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Correlative Microscopy Reveals Air-Stable 2D Gallium-Intercalated Monolayer Epitaxial Graphene

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The fabrication of various 2D metals 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 inside a tube furnace, typically at 800 °C. The intercalation of a monolayer EG results in passivating the Si dangling bonds of the Si-face SiC, which consequently detaches a carbon-rich buffer layer and form a new graphene layer after the intercalation (Fig. 1a). To enable large area intercalation, the EG surface is deliberately damaged before the intercalation using plasma (3:1 O_2/He mixture at 50 Watts for 60 seconds), which facilities scalable fabrication of 2D metals and refractory compounds over millimeter-scale [2]. The 2D CHet layers exhibit novel properties such as superconductivity [3], enormous second harmonic generation [4], and epsilon-near-zero behavior [5]. To make use of these materials in electronic or optical applications, the layers should be environmentally air-stable.

Although the air-stability of 2D metals intercalation of monolayers EG has been studied using X-ray photoelectron spectroscopy (XPS) techniques [1], the presence of oxygen signal in XPS at the time of fabrication is still confusing. This confusing signal (Fig. 1.b) was interpreted to come from oxidized micrometer-size metallic particles on the sample's surface. However, our plan-view auger electron spectroscopy (AES) maps from a 2D gallium (2D-Ga) surface in Fig. 1c-e show significant oxygen signals co-locates at the confined Ga regions. The AES maps were acquired using JEOL JAMP-9500F at 10 kV, 10−20 nA, and $<10^{-6}$ mbar where the Auger electrons are analyzed using a hemispherical analyzer equipped with a seven-channel detector. Here we utilize correlative microscopy workflows to reveal that the 2D-Ga regions has an oxygen signal but locates above the metal in cross-section view – without actual oxidation of the 2D-Ga. By preparing a site-specific cross-section from the 2D-Ga surface [2], we could employ aberration-corrected scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) investigations to understand the role of bilayer graphene in protecting the 2D-Ga.

A pristine 2D-Ga surface was scratched using tweezers to peel off the graphene from a region and then to expose the surface in the air and room temperature for more than six weeks. Because of the graphene has weak bonding with the metal, it can be exfoliated without damaging the Ga layer within few micrometers area besides the actual sever scratch. Then, an FEI Helios G4 PFIB system with a Xe+ plasma ion source is used to prepare a cross-section from a site that covers both peeled and unpeeled regions as illustrated in Fig. 2a,b. Identifying this site and its contents is possible using the SEM contrast as previously studied [2]. A double-corrected FEI Titan STEM (operated at 200 keV and 50-100 nA screen current) is used to acquire high annular angle dark field (HAADF) images from both the peeled and unpeeled regions in the cross-section view. The HAADF image in Fig. 2c confirms that graphene is essential to preserve air-stable epitaxial gallium structure on the SiC. In addition, EELS maps in Fig. 2f confirm that Ga at the peeled region is oxidized and forms a non-crystalline Ga_xO_y as seen in Fig. 2d. For the unpeeled region, a weaker oxygen signal exists (Fig. 2e) and is spatially co-located with the graphene, which indicates that the plasma process, used prior to the intercalation to damage the EG, incorporates few oxygen traces into the graphene. This site-specific experiment explains the confusing oxygen signal that is usually detectable in XPS and AES at the time of preparation.

Our correlative microscopy work confirms that the bilayer graphene encapsulation is the key factor in the protection of the confined metallic Ga from oxidation in the air in addition to epitaxially stabilizing the Ga layers on the SiC substrates. Moving forward, air-stable 2D-Ga can be integrated into next-generation quantum devices, high-frequency electronics, new optical devices, and sensing technologies [6].

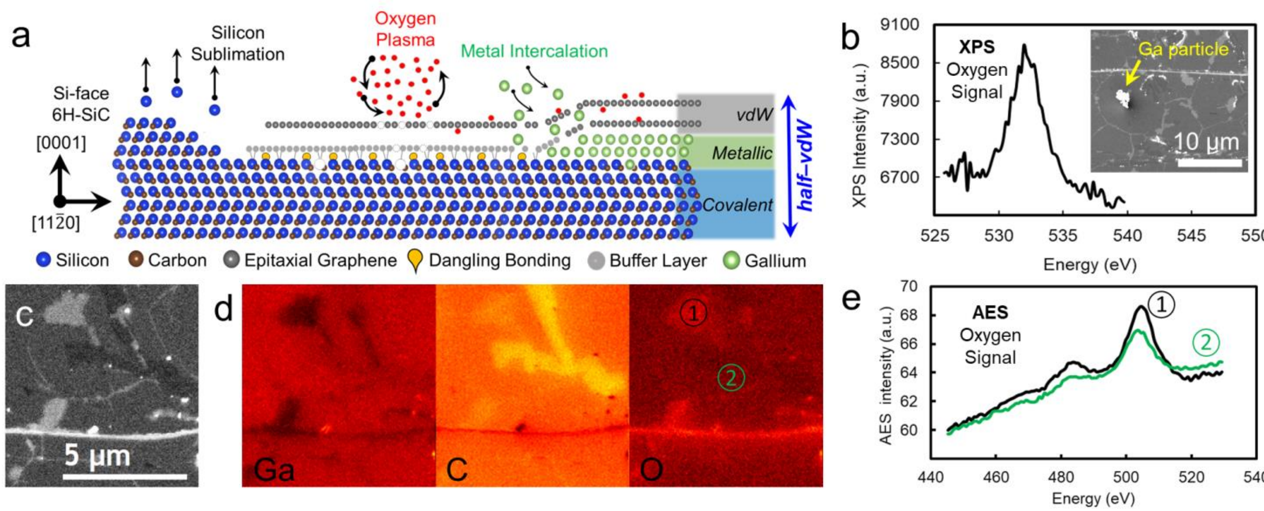

Figure 1. Presence of oxygen signal in 2D gallium-intercalated of epitaxial graphene. (a) a schematic represents the fabrication steps of Ga interaction of a monolayer epitaxial graphene. The buffer layer is detached and forms a bilayer graphene cap over a bilayer Ga layer. The final structure is called half-vdW heterostructure because it achieves three bonding types across the interface. (b) XPS signal from 2D-Ga surface. The insert is an SEM image shows a micrometer-size oxidized Ga particle in the surface which could contribute to the XPS oxygen signal. (c) Higher magnification SEM image and (d) the corresponding auger electron spectroscopy (AES) maps for gallium, carbon, and oxygen. (e) AES point spectrum at the oxygen signals from sites 1 and 2 as indicated in the oxygen map in (d). The AES maps and the signal spectrum from site 2 confirm that there is oxygen co-located with the gallium. However, the plane-view AES characterization cannot confirm if the 2D-Ga layer is oxidized.

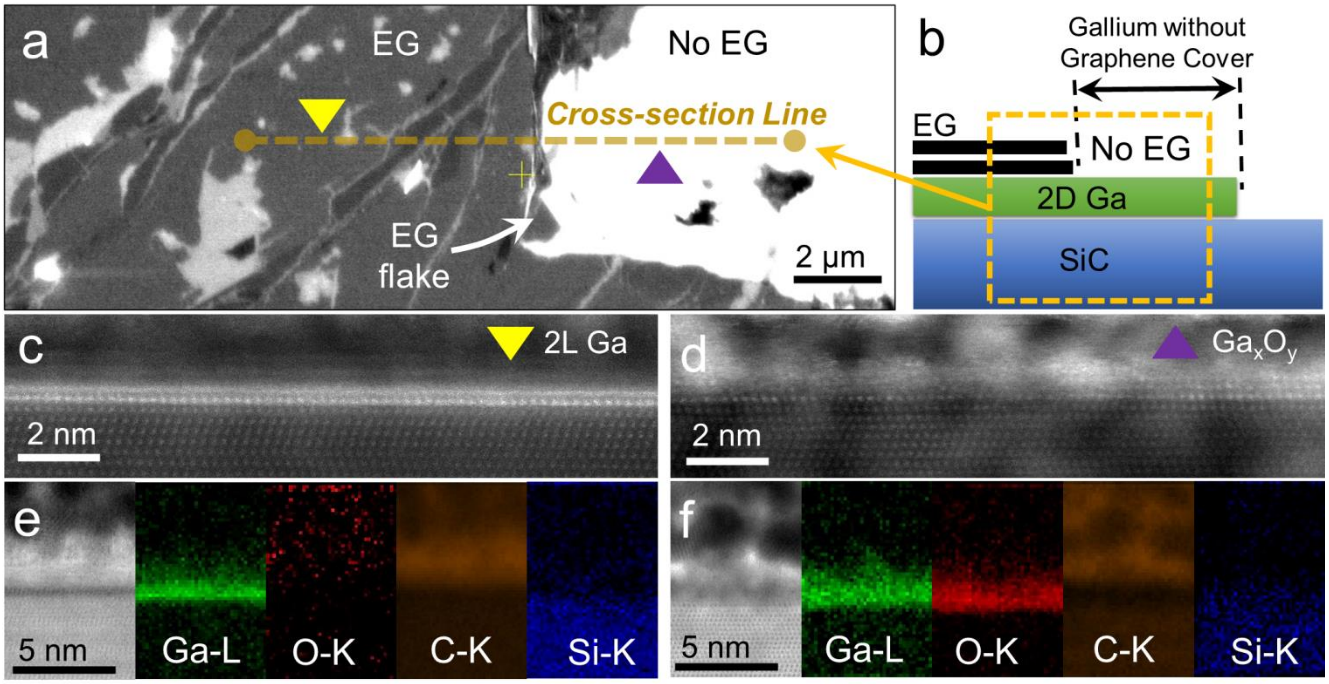

Figure 2. STEM and EELS investigation of a site-specific cross-section prepared near a peeled EG region. (a) SEM image shows graphene flakes at the peeled boundary. The right side has Ga layer that increases the secondary electron emission and saturate the SEM contrast at this region. A ~10 µm cross-section is prepared at the indicated with the orange line. (b) a schematic diagram shows the expected cross-section view for the site-specific preparation in (a). (c) and (d) are HAADF images from the unpeeled and peeled EG regions, respectively. The presence of graphene ensures the epitaxial structure of the 2D-Ga but the peeled EG region shows cloud-like non-crystalline gallium on the surface. (e) and (f) ADF images and the corresponding EELS maps of the Ga L-edge, O K-edge, C K-edge, and the Si K-edge from the unpeeled and peeled EG regions, respectively. The HAADF and EELS maps confirm that the graphene provides air-stability of the 2D-Ga. A few oxygen counts are present in the top of the Ga location of the unpeeled region which originates from the plasma applied before the intercalation.

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