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Direct patterning on reduced graphene oxide nanosheets using femtosecond laser pulses

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Abstract
Micro- and nanostructures were fabricated directly on graphene nanosheets by controlling the conditions of femtosecond laser pulse etching. High quality graphene micro- and nanostructures with a minimum width of 492 nm were obtained as the graphene nanosheets used in our experiments were large-scale, uniform and highly conductive. Various complex patterns were successfully created through femtosecond laser etching. Furthermore, by managing the laser energy, the graphene under the Au electrodes could be completely or partly removed. This technology of direct patterning of micro- and nanostructures on graphene through femtosecond laser technology might pave the way for the integration of graphene-based electronic microdevices.

Keywords: graphene, femtosecond laser, patterning, microdevice

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Graphene has been considered as a promising material for the greatly anticipated all-carbon-based electronic micro/nanodevices owing to its prominent intrinsic electronic, thermal, optical, structural and chemical properties in recent years [1–5]. The high mobility and optical transparency of graphene attract significant attention aimed at numerous potential applications in electronics and optoelectronics, such as transparent electrodes [6, 7], ultrafast photodetectors [8], supercapacitors [9], and so on. As an essential step in any form of microelectronic processing, the lithographical patterning of graphene with desirable configurations is an important and a challenging issue. To date, the existing methods of patterning graphene into desired geometries include electron beam lithography, plasma etching, chemical procedures by using nanometer-sized nickel, and tip-based thermochemical/mechanical nanolithography [10–14]. However, most of them involve complex steps, require harsh conditions, and suffer from photoresist contamination of the graphene surface. Furthermore, it is still difficult to fabricate graphene into complex patterns with desirable configurations, which constitutes the main restriction for its application in electronic microdevices [15].

Laser micromachining, as a non-contact patterning technique based on a direct-write process, is preferred for the production of micrometre-sized features and three-dimensional microdevices because of its advantages of fast material-processing speed, large scan area, nanometer spatial resolution and single-step capability [16]. Recently, continuous and femtosecond lasers have been used to construct graphene microstructures by patterning and reduction of graphene oxide

(GO) film [17, 18]. A femtosecond laser-based technique has also been used to image and pattern mechanically exfoliated graphene with high spatial resolution [19]. However, an unavoidable drawback of GO is that its resistance is exponentially higher than that of graphene, thus post-reduction of GO is essential for electrical application of graphene. Another drawback is that GO reduced by a femtosecond laser has a rougher surface and nonuniform conductivity. Therefore, direct patterning of solution-processed graphene obtained by reduction of GO, which meets the urgent requirement of graphene technologies as reduced GO (rGO) has an ultra-smooth surface and high and uniform conductivity [20], might boost the rapid development of graphenes. Here, we constructed patterns directly on rGO nanosheets on different substrates by employing a femtosecond laser. Various complex patterns were successfully created through femtosecond laser etching. Moreover, we demonstrated that the fabrication of graphene patterns can be realized under conditions with gold electrodes. The investigation probably paves a flexible as well as easy route for the patterning of rGO and its further applications in electronic microdevices.

2. Materials and experiments

Glass and quartz slides were cleaned in an ultrasonic bath with detergent, deionized water, acetone, and isopropyl alcohol, respectively, followed by extensive rinsing with deionized water, dried under a nitrogen stream, and stored in a vacuum oven at 80 °C until use, typically within a period of 2 h. Polyimide (PI) strips and silicon wafer were ultrasonicated in ethanol for 30 min, followed by dried under a nitrogen stream, and stored in a vacuum oven at 60 °C until use, typically within a period of 1 h. The GO was prepared by using a modified Hummers method from flake graphite. Firstly, GO was dispersed into solvent to form a stable solution, after which the slide was allowed to spin at 700 rpm for 12 s to cause uniform spreading of the solution on the substrate, then at 2000 rpm for 1 min to dry the film. After spin-coated deposition, the GO films on the substrates were reduced through exposure to hydrazine vapor. The substrates (the GO films were reduced by hydrazine) were heated at 1000 °C for the quartz substrates and at 400 °C for the glass, PI and silicon substrates for 1 h under Ar, and then cooled to room temperature over 3 h. Subsequently, gold electrodes were thermally evaporated onto the graphene nanosheets through a shadow mask. Finally graphene films with a thickness of about 20–40 nm were obtained, and then Au electrodes with an approximate thickness of 20 nm were coated though a shadow mask.

The femtosecond laser pulses at wavelengths of 800 and 400 nm with a repetition rate of 1 kHz and a pulse width of 120 fs were focused by a 50× or 20× objective lens with a numerical aperture of 0.5 or 0.4 onto the graphene film surface. The energy was less than 500 nJ. A neutral filter was used to adjust the energy of the pulse. The sample position was controlled by a computer-controlled 3D stage of type M-505.6DG or M-501.1DG produced by Princeton Instruments. By moving the computer-controlled 3D sample stage with respect to the focused laser beam, the preprogrammed patterns were written on the graphene film. The speed of the stage in the exposure region was 50 μm s^{-1}.

Observations of the optical images were performed by an axio observer D1 fluorescence microscope with a 100 W mercury lamp and a fluar 40× UV objective (Carl Zeiss). The Raman spectra were collected in a backscattering configuration by microscope using a 100× objective. SEM analysis was carried out on a Hitachi S-3500N scanning microscope at an accelerating voltage of 20 kV. Atomic force micrographs (AFM) were obtained using a MultiMode V AFM (Veeco Instruments Inc., USA).

3. Results and discussion

Experimentally, GO was prepared using the Hummers method from flake graphite. Compared with exfoliation of graphite and epitaxial growth on silicon carbide, easy chemical synthesis and solution processable GO can greatly facilitate the fabrication of graphene-based microelectronic devices. The conductivity of rGO film after pyrolysis at 1000 °C can reach approximately 400 S cm^{-1}, which is much larger than the highest conductivity (256 S cm^{-1}) of the graphene reduced by femtosecond laser pulses [18]. Moreover, in addition to this, the rGO film obtained by thermal reduction has an ultra-smooth and uniform surface [20], which cannot be obtained in laser reduced GO [18]. A perfect surface morphology of rGO film is crucial for optoelectronic device performance [21]. Therefore, direct patterning on rGO film with ultra-smooth surface and high conductivity will facilitate access to higher quality graphene microstructures.

The gold electrode lines were thermally evaporated onto the as-prepared rGO film under vacuum through a shadow mask. After this, the rGO nanosheets with and without gold electrodes were patterned by femtosecond laser pulses with a 20× objective lens (numerical aperture: 0.4). Figure 1(a) schematically illustrates the procedures of patterning rGO. Femtosecond laser micromachined graphene results from a process by which optical energy is transferred to the graphene. As a result of the irradiation, rGO can be removed from the substrates due to localized oxidative burning of the graphene [17], while the rGO that was not irradiated by the femtosecond laser can be retained. According to the preprogrammed patterns, the desired graphene patterns were fabricated by direct femtosecond laser cutting.

Optical microscopy images of periodic graphene lines on quartz substrate with microscale are given in figures 1(b)–(d). The widths and lengths of the retained graphene lines are tunable by controlling the energy of the femtosecond laser pulses and adjusting the laser-cutting position relative to the focus, as shown in figure 1(e). From figures 1(b) to (d), it can be seen that the width of the cut area increases from 2 to 13 μm with the energy of the pulses from the left to the right. The smallest width of the retained graphene lines is about 4 μm. The thickness of the rGO film is only 25 nm, thus it should be noted that when the laser-cutting position is about 5 μm above the focus, obvious damage of the substrate can be observed because the beam focus is located inside the substrate, as

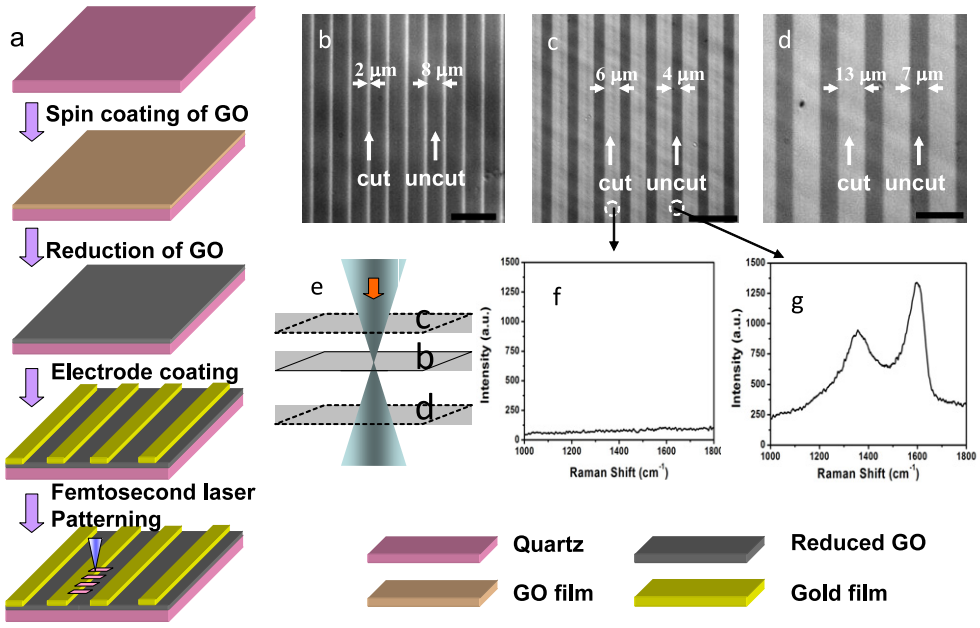

Figure 1. Preparation scheme and optical microscopy images of the reduced GO patterns. (a) Schematic illustration of the preparation procedure of micro/nanofeatures on reduced GO nanosheets with a focused femtosecond laser beam. (b)–(d) Optical microscopy images of the graphene lines under different femtosecond laser energies and different distances from the focus: (b) $E = 20$ nJ and $d = 0$ μm, (c) $E = 200$ nJ and $d = 5$ μm, (d) $E = 400$ nJ and $d = 10$ μm. The dark and light gray areas correspond to uncut (with graphene) and cut (without graphene) regions, respectively. Scale bars: 20 μm. (e) Illustration of the laser-cutting position relative to the focus for (b)–(d). (f) Raman spectrum of the cut area for graphene film on quartz. (g) Raman spectrum of the uncut area for graphene film on quartz. The Raman results show that all graphene materials are cleanly etched away in the trenches after laser direct-cutting.

shown in figure 1(c). To obtain a higher resolution of the patterns, the rGO film should be placed on the focal plane of the laser beam. Raman spectroscopy was performed on the cut and uncut regions shown in figures 1(f) and (g), respectively. We find that the Raman spectroscopy displays two bands at 1354 and 1596 cm^{-1} for the uncut region, corresponding to the G and D bands, which are the characteristic bands of graphene. But both of the bands disappear for the cut region, indicating that the graphene is completely removed after laser radiation.

Various simple or complicated graphene-based patterns were fabricated for the graphene films. It is interesting to notice that complex patterns like the school badge of Nan Kai University and the phrase 'Nan Kai University' can also be fabricated with high resolution by a simple step as shown in figures 2(a) and (b), indicating that laser etching is a flexible method to create any desired patterns. The optical microscopy images and scanning electron microscopy (SEM) images demonstrate the formation of periodic arrays of rGO square pillars of 8 μm $\times$ 4 μm and 16 μm $\times$ 16 μm (figures 2(c)–(f)).

Besides quartz substrate, this GO dispersion can be spin-coated onto clean glass and flexible polymer (PI) substrates and silicon wafers to form integrated GO films. In practice, this solution spin-coating process is suitable for almost all substrates, particularly flexible and large-area polymer-based substrates. The conductivity for reduced graphene films fabricated on glass, silicon and flexible polymer substrates can reach approximately 100 S cm^{-1}. Figure 3 displays a series of SEM images of laser direct-cutting patterns for graphene films on different substrates, including flexible PI, glass, silicon and quartz. This indicates that the femtosecond laser direct-cutting method is flexible and convenient for the patterning of graphene. Figures 3(a)–(c) show the microchannels of rGO on quartz cut under different pulse energies. The exposure energy used in figure 3(a) is 210 nJ and the width of the uncut graphene channels is about 13 μm; the exposure energy used in figure 3(b) is 103 nJ and the width of the uncut graphene channels is about 15 μm; the exposure energy used in figure 3(c) is 52 nJ and the width of the uncut graphene channels is about 17 μm. As the exposure energy increases, the width of the etched channels also increases, from 3 to 7 μm.

To obtain a better fabricating effect, we chose femtosecond laser pulses at 400 nm and a lower energy to cut the rGO nanosheets because the edges of microchannels fabricated using a femtosecond laser at 400 nm are smoother than those at 800 nm. A 50$\times$ objective lens with a numerical aperture (NA $=$ 0.6) was also used to obtain higher resolution. Figure 4(a) shows AFM images of the nanochannels of rGO nanosheets fabricated using a femtosecond laser at 400 nm with about 5 nJ pulse energy. The profile property of the microchannels at the wavelength of 400 nm is shown in figure 4(b). AFM section analysis along the horizontal line shows that the height of the graphene channel is about 25 nm, which agrees with the thickness of the rGO film. And the section analysis along the vertical lines indicates that all the graphene is removed, while the etched surface of the quartz is smooth because of the high threshold of the quartz. Finally, the narrowest width of 492 nm of nanochannels on rGO nanosheets was obtained by a femtosecond laser at 400 nm. It should be noticed that to obtain a comparable resolution a 100$\times$ objective

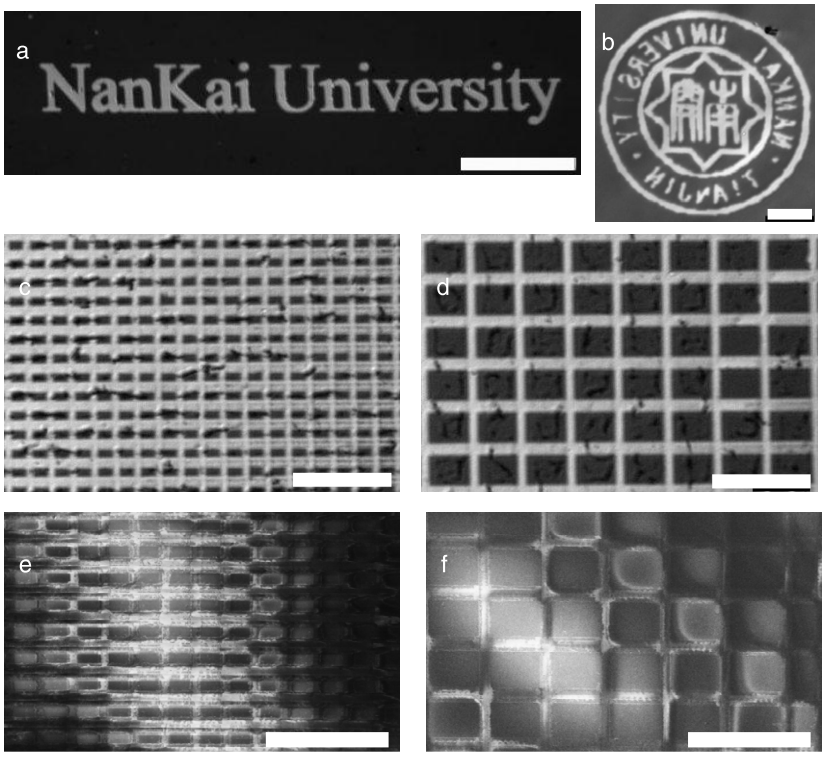

Figure 2. Optical microscopy images of the phrase (a), and school badge (b) of Nan Kai University. Optical microscopy images of square patterns of 8 μm $\times$ 4 μm (c) and 16 μm $\times$ 16 μm (d); (e) and (f) are the corresponding SEM images. The dark and light gray areas correspond to uncut (with graphene) and cut (without graphene) regions, respectively. Scale bars: 40 μm.

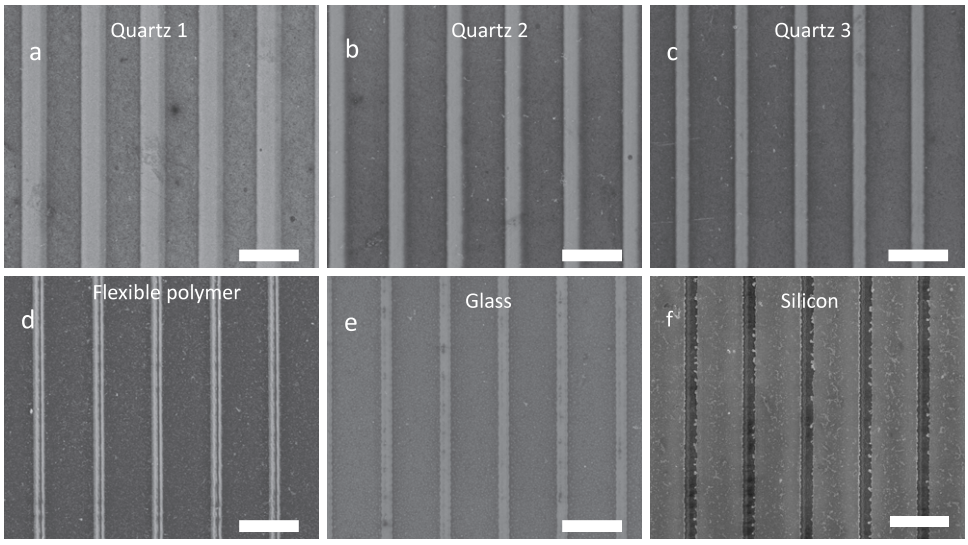

Figure 3. SEM images of the channel patterns on the substrates of quartz (a)–(c), flexible polymer (d), glass (e) and silicon wafer (f). The distance between the sample position and the beam focus is about 5 μm below the focus. Scale bars: 20 μm. Parts (a)–(c) are SEM images of the channel patterns for graphene films on quartz cut under different exposure energies.

with a higher numerical aperture (NA = 1.4) was used by Sun *et al* [18] to pattern and reduce GO by a femtosecond laser, which indicates that it is possible to reach high resolution by direct patterning of rGO film.

The microchannels we studied above were all directly etched on graphene nanosheets with quartz substrate. In microelectronic devices Au electrodes are always needed to fabricate different patterns. Figures 4(c)–(f) give AMF images and the profile properties of the microchannels etched on rGO nanosheets with and without Au film. The section analysis performed along the horizontal line shows that the height of the microchannels is 45 nm, which exactly equals the thickness of

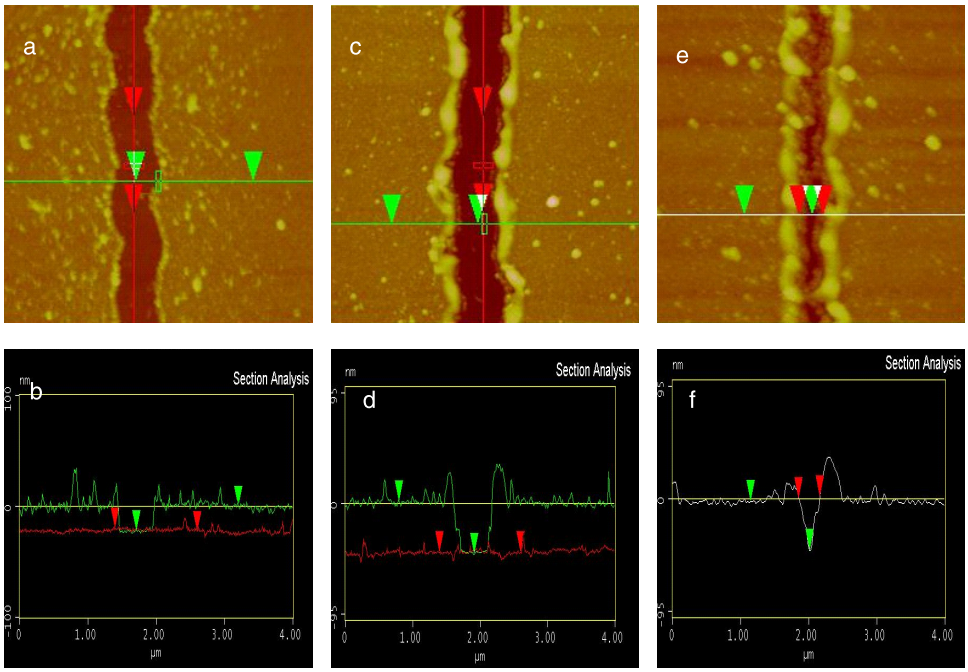

Figure 4. AFM characterizations of reduced GO nanochannels with and without Au film using a femtosecond laser at 400 nm. (a) AFM image of a reduced GO nanochannel without Au film, and with a laser pulse energy of about 5 nJ. (b) Height profile along the horizontal and vertical lines shown in (a); the height of the nanochannel is about 25 nm. (c) AFM image of a reduced GO nanochannel with Au film, and with a laser pulse energy of about 10 nJ. (d) Height profile along the horizontal and vertical lines shown in (c); the height of the nanochannel is about 45 nm. (e) AFM image of a reduced GO nanochannel with Au film, and with a laser pulse energy of about 5 nJ. (f) Height profile along the white line shown in (d); the height of the nanochannel is about 41 nm.

the Au film (20 nm) plus the G nanosheets (25 nm), indicating that the Au and the graphene are both cleanly removed. The width of this channel is 578 nm. The section analysis along the red line demonstrates that the bottom of the channel is very smooth, which implies that the entire G film is removed cleanly. It should be noticed that an obvious step can be observed in the interface between two films, the height of the step is 20 nm. The height of the step is the same as the height of the Au film, which means that the step is at the interface of the Au film and the rGO nanosheets, and the width of the rGO channels is smaller than the width of the Au channels. Using lower pulse energy, microchannels with the smallest width of 312.50 nm on Au electrodes were obtained as shown in figures 4(e) and (f). The height of the channel is about 41 nm, which is smaller than the total height of Au and G film. The AFM section analysis along the white line in figure 4(e) shows that the section of the channel is conical since most of the laser energy is absorbed by the Au film when the laser energy is low. So, through careful modulation of the laser pulse energy, the Au film can be removed and the rGO nanosheets can be partly retained; this provides a flexible, cheap and direct approach to fabricate graphene-based materials in electronic micro- and nanodevices.

4. Conclusion

In conclusion, using the direct femtosecond writing method, we have directly fabricated graphene together with Au electrodes. Graphene lines with different widths and periods and complex graphene patterns were created. The minimum width of the channels reaches 312 nm on Au/graphene and 492 nm on graphene. Thanks to the femtosecond laser, this process is very simple, flexible and direct. Furthermore, rGO nanosheets with and without Au electrodes can be either all cleanly removed or partly retained by laser ablating at the same time. Direct patterning on rGO by using a femtosecond laser may improve the applications of graphene-based materials in microelectronic devices.

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