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Pressure-induced Formation of an Ultra-Hard 2D Diamond Structure from Graphene and h-BN

The quest for materials with exceptional mechanical properties is the long-time focus of major efforts in the material science community. The study of the nanomechanical behavior of atomically thin graphene has led to the discovery of attractive mechanical properties, such as its outstanding in-plane stiffness and out-of-plane flexibility, although its hardness and transverse stiffness are inferior to those of diamond. Here we explore the elastic properties of supported 2D films of graphene by modulated Å-Indentation, an Atomic Force Microscopy (AFM)-based technique capable of achieving sub-Å indentations depths during force-indentation measurements. 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, it is resistant to perforation by a diamond indenter and shows a reversible change in electrical conductivity upon indentation. Density functional theory (DFT) calculations indicate that the 1+buffer layer graphene film undergoes a pressure-induced reversible phase transformation to a new ultra-stiff, ultra-hard 2D diamond structure, named diamene, followed by sp2-to-sp3 chemical bond transitions. DFT calculations also show that the transition to a 2D diamond structure is facilitated by the presence of the interfacial buffer layer, that strongly interacts with the reactive Si-terminated face of the SiC substrate, and that does not require the presence of adsorbates to stabilize the film surface in contact with the indenter. This finding casts light on the importance of the physics of the interface between graphene and the substrate in the emergence of the hardening effect. Recent experiments indeed demonstrate the absence of the graphene-diamene transformation in exfoliated graphene films of any thickness on SiO2.
Besides graphene, other 2D materials possess the structural characteristic necessary for sustaining a similar pressure-induced sp2-to-sp3 phase transition. In particular, hexagonal boron nitride (h-BN) may be converted to a stable cubic phase (c-BN) under pressure. Our most recent Å-indentation experiments demonstrate that 2-layer h-BN flakes, mechanically exfoliated on a SiO2 substrate, consistently exhibit a transverse elastic modulus almost two times bigger than that of the bare substrate. This stiffening effect is observed only for flakes of thickness between 2 to 5 atomic layers, but not in single- nor multilayer (> 6-layer) h-BN. MD simulations also show that the transition is not uniform but it starts in nuclei under and around the tip-sample contact..

References

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