n-Type Doping of Graphene Monolayer

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Abstract

A prerequisite for the development of graphene based electronics is how to dope pristine graphene. Here we present a method for the synthesis of large-area, monolayer n-doped graphene via chemical exfoliation of HOPG in various solvents. Monolayer graphene has been confirmed by scanning electron microscopy and confocal Raman spectroscopy. The doping was probed by analyzing shift in Raman peak positions and transistor transfer ($I_{DS}-V_{GS}$) characteristics. Very high electron mobility of 5,000cm²/V-s has been achieved in n-doped graphene.

Keywords:-Graphene, Doping, Raman, g-FET

1. Introduction

Graphene, a two-dimensional network of sp²-hybridised carbon atoms, is an excellent material for the next generation of electronic devices ^[1], due to its unique electronic structure resulting in extremely high carrier mobility. Till now several methods have been employed for controlling the carrier type and modifying the carrier concentrations in graphene by covalent functionalization, surface modification of substrates, or by using metallic ultrathin films. In general it is difficult to obtain a n-type graphene compared to p-type graphene. Here, we present a method based on chemical exfoliation for growing high quality graphene monolayers on desired substrates.

2. Experimental Details

Monolayer graphene has exfoliated from HOPG (Highly Ordered Pyrolytic Graphite) in organic solvents by sonication. [3] Thick flakes were precipitated out by centrifugation and solution contains dispersed graphene layers at the top of the solution. Graphene layers were transferred to SiO₂ substrates by simple drop casting method. The organic solvents used for exfoliation can be used as dopants to graphene layers. The solvents with high dipole moment foramide(DMF), like dimethyl Propylene Carbonate (PC), Acetone inject electrons into graphene layer making them n-type while solvent with low dipole moment like toluene withdraw electrons from graphene layers turning them into p-type graphene. Layered structure was confirmed by confocal Raman spectroscopy. Subsequently, graphene field effect transistors (g-FETs) on monolayer graphene were fabricated with Cu source-drain electrode in order to probe the doping of the graphene layers.

3. Result and Discussions

Figure 1a shows, Raman spectra of graphene exfoliated in toluene having G band at ~ 1580 cm⁻¹ and 2D band at 2700 cm⁻¹ with $I(G)/I(2D) \sim 0.3$. We do not observe any significant shift in energetic positions of G and 2D peaks with respect of those in graphite. Raman spectrum of graphene exfoliated in PC (g- PC) is shown in Figure 1b. Here we observed G band at ~ 1577 cm⁻¹ and 2D band at ~ 2714 cm^{-1} having I (G)/I(2D) ~ 0.5 indicating monolayer graphene with substantial shift in the energetic positions of G and 2D peaks. This shift in the 2D peak is attributed to the incorporation of the n-type dopants in the graphene layer. Inset shows the scanning electron microscopy image for g-toluene and g-PC respectively.

In order to go to further insight into how graphene is doped, current-voltage characteristics have been obtained in field effect transistors fabricated on n-doped graphene and compared with undoped pristine graphene.



FIGURE 1. Confocal Raman spectra of (a) g-Toluene and (b) g-PC. Inset shows scanning electron microscopic images.

Figure 2 shows the transfer characteristics (I_{DS} - V_{GS}) of g-FET fabricated with PC. Figure 2 clearly shows the sharp increase in I_{DS} with negative V_{GS} indicating strong n type doping.^[2] Whereas, transfer characteristics shown by g-FET fabricated with Toluene (inset) shows ambipolar behavior where I_{DS} increases linearly with V_{GS} on both sides of conductivity minima (0.2V).

These observations of Raman spectroscopy and electrical measurements can be explained by doping of graphene exfoliated in PC. For this to happen there should be an electron donating or injecting group. Toluene has stable structure with low polarity (molecular structure shown in inset of Figure 2). When graphene comes into contact with toluene during sonication, no charge transfer takes place between graphene and toluene molecule. As a consequence, we do not observe any shift in Raman spectra and conductivity minima is at 0.2V showing negligible doping effect.



FIGURE2. I_{DS} - V_{GS} characteristics of g-FET fabricated with g-PC green curve) and g-Toluene (inset-blue curve). Molecular structures of PC and Toluene are also shown.

On the other hand, PC has a polar character with high dipole moment (molecular structure shown in inset of Figure 2). As shown in the schematic above, the structure of PC is having oxygen atom with lone pair of electron, when graphene comes into contact with PC during sonication, due to electron donating nature of oxygen atom, PC donates electrons to graphene layers making it n-type doped graphene.

4. Conclusions

In conclusion, it has been shown that due to polar nature of the PC, graphene layers can be doped with electrons during exfoliation due to presence of lone pair of oxygen in PC. Doped graphene has been characterized with Raman spectroscopy and typical transfer characteristics.

5. Acknowledgement

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6. References

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