The electrical properties of graphite oxide (GO) can be tuned consecutively by treating samples with ammonia and hydrogen plasma. When altering ammonia plasma time from 10 to 4.5 min, large area (greater than $100 \times 100 \mu m^2$), n-type, ambipolar and p-type semiconducting reduced graphite oxide (RGO) sheets could be obtained. The highest mobilities of the electron and hole are 5.41 and 2.10 cm$^2$ V$^{-1}$ s$^{-1}$ at low operational voltage (3 or $-3$ V, respectively). When treating a GO film with hydrogen : argon (9 : 1) plasma, high conductivity RGO was obtained with conductivity around 630 S cm$^{-1}$. It is anticipated that this study could pave the way towards carbon-based electronics.

1. Introduction

Silicon-based electronics are indispensable elements in our daily life. Insulators, semiconductors and conductors are essential components to build traditional electronics. By oxidizing silicon, insulator SiO$_2$ will be obtained, which is one of the most important components in field effect transistors (FETs) [1]. By doping elements, the electrical properties of semiconducting silicon can be tuned between the n- and p-type. Tunable electrical properties in silicon are the functional basis for traditional electronics. However, the limited capacity of silicon electronics (Moore’s law [1,2]) and the problems that arise during the fabrication processes of silicon-based materials, such as environmental pollution and energy demand, have encouraged scientists to seek alternative substitutes. Carbon-based materials, such as graphene [3], the thinnest and strongest material [4], exhibit giant intrinsic charge carrier mobility [5, 6], which enables faster and smaller transistors to be constructed that use less power and dissipate
heat faster than current silicon-based devices [7]. To develop carbon-based electronics [8–10], the tunability of semiconductor electrical properties is one of the critical issues facing scientists. However, until now, no report has been published about tuning the electrical properties of carbon-based materials consecutively by the insulator, semiconductors (n-type, ambipolar and p-type) and conductors, compared with the tunable electrical properties of silicon semiconductors in current application electronics. Herein, we have developed a simple, efficient method to tune the electrical behaviours of graphite oxide (GO) by treating samples simply with less energy-consuming plasma. By means of ammonia plasma treatment, semiconducting reduced graphite oxide (RGO) with n-type, ambipolar and p-type electrical properties can be achieved. By using hydrogen:argon (9:1) plasma treatment, we obtained high-conductivity RGO [11,12]. Tunable electrical properties of carbon-based materials provide a considerable opportunity for building carbon-based electronics.

2. Material and methods

(a) Reduced graphite oxide sample preparation

GO was prepared by the modified Hummers & Offeman [13] method from graphite flakes (less than or equal to 230 mesh). GO powder (20 mg) was dissolved in 10 ml distilled water to obtain 2 mg ml\(^{-1}\) GO solution, which was spin-coated onto pre-cleaned Si substrate with 300 nm SiO\(_2\) on the surface. GO film was annealed at 70\(\degree\)C under vacuum for 1 h to eliminate rudimentary water. Large RGO sheets were obtained by reducing GO film with ammonia and hydrogen:argon (9:1) plasma with a GaLa Instrumente plasma Prep2 plasma cleaning machine.

(b) Device fabrication and characterization

Field effect transistors (FETs) of RGO were fabricated by an ‘organic ribbon mask’ method, which is briefly summarized in four steps. (i) Micro-organic ribbons were prepared using a physical vapour transport technique. (ii) An individual ribbon standing on the substrate was picked up by a mechanical probe and dropped over the RGO surface as a shadow mask. (iii) Gold source and drain electrodes (40 nm) were vacuum deposited on the sample surface. (iv) The ‘organic ribbon mask’ was peeled off, using the mechanical probe. The electrical properties of the as-produced RGO FET were characterized with a Keithley 4200 SCS system.

3. Results and discussion

Figure 1a shows a typical atomic force microscopy (AFM) image of GO film spin-coated onto pre-cleaned Si/SiO\(_2\) (300 nm) substrate. Single GO sheets with thickness approximately 1.43 nm could be obtained by diluting GO solution (figure 1b). Figure 1c is a typical scanning electron microscope (SEM) image of a large RGO sheet with size larger than 100 \(\times\) 100 \(\mu\)m\(^2\) after reducing GO film with plasma at a power of 160 W for 8.5 min with a gas flow rate of approximately 8 standard cubic centimetres per minute (scm). Arrow (i) and arrow (ii) are pointing to the region of SiO\(_2\)/Si substrate and the thin RGO sheet, respectively. Here, RGOs are obtained with different thickness ranging from 1.54 to 15 nm. For the sake of convenience when building electronic devices, RGO sheets with thickness around 8 nm were chosen in this study. Figure 1d is a thin RGO sheet with height approximately 1.54 nm (inset: AFM image).

Figure 2a shows the Raman spectra of GO (top curve) and RGO (bottom curve). Comparing these two curves, it was found that the D/G ratio of GO is smaller than that of RGO, which might be due to increased disorder of the sp\(^2\) carbon framework in the processes of plasma treatment [14]. RGO sheets were used to fabricate FETs with the ‘organic ribbon mask’ technique developed by Jiang et al. [15]. The electrical properties of devices were characterized by a Keithley 4200 SCS machine with a micromanipulator 6150 probe station in a clean and shielded box at room temperature in air. If not specified, then all the electrical measurements were carried out in air.
Figure 1. Morphology of GO and RGO sheets. (a) Optical microscope image of GO film spin-coated onto an SiO$_2$/Si substrate; (b) AFM image of a typical thin GO sheet with thickness approximately 1.43 nm; (c) SEM image of RGO sheets with size larger than 100 × 100 µm$^2$ and (d) a thin RGO sheet, and an AFM image (inset) of an RGO sheet, with thickness around 1.54 nm. In (c,d) arrow (i) and arrow (ii) indicate the SiO$_2$/Si substrate and RGO sheet, respectively. (Online version in colour.)

at room temperature. Typical output curves of n-type RGO are shown in figure 2b. A schematic and an SEM image of the RGO FET device are shown in the top left and bottom right inset of figure 2b, respectively. Figure 2c, d shows the tunable electrical properties of RGO FET devices with various ammonia plasma times. The 8.5 min curve in figure 2c is the transfer curve of the FET device based on RGO sheets treated with plasma for 8.5 min. The device exhibits n-type behaviour with electron mobility of approximately 5.41 cm$^2$ V$^{-1}$ s$^{-1}$ by applied low-bias voltage $V_{ds} = 3$ V. It is worth noting that n-channel transistors exhibit good air stability when stored in air for 180 days. As we know, it is highly desired that both p- and n-type semiconductors have similar mobilities for the construction of high-speed complementary circuits. However, retardant effects on electron mobility by water and oxygen in air has still hindered the development of high-performance organic n-type semiconductors [16]. Moreover, synthesizing new n-type organic semiconductors is also a complex, time-consuming and expensive process. Here, we present a simple and less energy-consuming method to develop air-stable n-type semiconductors with mobility comparable to that of amorphous silicon.

Interestingly, it was found that when decreasing the plasma time from 8.5 to 7.5 min at $V_{ds} = 3$ V, ambipolar electrical behaviour was demonstrated, as shown in figure 2d (7.5 min curve). Both electron and hole conduction appeared in this device but electron conduction dominated. Further shortening the plasma time to 6.5 min, ambipolar electrical behaviour occurred but hole conduction dominated (figure 2d, 6.5 min curve). Decreasing the plasma time to 5.5 min, FET devices demonstrating only p-type behaviour were obtained with mobility of approximately 2.10 cm$^2$ V$^{-1}$ s$^{-1}$ with $V_{ds} = -3$ V (figure 2c, 5.5 min curve). The results demonstrate that, through the facile ammonia plasma treatment, RGO with n-type, ambipolar and p-type electrical properties can be achieved.

Given these interesting results, the question arises of what the mechanism is behind the tunable electrical properties of RGO. In previous reports, ammonia plasma has been used to generate a variety of atomic and molecular species such as H·, N·, NH·, and NH$_2$.[14,17,18].
Three roles played by these ammonia plasma species have been proposed, which were proved by further experimental results. (I) Reduced GO by eliminating oxygen-containing functional groups (OCFGs) from the graphite carbon framework (GCF), which is responsible for the improved conductivity of RGO sheets with respect to GO films. (II) Doping nitrogen atoms into the GCF, which is responsible for n-type or ambipolar behaviours of RGO FET devices. This role can be confirmed by the N1s X-ray photoelectron spectroscopy (XPS) spectrum: the peak centred around 398.2 eV is consistent with earlier reports [14,19]. (III) Covering a layer of those species on the RGO surface to protect the nitrogen-doped carbon framework from the influence of water and oxygen in air. This role can be proved by N1s XPS spectra and electrical characterization.

First, we fabricated n-type FET devices based on RGO under ammonia plasma for 8.5 min and further characterized by XPS. The N1s spectrum of the RGO sheets after 8.5 min of plasma treatment is shown in figure 3a, and it is split into two major subpeaks. The peak centred at 398.2 eV could be assigned to the in-plane ‘pyridine’-like nitrogen atoms [14,19,20], which was the main reason for n-type behaviour in FET devices [21]. The main peak centred at 402.8 eV could be attributed to out-of-plane nitrogen atoms on the surface of the RGO sheets [14,22]. Devices based on these RGO species could exhibit n-type behaviour. Second, the device was annealed

Figure 2. (a) Raman spectra of graphite oxide (top curve) and fabricated RGO (bottom curve) sheets; (b) the SEM image of an RGO FET device; inset, sketch map of an RGO FET device; (c) transfer curve of air-stable n-type and p-type RGO sheets obtained with plasma times of 8.5 min and 5.5 min; (d) transfer curve of air-stable ambipolar RGO sheets obtained with plasma times of 7.5 and 6.5 min. All the RGO sheets obtained under a plasma power of 160 W with an ammonia gas flow rate of approximately 8 sccm; (e) the transfer curves of the annealed device measured in air and under vacuum and (f) the I–V of GO thin film and RGO obtained with hydrogen plasma.
Figure 3. (a) The N1s spectrum of RGO obtained with an ammonia plasma treatment time of 8.5 min; (b) N1s spectrum of RGO annealed under a hydrogen atmosphere at 300°C for 3 h; (c) the N1s spectrum of RGO obtained with ammonia plasma treatment times of 7.5 min and 6.5 min; (d) the N1s spectrum of RGO obtained with an ammonia plasma treatment time of 5.5 min; (e) the sketch map of RGO obtained with ammonia plasma treatment and (f) the relationship between the number of devices with different electrical behaviour and the treatment time.

in a home-made quartz tube furnace under a hydrogen atmosphere at 300°C for 3 h. The N1s spectrum of annealing RGO and the electrical properties of the corresponding devices are shown in figures 3b and 2e, respectively. In figure 3b, it was found that peaks centred around 398.2 eV still existed after annealing, whereas peaks centred at 402.8 eV disappeared. Comparing figure 3a with 3b, it was found that role II nitrogen-containing species doped in the sp² carbon framework are more stable than the role III nitrogen-containing species. The content of elemental nitrogen in the RGO sheets will drop from the original 2.67% to the annealed 1.58%. The annealing process will eliminate the role III nitrogen-containing species from the RGO surface, and nitrogen doping and oxygen doping (arising from the oxidizing process of graphite) will both take effect to make the device demonstrate ambipolar behaviour under a nitrogen atmosphere (figure 2e). When the electrical properties in air are measured, the electron-conducting channel will be hindered by oxygen and water with the elimination of the role III nitrogen-containing species, and only oxygen doping will take effect, thus the device will exhibit only p-type behaviour (figure 2e).
According to the above-mentioned experimental results and discussions, we propose a mechanism of time-dependent tunable electrical properties of RGO as follows. (i) When GO is treated with ammonia plasma for 8.5 min, role I and II ammonia plasma species will cooperate to make the RGO device show n-type behaviour. Role III species will protect the nitrogen-doped RGO from interference by water and oxygen in air. Thus, the obtained RGO will demonstrate air-stable n-type behaviour. The content of nitrogen atoms in this sample will be approximately 2.67% (shown in figure 3a). (ii) When GO is treated for 7.5 and 6.5 min, the amount of role I and II ammonia species is decreased, oxygen doping and nitrogen doping will cooperate together to make devices that show ambipolar behaviour. Comparing the 7.5 min curve and the 6.5 min curve in figure 2d, it was found that the electron-conducting behaviour will dominate in RGO treated for 7.5 min; when the plasma time is decreased to 6.5 min, hole-conducting behaviour will dominate in the ambipolar devices. Role III species can also isolate the RGO from water and oxygen in air. Thus, this style of RGO device will demonstrate air-stable ambipolar behaviour. The content of nitrogen atoms will be approximately 2.12% for the 7.5 min treatment and 2.02% for the 6.5 min treatment. The N1s spectra of 7.5% and 6.5% were a similar shape, as shown in figure 3c. (iii) When the treatment time is further reduced to 5.5 min, the amount of ammonia plasma species will be further decreased. In figure 3d, there are no obvious role II species in the sample. In this case, oxygen doping will dominate in the device. The content of nitrogen atoms in this sample is approximately 1.83%. Figure 3e is a schematic diagram of the RGO obtained. The right arrow represents the role II ammonia plasma species, and the left arrow represents the role III ammonia plasma species.

It was found that the OCFGs existing in GO play critical roles during the plasma treatment processes [19]. The oxygen-containing functional groups make it easy for nitrogen atoms to be doped into the sp² carbon framework even under mild conditions, and even with low-power plasma in our experiment. We tried to remove some OCFGs first by annealing the GO film at 300°C for 3h under a hydrogen atmosphere. Then, ammonia plasma at 160 W for 8.5 min was used to further treat the GO film for preparing RGO. Although the RGO sheets still demonstrated n-type properties, the highest electron mobility was only 0.2 cm² V⁻¹ s⁻¹. The reason for the poor performance of RGO FET devices might be attributed to elimination of the OCFGs in the annealing process. Hence, there would be fewer opportunities for N-containing plasma species to replace OCFGs or to dope the carbon framework. By using ammonia plasma, more structural damage will be induced in less OCFG-protected RGO carbon frameworks annealed under hydrogen gas. Such structural damage might be one of the major reasons for poor mobility in the FET devices based on pre-annealed RGO.

In order to investigate device reproducibility, we spin-coated 2 mg ml⁻¹ GO solution onto 15 pieces of SiO₂/Si substrate; we then reduced one piece of substrate with ammonia plasma every 30 s (starting from 4.5 to 10 min). Five RGO sheets (with thickness approx. 10 nm) on every piece of substrate were chosen to build FET devices. Thirty-five of 75 devices worked and exhibited n-type, ambipolar and p-type behaviours. In the time span from 4.5 to 6.5 min, 15 devices exhibited p-type behaviour; in the time span from 6.5 to 8.5 min, nine devices exhibited ambipolar behaviour; in the time span from 8.0 to 10.0 min, 11 devices showed n-type behaviour (shown in figure 3f). To investigate the stability of charge carrier mobility in the three types of semiconductors, n-type, ambipolar and p-type RGO sheets were used to build FET devices. After being stored in air for 180 days, the mobility of the charge carriers in all these semiconductors demonstrated high stability, with mobility varying less than 1%.

Considering the tunable semiconducting properties of the RGO sheets, the question arises of whether it is possible to reduce GO from insulator to conductor via plasma treatment? This flexible super-thin, carbon-based conductor could be applied as the electron conductor in future carbon-based electronics, just as copper is used in silicon-based electronics. Herein, RGO could be obtained by reducing GO film with hydrogen:argon (9:1) mixing plasma at a power of 160 W for 8.5 min with a gas flow rate of approximately 8 sccm. Figure 2f shows the electrical properties of the hydrogen and argon plasma-treated RGO with electric conductivity of about 630 S cm⁻¹ (RGO curve). The GO film (film thickness was approx. 30 nm, GO curve) with electric
conductivity is only around $4.05 \times 10^{-6} \text{ S cm}^{-1}$. The results demonstrate that the conductivity of the hydrogen plasma-treated RGO semiconductors improves by more than eight orders of magnitude compared with GO.

4. Conclusions

We successfully tuned the electrical properties of GO from insulator to semiconductor and conductor with mild plasma treatment. When treating GO with ammonia plasma, it can be used to produce semiconducting RGO with tunable electrical behaviours in FET devices. By changing the plasma time, n-type, ambipolar and p-type RGO semiconductors could also be obtained. In addition, by reducing GO film with hydrogen:argon (9:1) plasma, conducting RGO with a conductivity of approximately $630 \text{ S cm}^{-1}$ can be prepared. The tunable electrical properties of RGO from insulator, to semiconductor to conductor, as prepared by facile plasma treatment, could be integrated into all carbon electronics, which is a potential alternative to traditional silicon-based electronics.

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