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Elasticity Measurements of Ultra-hard, Ultra-stiff Graphene Films via Atomic Force Microscopy Modulated Å-Indentation

The ability to characterize and manipulate materials down to the atomic scale for tuning their mechanical and physical properties is the cornerstone of material science. Here we explore the elastic properties of supported 2D graphene films by the use of modulated Å-Indentation, a novel Atomic Force Microscopy (AFM)-based technique capable of achieving sub-Å indentation depths during force-indentation measurements. In conventional nanoindentation experiments, the indentation depths are usually in the order of units of nanometers, which hinder the possibility of studying ultra-thin films (<10 nm) and atomically thin 2D materials supported on substrates. By using extremely small amplitude oscillations (<<1 Å) at high frequency, achievable by combining a commercially available lock-in amplifier and AFM, we show how Å-Indentation enables non-destructive local accurate measurements of the contact stiffness and out-of-plane elastic moduli of ultra-thin ultra-stiff films, including CVD diamond films (thus even up to TPa range stiffness), as well as the transverse moduli of supported graphene and other 2D materials (<1 nm thickness). Å-Indentation thus obtains in-situ indentation curves combining superior resolution and indentation depths as small as 0.3 Å (Fig.1) with AFM nanoscale topographical imaging. Thanks to this technique, we experimentally demonstrate that at room temperature and under localized indentation pressure, a single layer of graphene on top of a carbon interface layer (buffer layer), both epitaxially grown on the Si-face of a SiC(0001) substrate, exhibits transverse stiffness superior to that of CVD bulk diamond (Fig.1). Backed by density functional theory (DFT) calculations, these results indicate that the 1+buffer layer graphene film undergoes a pressure-induced phase transformation to a new ultra-stiff, ultra-hard diamond structure, named *diamene*, followed by a sp^2-to-sp^3 chemical bond transitions. Furthermore, we find that the formation of ultra-stiff *diamene* is exclusive of 1-layer epitaxial graphene plus buffer layer films grown on SiC(0001), and it is not observed in the buffer layer alone, nor in thicker epitaxial graphene (2-layer or more – see Fig.1), nor in exfoliated graphene films of any thickness on SiO_2 substrate. Extending the capabilities of the Å-indentation technique to the analysis of other 2D materials, our ongoing studies explore the possibility of similar pressure-induced phase transition in hexagonal boron nitride (h-BN). Recent experiments demonstrate that 2-layer h-BN flakes, mechanically exfoliated on SiO_2 substrate, consistently exhibit a transverse elastic modulus almost two times larger than that of the bare substrate. This stiffening effect thus appears to be related to the conversion of h-BN to cubic BN (c-BN) induced by the pressure applied through the indenter.

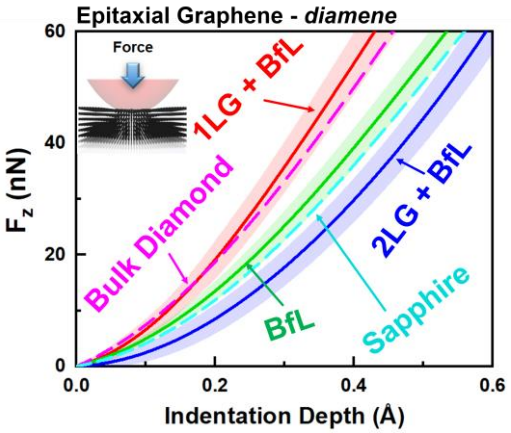

Figure 1: Experimental force vs indentation curves showing that *diamene* (1-layer graphene + buffer layer) exhibits stiffness larger than CVD bulk diamond. The ultra-high stiffening effect is not obserbved for 2-layer graphene + buffer layer.

References

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