

Nitric Acid doping of epitaxial graphene on SiC(0001) substrate

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Abstract

Chemical doping by surface charge transfer is an effective way to modulate graphene's electrical properties through p or n-type doping. Nitric Acid (HNO_3) is an efficient acidic doping agent that manipulates work function (WF) of graphene^{1,2}. Although HNO_3 is known as a p-type dopant for CVD-graphene increasing the conductivity by surface charge transfer, it may behave different on intrinsically n-type epitaxial graphene on SiC(0001) surface due to the difference in surface potentials³. In this work, the doping behavior of HNO_3 solutions with several concentrations on n-type epitaxial graphene was investigated. Three different concentrations of 15 vol%, 30 vol%, and 70 vol% of HNO_3 solutions in DI water were applied on the surface of epitaxial graphene and compared with pristine samples. The samples used for each concentration were separately measured by Raman spectroscopy before and after doping to avoid errors due to the structural differences on each sample affecting the peak positions. In Figure 1, Raman results show that after the 15 vol% of HNO_3 resulted in no-change in G-band position and a red-shift at higher concentrations. 2D-band positions of Raman spectra all exhibit a red-shift after doping regardless the concentration indicating n-type doping behavior^{4,5}. D-band intensities of Raman spectroscopy are increased after doping with concentration of HNO_3 above 15 vol%. AFM image in Figure 2 shows the surface morphology of SiC(0001) consist of micron size parallel steps. To confirm Raman spectroscopy results, ultraviolet photoelectron spectroscopy (UPS) (Fig.2) and X-ray photoelectron spectroscopy (XPS) (Fig.3) were utilized to investigate the chemical environment of the graphene surface and to observe the change in WF for each concentration. The UPS results clearly confirmed the trend as it was observed in Raman spectroscopy where WF is decreasing at all concentrations. It is worth noting that considering Raman and UPS results (Fig.2), Fermi level shifted up more severely into the conduction band in the case of 30 vol% HNO_3 than that of 70 vol% HNO_3 doping. It is also noteworthy that doping of epitaxial graphene on SiC could be more complex than that of CVD-graphene doping due to strong covalent bonding with the substrate. Acidic solutions could interact with the SiC that may result in decoupling of graphene by strong oxidation. This complex behavior of WF changes could be implemented into apparent compensation effects from two simultaneous chemical reactions of oxidation/nitrogenation which occur via: i) stronger nitrogenation for concentrations below 50 vol% HNO_3 , and weaker for concentrations above 50 vol% HNO_3 , ii) increasing oxidative effect as the concentration of HNO_3 is increasing as demonstrated by the O1s XPS data.

References

- [1] Güneş, F. *et al.* *ACS Nano* **4** (2010) 4595–4600.
- [2] Bae, S. *et al.* *Nature Nanotechnology* **5** (2010) 574–578.
- [3] Ohta, T. *et al.* *Physical Review Letters* **98**, (2007) 206802.
- [4] Voggu, R. *et al.* *J. Phys.: Condens. Matter* **20** (2008) 472204.
- [5] Panchakarla, L. S. *et al.* *Advanced Materials* **21** (2009) 4726–4730.

Figures:

Fig.1

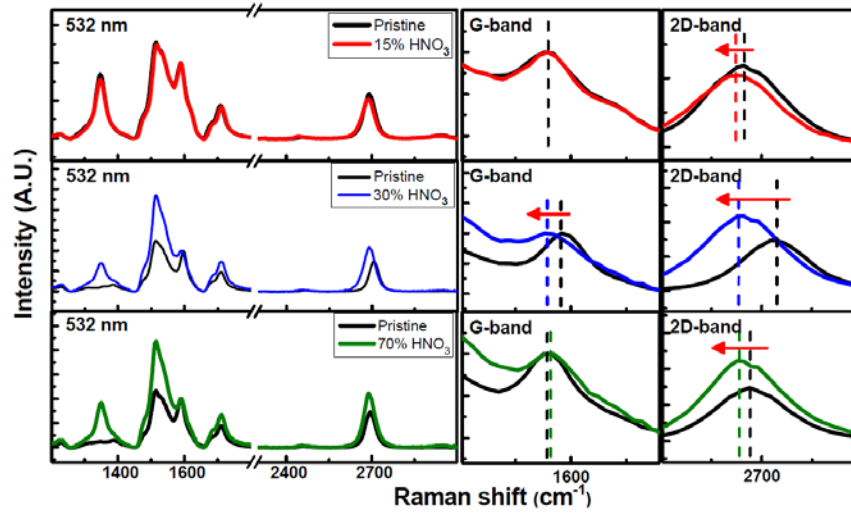


Fig.2

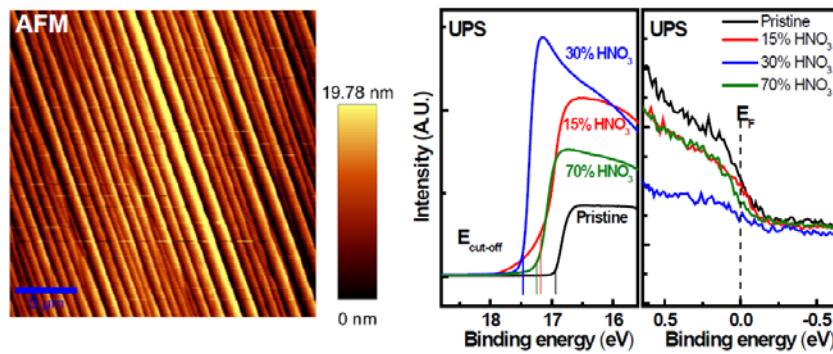


Fig.3

