Screen-Printable Electronic Ink of Ultrathin Boron Nitride Nanosheets

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ABSTRACT: Two-dimensional materials play a vital role in the current electronic industry in the fabrication of devices. In the present work, we have exfoliated and stabilized the insulating hexagonal boron nitride (hBN) by means of a polymer-assisted liquid-phase technique. Further, the highly viscous ink of hBN was prepared, and its printability on various commercially available substrates was studied. The morphology of the printed patterns reveals the layered arrangement of hBN. The various electrical and dielectric characterizations, carried out on a metal–insulator–metal capacitor, testified its potential applications in various fields of printed electronics.

INTRODUCTION

The exfoliation of graphite into graphene in 2004 by Geim and Novoselov has revolutionized the domains of electronics and paved the way for a new area of research on ultrathin two-dimensional (2D) materials.1,2 These atomically thin materials are generally obtained by the different exfoliation techniques such as mechanical cleavage, liquid-phase exfoliation, ion intercalation, etc. from their bulk-layered counterparts.3–5

The extraordinary performance of a single-layer graphite, which is an electrically conducting material, became the seed for the growth of other 2D materials such as boron nitride, transition-metal dichalcogenides, black phosphorous, and many more, which display a broad range of electrical properties from insulating to conducting. Interestingly, the single- and few-layered materials generally exhibit much better mechanical, electrical, and optical performances compared to those of their bulk counterparts, and this led to a resurgent interest in the research on atomically thin materials in recent years.6–9

Among the layered materials, hexagonal boron nitride (hBN) is the insulating analogue of graphene with boron and nitrogen atoms in the alternate positions of a regular hexagon. This atomically flat material possesses extremely high thermal conductivity, very high thermal stability, and exceptional dimensional stability.10–12 This unusual combination of properties, such as electrical insulating nature, together with high thermal conductivity of BN, qualifies it for use in a plethora of applications such as electronic packaging materials, coatings, lubricants, and also as an ideal substrate for high-performance graphene electronics.13–17 Boron nitride nanosheet films have also been widely used industrially as a water repellent and as self-cleaning materials.18 BN has been utilized for the preparation of highly thermal conductive, thermally stable, and mechanically robust polymer composites for various applications.19–22 For specific PMMA-based polymer composites with 80 wt % functionalized BN, a thermal conductivity of >10 W m⁻¹ K⁻¹ was reported.23 The graphene devices fabricated on hBN substrates showed better mobilities and carrier inhomogeneities than those on SiO₂ substrates,24 and the breakdown field of the hBN dielectric is comparable to that of SiO₂.25–27 Recently, Lee et al. developed a flexible and transparent field effect transistor using hBN as the dielectric, graphene as the top and bottom electrodes, and MoS₂ as the channel.26

In this way, ultrathin 2D structures and flexible electronic devices were realized and are constantly pushing the limits of knowledge into newer horizons.

In conventional flexible electronics, functional nano inks are printed onto flexible substrates, thereby generating various devices and components for energy harvesting, radiofrequency (RF) communication, smart packaging, and flexible display applications.28,29 Among the various printing technologies available, screen printing allows large-area printing under ambient conditions, often resulting in thick printed layers of...
few micrometers, and is compatible with a wide variety of substrates and functional inks. Here, inks of suitable viscosity are pressed on patterned meshes with the help of a squeegee in order to obtain the predesigned pattern of interest on top of various substrates. Recently, Hyun et al. prepared graphene inks of different viscosities and has been screen printed with good resolution, which was further used for the fabrication of printed thin-film transistors (TFTs). Jobin et al. developed dielectric inks of silica and zirconium silicate, which possess suitable viscosity for screen printing and were curable at room temperature as well. Screen printing has also been utilized for the realization of many applications such as the preparation of flexible conductive electrodes, flexible transistors, etc.

Just like the conducting materials are important for device fabrication such as TFTs, the insulating materials also play a vital role in determining the device performance. The quality of the interface between the dielectric and the semiconductor is very important as the carrier transport takes place at these interfaces. Lee et al. utilized a sol–gel-derived metal-oxide material as the gate dielectric, and they printed the material using the wire bar printing technique. The ink formulation of layered materials is again a largely unexplored area, probably due to the reaggregation of the exfoliated layers when formulated into the ink of enough viscosity. A series of layered material exfoliation in water and their subsequent ink formulation with polyethylene oxide as the binder have been studied by Kim et al. Here, not many properties of the printed patterns were explored except the conductivity of graphene. Graphene was also used for screen printing by the gelation of the exfoliated nanosheets in the presence of the polymer binder, which is capable of preventing the aggregation of the exfoliated sheets and also provides higher viscosity suitable for screen printing. In contrast, owing to the complexities involving 2D structures, there are no significant efforts on the colloidal ink formulation using hBN as the filler. In 2014, Withers et al. directly used the liquid-exfoliated nanosheets of different materials including hBN for the fabrication of heterostructures using the inkjet printing technique. In an another approach, hBN has been made into an ink by the density-gradient ultracentrifugation technique in the presence of an amphiphilic block copolymer, and subsequently ultrathin dielectric films were deposited through a layer by layer approach. In the present investigation, we take up the challenge of formulating a screen-printable ink using ultrathin BN nanosheets, by adopting a polymer-assisted delamination mechanism followed by centrifugation and later adjusting the viscosity suitable for conventional screen printing. Here, dimethyl formamide (DMF) was selected as the solvent for exfoliation, whereas chloroform was used as the main vehicle in the ink formulation. Polycarbonate (PC) was chosen as the polymer binder because of its high glass-transition temperature and room temperature solubility in the selected solvents. Printed patterns were well characterized for the morphology, electrical properties, temperature stability, etc. In addition, dielectric properties in the RF and microwave frequency regions were thoroughly analyzed for the printed patterns of the hBN ink.

RESULTS AND DISCUSSION

The exfoliation of the layered material was started with continuous sonication of the bulk-layered BN in DMF. The polar nature of DMF was reported to be effective in the exfoliation process of BN, because of the interaction between the particle surface and the solvent molecule. In principle, the matching surface energy of the solvent and the energy per unit area of the layered material helps to overcome the van der Waals forces of attraction between the layers, and this is the reason behind the delamination of the bulk material into single or a few layers. This sonication-assisted delamination is considered to be the simplest but efficient way of exfoliation, which can result in high-quality 2D sheets. During sonication, the high-energy waves will generate cavities, which will collapse into high-energy jets, which in turn will break the bulk material into individual layers. Transmission electron microscopy (TEM) is a convenient technique to dig deep into the exfoliation characteristics of layered materials. Figure 1a,b shows the TEM images of the exfoliated BN before adding the polymer solution. When the bulk material is delaminated into thin sheets of 2D nature, the thickness usually decreases down to less than 1 nm. Because of this extremely thin nature, it will be transparent to electron beams, which is evident from the low-magnification images of TEM (Figure 1a,b). This transparent nature is a clear evidence for the effective exfoliation of hBN. The lateral dimensions of the delaminated sheets were reduced when compared to that of the bulk hBN powder. The bulk material used was of ~1 μm in the lateral dimensions. The continuous sonication in a congenial solvent can result in the reduction of the thickness along with a reduction of the lateral dimensions, which is common in liquid exfoliation. The high-resolution transmission electron microscopy (HRTEM) images shown in Figure 1c,d deliver more testimonial information about the already exfoliated nanosheets. The individual atoms of B and N can be clearly delineated from the respective electron densities of the individual atoms. Here, it is quite logical to assume that the brighter atoms are nitrogen, whereas the darker ones are boron. Moreover, from the HRTEM, the B–N bond length is

Figure 1. (a, b) TEM images of exfoliated hBN nanosheets (inset of (b) is the corresponding FFT). (c, d) HRTEM images of exfoliated nanosheets. (Red balls correspond to nitrogen atoms, and green balls correspond to boron atoms.)
calculated to be ∼1.45 Å°, which matches well with the literature.47 Interestingly, the distance between two neighboring white dots in Figure 1c is actually equal to the distance between any two nearest N or B atoms. This corresponds to a d spacing of 0.22 nm, which matches well with the (hkl = 100) lattice constant of BN too.42,48 The fast Fourier transform (FFT) given in the inset of Figure 1b and the image in 1d reveals the typical sixfold symmetry or the honeycomb nature of the hBN without any defects or dislocations in the crystalline nature, despite the reduction in the thickness and the size.

Another key technique to identify the exfoliation and the film thickness of the 2D materials is the atomic force microscopy (AFM). An AFM image in the tapping mode that recorded the exfoliated nanosheets drop-casted onto a mica sheet is given in Figure 2a. The height profile (Figure 2b) indicates that the approximate thickness of the sheets varies around 0.85 nm, which is in close agreement with the reported values for the monolayer BN.46,49,50

Figure 2. (a) AFM height image of the exfoliated nano-hBN sheets in the tapping mode. (b) Cross-section of exfoliated nanosheets.

For a material to be effectively screen printed, it should be of very high viscosity (>10 Pa s). Many of the polymeric materials, such as polyvinyl butyral, poly(methyl methacrylate), copolymer of poly(vinyl acetate), etc., have been commonly used as a binder in the printing technology to maintain the colloidal stability and also for the proper adhesion of the ink onto the substrate.33,39,51 In this attempt, we have utilized PC as the binder, which is a widely used polymer in many fields of electronic devices possessing exciting properties such as a very high glass-transition temperature of around 150 °C, easy solution processability, optical transparency, and low cost. When the polymer solution is added into the delaminated layered nanostructure in the solvent, the polymer chains will get physically attached to the surface of the layered material, and the steric hindrance induced by the macromolecules will prevent further aggregation of the layered materials into clusters, even when it is centrifuged. It is already known from the literature that PC is capable of effective exfoliation of the bulk material through a polymer-assisted delamination mechanism, and is ideal to stabilize the nanosheets through steric hindrance.32 After centrifuging, the solution containing the delaminated nanosheets with the polymer chains adsorbed on it will be like a highly viscous paint. The viscosity of the colloid is tuned with the help of chloroform, a low boiling point solvent, which can facilitate the room-temperature drying of the ink and faster adhesion of the ink on the substrates. This tricky selection of solvent enables a smooth printing on flexible substrates like BoPET, as it does not need any pre- or post-printing heat treatments. The photographic images of the printed film on the BoPET substrate are given in the Supporting Information (Figure S1).

The final ready-to-print ink composition consists of about 83 mg/mL of hBN nanosheets along with adsorbed polymer chains in chloroform. The viscosity of the ink was studied using the rheological measurements. Ideally, for a standard screen-printable ink, it should exhibit a pseudoplastic behavior, that is, the viscosity should decrease with increase in the shear rate.53 The overall higher viscosity and pseudoplastic behavior will eventually help in the high resolution of the printed patterns without any smudging at the sides and edges. In our study, the ink showed a high viscosity of 12 Pa s at a shear rate of 10 s⁻¹, whereas the viscosity reduced to less than 1 Pa s at higher shear rates (Figure 3a). This observed shear-thinning behavior helped in the printing of high-resolution patterns as the ink ceases to flow once the pressure applied on the squeegee is removed. This immobilization is partly supplemented by the high evaporation rate of the less volatile solvent used. The photographic image given in the inset of Figure 3a clearly testifies the highly viscous nature of the colloidal ink. The dynamic viscoelastic properties of the ink are shown in Figure 3b. It is observed that the loss modulus, which indicates the viscous nature of the material, dominates over the storage
modulus or the solid-like behavior in the entire strain region. This viscous nature helps in the effective printing of the ink with a good homogeneity over a larger area.

The surface morphology of the printed pattern on the BoPET substrate was visualized with the aid of scanning electron microscopy (SEM) and AFM, which are given in Figure 4. The photographic image of the hBN ink screen-printed on the Mylar film under optimal conditions is given in Figure 4a. The morphology of the printed pattern at a lower magnification is shown in Figure 4b. The printed hBN consists of stacked BN layers, which is clear from Figure 4c. Almost all the sheets lie horizontally, whereas very few lie randomly oriented to the plane of the substrate. This can be due to the pressure applied on the squeegee while printing, which helps the ink to strike down to the substrate surface effectively. Furthermore, during the free fall of the ink onto the substrates, the delaminated BN sheets would prefer to assume the low potential energy orientations, resulting in the horizontal stacking of BN layers one on top of the other. This is more or less like the stacking of 2D sheets, and this is the common morphology exhibited by other 2D inks like graphene specifically in screen-printed patterns. The horizontally levelled arrangement of electrically insulating and thermally conducting BN sheets that are connected to each other over a large surface area is supposed to provide reliable electrical, thermal, and mechanical properties for the printed pattern. The thickness of the printed pattern is estimated to be around 14 μm, which was computed using the scanning electron micrographs recorded from the different portions of the printed thick film (Figure 4d). The obtained thickness is a result of three strokes of printing. The presence of the polymer content is comparatively less in the ink formulation (less than 20 wt %) and hence was almost invisible in the SEM images but can be identified from the TGA discussed in the later section.

AFM images given in Figure 4e,f also shed light on the surface morphology of the printed pattern, and they are quite similar to those obtained from the SEM analysis. The nanosheets are arranged in a visibly close-packed manner. The surface roughness of the printed pattern was also investigated with the help of AFM analysis of the hBN ink screen-printed on the BoPET substrate. The printed pattern possesses an average surface roughness value of around 201 nm, and the root-mean-square surface roughness is around 282 nm.

The thermal stability of the printed pattern against peeling off, cracking, etc. is a critical parameter in real electronic devices. To understand the effect of heating in the printed patterns, we annealed the samples at temperatures of 50, 100, and 150 °C for 1 h and performed systematic SEM analysis of all the samples, which are depicted in Figure 5. It is evident from the images that all the samples have a similar morphology in comparison to that of the samples printed and aged at room temperature, without any visible cracks or peeling off from the

Figure 4. (a) Photographic image of the printed hBN ink on the BoPET substrate. (b, c) Surface of the printed patterns in different magnifications. (d) Cross-sectional image of printed hBN. (e, f) AFM images of the surface of the printed hBN on the BoPET substrate.

Figure 5. SEM images of the surface of the printed patterns annealed at (a) room temperature, (b) 50 °C, (c) 100 °C, and (d) 150 °C for 1 h.
flexible BoPET substrate. This enhanced thermal stability is attributed to the high thermal stability of hBN and also to the high thermal stability of the polymer used for binding the nanosheets together and to the substrate. The binder, PC, used in this study has a glass-transition temperature of around 150 °C, and thus the annealing of the printed pattern up to 150 °C will not cause any significant expansion or segmental mobility of the polymer chains. Up to this temperature, the adhesion of the ink to the BoPET was also found to be unaffected.

The overall thermal stability of the hBN ink was evaluated with the help of the thermogravimetric analysis after drying a very small portion of the ink before printing (see Figure S2). It is understood from the thermogram that the final composition of the ink contained only around 15% of the polymer, and the remaining was thermally stable hBN that resulted in an enhanced thermal stability of above 400 °C for the hBN ink. The 10% weight loss temperature of the final ink composition and that of the binder are given in Table S1. From the TGA analysis, it is understood that there is an improvement of more than 100 °C in the thermal stability of the newly developed ink when compared to that of the pure polymer.

As shown in Figure 6, various electrical and dielectric properties of the printed hBN were investigated. The variation of the dielectric loss and dielectric constant of the printed hBN on the copper foil with printed silver as the top electrode is given in Figure 6a,b. It is clear that both these properties decrease with increase in frequency. The “exponential-like” decrease of the dielectric constant can be explained on the basis of the various polarization mechanisms acting on the composite film at the lower RF region. Up to a few tens of hertz, all the four polarization mechanisms (interfacial, dipolar, ionic, and electronic) do contribute to the net dielectric constant, with interfacial polarization being the strongest as the otherwise porous printed film can contain a lot of highly polarizable mobile charge carriers. These molecules respond quickly to the applied frequency, resulting in a higher dielectric constant at the lower end. As the frequency increases, the polarity switching of these molecules fall behind that of dipolar polarization, resulting in an obvious decrease of the dielectric constant. At these frequencies, the polar nature of the B—N bond dictates the dipolar polarization. The dielectric constant of the printed hBN is found to be 2.57, and the dielectric loss obtained is 0.09 at 1 MHz. The dielectric constant for the bulk hBN reported is between 2 and 4.5 The comparatively reduced value of the dielectric constant for the printed hBN ink at 1 MHz can be attributed to the ordered arrangement of a few layers of the 2D material combined with the low dielectric constant of the polymer used. The capacitance and the impedance values also reduce with respect to frequency (Figure 6c,d). All these properties were measured for comparatively thicker printed layers of approximately 22 μm thickness.

Microwave dielectric characterizations of the delaminated low-dielectric-constant structures are far more reliable than conventional RF characterizations as the detrimental influence of interfacial and dipolar polarizations damp out to ionic polarizations at the GHz frequency range. However, there is a surprising scarcity of literature pertaining to the high-frequency dielectric properties of 2D structures, believed to be primarily due to the complexity and less popularity of the measurement techniques involved. The dielectric properties of the printed BN ink were studied for the first time in the microwave frequency region, with the help of a split-post dielectric resonator (SPDR) at three different frequency regions (5, 10, and 15 GHz) using BN printed on a flexible BoPET substrate having a thickness of 17 μm. It should be noted that this thickness of the film is slightly lower than that used in low-frequency measurements. This should not be a problem because SPDR enables accurate microwave dielectric measurement of thin dielectric films having high surface resistance. Here, the BoPET film has been taken as the reference for the resonant cavity, and the microwave dielectric constant of the flexible substrate used is estimated to be 3. The dielectric properties of the printed pattern were evaluated and are listed in Table 1. As expected, the apparent dielectric constant and dielectric loss of the printed pattern are slightly lower in the microwave frequency region when compared to those in the RF region, obviously due to the decreased net polarization, wherein

| material | dielectric constant ± 0.02 | dielectric loss ± 0.003 |
|----------|---------------------------|-------------------------|
| BN (15 GHz) | 1.96                      | 0.017                   |
| BN (10 GHz) | 2.14                      | 0.015                   |
| BN (5 GHz) | 2.22                      | 0.015                   |
the ionic polarization is the main component contributing to the dielectric constant. The ac conductivity measured for the printed film by making it into a metal–insulator–metal (MIM) capacitor is shown in Figure 7a. As shown, the ac conductivity increases with frequency, the lower values of which evidence the high-insulation behavior of the printed exfoliated hBN ink. The $I$–$V$ characteristics of the film printed on a copper foil are given in Figure 7b. The schematic of the experiment is given in the inset of Figure 7b. It is observed that the current density increases in an exponential manner after a particular applied field, which is common in the case of many dielectrics. Moreover, it is clear that the material possesses a comparatively lower leakage current density. This is to be understood, considering the lamellar arrangement of the exfoliated BN nanosheets between two high-voltage electrodes, wherein electrons have to travel a longer path to drift through the edges of the nanosheets in comparison with the nanoparticles. In the latter case, leaking through the nanoparticle grain boundaries is rather more facile. The DC conductivity of the printed hBN ink at 100 V is around $2.5 \times 10^{-6}$ A.

The reliability of the dielectric properties of the printed pattern against folding of the samples and also after annealing is worth studying for practical flexible electronics applications. To understand the effect of bending on the dielectric properties, the printed film on the flexible substrate was folded randomly in all the directions, and the properties were analyzed at 15 GHz as given in Figure 8a. It is found that both dielectric constant and dielectric loss remain more or less constant, within the experimental error limit of the instrument used for the measurements, even after folding up to 200 cycles. The effect of annealing on the dielectric properties was also explored with the help of a SPDTR by heat-treating the samples at 50, 100, and 150 °C for 1 h, and the results are given in Figure 8b. As the glass-transition temperature of the polymer used is around 150 °C as mentioned elsewhere, we did not expect much change in the dielectric properties, and the results are as expected.

**CONCLUSIONS**

The effective exfoliation of the insulating hBN has been carried out in DMF solvent and understood with the help of various techniques. The morphological, thermal, and electrical properties of the printed films offer an easy fabrication process for a good dielectric layer for various electronic devices. The lower dielectric constant of the printed film (2.57 at 1 MHz) with promising low dielectric loss and the favorable capacitance can make this material an effective substrate for various applications including printed graphene-based electronics.

**EXPERIMENTAL SECTION**

**Materials.** Boron nitride powder of ~1 μm size was used as the starting material (Aldrich Chemicals Co). DMF and chloroform were received from Merck Chemicals, India, whereas the PC used in this study was received from DuPont.
The substrates used are commercially available biaxially oriented PET (Mylar) and copper foil.

**Ink Formulation.** The exfoliation of BN was done through the liquid exfoliation method using DMF as the solvent. A concentration of 2.5 mg/mL of the layered material was sonicated in an ultrasonic bath for 48 h, so as to yield effective exfoliation. After 24 h of sonication, the PC dissolved in DMF (20 wt %) was added to the same, and the sonication was continued. After the exfoliation, the solution containing the BN nanosheets was centrifuged first at a lower rpm of 3000. The unexfoliated powder that settled down was discarded, and the supernatant was collected and centrifuged at a higher rpm of 10 000. This BN nanopowder was used for screen printing on the BoPET and the copper foil by adjusting the viscosity using chloroform. The screen used was a silk screen with the desired pattern fabricated by a photoresistive masking. A rubber squeegee was used for the uniform spreading of the ink through the shadow mask onto the substrate.

**Characterization.** The exfoliated layered materials were clearly imaged using TEM, and the lattice parameters were identified using HRTEM (FEI Tecnai G2 30STWIN; FEI Company, Hillsboro, OR). To understand the delamination and to find out the thickness of the exfoliated layers, AFM analysis in the tapping mode was carried out (Bruker Multimode, Germany). The morphology of the printed patterns was viewed using a scanning electron microscope (JEOL-JSM 5600 LV) and an atomic force microscope (Bruker Multimode, Germany). The colloidal stability of the ink with the polymer binder was measured at 15 °C using a rheometer (Rheo plus32, Anton Par) provided with a chiller. The thermal stability of the ink and the actual weight percentage of the polymer binder was measured at 15 °C using a rheometer (Hioki LCR HiTESTER, Hioki Company, Hillsboro, OR). To understand the delamination characteristic of the printed hBN film, and Pt–hBN ink calculated from TGA analysis (Table S1) (PDF)

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**Notes**

The authors declare no competing financial interest.

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