

The two-dimensional phase of boron nitride: Few-atomic-layer sheets and suspended membranes

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We describe the synthesis of very thin sheets (between a few and ten atomic layers) of hexagonal boron nitride (*h*-BN), prepared either on a SiO₂ substrate or freely suspended. Optical microscopy, atomic force microscopy, and transmission electron microscopy have been used to characterize the morphology of the samples and to distinguish between regions of different thicknesses. Comparison is made to previous studies on single- and few-layer graphene. This synthesis opens the door to experimentally accessing the two-dimensional phase of boron nitride. © 2008 American Institute of Physics. [DOI: 10.1063/1.2903702]

The recent experimental isolation of graphene,¹ a single sheet of graphite, has attracted much scientific attention. The relativistic nature of charge carriers in graphene^{2–6} underlies physical phenomena such as high room-temperature mobility and holds promise for applications in future electronic devices.^{7,8} While the physics of graphene is undeniably rich, the possibility of extracting and isolating two-dimensional (2D) ordered crystals composed of elements other than carbon is itself a new frontier of physics.

Before the isolation of graphene in 2004, the experimental study of 2D systems primarily dealt with artificial structures grown on surfaces and interfaces,⁹ or with highly anisotropic, quasi-2D materials including graphite, transition metal dichalcogenides, and perovskites. Lacking were analogs of the one-dimensional materials such as nanotubes and nanowires.¹⁰ In the 2D cases, theoretical models of these systems often approximated to zero in the third dimension, although their contributions were never experimentally removed. The notion that a true 2D system was unlikely to physically exist was supported by many theoretical investigations, which started more than 70 years ago. Peierls¹¹ and Landau and Lifshitz¹² predicted that a 2D lattice could not survive at any finite temperature. Indeed, some experimental investigations apparently confirmed that it was not possible to thermodynamically stabilize a single layer of atoms unless they were coupled to a three-dimensional system, such as a monolayer on top of a bulk substrate with a matching lattice.^{13–15} Graphene is the first known 2D material that can exist without a matching crystalline substrate and, indeed, even freely suspended.^{16–19} It is likely that other 2D materials can similarly be isolated, with perhaps highly contrasting physics. Indeed, Novoselov *et al.*²⁰ suggested the possibility of extracting single sheets of other layered materials by the simple technique of micromechanical cleavage. They performed microscopy investigations of dichalcogenides (NbSe₂ and MoS₂), layered superconductors (Bi₂Sr₂CaCu₂O_x), and commented on the possibility of obtaining similar results on layered boron nitride compounds.

Boron nitride (BN), a III-V compound, is similar to carbon in that it exists in both hexagonal- and cubic-bonded structures. Structural similarities between carbon and BN-based materials are well known and supported, for instance, by the theoretical prediction²¹ and experimental realization²² of BN nanotubes. The *hexagonal* boron nitride (*h*-BN) phase (sometimes called white graphite) is isostructural to graphite except for the different stacking sequences of the atomic planes: well-crystallized graphite displays the Bernal (*AB*) stacking sequence, while hexagonal boron nitride is stacked with boron on top of nitrogen and vice versa (*AAA*···stacking). *h*-BN was recently found to be a promising deep ultraviolet (DUV) light emitter²³ and a new route of synthesis was found to produce high quality crystals.²⁴ Boron and nitrogen atoms, analogous to carbon atoms in graphite, form in *h*-BN a 2D honeycomb structure with strong covalent bonds in the plane and weak bonds between different planes, slightly ionic in *h*-BN. Although the BN- and carbon-based materials have very similar crystal structure ($a_{\text{BN}}=0.250$ nm and $a_{\text{C}}=0.246$ nm; $c_{\text{BN}}=0.666$ nm and $c_{\text{C}}=0.674$ nm), their electronic properties are very different, as *h*-BN is an insulator with a direct energy gap of about 5.9 eV,^{23,25} while graphite is a semimetal.

Here, we report the first isolation and experimental study of thin sheets of *h*-BN and establish their crystallinity and continuity over several microns. We report both thin (few-atomic-layer-thick) BN sheets deposited on oxide surfaces and similarly thin BN membranes freely suspended across circular apertures.

Our experimental procedure to obtain thin sheets of *h*-BN is the micromechanical cleavage technique, reported by Novoselov *et al.*²⁰ Layers of *h*-BN are peeled off with adhesive tape, attached to a 300 nm thick SiO₂ substrate, and identified by using simple optical microscopy (OM). The main difference here is that we applied the cleavage technique to powdered raw material instead of using bulk raw materials, as reported for graphene. Our best results in terms of dimension and thickness of flakes were achieved by using *h*-BN powders of grade AC6004, with an average crystal size of about 10 μm, purchased from Momentive Performance Materials, Inc.

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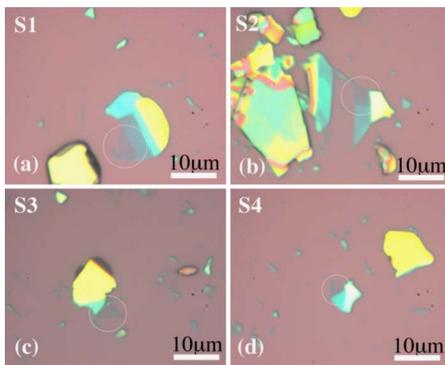


FIG. 1. (Color online) Optical images of four different samples [(a) S1, (b) S2, (c) S3, and (d) S4] showing BN flakes containing regions with different thickness. Light green corresponds to thin regions. White circles show the thinnest regions for each sample.

Figure 1 shows four OM pictures of selected thin, crystalline BN flakes and Fig. 2 shows atomic force microscopy (AFM) images of the first sample [S1, Fig. 1(a)] obtained in tapping mode in air. The topography image in Fig. 2(a) shows that the micromechanical cleavage procedure can produce clean, well ordered BN samples. The root-mean-square (rms) surface roughness of the thinnest region is 0.14 nm, the noise limit of the instrument. In comparison, the rms roughness of the gate quality SiO layer is 0.3 nm. From the line profile of Fig. 2(b), the thinnest region is 3.5 nm thick, and since any water adsorbed between the sample and substrate contributes to the measured thickness, the number of layers is at most ten. The thickest region measures roughly 80 nm.

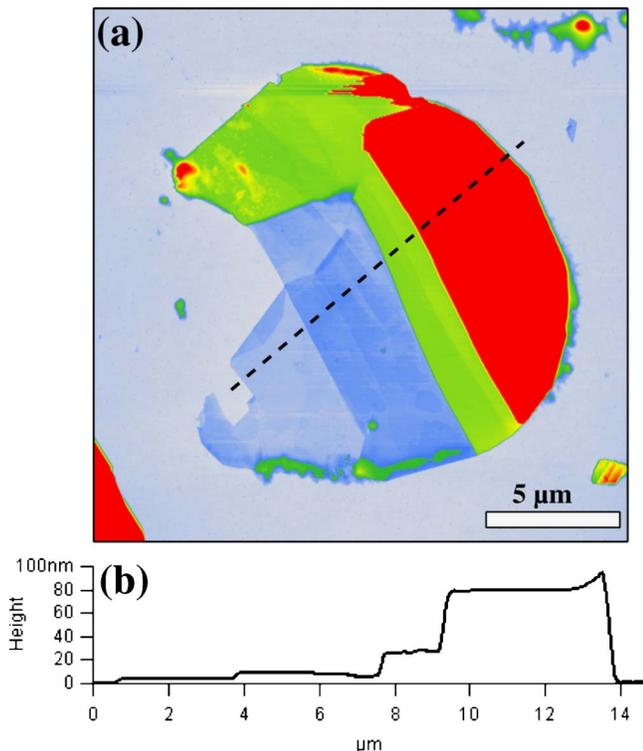


FIG. 2. (Color online) (a) AFM tapping mode topography image of S1. (b) The dashed lines indicate the position of the line profile. The thinnest region is 3.5 nm thick or roughly ten layers. The rms roughness of the thinnest region is 0.14 nm, whereas the silicon oxide substrate itself has a roughness of 0.30 nm.

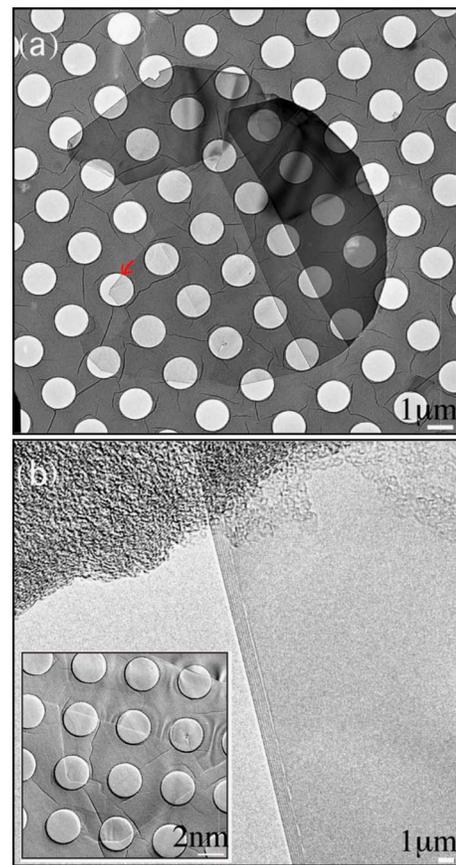


FIG. 3. (Color online) TEM images of S1. (a) Overview performed at low magnification and large defocus. (b) The folding indicated by red arrow in the overview image. Here, the number of dark lines (seven) indicates the number of layers in the thinnest area. The inset shows a close up on the thinnest region of the sample.

The flake of S1 [Figs. 1(a) and 2(a)] was transferred to a transmission electron microscopy (TEM) grid as follows. The flake was located under an OM and a Quantifoil™ gold grid with 1.3 μm sized holes in the carbon film was carefully placed on top of the flake. A drop of isopropanol was placed onto the grid and left to evaporate, thereby pulling the perforated carbon foil of the TEM grid into contact with the substrate and boron nitride flakes. Heating on a hot plate at 200 °C for 10 min improved the contact between the flakes and the grid. Next, the grid and flakes were covered with polyimide by placing a drop of polyimide dissolved in methylpyrrolidone onto the sample and heating to 110 °C for 10 min. The polyimide along with the TEM grid and the BN sheets could then be peeled off in one piece. The polyimide was dissolved again by a methylpyrrolidone bath (60 °C, 2 h) and the TEM grid was transferred to isopropanol and then dried. Figure 3(a) shows the corresponding bright-field TEM image. The general shape of our flake, including thickness distribution and folding, is maintained after the transfer. Figure 3(b) shows a high resolution TEM image taken on the folded region indicated by a red arrow in Fig. 3(a). This folding shows seven parallel dark lines providing a clear signature of the number of BN layers in the thinnest region of S1. Because the height of this region as measured by AFM is 3.5 nm, we conclude that there is a roughly 1 nm thick layer of adsorbate between the sheet and substrate.

According to the contrast method recently proposed to count the number of graphene layers,²⁶ it is possible to have

a rough evaluation of the number of BN layers of our samples. Although the contrast provided by a single BN layer is missing and the fit procedure reported for graphene²⁶ would require a higher number of experimental points, we take as reference the number of layers determined for S1 [Fig. 3(b)]. Applying the contrast method to our images and comparing the results to that of S1, we estimate that the thinnest part of S2 is below ten layers, while S3 and S4 have an even lower number of layers (below six).

The physics of low-dimensional BN is expected to be exceedingly rich. With respect to graphene sheets, where, for instance, the absence of a gap represents a complication for graphene-based electronic devices, BN may have attractive potential as a wide-band-gap material. Beside promising applications as DUV light emitters,²³ thin sheets of *h*-BN can also be tested for other applications. One possible route, successfully achieved for boron nitride nanotubes,²⁷ is the chemical functionalization via active molecular groups, in order to realize nanoscale scaffolds for the assembly of technologically relevant materials (transistors, biosensors, etc). Another more challenging possibility might be to make composite materials of graphene and *h*-BN, where BN acts as template of a single graphene sheet, breaking the equivalence of the two carbon atoms sublattices and opening a gap at the Dirac point.²⁸

Our experimental study demonstrates the ability to isolate samples consisting of just a few layers of hexagonal BN, including freely suspended membranes. It should be possible to isolate single-atomic-layer sheets as well. Samples as presented here open the possibility to fully characterize the physical properties of 2D phases of boron nitride underlying the bulk structure.

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