Soft-lithographic processed soluble micropatterns of reduced graphene oxide for wafer-scale thin film transistors and gas sensors†

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PDMS based imprinting is firstly developed for patterning of rGO on a large area. High quality stripe and square shaped rGO patterns are obtained and the electrical properties of the rGO film can be adjusted by the concentration of GO suspension. The arrays of rGO electronics are fabricated from the patterned film by a simple shadow mask method. Gas sensors, which are based on these rGO electronics, show high sensitivity and recyclable usage in sensing NH3.

Introduction

Patterning of nanostructure materials to generate a functional microstructure on a large area is promising for mass production of micro/nanoscale devices. Graphene discovered in 2004 is a two dimensional material of sp² bonded carbon atoms and has aroused huge research interest in a wide field of physics, material science, biology and electronics.1-3 Graphene exhibits excellent electrical properties and great chemical stability, and may be considered as the building block of future electronics and sensors. Graphene transistors show carrier mobilities between 3000 and 27 000 cm² V⁻¹ s⁻¹, which makes graphene a promising material for nanoelectronics. Mechanically exfoliated graphene has been demonstrated to have the ability to detect gases down to a single molecular level.4 For these microelectronics and sensor applications, large area and selective patterning of graphene on a substrate is urgently in need. The most popular method to produce graphene for research purposes is through “scotch tape” or mechanical cleavage of graphite.5 However, this technique has a very low yield, in which monolayer graphenes have to be discerned from a mixture of thick graphene flakes. Therefore, the “scotch tape” process is unsuitable for large-scale production of devices. Pattermed graphene can be produced by a chemical vapor deposition method (CVD) on the patterned metallic film from a hydrocarbon source.6 The device array can be made of those grown graphene patterns. However the patterned metallic films for graphene growth are made using a complex photolithographic technique; and a complex procedure is required to transfer patterned graphenes to the insulating substrate prior to device fabrication6-8 since metallic substrates are unsuitable for electrical devices application.

Reduced graphene oxide (rGO) produced from chemical or thermal reduction of graphene oxide (GO) is competitively alternative material for graphene. GO prepared from graphite via a chemical exfoliation method emerges as single- or few-layered graphene with high yield production dispersions (~4 mg ml⁻¹).9 The solution processability of GO offers unique advantages since it is readily amenable for spin-coating, casting, transferring, imprinting onto substrates for large-scale production of graphene electronic circuits. Especially, residual chemically active defect sites render rGO as promising material for functional electronic sensors.10-14 Some chemical/biological sensors made from single-layer rGO or few-layers rGO have been demonstrated.10-14 Up to date, most of those studies are focused on a single electronic device or sensor. For real-life applications, it is essential to produce highly integrated electronics and sensors, for which research into patterning of continuous rGO films is urgently needed.

Patterning GO have been performed using micromolding in capillaries (MIMIC).15 This method mainly exploits a weak capillary force which produces the limit area of micropatterns (<20 cm × 20 cm). In addition, a limit geometric structure of stripe type can be made by the MIMIC method. Nanoimprinting, which is a most widely used soft-lithography technique, allows fabrication of two- or three-dimensional structures with micro/nanoscale resolution.16-20 Polydimethylsiloxane (PDMS) is the most popular soft elastomeric and conformable stamp for nanoimprinting. In the imprinting procedure, pressure is applied to make the PDMS stamp contact with the solution (or soft solid materials) coated substrate and various geometric patterns can be replicated to the substrate from the PDMS stamp.
(shown in Fig.1a). Compared to MIMIC, the advantages of this technique include simplicity, large area (depending on the size of stamp) and possible production of various geometric micro-patterns. To our best knowledge, up to date, there is no report about exploitation of this imprinting technique for GO patterning. In this paper, we present PDMS based imprinting to fabricate wafer-scale continuously conductive rGO micro-patterns. Highly integrated thin film transistors (TFTs) are made based on these rGO micropatterns. And the applications of our rGO TFT for gas sensors are also demonstrated.

**Experimental details**

Graphite oxide was synthesized from natural graphite flakes using a modified Hummer's method. Graphite oxide was then fully exfoliated in water to produce suspension of graphene oxide (GO) sheet for imprinting. The glassy carbon toolsets were prepared via a previously reported laser machining. A 10 : 1 (PDMS : curing agent) mixture of the PDMS and silicon elastomer kit (Dow Corning) was poured onto the glassy carbon mold. Then, the PDMS was cured at 80°C for 2 h. After curing, the PDMS stamp was carefully lifted off the glassy carbon master. To fabricate the rGO pattern (shown in the schematic drawing of Fig. 1): a GO suspension was dispersed onto the substrate, then the PDMS stamp (length × width × thickness: 10 × 10 × 3 mm; depth of pattern structure: 1 μm) was pressed onto the GO suspension and pressure of 0.2 N was used to ensure close contact between the PDMS and the substrate. After water was evaporated by heating at 80°C for 1 h, the PDMS stamp was carefully lifted off the substrate, leaving the GO patterns on the substrate intact. Patterned GO films were annealed in H2/Ar (10/40 sccm) under ambient pressure at 800°C for 30 min. The patterned GO and rGO films were characterized using optical microscopy (Leica DM4500P), scanning electron microscopy (SEM, Hitachi S-4200), atomic force microscopy (Nanoscope IIIa Vecco) and Raman spectroscopy (LabRAM XploRA, power 0.15 mW, excitement wavelength 532 nm). The element components and structure analysis was performed using X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha XPS, using Al (Ka) radiation as a probe). Cr/Au electrodes on the patterned film were fabricated using film-plating machines (ZHD-300) by a shadow mask. Electrical measurements of these devices were performed using a semiconductor analyzer (Keithley 4200 SCS) combined with a Lakeshore probe station.

**Results and discussion**

The significance of our work is in demonstrating the fabrication of continuous patterned thin film consisting of single or few layered rGO by an imprinting procedure of soft-lithography and the simplicity to make the array of graphene electronics from these patterns. The imprinting procedure is schematically shown in Fig.1. Graphene oxide for imprinting is synthesized from natural graphite flakes using modified Hummer’s method. We can prepare single-layer GO with different concentrations (Fig. S1).† A high quality and large area rGO pattern (depending on the size of PDMS mold) can be made on solid or flexible substrates by this PDMS imprinting procedure. Stripe and square shaped micropatterns of GO film are generated from PDMS replication. The morphologies of patterned films are characterized using optical microscopy, SEM, AFM. A series of typical images of the rGO pattern that were made using 0.3 mg ml⁻¹ GO suspension are shown in Fig. 2. Fig. 2a gives a low magnification view of stripe shaped rGO patterns. The stripe structure has a width of 15 μm and length up to 5 cm. The array of the square shaped rGO pattern is shown in Fig. 2b. Each microscale square has a size 30 × 30 μm. A magnified image (Fig. 2c) shows that the patterned film is continuous and composed of stacked individual rGO flakes with a size range of

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**Fig. 1** Schematic illustration of (a) a soft-lithographic procedure for patterned rGO film, (b) an rGO electronics array fabricated using a shadow mask.

**Fig. 2** Optical image of patterned rGO films: (a) striped shape, (b) square shape. (c) A magnified SEM image indicates that rGO films are composed of one- to a few-layer randomly stacked rGO sheets. (d) AFM image of the film edges. (e) Section analysis indicates that the thickness of rGO sheets is ~3 nm. (f) Raman spectra of GO and rGO film.
1–15 μm. The AFM images of the film edge (Fig. 2d, Fig. 2e) indicate that the film thickness is ~3 nm, which corresponds to 2–3 layers of rGO. These patterned films exhibit nonuniformity in colours under optical microscopy, which indicates nonuniformity in the film thickness (shown in Fig. 2a and Fig. 2b). Deeper colours mostly observed at the film edges reflect a little bigger thickness at the rim. GO pattern are formed in the patterned PDMS stamp, in which GO suspension is evaporated. The generation of nonuniformity in GO film thickness may be accounted for by the coffee ring effect that occurred in the microscale chamber which formed by compact contact of PDMS stamp with substrate. GO suspension evaporates on a solid surface. As the three-phase contact line (CL) of the GO suspension droplet is pinned on the surface in the microscale chamber due to physical roughness or surface heterogeneities, the evaporation induces a capillary flow within the droplet which drives the suspended GO flakes toward the CL and leaves a little thicker structure at the rim (shown in Fig. 2a, b). In addition, there are no GO residues left on the surface of PDMS stamp after imprinting (shown in Fig. S2). This is attributed to the low surface energy of the PDMS interface (19.8 mJ m⁻²). Therefore, the low surface energy of the PDMS interface enhances the formation of a high quality GO pattern.

The structure of GO and rGO is characterized using Raman spectroscopy. Raman spectra taken from a GO film and the corresponding chemically reduced GO film are shown in Fig. 2f. Compared to GO, the G band (~1600 cm⁻¹) of rGO is sharper and more symmetrical and has an up-shift of ~2 cm⁻¹. The intensity ratio of D (~1350 cm⁻¹) and G band (I_D/I_G), which is utilized to determine the extent of defects in graphene, decreases from 1.2 to 0.92. This implies an increase in the size of sp² domains in rGO. This can be explained by the removal of epoxide and hydroxyl groups on the basal plane and carbonyl and carboxyl groups on edges of GO via chemical reduction, leading to the restoration of sp²-hybridized carbons. The structure and components of GO and rGO are further analyzed by XPS. The analytic results are shown in Fig. S2: the oxygen content in GO is more than 24.9% as compared with 17.11% in rGO (calculated from Fig. S3a). The high-resolution XPS spectra of C1s of as-prepared GO sheets (Fig. S3b) shows that oxidized carbon atoms exist in form of different functional groups: aromatic or conjugated C (284.5 eV), the C in C–O bonds (286.8 eV), the carbonyl C (C==O, 283.3 eV), and the carboxylate carbon (O=C==O, 289.0 eV). These oxygen containing groups are produced from harsh oxidation, which destroyed the sp² atomic structure of graphene. Those oxygen containing groups are also observed from rGO (Fig. S3c), but the intensities of those oxidized carbon groups are much weaker than that in the GO, proving considerable de-oxygenation and restoration of the sp² carbon sites by the reduction treatment.

In previous reports on the rGO film prepared by filtration or transfer printing, the thickness of the as-made rGO film, which can be controlled and adjusted by the concentration of GO suspension, is the key for the field effect properties. We perform the experiments in the thickness and conductance of the rGO film as a function of the concentration of GO suspension (shown in Fig. 3). The thickness shows a linear increase with concentration of the GO suspension (Fig. 3a). The rGO films fabricated from GO suspension with concentrations 0.5 mg ml⁻¹ and 1 mg ml⁻¹ are continuous and exhibits respective average thicknesses of 6 nm and 10 nm (shown in Fig. 3a, Fig. 3d, Fig. 3e), while a discontinuous film with an average thickness of 2 nm is obtained when the concentration of GO suspension is below 0.1 mg ml⁻¹ (shown in Fig. 3a, Fig. 3c). From Fig. 3b, the conductivity of rGO increases from 1.2 × 10⁻¹¹ to 1 × 10⁻⁸ S m⁻¹ in the GO concentration range of 0.05–0.5 mg ml⁻¹, and higher concentrations (>0.5 mg ml⁻¹) lead to a nearly constant conductivity of ~7 ± 3 × 10⁻⁸ S m⁻¹.

Multilayered graphene reaches the 3D limit of graphite in terms of its electronic and dielectric properties at about 10 layers, which theoretically corresponds to a thickness below 3.4 nm for the pristine graphene since a single graphene has a thickness of 0.34 nm, while owing to the oxygen functional groups in both sides, single layer GO and rGO show a much larger thickness of ~1 nm, which is reported in the previous theoretical and experimental research. Our experimental results (Fig. 3a) show that a dense rGO flake film with a stacked layer number above 10 can be fabricated using a high concentration (1 or 2 mg ml⁻¹) solution, which has the characteristics of a good conductor. And a rGO film made using GO solution with concentration of below 0.5 mg ml⁻¹ can be used for transistor application since its average stacked layer number is estimated to be below 5.

The parallel array of graphene electronics for the gas sensor is made from patterned film using a shielding mask (shown in Fig. 1b and Fig. 4a). This provides a simple and efficient approach for scalable production of rGO electronics and sensors. The devices with a channel length (L) of 60 μm and a width (W)
of 15 μm are made on a doped silicon substrate with a 300 nm thermally grown SiO₂ layer. The silicon wafer layer is used as the back gate. The conductivity of the patterned rGO film is in the range of 100 ~ 1000 S m⁻¹. The electrical transport properties of rGO film TFT in air and in vacuum are measured. The transfer characteristics (Iₘₛ−Vₚₖ) of a typical rGO device are shown in Fig. 4b. It has high conductance under a negative gate bias and almost no conduction under a positive gate bias when the device is measured in air, indicating that the carriers in this condition are holes and the device behaves as p-type semiconductor. 

![Image](https://via.placeholder.com/540)

**Fig. 4** (a) SEM images of the array of rGO TFT, the insert SEM image in (a) is a magnified TFT device, bar = 15 μm. (b) Transfer curves of rGO TFT measured in air and in vacuum. (c) Output curve of rGO TFT in vacuum. (d) Current variance of rGO TFT versus exposure to 1000 ppm NH₃. (e) Resistance variance of rGO TFT as a function of NH₃ concentration. (f) Adsorption and desorption of NH₃ on the rGO sensor.

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**Fig. 4** (a) SEM images of the array of rGO TFT, the insert SEM image in (a) is a magnified TFT device, bar = 15 μm. (b) Transfer curves of rGO TFT measured in air and in vacuum. (c) Output curve of rGO TFT in vacuum. (d) Current variance of rGO TFT versus exposure to 1000 ppm NH₃. (e) Resistance variance of rGO TFT as a function of NH₃ concentration. (f) Adsorption and desorption of NH₃ on the rGO sensor.

This strong p-type behaviour is resulted from the adsorption of oxygen or water from the ambient or hydroxyl group of the substrate. In order to exclude such ambient impact, the device is placed inside a high vacuum chamber (<5 × 10⁻⁵ Torr) for 24 h before electrical measurement. Ambipolar behavior, which has been reported in single-layer reduced GO transistor, has been observed from the rGO film transistor (shown in Fig. 4b). The observed transport characteristics (Iₘₛ−Vₚₖ) exhibits a large linear region in Fig. 4c, implying a good ohmic contact between the C/t/Au electrodes and the rGO. The mobility (μ) of hole or electron can be extracted from the two branches of the transfer characteristics using the following equation:

\[ μ = \frac{\Delta I_m}{\Delta V_{pg}} \left( \frac{L}{W} \right) / (V_{ds} C_{ox}) \]  

(1)

where Cₜox is the silicon oxide gate capacitance (which is 1.15 × 10⁻⁸ F cm⁻² for a gate oxide thickness of 300 nm). The room temperature-field effect mobilities of as-made rGO TFTs are ~2.3 cm² V⁻¹ s⁻¹ for holes and ~0.84 cm² V⁻¹ s⁻¹ for electrons. Compared to the pristine graphene, rGO exhibits very low mobilities, which may result not only from the scattering by doping defects, growth defects, and other imperfections or adsorbates, but also from the scattering at junctions of two or more rGO sheets overlapped.

Current interest in rGO sensors can be attributed to two main reasons. First, its every constituted atom is at surface which makes its electrical transport properties sensitive to the environment, which is similar to pristine graphene. Second, the existence of chemically active defects such as vacancies or small holes may render more adsorption sites for gaseous molecules, which enhances the sensing capability. To test the sensing performance of as-fabricated rGO TFFs, we use NH₃ gas as the sensing target in this study. Sensing performance of the devices is characterized against the low concentration of NH₃ diluted in N₂ gas. The rGO sensor shows a strong response to NH₃ and exhibits a decrease of about 10% in conductance with the exposure to 1000 ppm NH₃. This is verified by the measurement of Iₘₛ−Vₚₖ curve of the devices at the gate voltage of 0.1 V as shown in Fig. 4d. This conductance variance is due to the depletion of holes in rGO by the NH₃ adsorption. Resistance variance of rGO film as a function of NH₃ concentration is given in Fig. 4e. The resistance of rGO film increases linearly with the NH₃ concentration. The lowest detection concentration of 400 ppm has been achieved in our experiments, which is not even optimized. Compared to other NH₃ sensors such as oxide sensor which are operated at high temperature of 100~300 °C, the rGO film sensors work at room temperature, which greatly facilitates the operation.

To test the stability, the adsorption and desorption of NH₃ on rGO film device are performed several times (shown in Fig. 4f). A flow of pure N₂ is applied to clean the device after each run. The sensor demonstrates stable sensing capability after several circles of adsorption and desorption of NH₃. The adsorption behavior of the molecules on graphene is proposed to be closely related to the structure. Adsorption on sp²-bonded carbon (the low-energy binding sites) occurs through weak dispersive forces, which is a recoverable process; while adsorption onto higher energy binding sites (e.g. vacancies, structural defects, and oxygen functional groups) is usually nonrecoverable without moderate thermal treatment. For example, a carboxylic acid group with single- and double-hydrogen bonding allows binding energies of at least several hundred meV molecule⁻¹ for adsorption of a molecule. Our recoverable sensor is here attributed to the fully reduced treatment, which increases the number of sp²-bonded carbons. This fully reduced treatment can be evidenced by the analysis of Raman spectra and XPS (shown in Fig. 2f and Fig. S3f). As for the sensing mechanism, the sensing behavior can be attributed to the effective adsorption of NH₃ on the surface of p-type rGO. NH₃ is an electron donator because of the existence of the lone pair of electrons. Electron transfer from the adsorbed NH₃ to the rGO leads to depleted hole concentration and decreased electrical conduction in rGO film.

**Conclusions**

In summary, we demonstrate that the PDMS based imprinting enables large area patterning of rGO film, which makes scalable...
fabrication of rGO electronics a reality. Microscale features with stripe and square geometries are successfully fabricated by the PDMS based imprinting. An array of rGO TFTs are made using the patterned film following a simple mask shielding process and a gas sensor is then fabricated. The sensor is quite sensitive even at the non-optimized stage, and the sensing capability is very stable. Our results are significant because this PDMS based imprinting method make scalable fabrication of electronics and sensors of rGO an easy task.

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References