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A simple and scalable route to wafer-size patterned graphene

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Abstract

Producing large-scale graphene films with controllable patterns is an essential component of graphene-based nanodevice fabrication. Current methods of graphene pattern preparation involve either high cost, low throughput patterning processes or sophisticated instruments, hindering their large-scale fabrication and practical applications. We report a simple, effective, and reproducible approach for patterning graphene films with controllable feature sizes and shapes. The patterns were generated using a versatile photocoupling chemistry. Features from micrometres to centimetres were fabricated using a conventional photolithography process. This method is simple, general, and applicable to a wide range of substrates including silicon wafers, glass slides, and metal films.

Introduction

Graphene is a promising nanomaterial due to its unique properties such as stable crystal structure, optical transparency, and exceptional electronic properties of high electron mobility and high saturation velocity for both electrons and holes.^{1,2} Producing large-scale graphene films with controllable patterns is an essential component of graphene-based nanodevice fabrication. Among various reported methods for preparing graphene films, mechanical cleavage of highly oriented pyrolytic graphite (HOPG)³ or exfoliation of graphite crystals^{4,5} remain the most popular and successful in producing single- and few-layer pristine graphene. The graphene films prepared by these methods are physisorbed or dispersed randomly on the substrate, and could be easily removed by solvent washing or sonication.^{6,7} Although these approaches are adequate for making measurements for fundamental studies, they are not amenable to high-throughput fabrication of graphene-based devices due to the size limitation, the lack of site-specific placement of graphene films on the substrate, and ease of removal from the surface. It is highly desirable to assemble graphene at designated locations and into desired patterns for the rational design of functional graphene-based devices on a large scale. Several methods have been reported for patterning graphene films, including contact printing using a patterned HOPG stamp generated by O₂ reactive ion etching (RIE),^{8,9} chemical vapor deposition through a mask,¹⁰

and electron-beam lithography on the hydrogen silsesquioxane (HSQ)-masked graphene.¹¹ However, these methods involved either relatively high cost and low throughput lithographic patterning processes, or required sophisticated instruments, hindering their large-scale fabrication and practical applications.

Herein, we report a simple, effective, and reproducible approach for patterning graphene films with controllable feature sizes and shapes on various substrates. The fabrication of patterned graphene structures consists of four simple steps as illustrated in Fig. 1. The substrate was first treated with a functionalized perfluorophenylazide (PFPA) such as PFPA-silane for silicon wafers and glass slides¹² or PFPA-disulfide for gold films.¹³ Graphene flakes suspended in *o*-dichlorobenzene (DCB) were then spin-coated or dip-coated onto the PFPA-functionalized substrate. After drying in vacuum, the sample was subjected to UV irradiation in the presence of a photomask. It was then sonicated in DCB for 10 min, rinsed with DCB and ethanol, and dried with nitrogen to generate the patterned graphene structures. This method has the following advantages: (1) simple, efficient, and fast *via* a clean and unique photocoupling reaction, (2) low cost and high throughput, (3) compatible with current microfabrication and lithography processes, (4) scalable from micrometres to centimetres to a full wafer, and (5) applicable to a wide range of substrates by simply using a different anchor group on PFPA.

Experimental

Preparation of PFPA-functionalized substrate

PFPA-silane was synthesized as previously reported.¹⁴ Silicon wafers with an oxide layer thickness of ~275 nm or microscope glass slides were cleaned with Piranha solution (7 : 3 v/v conc. H₂SO₄/35 wt% H₂O₂, **Caution!** *Piranha solution reacts violently with many organic compounds; use extreme care when handling it.*), followed by thorough washing with boiling water and dried under flowing nitrogen. The substrates were then incubated with a solution of PFPA-silane in toluene (12.6 mM) at room temperature for 4 h, washed with toluene, dried under flowing nitrogen, and cured at room temperature overnight.

Preparation of exfoliated graphene

Graphite flakes (50 mg, Sigma) were added to DCB (20 mL) and the mixture was sonicated using a sonication probe (SONICS, VCX130) for 1 h and settled for 1 week. The supernatant of the mixture was then centrifuged at 4500 rpm for 30 min. The upper solution was collected and used for the subsequent pattern fabrication. The graphene flakes were imaged with transmission electron microscope (TEM) by depositing the solution onto a TEM grid (Fig. 1). To determine the concentration of the solution, DCB was removed by rotary evaporation. The solid was then dried under vacuum and weighed, from which the concentration was calculated to be 0.01 mg mL⁻¹ graphene in DCB.

Fabrication of graphene patterns

Graphene flakes were deposited onto PFPA-functionalized wafer by spin-coating the solution of exfoliated graphene flakes in DCB at 1000 rpm for 2 min or by dip-coating. Samples were then dried under vacuum for 30 min. A photomask was placed on top of the graphene-coated wafer, and was irradiated under ambient conditions with a 450 W medium pressure Hg lamp (Hanovia) for 10–30 min. The lamp reached its full power of 5.0 mW cm⁻² after a 2 min warm-up, as measured by a model UVX radiometer and UVX-36 sensor (Upland, CA). A 280 nm optical filter was placed on the sample surface during irradiation. Samples were then sonicated in DCB for 10–30 min followed by washing with DCB and ethanol, dried under vacuum for an hour, and finally stored in a desiccator.

Plasma etching

The experiment was carried out by placing the patterned graphene sample in a home-built up-stream RF excited plasma for 3 min at an air pressure of 400 m Torr at 400 °C.

General characterization

Atomic force microscope (AFM) images were recorded on a XE-70 AFM (Park systems, non-contact mode) with a NCS15/Pt tip and a scan rate of 0.1 Hz. Raman spectra were recorded on a Horiba HR800 UV Raman System with a 100× objective and a 100 mW 532 nm laser having a 750 nm spot size. Spectra were recorded at various locations in the patterns at room temperature. UV-Vis transmittance spectra were recorded on a Lambda 45 UV-Vis spectrometer (Perkin Elmer). The samples were prepared on glass slides (1×2.5 cm²) using the same fabrication protocols as described above for silicon wafers except that no photomask was used during irradiation. TEM images were obtained on a JEOL 100CX TEM operating at an accelerating bias voltage of 100 kV. The specimens were prepared by dropping the exfoliated graphite solution onto 300-mesh grids (lacey formvar/carbon on copper support, Ted Pella, Inc.). X-Ray photoelectron spectroscopy (XPS) studies were carried out on a Surface Science Instruments S-probe spectrometer. This instrument has a monochromatized Al K α X-ray source, a hemispherical analyzer, a multichannel detector and a low-energy electron flood gun for charge neutralization. The X-ray spot size used in these experiments was approximately $800 \mu\text{m} \times 800 \mu\text{m}$. Pressure in the analytical chamber during spectral acquisition was less than 5×10^{-9} Torr. The take-off angle (the angle between the sample normal and the axis of the analyzer lens) was 55°. Spectra used to determine surface elemental compositions were acquired at an analyzer pass energy of 150 eV. The high-resolution spectra were acquired at an analyzer pass energy of 50 eV. Peak fitting of the high-resolution spectra were performed using the XPSPEAK4.1 software, and the binding energy was calibrated by assigning the hydrocarbon peak in the C 1s high-resolution spectra to 285.0 eV. The XPS results are average values from analyzing three spots on at least two replicates of each sample type.

Results and discussion

Solution-exfoliated graphene was used as the starting material to demonstrate this patterning technique. Compared to other graphene preparation methods, solvent exfoliation does not involve high temperatures or low vacuum, and can be easily carried out under ambient conditions in a conventional fume hood. An important parameter to consider is the solvent. The solvent should be graphene compatible, able to efficiently exfoliate graphite, and volatile so it is readily evaporated after coating the substrate. *N*-Methyl-2-pyrrolidone (NMP)⁴ and *N,N*-dimethylformamide (DMF)¹⁵ are the two most popular solvents used in the preparation of liquid-exfoliated graphene flakes. However, both solvents have high boiling points and low vapor pressures, thus are difficult to evaporate under ambient conditions, which is not ideal for this study. DCB was recently used to exfoliate graphite and produce pristine graphene flakes in high yield.¹⁶ In addition, it readily evaporates during spin-coating or after dip-coating, producing samples that are homogeneous and uniform. The density of the spin-coated or dip-coated graphene flakes can be controlled by adjusting the solution concentration and the number of coating cycles. By using a higher concentration or coating multiple times, higher graphene coverage on the substrate can be achieved. Additionally, the strong electron-withdrawing F atoms on PFPA may help provide an electron-deficient surface for the absorption of electron-rich graphene by π - π stacking forces.¹⁷

The graphene patterns were generated by photolithography and graphene was covalently attached to the substrate using a photochemically initiated coupling chemistry. Upon light

activation, the azido group on PFPA is converted to the highly reactive singlet perfluorophenylnitrene that can subsequently undergo C–C addition reactions with the neighboring graphene sp^2 C network to form the aziridine adduct (Fig. 1).¹⁸ The reaction occurs at the interface of the functionalized wafer and graphene, and excess graphene flakes can be removed by sonication and solvent washing. In principle, only a monolayer of graphene becomes covalently attached to the surface, regardless of the number of graphene layers initially deposited.

Fig. 1 shows the coated graphene flakes on PFPA-functionalized substrates before (Fig. 1a) and after photopatterning (Fig. 1b–f). Graphene remained in the areas that were transparent to UV light where the photocoupling reaction occurred between the surface azido groups and graphene. In the regions where the UV light was blocked, the coated material was completely removed after sonication and solvent washing. The photocoupling process faithfully copied the features on the photomasks, generating patterns with sizes ranging from millimetres to micrometres depending on the configuration of the photomasks. The contact edges of the patterned structures were sharp and regular, and the masked areas were clean. These results demonstrated that the photocoupling chemistry was highly efficient, producing patterns with high spatial resolution. Without a photomask, graphene flakes covering the entire substrate could be obtained after UV irradiation. Because the patterned graphene flakes were covalently immobilized, they remained intact on the substrate after extensive sonication and repetitive solvent washing. For example, the graphene remained attached after sonicating in DCB for 30 min or plasma etching for 3 min. These results demonstrated that the bonding between the graphene flakes and the substrate was strong and highly stable.

Further evidence confirming the covalent bond formation between the graphene flakes and the PFPA-functionalized wafer was provided by XPS of unpatterned substrates. The fluorine to nitrogen atomic ratios were calculated from XPS determined surface elemental compositions before and after the reaction between the PFPA and the graphene. Values of 0.8 and 1.3, respectively, indicate, as expected, that the amount of nitrogen decreased due to loss of two nitrogen atoms during the grafting reaction. The high-resolution N 1s spectrum of the PFPA-functionalized wafer exhibited three peaks (Fig. 2b). The two highest BE peaks (402.1 and 406.5 eV) are attributed to the N atoms in the azide structure (two N atoms in the azide species have the same nominal N 1s BE, thus these two peaks have a 2 : 1 intensity ratio) and both peaks decreased significantly in intensity after UV activation and attachment of the graphene flakes (Fig. 2e). The lowest BE peak (400.5 eV) is attributed to the amide N atoms as well as any amine N atoms formed by partial decomposition of the azide due to sample exposure to ambient conditions during sample transfer and X-ray exposure during XPS analysis. The change of the N 1s spectrum after reaction with the graphene overlayer is consistent with conversion of $Ar-N_3$ to $Ar-N$ (*i.e.*, loss of central and outer N atoms) upon UV activation.^{18,19} Three peaks at 285.0, 286.4 and 288.1 eV were present in the C 1s core level spectra (Fig. 2c and f). The C 1s peaks, in order of increasing BE, are attributed to C–C, C–N, C–F and N–C–O species (the C–F and N–C–O species have similar BEs and both contribute to the highest BE C 1s peak). The C–N to C–F/N–C–O ratio in the PFPA-functionalized wafer was 1 : 2 (Fig. 2c). After the graphene was attached to the surface, an increase of the 285.0 eV component (C–C) was observed due to the added C–C species in the graphene layer. In addition, the C–N to C–F/N–C–O ratio changed to 5 : 4 (Fig. 2f). The relative increase in the C–N peak can be attributed to the formation of additional C–N bonds (aziridine) upon reaction of PFPA with graphene (Fig. 2d).

The patterning technique can be applied to other substrates simply by changing the anchor group on PFPA. We have synthesized a series of PFPA derivatives for silicon wafers and glass slides,²⁰ metal oxides,²¹ and metal films.^{22,23} These PFPAs, when applied to the corresponding substrates, generate PFPA-functionalized substrates that can be subsequently

used to pattern graphene. We have successfully fabricated patterned graphene structures on silicon wafers and glass slides using PFPA-silane (Fig. 1) and on gold films using PFPA-disulfide.

The patterns were analyzed by AFM and Raman spectroscopy. AFM section analysis of patterned structures shown in Fig. 3a and 3b indicated that the thickness of graphene in the patterned areas was 4–20 nm (Fig. 3c and 3d), corresponding to a mixture of 4–6 layers of graphene to thin graphite.^{16,24,25} Raman spectra were recorded at different locations in the patterned region; a typical spectrum is shown in Fig. 4a. The presence of the D peak at 1345 cm^{-1} and D peak at 1620 cm^{-1} , corresponding to defects in the patterned graphene structure.²⁶ This was consistent with a sample containing numerous surface edges. The position and the shape of the Raman 2D peak offer a simple, non-destructive means for analyzing the number of graphene layers.^{27,28} For the single-layer graphene, the band centers at 2668 cm^{-1} , and shifts gradually to higher wavenumbers as the number of graphene layers increases (2682 cm^{-1} for two layers, 2692 cm^{-1} for three to five layers, and 2720 cm^{-1} for more than five layers of graphene and bulk graphite, respectively).^{18,27,28} Fig. 4b–4e show the Raman 2D peaks recorded at different locations in the patterned area. The position of the 2D peaks ranges from 2690 cm^{-1} to 2710 cm^{-1} , indicating that the flakes in the patterned regions consisted primarily of four to five layers of graphene and thin graphite. This is consistent with the AFM analysis that showed the thicknesses of patterned graphene to be from ~4 nm (4–6 layer graphene) to ~10–20 nm (thin layer graphite) (Fig. 3).

The optical transmittance property of the graphene film was also evaluated. Samples were prepared where graphene flakes coated on PFPA-functionalized glass slides were irradiated without a photomask. The PFPA-functionalized glass slide had a similar UV-Vis spectrum as the unfunctionalized glass slide (Fig. 5, curve I). When coated with graphene flakes, the transparency of the resulting glass, defined as the transmittance at 800 nm, decreased to 68% (Fig. 5, curve II). After UV irradiation and removal of excess graphene flakes, the transparency of the attached graphene increased to 82% (Fig. 5, curve III), a value similar to those reported in the literature.^{10,29,30}

Conclusions

In conclusion, we developed a simple and scalable approach to the fabrication of patterned graphene structures using a versatile photocoupling chemistry. Using solvent-exfoliated graphene flakes as the starting material and a photomask, patterns were generated with feature sizes ranging from micrometres to centimetres. The process is low-cost, occurs at room temperature, and is induced by a fast and tunable light activation. Since the coupling chemistry can be initiated by other energy sources such as electrons³¹ and heat,³² nanoscale patterns are possible by using higher resolution lithography tools such as electron beam or near-field probes. The quality of the generated patterns is highly dependent on the initial graphene starting materials used. With the improved synthesis and the quality of the graphene, single-layer patterned graphene nanostructures can be readily produced using this method. Such a simple and scalable route to highly ordered graphene patterns will open immense opportunities for fabricating graphene-based nanomaterials and functional devices.

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Fig. 1. Fabrication of patterned graphene: (1) functionalization of the substrate with PFPA; (2) spin-coating graphene flakes onto the substrate. Insert is the TEM image of the graphene flakes, scale bar = 200 nm; (3) UV irradiation through a photomask; (4) development of the patterned graphene by sonication and solvent washing. Inset: UV-initiated reaction of PFPA and examples of synthesized PFPA coupling agents. Optical images of (a) coated graphene flakes on a silicon wafer; (b-e) graphene patterns with various features and sizes fabricated by photolithography; and (f) graphene patterns on a glass slide.

Fig. 2. PFPA-decorated wafer (a) and the corresponding high-resolution XPS N 1s and C 1s core level spectra (b and c); covalently attached graphene (d) and the corresponding high-resolution XPS N 1s and C 1s core level spectra (e and f). See text for the discussion of peak assignments.

Fig. 3. Optical images of graphene patterns (a, b), and the corresponding AFM images and height profiles (c, d). The height profiles were recorded along the horizontal lines shown in the AFM images in c and d.

Fig. 4. Raman spectra of the patterned graphene: (a) Typical Raman survey scan of the patterned structures; (b–e) representative Raman 2D peaks recorded at various locations in the patterns ($\lambda_{\text{laser}} = 532$ nm, laser spot size: 750 nm).

Fig. 5. UV-Vis spectra of glass slide functionalized with PFPA (I), dipcoated with graphene flakes (II), and after covalent attachment of graphene (III).