Quasi-freestanding Epitaxial Graphene on SIC (0001) Via Fluorine Intercalation from a Molecular Source

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The process of graphene formation via fluorine intercalation and its properties was investigated using Low Temperature Scanning Tunneling Microscopy (LT-STM), Scanning Tunneling Spectroscopy (STS) and Photoemission Spectroscopy (PES). Quasi-freestanding epitaxial graphene with dilute fluorination was achieved after intercalation using $C_{60}F_{48}$ as a source of fluorine. This is confirmed by the absence of the underlying SiC 6√3 x 6√3 R 30° reconstruction and presence of novel structures observed under LT-STM. PES reveals that fluorine exists as a passivation layer at the graphene-substrate interface. STS measurements reveal the effect of a localized impurity potential on the electronic structure of graphene due to possible fluorine adsorption from below.

Introduction

Graphene, a single atomic layer of carbon, has attracted lots of attention in recent years due to its impressive electronic, optical, mechanical and thermal properties[1]. Those grown on hexagonal SiC (0001) wafers provide a means for integration in existing device technology[2]. However, a limiting factor in the usage of such wafers is the high intrinsic electron doping and low electron mobility due to the presence of a buffer layer[3].

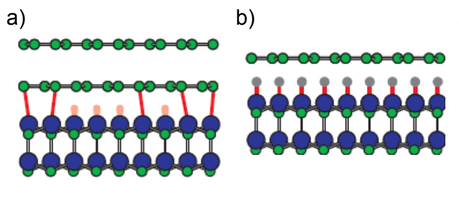

Fig. 1a) Model of an as-grown epitaxial graphene with an underlying buffer layer on SiC(0001)
1b) Quasi free-standing graphene after hydrogen intercalation. Figure from ref. 3.

Removal of this buffer layer has been performed using hydrogen[4] and other elements. These products have been intensively studied using averaged PES and LEEM[4] measurements but STM experiments have not been done to study local nanoscale effects of intercalation on graphene and the interfacial layer. In this work, we demonstrated successful fluorine intercalation using $C_{60}F_{48}$ as fluorine source and observed the associated structural and electronic changes via Low Temperature Scanning Tunneling Microscopy (LT-STM) and Scanning Tunneling Spectroscopy (STS). The intercalated product is confirmed via Photoemission Spectroscopy (PES).

Methodology

A sample having surfaces containing both epitaxial monolayer graphene and buffer layer were used as the substrate for intercalation. A reference sample having an epitaxial monolayer graphene surface was also prepared for comparison in PES studies.

- Both samples were grown via graphitization from the SiC (0001) face under UHV conditions.
- $C_{60}F_{48}$ was first deposited on the sample in-situ.
- Initial annealing at 150°C to allow fluorine migration from the molecule to the interface below the buffer layer.
- Annealing at a higher temperature of 800°C to complete the decoupling process.
- LT-STM and STS was measured at 77K with a base pressure lower than 1.0 x 10^{-10} mbar with a chemically etched tungsten tip.
- PES measurements were performed at the SINS beam line in the Singapore Synchrotron Light Source with a resolution of 0.05 eV.

Results and Discussion

LT-STM

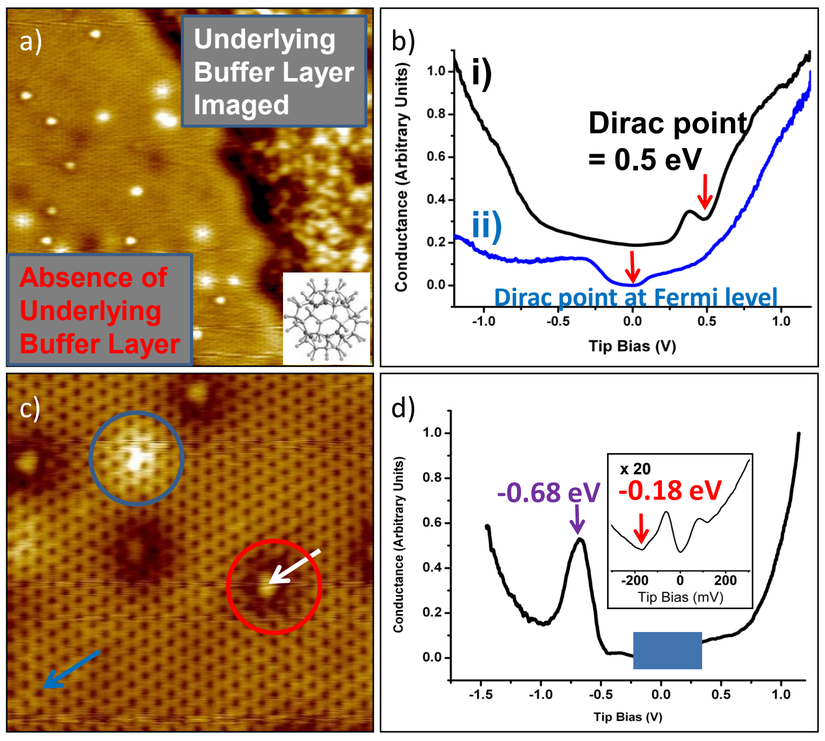

Fig. 2a) 20 x 20 nm STM image showing both quasi free-standing graphene and pre-existing graphene after intercalation.
b) Averaged dI/dV spectra taken on i) pre-existing graphene and ii) decoupled graphene, indicated by a blue arrow. c) 7nm x 7 nm STM image of surface. d) dI/dV spectra taken over bright spots on decoupled graphene, as indicated by a white arrow.

- Absence of buffer layer under graphene indicates successful intercalation and decoupling of the buffer layer to form quasi free-standing graphene. Intercalation only occurs on buffer layer and not pre-existing graphene.
- Quasi free-standing graphene is charge neutral compared to pre-existing coupled graphene with electron doping.
- Novel structures formed on quasi free-standing graphene. Diffusive bright spots (circled blue) are undulations of graphene sheet and protrusions (circled red) are due to impurities adsorbed below graphene layer.
- STS done on protrusion show local hole doping and resonance peak at 0.68 eV above Fermi Level.
- Indicates possibility of perturbation by a highly localized potential[5] in the form of electron withdrawing fluorine adsorbed below the graphene sheet.

Synchrotron PES

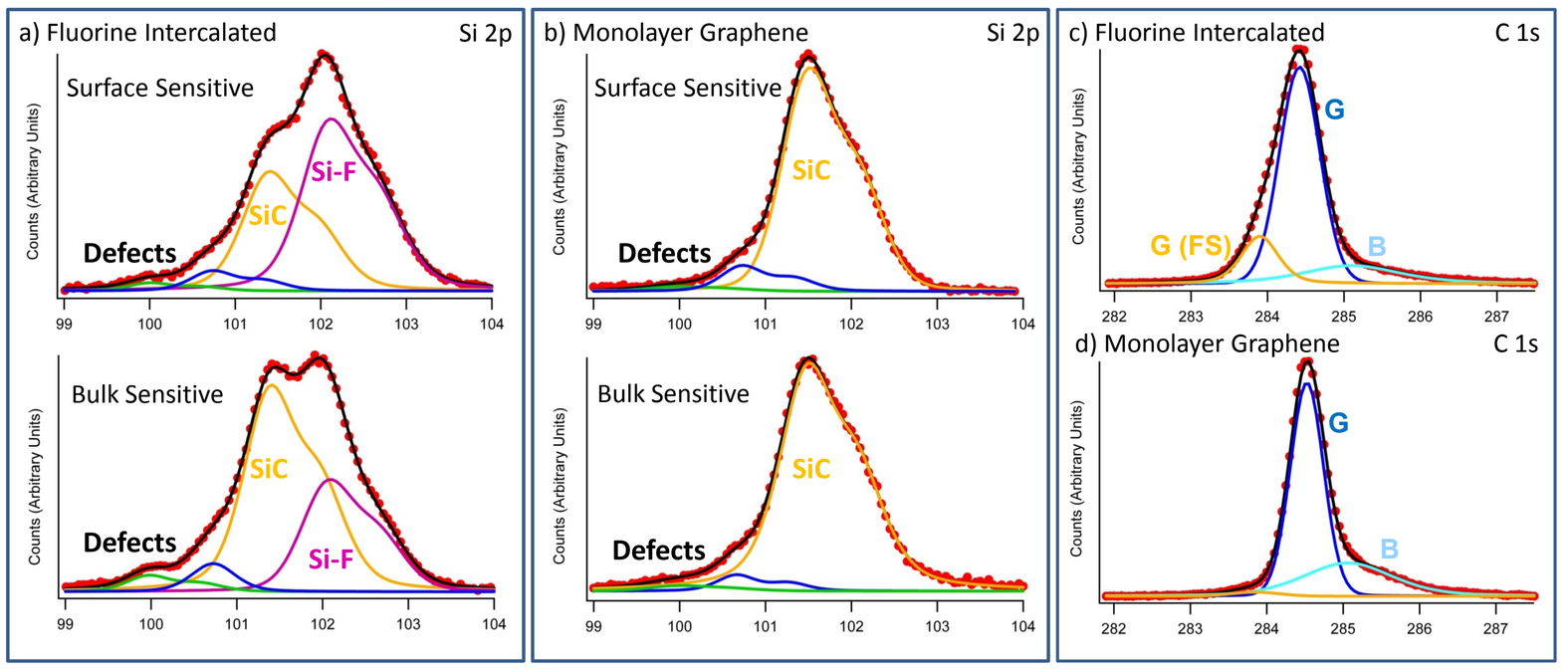

Fig. 3) Core level spectra for a) fluorine intercalated graphene sample and b) monolayer graphene. The spectra in the top panel is collected with the beam entering at normal incidence (surface sensitive) while the spectra in the bottom panel is with the detector placed at normal emission (bulk sensitive). c) Fluorine intercalated graphene sample and d) monolayer graphene. Experimental data are displayed in red dots. The black solid line is the envelope of the fitted components which are labeled accordingly.

- Presence of new Si 2p component at higher binding energy because of electronegative Fluorine bonded to Si.
- Surface sensitive measurements show higher ratio of Si-F : Si-C component which is inverse of that in bulk sensitive measurements, indicating Si-F is present at the interface between graphene and SiC substrate.
- New C 1s peak belonging to quasi free-standing graphene labeled G(FS) at binding energy 0.5 eV lower than the main C1s graphene peak matches difference in Dirac points as measured from STS.
- PES measurements confirm hypothesis of a Si-F interface layer formed after intercalation with a reduced in electron doping of the as-formed quasi free-standing graphene.

References

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Conclusion

In conclusion, we have successfully performed fluorine intercalation to form quasi free-standing graphene using a molecular source and have confirmed it from PES and STM observations. This process is highly selective due to its weaker nature of intercalation and only takes place on the buffer layer. This demonstrates the possibility for use of other molecules with different functionalities for such intercalation at designated locations on the surface. The intercalated interfacial layer is stable up to 1200°C and under ambient conditions, therefore being suitable for electronic applications.