

# Transport Properties of Graphene Decorated with Oxygen Molecules

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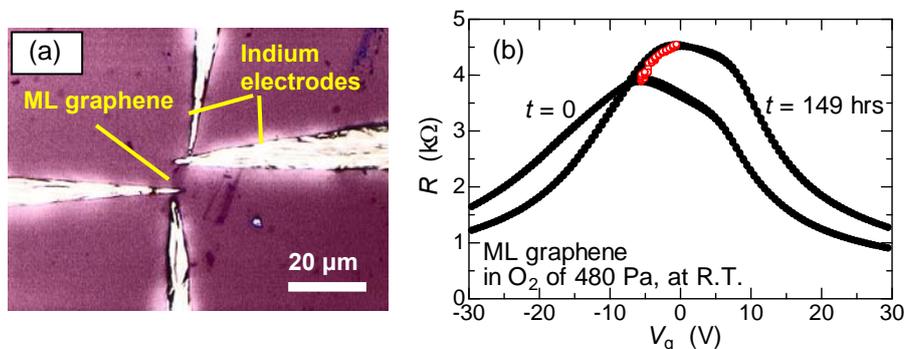
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Graphene is attracting considerable interests in various aspects. Carriers in an ideal graphene sheet behave like the massless Dirac fermions, and exhibit a series of unique electronic properties such as the anomalously quantized Hall effects, the absence of weak localization, and the existence of a minimum conductivity. Moreover, it is a promising material for the future electronics. The high carrier mobility and chemical and mechanical robustness suggest important applications. The next important step of graphene research is to find ways to control the physical properties. One of the strategies is depositing atoms or molecules on graphene. For example, band gap opening due to the chiral symmetry breaking is expected when the adsorbates form the  $(\sqrt{3}\times\sqrt{3})R30^\circ$  structure on graphene. On the other hand, it is well known that some adsorbates transfer either electrons or holes into graphene and change the conductance, which makes graphene applicable to gas sensor. To elucidate the mechanism of the chemical doping, Sato *et al.* [1] measured the two-terminal conductivity of bilayer (BL) graphene when it is exposed to 1 atm of molecular oxygen ( $O_2$ ) at room temperature. They repeated the  $O_2$  exposure with a short-time interval at a certain gate voltage ( $V_g$ ) and measured a  $V_g$  dependence of conductivity after evacuating the  $O_2$  gas. They showed that the hole doping proceeds faster at higher  $V_g$ , and the doping rate follows a power-law in time rather than exponential. They also noticed that the  $V_g$  dependence of conductivity is restored by annealing graphene in vacuum at 200 °C.

Here, we studied the effect of  $O_2$  exposure on both monolayer (ML) and BL graphene samples which are installed in a vacuum chamber. Three ML and one BL graphene samples were fabricated by micro-mechanical cleavage on a surface  $SiO_2$  layer of 285 nm thick of a highly doped Si which is used as a back gate electrode. The thickness of graphene samples were determined both from the contrast of green component in optical microscope image and the Raman spectroscopy. The time evolution of conductivity was measured by sweeping  $V_g$  within  $\pm 10$ -25 V about the Dirac point (DP) under a fixed pressure of  $O_2$  of 200-500 Pa at room temperature. Since the surface cleanness is extremely important to study the effect of adsorption, micro-electrodes of fine indium wires were soldered directly onto graphene [2] as shown in fig. 1(a). This so-called the *dry process* may keep the graphene surface as was exfoliated without contaminations of resist residue or solutions in ordinary *wet process* like photolithography. Not to measure the contact resistance of the indium electrodes, the conductivity was measured with four-terminal configuration.

Figure 1(b) shows a measured  $V_g$  dependence of resistance ( $R$ ) in one of the ML graphene samples during the  $O_2$  exposure, in which the shift of DP is marked with the red circles. One can easily see that both the energy ( $V_{DP}$ ) and resistance ( $R_{DP}$ ) at the DP increase monotonically by time. In addition, the  $R$ - $V_g$  curve is modified by the  $O_2$  exposure. We analyzed the data in terms of the shift of DP ( $\Delta V_{DP}$ ),  $R_{DP}$  and resistance drop ( $\Delta R$ ) from the DP at  $V_g = V_{DP} \pm 5$  V. Here, positive  $\Delta V_g$  means hole doping, while larger  $R_{DP}$  indicates increasing scattering centers. On one hand, the increasing  $\Delta R$  or sharpening of the  $R$ - $V_g$  curve naively suggests higher mobility.

Figure 2 shows measured time evolutions of  $\Delta V_{DP}$ ,  $R_{DP}$  and  $\Delta R$  for BL (a)-(c) and for ML graphene



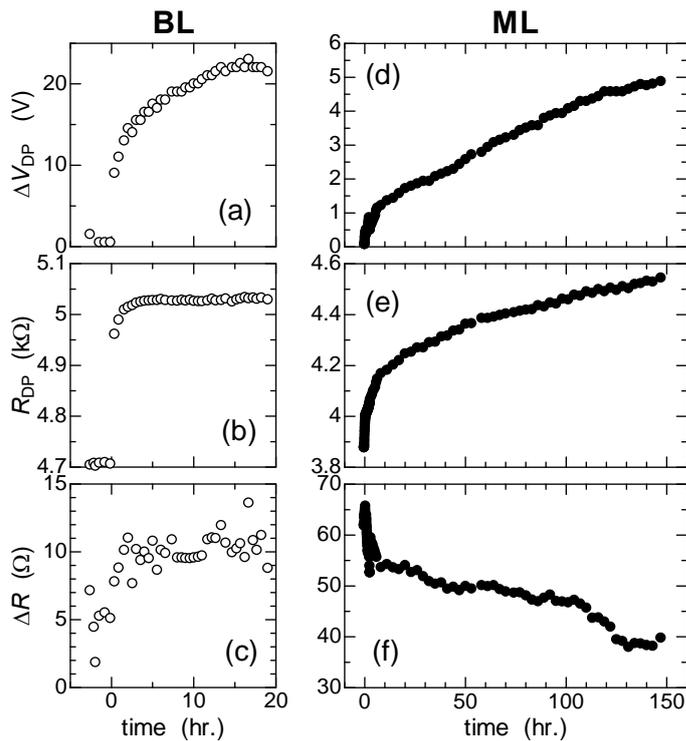
**Figure 1.** (a) Optical microscope image of a ML graphene sample with indium micro-electrodes. (b) Resistance of ML graphene as a function of  $V_g$  before ( $t = 0$ ) and 149 hours after exposing to an  $O_2$  gas of 480 Pa. The change of the Dirac point during the  $O_2$  exposure is represented by the red circles.

(d)-(f). As shown in fig. 2(a),  $\Delta V_{DP}(t)$  for BL graphene follows a power-law in time rather than exponential as reported previously [1]. The power ( $\sim 0.25$ ) is also comparable to the previous report [1]. We found that ML graphene has a similar time dependence but with a roughly two times larger power ( $\sim 0.5$ ) than in BL graphene. This suggests stronger chemical reaction with  $O_2$  due perhaps to larger deformation by  $SiO_2$  substrate in ML than in BL graphene, which is consistent with the fact that oxidative etching of graphene in  $O_2/Ar$  environment proceeds at lower temperature in ML ( $\sim 450^\circ C$ ) than in BL ( $\sim 600^\circ C$ ) graphene [3].

On the other hand,  $R_{DP}$  and  $\Delta R$  are found to behave rather differently from  $\Delta V_{DP}$  and showed strong sample dependence. At first glance, since adsorbed  $O_2$  would act as scattering centers in transport, one may expect that  $R_{DP}$  should increase and  $\Delta R$  should decrease in time. However, as shown in fig. 2(c),  $\Delta R$  sometimes increases in time. While  $R_{DP}$  and  $\Delta R$  of ML graphene change gradually in time (figs. 2 (e)(f)), those of BL graphene change rather rapidly and saturate as shown in figs. 2 (b)(c).

The changes of  $\Delta V_{DP}$ ,  $R_{DP}$  and  $\Delta R$  caused by the  $O_2$  exposure are restored only partially even after evacuation of the chamber with samples at about  $100^\circ C$  for 6 to 70 hours, and the subsequent  $O_2$  exposure provides smaller changes. Such a tendency seems to continue at least up to five  $O_2$  exposure/evacuation cycles. These results probably indicate the existence of qualitatively different adsorption or catalytic sites for adsorption or dissociation such as defects, edges, etc., and adsorption processes such as surface diffusion, chemical reaction, etc.

In this presentation, we will also show strong temperature dependence of conductivity in graphene exposed to  $O_2$  at room temperature down to  $T = 1.6$  K. The resistivity decreases slowly with decreasing temperature until  $\sim 80$  K, below which it turns to increase with a dependence of  $R \propto \exp(T^{-1/3})$  suggesting the variable range hopping in two dimensions. In addition, a complicated structure with many sharp peaks appears in the  $V_g$  dependence in this low temperature regime. The peak amplitude becomes larger at lower temperatures. It suggests stronger localization of carriers at low temperatures after the  $O_2$  adsorption.



**Figure 2.** Time evolution of  $\Delta V_{DP}$ ,  $R_{DP}$  and  $\Delta R$  for BL graphene after exposing to an  $O_2$  gas of 480 Pa (a)-(c) and for ML graphene to  $O_2$  of 416 Pa (d)-(f) at room temperature. The data in (d)-(f) are extracted from those shown in fig. 1(b).  $\Delta V_{DP}$  varies with a power-law in time for both ML and BL, while time dependences of  $R_{DP}$  and  $\Delta R$  vary sample to sample.

## References

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- [3] L. Liu *et al.*, *Nano Lett.*, **8** (2008) 1965.