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Scalable and site specific functionalization of reduced graphene oxide for circuit elements and flexible electronics



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ABSTRACT

We demonstrate a rapid and facile approach towards scalable patterning of reduced graphene oxide (rGO) for interconnects in flexible electronic applications. We have used controlled UV light exposure for patterning of rGO over spin coated GO film, which has been demonstrated by various patterns of GO-rGO. Optical and conductivity contrast has been supported by spectroscopic data for GO and rGO regions. Electrical conductivity of completely exposed rGO (60 mS/m) is significantly (~150 times) higher than unexposed GO, which is suggesting effectiveness of rGO for circuit elements and interconnect applications. The tunable GO reduction is used for fabrication of rGO-FET, on flexible substrates, with completely exposed rGO as source/drain/gate electrodes and partially exposed rGO as semiconducting channel. The site specific and large area patterning of GO-rGO is advantageous for its usage in lighter and wearable flexible electronics.

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1. Introduction

Major improvements in the field of electronics have been achieved by exploring alternative technologies, while silicon-based electronics continued to be on the forefront, for past few decades. Graphene and its derivatives (graphene oxide (GO), reduced graphene oxide (rGO)) have shown a notable potential for electronic applications [1,2], devices for energy conversion and storage such as, solar cells, supercapacitors, batteries and fuel cells [3-5]. Study of graphene based materials for device applications is an emerging field due to availability of low cost and large area films on flexible substrates [2]. Currently, the device fabrication on flexible substrates is in its infancy owing to involvement of organic solvents, high temperature process technologies and site specific metal deposition for robust interconnects [6-8]. Thus, synthesis and processing of graphene and its derivatives as channel material as well as metallic interconnects remained an important challenge. The synthesis of graphene has evolved with time and several methods have been adopted, for instance, mechanical exfoliation, chemical vapor deposition (CVD) [4], reduction of GO into rGO by solution processes [9]. The major challenges in graphene research are (i) large area growth for device fabrication, (ii) scale up synthesis for photovoltaic and storage applications and (iii) localized functionalization for sensor applications [10]. The mechanical exfoliation and CVD provided a good quality graphene but in a very limited quantity, while the solution based synthesis methods are otherwise advantageous for mass production [9].

Generally, chemical exfoliation of graphite in a solution under oxidizing conditions produces thin sheets of GO, which are hydrophilic and nonconductive in nature due to attached carboxylic, carbonyl, hydroxyl and ether functional groups at the plane and edges [9,11–13]. The insulating nature and existence of functional groups in GO restricts its applications, especially, in the field of electronics [2,14]. In this context, a more hydrophobic and conductive counterpart, rGO can be obtained by thermal and chemical reduction of GO [15-22]. However, the reduction of GO involves strong reducing agents, high temperatures, harmful contaminants and adverse reaction conditions, making the process non-environment friendly [15,17,18,23,24]. Additionally, researchers have adopted various site-specific strategies for solidstate photoreduction of GO based on laser assisted writing, scribbling and patterning [19]. Besides being expensive, the laser irradiation also heats-up the local temperature of GO to ~1000 °C, which in turn damages the GO film and the substrates, thus not suitable for flexible electronic applications [19,25]. Table 1 summarises the comparison among different approaches for patterning



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Table	1
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Comparison of different approaches for patterning of GO-rGO.

Patterning method	Time elapsed	Patterns (in µm)	Remarks	Ref
Electro-erosion	-	~25	Complex/Expensive Setup (requires 60 V), Incompatible with Flexible substrates	[33]
Laser ($\lambda = 532$ nm) and under heating at 100 °C	-	20-50	Expensive Set up, Damages the GO film and substrates, Incompatible with flexible substrates	[34]
Eximer laser ($\lambda = 248$ nm) and under heating at 100 °C	20 ns PW, 200 μm/s scan speed, repetition rate of 1 Hz	15		[35]
Femtosecond laser oscillator central $\lambda = 780 \text{ nm}$	120 fs pulse duration & 80 MHz repetition rate	100		[25]
Eximer laser ($\lambda = 248 \text{ nm}$)	20 ns PW repetition rate of 1 Hz	10	Expensive Set up with ambient Conditions (Vacuum and N ₂)	[36]
Femtosecond laser λ between 400 & 800 nm	120 fs PW and repetition rate of 1 kHz	2–20	Expensive Set up, Damages the GO film and substrates, Incompatible with flexible substrates	[37]
Laser ablation $\lambda=532\ nm$	500 fs pulse duration, & repetition rate of 500 kHz	-		[38]
Patterning of PR followed by etching and transfer	-	5-100	Complex processes, multiple steps, ambient Conditions (Vacuum and N_2)	[39]
Patterning of PR followed by etching and transfer	-	50		[40]
UV lamp	1–24 h	50-100	Long reduction Time	[5]
UV lamp ($\lambda = = 253$ nm,	45 min	5–100	Rapid, low temperature, tunable approach	Present
power 130 W)			for patterning	Work

of GO-rGO. Therefore, a material friendly irradiation method is highly essential for tailoring the physiochemical and conductivity contrast between GO and rGO for potential applications in flexible electronics [5,22].

The fabrication of electronic devices, field effect transistors (FETs) using graphene related materials involves complex lithography process such as spin coating of photoresist, transferring to suitable substrates at specific sites and electrode patterning using lithography followed by metal deposition [26–28]. Conventionally, metal electrodes used for making electrical contact with graphene result into serious contact resistance, leading to Schottky barrier and Joule heating under the contacts [28–31]. In this process, the elimination of contact resistance between metal and graphene is a major difficulty, while the performance of contacts under multiple electrical stress is challenging, especially, for devices on flexible substrates [28-31]. For interconnects, the metal films are susceptible for electro-migration resulting in loss of connection and failure of circuit components [28-31]. In order to overcome the challenges of contact resistance, electro-migration and flexibility for metal contacts, the rGO based metallic and semiconducting regions are expected to be advantageous for interconnects and channel materials [32]. Thus, exploring alternative approach for allcarbon devices with a range of physical properties such as tunable conductivity based on degree of reduction and suitability for flexible substrates, altogether, is useful for device and interconnects fabrication.

Here, we demonstrated a cost effective and scalable method for tunable micro patterning of rGO circuit elements for flexible electronics. The insulating GO will not allow cross talk of signals between conductive rGO lines, therefore rGO can be used as interconnects and also for repairing of broken contacts. Major highlight of the proposed process is scalable and tunable micropatterning of GO-rGO under single exposure. GO-rGO patterning approach is extended for fabrication of metal free all-carbon rGO-FET. The fabrication of rGO-FET is free from complex lithographic processes such as site-specific writing, development and baking of photoresist, transfer on suitable substrates, followed by metal deposition. Metallic (source, drain, gate) and semiconducting (channel) rGO regions for the fabricated rGO-FET are obtained by tuning the grey scale value of mask, with single exposure to UV light. However, admitting modest device characteristics for the fabricated rGO-FET [25], but reasonably good for first time demonstration.

2. Experimental

2.1. Materials

All the chemicals used were of analytical grade, De-ionized water (resistivity ~18.2 M Ω -cm) was used for cleaning and solution preparation. The UV light source (130 W and λ ~ 253 nm, G64H075), purchased from Arklite with an intensity of ~5 mW/cm² at distance of ~5 cm (measured using UVC Light Meter 850010, SPER Scientific make), was used as a light source for GO-rGO patterning [9].

2.2. Synthesis of GO powder

GO powder was synthesized using modified Hummers method, as discussed in earlier reports [9,42]. To obtain aqueous GO dispersions, the final GO powder was sonicated (Rivotek, 33 KHz) in deionized water (0.1–1 mg/ml) for 2 h. Size uniformity of GO in dispersion was achieved by filtering the final solution twice using PTFE membrane (~0.2 μ m pore size).

2.3. GO-rGO patterning

Substrates were properly cleaned before spin coating the GO solutions [43]. A mixture of aqueous GO solution and *N*-Methyl-2-Pyrrolidone (NMP) in a typical ratio of 10:1 was prepared for further processing. Final solution was spin coated, at 500 rpm for 120 s, as a smooth film on desired substrates, including flexible, followed by drying at 100 °C for 5 min. After drying, the estimated thickness of GO film is ~1 μ m. For the lower thickness of GO layer, it was very difficult (i) to identify the patterned/reduced regions using an optical microscope, (ii) to obtain a good conductivity among the nanosheets with the presence of grain boundaries, and (iii) to protect substrate to be exposed to UV light. We observed that having a higher thickness of GO is better for further device fabrication. The spin coated GO films over flexible substrates were found

to be uniform, with negligible thickness variation, hence the process may easily be used for future high resolution lithography and next generation semiconductor processes. The film on substrate was exposed to UV light, a fixed distance (~5 cm), in the presence of a desired photo mask, for 45 min. Finally, the GO–rGO patterning was obtained after a careful removal of photomask, without any solution based developmental/lift-off processes.

2.4. Material characterizations

Optical microscopy and scanning electron microscopy (SEM) images were obtained on the patterned substrates using Olympus BX-51 microscope and Nova Nano-SEM-450 instrument. Raman spectroscopy was performed using Horiba LabRAM HR-evolution confocal Raman spectrometer with 532 nm excitation laser, in the range 800–2000 cm⁻¹. Raman mapping was done with a very low LASER power ~0.17 mW on sample.

2.5. Devices fabrication and electrical characterization

For electrical conductivity measurements of GO and rGO, contact pads of Aluminum (thickness ~ 200 nm) was thermally evaporated (pressure of $\sim 1.5 \times 10^{-6}$ mbar) over the patterned substrates. Geometrical factor for in-plane electrical measurements was estimated with a predefined electrode separation length and width of ~100 µm and ~1000 µm, on GO and rGO films, separately. For the rGO-FET fabrication, aqueous GO + NMP was spin coated over cleaned PET substrates and dried. Followed by this, the samples were exposed under UV ($\lambda \sim 365 \text{ nm}$) using a grey scale mask and Intelligent Micropatterning (IMP) system. The tuning of the UV exposure was done using a grey scale mask with values of 0 (fully exposed) and 110 (partially exposed). The region of GO fully exposed to UV was conductive while the partial exposed portion was semi-conducting. Afterwards, PMMA (950, A1) is spin coated over GO-rGO patterns and dried, to serve as a gate dielectric, followed by spin coating of aqueous GO + NMP solution and dried on hotplate. Electrical measurements were carried out using a cascade probe station attached to the Keithley 4200 SCS semiconductor parameter analyzer at room temperature.

3. Results & discussions

For writing patterns of GO-rGO, a photomask with desired features is placed over the flexible substrate, spin coated with GO ((GO + NMP)/PET). The whole assembly is exposed to UV light $(\lambda \sim 253 \text{ nm})$ and the process schematic of GO-rGO patterning is shown in Fig. 1(a). Final obtained patterns are shown in Fig. 1(b). where the dark brown portion is exposed to UV and the bright pale yellow part is blocked by the photomask. We understand that the UV exposed part is photocatalytically reduced-GO (rGO), while the unexposed yellow part is GO. The similar color contrast has been observed for liquid dispersions of GO and rGO [44,45], where the role of NMP is emphasised in details [9]. To a brief note, electron hole pair generated in NMP enhances the photocatalytic reduction of GO by reacting with oxygen containing functional groups and thus resulting in GO-rGO patterning, under UV exposure. Due to inductive effect of methyl group, lone pair of N could easily donate its electron to the O atom in C=O via conjugation, thus forming NMP* (as shown in Fig. 2) [46,47]. The obtained NMP*, in the presence of H₂O molecules, reacts with the functional groups attached to GO sheets and resulting in rGO. To understand the patterning of GO-rGO, we have further exposed the GO films with various masks including transmission electron microscope (TEM) grid and virtual/photo mask designed in mask-less lithography. To our excitement, we could make patterns with various feature sizes down to submicron range.

Optical microscope and SEM images for 100 μ m GO-rGO patterns are shown in Fig. 3(a) and (b), respectively, where the change in color of exposed region is assigned to the rGO patterning with desired feature sizes. We also attempted patterning with ~ 6–8 μ m features using designed photomask (Fig. 3(c)), and rGO pads with ~20 μ m features made from a TEM grid (Fig. 3(d)), where dark and bright regions correspond to rGO and GO, respectively. Similarly, various complex patterns such as resistive circuit and IIT Mandi logo have been attempted for demonstration. Further, being photoactive to UV light, going down to sub 100 nm is a real challenge at the moment, on the other hand the possible laser writing seriously damages the sample and substrate.

After satisfactory demonstration of patterning, we have characterized different patterns using Raman spectroscopy and mapping to confirm the formation of rGO after exposure (Fig. 4(a)-(c)).



Fig. 1. Process schematic (a) for patterning of GO-rGO films on a flexible substrate under UV illumination. A homogeneous dispersion of GO + N-Methyl-2-Pyrrolidone (NMP) spin coated and dried at 100 °C, before subjected to UV radiation for 45 min after masking with desired pattern. (b) Photograph of representative pattern obtained on the flexible substrate. (A colour version of this figure can be viewed online.)



Fig. 2. Reduction of GO in presence of NMP under UV illumination. Here, NMP acts as a photo-catalyst for rapid reduction of GO to rGO. (A colour version of this figure can be viewed online.)



Fig. 3. Patterning of GO-rGO using photomasks with various feature sizes; (a) Optical microscope image on flexible substrates (2 × 2 cm); (b) SEM image of pads in (a); (c) Optical image of patterns from photo mask; (d) SEM image of patterns made by TEM grid (e) optical image of resistive circuit and (f) logo of IIT Mandi. (A colour version of this figure can be viewed online.)



Fig. 4. Raman characterization of GO-rGO. (a) Optical image of GO-rGO patterns, on flexible PET substrate, used for Raman mapping. Inset shows the low magnification image of patterned electrodes of rGO (black color) and GO (grey color); (b) Raman spectra of rGO and GO at specified green spots in (a); (c) Raman mapping of I_D/I_G ratio for the area shown in (a). (A colour version of this figure can be viewed online.)

Generally, graphene based materials have two characteristic Raman peaks corresponding to first order (i) breathing mode of sp² hybridized carbon atoms in the hexagonal ring along with the local defects and disorder called D Band (~1338 cm⁻¹), and (ii) E_{2g} symmetry of sp² hybridized carbon atoms known as G band (~1586 cm⁻¹) [9,44]. By analyzing the intensity ratio (I_D/I_G) of Raman peaks corresponding to D and G band, a clear distinction of GO and rGO has been demonstrated [9]. In present case, the estimated I_D/I_G ratio of GO is 0.96 and rGO is 1.11. The dark (rGO) and bright (GO) regions in optical images (Fig. 3) are showing two different intensity ratio of D and G bands, around 1338 and 1586 cm⁻¹, respectively [16,20,48]. Moreover, the broadening of the D band (peak at ~ 1338 cm⁻¹) in rGO is attributed to the presence of structural defects and imperfections due to detachment of functional moieties at edges and basal plane from GO. The absence of Raman signature peaks of NMP in GO and rGO, rules out the possibility of traces of NMP after UV exposure and drying, shown in Fig. S1 (supplementary information).

Further, reduction of GO has been reported by laser irradiation in earlier reports [49]. To rule out the feeble possibility of GO reduction by laser, during Raman measurements, a Raman mapping has been carried out over the region, shown in Fig. 4(a), at one of the corners of GO-rGO pattern. Based on the I_D/I_G ratio map, the region with I_D/I_G ratio higher than one (rGO) is clearly demarcated from the region with I_D/I_G less than one (GO), which rules out the possibility of further reduction by laser exposure (Fig. 4(c)). Thus, I_D/I_G Raman mapping is demonstrating a clear distinction of two separate regions of patterned GO-rGO, in line with conclusion from Fig. 3.

With a limited number of functional groups attached, rGO is expected to show a higher electrical conductivity than GO, thus current-voltage (I–V) characteristic are performed on two regions to investigate the conductivity contrast between GO and rGO patterns. Fig. 5(a) shows I–V characteristic with aluminum (Al) contacts pads on GO and rGO patterns. The linear I–V curves (shown as log-I vs V for clarity here) confirm a good ohmic contact between Al electrodes and rGO. For a constant voltage of 1 V, the current value in case of rGO (~0.6 μ A) is ~2 orders higher than GO (~4.4 nA) while the calculated electrical conductivity for rGO (60 mS/m) is ~150 times higher for GO (0.4 mS/m). Thus, the color contrast between the two patterns is also associated with the conductivity contrast.

To demonstrate the potential application of this simplified and rapid patterning approach, the method is utilized for the fabrication of flexible, all carbon and metal-free rGO-FET using grey scale lithography. The optical photograph of the device structure is presented in Fig. S2 (supplementary information). The device structure has been dried after patterning to rule out the possible contribution coming from NMP (Fig. S1 (supplementary information)). Schematic for the fabrication of metal-free, all-carbon rGO-FET is shown in Fig. 5(b), where three different regions depicting the whole device structure. First, region covered with mask and unexposed to UV is GO (with grey scale value 255); second, region completely exposed to UV (with grey scale value 0) corresponds to



Fig. 5. Electrical characterization of GO-rGO and metal-free all-carbon rGO-FET. (a) Current-Voltage characteristic for GO and rGO patterns with Al electrodes, inset is a device structure, (b) Schematic for fabrication process of rGO-FET on flexible substrate, (c) Output characteristic ($I_{DS}-V_{DS}$) as function of gate voltage (V_{GS}), and (d) Transfer Characteristics ($I_{DS}-V_{CS}$) at $V_{DS} = -1$ V, for the fabricated rGO-FET. (A colour version of this figure can be viewed online.)

conductive rGO (drain, source and gate); and third, partially exposed region (with grey scale value 110) corresponds to semiconducting channel of rGO. In present investigations, channel length and width patterned for the rGO-FET is 100 and 1000 μ m, respectively.

Output $(I_{DS}-V_{DS})$ characteristic as a function of gate to source voltages (V_{CS}) and transfer $(I_{DS}-V_{CS})$ at $V_{DS} = -1$ V for all-carbon rGO-FET is as shown in Fig. 5(c) and (d), respectively. Linear $I_{DS}-V_{DS}$ modulates with field effects of V_{GS} applied across the PMMA as gate dielectric. With increasing V_{CS} , I_{DS} decreases at a constant V_{DS} suggesting holes as majority charge carriers in the channel. $I_{DS}-V_{DS}$ as a function of V_{CS} demonstrates a characteristics similar of p-MOSFET. Further, the transfer characteristic of the fabricated rGO-FET shows an ambipolar nature with I_{DS} minimum at ~ - 2.5 V. The transfer characteristics shows an I_{ON}/I_{OFF} ratio of ~1000, which is reasonably alright for demonstration of the rGO-FET device. The formation of p-channel rGO-FET is attributed to the presence of functional groups in semiconducting rGO as compared with the fully exposed, conductive rGO.

4. Conclusion

In summary, we have developed a facile and low cost method for GO-rGO patterning, under UV exposure, for simultaneous fabrication of metal-free, all carbon rGO-FET device and metallic interconnects, which is useful for large scale production of multifunctional flexible and wearable electronic devices. Reduction of GO under UV-irradiation is confirmed by Raman spectroscopy, Raman mapping and electrical measurements. Patterned rGO has an enhanced electrical conductivity than GO, while the fabricated metal-free and all-carbon rGO-FET device has shown an ambipolar characteristics. The advantage of the present approach is reliable and metal-free patterning of rGO-FET device and rGO interconnects for flexible electronic applications. Proposed controlled reduction and site specific patterning strategy can be further extended for the fabrication and integration of future GO-rGO based flexible electronic devices, sensors and circuit components.

Appendix A. Supplementary data

Supplementary data related to this chapter can be found at https://doi.org/10.1016/j.carbon.2017.11.087.

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