Stabilizing Phosphorus Oxides at Confined Heterointerfaces

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A clean interface is crucial to obtain complex heterostructures with pre-determined properties. Intercalation, a polymer-free method to realizing vertical stacks with a clean interface, remained challenging for large intercalants. In this work, we reported the intercalation of P_2O_5 via chemical reactions at the graphene-Ge (110) heterointerface. Strong P and O signals from energy dispersive X-ray spectroscopy (EDS) were detected underneath the graphene layer on the cross-section of the graphene-Ge (110) heterointerface. A two-step mechanism for the intercalation process was that P_2O_5 decomposed into small fragments (i.e., P, O). These small fragments intercalated through graphene, reacted, and formed P_2O_5 at the graphene-Ge (110) interface. The P_2O_5 intercalated not only tunning the electronic structure of graphene on top with charge transfer but also converting metal (e.g., Ga) to its phosphate form. This study offers an important opportunity for advancing the understanding of mechanism for unstable large molecule intercalation at the graphene-substrate heterointerface.

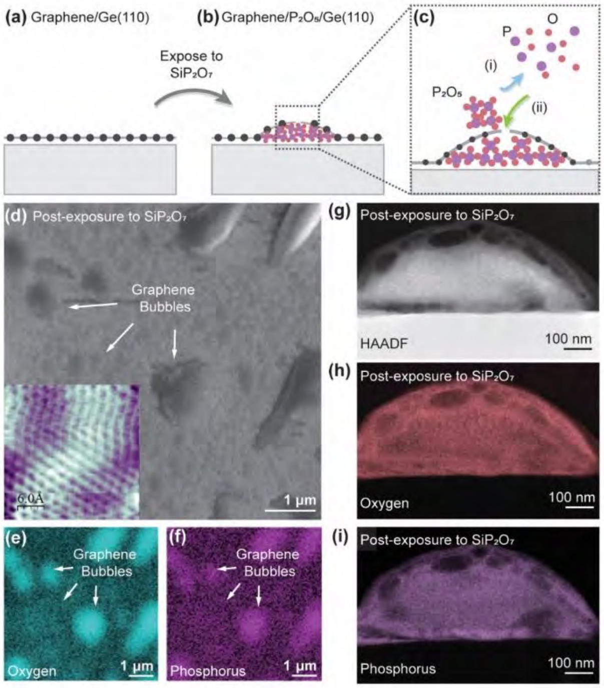

Figure 1 (a, b, and c) Schematic illustration for the intercalation process. (d) SEM and (inset) STM image for graphene bubbles (white arrows). SEM-EDS elemental mappings of (e) oxygen, (f) phosphorus for the region shown in (d). Graphene bubbles were marked with white arrows. Scale bar is 1 μm. (g) STEM-HAADF image and STEM-EDS elemental maps of (h) oxygen, and (i) phosphorus within graphene bubbles.

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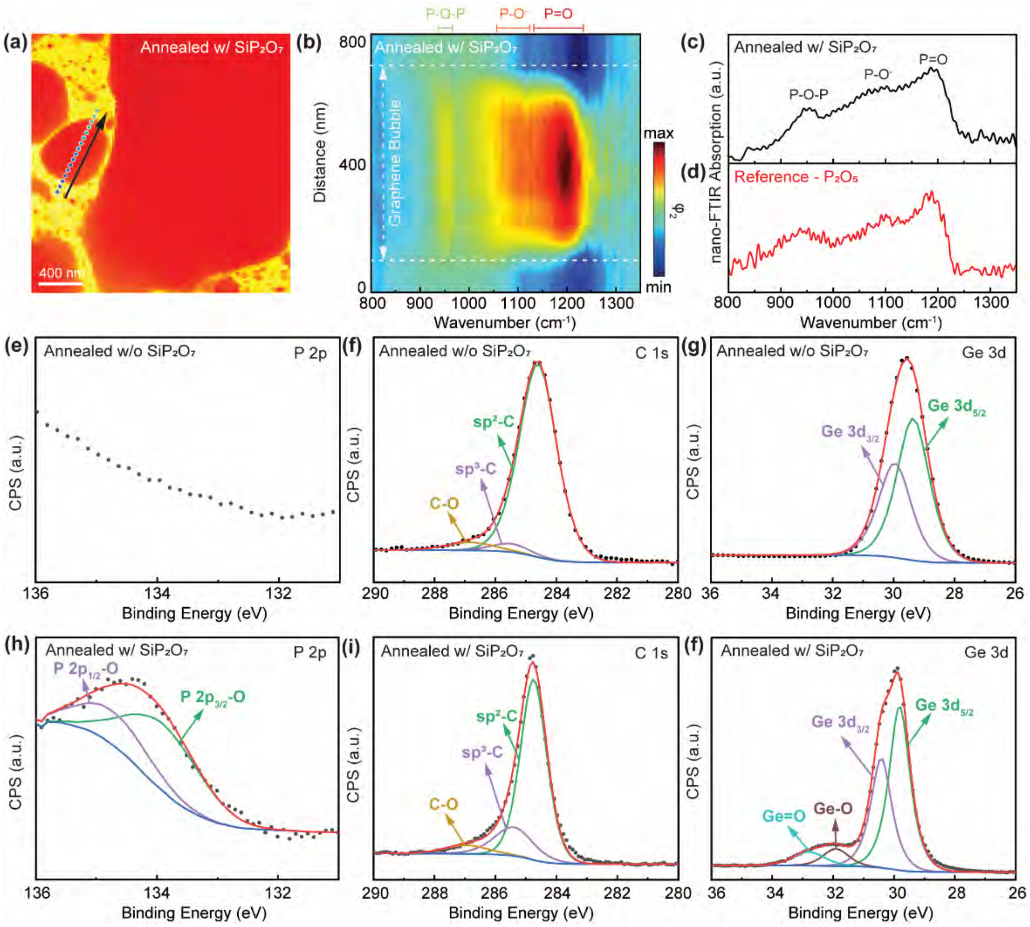

Figure 2. Chemical environment for graphene/P_2O_5/Ge (110) system. (a) Near-field white light IR image in a region containing graphene bubbles. The white light IR image is the near-field amplitude (S_2) image, which is spectrally averaged over approximately 610-1400 cm^{-1} by setting the interferometer at the white light position (WLP). The scale bar is 400 nm. **(b)** Color map representation of nano-FTIR spectra for different vibration modes for bonding between phosphorus and oxygen acquired at 50 nm intervals along the *blue-to-green dot line* and *black solid arrow* in **(a)**. The spectra displayed here are the near-field phase channel (φ_2), which correspond to the absorption spectra of the material. The graphene bubble region is highlighted with *white dash lines and dash arrow*. Comparison of a nano-FTIR measurement of **(c)** a graphene bubble with **(d)** P_2O_5 solid. XPS spectra for graphene on Ge (110) annealed **(e**, **f**, and **g)** without SiP_2O_7 and **(h**, **i**, and **j)** with SiP_2O_7, respectively. High-resolution XPS spectrum for core-levels of **(e** and **h)** P 2p, **(f** and **i)** C 1s, and **(g** and **j)** Ge 3d. All data were collected after annealing treatment.

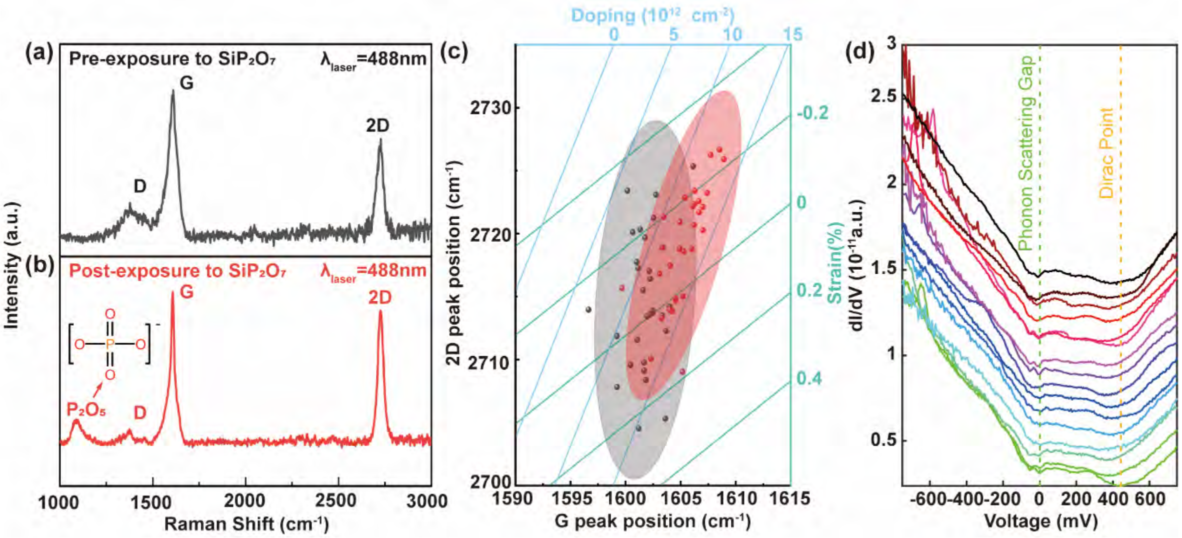

Figure 3. Modulation of graphene doping level with P_2O_5 intercalated. Raman spectra for graphene on Ge (110) **(a)** before and **(b)** after exposure to SiP_2O_7. **(c)** 2D peak position versus G peak position for spatially resolved Raman spectra of graphene on Ge (110) before (black dots) and after (red dots) exposure to SiP_2O_7. **(d)** dI/dV tunneling point spectroscopy for graphene on Ge (110) after exposure to SiP_2O_7. The corresponding phonon scattering gap and Dirac points are highlighted with green dash line and yellow dash line, respectively.

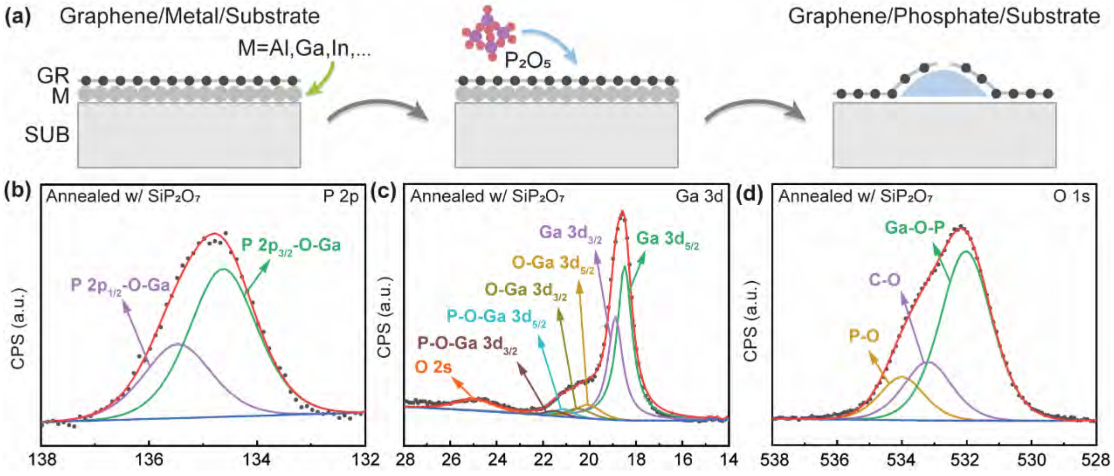

Figure 4. Synthesis of metal phosphate at heterointerface. **(a)** Schematic illustration for the conversion of metal (e.g., Ga, Al, In, etc.) to its phosphate form at heterointerface. (**b**, **c**, and **d**) High resolution XPS spectra for gallium embed at graphene-SiC (0001) interface after annealing with SiP_2O_7 for: (**b**) P 2p, (**c**) Ga 3d, and (**d**) O 1s. All data were collected after annealing treatment.