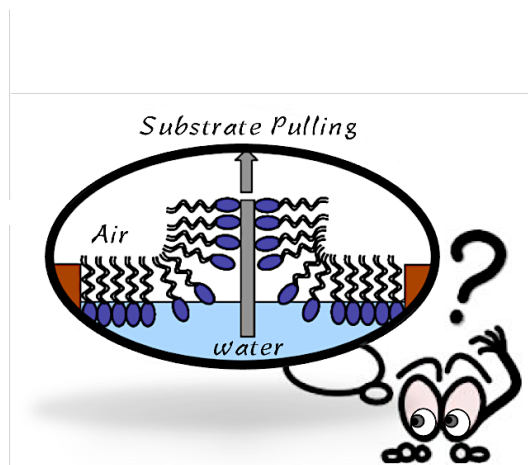
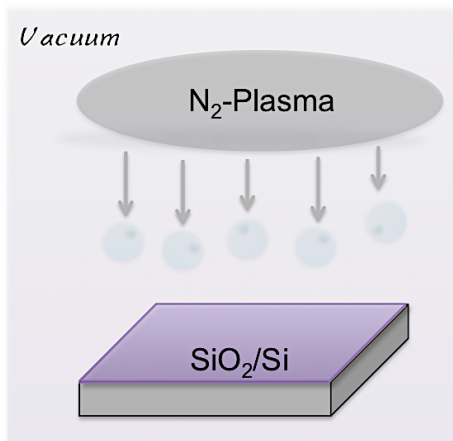


5

Effect of N₂-Plasma on Hydrophilization of SiO₂/Si

*“Anyone who has never made a mistake has never tried anything new”
- Albert Einstein*



This chapter deals with the influence of different plasma systems on SiO₂/Si for selective area hydrophilization under different chamber pressure conditions. A comparative study was performed between air and N₂-plasma systems using OES and SEM to elucidate the effectiveness of this technique. Amongst all plasma systems, N₂-plasma was found to be more efficient for specific placement of GO and to promote its better adhesion to the substrate at 60 Pa.

5.1 Introduction

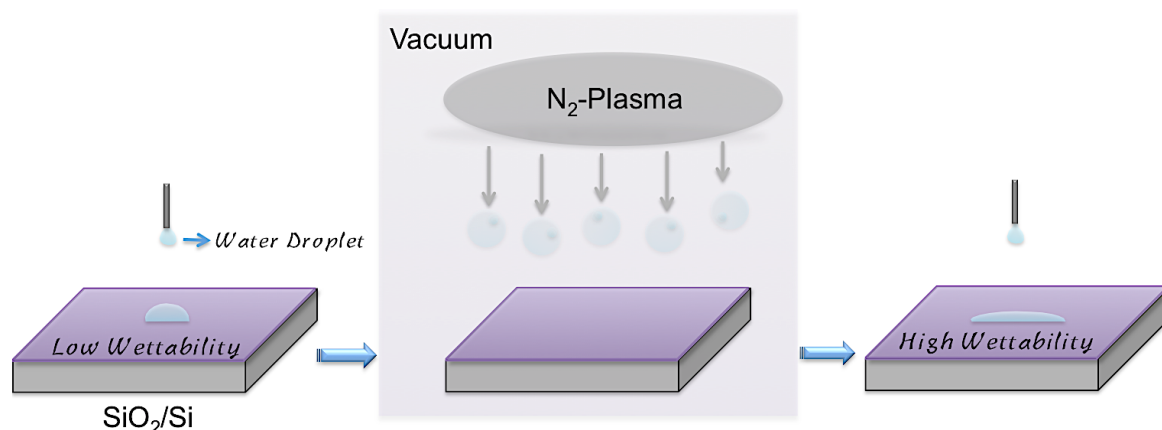
GO is used to make graphene — a wonderful material that scientists believe has immense potential for various electronics and biomedical applications. Like graphene, GO is essentially a sheet that is only one atom thick with oxygen moieties attached to it, but can be as wide as tens of micrometers. Among various methods employed to synthesize graphene or its derivatives [1–4], CVD [5] technique is known to yield high-quality and large-size graphene flakes for patterning and creating transparent conducting films (TCFs) that includes substrate transfer to produce flexible TCFs. The present strategies employed to pattern graphene includes EBL, UVL, SPL, block copolymer lithography, soft transfer printing, direct laser patterning, ink-jet printing, etc. [6–13]. Despite some degree of success in patterning through the present methodologies, all of them lack simplicity, achieving large-scale monolayer graphene arrays and cost effectiveness. Moreover, successful transfer of large graphene films without contamination, wrinkling or damage poses formidable technological challenges. Nevertheless, TCFs made from graphene or rGO sheets largely underperform in comparison to those made from ITO in terms of their opto-electrical properties. This is because the graphene thin films have fundamental limitations for 2D conductivity due the defects and grain boundaries present in the large-area graphene sheets grown by CVD [14], a large number of inter-sheet junctions between the relatively small GO sheets and presence of inter-layer gaps between the stacked layers [15]. Several solutions to these issues have been successfully proposed, including the synthesis of ultra-large size GO sheets [16, 17] and doping with elements that can function as an electron donor [18–20].

The use of GO sheets derived chemically from NG via oxidation and subsequent reduction is considered a low-cost, aqueous-processable alternative to the CVD method without the need for substrate transfer. Direct deposition of GO sheets on a substrate has been achieved via several well-established techniques with varying levels of success, including spin- or spray-coating [21], electrophoretic deposition [22], transfer printing [23–24], dip-coating [25] and LB assembly [26–28]. Among these approaches, LB assembly technique is versatile for the deposition of GO sheets on various substrates, including both rigid and flexible substrates on a large scale, as we have already discussed in *Chapter 1 and 4*.

It is noteworthy that the substrate surface needs to be hydrophilic for proper wetting to take place by water and efficient deposition of GO sheets. In this

regard, for rigid substrates like quartz, glass and Si, piranha solution (traditionally, a 3:1 mixture of H₂SO₄ and 30 % H₂O₂) was quite often used to increase the hydrophilicity. However, piranha solution has its own limitations such as it is highly corrosive in nature, and can destroy poly(ethylene terephthalate) (PET) substrate, could lead to poor reproducibility and is not suitable for selective area treatment of any substrate. Although, plasma—*the fourth state of matter*, has a massive potential for surface modification and deposition of various materials for microelectronics, optoelectronic and a number of chemical processing applications [29]. Plasma surface modification involves the interaction of the plasma-generated excited species with a solid interface. Plasma is created when a neutral gas is given sufficient energy from an electronic discharge source to create new product ions and radicals. The source of free electrons is generally a high-energy glow discharge such as a high voltage electrode. The resulting collisions of electrons and gas molecules result in a net energy transfer to the molecules producing metastable fragments and energized ions. The resulting product is a mixture of highly excited ions consisting of fragmented portions of the parent molecule. Like, plasma generated from N₂ carrier gas typically consists of N, N₂, N₂⁺. The plasma particles are extremely unstable and their energetic states cause them to be highly reactive with particles or surfaces that they contact [30]. The plasma process results in a physical and/ or chemical modification of the first few molecular layers of the surface, while maintaining the properties of the bulk.

The present study presents a one-step facile technique using the N₂-plasma that promotes surface modification and increases the surface wettability of SiO₂/Si (**Scheme 1**) and enhances the adhesion of GO to the substrate. This technique has been employed to create partially hydrophilic surface with the aid of various templates, enabling selective deposition, alignment and formation of desired monolayer GO-sheets patterns through LB deposition technique over large area without the need of any sophisticated equipment. It is well known the plasma generated under low-pressure environment promotes stability of formed ionic radicals. This low-pressure stability is achieved by effectively increasing the mean free path between the active components. Various plasma parameters were optimized to evaluate the effectiveness of the N₂-plasma system and enable selective deposition of GO using LB technique on partially hydrophilized SiO₂/Si substrate. This technique provides a cost effective and environment friendly alternative to many important industrial processes because the method produces



Scheme 1. Schematic representation of the hydrophilization process of SiO₂/Si.

no unwanted waste products and in most cases exposes operators to no significant hazards and therefore can provide an excellent platform to utilize GO and many other amphiphilic molecules that can float on the surface of water for the forthcoming smart Bio-Nano Electronics applications.

5.2 Influence of Various Plasma Parameters on SiO₂/Si for Selective Placement of GO via LB technique

Hydrophilization of SiO₂/Si was carried out using Jeol Datum, HDT-400 Hydrophilic Treatment Device (all the plasma parameters are already fixed) and Basic Plasma Kit (BPK) (Model BP-1) equipped with RF generator of 13.6 MHz, Model RFG-300 (Samco, Japan), where the plasma parameters can easily be regulated. In BPK, gap between the two electrodes was fixed at 23 mm. The N₂ gas used throughout the experiment was of ultra-high purity G1 grade. N₂ was introduced into the plasma chamber with a constant flow rate of 40 ml/min during the entire experiment by varying the chamber pressure (15 Pa, 60 Pa and 1KPa). The operating plasma power was generated at 150 W and the sample was exposed for 30 sec. To detect electronically excited atomic and molecular species in the plasma system, optical emission spectroscopy (OES) studies were conducted from 200–900 nm region. The wettability of as such and N₂-plasma treated SiO₂/Si substrate was recorded using contact angle studies. LB deposition technique and SEM studies were performed to find the effectiveness of the processed parameters for the selective area deposition of monolayer GO.

Selected area deposition of LB film. An optimized solution concentration of 0.1 mg/ml, 5 ml solution volume of GO was used throughout the experiments as

deduced from Chapter-4. Vertical dipping was performed to transfer monolayer GO-film on plasma treated SiO₂/Si substrate. It is well known that surface modification is often sensitive to time and environmental exposure, where the surface may lose its plasma-induced physical and chemical properties. Considering the possible ageing of plasma treatments, the substrates were treated just before the LB assembly.

5.3 Results and Discussion

Plasma Diagnostic by OES. Figure 1 shows typical OES spectra monitored *in situ* from Joel Datum HDT-400 system where the plasma source is air which mainly consists of N₂ (~ 78 %) + O₂ (~ 21 %) + < 1 % of Ar, CO₂, and other gases. This spectrum exactly resembles with the OES spectra for N₂ plasma where the N₂ 1st and 2nd positive emission bands as well as N₂⁺ 1st negative emission lines are observed in spectra where four bands in the visible region, with band heads at ~ 540, 580, 650, and 750 nm that are commonly associated with the first positive system of the neutral nitrogen molecule. The peaks in the UV region centered at 316, 337, 380, 400 and 420 nm corresponds to the most intense peaks of the second positive molecular series of neutral nitrogen and the sharp peaks at 392.42 and 428.68 nm originated from first-negative system of N₂⁺ molecular ion

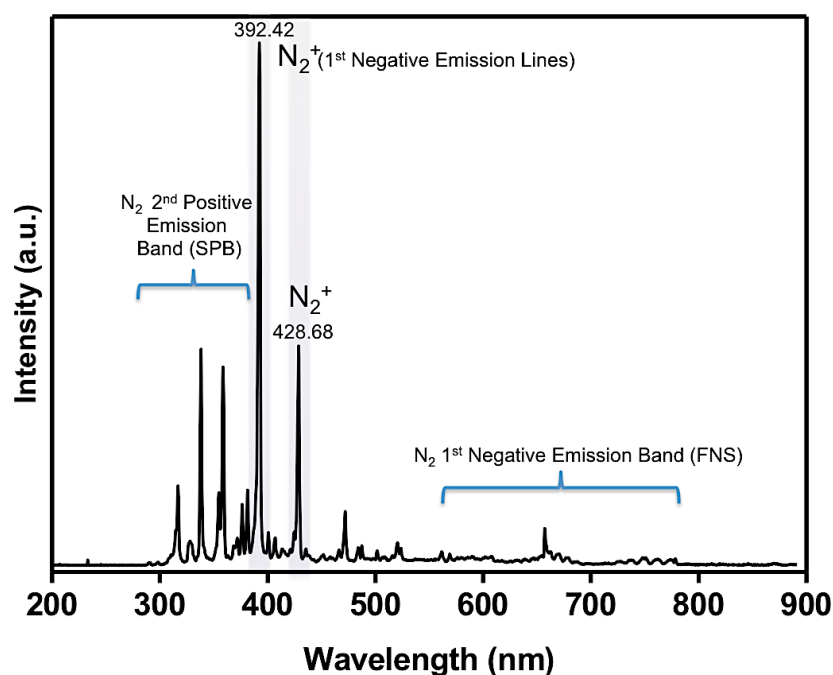


Figure 1. Typical Optical Emission spectra from Joel Datum, HDT-400, hydrophilic treatment device.

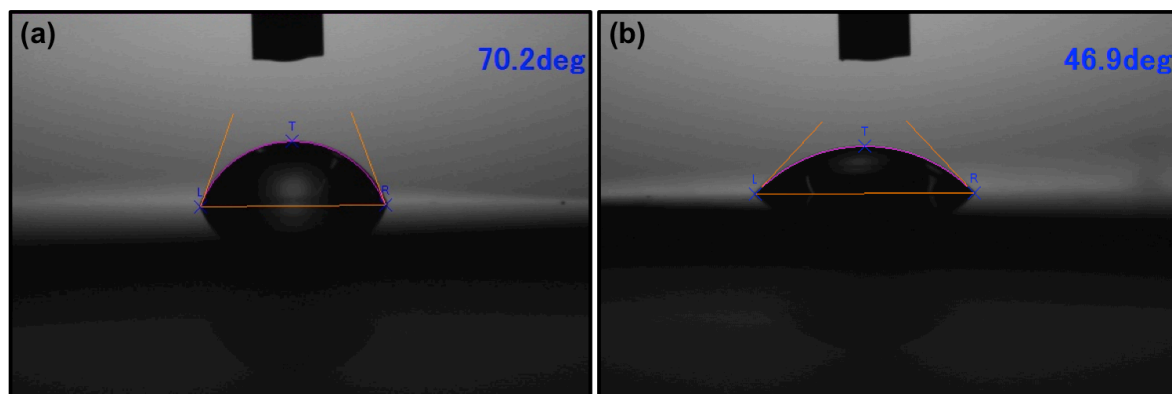


Figure 2. Contact angle measurement of (a) bare SiO₂/Si and (b) after treatment with the hydrophilic treatment device for 30 sec.

transitions [30]. N-atoms and N₂⁺ ions are the primary species in N₂-plasma that contribute to the nitridation of SiO₂ thin film. However, N₂⁺ species are responsible for top surface nitridation on SiO₂/Si [31].

For contact angle measurements, the sessile drop technique was used, [32] in which a 1 μl-distilled water from a syringe was dropped on the sample surface at room temperature. The water droplet formed an equilibrium dome shape on the sample surface and was imaged by an optical microscope. **Figure 2** shows the experimental results of the water droplet contact angle measurements on SiO₂/Si surfaces before and after hydrophilic treatment.

The morphology of selective area deposition of monolayer GO film using LB deposition technique on SiO₂/Si was characterized using SEM as shown as **Figure 3**. The edge of the patterned area does not seem to be sharp enough. To understand the mechanism behind this whole process, we have monitored the effect of

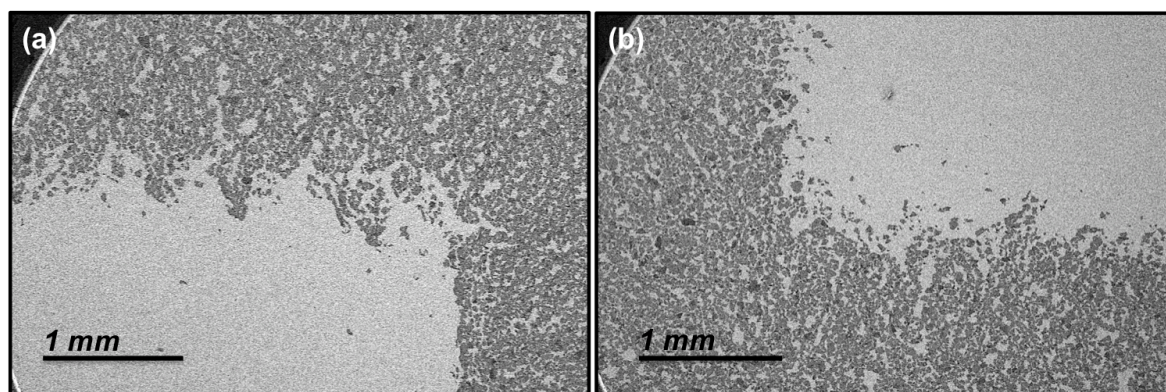


Figure 3. SEM image of selective area deposition of GO using hydrophilic treatment device via LB technique.

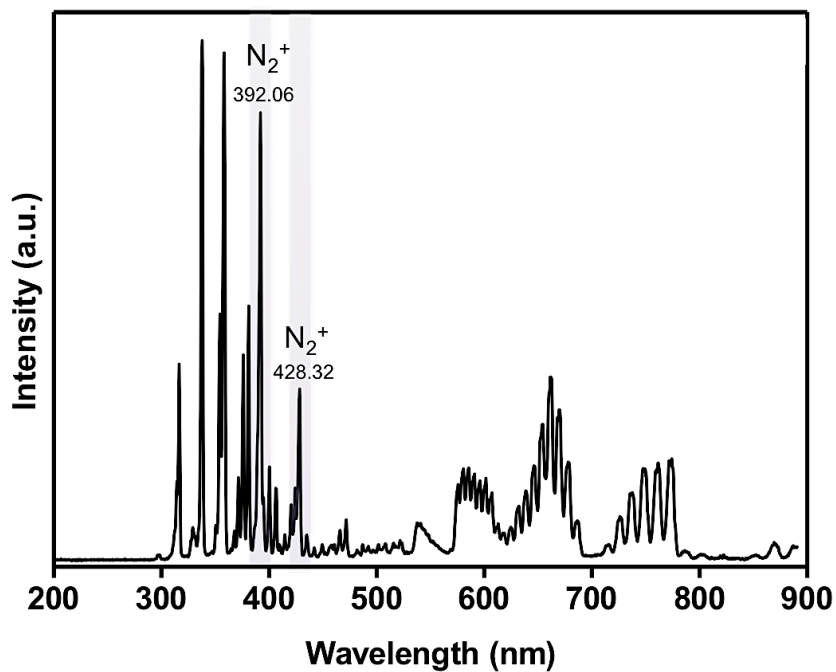


Figure 4. Emission spectra of N₂-plasma @ 15 Pa.

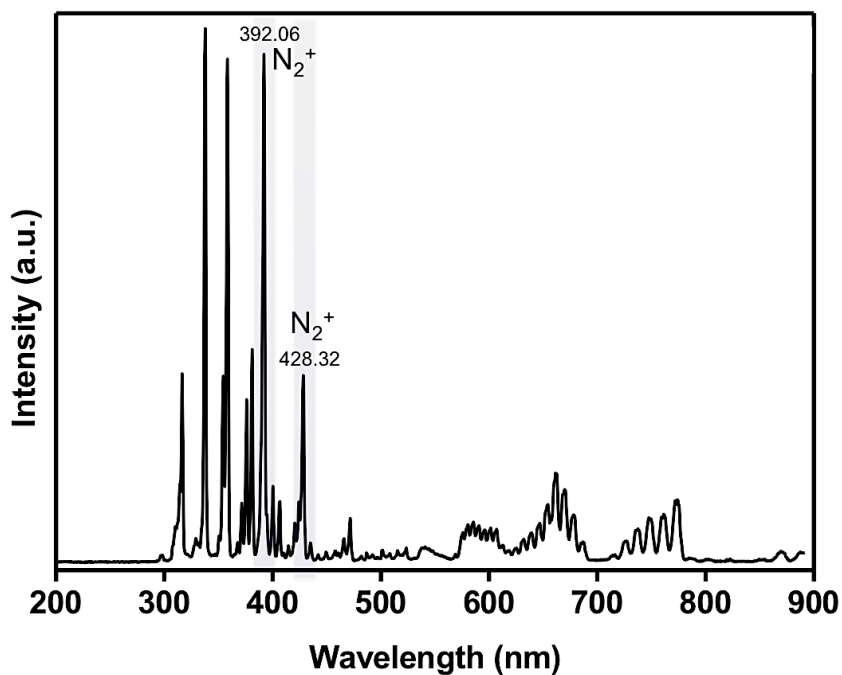


Figure 5. Emission spectra of N₂-plasma @ 60 Pa.

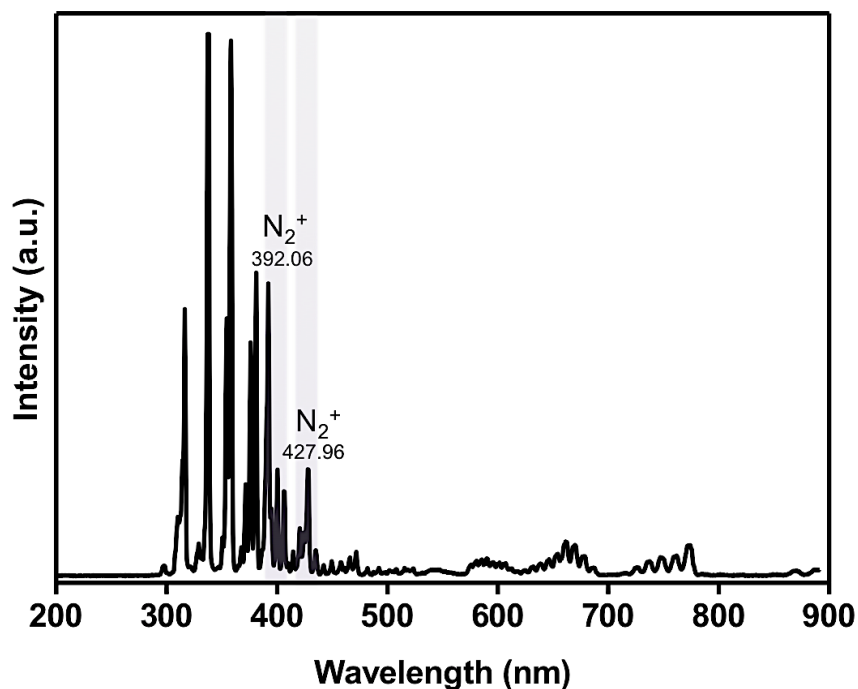


Figure 6. Emission spectra of N₂-plasma @ 1K Pa.

chamber pressure (15 Pa, 60 Pa and 1 KPa) of N₂-plasma generated using Basic Plasma Kit on the patterned areas while keeping gas flow rate and plasma power constant. It can clearly be observed from OES spectra of N₂-plasma at different pressure (Figure 4–6) and the respective SEM images of patterned GO (Figure 7–9) that the intensity of N₂⁺ species does matter in the proper alignment and selective area deposition of GO sheets. The patterned areas appeared to be highly regular and clean as shown in Figure 8. Moreover, Figure 10 shows the contact angle measurements on SiO₂/Si surfaces before and after hydrophilic treatment.

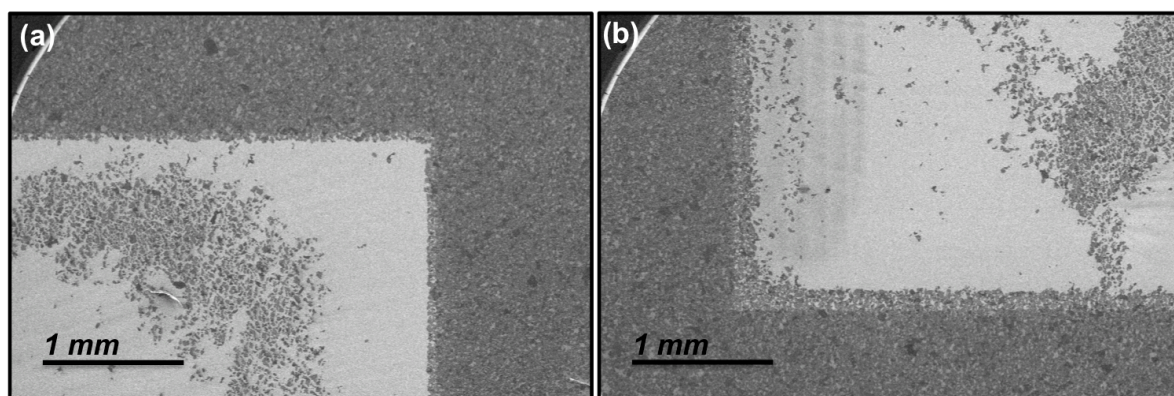


Figure 7. SEM image of N₂-plasma assisted selected area deposition of GO @ 15 Pa.

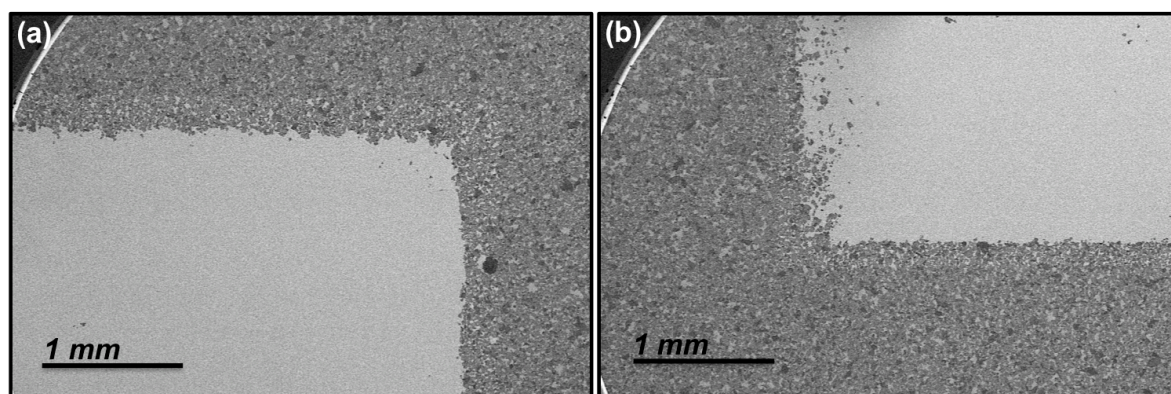


Figure 8. SEM image of N₂ Plasma assisted selected area deposition of GO @ 60 Pa.

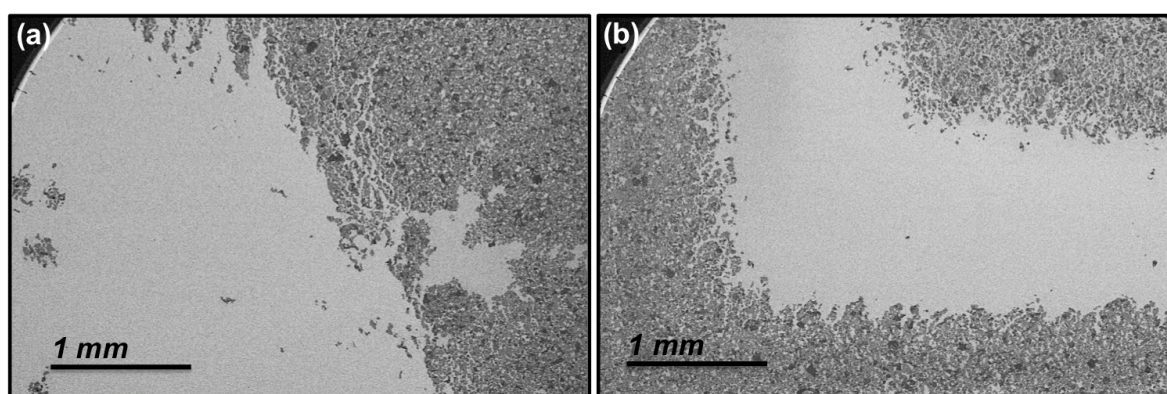


Figure 9. SEM image of N₂ Plasma assisted selected area deposition of GO @ 1K Pa.

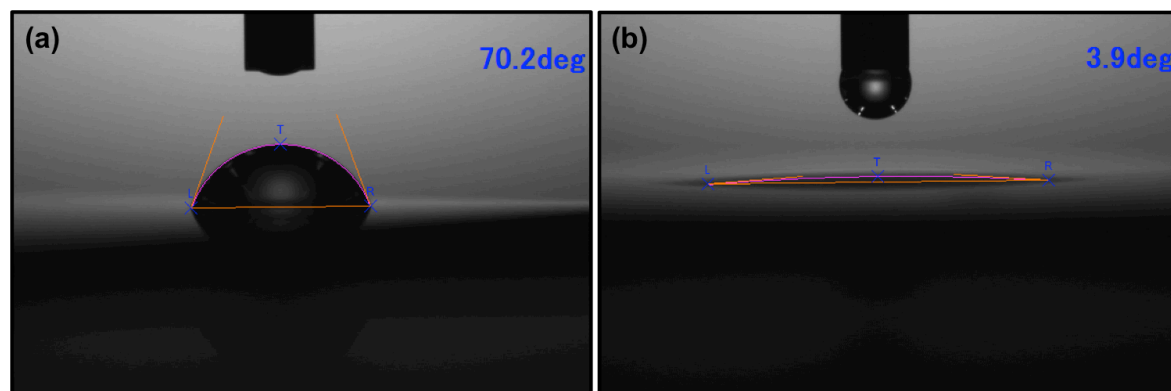


Figure 10. Contact angle measurement of (a) bare SiO₂/Si and (b) after treatment with the N₂ Plasma @ 60 Pa for 30 sec.

5.4 Conclusion

The influence of different plasma systems on SiO₂/Si towards its selective area hydrophilization under various chamber pressure conditions was monitored. A comparative study has been performed between air and N₂-plasma systems using OES and SEM to elucidate the effectiveness of specific area monolayer GO

deposition through LB technique. This study reveals that the activation plasma process occurs when SiO₂/Si surface is treated with air or N₂-plasma. Thus, suggesting the incorporation of some molecular species present in plasma system on the surface of substrate, changing its hydrophobic nature to hydrophilic. The N₂-plasma found to be more efficient for specific placement of GO @ 60 Pa, having capability to further promote better adhesion of GO to the substrate (detail studies have been performed in the upcoming chapters). The combination of N₂-plasma and LB assembly technique is highly versatile and could be applied for large-scale patterning and selective area placement of monolayer GO for commercial applications.

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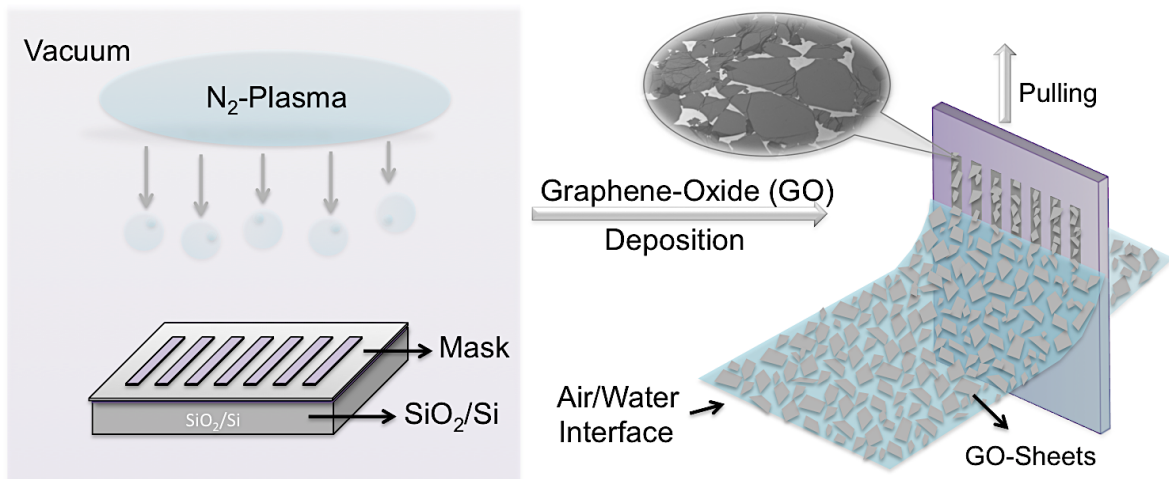
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6

N₂-Plasma Assisted One-Step Alignment and Patterning of GO on SiO₂/Si via LB Technique

*“Genius is one percent inspiration & ninety- nine percent perspiration”
- Thomas A. Edison*



The present study demonstrates a one-step plasma-assisted selective placement, which is very simple, high throughput, time saving, and cost effective technique for efficient fabrication of 2D patterned graphene over large area. This technique was employed to create partially hydrophilic surface with the aid of various templates, enabling selective deposition, alignment and formation of desired monolayer GO-sheets patterns via LB deposition technique without the need of any sophisticated equipment. The efficacy of this methodology was evaluated through, SEM, TEM, AFM, XPS, Raman spectroscopy and I-V. We believe that this avenue could provide an excellent platform for the forthcoming smart electronics and biological applications.

6.1 Introduction

Precisely controlled placement and patterning of graphene on various substrates will be highly desired in many applications such as nanoscale electronics, multifunctional optoelectronic devices and molecular sensing. However, from the industrial point of view, a enormous challenge still exists in its selective placement, self-assembly and patterning for application in electronics, photonics, optoelectronic devices, biological and chemical sensing, energy conversation etc. It is extremely desirable to develop successful selective placement and patterning technique for low cost and high throughput fabrication of large area 2D patterned graphene and GO with controllable dimensions.

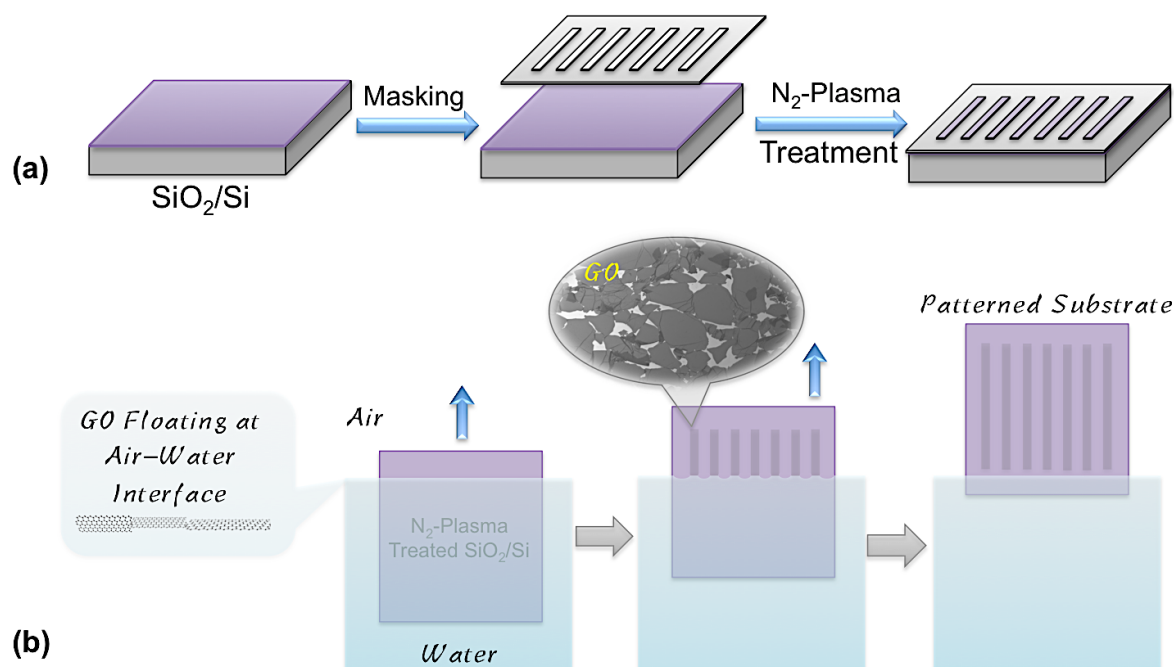
To date, extensive work has been devoted to the self-assembly and patterning of GO and graphene, using various techniques including EBL, UVL, SPL, block copolymer lithography, soft transfer printing, masked laser patterning, direct laser patterning, combination of wettability modulation and spin-coating, ink-jet printing, etc. [1-8]. The complex patterned structures can be formed using the current lithography and metal evaporation deposition techniques. However, this technique involves photoresists, which is undesirable due to the presence of residual polymers that may contaminate the graphene surface and interfere with subsequent metallization steps. Apart from that, these processes are time consuming and involve highly expensive, sophisticated equipment's with low throughput. Hence, there is an urgent need for a simple, time saving, cost effective method that can yield high throughput with greater reproducibility for an efficient fabrication of 2D patterned graphene and various nanostructures in large area.

Besides that, another important issue yet to be resolved is the precise control over the alignment and positioning of GO-sheets from its stock solution on to the substrate, which is one of the vital steps in the processing of graphene based devices especially for large-scale fabrication of parallel device arrays [9], that is highly desirable from an industrial point of view.

Recently, extensive efforts have been made to achieve continuous films of GO using numerous methods and techniques such as drying of a suspension droplet i.e., via drop casting, spin coating by means of functionalization [10], vacuum filtration [11], electrophoretic deposition [12], dip coating [13], layer by layer assembly [14] and LB [15] for transparent electronic and bio-electronic applications. Among these techniques, LB is the most widely employed technique to achieve high density and even close-packed monolayer of GO for large-scale deposition without

the need of a stabilizing agent [16]. It is important to mention that the substrate size is virtually unlimited since the dimension of the LB trough is the only restricting factor for large-scale film deposition. The thin film performed in such a way can then be transferred onto a substrate either by vertical dipping or horizontal dipping. This simple and general process has led to various applications based on mono and multilayer films of graphene [17]. However, a single-step selective placement and patterning of monolayer GO with controlled dimensions without the need of special equipment and process has not been demonstrated yet.

It is well known that upon exposure to N₂-Plasma, the surface properties of Si or SiO₂ can be modified [18, 19]. In this chapter, we demonstrate N₂-plasma treatment on masked substrate prior to LB deposition that enables high-resolution selective-placement and patterning of GO-sheets thus overcoming the limitations of functionalization and lithography processes (**Scheme 1**) and yet very cost effective. To preserve the native surface properties of SiO₂/Si substrate, we have studied the effects of several experimental parameters (already discussed in *Chapter 5*) and have optimized them for best results, which include the effect of N₂-plasma power, chamber pressure, exposure time, contact angle measurements and roughness evaluation through AFM studies. The optimized solution



Scheme 1. Schematic illustration of (a) the approach to enable selective placement and patterning of GO and (b) Selective deposition of GO on N₂-plasma exposed site during gradually moving SiO₂/Si upward.

concentration and volume of GO solution was used throughout the experiment (deduced from *Chapter 4*). This approach facilitates the selective and close-packed placement of the GO monolayers directly on the N₂-plasma exposed substrates, thus providing a facile, inexpensive lithography-free approach that allows easy control of patterned dimensions and therefore can boost the development of GO based devices at wafer-scale in a short turnover time.

The pivotal aspect of this technique includes simplicity, large area deposition, and fabrication of various geometric micro-patterns. Moreover, this cost effective avenue could provide an excellent platform to utilize GO and many other amphiphilic molecules that can float on the surface of water for the forthcoming smart Bio-Nano Electronic applications.

6.2 Fabrication of Various Geometric Patterns of GO

Surface Modification of SiO₂/Si.

Plasma treatment of SiO₂/Si was carried out using BPK (Model BP-1) equipped with RF generator of 13.6 MHz, Model RFG-300 (Samco, Japan). Various parameters have been optimized to deduce the overall performance and reliability of SiO₂/Si as discussed in *Chapter 5*. Briefly, N₂ gas was introduced into the plasma chamber at a flow rate of 40 ml/min with a chamber pressure maintained at 60 Pa. The operating plasma power was generated at 100 W and the sample was exposed for 30 sec.

Partial Hydrophilization of SiO₂/Si.

In a typical experiment, SiO₂/Si substrate was placed on the lower electrode in the plasma system and covered with a desired mask to be patterned. The mask was taped down around the edges to prevent the penetration of plasma under the mask. After the system was evacuated to lower than 10 Pa, N₂ gas was introduced into the chamber and exposure was performed at aforementioned parameters. The structural changes in the pretreated SiO₂/Si have been studied using AFM, contact angle measurement, OES and XPS analysis.

Preparation of LB Films.

For the preparation of LB films, 0.1 mg/ml concentration of GO solution was prepared in stock and all the suspension were centrifuged @ 2500 rpm for 20 min in order to remove all the debris, if any. Methanol was used to form a stable GO solution with a final ratio of 1:5 (water/methanol) to enable rapid spreading on

the surface of de-ionized water subphase [20, 21]. Before performing each experiment, LB trough and barriers were cleaned with ethanol and thoroughly rinsed with DI water in order to avoid any contamination.

The isotherm for GO solution was taken by dropping 5 ml solution using a glass micro-syringe on the water surface. After stabilizing it for ~ 30 min the film was compressed by the barriers at a speed of 5 mm/min and the SP was recorded using tensiometer attached to the Wilhelmy's plate.

The vertical dipping was performed to transfer monolayer GO-film on N₂-plasma treated SiO₂/Si substrate at SP of 2 mN/m. It is worth noting that for the dipping of N₂-plasma treated SiO₂/Si substrate; the first cycle was executed beneath the subphase because of its hydrophilic nature. At least 20 min was allowed for solvent evaporation and the monolayer was compressed at different values of SP to yield tightly packed monolayer film of GO while pulling it out of the solution at 0.5 mm/min. Once the deposition was achieved, the sample was air-dried and used for further characterization.

6.3 Results and Discussion

One-step plasma assisted route for selective placement and patterning of monolayer GO film in the required geometry, using LB deposition technique, is shown and also schematically illustrated in **Figure 1 and scheme 1(b)**, respectively.

The typical optical emission spectra monitored *in situ* from the N₂-plasma at 60 Pa, 100 W and 40 ml/min flow rate of N₂ gas is shown in **Figure 2**. The N₂ 1st and 2nd positive emission bands as well as N₂⁺ 1st negative emission lines are observed in spectra where four bands in the visible region, with band heads at approximately 540, 580, 650, and 750 nm which are commonly associated with the first positive system of the neutral nitrogen molecule. The peaks in the UV region centered at 316, 337, 380, 400 and 420 nm corresponds to the most intense peaks of the second positive molecular series of neutral nitrogen and the sharp peaks at 391 and 428 nm originated from first-negative system of N₂⁺ molecular ion transitions [18]. N-atoms and N₂⁺ ions are the primary species are responsible for top surface nitridation on SiO₂/Si [18], which is further affirmed by XPS results.

The thickness measurements were recorded to determine the SiO₂ thickness before and after N₂-plasma treatment. Measurements recorded across randomly selected regions of the SiO₂/Si substrate indicated a SiO₂ layer thickness before and

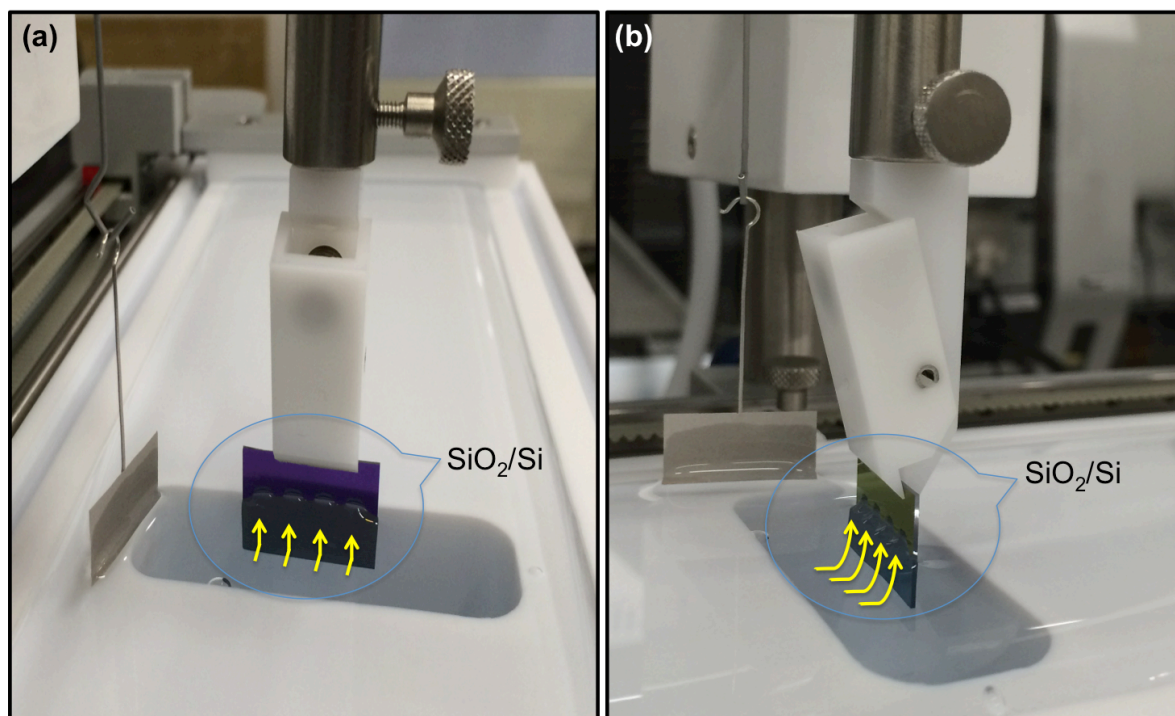


Figure 1. Selective area deposition and patterning of GO at air–water interface on partially hydrophilic substrate (marked with arrow) using LB technique (a) Front view and (b) side view.

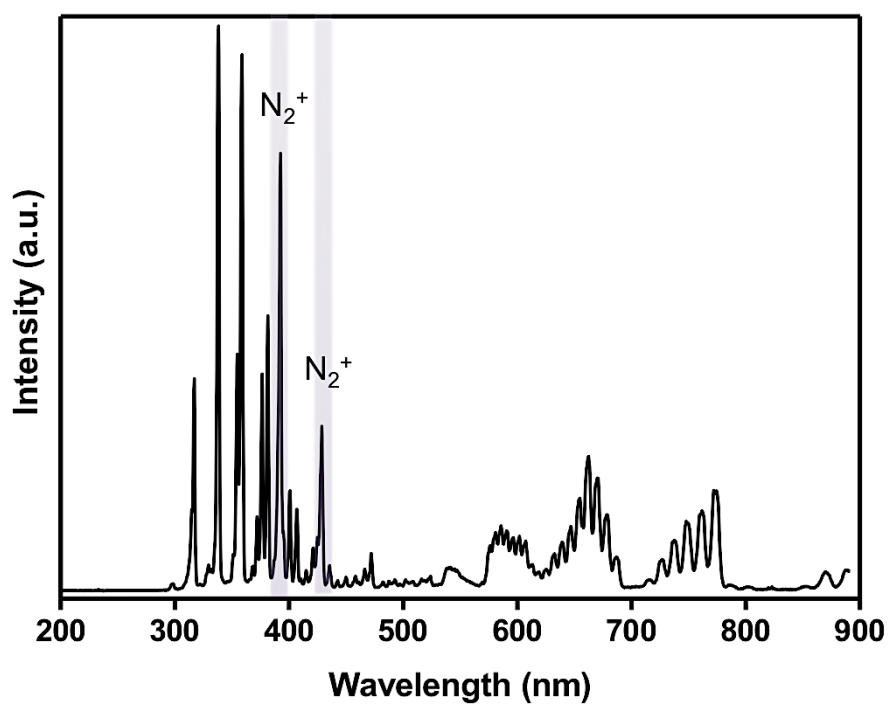


Figure 2. Emission spectra from N₂-plasma at a power of 100 W, gas flow rate: 40 ml/min with a chamber pressure of 60 Pa.

after measurement as 298.233 ± 0.00223 nm and 298.097 ± 0.00105 nm respectively, which clearly reveals that as such there is no etching of SiO₂ taking place on the exposure of N₂ plasma.

For contact angle measurements we have used the sessile drop technique [22] in which a 1 μ l-distilled water from a syringe was dropped on the sample surface at room temperature. The water droplet formed an equilibrium dome shape on the sample surface and was imaged by an optical microscope. **Figure 3 (a and c)** shows the experimental results of the water droplet contact angle measurements on SiO₂/Si surfaces before and after treatment with N₂-plasma. A significant dip in the contact angle was observed from 70 ± 1.2 (untreated SiO₂/Si surface) to 4.14 ± 0.96 (N₂-plasma treated surfaces). The decrease of the water droplet contact angle suggests that the SiO₂/Si surfaces have been transformed from hydrophobic to hydrophilic after this surface treatment. It is well known that the water droplet contact angle depends on both the surface morphology and surface chemistry [23]. The change of either the surface morphology or surface chemistry of a given surface would modify its surface energy leading to the change in the water droplet

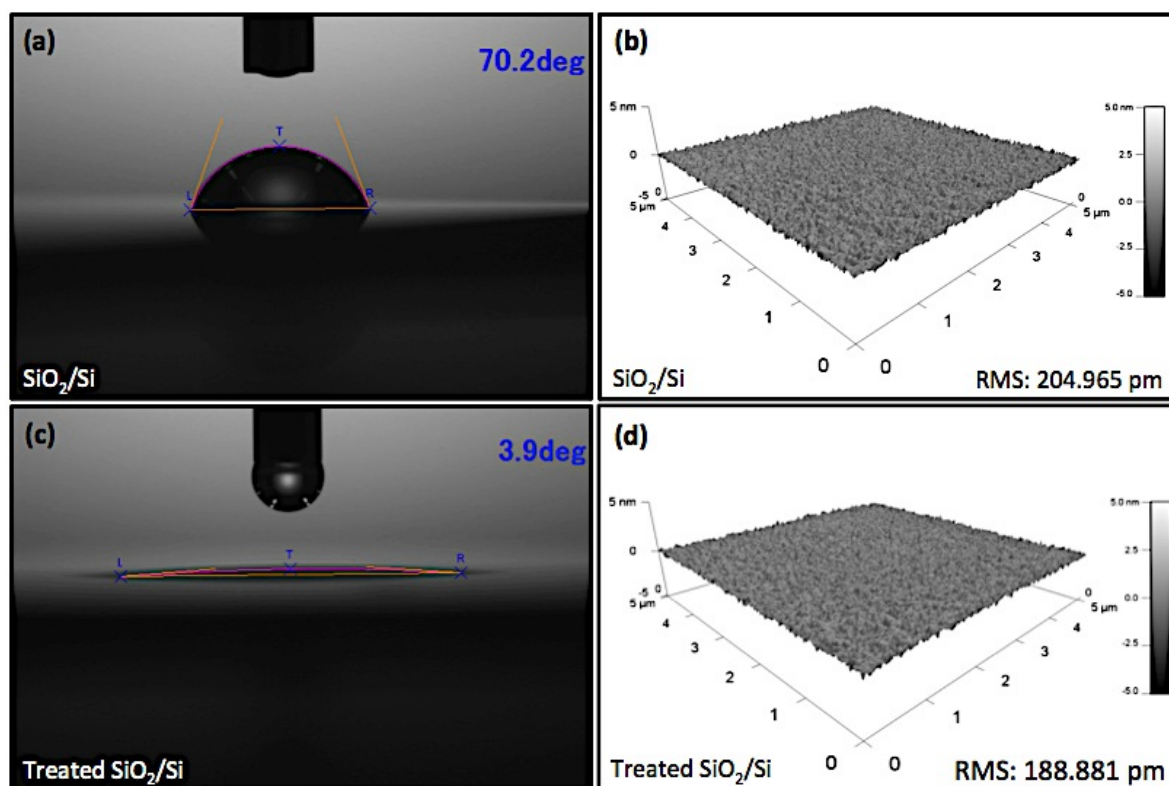


Figure 3. Contact angle measurement and 3D RMS surface AFM image of (a and b) bare SiO₂/Si, (c and d) after N₂-plasma exposure for 30 sec.

contact angle [24].

Normally, in the plasma irradiation process, the ion bombardments physically modify the wafer surface, and may cause damage to layer and increase the surface roughness [25]. To check this, root-mean-square (rms) surface roughness was measured by using AFM before and after plasma treatment of the substrate. For each sample, we have randomly selected five points as the scanned zones, and the scanned size was 5 $\mu\text{m} \times 5 \mu\text{m}$. It was found that for SiO₂/Si the rms surface roughness does not evidently change after N₂-plasma treatment or plasma activation. **Figure 3 (b and d)** shows the surface roughness of SiO₂/Si treated by N₂-plasma. The original wafer's rms roughness was found to be 202.577 ± 3.250 pm. However, on 30 sec plasma exposure, rms surface roughness value improved to 186.668 ± 5.885 pm. The corresponding rms value obtained from the AFM analysis shows that the surface morphology of SiO₂/Si treated with N₂-plasma appears to have no significant changes (difference of only about 20 pm), which agrees well with Ma et al. [26].

It is worth to note that the surfaces treated with plasma should be used for LB deposition immediately, since they may revert to their original characteristics with prolonged exposure to air. Contact angle measurement studies have been performed to determine the aging effect on N₂-plasma treated substrates. There was an increase in water contact angle with the aging of sample, results shown in

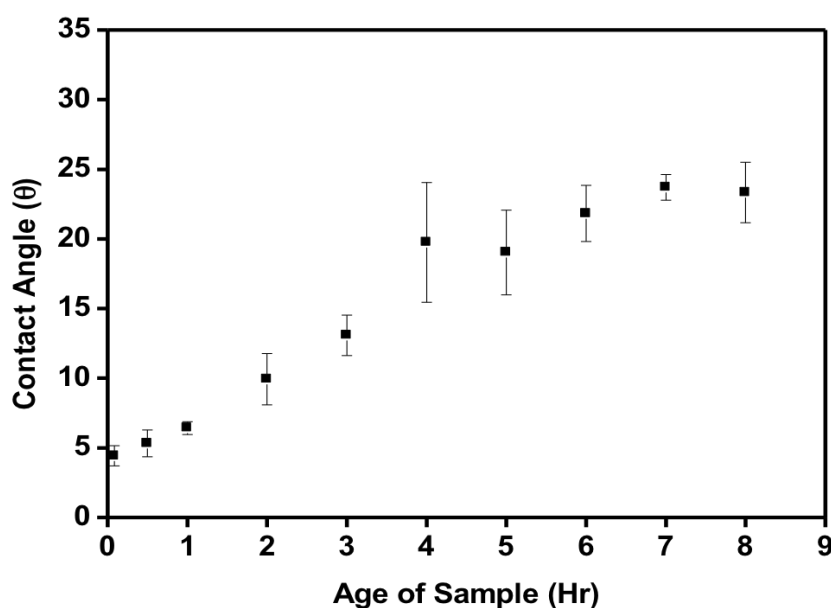


Figure 4. The contact angle measurement of N₂-plasma treated SiO₂/Si as a function of sample age.

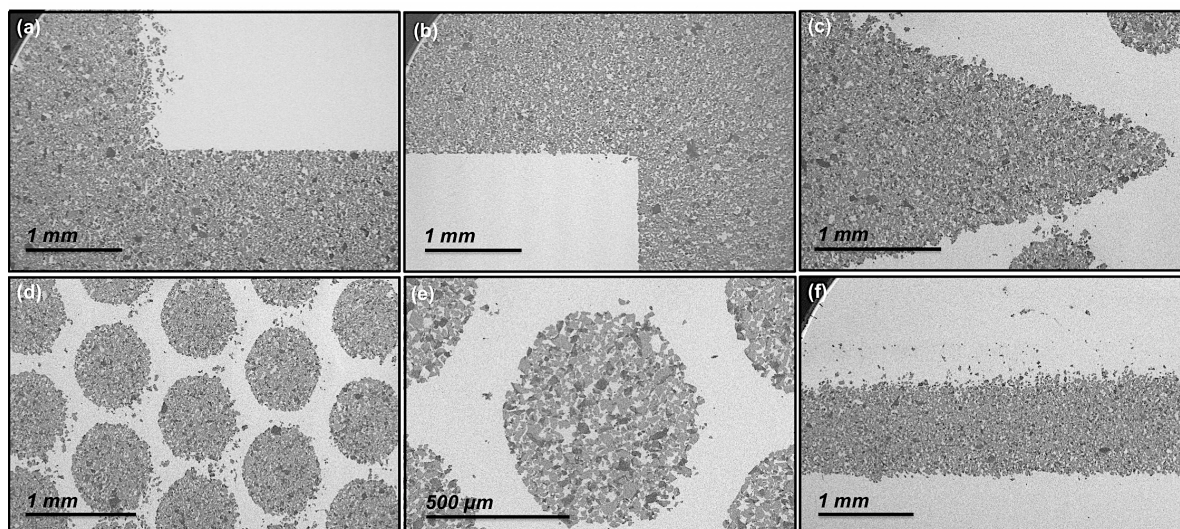


Figure 5. SEM images of large-scale patterned monolayer GO arrays of various shapes through LB technique.

Figure 4. Thus, all the treated samples were utilized immediately after plasma treatment in order to minimize the aging effect.

The above results suggest that N₂-plasma treatment of SiO₂/Si at aforementioned parameters leads to a highly hydrophilic surface with extremely high surface wettability. Moreover, it maintains a reduced surface roughness, which is suitable to preserve the electronic integrity of SiO₂/Si substrate.

The morphology of various geometric patterns of monolayer GO film on SiO₂/Si was characterized using SEM (**Figure 5**). The patterned areas appeared to be regular and clean. The gap between the GO sheets can be tuned by varying LB parameters during deposition. As expected, without any masking to the substrate during plasma exposure, a uniform monolayer GO film can be formed throughout the substrate as revealed by **Figure 6**.

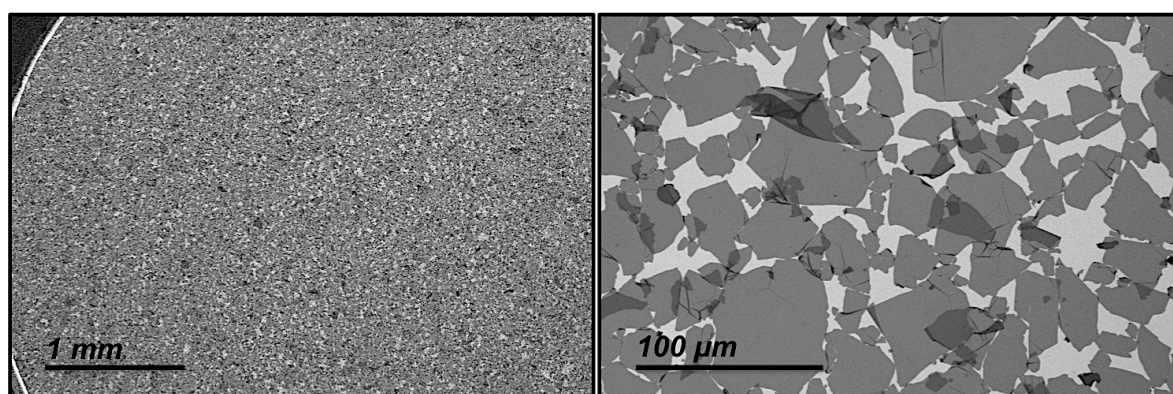


Figure 6. GO film formation using LB technique without masking SiO₂/Si during plasma treatment.

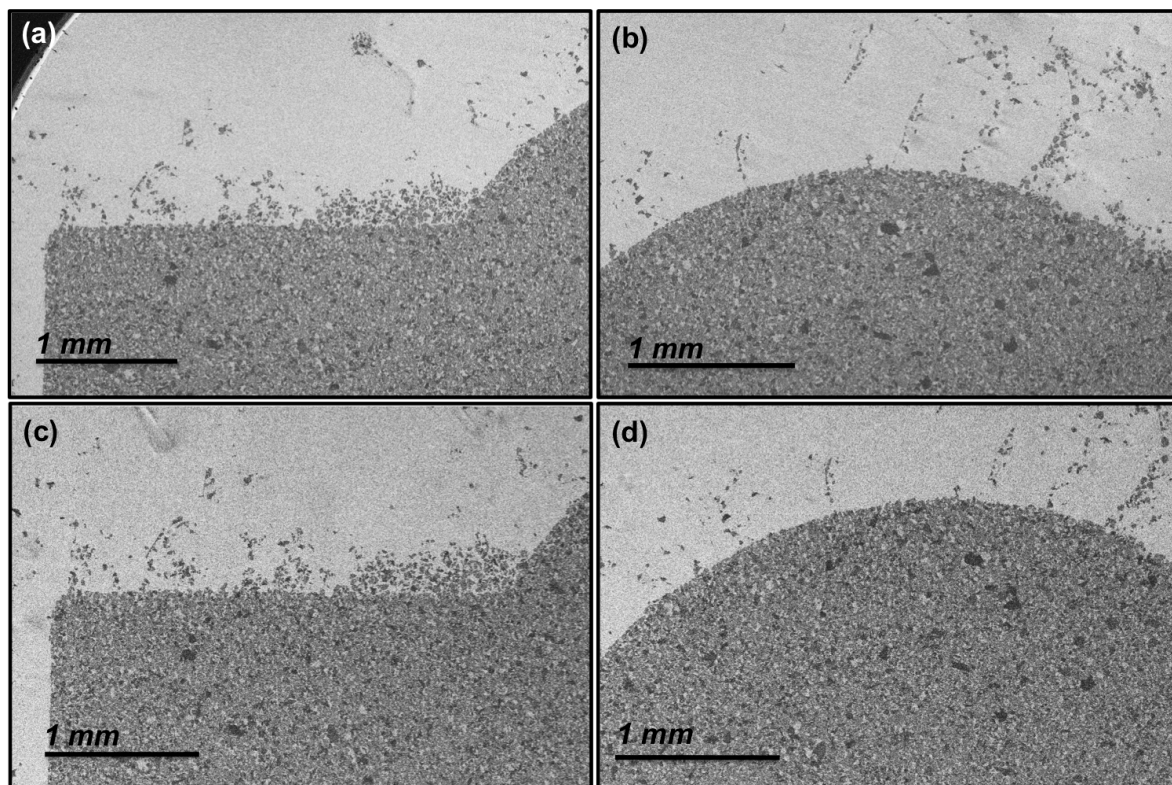


Figure 7. Patterned GO film on SiO₂/Si (a,b) before (c,d) after sonication treatment with IPA for ~ 30 min.

The patterned substrate was analyzed to elucidate the bonding strength of GO sheets with N₂-plasma treated SiO₂/Si surface, before and after sonication in IPA for ~ 30 min. The results demonstrated that the bonding strength of GO with N₂-plasma treated SiO₂/Si surface is strong and highly stable to hold high frequency sonication treatment (43 KHz). SEM images of patterned GO taken before and after sonication treatment are illustrated in **Figure 7**.

To elucidate the incorporation of nitrogen on the surface of SiO₂/Si after N₂-plasma treatment, XPS study was performed. The photoelectrons were separated by a hemi-spherical analyzer with a pass energy of 80 eV. All XPS binding energies were normalized to Si 2p (oxide) peak. **Figure 8** shows the Si 2p and N 1s core level spectra collected from SiO₂/Si before the plasma treatment. The result depicts a strong emission from Si 2p and absence of nitrogen peak. After plasma treatment, a very low atomic concentration of 0.77 % nitrogen was observed and the corresponding spectra is shown in **Figure 8**, which is consistent with the previous reports [18, 27]. The results reveal a slight modification of SiO₂/Si surface with nitrogen group that is interacting with oxygen moieties present on GO surface and thereby probably contributing towards strong adhesion of GO to SiO₂/Si surface.

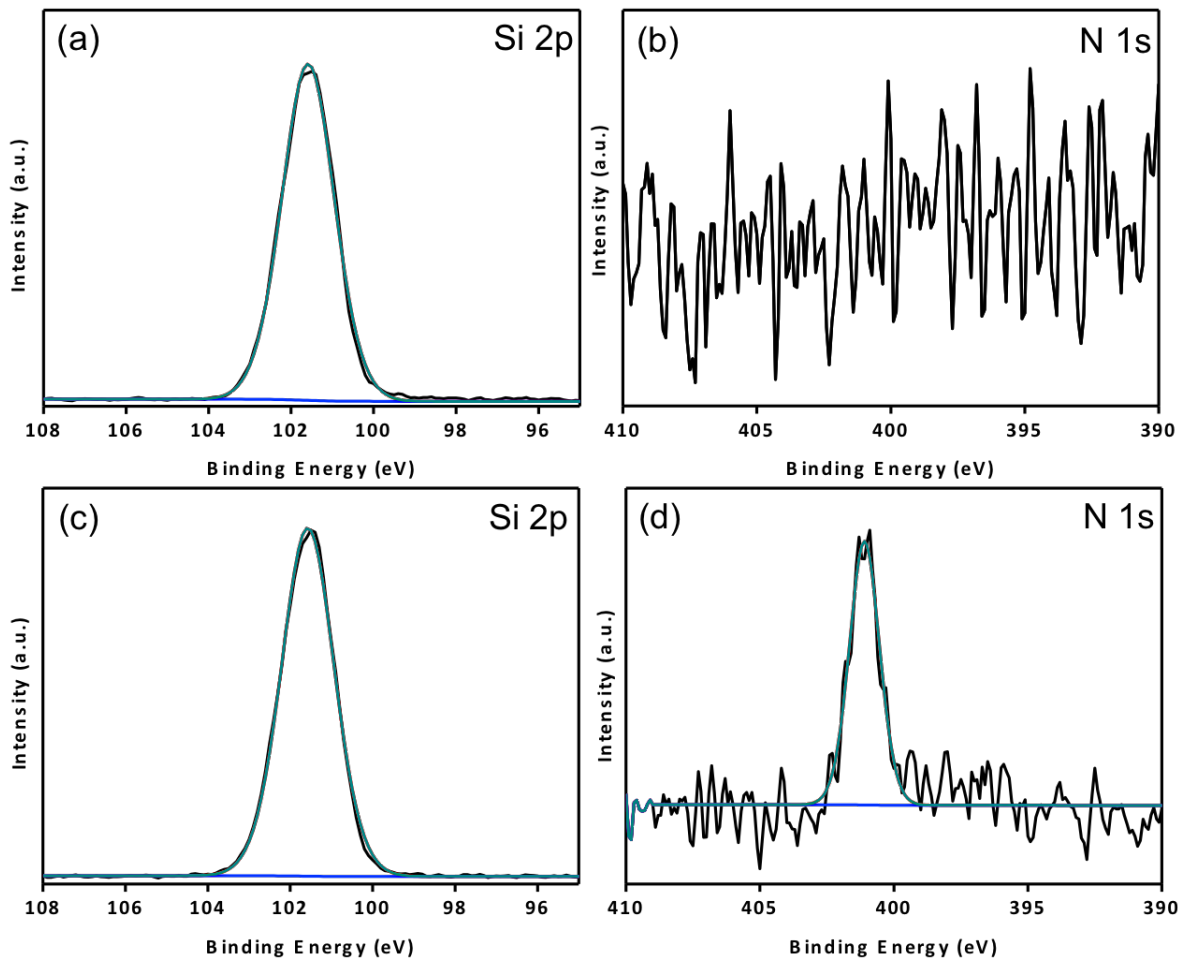


Figure 8. XPS spectra for (a–b) Si 2p and N 1s spectra of as such SiO₂/Si and (c–d) Si 2p and N 1s spectra of as N₂-plasma treated SiO₂/Si.

XPS results reveal that N₂-plasma treatment creates chemically reactive sites on the surface of SiO₂/Si, hence increasing the surface hydrophilicity and significantly enhancing the bond strength between SiO₂/Si and GO.

6.4 Conclusion

We have demonstrated a simple technique for selective placement and patterning of monolayer GO over large area without utilizing sophisticated instruments and thus makes scalable fabrication of rGO electronics a viable reality. Selective N₂-plasma assisted treatment of SiO₂/Si substrate has transformed non-uniform sized GO into an ordered, large-area array by LB technique, which has been characterized using various techniques. It offers a flexible pathway for developing highly integrated and hierarchically organized nanodevices that could be regarded as a general approach towards various patterned nanomaterials for a

broad range of functional nanosystems including nanoelectronics, multifunctional optoelectronic devices and bionics. A very low concentration of GO is required to assemble monolayers at air–water interface and the patterns prepared in the present study show highly ordered arrangement.

Our approach has the convenience of being inexpensive, simple, lithography–free, and rapid and has capability of large area fabrication of various geometric micro–patterns. We believe that this cost effective avenue could provide an excellent platform to utilize GO and many other amphiphilic molecules that can float on the surface of water for the forthcoming smart Bio–Nano Electronic applications. Although this technique offers a lot of advantages, however it is still a naïve beginning and significant efforts are further required to create higher–resolution patterns. Extensive research is going on in our laboratory to enhance the resolution of realized patterns without affecting rGO and substrate properties.

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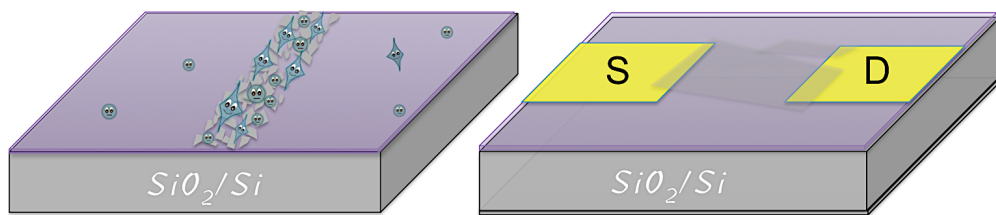
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7

Site-Specific Disposition of GO for Bio-Nano Electronics Applications

*“There is no substitute for hard work”
- Thomas A. Edison*



This chapter describes how specific area placement and patterning of GO via N₂-plasma-assisted surface modification of SiO₂/Si can contribute towards electronics and biomedical applications. Cytotoxicity assay revealed that the synthesized large area monolayer GO sheets are non-toxic to L929 and HCN cells and are highly biocompatible. A proof of concept experiment was performed in which the patterned GO substrate was subjected to specific area cellular growth of L929 cells. Moreover, a straightforward way to make graphene-based device using UVL and electron evaporation technique was followed to define Au/Ti electrodes for electrical contacts. The plasma enhanced surface modification of SiO₂/Si approach was adapted to selectively place GO on the pre-fabricated electrodes using the LB technique. The results revealed a successful specific area cellular growth on the patterned substrate and placement of GO on the pre-fabricated electrodes. This facile and quick approach can precisely assemble GO sheets directly from dispersion onto the desired area, thus significantly decreasing the processing steps required for making devices.

7.1 Introduction

Graphene, a versatile material, can be integrated into numerous applications [1]. Electronics and bioengineering will undoubtedly be a field in which graphene will play a vital role in future; though some imperative hurdles need to be rectified before it can be used for commercial applications. Graphene can revolutionize these application areas in a number of ways as it offers large surface area, good electrical conductivity, transparency and biocompatibility [2]. The unique features of graphene and GO have motivated researchers to explore various applications such as; for the development of fast and efficient electronic devices [3], electrochemical devices [4, 5], energy storage [6,7] catalysis [8], adsorption of enzyme [9], biological interaction, cell imaging, drug delivery [10–12], and biosensors [13]. However, the potential of site-specific disposition of GO and rGO for electronic as well as biomedical applications have not been explored much.

It is quite explicable that the electrical characteristics and bandgap of rGO can be controlled by the degree of thermal reduction of GO [14]. Based on the recovery of sp^2 conjugation and degree of reduction, electrical properties of rGO FET (ambipolar, p- or n-type) can be easily tuned [15, 16]. FETs are primarily attractive for sensing applications due to their swift response, high sensitivity, and real-time monitoring features [17]. Usually, conventional methods for the fabrication of FET devices involve deposition of rGO from its stock solution to SiO_2/Si substrate followed by UVL or EBL process to create metal electrodes or vice-versa [14, 17–19]. Formerly, fabrication of rGO devices has been demonstrated using the drop-casting method or the spin-coating method [20, 21]; alternatively, dielectrophoresis has been used to trap GO sheets at predefined electrode position [22]. A thin layer of GO sheets can be easily deposited on the Au electrode through electrostatic attractions between the charged self-assembled monolayers (SAMs) and the charged GO sheets. By using simple solution processes to prepare GO films, the single-layer GO sheets tend to fold and wrinkle at edges to resist collapsing into multilayers or randomly overlaying monolayers during the evaporation of solvents [23]. Yang et al have developed a facile method for the fabrication of rGO FET with SAMs, due to the strong electrostatic adsorption between the NH_2 -modified electrodes and the first layer of the deposited GO sheet [24]. However, to create FET array devices, rGO need to be selectively placed between the electrodes that actually complicates the whole process and requires exquisite skills.

Besides that, for tissue engineering applications – to cultivate, cells of most types need to adhere to some substrate. *In vivo*, the substrate is the extracellular matrix (ECM) or other cells [25]. Thus, for *in vitro* studies and to boost cell growth for tissue engineering [26, 27] we need to provide substrates that imitate at least some properties of the ECM. Interactions with the ECM, or with artificial mimics of it, play a vital role in fundamental cellular functions, including cell migration [28, 29], proliferation [30, 31], differentiation [32], and apoptosis [33, 34]. Cell adhesion and cellular organization have been extensively studied as a function of the available adhesive area and shape on a substrate using micrometer-scale patterns [35, 36]. Various techniques of cell patterning have been developed that allows the control of the cell shape and size of cell adhesion [37, 38]. Amongst various micro-patterning techniques, cells are typically plated on 2D surfaces. Cell micro patterning has become a useful method in fundamental studies to investigate both cell to cell and cell to matrix interactions [39]. Topography and physical properties of the substrate dramatically affect the cell's functions. The potential applications of graphene are not only restricted to physicochemical materials but also extend to biological uses. Ruiz et al have demonstrated that GO can act like a general enhancer for cellular growth by increasing cell attachment and proliferation [40]. There are many reports available where graphene has been used for tissue engineering [41, 42]. Previous literature report showed that UVL and EBL has become a major technique for making patterns. However, it requires highly sophisticated instruments, clean room facilities and highly expensive equipment, which makes it inconvenient for many researchers including biologists. Additionally, chemicals used in UVL and EBL processes may denature and deactivate biomolecules [43].

In this work, we have utilized a facile and quick approach that can precisely assemble GO sheets directly from dispersion to the specified area, thus significantly decreasing the processing steps as cited in *Chapter 6*. This approach allows us to assemble monolayer GO with high density at a specific area using minimal concentration of the GO solution. Here, we describe how specific area placement and patterning of GO via N₂-plasma-assisted surface modification of SiO₂/Si can contribute towards electronics and biomedical field to fabricate FET array devices and create specific area cell adhesion and proliferation respectively. A straightforward way to make graphene-based device using UVL and EB evaporation technique has been followed to define Au/Ti electrodes for the electrical contacts.

The plasma enhanced surface modification of SiO₂/Si approach was adapted to selectively place GO on the pre-fabricated electrodes using LB technique. Cytotoxicity assay has been performed to check the biocompatibility of as-synthesized large area monolayer GO sheets against mouse connective tissue (L929) fibroblast like cells and human cortical neurons (HCN-1A) cells. A proof of concept experiment was performed in which the patterned GO substrate was subjected to specific area cellular growth of L929 cells. The primary studies have revealed that the cells could be located accurately by micro-patterning GO over large area on any substrate, which can significantly aid the development of tissue engineering, neural generation, cellular and molecular sensors.

7.2 Selected Area Placement of GO on Pre-patterned Electrodes

The optimized parameters were used for the preparation of GO LB films on selectively treated areas of SiO₂/Si as discussed in *Chapter 6*. For device fabrication, electrodes were fabricated using UVL process and EB evaporator system on SiO₂/Si wafer with Al (300 nm) as the BG and Au/Ti (50 nm/ 10 nm) as S and D.

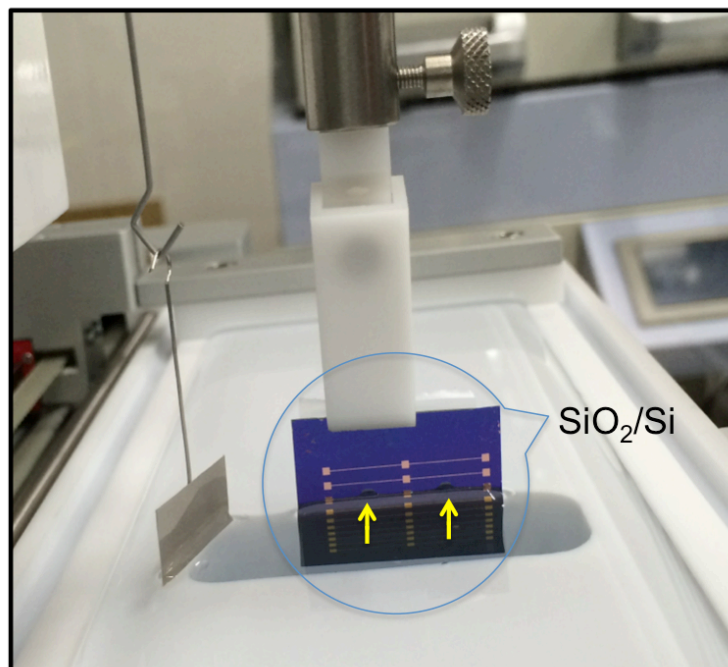


Figure 1. The image showing selective placement of GO between Au/Ti electrodes on SiO₂/Si/Al Substrate.

7.3 *In vitro* cytotoxicity and specific area cell adhesion and imaging studies

Cell Culture.

Biocompatibility in terms of viability, proliferation and attachment of mammalian cells to GO as scaffolding materials can be analyzed using cell culture studies. Cytotoxicity of the GO synthesized was tested using two different cell lineages, like HCN-1A and, L929 cells.

HCN-s1A and L929 cells were cultured and maintained using T33 tissue culture flasks in complete media consisting of Dulbecco's Modified Eagle's Medium (DMEM) with 1% l-glutamine supplemented with 15 % FBS and 1 % antibiotics-antimytotics (final concentration: penicillin 100 µ/ml, streptomycin 100 µ/ml and amphotericin B 0.25 µ/ml). Cells were cultured in a 5 % CO₂ incubator at 37 °C and the medium were replaced once in every 2 days.

In vitro cytotoxicity assay-Alamar blue assay.

In vitro cytotoxicity of the GO synthesized were studied using alamar blue reduction assay in a 96-well microtiter plate. The method involves the quantification of the metabolically active cells that has the ability to convert resazurin to the fluorescent molecule resorufin. The viability of the cells in turn depends upon the dosage of the GO samples that are under study. Alamar blue assay was performed as follows: HCN- 1A and L929 cells were seeded separately in the order of 3-6 × 10³ cells/well and incubated at 37 °C in 5 % CO₂ atmosphere. After 24 hours, medium in the wells were replaced with fresh medium containing GO samples of 4 different concentrations (25 µg/ml, 50 µg/ml, 100 µg/ml, 200 µg/ml and 400 µg/ml, all the solution volume were centrifuged @ 2500 rpm for 10 min to remove debris, if any and the supernatant was collected). After addition, cells were incubated for another 24 hours under same conditions. At the end of incubation, 10 % of alamar blue dye was added to all wells and after 4 hours incubation; fluorescence was measured at 580-610 nm, using a multi detection microplate reader (Dainippon Sumitomo Pharma, Powerscan HT). Assay was performed in duplicates and percentage of cell viability was calculated using the formula,

$$\% \text{ of Cell Viability} = \frac{[A]_{\text{test}}}{[A]_{\text{control}}} \times 100$$

where, [A]_{test} is the absorbance of the test sample and [A]_{control} is the absorbance of control sample.

Adhesion and Proliferation Studies.

Mouse fibroblast like cells were seeded into three different substrates: bare SiO₂/Si, specific area N₂-plasma treated SiO₂/Si and GO patterned on SiO₂/Si on the order of 1.5 × 10⁴ cells/ml, in duplicates. 100 µl of culture in DMEM medium was added on to the top of the substrate and incubated at 37 °C with 5 % CO₂ for 48 hours. Culture medium was replaced after 24 hours with fresh medium. At the end of incubation after 48 hours, cells were stained with Hoechst nuclear stain and excess stain was washed using 1x PBS solution. Cells adhered to the GO coated area was observed under confocal microscope. Primarily, optical images were taken and reported.

7.4 Results and Discussion

GO-based FET was fabricated by the deposition of GO sheets across the Au/Ti electrode gap using LB technique (**Figure 1**). The device was annealed at 300 °C under N₂ environment (200 ml/min) for 2 hours to improve ohmic resistivity and reduce oxygen moieties in order to enhance the semiconducting properties. **Figure 2** shows the SEM images of GO placed over Au/Ti electrodes at different magnifications. To further examine the electrical characteristics of GO FET device, V_g was applied to the devices from -2V to 2V in steps of 1V. The typical I_{ds}-V_{ds} of rGO FET device is shown in **Figure 3**, where I_{ds} modulates with increasing V_g, which indicates that the device response is sensitive to the V_g. The decrease in I_{ds} with increasing V_g indicates that rGO sheets are p-type semiconductor in nature. Out of 20 pre-patterned Au/Ti electrodes on SiO₂/Si/Al (imaged in **Figure 1**), we were able to fabricate 14 working rGO based FET devices on the same wafer by adapting this selective deposition technique.

Alamar blue assay revealed that the GO concentrations tested for growing HCN- 1A and L929 cells are not causing any observable toxicity. This can be clearly demonstrated using the graph plotted for percentage cell viability against concentration of GO for both the cell lines (**Figure 4**). Graph shows that the test concentrations of GO that favors cell growth, as the percentage of viability across different test concentrations were > 90%. However, a slight dip in cell viability

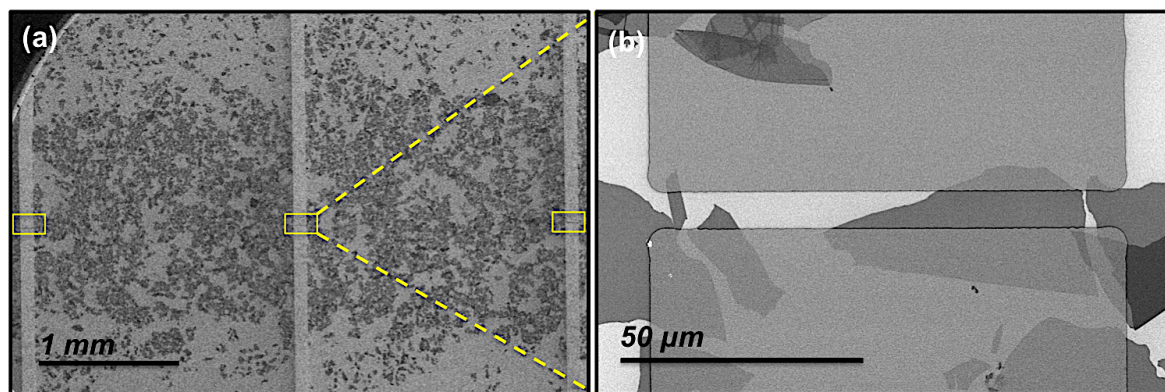


Figure 2. SEM images of selectively placed GO across the Au/Ti electrode gaps.

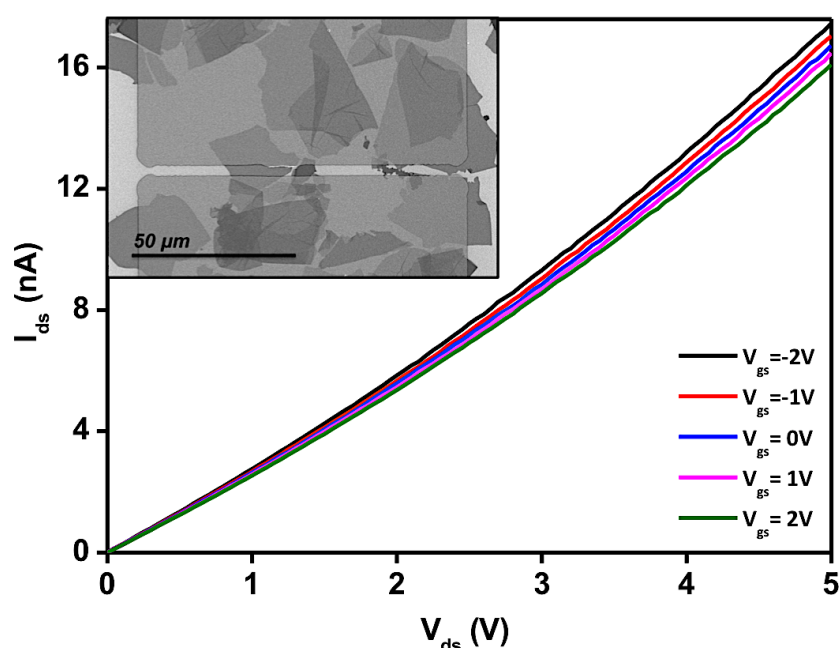


Figure 3. The FET I_{ds} - V_{ds} curve of GO on SiO_2/Si substrate. The inset shows an SEM image of a monolayer GO sheet bridging the electrode gap.

was seen beyond 100 $\mu\text{g}/\text{ml}$ concentration. Thus, the GO concentrations tested for cytotoxicity is highly biocompatible in nature and hence can be applied as a scaffold material for growing mammalian cell lines for biosensor applications. Microscopic images captured after growing L929 cells on patterned GO substrates showed very promising results of adhesion and proliferation of mammalian cells (Figure 5). It is clearly observed that the area with N_2 -plasma treated GO monolayers (Figure 5(c and d)) were having more number of cells adhered to it compared to the simply N_2 -plasma treated SiO_2/Si (Figure 5 (b)) and bare SiO_2/Si substrate (Figure 5 (a)).

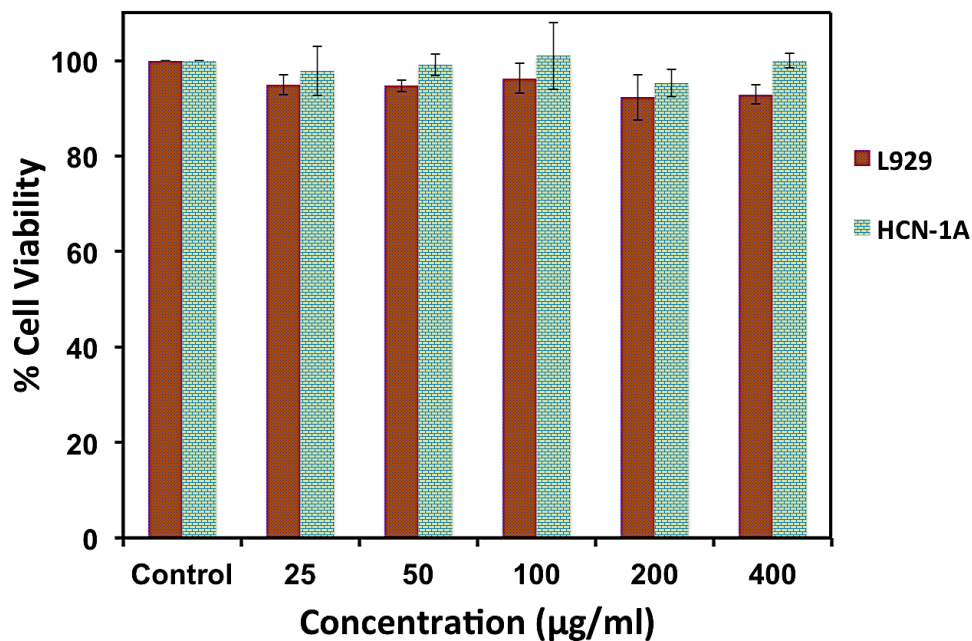


Figure 4. Cytotoxicity assay results showing the viability of L929 and HCN cells under various concentrations of large area GO.

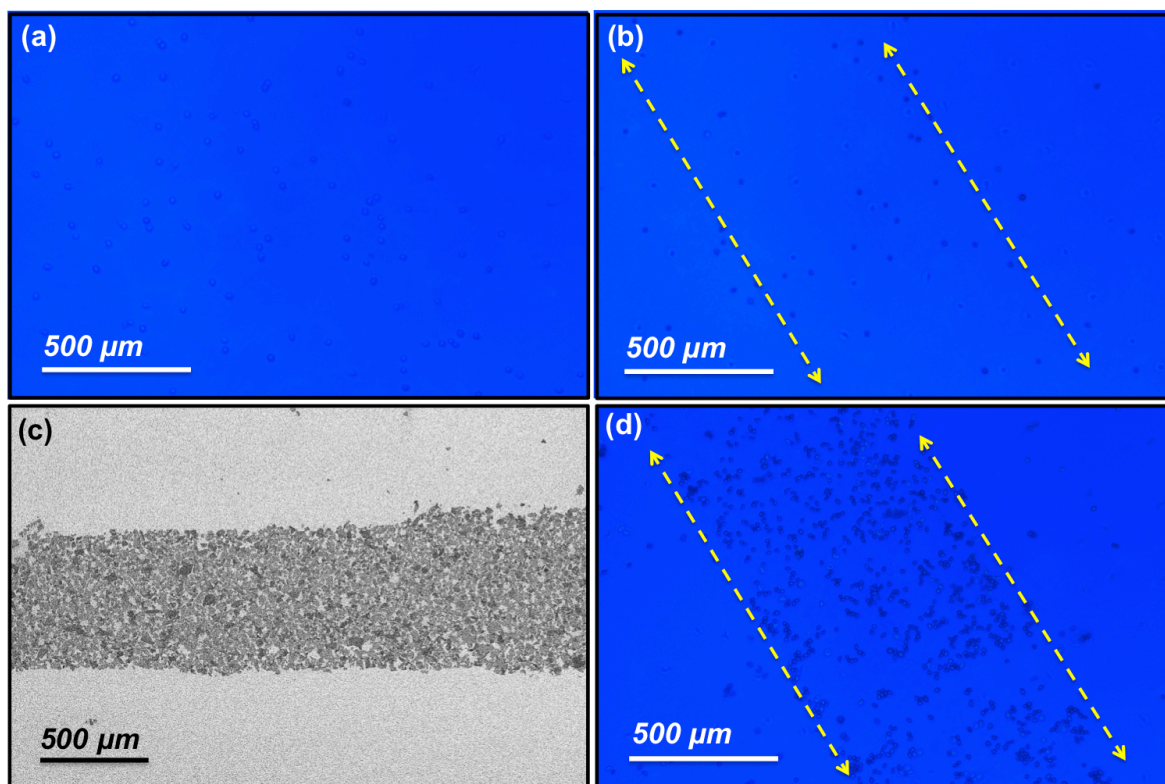


Figure 5. Optical images of specific adhesion of L929 cells on (a) As such SiO_2/Si , (b) N_2 -plasma treated SiO_2/Si on specific area (marked with yellow arrow), (c) SEM image of N_2 -plasma assisted placement of GO on SiO_2/Si and (d) optical image of specific area cell adhesion on (c).

Thus, indicating that the bare SiO₂/Si or N₂-plasma treated SiO₂/Si substrate alone cannot contribute towards the cell adhesion. Probably, the oxygen moieties present on patterned GO monolayers are playing an important role for the effective cell adhesion and proliferation. This supports the results obtained from the alamar blue assay that GO concentrations tested are highly biocompatible as a scaffold material. However, the proper mechanism behind this whole process still needs to be investigated.

7.5 Conclusion

In conclusion, our preliminary studies have indicated that the selective placement of GO on pre-fabricated electrodes, a major concern for graphene related electronic applications, is feasible. *In vitro* cytotoxicity has indicated good cell viability with L929 cells, while the cell adhesion and proliferation studies have shown that selective area cell adhesion on a substrate can be achieved using this facile technique. Through this study, we have shown the interaction of cells with specific GO surface only, which can hold immense potential for biomedical applications from cell patterning to biosensors.

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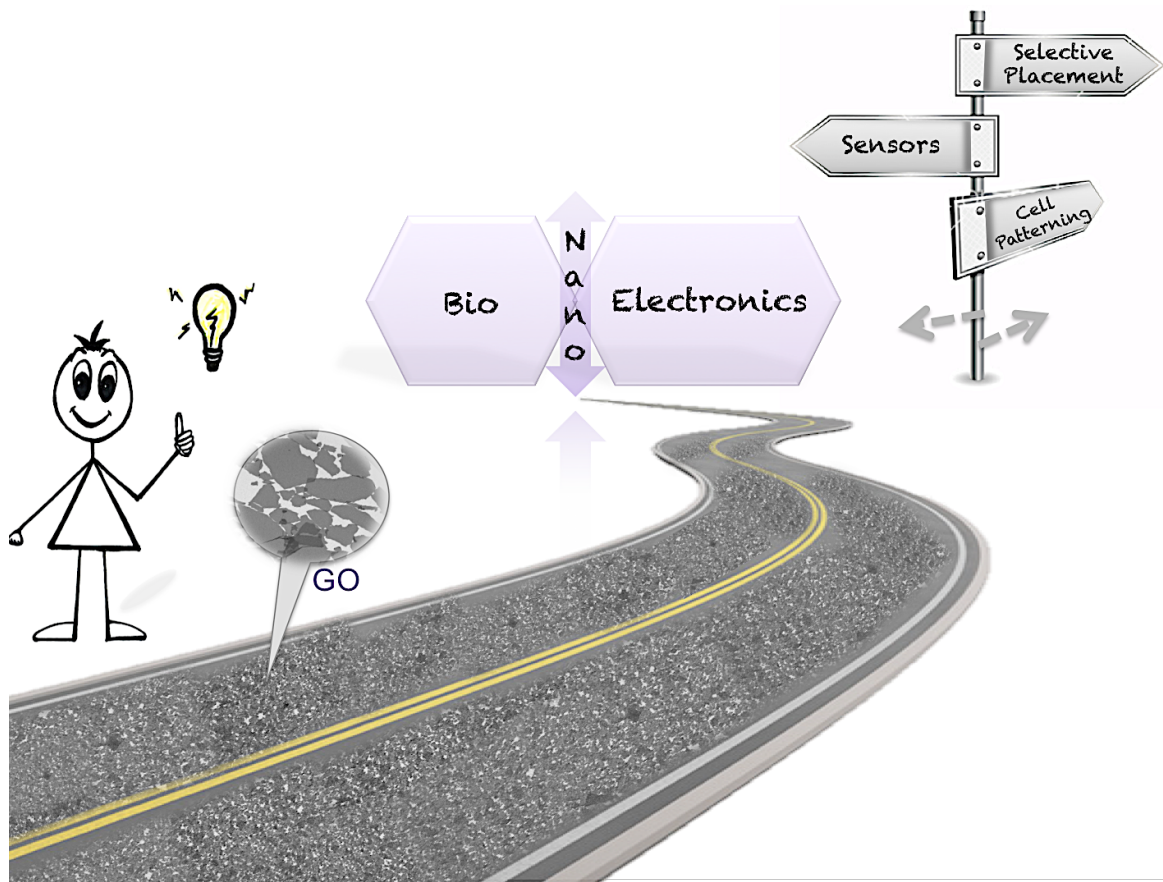
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8

Conclusions

"The value of an idea lies in using it"
- Thomas A. Edison



This chapter outlines the salient features of the work described in this thesis and emphasizes on the future scope of our work.

8.1 Summary of the Work

The large area synthesis and 2D assembly of monolayer GO for Bio–Nano Electronics applications, using the LB technique, on a selected area of SiO₂/Si was the prime intention of this thesis. There were many reports available for the 2D assembly of GO using the LB technique, where, assembly of GO on various substrates was the main focus of concern amongst most of the researchers, particularly for TCFs. Though, progress in the direction of patterning of graphene and GO has been made by many researchers using various techniques including EBL, UVL, SPL, block copolymer lithography, soft transfer printing, masked laser patterning, direct laser patterning, combination of wettability modulation, spin coating, ink–jet printing, etc. Despite some degree of success in patterning using the present strategies, all of them lack simplicity, ability to achieve large–scale monolayer graphene arrays and cost effectiveness. Surprisingly, the use of air–water interface for achieving successful selective placement and patterning of large area 2D patterned graphene and its related derivatives with controllable dimensions remains largely unexplored.

We have developed a feasible and cost–effective ecofriendly approach for the bulk reduction of GO by extremophiles to produce rGO with high electrical conductivity and large surface area. This gives us an insight of its tolerance and acceptance by a biological system since it doesn't hamper the growth of fibroblast cell lines under *in vitro* conditions. Hence, it could be effectively used for green electronics and bioscience applications. Moreover, to control the edge density of GO and evaluate its viability and practicality, large area monolayer GO sheets were successfully prepared having mode of area as 1016 μm². The influence of N₂–plasma system on SiO₂/Si towards its selective area hydrophilization has been studied under various chamber pressure conditions. We optimized various parameters for the selective placement and desired geometric patterns of monolayer GO sheets over large area using LB technique. The selective area N₂–plasma assisted hydrophilization of SiO₂/Si substrate could transform not only the non–uniform sized GO into an ordered form but also in large–area arrays by LB technique without employing any complex instruments. This makes it a facile, realistic and a quick approach for numerous electronics and biomedical applications.

The additional advantage that LB technique offers is a flexible pathway for developing highly integrated and hierarchically organized nanodevices. This could

be regarded as a general approach towards various patterned nanomaterials for a broad range of functional nanosystems including nanoelectronics, multifunctional optoelectronic devices and bionics.

Besides that, our preliminary studies have demonstrated the placement of GO between pre-patterned electrodes, which is one of the foremost concerns for device fabrication. *In vitro* cytotoxicity studies have shown good biocompatibility and the selective area cell adhesion on patterned GO substrate has also been achieved, which could allow us to have better control over the cell behavior. This approach can significantly aid the development of tissue engineering, neural generation, and cellular and molecular sensors.

8.2 Future Prospects of Patterning of Large-Area Monolayer GO

Our approach has the convenience of being inexpensive, simple, lithography-free, rapid and large area fabrication of various desired geometric micro-patterns. Though this technique presents a lot of advantages, it is still a naïve beginning and a significant research focus is required to create high-resolution patterns. Extensive research is going on in our laboratory to enhance the resolution of realized patterns without affecting rGO and substrate properties.

We believe that this cost effective avenue could provide an excellent platform to employ GO and many other amphiphilic molecules that can float on the water surface for the forthcoming smart Bio-Nano Electronic applications.

The study of interparticle interactions in 2D assembly of nanomaterials could be interesting in order to explore their potential applications in electronic transport systems. One of the most attractive prospects of this strategy of hydrophilization of specific area of the substrate is that any kind of nanoparticles that can be charged using suitable surfactant can be organized at air-water interface to form a 2D assembly using LB technique. In particular, this method can be extended to achieve multicomponent patterned nanomaterials in one plane, which could bring revolution in the field of Bio-Nano Electronics applications.

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Publications

1. Sreejith Raveendran, **Neha Chauhan**, Yoshikata Nakajima, Higashi Toshiaki, Shunji Kurosu, Yuji Tanizawa, Ryugo Tero, Yasuhiko Yoshida, Tatsuro Hanajiri, Toru Maekawa, Pulickel M. Ajayan, Adarsh Sandhu, and D. Sakthi Kumar. *Ecofriendly route for the synthesis of highly conductive graphene using extremophiles for green electronics and bioscience*. Part. Part. Syst. Charact. **2013**; 30(7): 573–578. DOI: 10.1002/ppsc.201200126. (Equally Contributed)
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7. Vivekanandan Palaninathan, **Neha Chauhan**, Sreejith Raveendran, Yasushi Sakamoto, Toru Maekawa, D. Sakthi Kumar. *Versatile bacterial cellulose sulfate film incorporated with silver nanoparticles for food packaging and biomedical applications. (Communicated)*

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2. Vivekanandan Palaninathan, Sreejith Raveendran, **Neha Chauhan**, Toru Mizuki, Yasuhiko Yoshida, Toru Maekawa, D. Sakthi Kumar. (Poster). *Mass cultivation of Komagataeibacter sucrofermentans and cellulose production through fermentation for wound healing applications*. The 11th International Symposium on Bioscience and Nanotechnology. 15 Nov, **2013**, Hakusan Campus, Toyo University, Japan.
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Glossary

0–9

0D: Zero-Dimensional
1D: One Dimensional
2D: Two-Dimensional
3D: Three-Dimensional

A

AES: Auger Electron Spectroscopy
AFM: Atomic Force Microscopy
Al: Aluminum
Al₂S₃: Aluminum Sulphide
Ar: Argon
ATR: Attenuated Total Reflection
Au: Gold

B

BE: Binding Energy
BG: Back Gate
BHA: Buffered Hydrofluoric Acid
BHF: Buffered Hydrofluoric Acid
BPK: Basic Plasma Kit
BRGO: Bacterially Reduced Graphene Oxide
BSE: Backscattered Electrons

C

CH₃NO₂: Nitromethane
CNT: Carbon Nanotube
CO₂: Carbon Dioxide
Cr: Chromium
CVD: Chemical Vapor Deposition

D

D: Drain
DI: De-Ionized
DLS: Dynamic Light Scattering
DMF: Dimethylformamide
DMEM: Dulbecco's Modified Eagle's Medium

E

EB: Electron Beam
EBL: Electron Beam Lithography
ECM: Extracellular Matrix
EDS: Energy Dispersive X-ray Analysis
EDP: Electrophoretic Deposition
EG: Expanded Graphite
ERGO: *Halomonas eurihalina* reduced GO

F

FBS: Fetal Bovine Serum
FeCl₃: Iron chloride
FeCl₃.6H₂O: Iron (III) Chloride Hexahydrate
FET: Field Effect Transistor
FLG: Few-Layer Graphene
FTIR: Fourier Transform Infra-red Spectroscopy

G

G: Gate
GICs: Graphite Intercalated Compounds
GO: Graphene Oxide

GNR: Graphene Nanoribbons

H

HCl: Hydrochloric Acid

HCN-1A: Human Cortical Neuronal

H₂O₂: Hydrogen Peroxide

H₂SO₄: Sulfuric Acid

I

ILC: Ionic liquid crystals

IR: Infrared

K

KCl: Potassium Chloride

KE: Kinetic Energy

KMnO₄: Potassium Permanganate

KOH: Potassium Hydroxide

K₂S₂O₈: Potassium Persulfate

L

l: Length

LaB₆: Lanthanum Hexaboride

LB: Langmuir Blodgett

LS: Langmuir-Schaefer

M

MgSO₄.7H₂O: Magnesium Sulfate

MRGO: *Halomonas maura* reduced GO

N

N₂: Nitrogen gas

NaBr: Sodium Bromide

NaCl: Sodium Chloride

NaHCO₃: Sodium Bicarbonate

NaNO₃: Sodium Nitrate

NG: Natural Graphite

NMP: N-methyl-pyrrolidone

O

O₂: Oxygen gas

OD: Optical Density

OES: Optical Emission Spectroscopy

OFETs: Organic field effect transistors

P

PAHs: polyaromatic hydrocarbons

PAN: Polyacrylonitrile

PBS: Phosphate Buffer Solution

PDMS: poly(dimethylsiloxane)

PET: poly(ethylene terephthalate)

PV: Photovoltaic

PL: Photoluminescence

P₂O₅: Phosphorous Pentoxide

R

rGO: Reduced Graphene Oxide

rms: root-mean-square

S

S: Source

SAED: Selected Area Electron
Diffraction

SAMs: Self-Assembled Monolayers

SE: Secondary Electrons

SEM: Scanning Electron Microscopy

SiC: Silicon Carbide

Si: Silicon

SiO₂: Silicon Dioxide

SLG: Single Layer Graphene

SP: Surface Pressure

SPL: Scanning Probe Lithography

STM: Scanning Tunneling Microscope

STM: Scanning Tunneling Microscope

T

t: Thickness

TCFs: Transparent Conducting Films

TEM: Transmission Electron Microscopy

THF: Tetrahydrofuran

Ti: Titanium

TR: Transfer Ratio

U

UHV: Ultra-High Vacuum

UVL: Photolithography

V

V_{ds} : Voltage across drain and source

V_g : Gate voltage

W

w: width

X

XPS: X-ray photoemission spectroscopy, also known as ESCA (Electron Spectroscopy for Chemical Analysis)

