Controlled Island Formation of Large-Area Graphene Sheets by Atmospheric Chemical Vapor Deposition: Role of Natural Camphor

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ABSTRACT: Camphor-based mono-/bilayer graphene (MLG) sheets have been synthesized by very facile atmospheric chemical vapor deposition processes on Si/SiO₂, soda lime glass, and flexible polyethylene terephthalate films. The effect of camphor concentration with respect to distance between camphor and the Cu foil (D) has been varied to investigate the controlled formation of a homogeneous graphene sheet over a large area on Cu foil. Raman studies show a remarkable effect of camphor at a typical distance (D) to form a monolayer to multilayer graphene (MULG) sheet. The signature of MLG to MULG sheets appears due to increase in the number of nucleation sites, even over the subsequent domains that contribute stacks of graphene over each other as observed by high-resolution transmission electron microscopy images. Moreover, the increase in camphor concentration at a particular distance generates more defect states in graphene as denoted by D band at 1360 cm⁻¹. Uniform distribution of large-area MLG demonstrates an intense 2D/G ratio of ~2.3. Electrical and optical measurements show a sheet resistance of ~1 kΩ/sq with a maximum transmittance of ~88% at 550 nm for low camphor concentration. An improvement in the rectification and photodiode behavior is observed from the diodes fabricated on n-Si/MULG as compared to n-Si/MLG in dark and light conditions.

1. INTRODUCTION

Since the invention of graphene in 2004, it has attracted a great attention because of its extraordinary quantum transport, optical transmittance, superior mobility, thermal conductivity, and superior mechanical properties. A honeycomb lattice arrangement consists of a long chain of carbon atoms in sp² hybridization, enabling its use in optoelectronic applications such as transparent conducting electrodes, solar cells, photodetectors, and field-effect transistors.¹⁻⁴ All these high-accuracy and large-scale-scalable devices demand graphene films with very high quality and large domain size on a larger area. Motivated by all these superior properties, different processes are currently under development to achieve mono-/bilayer graphene (MLG) sheets over a larger area to attain a low sheet resistance and high transmittance values.⁵⁻⁶ Among all the synthesis processes established so far, the chemical vapor deposition (CVD) process has been considered as one of the most versatile technique to synthesize large-area graphene with controllable layer numbers and single crystal domains. In this technique, the carbon precursors are decomposed on the Cu surfaces because of its low carbon solubility and the self-limiting factor.⁶⁻¹⁰ The resulting graphene on the metal substrate can be easily transferred to any desirable substrates by a simple transferring process without affecting much of the properties of graphene. Recently, gaseous hydrocarbons and liquid carbon sources have been replaced by forthcoming solid carbon sources such as camphor (C₁₀H₁₆O), polystyrene, and so forth by a very facile and low cost approach to achieve a large-area MLG on Cu foil with an optimum optoelectronic properties.¹¹⁻¹⁵ Kalita et al. have initiated the growth of mono-/bilayer graphene by employing camphor as a carbon source on different metal substrates.¹⁶⁻¹⁸ In recent years, significant efforts have been made to synthesize large single crystal MLG sheets from camphor on Cu foil to form a large area by the atmospheric chemical vapor deposition (APCVD) process. However, there are various factors that have affected the graphene nucleation and growth on the Cu surface grown by APCVD, such as gas composition, growth temperature, flow rate of carbon source, and substrate surface purity.¹⁵,¹⁶,¹⁹⁻²² There are various reports on the variation of annealing and gaseous flow rates to control the nucleation and growth kinetics of graphene crystals on substrate surfaces.¹⁰,²³⁻²⁶ In addition, various temperature conditions give an indication on the control formation of monolayer, bilayer, hexagonal structure, layer-stacking, and dendrite growth of graphene.²⁷,²⁸ In this regard, the key point for the present investigation is to achieve MLG on Cu foil with a large domain size that can deliver good optical and electrical...
properties. An efficient, low-cost, and facile approach of using camphor as a carbon precursor has been utilized to develop an MLG sheet with a large domain size on a Cu foil and transfer it to glass and flexible polyethylene terephthalate (PET) substrates. The nucleation and growth mechanism to optimize an MLG has been further explained in detail by varying the concentration of camphor at various source-to-substrate distances \((D)\). Finally, superior optical and electrical properties have been identified in correlation with the growth mechanism for various camphor concentrations.

2. RESULTS AND DISCUSSION

The synthesis and formation of large-area graphene sheets (\(\sim 1 \text{ cm} \times 1.5 \text{ cm}\)) were performed using camphor, a botanical hydrocarbon source, by pyrolysis in a high-temperature atmospheric CVD system. Camphor is a natural solid, low-cost, and environmental friendly hydrocarbon. It consists of hexagonal and pentagonal rings along with a methyl carbon structure, which plays an important role in graphene formation as shown schematically in Figure 1. During pyrolysis, methyl carbon can be easily detached and hexagonal carbon ring can be fused to form a larger graphene sheet on Cu foil. During the growth process, at a certain distance \((D)\) and evaporation temperature, \(T_e = \sim 350 - 400 \, ^\circ \text{C}\), transformation of solid camphor to camphor vapor phase takes place, and under the Ar/H\(_2\) flow, the camphor molecules are transported to Cu foil as schematically shown in Figure 2. It is to be noted that the graphene nucleation from camphor vapor on a Cu foil is a surface reaction mechanism, as demonstrated in the synthesis of methane-based graphene by Li et al.\(^\text{21}\) Catalytic decomposition of camphor to carbon atoms on a Cu foil takes place at a very high temperature of 1020 \(^\circ\)C. By optimizing the camphor concentration, a continuous formation of single-chain hexagonal rings of carbon atoms creates an MLG on a large surface and bilayer growth at a few regions on the Cu substrate. In order to understand the effect of camphor concentration to form an MLG, the source to substrate distance was varied and kept at 15, 16, and 17.5 cm. For each distance \((D)\), the camphor concentration was varied from 1 to 5 mg. Figure 3 shows the evaporation rate \((\text{mg/min})\) \((R_e)\) of camphor at the above-mentioned distances to form a homogenous and uniform graphene sheet. As the camphor concentration increases from 1 to 5 mg, the \(R_e\) linearly decreases for a particular distance due to an increase in the camphor weight as seen in Figure 3a–c. The observations can be expressed in terms of camphor weight \((W_c)\), as follows

\[
W_c = R_e^{-1}
\]

It is observed that a very low camphor concentration is not sufficient and appropriate for covering a homogeneous graphene sheet on Cu foil. Therefore, further experiments were carried out by considering 3, 4, and 5 mg of camphor at 16 and 17.5 cm distances. Figure 3d provides an easy understanding on the transition of inhomogeneous to homogeneous and uniform growth of graphene with respect to camphor concentration. To further understand the effect of camphor on the formation of homogeneous MLG sheets, we have carried out optical microscopy and micro Raman spectroscopy studies for all the above-mentioned parameters which will be discussed in the subsequent sections.

Optical microscopic studies have been carried out to explore and elucidate the nucleation, growth, and morphology of the homogeneous graphene sheet for various camphor concentrations as shown in Figure 4A. To clearly visualize the graphene crystals with an optical microscope, selective
oxidation of the Cu surface was performed by annealing at 180 °C for 5 min in atmospheric conditions. Low-temperature oxidation does not change pristine quality of graphene but changes Cu foil to copper oxide and leads to visible graphene domain due to color contrast. Initially, for low camphor concentration of 1 and 2 mg at $D = 15$ cm, most of the portion is uncovered by graphene as highlighted by domain (a) and in some of the portion, a presence of hexagonal growth of graphene crystals over a Cu foil can be observed and it is highlighted in domain (b). Further increasing the camphor concentration to 3 mg, most of the part is covered by graphene crystals except few. For 3.5 mg, it is found that there is no uncovered domain left by the graphene. Nevertheless, in most of the regions, there are low nucleation sites of graphene, which are distinguished and highlighted as domain (c). In addition, there are some regions at this particular concentration where we found homogeneous nucleation of graphene, where merging of the crystals to form larger clusters has been verified and highlighted as domain (d). Again increasing the concentration to 4 and 5 mg leads to increase in the number density of nucleation sites even over graphene domains and hence a possibility of forming a homogeneous growth of few layers of graphene on Cu foil. In this regard, micro Raman measurements as shown in Figure 4B were carried out on Cu foil to identify the crystalline nature, number of layers, and defects states of graphene for various camphor concentrations with the utilization of 1% of the total laser power for 30 s of exposure time. Raman spectra were taken at different locations in an as-grown graphene sheet. For very low camphor concentrations, the spectra were taken at a spot where graphene crystals are easily distinguished [see Figure 4A highlighted as (b)]. Raman spectra show almost no defect-
induced D band at $\sim 1360$ cm$^{-1}$ at the particular spot, presenting a high quality of graphene crystals. Moreover, there is presence of a characteristic graphitic G and second-order 2D Raman peak at $\sim 1590$ and $\sim 2700$ cm$^{-1}$, respectively. It is well reported in the literature that the 2D peak position experiences a blue shift with increasing number of graphene layers, providing a signature of multilayer graphene (MULG), which is observed in our present investigation as well.\textsuperscript{13,31,32} This may be due to an increase in the number of nucleation sites of graphene crystals which can form stacks of graphene layers. This effect introduced more defect states described as D band at $\sim 1360$ cm$^{-1}$ for high camphor concentration. Also, with the increase in the number of layers due to increase in the camphor concentration, the 2D band experiences a significant broadening due to enhancement of the allowed double resonance processes as a result of the splitting of both the in-plane transverse optical phonon and electronic branches.\textsuperscript{16,17,31} Similarly, the Raman spectra were carried out to study the overall effect of camphor concentration by varying $D = 16$ cm (Figure 5a) and 17.5 cm (Figure 5b). It has been observed that, the growth is more uniform and homogenous for $D = 16$ cm, which is confirmed by taking Raman results at various spotted areas. Eventually, as discussed above, as the camphor concentration increases to 3.5 mg and more, the defect-induced D band increases due to more number of graphene layers. On the other hand, 2D band shows a more intense peak for low camphor concentration (3.5 mg). It has been observed that 2D band is much more intense than that of the G band, which indicates a monolayer graphene. It is to be noted that at most of the places, we found a single-layer graphene, but at some places a possibility of bilayer graphene has been confirmed. On the other hand, the intensity has found to be reduced with a significant broadening of 2D band, which is in agreement with an increase in the number of graphene layers as the camphor concentration increases above 3.5 mg. As it is evident from Figure 5a, the 2D/G ratio for the MLG sheet is found to be 2.3, which suggests a single layer of the graphene sheet with the corresponding full width at half-maximum of 2D peak to be 24 cm$^{-1}$. Interestingly, as we increase the distance to 17 cm, there is no defect-induced D peak observed as the camphor concentration increases, as observed for the previous two distances. Carbon radicals have to travel more distance to nucleate themselves over a Cu foil and may certainly not be able to grow homogeneously at high camphor concentration. The presence of the broadening of 2D band is mostly observed, which indicates the existence of more number of layers above 3 mg. Our observations suggest that one needs to optimize the growth rate, distances, and camphor concentrations to identify the best possible nucleation to achieve a homogeneous and uniform MLG. Therefore, the results clearly show that control of camphor vapor flowing to the high-temperature furnace at a particular distance can produce graphene with different number of layers.

**Figure 5.** (a) Raman spectra of the as-grown graphene for various concentrations of camphor of 3, 3.5, 4, and 5 mg kept at (a) 16 and (b) 17.5 cm.

**Figure 6.** (a) Surface morphological images of the as-grown graphene for (a) 3.5 and (b) 5 mg camphor kept at 16 cm distance.
evaluated by atomic force microscopy (AFM) analysis. Figure 7 shows the surface topographic images of graphene sheets for 3.5 and 5 mg of camphor concentration at $D = 16$ cm. From AFM images, the root mean square roughness ($R_{\text{rms}}$) has been determined in a selected region for mono-/bi layer (3.5 mg) and MULG (5 mg) and it is found to be 1.07 and 1.17 nm, respectively, which is identical with the earlier reported literature.\textsuperscript{12,24,33,34} In addition, from Figure 7a,b, it is also confirmed that there is an existence of a few wrinkles on the surface of graphene grown at low camphor concentration (3.5 mg), but more on the surface of graphene grown at higher concentration (5 mg). Further, the selected line scan profiles

Figure 7. (a) AFM analysis of the as-grown graphene grown with (a) 3.5 and (b) 5 mg camphor kept at 16 cm distance on Si/SiO$_2$ substrate. On the right of (a,b), a line scanning profile has been shown for two different regions as indicated by blue and red. The regions indicated with blue color are without graphene wrinkles and the regions with red color are with graphene wrinkles.

Figure 8. Transmittance spectra of a graphene sheet transferred on: (a–c) flexible PET substrates and (d–f) glass substrates for various camphor concentrations of 3, 3.5, 4, and 5 mg kept at $D = 15$, 16, and 17.5 cm distances. Insets of (b) and (e): optical image of transferred graphene on PET and glass substrates.
Table 1. Electrical Properties of Graphene Sheets Transferred on Glass Substrates at Various Distances for a Typical Camphor Concentration

| camphor concentration (mg) | sheet resistance ($R_s$) (kΩ/$\square$) | mobility ($\mu$) (cm$^2$/V·s) |
|----------------------------|------------------------------------------|-------------------------------|
|                            | 15 cm | 16 cm | 17.5 cm | 15 cm | 16 cm | 17.5 cm |
| 3                          | 1.06  | 1.8   | 1.9     | $1.2 \times 10^1$ | $3.8 \times 10^2$ | $4.1 \times 10^2$ |
| 3.5                        | 1.45  | 1.50  | 2.01    | $3.1 \times 10^2$ | $1.7 \times 10^2$ | $4.6 \times 10^2$ |
| 4                          | 1.31  | 2.63  | 4.76    | $5.3 \times 10^2$ | $2.3 \times 10^2$ | $2.0 \times 10^2$ |
| 5                          | 1.90  | 2.12  | 1.73    | $1.7 \times 10^2$ | $3.2 \times 10^2$ | $3.1 \times 10^2$ |

The chemical states of the MLG sheet have been determined by the X-ray photoelectron spectroscopy (XPS) technique as shown in Figure 9. The core-level peak of the C 1s shown in Figure 9 is divided into three major components corresponding to carbon atoms at different chemical environments. The convoluted peak consists of two broad peaks at binding energies 284.7 and 285.2 eV. The sharp peak at binding energy 284.7 eV represents graphitic carbon, that is, $sp^2$ hybridized, while the characteristic feature attributed to the presence of defects states, that is, $sp^3$ hybridized, is observed at 285.2 eV. The break in the ring of resonating aromatic carbon bonds as schematically shown may be the additional reason for the existence of such a broad defect peak in the sample. Moreover, the oxidized states of carbon ($C_{ox}$) are also observed at 288.3 eV. Thus, the occurrence of more number of defect states in the aromatic chain of carbon bonds can also be the possible reason for such high sheet resistance values for graphene samples. Moreover, Figure 10 presents the high-resolution transmission electron microscopy (HRTEM) images of graphene samples grown at camphor concentrations of 3 and 5 mg in order to identify the number of layers to support the Raman observations. A low magnification image as shown in Figure 10a,d indicates that the graphene has been successfully transferred on the TEM grid. The edge of the graphene film folds back, allowing us to identify the cross-sectional view of the graphene sheet. Figure 10b confirms two to three layers of graphene for low concentration of camphor as highlighted in the red circle at few places, whereas another region contributes to the MLG sheet as demonstrated in Figure 10c. In contrast, Figure 10e indicates that high concentration of camphor will lead us to more than 10 layers of the graphene sheet. From the observations, the interplanar spacing of 0.38 nm for MULG was estimated, which is exactly similar with the existing literature. The zoomed-in image of Figure 10e indicates the detailed atomic arrangement.
It is to be noted that the fabricated device made from MULG obtained by 5 mg camphor as displayed in Table more number of graphene layers and a very high mobility of for the Si/MULG structure as compared to Si/MLG, due to forms a Schottky barrier. The typical dark the Gr/n-Si heterojunction device is shown in Figure 11a. Excellent recti
dation behavior is observed for the fabricated device. It is observed that the $J_{SC}$ value increases exponentially for the Si/MULG structure as compared to Si/MLG, due to more number of graphene layers and a very high mobility of MULG obtained by 5 mg camphor as displayed in Table 1.2,4,18,30 It is to be noted that the fabricated device made from camphor-based graphene is rather novel, which has been reported for the first time in our present article. When the device is illuminated under AM 1.5 condition, it shows an excellent rectification and photovoltaic performance. The enhancement in the $J_{SC}$ values from 0.16 to 11 $\mu$A/cm$^2$ signifies more number of graphene layers that can help to contribute more current.

3. CONCLUSIONS

In conclusion, we present a study to explain the effect of camphor concentration along with the source position for achieving a homogenous island growth of MLG sheets using natural camphor by the very facile APCVD technique. The Raman study confirms the existence of intense 2D band at $\sim$2700 cm$^{-1}$ and G band at 1590 cm$^{-1}$ for the slow growth process at the rate of $\sim$20 mg/min with 3.5 mg camphor kept at 16 cm. The existence of mono-/bilayer and multilayer formation of homogeneous graphene sheets has been confirmed by HRTEM images. Moreover, the XPS study confirms the defect peak generated at 285.2 eV, which gives the direct evidence of such a high sheet resistance value. Synthesized graphene sheets at various camphor concentrations at typical distances were transferred onto glass and flexible PET substrates to identify the optimum electrical and optical properties. The measurement shows a decent sheet resistance value of $\sim$1 k$\Omega$/sq with a maximum transmittance of $\sim$88% at 550 nm for low camphor concentration. The excellent rectification and Schottky behavior of n-Si/Gr signifies that graphene layers contribute to an excellent enhancement in the current up to 11 $\mu$A/cm$^2$. This novel approach of obtaining a large-area MLG sheet by natural botanical camphor can be easily scalable for various optoelectronic applications.

4. EXPERIMENTAL SECTION

4.1. Substrate Preparation. Copper foil (13382; 25 $\mu$m) from Alfa Aaser, USA was used as a metal substrate for the graphene growth. First, the Cu foil of 2.5 cm $\times$ 2.5 cm was precleaned by acetone and deionized (DI) water and then immersed in 2:1 DI H$_2$O/HCl at room temperature for 15 min. Then, the Cu foil was rinsed with DI water three times and then washed with isopropanol (IPA). Cu foils were then dried under the slow stream of Ar gas before loading into a high-temperature zone furnace. In the CVD chamber, first, the Cu substrate was pre-annealed until the temperature reaches 1020 °C, as represented in Figure 12. Then, Cu foil was annealed at a constant temperature (1020 °C) for 15 min under an H$_2$ (100 sccm) atmosphere to enlarge Cu grain size and reduce lattice mismatch and dislocations that help to limit the number of nucleation sites. During the growth process, the camphor was introduced and kept at a certain distance for the number of nucleation sites. During the growth process, the camphor was introduced and kept at a certain distance for the number of nucleation sites. When the camphor was introduced and kept at a certain distance for the number of nucleation sites. When the camphor was introduced and kept at a certain distance for the number of nucleation sites.
Finally, under the cooling process, the gas composition was kept constant.

4.2. Graphene Growth and Transfer Process. For the graphene growth process, a quartz tube with length around 1250 mm and diameter 55 mm is used as a CVD reactor and kept horizontally inside the high-temperature zone furnace as shown schematically in Figure 1. For the synthesis of graphene, as-cleaned Cu foils were kept with an angle of 10°−15° inside the high-temperature zone facing toward the gas flow and the carbon source material (camphor) was put in a quartz boat at a typical distance (D). In our present work, Cu foil inclination predominantly supports the uniform growth of graphene coverage over a large substrate as compared to no inclination. In these experiments, the concentration of camphor and the distance between source and the substrates (D) were varied to obtain MLG sheets on glass and PET substrates with suitable electrical and optical properties. The Cu foil was heated from room temperature to 1020 °C at a heating rate of ~15 °C/min under the flow of 200 sccm high purity Ar, followed by annealing for 15 min under the flow of 100 sccm H2. Then, camphor is moved with a magnet and kept at a typical distance (D) to evaporate above its melting point under Ar/H2 as the carrier gas. For the growth of graphene, the gas composition was changed to Ar/H2 98:2 ratio. The total growth time [evaporation rate (Rv)] was calculated accordingly, for all the experimental variations. After growth, the operation was switched off and the chamber was allowed to cool naturally under the flow of Ar and H2 gases.

The graphene-covered Cu was coated with polymethyl methacrylate (PMMA) by spin coating at 3000 rpm for 60 s and 1000 rpm for 60 s, followed by baking of PMMA/graphene/copper at 180 °C for 2 min. Then, the copper was etched by placing the samples over 0.5 M (NH4)2S2O8 for 6 h. The graphene grown on the back side of the Cu was removed by washing under the stream of DI water and placed again on the substrates. The substrates were kept overnight for the complete adhesion to the substrate. Finally, the PMMA layer was removed by dipping in acetone for 30 min and after that repeatedly washed with DI water and IPA.

5. CHARACTERIZATION DETAILS

To identify the formation of MLG, Raman measurements were carried out at various spots by using a 532 nm laser source with a micro Raman (inVia, Renishaw, UK) with an attached optical microscope (Leica Microsystems). The laser power used was 2.5 mW, with an accumulation time of 30 s. The sheet resistance and mobility of all the variations were measured using a Hall Effect measurement system (Ecopia, model HMS-5000) with the van der Pauw configuration. Optical transmittance of the graphene sheet was measured using a (UV-2600, Shimadzu) UV–vis spectrophotometer. The optical measurements were carried out on graphene transferred onto glass and flexible PET substrates. FE-SEM analysis was carried out using a (Zeiss, Ultra-55) microscope at 5.0 kV acceleration voltage. X-ray photoelectron spectroscopic measurements for one of the graphene transferred on Si samples were performed in multiprobe surface analysis ( Scienta Omicron, Germany) using the monochromatized Al Kα (1486.7 eV) radiation source. The pass energy of the scans was kept at 20 eV with an ultimate spectral resolution of ~0.02 eV. The transmission electron microscopic analysis (JEOL 2100) was conducted at 200 keV with a point-to-point resolution of 0.19 nm. Graphene samples were successfully transferred on the carbon-coated Cu grid by the standard transfer method process, AFM analysis was performed to analyze the air/Si surface roughness interface by using Bruker MultiMode 8.0, nanoscope ScanAsyst mode (using PeakForce Tapping mechanism). The device characterization was measured under a solar simulator (SS80AAA, Photoemission Tech., USA) equipped with an AM 1.5G filter and a source measuring unit (U2722A, Agilent) by applying the bias of −1 to +1 V.

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Notes
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