Self healing of defected graphene

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For electronics applications, defects in graphene are usually undesirable because of their ability to scatter charge carriers, thereby reduce the carrier mobility. It would be extremely useful if the damage can be repaired. In this work, we employ Raman spectroscopy, X-ray photoemission spectroscopy, transmission electron microscopy, and electrical measurements to study defects in graphene introduced by argon plasma bombardment. We have found that majority of these defects can be cured by a simple thermal annealing process. The self-healing is attributed to recombination of mobile carbon adatoms with vacancies. With increasing level of plasma induced damage, the self-healing becomes less effective. © 2013 American Institute of Physics.

Graphene’s unique band structure endows it with extraordinary electrical transport properties, owing to which it is believed to find applications in the next generation electronics and has thus drawn enormous attention.1 In particular, graphene possesses a very high mobility, the highest one at room temperature among all other materials.2 A high mobility means less resistive to electrical current and a faster switching ability for transistors. Therefore, circuits built from graphene can be potentially of low power consumption and high speed.3 However, graphene’s mobility is affected by various types of scatterers, i.e., charge impurities and crystalline defects. Defects are especially harmful, because they can backscatter electrons.4,5 To build either individual devices or integrated circuits, many steps of lithographic processes are required. It has been found that these processes can cause damage to graphene.6–9 The mobility is then reduced. To fully exploit the high mobility of graphene, it is important not only to grow high quality materials but to develop lithographic processes to maintain its original quality. For the latter, an alternative approach is to cure the damage, if it is difficult to avoid. In a related topic, methods have been developed to reduce graphene oxide.10,11 However, the main process there is reduction of oxide, e.g., removal of functional groups. To study how structural defects in graphene can be healed, it is much more relevant to study repair of well defined defects. Ion bombardment has been extensively used to study damage in graphite and graphene and known to produce vacancies.12–20 Although repair of these defects has been investigated in graphite,21,22 the defect there can be more stable due to bond formation between layers, hence more difficult to repair.15

In this work, we employ plasma bombardment to introduce structural defects in monolayer graphene films. We perform thermal annealing to study healing effects on these defects. By Raman, X-ray photoemission spectroscopy (XPS), high resolution transmission electron microscopy (HRTEM), and electrical transport measurements, it is found that vacancies can be healed simply by thermal annealing. The effect can be explained by annihilation of displaced carbon atoms with vacancies with assistance of thermal energy. When the size of the vacancy increases, healing becomes more difficult.

Graphene samples were prepared on SiO2 by mechanical exfoliation. The thickness of graphene flakes was estimated by optical images and confirmed by Raman spectra. Samples were loaded into a Femto plasma system. 99.99% high impurity argon gas was used to generate plasma. Low pressure plasma (17 Pa) was used to increase the ion energy, thereby enhance the bombardment effect. The plasma power was 20 W and the treatment time ranged from 5 to 60 s. The dosage per second is estimated to be 2 × 1014/cm2 from the power of the plasma generator and the area of the electrode.21 Thermal annealing was carried out in an argon environment (300 Pa) in a tube furnace. The intake of the pump was fitted with a custom made filter to reduce carbon contamination. Raman spectra were taken on a Renishaw confocal Raman system and the excitation was 514 nm. Samples for HRTEM imaging were large area graphene films grown by chemical vapour deposition on copper substrates. Pristine graphene films were transferred to TEM copper grids, followed by plasma treatment and annealing. The HRTEM images were taken on Titan 80–300 TEM at an acceleration voltage of 80 kV to avoid damage by electron beam irradiation. For the transport study, samples were patterned into 1 μm × 6 μm wide Hall bars by e-beam lithography. Electrical measurements were performed using a standard lock-in method in an Oxford cryostat.

Graphene samples were subjected to argon plasma treatment for various time durations. Raman spectra of pristine graphene and treated graphene are shown in Fig. 1. A D peak, centered at 1350 cm−1, is significantly enhanced by plasma treatment. The D peak is commonly known as a disorder peak, as it is associated with disorder in the sp2 bonded carbon network.19,22 The development of a strong D peak
indicates that substantial damage is introduced in graphene. Two new peaks, appearing at 1623 cm\(^{-1}\) and 2939 cm\(^{-1}\), are the \(D'\) peak and the \(D + D'\) peak. The amplitude of the \(D'\) peak is about one fifth of that of the \(D\) peak, indicating that the type of the defects is not \(sp^3\)-defects due to functionalization but mainly vacancies. Moreover, we have also taken spectra on bilayer regions after the plasma treatment. As shown in Fig. 1, the Raman spectrum of a bilayer region displays a strong \(D\) peak as monolayer regions do, indicating that both layers experienced considerable damage. Note that surface chemical modification will be very different for monolayer and bilayer graphene. This provides evidence that the damage is mainly caused by energetic argon ions, and some ions are capable of penetrating through two layers. We want to point out that the damage is severe, because graphene films were completely removed after 60 s plasma bombardment.

We then carried out thermal annealing on damaged films. In Fig. 2(a), Raman spectra taken after annealing at different temperatures are plotted. Starting from 300 °C, all three disorder related peaks, \(D\), \(D'\), and \(D + D'\), decrease as the annealing temperature increases. For the highest annealing temperature, 900 °C, the two peaks that appeared after plasma treatment, \(D'\) and \(D + D'\), almost completely disappear, while the \(D\) peak is greatly reduced. This indicates that large portion of the defects has been repaired. On the other hand, the recovery of \(G\) and \(2D\) peaks signals that the \(2D\) \(sp^2\) bonded carbon network has been restored. The ratio between the \(D\) peak intensity and the \(G\) peak intensity, \(I_D/I_G\), is inversely proportional to the domain size of graphene. To quantitatively estimate the extent of repair, we have calculated the domain size \(L_d\) as a function of the annealing temperature from the \(I_D/I_G\) ratio, which are plotted in Fig. 2(b).

XPS is employed to gain insight on the structure transformation by annealing. C 1s spectra were taken for pristine graphene, plasma treated graphene, and annealed graphene, as seen in Fig. 2(c). The plasma treatment results in growth of spectral weight on the high energy side of the C-C \(sp^2\) peak. By deconvolution, three peaks, centered at 286.6 eV, 288.1 eV, and 289.1 eV, are identified. The spectral weight around 286.6 eV and 288.1 eV can be attributed to C-OH, C=O, or structural damage. We want to emphasize the pronounced peak at 289.1 eV. It is assigned to COOH, which only appears at graphene edges. In sharp contrast, this peak appears at 288.1 eV, indicating that the damage is severe, because graphene films were completely removed after 60 s plasma bombardment.

![FIG. 1. Raman spectra for graphene monolayer and bilayer films under 5 s, 10 s, and 15 s argon plasma treatment.](image1)

![FIG. 2. Repair of defected graphene. (a) Raman spectra for monolayer graphene samples subjected to 5 s plasma treatment after annealing at different temperatures. (b) Domain size \(L_d\) as a function of the annealing temperature, showing gradual healing of defects in the graphene film. The solid line is a guide to eye. In the inset, \(\log(I_D/I_G)\) is plotted against \(1/T\). The red line is a linear fit excluding the lowest temperature point. XPS spectra of a graphene film before (c) and after (d) annealing at 750 °C.](image2)
is much lower than C-OH and C=O in graphene oxide.\textsuperscript{27,28} It is apparent that our samples possess significant amount of vacancies, in agreement with the Raman results. The formation of COOH likely took place when damaged samples were exposed to air. After annealing, the amplitudes of these peaks are substantially reduced and the spectrum displays only slight difference from that of the pristine graphene film, seen in Fig. 2(d). It is evidenced that considerable amount of vacancies have been repaired.

HRTEM images confirm the production and healing of defects. Fig. 3 shows HRTEM images for samples before and after plasma treatment and after annealing. Amorphous materials on the graphene surfaces are residue of poly(methyl methacrylate) (PMMA) that were used for transfer. In the clean region, the honeycomb lattice of graphene can be seen. The pristine graphene film shows high crystalline quality with no apparent defect. After the plasma treatment, a large amount of vacancies were introduced. The average distance between these defects is on the order of 10\,nm, consistent with the Raman result. Note that the distance is most likely shorter as single vacancies can hardly be identified and part of the surface is covered by residue. After annealing at 750\,°C, the defect density is substantially reduced. Only a few vacancies can be unambiguously identified on the surface.

The restoration of the graphene structure is further supported by electrical transport measurements. The transport data of a monolayer graphene sample are shown in Fig. 4. The pristine sample exhibits characteristics of high quality graphene, i.e., a weak temperature dependence of the resistance and the half integer quantum Hall effect. The mobility
Displaced carbon atoms are absorbed on graphene and lead to formation of vacancies in graphene, only ions with sufficient energy ($E_m > 4.7$ eV) can displace carbon atoms and diffuse. Because of the high energy cost of recombination, the migration barrier for carbon atoms is large. The formation energy for a single isolated vacancy in graphene is about 7.6 eV. For argon, only ions with sufficient energy (> 4.7 eV) can displace carbon atoms and lead to formation of vacancies in graphene. Displaced carbon atoms are absorbed on graphene film and diffuse. Because of the high energy cost of the dangling bond, recombination between adatoms and vacancies is energetically favourable. Assume that the migration barrier for carbon atoms is $E_m$ and the vacancies are fixed, the change rate of vacancies density $n$ due to recombination can be described by a bimolecular equation: 

$$\frac{dn}{dt} = -C n^2 e^{-E_m/k_B T}.$$  

Here, $C$ is the frequency factor, $k_B$ is the Boltzmann constant, and $T$ is the temperature. Thus, we have $1/n - 1/n_0 = C t e^{-E_m/k_B T}$, where $n_0$ is the initial defect density after plasma treatment. Assume $n = 1/L_{\text{local}}^2$, it becomes $L_{\text{local}}^2 - L_{\text{local}}^2 = C t e^{-E_m/k_B T}$. By plotting $L_{\text{local}}^2 - L_{\text{local}}^2$ as a function of $1/T$ in a semilog scale, we obtain the migration barrier $E_m = 0.95$ eV. Theoretical studies gives various values for the barrier, from 0.47 eV to 0.6–1 eV in carbon nanotubes, to <1.5 eV. Recent studies predict a barrier of 0.53 eV on graphene, 0.25 eV inside carbon nanotubes. Previous experiments on graphite have indeed shown that carbon adatoms can annihilate with vacancies at elevated temperatures. Most recently, such self-healing processes have been visualized by transmission electron microscope. Our experiments provide further evidence in a macroscopic scale that healing of defects in graphene by thermal annealing is very effective.

In conclusion, we employ argon plasma bombardment to produce structural defects in graphene and study healing of defects by thermal annealing. By comparing the Raman, XPS spectra, and HRTEM images before and after annealing, we show that the defect density is significantly reduced due to a self-healing process. Electrical measurements demonstrate that the healing process is very effective as the mobility is recovered to $9 \times 10^2 \text{cm}^2/\text{Vs}$ when the annealing temperature is only 500 °C. Repair of graphene without external carbon source is advantageous in micro-fabrication in that graphene is likely covered by an overlayer during the lithographic processing, which blocks the feed pathway of any external carbon source.

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21The effective dosage per second is much less than $\frac{2 \times 10^{14}}{cm^2}$ due to three factors. First, the power that is converted to the ion energy in the dark sheath is over-estimated because of the transfer efficiency. Second, in 17 Pa, the mean free path of Ar$^+$ ions is about 1 mm, much shorter than the dark sheath width. Multiple collisions that ions experience effectively reduce their energy. Third, the energy threshold for an Ar$^+$ ion to displace a carbon atom is 47 eV. In our setup, Ar$^+$ ions of energy less than 30 eV dominate. Therefore, majority of ions have no impact on graphene.