PERSPECTIVE

Insight into the mechanisms of chemical doping of graphene on silicon carbide

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Insight into the mechanisms of chemical doping of graphene on silicon carbide

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Abstract
Graphene (Gr) is currently the object of intense research investigations, owing to its rich physics and wide potential for applications. In particular, epitaxial Gr on silicon carbide (SiC) holds great promise for the development of new device concepts based on the vertical current transport at Gr/SiC heterointerface. Precise tailoring of Gr workfunction (WF) represents a key requirement for these device structures. In this context, Günes et al. (2015 Nanotechnology 26 445702) recently reported a straightforward approach for WF modulation in epitaxial Gr on silicon carbide by using nitric acid solutions at different dilutions. This paper provides a deep insight on the peculiar mechanisms of chemical doping of epitaxial Gr on 4H-SiC (0001), using several characterization techniques (Raman, UPS, AFM) and density functional theory calculations. The relevance of these findings and their perspective applications in emerging device concepts based on monolithic integration of Gr and SiC will be discussed.

Keywords: graphene, silicon carbide, workfunction, doping

Graphene (Gr), a single layer of C atoms with sp² hybridization, holds great promise for applications in several fields, including high frequency and flexible electronics, optoelectronics, MEMS/NEMS, environmental sensing at the single molecular level and high precision metrology [1]. This is due to the unique combination of many interesting physical properties, such as high optical transparency (97.7% over a wide wavelength range), outstanding carrier mobility (up to \( \sim 10^8 \text{cm}^2\text{V}^{-1}\text{s}^{-1} \)), excellent thermal conductivity, mechanical robustness and flexibility, as well as the highest surface-to-volume ratio.

To date, several scalable methods have been developed to produce Gr for the above mentioned applications. In particular, two main approaches are able to provide high electrical quality Gr with a large area, i.e. (i) chemical vapour deposition (CVD) from hydrocarbon precursors on catalytic substrates (typically metals, such us Cu, Ni...) [2] and (ii) controlled graphitisation of hexagonal silicon carbide (4H- and 6H-SiC) by high temperature thermal treatments [3]. Gr obtained by the first approach is a polycrystalline material formed by domains separated by grain boundaries. Furthermore, Gr grown by CVD on metals needs to be transferred from the original substrate to an insulating or semiconducting one for electronics applications. This manipulation, usually performed using a PMMA film as carrier layer for Gr and chemical etchants to detach Gr from metal, results in the presence of polymer/metal contaminations on Gr, which typically introduce an unintentional (p-type) doping. On the contrary, thermal decomposition of SiC provides Gr directly on a semiconducting or semi-insulating substrate ready for electronics and/or optoelectronics applications. The structural and electrical properties of Gr on hexagonal SiC strongly depend on the substrate orientation, i.e. the Si face (0001) [3], the C face (000-1) [4] or the non-polar faces (11-20) and...
In particular, highly uniform single or few-layer Gr films with excellent thickness uniformity on the wafer scale and very precise epitaxial orientation with respect to the substrate can be obtained in a controllable way on the (0001) face of SiC [3]. This is a result of the peculiar growth mechanism of Gr on this SiC orientation, i.e. the formation of a \((6√3 \times 6√3)\)R30 carbon reconstruction of the (0001) face, the so-called C buffer layer, which acts as the precursor of Gr formation [4]. The presence of the interfacial buffer layer between Gr and the SiC(0001) surface is also responsible for the n-type doping (typically in the order of \(10^{13} \text{ cm}^{-2}\)) of Gr.

In spite of its excellent uniformity and crystalline quality, epitaxial Gr on SiC has been employed so far only for a limited number of applications, such as high precision metrology (quantum Hall effect measurements) [6], gas sensing [7] and high frequency (RF) transistors [8]. The main reason is the relatively high cost of SiC wafers and the difficulty of transferring Gr grown on SiC to other substrates, which makes Gr grown on metals the preferred solution for large area applications, i.e. flexible electronics, touch screens, transparent conductive electrodes etc. On the other hand, future developments of epitaxial Gr are related to the possibility of exploiting the properties of Gr in combination with those of the SiC substrate (i.e. the wide-bandgap, high critical electric field, high saturation velocity and excellent thermal conductivity). New functional devices based on the concept of ‘monolithic integration’ of Gr and SiC technologies have been proposed in recent years. As an example, S Hertel et al [9] recently proposed a metal semiconductor field-effect transistor structure in which n-doped SiC plays the role of semiconducting channel material, as-grown epitaxial Gr is used as source and drain electrodes and hydrogen intercalated Gr as Schottky gate. The proposed monolithic integration scheme is suited to form complex circuits which adds full digital functionality to Gr high frequency electronics on the wafer scale. Other device concepts jointly exploiting the unique properties of Gr and SiC have been proposed, such as a Gr/SiC heterojunction UV photodetector [10], where the Gr transparent contact minimizes absorption losses, resulting in high-efficiency sensing while maintaining the low dark current associated with the wide bandgap of SiC.

As a matter of fact, precise tailoring of the Gr workfunction (WF) is a key requirement for these devices based on the vertical current injection at Gr/SiC heterojunction. In their paper published in volume 26 of Nanotechnology, Günes et al [11] reported a straightforward approach to modulate the WF of monolayer Gr grown on 4H-SiC(0001) using nitric acid (HNO₃) solutions at different dilutions. Raman spectroscopy and ultraviolet photoemission spectroscopy (UPS) were employed to evaluate the defects density, doping and workfunction variation both in the case of pristine Gr and after dips in HNO₃ at dilutions of 15%, 30%, 70% and 100%. Interestingly a non-monotonic behaviour of the WF as a function of HNO₃ dilution was observed, with a decrease of the WF (i.e. an increase of n-type doping) from pristine Gr to 30% dilution, followed by an increase of the WF for HNO₃ dilutions from 30 to 100% (see schematic in figure 1).

Treatments with HNO₃ solutions have been already reported in the past as a very efficient method for p-type doping of CVD grown Gr [12]. This study on epitaxial Gr presents striking differences compared to previous works on CVD Gr, demonstrating how the two Gr systems react differently to an identical chemical functionalization. As a matter of fact, the doping behavior of epitaxial Gr on SiC depends on the peculiar structural properties of this material. Epitaxial Gr on SiC(0001) follows the typical surface morphology of the substrate, characterized by the presence of (0001) oriented terraces separated by nanometer high steps or facets with (11-20) or (11-2n) orientations. Several investigations have demonstrated that these morphological features, originating from the miscut angle of the SiC wafer with respect to crystal growth axis, introduce local non-uniformities both in the number of Gr layers and in the structural and electrical properties Gr/
SiC interface [13, 14]. From the electrical point of view, this causes an anisotropy in the conductance of Gr with respect to step orientation [13]. Günes et al explained the HNO₃ doping behavior of Gr on SiC as a result of two competing effects, i.e. the preferential incorporation of nitrogen atoms (n-type dopants) in Gr defective sites corresponding to SiC step edges at lower HNO₃ concentration, and the physisorption of HNO₃ molecules (acting as p-type dopants) on Gr residing on (0001) SiC terraces, which becomes dominant for higher HNO₃ concentrations. This scenario is supported by density functional theory calculations.

This paper is especially interesting because it provides a deep insight on the peculiar mechanisms of chemical doping of epitaxial Gr on 4H-SiC (0001). Further investigations will be required to evaluate the stability of the doping as a function of temperature and time, in order to integrate these processes in the fabrication of functional devices based on Gr/SiC heterostructures.

References

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Figure 1. Schematic representation of the WF changes in Gr on SiC(0001) as a function of the HNO₃ concentration. Adapted from [11].
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