

Atomic Arrangement of Contamination on Graphene

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Graphene is an ideal sample support since it has the thickness of a single atom and is stable under low-voltage irradiation that is below the knock-on damage threshold of graphene. However, the surface of free-standing graphene frequently becomes contaminated during long periods of electron microscopic observation, and this contamination interferes with the observation of the target. Such contamination is thought to consist of amorphous carbon, but its atomic structure is not clear. On the other hand, crystalline graphene grows at the step-edge of bilayer graphene at high temperature [1]. In this paper, we report the atomic-resolution observation of contamination grown on monolayer graphene at room temperature and the contamination's atomic arrangement.

Graphene was grown by chemical vapor deposition (CVD) using an optimized recipe on Cu substrates. The graphene grown on one side of the substrates was removed by a mixed solution of hydrogen peroxide and sulfuric acid, followed by etching in ammonium persulfate solution to remove the Cu substrates. After the ammonium persulfate solution was exchanged for distilled water, the graphene was transferred to a Quantifoil holey carbon film TEM grid (R1.2/1.3 Cu 400 mesh) by using a scoop. The free-standing graphene sample was studied using aberration-corrected TEM/STEM (FEI Titan cubed G2 60-300) operating at 80 kV. After contamination was grown on monolayer graphene by a scanning electron beam, the monolayer graphene area including the contamination was pretreated with an electron beam shower. Next, we observed atomic-resolution annular dark-field (ADF) images of the contamination and analyzed its atomic structures.

Figure 1A is an ADF image of the boundary between the monolayer graphene and its contamination. Figure 1B shows the line profile of the dashed-line arrow in Figure 1A. The intensity is integer multiples of the monolayer graphene area, as with the dark-field image intensity of multilayer graphene [2]. Next, 50-frame atomic-resolution ADF images were observed in the monolayer graphene area under the conditions of 1.97 sec frame time and 6 sec dwell time. The observed images were filtered by a low-pass filter in Fourier space. Figure 1C and 1D show ADF images of a first-frame and 37th-frame, respectively. Moreover, the contamination grew on it during the observation. The dashed line in Figure 1D indicates the boundary between the contamination and the graphene. The structures of the contamination area, corresponding to AA stacking, pentagon, heptagon and mono-vacancy, are obtained by removing a hexagonal spot from the Fourier transform of the image in Figure 1D. In addition, the intensities of the convex points extracted from Figure 1D are integer multiples of a single carbon atom. Several of these points had three times the intensity of a single carbon atom. Therefore, the contamination consisted of a few layers of carbon, similar to multilayer graphene. From these results, we can draw the atomic arrangement of Figure 1D as shown in Figure 1E. In conclusion, contamination on graphene is not amorphous, but consists of nanographene.

References:

- [1] Z. Liu *et al.*, *Nat. Commun.* **5** (2014) 4055.
[2] J. C. Meyer *et al.*, *Solid State Commun.* **143** (2007) 101.

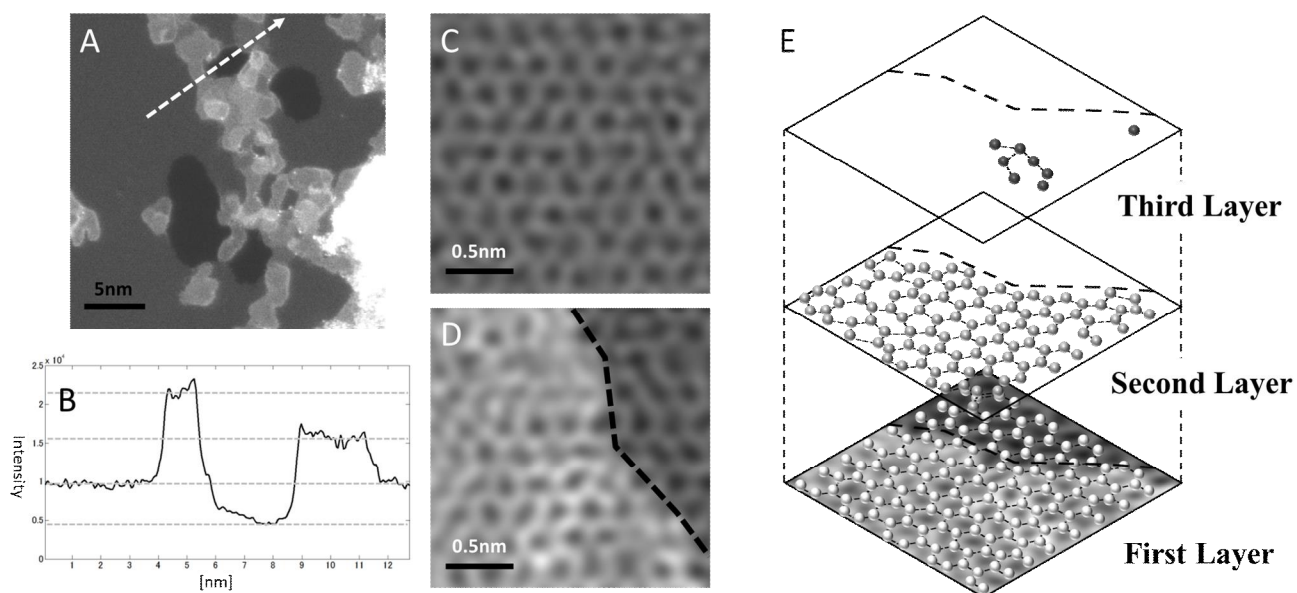


Figure 1. A: ADF image of monolayer graphene and contamination. B: Line profile of the dashed-line arrow in A. C: Filtered ADF image of monolayer graphene. D: Filtered ADF image of contamination on the graphene. E: Atomic arrangement of D.