Metal to semiconductor transition in graphene by oxygen plasma treatment: a building block for graphene-based electronics

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Graphene is considered a promising material in both fundamental science and technology because of its unique electronic and chemical properties[1] In particular, single- and bi-layer graphene are being investigated to fabricate various devices such as field-effect transistors (FETs),[2] biosensors,[3] and photodetectors.[4]

In this work the results of experiments devoted to the modification of the pristine electronic properties of single-layer graphene by means of an oxygen plasma will be illustrated. Electrical characterization and photoluminescence measurements are carried out to investigate the opening of a bandgap in plasma-treated graphene. figure 1(a, b) show room-temperature output characteristics of a SLG FET collected in pristine conditions and after steps of O2 plasma treatment. The symmetric rectifying behavior observed in figure 1(b) can be explained by building an equivalent circuit of the plasma-treated metal/SLG/metal structure, comprising two identical Schottky diodes connected back-to-back.
The PL maps in figure 2(b) shows the emission from the two SLG areas of the flake in figure 2(a), while no emission is collected from the thicker graphene areas. A corresponding PL spectrum representative of the bright PL emission from the SLG areas is shown in figure 2(d). It shows a broad peak lying in the visible range and centered at ~620 nm, corresponding to a ~2 eV optical bandgap. After two steps of O2 plasma treatment, the graphene sample shows PL emission (figure 2(c)) from the regions previously indicated as bilayers in figure 2(a). The analysis of the evolution of the PL maps upon O2 plasma treatment suggests that: (a) the plasma progressively renders the SLG regions photoluminescent; (b) as the O2 plasma is believed to affect the entire graphene surface in a similar fashion, regardless of the thickness of the flake, the absence of PL from the plasma-treated FLG is indicative of an emission quenching of the topmost layer by subjacent untreated layers. The experimental results are explained in terms of a functionalization of the pristine sp^2 graphene lattice with chemisorbed epoxy groups.The effects of epoxidation on graphene optoelectronic properties are further investigated by *ab initio* calculations. Figure 3 shows electronic band structure and electronic density of states (DOS) calculated for different oxygen densities. They confirm that progressively larger bandgaps are introduced in graphene upon functionalization with increasing amount of oxygen.

Furthermore, we demonstrate the potential of metal-contacted plasma-treated graphene rectifying junctions to fabricate Schottky diodes with turn-on voltages below 0.5 V. The use of low- (Al, Yb) and high- (Pd) work function metals, directly in contact with modified graphene, allows for the modulation of the Schottky barrier height. Figure 4(a, b) illustarte the diagrams of the band alignment in the cases of a *p*–doped semiconductor (work function φ_S) contacted with (a) two identical metal electrodes ($\varphi_M < \varphi_S$), and (b) two metal electrodes M_1 and M_2 with different work functions ($\varphi_{M1} < \varphi_S < \varphi_{M2}$, $\varphi_S \sim \varphi_{M2}$). The Schottky barrier height φ_B is indicated. Figure 4(c) dispalys output characteristics of Al–SSLG–Pd and Yb–SSLG–Pd devices, whereby the rectifying behavior is visible. Our results suggest that an oxygen plasma treatment represents a valid approach to control graphene chemistry toward tunable-bandgap graphene-based electronics.

References

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[3] Liu, Y., et al., Langmuir, **26**(2010) 6158-6160.
[4] Xia, F.N., et al., Nature Nanotechnology, **4**(2009)839-843.

Figures

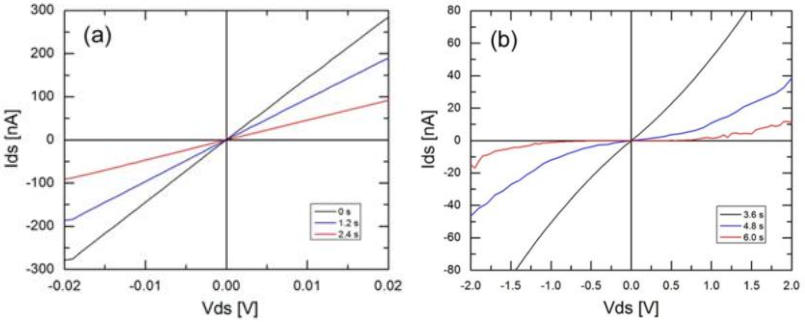

***Figure 1**: output characteristics of a SLG-FET collected in pristine conditions and after steps of O_2 plasma treatment (15 W, 1.2 s interval). The curves shown in (b) for longer O_2 plasma treatment times are indistinguishable from the X-axis in panel (a), measured in the cases of shorter O_2 plasma treatment times.*

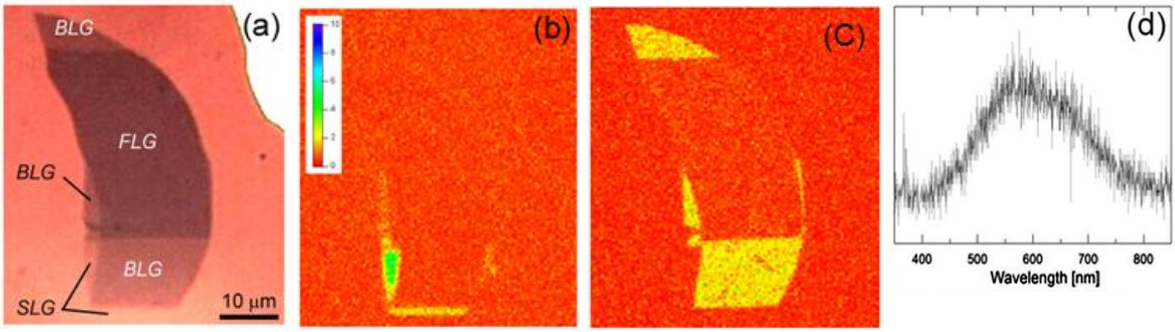

***Figure 2**: PL measurements on a graphene sample subjected to O_2 plasma for increasing time duration.*

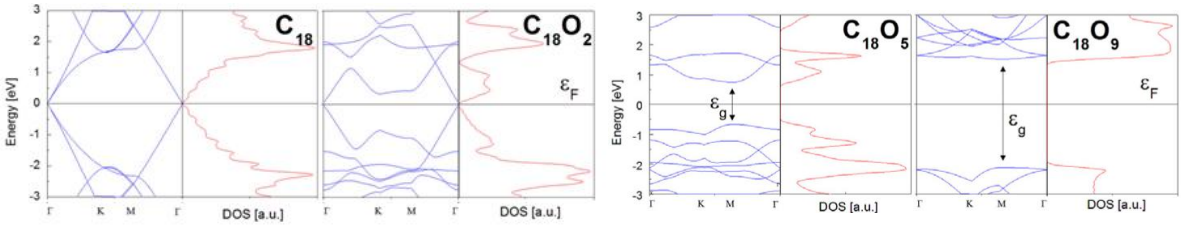

***Figure 3**: Electronic band structure and electronic density of states (DOS) calculated for different oxygen densities.*

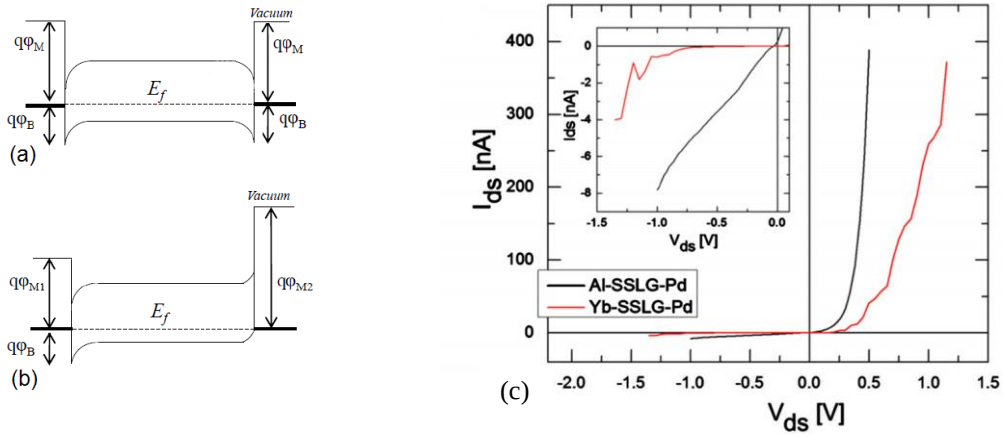

***Figure 4**: Diagrams of the band alignment in the cases of a p–doped semiconductor (work function φ_S) contacted with (a) two identical metal electrodes ($\varphi_M < \varphi_S$), and (b) two metal electrodes M_1 and M_2 with different work functions ($\varphi_{M1} < \varphi_S < \varphi_{M2}$, $\varphi_S \sim \varphi_{M2}$). The Schottky barrier height φ_B is indicated. (c) Comparison of the room-temperature, output characteristics of Al–SSLG–Pd and Yb–SSLG–Pd devices, whereby the rectifying behavior is visible. A detailed behavior of the two devices in reverse bias is shown in the inset.*