

Observation of 2D Si-Vacancies Filled by Gallium Intercalation of Epitaxial Graphene

Hesham El-Sherif¹, Natalie Briggs², Brian Bersch², Joshua Robinson², Nabil Bassim^{1,3}

¹ McMaster University, Materials Science and Engineering department, Hamilton, ON, Canada

² The Pennsylvania State University, Department of Materials Science and Engineering, State College, PA, USA

³ Canadian Center for Electron Microscopy, Hamilton, ON, Canada

Recently, the synthesis of various 2D materials confined at the epitaxial graphene interface has been realized through confinement heteroepitaxy (CHet) [1]. In this technique, atoms intercalate at the interface of epitaxial graphene (EG) and silicon carbide (SiC) substrates via a thermal evaporation process, typically at 800 °C. Although the EG is deliberately damaged using plasma to open intercalation holes prior to the CHet process, the EG is found to be healed after the metal intercalation due to a metal catalytic effect. The CHet process facilitates scalable and environmentally air-stable 2D metals and alloys over millimeter-scale [2,3]. CHet metals and alloys exhibit novel properties, such as enormous second harmonic generation [4], superconductivity [1], and epsilon-near-zero behavior [5]. The air-stability, due to the graphene cap, is a critical factor for integrating these materials for next-generation quantum devices, high-frequency electronics, and sensing technologies. Although the CHet materials have been studied by scanning transmission electron microscopy (STEM) techniques, the understanding of the SiC–metal interface is still challenging. Here we use aberration-corrected STEM and many cross-section samples thinned below 50 nm (using a Helios G4 Xe+ PFIB system) to observe that the CHet interface structure is not a superficial epitaxial metallic layer on a perfect 6H-SiC stacking.

Figure 1a shows a high annular angle dark field (HAADF) image of the plasma-treated EG interface before the intercalation process. The HAADF images are acquired using a double-corrected FEI Titan Cubed STEM microscopy operates at 200 keV and has 50-100 nA screen current. The topmost SiC layer does not follow the same 6H-SiC stacking but has a 3C stacking order instead. The HAADF intensity in Fig. 1b indicates that the topmost SiC layer has less Si intensity compared with the bulk SiC which means that this layer is more likely to have Si-vacancies. The loss of Si atoms from this layer can be due to the EG formation mechanism [6], which is associated with surface reconstructions evident in the out-of-plane selvedge (~ 2.75 Å) distance at this layer. Moreover, the broken Si-C bonds at the selvedge plane are detectable in the electron energy loss spectroscopy (EELS) signal in Fig. 1c where the C-K edge shows the weak bond signature (π bond) co-located from the topmost SiC layer. This EELS signal is collected from a spectrum image with 0.5 Å spatial resolution, and the signal is acquired by the Gatan's K2 IS direct electron detector.

Figure 2a shows the EG interface after Ga intercalation. Gallium passivates the Si-face SiC surface and heals the plasma-treated EG to form higher-quality graphene cap. The 3C stacking at the topmost layer is still observable after intercalation, but the HAADF contrast at this layer is higher than the bulk SiC. An EELS compositional profile across the interface shows a significant Ga signal (Fig. 1b and c) co-located at the topmost SiC layer. This indicates that the Si-vacancies in the topmost SiC layer are filled with the Ga atoms due to the intercalation process. With these observations, we could explain repeatable STEM-HAADF images of a variety of CHet interfaces, including 2D Gallium, Indium, and InGa alloys that show metal-SiC intermixing only at the topmost SiC layer. The control of this intermixing could provide local tuning of the electronic structure of the CHet layers. Further in-situ heating STEM experiments will be conducted to understand the interface intermixing [7].

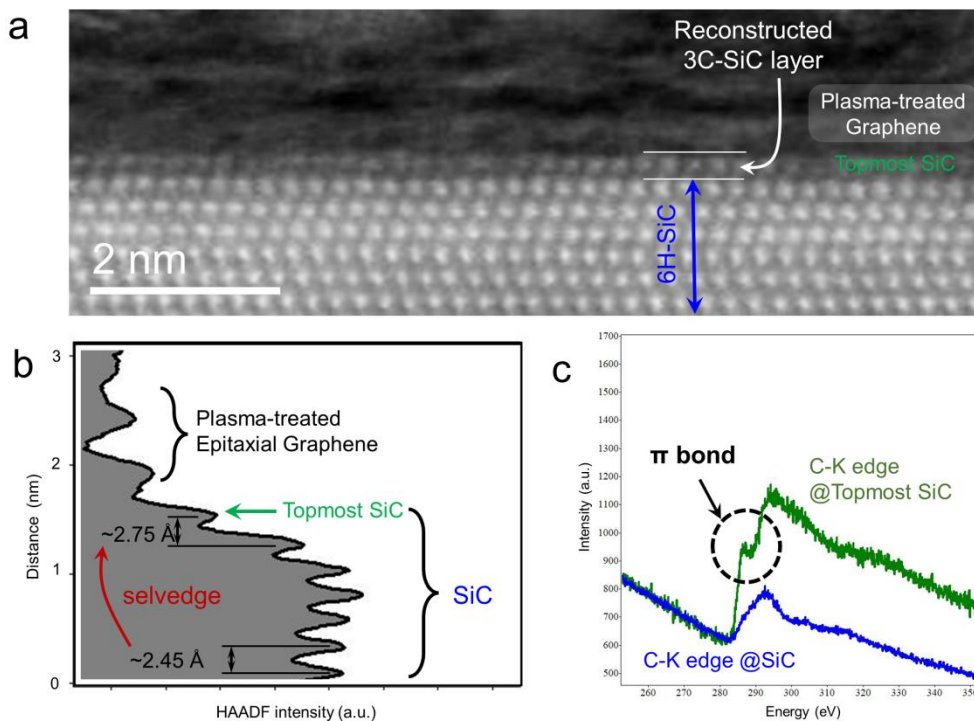


Figure 1. Evidence of silicon vacancies in the topmost SiC layer before the metal intercalation process. (a) STEM-HAADF image of plasma-treated EG. The SiC has 6H stacking while the topmost layer is reconstructed into a 3C stacking. (b) HAADF intensity profile from the image in (a) shows lower contrast of the topmost SiC layer than the rest of the bulk SiC crystal in addition to a selvedge distance at the topmost SiC layer as a result of possible surface reconstruction seen in cross-section view. (c) Core-loss EELS signals of carbon K-edge collected from the topmost SiC layer and the bulk SiC crystal.

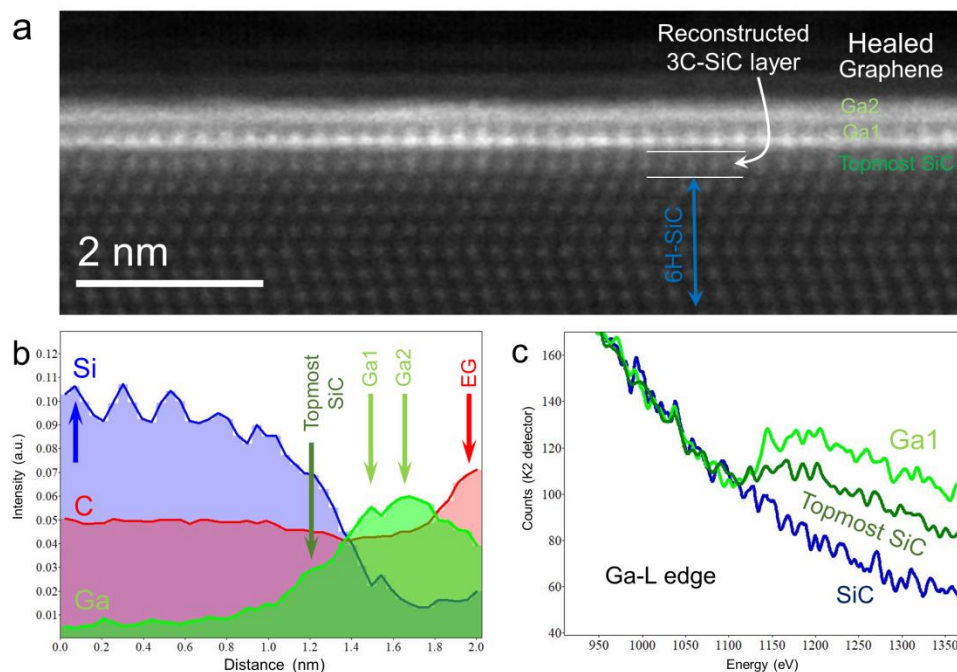


Figure 2. Evidence of metal filling the Si-vacancies at the topmost SiC layer. (a) STEM-HAADF image shows bilayer gallium encapsulated between the bilayer EG and SiC. The topmost SiC layer has 3C stacking order compared with 6H stacking for the rest of the substrate. A slightly higher HAADF intensity at the 3C layer can be observed. (b) EELS profile across the interface shows significant gallium co-located with the topmost SiC layer. (c) Core-loss EELS signal at the Ga L-edges collected from the intercalated gallium, the topmost SiC layer, and the SiC substrate. The Ga signal and its spatial location indicate that the possible Si-vacancies at the topmost SiC layer are filled by metal.

References:

- [1] N Briggs et al., *Nature Materials* **19** (2020), p. 637. doi:10.1038/s41563-020-0631-x
- [2] H El-Sherif et al., *ACS Applied Materials & Interfaces* **13** (2021), p. 55428. doi:10.1021/acsami.1c14091
- [3] S Rajabpour et al., *Advanced Materials* **33** (2021), p. e2104265. doi:10.1002/adma.202104265
- [4] M Steves et al., *Nano Letters* **20** (2020), p. 8312. doi:10.1021/acs.nanolett.0c03481
- [5] K Nisi et al., *Advanced Functional Materials* **31** (2020), p. 2005977. doi:10.1002/adfm.202005977
- [6] D Wang et al., *Nanoscale* **7** (2015), p. 4522. doi:10.1039/c4nr07197b
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