating (H$_2$) in sccm</th>
<th>Growth (CH$_4$:H$_2$:Ar) in sccm</th>
<th>Cooling (H$_2$:Ar) in sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$/Si TCVD-S1</td>
<td>200</td>
<td>50:150:200</td>
<td>150:200</td>
</tr>
<tr>
<td>SiO$_2$/Si HFCVD-S2</td>
<td>10</td>
<td>1:50:0</td>
<td>10:0</td>
</tr>
</tbody>
</table>

As-produced FLG samples on SiO$_2$/Si substrates were characterized by atomic force microscopy (AFM) (PicoIC), field emission scanning electron microscopy (FESEM) (JEOL 7600F), micro-Raman spectroscopy (Renishaw 2000) and four probe (Jandel multiheight) measurements. Dark current-voltage (I-V) characteristic of graphene-on-Si device was recorded using Keithley 4200-SCS. For Raman measurement, an Ar$^+$ laser of wavelength, $\lambda$=514 nm was used as the excitation source at an incident power of 3.6 mW. The laser beam was focused onto FLG sample by a 20X microscope objective lens and the scattered light was
collected and collimated by the same objective. The scattered signal was detected by a liquid-nitrogen-cooled master charge-coupled-device (CCD) camera detector. Field emission measurements were carried out using a stainless steel anode with a hemispherical tip of radius 1 mm at a distance of 25 µm from the free-standing graphene films in a vacuum chamber evacuated to 1X10\(^{-7}\) Torr. The emission current vs. applied field (I-E) characteristic properties were measured using a Keithley 237 source measure unit (SMU).

6.3 Characterization of Graphene

The AFM and FESEM images for as deposited FLG thin films are shown in Figure 6.2 and 6.3, respectively. Horizontally aligned morphology of FLG is clearly observed from AFM and FESEM images [Figure 6.2 (a) and 6.3 (a)] for TCVD grown films, whereas vertically aligned FLG, which are entangled with each other is noticed for the HFCVD grown films [Figure 6.2 (b) and 6.3 (b)]. The difference in morphologies between TCVD and HFCVD-grown graphene samples may be attributed to the effect of mass flow direction towards the substrate as discussed in the next section. The vertically aligned morphology exhibits maximum step height of 600 nm and is similar to the carbon nanowalls [79]. The horizontally oriented morphology possesses an average surface roughness of 20 nm. The white colour spots on the TCVD and HFCVD-grown graphene films are attributed to the adsorption of ambient species such as, nitrogen, oxygen, argon or water.

Figure 6.2: AFM topography images of (a) FLG-TCVD and (b) FLG-HFCVD on SiO\(_2\)/Si substrates.
Figure 6.3: FESEM micrograph images of (a) FLG-TCVD and (b) FLG-HFCVD on SiO$_2$/Si substrates.

The structural defects and number of layers of the as-formed graphene films can be determined using the Raman spectrum (514 nm), which is shown in Figure 6.4 (a) and (b). The presence of two intense peaks, G and 2D-band at 1593 and 2700 cm$^{-1}$, respectively indicate the formation of graphene films. The D-band at 1353 cm$^{-1}$ corresponds to the defects in the synthesized FLG, because the D-band originates from the backscattering of phonon by disorder sites (such as edges and defects). The detailed explanation on Raman modes has been presented in Appendix II. The intensity ratio between G and 2D-band (i.e., $I_G/I_{2D}$) is ~0.77 and the full width at half maximum (FWHM) of the 2D peak is ~50 cm$^{-1}$, indicating that the formation of FLG by both the systems [44, 45]. In addition to the above peaks, few more peaks such as, D’ and D+G-band at 1620 and 2920 cm$^{-1}$, respectively are found in the samples. The D’-band is due to an intravalley double-resonance process only in the presence of defects [121] and corresponds to SiC [122]. The D+G-band is the combination of D and G mode [79]. The presence of D, D’ and D+G-band in the Raman spectra indicate that FLG films are hydrogenated [123]. Hydrogenated FLG films are electron doped since carbon is slightly more electronegative than hydrogen [123, 124].
Figure 6.4: Raman spectrum (514 nm) of (a) FLG-TCVD and (b) FLG-HFCVD on SiO$_2$/Si substrates.
The electrical properties of FLG were measured using a four-probe method at room temperature. The sheet resistance ($R_s$) of FLG-HFCVD film is 44.42 Ω/□ compared to 20.1 Ω/□ for FLG-TCVD film. This is due to the fact that, the nearly horizontally aligned structure produced by TCVD through VW growth mechanism is compact and smooth. Thus, the film becomes more conducting due to better connectivity among the crystallites throughout. However, in the case of HFCVD, due to island growth process, the interconnectivity among the crystallite is low and existence of void space become highly probable throughout the film. This, in turn, results in high resistance of the film grown by HFCVD.

6.4 Graphene Growth Mechanisms

Graphene synthesis on SiO$_2$ substrates involves a vapor-solid-solid (VSS) growth mechanism for both horizontal and vertical gas flow cases. The heat treatment of SiO$_2$ substrate in air, in case of TCVD and in hydrogen, in case of HFCVD enhances the activation of oxides and increases the number of nucleation sites [120]. The presence of oxygen can enhance the capture of CH$_x$ (x=0-4) fragments through C-O and H-O binding and helps in C-C coupling and graphene nucleation [125]. In the horizontal mass flow one observes a balance between the interaction of the deposited carbon particles and the substrate i.e. the interaction between carbon (C) and SiO$_2$/Si is almost of similar order to that of interaction between carbon and carbon. Hence the AFM [Figure 6.2 (a)] and SEM images [Figure 6.3 (a)] of the thin film obtained by horizontal flow shows similar to Volmer-Weber (VW) growth process i.e. a tendency of layer by layer growth [126]. However, in the case of vertical mass flow strong C-C interaction leads to the growth of vertically aligned FLG as is observed clearly from the AFM (Figure 1b) and SEM images (Figure 2b). Hence the vertical mass flow with respect to the substrate in the present investigation favours growth according to Stranski-Krastanov (SK) growth mechanism i.e. island growth model [127]. The above mechanisms can be supported by the comparison of the intensity ratio of D to G band (i.e. $I_D/I_G$) of the two samples. In the case of VW growth, one should have less value of $I_D/I_G$ while for SK growth process one should see more value of $I_D/I_G$ which is clearly observed from the Raman spectrum (Figure 6.4).
6.5 Fabrication and Characteristics of Graphene/p-Si Heterojunction Device

Two devices were fabricated from two FLG samples (S1 and S2). Since the FLG is on SiO₂ (300 nm)/ Si (500 µm) substrate, so it was essential to make an Ohmic contact on top of the device for effective current collection. First, a little portion of the FLG/SiO₂ from one side of the device was removed using hydrofluoric acid and then a contact of silver metal was screen printed and dried for 30 minutes. The schematic diagram for graphene-on-silicon (p-type) heterojunction device is displayed in figure 6.5 along with its energy-band diagram. Rectification behaviour is observed at the interface of graphene/p-Si device with the appearance of a barrier height (ΦSBH), which is calculated experimentally below.

![Figure 6.5](image)

**Figure 6.5:** (a) Schematic and (b) energy-band diagram of graphene-on-Si (p-type) heterojunction.

For a Schottky barrier diode with assumption that the current is due to thermionic emission, the relation between the applied forward bias and current can be expressed as:

\[ I = I_S \left[ \exp \left( \frac{V_D}{n k_B T} \right) - 1 \right] \]

Where \( I \) is the diode current, \( I_S \) is the reverse bias saturation current, \( V_D \) is the voltage across the diode, \( k_B T \) is the thermal voltage, \((k_B \) is the Boltzmann constant and \( T \) is the temperature in Kelvin), and \( n \) is the ideality factor. \( I_S \) can be extracted by extrapolating the straight line of \( \ln (I) \) to intercept the axis at zero voltage:

\[ I_S = AA^*T^2 \exp \left( -\frac{q \Phi_{SBH}}{k_B T} \right) \]

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Where \( A \) is the effective area of the device (0.5 cm\(^2\)), \( A* \) is the Richardson constant (32 A/(cm\(^2\)K\(^2\)) for p-Si substrates. By combining Eq. 6.1 and 6.2 and fitting the J-V curves of the devices in dark, the Schottky barriers are estimated to be 0.75-0.77 eV for the graphene/p-Si device at 300 K using the following formula:

\[
\Phi_{SBH} = k_B T/q \ln(AA^*T^2/I_S) \]

The typical dark current-voltage (I-V) and Ln (I)-V characteristic of graphene-on-Si heterojunction fabricated from both TCVD-FLG and HFCVD-FLG samples are displayed in Figure 6.6 and 6.7, respectively. At low voltages the forward bias I-V characteristics are linear in the semilogarithmic scale but when the applied voltage is large enough, they deviate considerably from linearity due to the effect of series resistance (\( R_s \)), the interfacial layer and interface states. The ideality factor (\( n \)) and reverse saturation current (\( I_s \)) are derived from the slope and y-intercept of the dark Ln (I)-V curve, which are mentioned in the Table 6.2. The rectification ratio for both the devices have been calculated and presented in Table 6.2.

![Figure 6.6: Dark I-V characteristic curves for TCVD-FLG and HFCVD-FLG based devices.](image-url)
Figure 6.7: Ln (I)-V characteristics of TCVD-FLG and HFCVD-FLG based devices.

Series resistance ($R_s$) is an important parameter that influences the electrical characteristics of Schottky diodes. In order to evaluate $R_s$, we used the efficient Cheung method i.e. the forward bias current-voltage characteristics due to thermionic emission of a Schottky barrier diode with $R_s$ can be expressed as Cheung’s functions [128].

$$\frac{dV}{d\ln I} = \frac{nkT}{q} + IR_s$$ .................................................................(6.4)

Figure 6.8 shows the plot of $dV/d\ln I$ and $R_s$ and the obtained results are given in Table 6.2.
Figure 6.8: dV/dLnI-I characteristic curves for TCVD-FLG and HFCVD-FLG based devices.

Table 6.2: Dark characteristic parameters of the graphene-on-Si device at 300 K.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>TCVD-FLG</th>
<th>HFCVD-FLG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current (mA)</td>
<td>0.65</td>
<td>1.1</td>
</tr>
<tr>
<td>Applied Voltage (V)</td>
<td>± 1</td>
<td>± 1</td>
</tr>
<tr>
<td>Ideality Factor</td>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td>Schottky Barrier Height (eV)</td>
<td>0.75</td>
<td>0.77</td>
</tr>
<tr>
<td>Reverse Saturation Current (A)</td>
<td>5.043X10⁻⁷</td>
<td>1.85X10⁻⁷</td>
</tr>
<tr>
<td>Series Resistance (kΩ)</td>
<td>0.5-7</td>
<td>0.3-4</td>
</tr>
<tr>
<td>Rectification Ratio (at ± 0.5 V)</td>
<td>6.90</td>
<td>15.99</td>
</tr>
</tbody>
</table>

In general, the I–V characteristics of both the devices clearly indicate an ideal Schottky diode behaviour, as the current rises rapidly with voltage in contrast to the slow rise expected in the non-ideal Schottky diodes. Now the question is why the FLG-HFCVD graphene-on-Si device is better than TCVD graphene-on-Si? The higher ideality factor and lower dark current for FLG-TCVD graphene/p-Si device may be attributable to the defects, interfacial states and metal atoms that once diffused across the interface act as trap centres and thereby contribute to recombination current.
6.6 Characteristics of Vertically Oriented Graphene Field Electron Emitter

Figure 6.9 (a) shows the J-E characteristics of the FLG sample. An emission current density of 25 µA/cm² is found for the vertically-oriented FLG at an applied electric field of 44 V/µm. The turn-on field as low as 22 V/µm is observed in the grown films, when current density is 10 µA/cm². Figure 6.9 (b) shows the corresponding Fowler-Nordheim (F-N) plot. The linear F-N plot indicates that the field emission from vertically-oriented FLGs has a metallic behaviour and obey tunneling mechanism. Moreover, the observed knee point in the F-N plot implies two subsequent phenomena in the applied electric field region, that take place within the validity of the F-N theory. This may be attributed to the heating of the FLG top surface as a rate limiting step in the high field region.

![Figure 6.9](image)

*Figure 6.9: (a) Room temperature J-E characteristics and (b) Corresponding F-N plot with a ca. field enhancement factor of 6520.*

The open surfaces and the sharp edges of the graphene film are good for field emission and the films, which are synthesized vertically to the substrate, are better than the flat graphene films due to the large content of high density sharp edges in the present samples [129]. The field emission schematic from the graphene film is shown in Figure 6.10 (a).
Field emission characteristics are generally analyzed by the F-N theory and described in Eq. 5.1. Field enhancement factor is generally related to the geometry of the emitters. The plot of \( \ln (J/E^2) \) vs. \( 1/E \) is called F-N plot (Figure 6.9 (b)) and its slope is given by the Eq. 5.2.

The field enhancement factor is calculated using the Eq. 5.2 and was found to be \( \approx 6520 \), considering constant and lowest work function of 4.5 eV for vertically-oriented FLG films, which are hydrogenated. To realize more about the field emission performance, the current density stability was also measured and shown in figure 6.10 (b). The current density stability at the maximum emission current density i.e. 25 µA/cm\(^2\) was tested over a period of 24 h and a nearly stable emission was observed with minimum current density fluctuation. Although low threshold fields (\( \approx 1 \) V/µm) have been reported for carbon field emitters of various types, careful experiments on individual or well-separated emission sources have revealed that the onset of field emission is related only to the field enhancement factor (\( \beta = h/r \) where \( h \) is the height and \( r \) is the radius) and the work function (\( \Phi \approx 4.5-5 \) eV for sp\(^2\) carbon) of the emitter. In unique cases, however, low threshold field emission is possible in ultrasmooth surfaces, due to intrinsically lower (or even negative) work functions. For example, hydrogenation of diamond leads to a negative electron affinity surface [93], and low threshold field emission can be readily observed [130]. In our case, due to the combination of hydrogenation and longer vertically-oriented FLGs, we have been able to achieve better enhancement in the electron field emission. This may be due to the fact that, the atoms at graphene edges may form a distorted sp\(^3\)-hybridized geometry instead of a planar sp\(^2\)-hybridized configuration. As a result, there should be localised states at graphene edges and
possible barriers to the electron emission are decreased. This may be supported by the fact that, surface barrier is lower for vertically oriented graphene films.

6.7 Summary

Horizontally and vertically oriented FLGs have been grown directly on SiO$_2$ coated Si substrates using horizontal gas flow TCVD and vertical gas flow HFCVD, respectively. The horizontally oriented FLG shows the VW growth process and vertically oriented FLG shows the SK growth process, which are confirmed from the structural, Raman and electrical studies. Electron doping due to hydrogenation is also confirmed from the Raman spectrum. The dark I-V characteristics of graphene/p-Si device fabricated from both the techniques, clearly shows the rectification behaviour which corresponds to Schottky barrier at the interface. In addition, FLGs, which are seen to be entangled with each other and having larger density of sharp edges, demonstrate field enhancement factor of $\approx 6520$ and an field emission current density of $25 \mu$A/cm$^2$ at an applied electric field of 44 V/µm. The turn-on field as low as 22 V/µm is also observed in the grown films.