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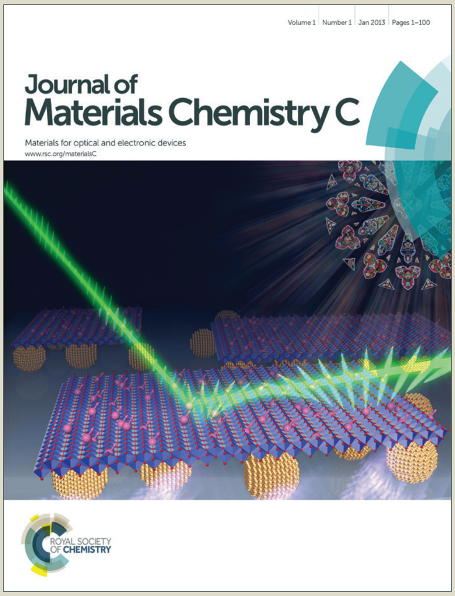

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Tuning the electrical properties of exfoliated graphene layers by deep ultraviolet irradiation

M. Z. Iqbal, M. F. Khan, M. W. Iqbal and Jonghwa Eom*

Department of Physics and Graphene Research Institute, Sejong University, Seoul 143-747, Korea

*Corresponding author. Tel: +82-2-3408-3794 E mail: eom@sejong.ac.kr

It is a fascinating subject in graphene-based nano- and optoelectronic devices to tune the electrical properties of graphene layers, while sustaining thier unique band structure and their electrical holdings. Here, we report the tuning of electronic properties of single-, bi-, and trilayer mechanically exfoliated graphenes by deep ultraviolet irradiation (DUV). Raman spectroscopy and electrical transport measurements revealed that DUV light imposes p-doping to single-, bi-, and trilayer graphenes. The shift of G and 2D peak wavenumber and intensity ratio of single-, bi-, and trilayer graphenes are examined as a function of irradiation time. The Dirac points shift are analyzed as a function of irradiation time, which indicates the p-type doping effect for all single-, bi-, and trilayer graphenes. Our investigation demonstrates that DUV irradiation is a non-destructive approach to tailor the electrical properties of single-, bi-, and trilayer graphenes, while maintaining their important structural and electrical characteristics.

Introduction

Graphene, a two-dimensional sp^2-hybridized network of carbon atoms with perfect crystalline structure, enables remarkable exploration of fundamental physics as well as the exciting potential applications for electronic devices.[1, 2] In addition, graphene possesses marvelous attentions due to its unique electronic properties such as ambipolar transport with high charge carrier mobility and transparency.[3-6] These distinctive properties made graphene as an ideal candidate for the application of transparent conducting electrode like other carbon-based materials.[7-9] The structural and electrical properties of graphene are extremely affected by chemical doping, metal doping, and high energy electron or ion irradiations.[10-13] The controlled tunability is essential to make graphene devices more suitable for technological applications. Chemical doping is one of the most common approach for the modification of structural and electrical properties, however it produces structural disorders.[14-18] The high energy electron or ion irradiations also induce the large structural defects in graphene.[12, 19-24] The exchange of carbon atoms in the graphene lattice with dopant atoms can be another route, but these substitutional doping may have some disadvantages that cause the disorder in honeycomb structure and potentially reduces the carrier mobility of the graphene.[12, 25, 26] The application of oxygen plasma treatment is able to tailor the electrical properties of graphene through oxidation, nevertheless the induced structural disorders are irrepressible.[27, 28] However, these complications can be avoided by employing an alternative approach while preserving the honeycomb structure of graphene. The theoretical predication suggests that the modification of graphene with photo oxidation is a conceivable approach to tune the properties of graphene.[29-31] Some experimental studies have gone so far to investigate the molecular photo-assisted desorption and absorption with ultraviolet light effect on pristine and functionalized graphene layers.[32-34] The interaction of oxygen with graphene was studied previously under the condition of atmospheric oxygen and dry O_2 gas flow.[35] The hole doping of graphene was observed for the exposure of dry O_2 or atmospheric oxygen and the doping was reversible by dry Ar gas flow. However, the experiment showed irreversible behavior with dry N_2 gas flow and that the hole doping effect becomes more stronger and irreversible in the presence of moisture. However, a comprehensive methodology is still demanded for the tunability of graphene to flourish applications.

In this work we concentrated on a nondestructive and less-defect-induced modulation of graphene with different number of layers. Recently graphene-based research has focused on investigating the modification of electrical properties as a function of number of graphene layers. The electronic structure and morphology becomes different by increasing the number of graphene layers.[36] For example, the electronic structure of single-layer graphene (SLG) is distinct from bilayer graphene (BLG), and trilayer graphene (TLG). The study of different number of graphene layers is very intriguing, because the optical, structural, and electrical properties obviously change from a linear dispersion relation for single-layer graphene to a parabolic dispersion relation for bi- or trilayer graphene. In addition stacking of more graphene layers reduces the sheet resistance, making graphene a more suitable material for conducting electronic devices.[37-39] The transparency of graphene layers decreases by 2.3 % as the number of layers increases by in the visible region, so transparency more than 90% can be still achievable up to three layers of graphene.[3]

Here we report the tuning of electronic properties of mechanically exfoliated single-, bi-, and trilayer graphenes by DUV irradiation without significantly degrading its charge carrier mobility. Raman spectroscopy and charge transport measurements revealed that the DUV irradiation effect tunes the properties of single-, bi-, and trilayer graphene layers towards p-type doping. The shift of charge neutrality point for single-, bi-, and trilayer graphenes are investigated as a function of DUV irradiation time. It is found that the charge neutrality point is shifted toward positive gate voltage with increase of DUV irradiation time for single-, bi-, and trilayer graphenes, which evidently confirms the p-doping effect. The results indicate that DUV irradiation is a non-destructive approach to tune the properties of single-, bi-, and trilayer graphenes, while preserving the optical, structural and electrical assets.

Device fabrication and characterization

Preparation of graphenes

The SLG, BLG, and TLG films were obtained by mechanical exfoliation of natural graphite flakes by using the adhesive tape and then transferred onto a 300 nm SiO_2 supported with Si wafer. The layer numbers of the graphene films were identified by optical microscope and Raman spectroscopy as shown in Fig. 1a, b and c. The big patterned electrodes (Cr/Au of 5/30 nm) for all SLG, BLG, and TLG were made by photolithography on Si/SiO_2 substrate. The contact electrodes were made by e-beam lithography and evaporation of Cr/Au (6/50 nm) for electrical transport measurements. The device structures of SLG, TLG, and BLG are shown in Fig. 1a, b and c, respectively.

Doping with DUV irradiation and characterization

The modification of graphene properties by DUV was investigated by transport measurements and Raman spectroscopy. The dominant wavelength of DUV light is 220 nm and its average intensity is 11 mW/cm^2. The gate voltage dependent resistivity measurements and Raman spectroscopy were implemented on pristine SLG, BLG, and TLG devices and the same devices after DUV treatment. Raman spectra were performed with a Renishaw micro spectrometer with the laser wavelength of 514.5 nm over wavenumber from 1100 to 3200 cm^{-1}. The laser power was kept at ~1.0 mW to elude the introduction of defects and local heating. The SLG, BLG, and TLG were exposed with DUV light for certain period of time and four terminal transport measurements were performed using a standard lock-in amplifier technique at room temperature in vacuum.

Results and discussion

The optical microscope images of the SLG, BLG and TLG field effect transistor devices fabricated on SiO_2/Si substrates are shown after photolithography and e-beam lithography in Fig. 1a, b, and c, respectively. Initially the number of graphene layers was identified on the basis of the optical contrast and then was further confirmed by Raman spectroscopy.[40, 41] Figure 1d shows the Raman spectra of pristine SLG, BLG, and TLG. The ratio of I_{2D}/I_G peaks are found to be 5.1, 1.34 and 0.96 for pristine SLG, BLG and TLG, respectively. The characteristic G and 2D peaks for pristine SLG appear around 1583.8 and 2680.2 cm^{-1}, for pristine BLG at 1584.75 and 2699.85 cm^{-1}, whereas the G and 2D peaks for pristine TLG appear around 1581.57 and 2703.18 cm^{-1}, respectively. A broad 2D peak is fitted with four Lorentzian curves as shown in Fig. 1e, which confirms the bilayer graphene. Figure 1f shows the six Lorentzian curve fitting of a broad 2D band of TLG. The absence of D peak in pristine SLG, BLG, and TLG is an indication of high quality graphenes.

Figure 2a shows the Raman spectra of SLG before and after different period of DUV irradiation time (5, 10, 15, and 30 min). The D peak is not observed even with increasing irradiation time, which indicates that DUV irradiation does not change the lattice structure of graphene. The upward shifting of G and 2D peak positions is responsible for p-doping as shown in Fig. 2b. It is already reported that the shifting of G and 2D peak positions toward lower wavenumber or upper wavenumber is attributed to n-type or p-type doping, respectively.[19, 20, 42-44] Raman spectra of BLG for pristine and after different period of irradiation time are shown in Fig. 2c. The intensity of D peak is not increased in BLG after DUV irradiation for different time duration as shown in Fig. 2c. The upward shifting of G and 2D peak positions is shown in Fig. 2d for clarity. The shifting of G peak position toward higher wavenumber is attributed to p-doping of bilayer graphene. Figure 2e shows the Raman spectra of TLG for pristine and after different period of irradiation time. The upward shifting of G and 2D peak positions is shown in Fig. 2f for clarity. The shifting of G peak positions toward higher wavenumber is also attributed to p-doping for trilayer graphene.

The shift of G and 2D peak positions of SLG, BLG, and TLG before and after DUV irradiation are summarized in Fig. 3a, b, and c, respectively. For all SLG, BLG, TLG, the G and 2D peak positions are shifted to higher wave number which attributed to p-doping. The general trend of the shifting of peak positions is similar for different number of graphene layers. Figure 3d shows the intensity ratio of 2D and G peaks (I_{2D}/I_G) before and after DUV irradiation for different periods for SLG, BLG, and TLG. The I_{2D}/I_G of SLG shows slight decrease with the increasing irradiation time, whereas I_{2D}/I_G in BLG, and TLG does not change significantly with increasing irradiation time. The decrease in the I_{2D}/I_G ratio may be due to the increase in the carrier density of graphene, as previously reported.[45]

The p-doping effect of exfoliated SLG, BLG, and TLG are further confirmed by Dirac point measurements. The resistivity as a function of gate voltage (V_g) before and after DUV irradiation treatment of SLG, BLG, and TLG is shown in Fig. 4. Figure 4a shows the Dirac point (V_{Dirac}) of SLG after DUV treatment for different period of time. After taking the measurements of pristine graphene, the devices were then exposed to DUV light for the desired amount time and then the electrical transport measurements were performed. The V_{Dirac} of the pristine SLG was found around V_g = -16 V and the V_{Dirac} shifted towards positive V_g with increasing DUV exposure time. It reached at V_g = 12 V after 30 minute, indicating p-type doping in exfoliated SLG. Figure 4b and c show the V_{Dirac} of BLG and TLG for different period of time. The V_{Dirac} of the pristine BLG was found around V_g = -15 V and V_g = -36 V for TLG. The V_{Dirac} shifted towards positive V_g with increasing DUV exposure time and reached at V_g= 8 V and -11V, respectively after 30 minutes, indicating p-type doping in exfoliated BLG and TLG.

The gradual shifts of V_{Dirac} with DUV irradiation time for SLG, BLG and TLG are shown in Fig. 5a. Figure 5b shows the change of charge carrier density (Δn) as a function of irradiation time. The charge carrier density is obtained from the relation $\Delta n= C_g|V_{Di} - V_{Dp}|/e$, where C_g is the gate capacitance, 115 aF/μm^2, obtained for our SiO_2/Si substrate. V_{Dp} represents the Dirac point of pristine SLG, BLG, and TLG, whereas V_{Di} is the Dirac point after different period of DUV irradiation time.[46] The Δn increases with the increasing DUV irradiation time. These modifications of charge carrier density are related to the tunability of Fermi level of graphene layers. The change of charge carrier densities of SLG, BLG and TLG shows a very similar trend as shown in Fig. 5b.

The mobility (μ) of different graphene layers was obtained by taking the slop of the conductivity around Dirac points before and after irradiation for different period of time using the relation $\mu=(1/C_g)(\delta\sigma/\delta V_g)$, where σ is the conductivity of graphene layers and V_g is the back gate voltage. Figure 5c shows the mobility of pristine and DUV doped single, bi- and trilayer graphenes. The mobilities are found to be sustainable of all graphene layers after different period of irradiation time. These results are in line with previously reported transport measurements of DUV irradiation on chemical vapor deposition grown single layer graphene.[44]

The hole formation in graphene is the result of photo-oxidation of oxygen molecules under DUV irradiation. It has been found from the theoretical investigations that oxygen molecules dissociate in the existence of UV light.[47] These dissociated molecules lead to the generation of oxygen containing groups that can easily attach to the most stable sites of graphene and offer a favorable conditions for p-doping of graphene.[35, 47, 48] During the photo-oxidation process with DUV light, the O_2 molecules absorb 220 nm photons to form two oxygen ions in the ground state, as the photon energy is enough to break the molecular bond. These dissociated oxygen ions attach to the most stable adsorption sites of the graphene.[49] The photon energy of DUV light is inversely proportional to the wavelength. Therefore the dissociation of oxygen molecules to form oxygen atoms will be smaller with increasing wavelength of light source. Since the total amount of DUV light determines the concentration of carriers in the graphene, for longer irradiation time with short wavelength light source makes an effective enhancement of the carrier concentration leading to a higher doping level. Recently, Y. Mulyana et al. have reported the oxidation of bilayer graphene through ultraviolet light treatment in ozone atmosphere.[50] Using X-ray photoelectron spectroscopy they have confirmed the π orbitals of graphene make C-O bonds. They have also found that these C-O bonds are thermally unstable. When the graphene devices were annealed in reductive hydrogen and argon environment. The hydrogen reacted with oxygen atoms to form H_2O, which caused C-O bonds to break, leaving the π orbitals to be unbounded and restored the graphene characteristics to its pristine level.

Conclusion

We have investigated the tunability of mechanically exfoliated single-, bi-, and trilayer graphene layers using DUV irradiation in atmospheric environment for different period of time. The Raman spectroscopy and transport measurements revealed that DUV irradiation induces the p-doping effect for all single-, bi-, and trilayer graphene layers. The shift of G and 2D peak position and intensity ratios for single-, bi-, and tri-layer graphene layers were examined as a function of irradiation time. The shift in the G and 2D bands in the Raman spectra towards higher wavenumber suggested p-doping in the graphene devices. The absence of D peak in Raman spectra after irradiation indicates the nondestructive modulation of graphene layers. The Dirac point shifted towards positive gate voltage for single-, bi-, and trilayer graphenes with increasing DUV irradiation time, which was attributed to the strong p-doping effect. Thus DUV irradiation significantly modulates the Fermi level of graphene layers while sustaining their mobility. The results indicate that DUV irradiation can significantly tailor the properties of graphene layers without degrading structural and electrical characteristics. Doping using DUV irradiation is believed to be a suitable photo-assisted scheme for modulating the electronic properties of graphene layers for future graphene-based transparent electronic devices.

Acknowledgments

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Figures captions

Figure1. Optical microscope images of (a) single layer (b) bilayer and (c) trilayer exfoliated graphene devices. (d) Raman spectra of pristine single-, bi-, and trilayer graphene. (e) Lorentzian curve fitting of 2D peak for bilayer and (f) fitting for trilayer graphene.

Figure 2. Raman spectra of (a) pristine and DUV irradiated SLG for time of 5, 10, 15, and 30 min, (b) G and 2D peaks of pristine and DUV modified SLG, (c) pristine and DUV irradiated BLG for time of 5, 10, 15, and 30 min, (d) G and 2D peaks of pristine and DUV modified BLG, (e) pristine and DUV irradiated TLG for time of 5, 10, 15, and 30 min, (f) G and 2D peaks of pristine and DUV modified TLG.

Figure 3. Raman shift of G and 2D peak positions of (a) SLG, (b) BLG, and (c) TLG as a function of DUV irradiation time. (d) G and 2D peak intensity ratio (I_{2D}/I_G) of SLG, BLG, and TLG for pristine and different periods of DUV irradiation time.

Figure 4. Resistivity as a function of back gate voltage (V_g) for (a) pristine and DUV irradiated SLG after different period of irradiation, (b) pristine and DUV irradiated BLG after different period of irradiation, (c) pristine and DUV irradiated TLG after different period of irradiation.

Figure 5. (a) The shift of Dirac point positions with different period of irradiation time for SLG, BLG, and TLG. (b) Change of charge carrier density (Δn) as a function of irradiation time for SLG, BLG, and TLG. (c) Electron and hole mobilities as a function of irradiation time for SLG, BLG, and TLG.

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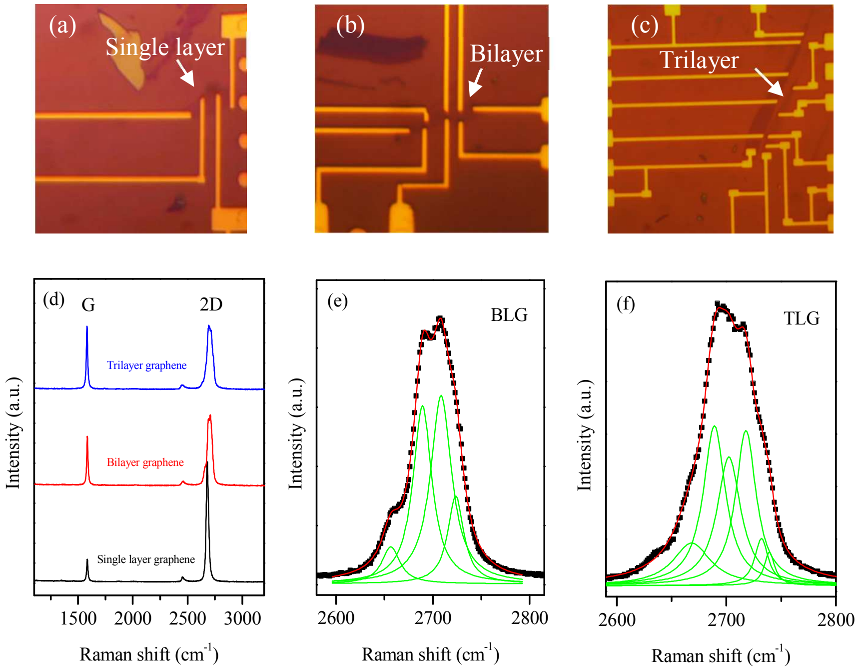
(a)
Single layer
(b)
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(c)
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(d)
G
2D
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Bilayer graphene
Single layer graphene
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2000
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3000
Raman shift (cm^{-1})
(e)
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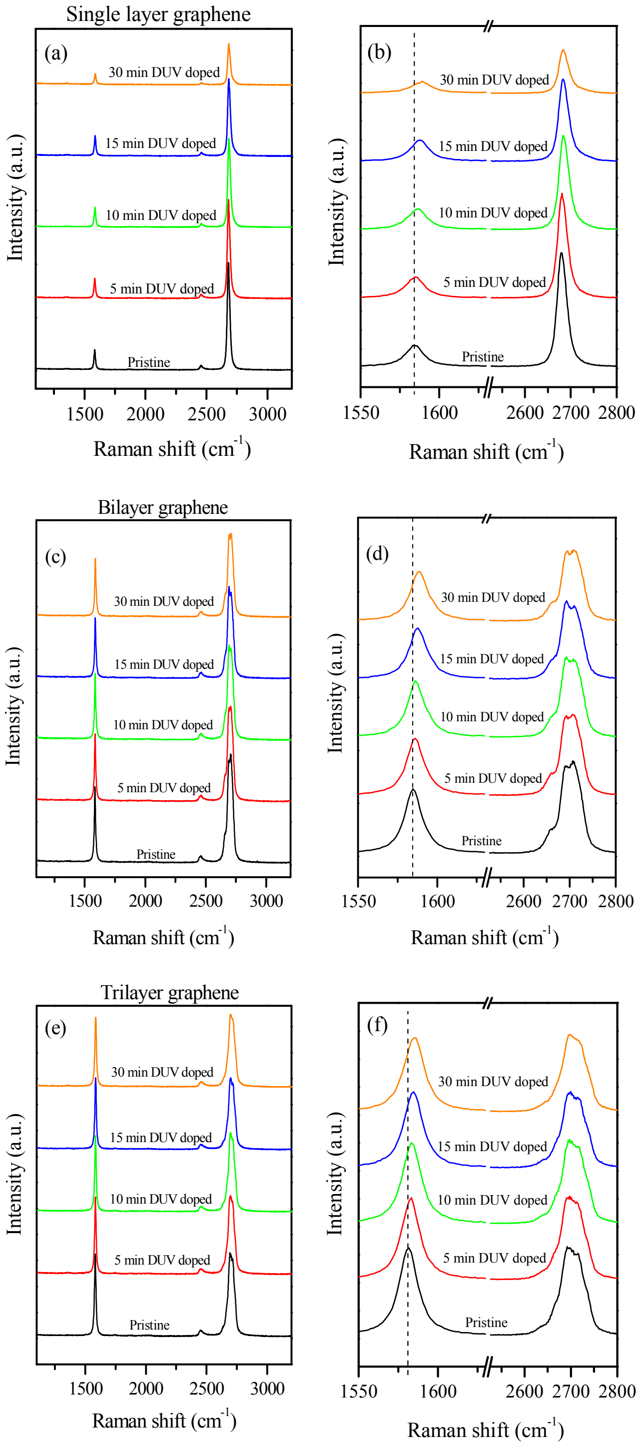
Raman shift (cm^{-1})

Fig. 1


Single layer graphene
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15 min DUV doped
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Pristine
Intensity (a.u.)
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Raman shift (cm^{-1})
(b)
30 min DUV doped
15 min DUV doped
10 min DUV doped
5 min DUV doped
Pristine
Intensity (a.u.)
1550 1600 2600 2700 2800
Raman shift (cm^{-1})
Bilayer graphene
(c)
30 min DUV doped
15 min DUV doped
10 min DUV doped
5 min DUV doped
Pristine
Intensity (a.u.)
1500 2000 2500 3000
Raman shift (cm^{-1})
(d)
30 min DUV doped
15 min DUV doped
10 min DUV doped
5 min DUV doped
Pristine
Intensity (a.u.)
1550 1600 2600 2700 2800
Raman shift (cm^{-1})
Trilayer graphene
(e)
30 min DUV doped
15 min DUV doped
10 min DUV doped
5 min DUV doped
Pristine
Intensity (a.u.)
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Raman shift (cm^{-1})
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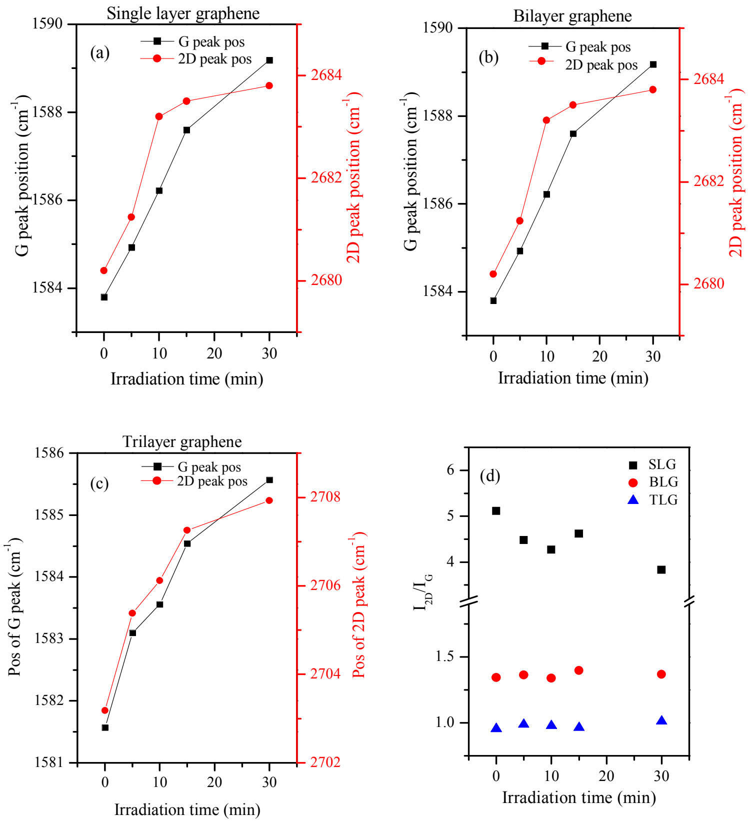
Raman shift (cm^{-1})

Fig. 2


Single layer graphene
(a)
G peak pos
2D peak pos
G peak position (cm^{-1})
2D peak position (cm^{-1})
1584
1586
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1590
2680
2682
2684
0
10
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30
Irradiation time (min)
Bilayer graphene
(b)
G peak pos
2D peak pos
G peak position (cm^{-1})
2D peak position (cm^{-1})
1584
1586
1588
1590
2680
2682
2684
0
10
20
30
Irradiation time (min)
Trilayer graphene
(c)
G peak pos
2D peak pos
Pos of G peak (cm^{-1})
Pos of 2D peak (cm^{-1})
1581
1582
1583
1584
1585
1586
2702
2704
2706
2708
0
10
20
30
Irradiation time (min)
(d)
SLG
BLG
TLG
I$_{2D}$/I$_G$
1.0
1.5
4
5
6
0
10
20
30
Irradiation time (min)

Fig. 3

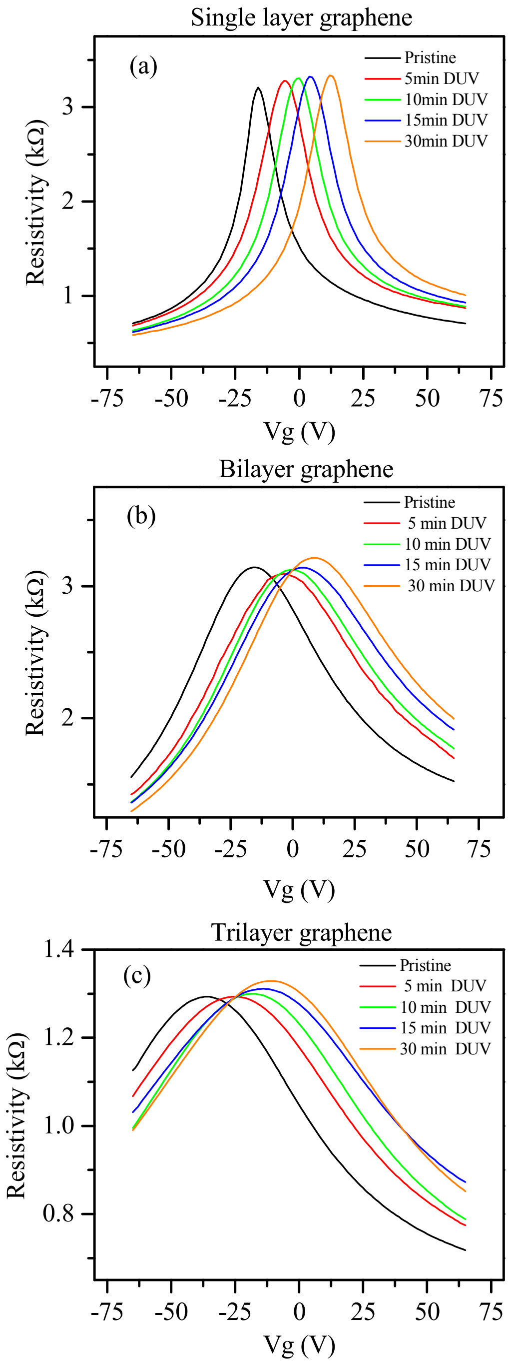

Single layer graphene
(a)
Pristine
5min DUV
10min DUV
15min DUV
30min DUV
Resistivity (kΩ)
1
2
3
-75
-50
-25
0
25
50
75
Vg (V)
Bilayer graphene
(b)
Pristine
5 min DUV
10 min DUV
15 min DUV
30 min DUV
Resistivity (kΩ)
2
3
-75
-50
-25
0
25
50
75
Vg (V)
Trilayer graphene
(c)
Pristine
5 min DUV
10 min DUV
15 min DUV
30 min DUV
Resistivity (kΩ)
0.8
1.0
1.2
1.4
-75
-50
-25
0
25
50
75
Vg (V)

Fig. 4

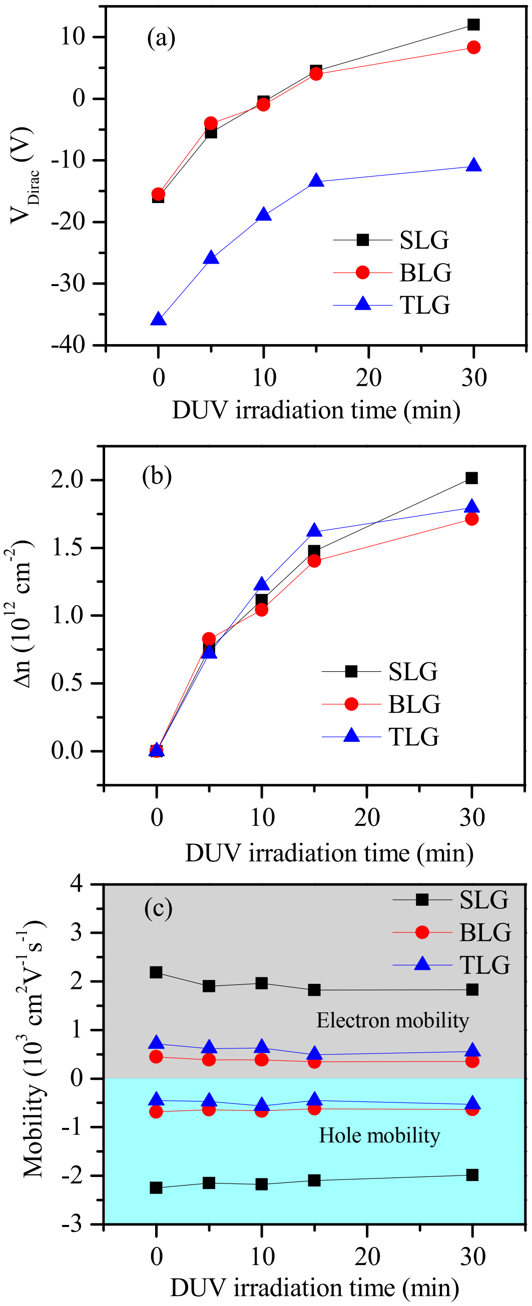
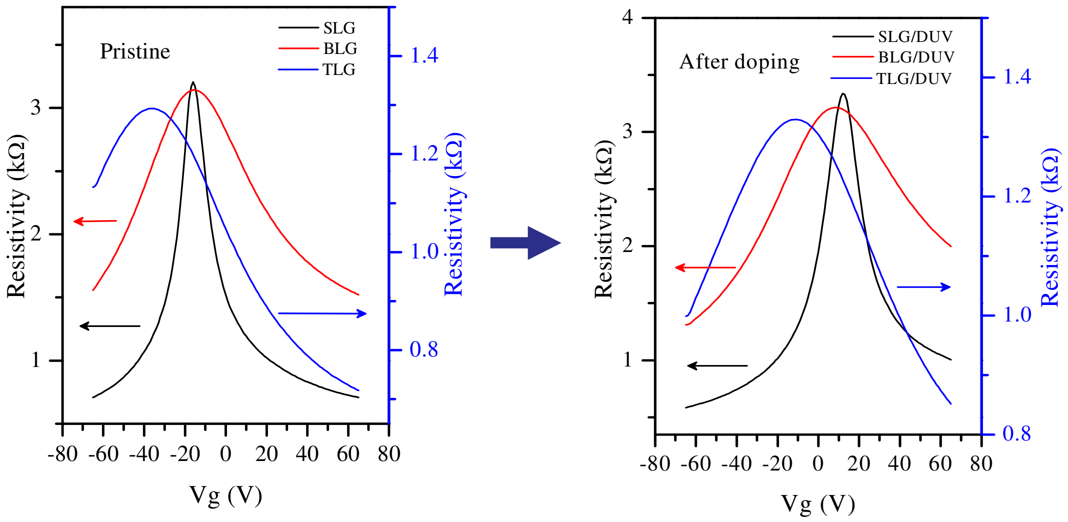

(a)
V_{Dirac} (V)
10
0
-10
-20
-30
-40
0
10
20
30
DUV irradiation time (min)
SLG
BLG
TLG
(b)
Δn (10^{12} cm^{-2})
2.0
1.5
1.0
0.5
0.0
0
10
20
30
DUV irradiation time (min)
SLG
BLG
TLG
(c)
Mobility (10^3 cm^{2}V^{-1}s^{-1})
4
3
2
1
0
-1
-2
-3
SLG
BLG
TLG
Electron mobility
Hole mobility
0
10
20
30
DUV irradiation time (min)

Fig. 5


Pristine
SLG
BLG
TLG
Resistivity (kΩ)
Resistivity (kΩ)
Vg (V)
-80 -60 -40 -20 0 20 40 60 80
1
2
3
0.8
1.0
1.2
1.4
After doping
SLG/DUV
BLG/DUV
TLG/DUV
Resistivity (kΩ)
Resistivity (kΩ)
Vg (V)
-80 -60 -40 -20 0 20 40 60 80
1
2
3
4
0.8
1.0
1.2
1.4