PCCP

PAPER

Check for updates

Cite this: Phys. Chem. Chem. Phys., 2017, **19**, 27353

Received 25th May 2017, Accepted 17th September 2017

DOI: 10.1039/c7cp03523c

rsc.li/pccp

1. Introduction

Accompanied with the quick development of high-quality largearea chemical vapour deposition (CVD)-grown graphene film,¹⁻⁶ properly cutting it into certain micro/nanostructures plays an important role in its applications in electronics and optoelectronics.1-13 Photo-/electron-beam lithography and direct laser writing are the two most popularly used approaches for micro/nanoscale graphene patterning.³⁻⁵ To overcome the obstacles of resist contamination and substrate damage, some new alternatives such as TiO2-film-based photocatalysis, soft lithographic patterning, and resist-free reactive ion etching (RIE) were proposed.⁷⁻¹² Recently, we proposed a solution toward resist-free, substrate non-damaging, and cost effective graphene patterning through stencil masks by magneticassisted UV ozonation under 172 nm irradiation of a xenon excimer lamp.13 In this process, the electrically neutral but paramagnetic oxygen radicals (O(³P)) and molecules $X^{3}\Sigma_{g}^{-}$ are

Exploring the working mechanism of graphene patterning by magnetic-assisted UV ozonation[†]

Huan Yue,^a Haihua Tao, ⁽¹⁾*^{ab} Yixuan Wu,^a Shubin Su,^a Hao Li,^a Zhenhua Ni^c and Xianfeng Chen*^a

When assisted with an inhomogenous vertical magnetic field, ultraviolet (UV) ozonation turns directional and is testified to be applicable to graphene patterning. Using a more cost-effective low-pressure mercury lamp, we further explore the underlying working mechanism by changing oxygen content, introducing reactive ozone or inert nitrogen molecules, and study the lateral under-oxidation impeded Dirac point shifts for a graphene field-effect transistor under UV irradiation. The paramagnetic oxygen molecule $X^3\Sigma_g^-$ accelerates toward graphene with the magnetic moment aligned parallel to the magnetic field. The O(³P) atoms, stemming from such a directional oxygen molecule, have a high initial velocity before being further accelerated, and therefore enhance the oxidation capability compared with those from weak diamagnetic ozone molecules. Intermolecular or atomic-molecular collisions between the high-speed oxygen molecules/atoms and the randomly moved weak diamagnetic molecules, including nitrogen and ozone, appear crucial in deteriorating graphene patterning by increasing the lateral under-oxidation. This study may shed light on our understanding of graphene patterning by magnetic-assisted UV ozonation.

magnetized, and they convert into directional photochemical reaction due to attractive magnetic forces toward graphene film in an inhomogeneous vertical magnetic field ($B_z = 0.31 \text{ T}$, $\nabla B_z =$ 90 T m⁻¹).^{13–16} The magnetic-assisted UV ozonation was testified to have a capability of patterning CVD–grown graphene film with an initial oxygen pressure of 10 Pa.¹³ However, because of the strong absorption of oxygen molecules $X^3\Sigma_g^-$ at 172 nm,^{17,18} a slight oxygen increase can severely deteriorate graphene patterning by weakening the photochemical reaction. Moreover, a minimum of 60 kPa nitrogen gas, even though inert under UV irradiation, is necessary to illuminate the xenon excimer lamp.^{13,19} These two traits make it hard to grasp the essential dynamic kinetics in the magnetic-induced directional photochemical etching of graphene.

Compared to the xenon excimer lamp, a cost-effective and low-power-consumption low-pressure mercury lamp is more widely used to modify graphene or improve graphene-based electronic properties in UV ozonation.^{20–24} Using a vacuum-type machine, oxygen can be precisely controlled to work at a certain atmospheric pressure after first vacuuming the chamber, since such a mercury lamp can work in a low vacuum condition (a few Pascals).²² Moreover, the photochemical oxidation intensity changes gently with oxygen content because of its low optical absorption at 184.9 nm.^{12,13,22}

In this report, we further explore the feasibility and underlying working mechanism of graphene patterning by magneticassisted UV ozonation under irradiation of the low-pressure



View Article Online

^a State Key Laboratory of Advanced Optical Communication Systems and Networks, Institute of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai 200240, China. E-mail: tao.haihua@sjtu.edu.cn, xfchen@sjtu.edu.cn

^b State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China

^c Department of Physics, Southeast University, Nanjing 211189, China

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/ c7cp03523c

mercury lamp. Tuning oxygen content, introducing ozone or nitrogen molecules in the magnetic-assisted UV ozonation can all affect graphene patterning. Experimental analyses indicate that the O(³P) atom has an initial velocity toward graphene after photodissociation from the accelerated oxygen molecule $X^{3}\Sigma_{e}^{-}$ in the vertical magnetic field. As a consequence, its oxidation capability is enhanced compared to that converted from $O(^{1}D)$ in the photolysis of randomly moved ozone molecule. Furthermore, intermolecular or atomic-molecular collisions between the directional oxygen molecules/atoms and the randomly moved weak diamagnetic nitrogen or ozone molecules become crucial in deteriorating the graphene patterning because of the increasing lateral diffusion and dissipation. Analyses of the electrical transport for graphene field-effect transistors (FET) reveal that ozone diffusion increases, and the Dirac point-shift toward the negative gate-voltage (n-doping) under UV irradiation is retarded by its lateral under-oxidation.

2. Experimental

CVD grown graphene film transferred onto the SiO₂/Si substrate (p⁺⁺, 0.001–0.004 ohm cm) was used for microstructure patterning as previously reported.^{13,25,26} A home-designed onechamber UV ozonation vacuum machine was used for graphene patterning under irradiation by a low-pressure mercury lamp. Oxygen and nitrogen gases can be individually controlled for feeding into the chamber after first pumping it down to 2 Pa. The UV lamp has an electric power of 200 W and a fixed distance of 20 mm to the graphene film. A cube magnet was placed underneath the SiO₂/Si substrate to provide an inhomogeneous vertical magnetic field ($B_z = 0.31$ T, $\nabla B_z = 90$ T m⁻¹) on the graphene surface.¹³ Graphene patterns were attained through the same magnetic steel mask (a hexagonal lattice of holes with a constant of 220 µm and rib width of 29 ± 2 µm at the surface).¹³ Three cycles of consecutive room-temperature UV ozonation treatments (10 min per cycle, with the same initial oxidation parameters) were carried out, if not otherwise specified. A home-made ozone generator was used to provide an oxygen-ozone mixture (O₃, 8% by volume). Graphene FET arrays were fabricated by first evaporating Cr/Au (5 nm/95 nm thick) metal contacts through a 20 μ m-thick steel mask and then patterning graphene film by the magnetic-assisted UV ozonation.¹³

The morphologies of graphene patterns were characterized using an optical microscope (Leica DM 4000) and a highly resolved scanning electron microscopy (SEM, Zeiss Ultra Plus) system under 3 kV biases. The lateral under-oxidation of graphene patterns was characterized *via* confocal micro-Raman spectroscopy (Senterra R200-L) under 532 nm excitation ($50 \times$ objective, 1.2 µm spot size) with a scanning step size of 1 µm. The electrical transport property was measured in a high vacuum chamber without or under irradiation by the 253.7 nm mercury line combined with the Keithley 6430 and 2400 electronic measurement system.^{13,22} When combined with a micro-Raman system (Jovin Yvon Labram 800002), the localized UV irradiation induced a Dirac point-shift toward n doping was measured in a flowing nitrogen atmosphere under irradiation by a 325 nm HeCd laser. The UV laser has a power of 120 µW, and its spot size is 10 µm.

3. Results and discussion

3.1 Influence of O_2 , O_3 , and N_2 content

As shown in the SEM topographical images of Fig. 1(a)-(d), changing the oxygen content can have a great impact on graphene patterning when an external magnetic field is applied in UV ozonation. The white dotted circles represent the stencil mask profile. When decreasing oxygen from 5 kPa *via* 2 kPa, 1 kPa to 0.5 kPa, we can see that a content of 2 kPa oxygen is



Fig. 1 SEM topographical images of the graphene pattern varying with an oxygen content of (a) 5 kPa, (b) 2 kPa, (c) 1 kPa, and (d) 0.5 kPa in the magneticassisted UV ozonation. (e) Micro-Raman map of the D band intensity in the region denoted by the red rectangle in (b), and (f) its Raman spectrum evolution for dots outlined with the black rectangle in (e). Red dotted lines represent graphene edges. a.u. indicates arbitrary unit.

optimal for obtaining the best conformal pattern. An increase or decrease of oxygen content can cause over-etching of graphene edges and weaken the oxidation intensity by leaving more graphene wrinkle residues.^{13,27} It is notable that the multilayer nucleii cannot be etched off under irradiation of the low-pressure mercury lamp because of its weak etching intensity compared to that of the xenon excimer lamp.

For the best conformal graphene, micro-Raman defect (D) band characterization for the region outlined with the red rectangle is shown in Fig. 1(e). Specific Raman spectrum evolution in Fig. 1(f) for dots outlined with the black rectangle indicates that the lateral under-oxidation is up to 9 μ m because of molecular/atomic diffusion underneath the mask. The lateral under-oxidation is larger than that obtained in a low pressure oxygen atmosphere (10 Pa) under irradiation of the xenon excimer lamp.

When the oxygen-ozone mixture is used to substitute oxygen, the microstructure graphene pattern appears over-etched (see Fig. 2(a)) after the same UV ozonation treatment as that shown in Fig. 1(b). The pattern degrades with part of its ribs broken as indicated by the blue arrows. In addition, an increase in graphene residues manifests the weakening oxidation intensity. When reducing the photochemical treatment to two cycles (10 min per cycle), the graphene pattern changes with the decreasing oxygenozone content (1 kPa, 0.5 kPa and 0.2 kPa in sequence) as shown in the SEM topographical images of Fig. 2(b)-(d). A conformal pattern is attained when reducing the mixture down to 0.5 kPa, though quite a bit of graphene wrinkle residues show up. Either an increase or decrease of the oxygen-ozone mixture leads to severe over-etching and blurring of graphene edges. Moreover, they also result in an increment of residues, demonstrating a continuous weakening of photochemical oxidation.

The graphene pattern in Fig. 2(c) is characterized by the micro-Raman mapping as shown in Fig. 2(e) and (f) for the

red-outlined region. The D band mapping and its corresponding Raman spectrum evolution for the black-outlined dots show that all graphene underneath the mask is oxidized.

When nitrogen molecules, which have a bond energy of 9.8 eV, are introduced into the magnetic-assisted UV ozonation, they can greatly affect graphene patterning as shown in Fig. 3 even though the 184.9 nm irradiation (single photon energy, 6.71 eV) is too low to dissociate them.²⁸ Fig. 3(a) shows a conformal graphene pattern etched by the magnetic-assisted UV ozonation with an initial oxygen pressure of 2 kPa, a zoomout SEM topographical image of Fig. 1(b). Keeping the oxygen pressure constant, an addition of 20 kPa nitrogen can weaken the oxidation intensity by shrinking the graphene pattern and leaving more residues, as shown in Fig. 3(b). Upon further increasing the nitrogen content to 40 kPa, the graphene pattern appears under-etched because of continuously weakening oxidation intensity (see Fig. 3(c)). Therefore, nitrogen molecules, though chemically inert in the directional photochemical oxidation, can impede graphene oxidation via some physical interaction mechanism as discussed in the next subsection.

It should be noted that the quality of graphene patterning deteriorates when no vertical magnetic field is applied during UV ozonation for the three cases discussed above (see ESI,† Fig. S1–S3).

3.2 Dissociation and collision model for the directional photochemical oxidation

In the traditional UV ozonation, a sequence of photochemical reactions occurs as described in eqn (1)–(5).^{20–22,29–31} Under irradiation by the low pressure mercury lamp, the paramagnetic ground state triplet oxygen molecule $X^3\Sigma_g^-$ dissociates into two ground state O(³P) atoms by absorbing photons at 184.9 nm. Then, the O(³P) atoms can react with oxygen molecules $X^3\Sigma_g$ to form ozone, an unstable molecule that can further dissociate



Fig. 2 SEM topographical images of the graphene pattern etched by the magnetic-assisted UV ozonation with (a) $2 \text{ kPa} O_2/O_3$ mixture after three-cycle treatment, and (b) 1 kPa, (c) 0.5 kPa, (d) $0.2 \text{ kPa} O_2/O_3$ mixture after two-cycle treatments. (e) Micro-Raman map of the D band intensity in the region denoted by the red rectangle in (c), and (f) its Raman spectrum evolution for dots outlined with the black rectangle in (e).



Fig. 3 SEM topographical images of the graphene pattern varying with nitrogen content in the magnetic-assisted UV ozonation. (a) 2 kPa O_2 ; (b) 2 kPa $O_2 + 20$ kPa N_2 ; (c) 2 kPa $O_2 + 40$ kPa N_2 .

with products mainly composed of the diamagnetic singlet oxygen molecule $\alpha^1 \Delta_g$ and $O(^1D)$ atom under irradiation at 253.7 nm. The electronically excited state $\alpha^1 \Delta_g$ and $O(^1D)$ can quickly convert into the ground state $X^3 \Sigma_g^-$ and $O(^3P)$, respectively, *via* nonreactive quenching collisions.^{31–33} Furthermore, in the abovementioned photochemical process, ozone generation and dissociation is thirty times higher than the dissociation of oxygen molecules.³⁰

Notably, for UV ozonation under irradiation of a xenon excimer lamp, a mixture of $O({}^{3}P)$ and $O({}^{1}D)$ atoms forms when absorbing photons at 172 nm as described in (eqn (1')).^{29,31}

$$O_2(X^3\Sigma_g^-) + h\nu(175.0 < \lambda \le 242.4 \text{ nm}) \to 2O(^3P)$$
 (1)

$$O_2(X^3\Sigma_g^-) + h\nu(\lambda \le 175.0 \text{ nm}) \to O(^1D) + O(^3P)$$
 (1')

$$O(^{3}P) + O_{2}(X^{3}\Sigma_{g}^{-}) + M \rightarrow O_{3} + M(N_{2} \text{ or } O_{2} \text{ or } O_{3})$$
(2)

$$O_3 + h\nu(\lambda < 310 \text{ nm}) \rightarrow O_2(\alpha^1 \Delta_g) + O(^1D)$$
 (3)

$$O(^{1}D) + M \rightarrow O(^{3}P) + M$$
(4)

$$O_2(\alpha^1 \Delta_g) + M \rightarrow O_2(X^3 \Sigma_g^-) + M$$
 (5)

The singlet $O({}^{1}D)$ and triplet $O({}^{3}P)$ atoms exhibit diamagnetic and paramagnetic properties, respectively, according to their individual electron configurations. Because of the severe collision quenching of $O({}^{1}D)$ atom,^{31–33} the ground-state $O({}^{3}P)$ atom acts as the major oxidant that can oxidize graphene into carbon monoxide (CO) or carbon dioxide (CO₂) molecule, as described in eqn (6). The oxidation intensity is related to the collision rate Z_{12} between the $O({}^{3}P)$ atom and the carbon atom in eqn (7).^{20,30}

$$C + O(^{3}P) \rightarrow CO_{2}(CO)$$
(6)

$$Z_{12} = p\pi b_{\max}^{2} v_r n_1 * n_2 *$$
(7)

where *p* is the steric factor, b_{max} is the sum of the hard-sphere molecular radii of O(³P) atom (r_1) and carbon atom (r_2), *i.e.*, $b_{\text{max}} = r_1 + r_2$, v_r is their relative velocity, and n_1^* and n_2^* are the mole concentrations of the O(³P) atom and carbon atom, respectively. The variants v_r and n_1^* can be described by eqn (8) and (9), respectively.

$$\nu_{\rm r} = \langle \nu_{\rm r} \rangle = (3kT/m_1)^{1/2} \tag{8}$$

$$n_1^* = (P/RT)N_A \tag{9}$$

In eqn (8), *k* is the Boltzmann's constant, *T* is the absolute temperature, and m_1 is the mass of O(³P) atom. In eqn (9), *P* is the atomic gas pressure, *R* is the gas constant equal to 8.314 × 10⁶ cm³ Pa mol⁻¹ K⁻¹, and N_A is the Avogadro number.

For graphene supported on the SiO₂/Si substrate, the sp² composed carbon atoms have a constant concentration n_2^* . The collision rate is determined by the velocity $\langle v_r \rangle$ and the concentration n_1^* of the O(³P) atoms. This model is consistent with the previous experimental reports that the higher the oxygen content (<1 atm) or the higher the reaction temperature, the stronger the traditional photochemical etching of graphene when no magnetic field is applied in UV ozonation.^{22,23}

When a vertical magnetic field is applied, oxygen molecules $X^{3}\Sigma_{\alpha}^{-}$ and $O(^{3}P)$ atoms are attracted to the magnetic field, resulting in an increasing concentration of n_1^* . In this process, ozone generation resulting from their collisions, shown in eqn (2), could be impeded because the directional motion can decrease their relative speed, particularly with an increasing magnetic gradient toward the substrate as shown in Fig. 4(a). In this circumstance, deviating from the conventional photochemical oxidation, the $O(^{3}P)$ atoms dissociated directly, or converted from $O(^{1}D)$ (eqn (1')), may play an important role in oxidizing graphene. According to the molecular orbital theory, two unpaired electrons of the oxygen molecule $X^3\Sigma_g^-$ are individually distributed in the π_{2p}^* orbital.³⁴ When magnetized, the oxygen molecule has a magnetic moment parallel to the external magnetic field. Moreover, considering energy and momentum conservation in the photolysis process, the O(³P)/O(¹D) atoms can acquire an initial velocity in the magnetic field after dissociation from the accelerated oxygen molecule $X^{3}\Sigma_{g}^{-}$. The O(³P) atoms directly dissociated under 184.9/172 nm irradiation, or converted from O(¹D) under 172 nm irradiation, keep accelerating (Fig. 4(b)). As a comparison, the O(¹D) atom dissociated from the ozone molecule moves randomly, and the subsequent product $O(^{3}P)$ has a low velocity when accelerated in the same magnetic field (Fig. 4(b)). Therefore, the magnetic-induced attraction and acceleration of paramagnetic oxygen molecules $(X^{3}\Sigma_{g}^{-})$ and $O(^{3}P)$ atoms result in an increase of n_{1}^{*} and $\langle v_{r} \rangle$ (a component perpendicular to the graphene film) and then improve the photochemical etching of graphene as experimentally demonstrated in Section 3.1.

In the vertical magnetic field, the increasing intermolecular or atomic-molecular collisions between the oxygen molecules/ atoms and the weak diamagnetic nitrogen/ozone molecules can

or



Fig. 4 Dynamic photochemical reaction in the magnetic-assisted UV ozonation ($B_Z = 0.31$ T, $\nabla B_Z = 90$ T m⁻¹) under irradiation of the low-pressure mercury lamp. (a) Dynamic motion of various molecules with green arrows denoting the velocity. (b) Photodissociation of ozone and oxygen molecule under different UV excitations in the magnetic field. (c) Collisions between the oxygen molecule/atoms and the diamagnetic molecules. The diamagnetic singlet oxygen molecule ($\alpha^1 \Delta_g$) and atom (O(¹D)) deactivate individually to their ground states *via* collisions.

impair the directionality of the photochemical reaction.^{13–15} As shown schematically in Fig. 4(c), oxygen molecule $X^{3}\Sigma_{g}^{-}$ is scattered after collision with nitrogen, and its acceleration in the magnetic field is impeded. Then, the velocity $\langle v_{r} \rangle$ of the O(³P) atom dissociated directly from the oxygen molecule, or subsequently converted from O(¹D), will decrease. The following collision between O(¹D)/O(³P) atoms and the diamagnetic molecules like ozone in Fig. 4(c) can also decrease the velocity $\langle v_{r} \rangle$. For ozone molecules, however, molecular collisions introduced by nitrogen up to 60 kPa may decrease the mean free path and contribute to the small lateral under-oxidation, as reported in ref. 13.

The abovementioned dissociation and collision model can well explain the experimental observations in Fig. 1–3. Specifically, introduction of either ozone (by addition of 8% ozone or increasing oxygen content) or nitrogen molecules can weaken the photochemical oxidation and degrade the quality of graphene patterning.

The vertical magnetic field can affect the collision rate Z_{12} between the O(³P) atom and graphene because of two opposite contributions. One is the increasing concentration of the O(³P) atom n_1^* and the other is its decreasing v_r aroused by collision with the diamagnetic molecules. In this circumstance, v_r and n_1^* can be described by eqn (10) and (11), respectively.

$$v_{\rm r} = \langle v_{\rm r} \rangle = f_1(B_Z, \nabla B_Z) \times f_2(Y, n_3^*) \times (3kT/m_1)^{1/2}$$
 (10)

$$n_1^* = g_1(B_Z, \nabla B_Z) \times g_2(Y, n_3^*) \times (P/RT)N_A$$
 (11)

Herein, $f_1(B_Z, \nabla B_Z)$ and $g_1(B_Z, \nabla B_Z)$ denote contribution from the non-uniform magnetic field, and $f_2(Y, n_3^*)$ and $g_2(Y, n_3^*)$ denote contribution from some specific diamagnetic molecule *Y* with concentration n_3^* .

As noticed, the photochemical oxidation intensity in Fig. 1 weakens compared with that reported in ref. 13, even though assisted with the same magnetic field ($B_Z = 0.31$ T, $\nabla B_Z = 90$ T m⁻¹). This indicates that the collision rate Z_{12} determined by two variants v_r and n_1^* in eqn (7) decreases. Since v_r increases upon decreasing atomic/molecular collisions (2 kPa O₂ vs. 60 kPa N₂ + 10 Pa O₂ atmosphere), a decreasing n_1^*

induced by the low optical absorption of oxygen molecule $X^{3}\Sigma_{g}^{-}$ at 184.9 nm should play a critical role.²⁹

3.3 Lateral under-oxidation affected Dirac point-shift under UV irradiation

Using the same oxidation parameters in Fig. 1(b), graphene FET arrays are fabricated and then characterized by micro-Raman spectroscopy and carrier transport measurements. As shown in the optical topographical image (see Fig. 5(a)), the graphene FET device has a dimension of $578 \times 165 \ \mu\text{m}^2$. The left and right blue dotted lines, L1 and L2, represent the two scanning routes under irradiation of 325 nm laser. The red rectangle represents the scanning scope for micro-Raman spectrum mapping as drawn in Fig. 5(b) and (c). We can observe that graphene is more severely damaged within twenty micrometers of the edge area. The uniformly oxidized graphene in the central area stems from molecular diffusion underneath the mask contributed by the 100 nm-thick metal contacts.

The graphene FET device is highly p-doped as indicated by the solid black conductivity curve varying with the back-gate voltage in Fig. 5(d). After 50 min irradiation under the mercury 253.7 nm line in a high vacuum condition $(4.5 \times 10^{-4} \text{ Pa})$, its Dirac point shifts and stabilizes at 7 V (slight p doping), as shown by the solid pink line.^{13,35,36} This observation deviates from the previous report that graphene became n doped under UV irradiation.^{34,35} The hole and electron mobilities are deduced to be 574 cm² V⁻¹ s⁻¹ and 640 cm² V⁻¹ s⁻¹, respectively, almost three times lower than those patterned under irradiation of the xenon excimer lamp.^{13,37}

Substituting the mercury lamp with the 325 nm laser, we can observe lateral under-oxidation induced electrical transport variation by scanning it between two metal electrodes with a dwell time of 2 s and a fixed step size of 7.2 μ m. When scanning along L1 adjacent to the central area, the Dirac point shifts monotonically toward n-doping, and it saturates at a value exceeding 60 V after 27 min irradiation. When scanning along L2 in the edge area, the Dirac point exhibits a slower shift toward n-doping after 3 min irradiation and then shifts slightly



Fig. 5 Characterization of a graphene FET device patterned by the magnetic-assisted UV ozonation. (a) Optical image. The blue dotted lines represent the micro-scale scanning of 325 nm laser. (b) Micro-Raman map of the D band intensity in the region denoted by the red rectangle in (a), and (c) the corresponding Raman spectrum evolution for the dots outlined by the black rectangle in (b). The white dotted line denotes the graphene edge. (d) Conductivity as a function of back-gate voltage for the graphene FET device varying with lateral under-oxidation after localized irradiation at 325 nm. The source-drain voltage is fixed at 0.1 V.

back after 27 min irradiation because of the readsorption of oxygen and water molecules on the defects.³⁸ The saturated p-doping is related to the lateral under-oxidation in graphene patterning. Furthermore, the more the graphene FET is oxidized, the slower and lesser the Dirac point shifts toward the negative gate voltage.

4. Conclusions

In summary, we have explored the working mechanism of graphene patterning in the magnetic-assisted UV ozonation by varying oxygen content and introducing reactive ozone and inert nitrogen molecules. A non-uniform vertical magnetic field, which makes oxygen molecules $X^{3}\Sigma_{g}^{-}$ and $O(^{3}P)$ atoms directional, can bring new vitality to the traditional photochemical oxidation. The O(³P) atom dissociated directly from oxygen molecule $X^{3}\Sigma_{g}^{-}$, or subsequently converted from O(¹D) atom via collisions under 172 nm irradiation, can obtain an initial velocity before being further accelerated in the magnetic field, and therefore it can enhance the oxidation intensity compared to that stemming from the randomly moved ozone molecule. Intermolecular or atomic-molecular collisions between the directional oxygen molecules/atoms and the randomly moved weak diamagnetic molecules play an important role in impeding the directional photochemical reaction. For ozone molecules, however, decreasing molecular collisions with the initial oxygen pressure being no more than a few kilopascals (at least an order

lower than nitrogen in ref. 13) can increase the mean free path and incur severe lateral under-oxidation.¹³ Compared with the previous work,¹³ a decreasing concentration of n_1^* induced by the low optical absorption of oxygen molecule $X^3\Sigma_g^-$ at 184.9 nm contributes to the weakening photochemical oxidation intensity. When the magnetic-assisted UV ozonation is applied to fabricating graphene FET devices, the metal contact induced 100 nm gap between the mask and graphene appears detrimental to graphene patterning because of severe lateral under-oxidation. We find that the more severe the graphene FET is oxidized, the more difficult it is to shift the Dirac point toward n-doping under UV irradiation.

In order to facilitate application of the low-pressure mercury lamp in graphene patterning, it is a prerequisite to simultaneously improve the photochemical oxidation intensity and restrain the lateral under-oxidation stemming from ozone diffusion and dissipation. This study may shed light on our understanding and designing of graphene patterning by magnetic-assisted UV ozonation.

Conflicts of interest

Shanghai Jiaotong University, along with the authors, has filed provisional patents on the technology and intellectual property reported here (patent number ZL 201310242512.4; patent application numbers CN 201610546722.6 and PCT/CN2016/102338; title: pattern graphene film by UV photochemical oxidation).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 11204173), the National Science and Technology Major Project (No. 2011ZX02707), and the Qingpu-Shanghai Jiaotong University (SJTU) Collaboration Fund. We thank Prof. H. Zheng, Prof. J. Chen, Prof. D. Qian, Prof. X. Y. Chen, and Prof. M. H. Shu from SJTU for fruitful discussions. We thank Prof. X. Xie from the Shanghai Institute of Microsystem and Information Technology (CAS), Prof. Y. Zhang from the Fudan University, and Prof. Z. Sheng from SJTU for their support. We thank Ms L. He from the Instrumental Analysis Center, Prof. Y. Wang from Advanced Electronic Materials and Devices (AEMD) and Prof. W. Shen and Dr Z. Jiang from SJTU for their technical support.

References

- S. Bae, H. Kim, Y. Lee, X. F. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y. J. Kim, K. S. Kim, B. Ozyilmaz, J. H. Ahn, B. H. Hong and S. Iijima, *Nat. Nanotechnol.*, 2010, 5, 574–578.
- 2 L. B. Gao, G. X. Ni, Y. P. Liu, B. Liu, A. H. C. Neto and K. P. Loh, *Nature*, 2014, **505**, 190–194.
- 3 Y. Hao, L. Wang, Y. Liu, H. Chen, X. Wang, C. Tan, S. Nie, J. W. Suk, T. Jiang, T. Liang, J. Xiao, W. Ye, C. R. Dean, B. I. Yakobson, K. F. McCarty, P. Kim, J. Hone and L. Colombo, *Nat. Nanotechnol.*, 2016, 11, 426–431.

- 4 T. Wu, X. Zhang, Q. Yuan, J. Xue, G. Lu, Z. Liu, H. Wang,
 H. Wang, F. Ding, Q. Yu, X. Xie and M. Jiang, *Nat. Mater.*, 2016, 15, 43–47.
- 5 X. Xu, Z. Zhang, Q. Lu, J. Zhuang, L. Zhang, H. Wang, C. Liao, H. Song, R. Qiao, P. Gao, Z. Hu, L. Liao, Z. Liao, D. Yu, E. Wang, F. Ding, H. Peng and K. Liu, *Nat. Nanotechnol.*, 2016, **11**, 930–936.
- 6 J. Sun, Z. Chen, L. Yuan, Y. Chen, J. Ning, S. Liu, D. Ma, X. Song, M. K. Priydarshi, A. Bachmatiuk, M. H. Rümmeli, T. Ma, L. Zhi, L. Huang, Y. Zhang and Z. Liu, *ACS Nano*, 2016, **10**, 11136–11144.
- 7 R. Sahin, E. Simsek and S. Akturk, Appl. Phys. Lett., 2014, 104, 4.
- 8 A. George, S. Mathew, R. van Gastel, M. Nijland, K. Gopinadhan,
 P. Brinks, T. Venkatesan and J. E. ten Elshof, *Small*, 2013, 9, 711–715.
- 9 L. M. Zhang, S. O. Diao, Y. F. Nie, K. Yan, N. Liu, B. Y. Dai, Q. Xie, A. Reina, J. Kong and Z. F. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 2706–2713.
- 10 M. C. Lemme, D. C. Bell, J. R. Williams, L. A. Stern, B. W. H. Baugher, P. Jarillo-Herrero and C. M. Marcus, ACS Nano, 2009, 3, 2674–2676.
- 11 A. Mahmood, C. S. Yang, J. F. Dayen, S. Park, M. V. Kamalakar, D. Metten, S. Berciaud, J. O. Lee and B. Doudin, *Carbon*, 2015, 86, 256–263.
- 12 Y. D. Tu, T. Utsunomiya, T. Ichii and H. Sugimura, ACS Appl. Mater. Interfaces, 2016, 8, 10627–10635.
- 13 Y. Wu, H. Tao, S. Su, H. Yue, H. Li, Z. Zhang, Z. Ni and X. Chen, *Sci. Rep.*, 2017, 7, 46583–46590.
- 14 M. Tinkham and M. W. P. Strandberg, *Phys. Rev.*, 1955, **97**, 951–966.
- 15 S. Ueno, M. Iwasaka, H. Eguchi and T. Kitajima, *IEEE Trans. Magn.*, 1993, **29**, 3264–3266.
- 16 O. E. Kurt and T. E. Phipps, Phys. Rev., 1929, 34, 1357-1366.
- 17 K. Watanabe, E. C. Y. Inn and M. Zelikoff, *J. Chem. Phys.*, 1952, **20**, 1969–1970.
- 18 Y. Tanaka, E. C. Y. Inn and K. Watanabe, *J. Chem. Phys.*, 1953, **21**, 1651–1653.
- 19 K. Stockwald and M. Neiger, *Contrib. Plasma Phys.*, 1995, 35, 15–22.
- 20 N. Leconte, J. Moser, P. Ordejon, H. Tao, A. Lherbier,
 A. Bachtold, F. Alsina, C. M. S. Torres, J. C. Charlier and
 S. Roche, *ACS Nano*, 2010, 4, 4033–4038.

- 21 Y. C. Cheng, T. P. Kaloni, Z. Y. Zhu and U. Schwingenschlogl, *Appl. Phys. Lett.*, 2012, **101**, 4.
- 22 Z. Zhang, H. Tao, H. Li, G. Ding, Z. Ni and X. Chen, Opt. Mater. Express, 2016, 6, 3527–3540.
- 23 H. Tao, J. Moser, F. Alzina, Q. Wang and C. M. Sotomayor-Torres, J. Phys. Chem. C, 2011, 115, 18257–18260.
- 24 W. Li, Y. R. Liang, D. M. Yu, L. M. Peng, K. P. Pernstich, T. Shen, A. R. H. Walker, G. J. Cheng, C. A. Hacker, C. A. Richter, Q. L. Li, D. J. Gundlach and X. L. Liang, *Appl. Phys. Lett.*, 2013, **102**, 5.
- 25 X. S. Li, W. W. Cai, J. H. An, S. Kim, J. Nah, D. X. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo and R. S. Ruoff, *Science*, 2009, **324**, 1312–1314.
- 26 X. L. Liang, B. A. Sperling, I. Calizo, G. J. Cheng, C. A. Hacker, Q. Zhang, Y. Obeng, K. Yan, H. L. Peng, Q. L. Li, X. X. Zhu, H. Yuan, A. R. H. Walker, Z. F. Liu, L. M. Peng and C. A. Richter, *ACS Nano*, 2011, 5, 9144–9153.
- 27 Z. H. Pan, N. Liu, L. Fu and Z. F. Liu, J. Am. Chem. Soc., 2011, 133, 17578–17581.
- 28 J.-X. Li and A.-H. Liu, J. Electron. Mater., 2011, 40, 2105–2110.
- 29 H. Okabe, *Photochemistry of small molecules*, John Wiley & Sons, Inc, 1978.
- 30 P. L. Houston, *Chemical kinetics and reaction dynamics*, McGRAW-HILL, international 1st edn, 2001.
- 31 B. J. Finlayson-Pitts and J. N. Pitts Jr., Atmospheric chemistry: fundamentals and experimental techniques, John Wiley & Sons, Inc., 1986.
- 32 R. Gilpin, H. I. Schiff and K. H. Welge, J. Chem. Phys., 1971, 55, 1087–1093.
- 33 R.-D. Penzhorn, H. Güsten, U. Schurath and K. H. Becker, Environ. Sci. Technol., 1974, 8, 907–909.
- 34 G. L. Miessler, P. J. Fischer and D. A. Tarr, *Inorganic chemistry*, Pearson Education, Inc., 5th edn, 2014.
- 35 Z. T. Luo, N. J. Pinto, Y. Davila and A. T. C. Johnson, *Appl. Phys. Lett.*, 2012, **100**, 4.
- 36 Y. J. Lin and J. J. Zeng, Appl. Phys. Lett., 2013, 102, 4.
- 37 S. Kim, J. Nah, I. Jo, D. Shahrjerdi, L. Colombo, Z. Yao,E. Tutuc and S. K. Banerjee, *Appl. Phys. Lett.*, 2009, 94, 3.
- 38 A. Tiberj, M. Rubio-Roy, M. Paillet, J.-R. Huntzinger, P. Landois, M. Mikolasek, S. Contreras, J.-L. Sauvajol, E. Dujardin and A.-A. Zahab, *Sci. Rep.*, 2013, 3, 2355–2360.