Nonlinear optical absorption and asymmetric charge carrier conduction in chemical vapor deposited single-layer graphene

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Abstract

In this work, we report the nonlinear optical absorption and asymmetric charge carrier conduction in single layer graphene films deposited by chemical vapor deposition (CVD) technique on copper foils with pretreated surface. XRD texture and pole figure analysis of the substrate are utilized for the visualization of the effect of the pretreatment on the substrate. The synthesised graphene is employed as a channel layer in a back gated field-effect transistor and the asymmetric behavior of charge carriers is analyzed. Nonlinear optical response of graphene is recorded after transferring it onto a quartz substrate. Open aperture Z-scan technique yields a nonlinear absorption coefficient of $5.34 \times 10^6$ cm GW$^{-1}$. The film exhibits saturable absorption in the visible range with a saturation intensity as low as 0.134 GW cm$^{-2}$.

1. Introduction

Graphene was considered only as an electronic material in its early stages of research. However, during the last few years, researchers started exploring its application in photonics and optoelectronics [1–4]. It is well proved that the important characteristics of the synthesized graphene film depend strongly on its quality. The difficulty in producing high-quality films over large area hinders the use of graphene in many possible applications. Hence, the sustained effort towards this direction became an active part of research in this field. In chemical vapor deposition (CVD) of graphene, pretreatment of the substrate surface is found to be an essential prerequisite to produce good quality films. Many pretreatment methods are reported for copper foil [5–9], which is a widely used substrate for CVD of graphene [10]. In addition to the removal of surface contaminants, etching of the rolling lines from the surface of copper foil and substrate annealing are the pretreatment processes. Understanding the surface morphology of substrate is very important to obtain high-quality graphene films with fewer defects, large domains and uniform coverage.

The polycrystalline nature of copper foils used as substrates for chemical vapor deposition (CVD) of graphene affects the properties of the graphene films [11]. After the first report on CVD of few-layer graphene on copper using methane, most of the studies were based on controlling the number of graphene layers irrespective of the polycrystalline nature of the graphene films [12–16]. Later, the attention was turned towards obtaining single-crystalline graphene films. Several substrate treatment studies are reported for this purpose [17–21]. Electrochemical polishing of copper is reported to remove the surface contamination and roughness of the as purchased foils [21]. Annealing of copper foil at high temperature in the presence of a high flow rate of hydrogen has been reported for getting substantial single domain growth [22]. Annealing causes an increase in the copper grain size and surface morphology modification, which in turn, facilitate better graphene growth [23]. A wide range of durations has been reported for annealing at various gas flow combinations of Ar and H$_2$ [24]. H$_2$ plays the leading role in the removal of surface oxide layers. In short, polishing improves the surface morphology of...
copper substrate and the annealing performed before CVD further improves the smoothness of substrate surface and domain size beneficial to the graphene growth.

Graphene’s biocompatibility, large electrochemical potential window and its ability to be functionalized along with other versatile properties make it suitable for biosensing applications [25]. Studies on the interaction of biomolecules with graphene paved the way for the development of graphene field-effect transistor (GFET) based biosensors [26]. In GFET, graphene acts as the channel layer. For sensing applications, it utilizes the variation of its transfer characteristics by a change in channel mobility. Field effect behavior of graphene was one of the first ground-breaking experiments reported on it [27, 28]. The nonlinear optical properties of graphene have gained attention in laser technologies and other optoelectronic applications. Third-order optical nonlinearities observed in graphene and the studies on gate tuned third-harmonic generation have promoted potential applications of this material in optoelectronics [29–31].

The present study covers the whole processes involved in the CVD of graphene, extending to its practical applications. Texture characterizations of pretreated copper foils are not reported related to the CVD process of graphene. In this study, copper foils are electrochemically polished and the effect of treatment is visualised by pole figure images recorded by x-ray diffraction (XRD) technique. Graphene is deposited on these pretreated copper substrates. A clear understanding of the behavior of charge carriers in graphene film on the application of an electric field is important in the design of practical sensing devices. The asymmetric behavior of charge carriers is analysed in this study using graphene as the channel layer in GFET. As the nonlinear absorption coefficient of single-layer graphene is less reported, we conducted open aperture Z scan measurements, which revealed the saturable absorption behavior and low saturation intensity of the material.

2. Materials and methods

2.1. Materials used
Copper foil (99.98%) of 25 μm thickness, purchased from Alfa Aesar, was used as the substrate. The hydrocarbon used for the synthesis was methane (99.995%). Hydrogen (99.995%) and argon (99.999%) were the other gases which assisted the growth of graphene on copper. As purchased 85% orthophosphoric acid (H₃PO₄) solution was used as the electrolyte for polishing the copper substrate. 1M ammonium persulphate was the copper etchant. Two wt% polymethyl methacrylate (PMMA) (11000 molecular weight) in anisole was used to support the graphene film while transferring it onto other substrates. Prior to copper etching, the graphene on the rear side of the substrate was removed using 11% nitric acid (HNO₃) solution. Deionized water was used for washing the sample throughout the transfer steps. Semiconductor grade acetone and isopropyl alcohol (IPA) were used for removing PMMA coating and remaining residues, respectively.

2.2. Electrochemical polishing of copper
The electrochemical polishing of copper substrate was performed using Biologic SP 300 potentiostat in 3-electrode configuration. Copper foil of 2 × 2 cm, which is to be electropolished, was used as the anode. A platinum foil of the same size served as the counter electrode while Ag/AgCl acted as the reference electrode. Polishing was achieved by running chronoamperometric electrochemical experiment for 30 min duration at a constant potential of 0.7 V in the electrolyte solution of 85% orthophosphoric acid at room temperature.

2.3. Texture analysis and CVD of graphene
The electrochemical polishing and annealing of copper substrates before graphene deposition were conducted to improve the surface morphology of the copper substrate. Phase analysis and texture measurements using x-ray pole figure analysis were carried out using PANalytical X’Pert PRO with Cu Kα radiation. Since the exposure of the annealed copper substrates to air can cause surface oxidation, texture measurements were performed on polished and annealed samples only after graphene deposition. Graphene prevents surface oxidation of the copper substrate. Two types of samples were considered for texture study: (1) unpolished copper foil (bare Cu) and (2) annealed polished copper foil with graphene coating (processed Cu). The graphene deposition was done at 950 °C and 20 mbar pressure using a home-built CVD system [32]. Polished copper foils of 1 × 1 cm were used as the substrate. After loading the substrate, the temperature of the CVD chamber was ramped upto 950 °C under 10 sccm H₂ and 100 sccm Ar atmosphere. Once the temperature reached 950 °C, the annealing of the substrate was done in a high H₂ ambient of 150 sccm along with 50 sccm Ar for one-hour. The CVD growth was initiated after this by letting methane into the CVD chamber at a flow rate of 7 sccm along with 600 sccm H₂ and 30 sccm Ar. The growth was immediately followed by a sudden cooling step. The sample was taken out when the substrate reached room temperature. The as-grown graphene films were analyzed using Raman spectroscopy and field emission scanning electron microscopy (FESEM). Horiba’s LabRAM HR micro-Raman spectrometer with 514.5 nm excitation laser and ZEISS Sigma microscope were used respectively.
2.4. Transfer of graphene
The graphene was transferred from copper foil to 300 nm thick SiO$_2$ coated silicon substrate using PMMA assisted wet transfer technique. 300 nm PMMA layer was formed on the graphene surface using spin coating technique. The graphene on the backside of copper was etched away using HNO$_3$ solution, and then 1M ammonium persulphate solution was used to etch away the copper. The PMMA layer was removed from the graphene transferred onto the SiO$_2$ surface using acetone. The same technique was employed for transferring graphene onto the quartz substrate for optical characterizations. Schematic of the transfer process is shown in figure 1. Raman spectroscopy was employed to confirm the transfer and quality of graphene. Optical microscopy and FESEM were used to understand the nature and quality of the film. Optical microscope images were captured by a Leica DFC 280 microscope.

2.5. GFET fabrication and characterization
Back gated GFET was fabricated on a p-type silicon wafer precoated with 300 nm thick SiO$_2$ Graphene is used as the channel layer. 100 nm thick gold source and drain electrodes were deposited through shadow mask by vacuum thermal evaporation technique. The deposition was carried out at a base pressure of $6 \times 10^{-6}$ mbar at a deposition rate of 5 Å s$^{-1}$ measured by a quartz crystal thickness monitor. GFET was fabricated with a channel length of 65 μm and width of 1000 μm. The schematic of the fabricated device is shown in figure 2. The electrical characterizations of the device were performed using Keithley 3200 semiconductor parameter analyzer. Gate voltage ($V_{GS}$) was swept from $-40$ to 100 V while recording the transfer characteristics. The drain-source current ($I_{DS}$) versus drain-source voltage ($V_{DS}$) characteristics were also noted at different values of $V_{GS}$. The

![Figure 1. Schematic of graphene transfer steps.](image1)

![Figure 2. Schematic of back gated GFET.](image2)
carrier mobility within the channel layer was estimated using the transconductance method. The same measurements were carried out under vacuum after heating the device at 100 °C.

2.6. Open aperture Z-scan study
Optical properties of the film were studied using the graphene transferred onto the quartz substrate. Jasco V350 UV–vis spectrophotometer was used to record the transmittance spectrum. Single beam Z-scan technique was used to measure the nonlinear absorption coefficient of graphene on quartz substrate. A Q-switched Nd:YAG laser (Spectra Physics LAB-1760, 532 nm, 7 ns, 10 Hz) was the laser source. The transmittance of the sample was measured by moving the sample in the direction of the incident light (Z-direction) through the focal point of the lens having a focal length of 20 cm. Measurement was performed in an open aperture mode, where all the light transmitted through the sample is collected on a photodetector. The open aperture regime enables the characterization of the intensity dependent absorption. The nonlinear absorption coefficient was determined after fitting the experimental Z-scan plot with theoretical plot [33].

3. Results and discussion

3.1. Texture analysis of surface-treated copper substrate
The x-ray diffraction patterns of bare and processed copper foils are shown in figure 3. The XRD patterns of processed copper foils have a single sharp peak centered around 50.5° corresponding to (2 0 0) plane. But additional peaks corresponding to (1 1 1) c.a. 43.3° and (2 2 0) c.a. 74.1° planes are observed for the bare copper foil. It indicates a preferred orientation of planes in processed copper foil when compared to the bare copper foil.

Further, on pole figure analysis, the distinct spots typical to cubic Cu structure were observed. Figures 4(a)–(c) corresponds to (1 1 1), (2 0 0) and (2 2 0) poles, respectively performed on untreated Cu foil. Figure 4(a) reveals four broad and prominent equidistant spots corresponding to (1 1 1) which are seen at a ψ angle of 54.7°. Another four weak traces are seen near the ψ angle of 16°. Figure 4(b) shows a single spot at the center corresponding to (2 0 0) plane. In figure 4(c), four equidistant prominent spots corresponding to (1 1 1) at a ψ angle of 45° and some fused spots in between can be observed. In the three figures at the bottom (d, e and f) which corresponds to pretreated Cu foil, the poles of (1 1 1), (2 0 0) and (2 2 0) are observed. Compared to the untreated foil, the processed foil shows only the prominent spots, and the fused weak spots are not observed. A single spot at the center of (2 0 0) pole figure suggests that the plane is parallel to the foil surface. This indicates an improvement in the ordering of planes in copper foil after processing. The weak pattern seen on the untreated foil suggests the presence of defects, which are removed on surface processing. The distinct pattern of weak spots suggests that the surface defects may be created at the time of production of the foil. While making the foil, some atoms at the surface may have experienced a shearing force which might have added tilting defects on few surface atomic layers. From the texture analysis, it is found that the substrate surface defects are removed by the pretreatment of the copper foil.

An optimized electrochemical polishing provides a smooth surface through etching of protrusions without the formation of pits on the copper foil. The polishing is taken place at the mass transfer limit, which enables
controlled etching [34]. So, by electrochemical polishing in addition to the removal of surface contaminants, surface defects are also eliminated. The annealing of copper foil improves surface characteristics by reducing surface oxides and volatile impurities. Annealing in the presence of hydrogen for a specific duration results in the smooth and flat copper surface due to the reduction of rolling lines and associated recrystallization of large grains [35]. Exposure of this fresh Cu surface to ambient growth conditions of graphene will lead to ordered stitching of graphene-hexagons and decreased defects in the deposited film. Also, the decreased density of nucleation sites resulting from the surface treatment hinders multi-layer graphene nucleations. Hence it can be concluded that pretreatment of the foil makes the surface suitable for the growth of good quality graphene.

3.2. Characterization of graphene film
Raman spectra of graphene on copper foil is shown in figure 5. The characteristic Raman peaks of graphene [36, 37] centered around 1580 cm$^{-1}$ (G peak) and 2680 cm$^{-1}$ (2D peak) are observed. The D peak ($\sim$1350 cm$^{-1}$) representing the defect, observed in disordered graphene [37, 38] is absent. The higher intensity of 2D peak compared to the G peak is a significant pointer to the formation of single-layer graphene. The Raman spectrum of graphene on SiO$_2$ surface is shown in figure 6(a). The 2D peak is symmetric and it can be fitted well with the single Lorentzian peak. The full width at half maximum (FWHM) is found to 26.5 cm$^{-1}$. All these characteristics of Raman spectrum agree to that of single layer graphene [36, 38, 39]. The graphene domains are visible in the FESEM image of graphene on copper (inset of figure 5). The FESEM image of graphene on SiO$_2$ is shown in figure 6(b), which shows some cracks on the film surface, but the uniform color contrast represents uniform monolayer graphene. The optical microscope image of graphene on SiO$_2$ (figure 6(c)) has uniform color contrast except for small marks of few layers. All these analyses confirm high quality of the present samples.
Figure 6. (a) Raman spectrum of graphene on a SiO$_2$/Si substrate. The inset figure shows the 2D peak curve fitted on single Lorentzian peak. (b) FESEM image and (c) Optical microscope image of graphene on SiO$_2$/Si.

Figure 7. (a) Transfer and (b) output characteristics of GFET measured under ambient conditions.
3.3. GFET characterization

GFET is the simple form of a sensor in which the entire surface of graphene in between two metal electrodes is exposed to the surroundings. The GFET with an intrinsic graphene film as a channel layer should exhibit symmetric $I_{DS} - V_{GS}$ characteristics about the charge neutrality point at $V_{GS} = 0$. The transfer characteristics

![Figure 8](image)

Figure 8. (a) Transfer and (b) output characteristics of annealed GFET measured under vacuum. The inset figure shows the different regions of output characteristics at $V_{GS} = -40$ V.

![Figure 9](image)

Figure 9. The comparison of transfer characteristics of unannealed GFET measured under ambient conditions and annealed GFET measured under vacuum.
of the present GFET recorded by sweeping gate voltage from $-40$ V to 100 V at different drain-source voltages are shown in figure 7(a). A minimum $I_{DS}$ corresponding to the charge neutrality point is observed at $V_{GS} = 60$ V. The positive charge neutrality indicates that the graphene is highly p-doped. In ambient conditions, GFETs show p-doped characteristics due to the surface adsorbents such as oxygen, water molecules or other contaminants introduced during transfer process [40]. The exposure to air, chemical vapor or water vapor during transfer will result in charge trapping within or near the graphene-SiO$_2$ interface. These surface contaminants can induce a higher hole carrier concentration in graphene. It causes the charge neutrality point (Dirac point) to shift towards a positive direction. Gonisewski et al have reported that CVD graphene is inherently p-doped due to the adsorbates in contact with graphene [41]. The GFET output characteristics are shown in figure 7(b). It shows ohmic behavior. For the present device, oxide capacitance is 11.5 nF cm$^{-2}$ with 300 nm-thick SiO$_2$. The mobility of GFET in the linear region of the output characteristics is estimated to be $\approx 1500$ cm$^2$V$^{-1}$s$^{-1}$.

The transfer and output characteristics of GFET with measurements performed in vacuum after annealing are shown in figures 8(a) and (b). The inset figure 8(b) shows the different regions of output characteristics in the case of $V_{GS} = -40$ V. The presence of a ‘kink’ observed represents the transition to ambipolar channel [42]. The transfer characteristics of unannealed GFET measured under ambient conditions and annealed GFET measured under vacuum are plotted in figure 9. A shift in charge neutrality point towards zero is visible in the latter case.
comparison with air exposed GFET, the ambipolar behavior in transfer characteristics is regained with an asymmetry on measurement in vacuum of annealed devices. Hydrocarbons in ambient air are a source of contamination in graphene and most of the substrates adsorb them \[^{[43]}\]. Annealing removes these adsorbed hydrocarbons along with other contaminants (including PMMA residues). Annealing of graphene at medium temperatures has been reported as a reason for the transition from unipolar to ambipolar behavior \[^{[44]}\]. The reverse (ambipolar to unipolar) is possible by attaching suitable molecules onto the surface of graphene. The shift in the charge neutrality point with adsorbed molecules is the basis of GFET based sensing. Even though the sensing of biomolecules using GFET structure \[^{[45]}\] is straightforward, a detailed understanding of the device characteristics is essential. It was observed that the hole mobility in graphene exceeds 2000 cm\(^2\) V\(^{-1}\) s\(^{-1}\) on annealing the device. Thus an improvement in mobility is achieved with the annealing process and measurement under vacuum. The asymmetry in the transfer characteristics is a result of unintentional doping of graphene. This can be utilized in the selective sensing of molecules which can get attached to the graphene’s surface.

### 3.4. Nonlinear optical characterization

The transmittance spectrum recorded for graphene on quartz is shown in figure 10. The optical transmittance of graphene film in the visible range is found to be 97.1\%, which agrees with the theoretical value \[^{[46]}\]. The linear absorption coefficient is obtained from the corresponding absorption spectrum. The thickness of the graphene film is taken as 0.34 nm while calculating the optical parameters of the film. Figure 11 shows a typical Z-scan trace obtained when the sample is translated through the beam focus. The transmission peak observed when the sample passed through the focus is characteristic of saturable absorption. After fitting the experimental Z-scan plot with the theoretical plot, the fitting parameter is estimated as \(-0.1172\). The beam waist radius is calculated to be 21.28 \(\mu\)m. The obtained Rayleigh length of 2.67 mm satisfies the condition for nonlinear refraction \[^{[33]}\]. The nonlinear absorption coefficient is calculated as \(-5.34 \times 10^6\) cm GW\(^{-1}\). The negative value confirms the saturable absorption property of graphene. The saturation intensity for graphene film is observed as 0.134 GW cm\(^{-2}\).

The measured saturation intensity is low when compared to the reported values in various spectral ranges, especially at visible range \[^{[47-54]}\]. However, it is comparable with the theoretical value \[^{[55]}\]. The highest reported values is close to 4 GW cm\(^{-2}\) for single layer graphene \[^{[47]}\]. Podila et al have reported that graphene films having less disorder will have the highest saturation intensity owing to its longer recombination time \[^{[48]}\]. They reported the lowest value for graphene film having the maximum disorder. However it is higher than the value obtained in the present study for the graphene film with minimum disorder. The enhanced nonlinear optical response with a saturation intensity of 1.28 GW cm\(^{-2}\) observed for modified graphene \[^{[52]}\] is ten times higher than the value obtained in the present study. The saturable absorption in the visible range has great relevance in passive mode-locking applications. Further, gate tuned nonlinearity can contribute well to future optoelectronic applications.

### 4. Conclusion

Electrochemical polishing of copper foil and subsequent high pressure hydrogen annealing for one hour favor the growth of good quality graphene by CVD. X-ray pole figure analysis was used to examine the surface of pretreated copper foil. The Raman spectroscopy and other imaging tools confirm the formation of uniform defect free single layer graphene. The asymmetric behavior of charge carriers in graphene films is studied in various atmospheres by fabricating GFET. The hole mobility is found to exceed 2000 cm\(^2\) V\(^{-1}\) s\(^{-1}\). The transparency of the graphene film is 97.1\% in the visible range with good saturable absorption. The film exhibits nonlinear absorption with an absorption coefficient of \(-5.34 \times 10^6\) cm GW\(^{-1}\) and a low saturation intensity of 0.134 GW cm\(^{-2}\). These attributes of the graphene films find applications in various optoelectronic devices.

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