Ultrasound stitching of nanotwinned diamond and cubic boron nitride in C$_2$-BN composite

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Materials combining the hardness and strength of diamond with the higher thermal stability of cubic boron nitride (cBN) have broad potential value in science and engineering. Reacting nanodiamond with cBN at moderate pressures and high temperatures provides a pathway to such materials. Here we report the fabrication of C$_x$-BN nanocomposites, measuring up to 10 mm in longest dimension, by reacting nanodiamond with pre-synthesized cBN in a large-volume press. The nanocomposites consist of randomly-oriented diamond and cBN domains stitched together by sp$^3$-hybridized C-B and C-N bonds, leading to p-type semiconductivity. Dislocations near the sutures accommodate lattice mismatch between diamond and cBN. Nanotwinning within both diamond and cBN domains further contributes to a bulk hardness ~50% higher than sintered cBN. The nanocomposite of C$_2$-BN exhibits p-type semiconductivity with low activation energy and high thermal stability, making it a functional, ultrahard substance.

Superhard and ultrahard materials, presently defined as having Vickers hardness ($H_V$) greater than 40 and 80 GPa, respectively, are sought after for their potential use as extreme abrasives and other applications in high-pressure science and technology$^{1-4}$. Diamond is generally considered the hardest known substance, but due to graphitization in air at 800–900 K and reactivity with transition metals at high temperature, diamond has limited application in certain grinding environments. Cubic boron nitride (cBN), a diamond-structured compound, is widely used as an abrasive with much higher thermal stability than diamond (~1473 K) and low reactivity with steel, but the Vickers hardness of cBN (40–60 GPa)$^{5,6}$ is only about half that of diamond. Because of their similar ionic radii, B, C, and N may form diamond-like compounds in solid solution that are expected to be ultrahard with higher thermal and chemical stability than diamond$^{7-12}$. Based on theoretical predictions, experimental studies have attempted to synthesize a number of superhard B-C-N materials including diamond-like BC$_2$N$^{13}$, BC$_3$N$^{10}$, BC$_4$ and BC$_5$,$^{14,15}$ However, solid-solution B-C-N phases are generally considered metastable because syntheses usually lead to segregated carbon and boron compounds$^{17}$. The extremely high pressures (20–25 GPa) and temperatures (2000–2500 K) of many B-C-N syntheses ultimately limit production potentials and sample size$^{7,15,17}$.

Recently, it was discovered that nanotwinned (nt) diamond$^3$ and nt-cBN$^{2,18}$ possess ultrahigh hardness and toughness, mitigating the so-called reverse Hall-Petch effect by shear strengthening from compressive forces across nanospaced twin boundaries$^{14}$. Combining nt-diamond and nt-cBN to create an ultrahard nanocomposite would potentially lead to a material with optimized properties of each. Reacting diamond and cBN at high pressure and high temperature (HPHT) has been the typical route to synthesizing composites of diamond and cubic boron nitride (C$_x$-BN)$^{19-24}$, where $x$ is the proportion of diamond relative to cBN. The conditions and mechanisms of stitching diamond and cBN together remains the primary challenge. Recently, an epitaxial cBN/diamond heterojunction was produced by growing single-crystal cBN on diamond seed crystals using a temperature gradient method$^{34}$. A network of continuous stacking faults, arranged by hexagonal dislocation loops on the [111] heterointerface was found to accommodate the cBN/diamond lattice mismatch (~1.4 Å)$^{14}$. In this study, we fabricated...
highly uniform C\textsubscript{x}-BN (\(x = 2, 4, 6, 8\)) nanocomposites at 7.5 GPa and 2273 K, which consist of randomly oriented, ~50 nm domains of diamond and cBN (~250 nm). The bulk samples, measuring up to 10-mm diameter by 5-mm in height, combine several novel features from recent syntheses in the diamond-cBN system\textsuperscript{2,3,18,24}; in particular, the new C\textsubscript{2}-BN composite possesses nanotwinning in both diamond and cBN domains, which are stitched by \(sp^3\)-hybridized C-B and C-N bonds along randomly-oriented interfaces. Near the sutures, dislocations accommodate the lattice mismatch between diamond and cBN and, as recently predicted\textsuperscript{24}, the C\textsubscript{2}-BN nanocomposite is a \(p\)-type semiconductor with low activation energy. Among the suite of new nanocomposites, C\textsubscript{2}-BN is the hardest, with \(H_v = 85(2)\) GPa, placing it in the ultrahard class of materials.

We control the stoichiometry in C\textsubscript{x}-BN, by varying the proportions of starting powders of diamond (average grain size 50 nm) and cBN (average grain size 250 nm). Synthesis was conducted at 7.5 GPa while holding constant temperature of 2273 K for two hours (Table 1). The components of C\textsubscript{x}-BN composites consist of sintered nanodiamond (50 nm) and cBN (250 nm) with varying ratios (\(x\)) of diamond to cBN. For comparison, microcrystalline C\textsubscript{2}-BN composites from two different synthesis temperatures demonstrate the decrease in resistivity with increasing temperature between 1800 and 2273 K.

![Figure 1](image_url)

**Figure 1.** Characterization of C\textsubscript{2}-BN synthesized at 7.5 GPa and 2273 K. (a) XRD and (b) Raman spectra indicate two components, diamond and cBN. Rings in the CCD image (top-right inset in 1a) show the polycrystalline texture of well-sintered C\textsubscript{2}-BN composite.
The Fourier transform infrared (FTIR) spectrum (Fig. S2) shows two main peaks at 1065 and 1318 cm\(^{-1}\) together with one weak shoulder at 1208 cm\(^{-1}\), which correspond to stretching of the sp\(^3\) B-N bonds in cBN\(^2\), C-N bonds within the sutures of diamond and cBN domains\(^2\), and C-C bonds in diamond\(^2\), respectively. This characterization shows that the C\(_2\)-BN samples consist of diamond and cBN domains, consistent with XRD data (Fig. 1a).

The recovered samples from 7.5 GPa and 1500–2273 K were black and opaque, while transparent samples were achieved by subsequent annealing at 15–18 GPa and 2100 K (Fig. S3).

Scanning electron microscopy (SEM) confirms the C\(_2\)-BN composite is uniform and well sintered (Fig. 2a). Thin foils of C\(_2\)-BN synthesized at 7.5 GPa and 2273 K were prepared by focused-ion beam (FIB) techniques for transmission electron microscopy (TEM). Characteristic TEM and high-resolution TEM (HRTEM) images are shown in Fig. 2b–e. The TEM images in Fig. 2b,c show the absence of porosity in the C\(_2\)-BN sample, unlike many sintered diamond samples from which catalysts have been removed. The samples exhibit a nanopolycrystalline structure, consisting of hybridized, randomly distributed diamond and cBN domains (Figs S4 and S5).

Furthermore, HRTEM images reveal that nanotwinned structures have been produced during HPHT treatment (Fig. 2d,e). These multiple twins in the diamond and cBN domains are 1.5–2 nm and 6–8 nm wide, respectively. HRTEM images in Fig. 3 show that the two main domains of diamond and cBN have been stitched together by high-pressure sintering. The rigid lattice misfit between diamond and cBN domains is accommodated by the presence of partial dislocations and stacking faults at the interface between the two domains (Fig. S6). The sutures between diamond-cBN domains are typically 1–2 nm thick. HRTEM images and selected area electron diffraction (SAED) patterns (Fig. 3c,d) from the diamond-cBN junctions reveal that cBN domains twin to conjoin the adjacent diamond. Stacking faults and dislocations are observed in cBN in close proximity to the interfaces (Fig. S6). Through this misfit accommodation mechanism\(^2\), strain between diamond and cBN domains is released, leading to stability of the C\(_2\)-BN composite.

To determine the local bonding characteristics across the diamond-cBN sutures, we carried out inelastic X-ray scattering (IXS; beam size 20 μm) and electron energy-loss spectroscopy (EELS; beam size 1 nm) on the C\(_2\)-BN sample. The IXS spectra in Fig. S7 show that all three elements, B, C and N, are sp\(^3\) hybridized along the sutures. In contrast, pure diamond sintered under identical conditions (7.5 GPa and 2273 K) exhibits both sp\(^2\) and sp\(^3\) bonds (Fig. S8). This confirms that graphitization of sintered diamond can be effectively minimized or eliminated in C\(_2\)-BN by choosing the optimal synthesis conditions. EELS was conducted to analyze the interface between diamond and cBN from the selected area in the C\(_2\)-BN sample from 2273 K (Fig. 4a). Figure 4b shows the EELS spectrum and all the three bonds corresponding to the characteristic K-shell ionization edges of B, C and N in
the diamond-cBN interface. These EELS edge structures prove that bonding within the sutures are primarily $sp^3$-hybridized B-C-N bonds together with small amount of $sp^2$ C-B bonds.

X-ray photoelectron spectroscopy (XPS) was performed to study the stoichiometry of the hybridized diamond-cBN junctions. Figures 4c–e show XPS spectra of B, N and C, respectively. The shape and position of the spectra for all three elements are different from previous studies on pure diamond, cBN, and B-C-N compounds. The C 1s peak is located at 285.2 eV (Fig. 4c), which is similar to the value of C 1s in $sp^3$ C-C bonds observed in diamond. The full width at half-maximum (FWHM) is about 2.3 eV, suggesting different valence states of carbon are present. Two smaller peaks at higher (285.9 eV) and lower (284.5 eV) binding energy are due to C 1s in $sp^3$ C-N and C-B bonds, respectively. In addition, a higher binding energy at 289.0 eV is observed from the contribution of C 1s in C-O bonds. The main peak of the B 1s spectrum is located at 190.7 eV, very close to that of B 1s (191.0 eV) in pure cBN, suggesting the main bonding configuration in the C$_2$-BN composite produced at 7.5 GPa and 2273 K is similar to that of cBN, where one N atom is surrounded by four B atoms. However, a small shoulder at lower binding energy implies a contribution of B and C, because of the lower electronegativity of C atoms than N. A higher binding energy at 192.4 eV implies a contribution from the configuration of B 1s in B-O bonds. The N 1s binding energy is located at 398.4 eV (Fig. 4e), similar to the position of N 1s in cBN. However, two small shoulders are observed at higher binding energy of 400.3 and 402.1 eV, which are due to N 1s in C-N and C-O, respectively. All the C 1s, B 1s and N 1s spectra indicate that the main configuration for C, B and N atoms is $sp^2$ B-N bonding, together with a contribution from the bonding configuration in the boundary region between diamond and cBN domains. In addition to $sp^2$-hybridized C-N and C-B bonds produced during HPHT reaction, some C-O, B-O, and N-O bonds remain from the starting materials exposed to air.

Figure 3. Ultrahard sutures in nanocomposite C$_2$-BN. (a–c) HRTEM images at the junction between diamond and cBN domains. The FFT inset shows the rotation angles between adjacent diamond or cBN domains. (d) HRTEM and corresponding SAED pattern from a typical junction indicates that only nano-twinned diamond and cBN are present at the interface. Dislocations and stacking faults at the interface are found in the region marked by the white rectangle in (b) and (d).
Vickers hardness measurements were conducted on the Cx-BN nanocomposites using a standard square-pyramidal diamond indenter. We imaged and compared the indented surfaces using an optical microscope, SEM, and well-calibrated 3D optical microscope to determine the HV value. Figure 5a shows the hardness-load curve of C2-BN. The asymptotic region is reached at loads above 4.9 N and shows an ultrahard value of 82(3) GPa at 19.6 N. In a second C2-BN sample, the indentation at 19.6 N load corresponded to HV = 85(2) GPa, confirming the ultrahard value of our nanocomposite C2-BN. For other compositions of Cx-BN as well as cBN and sintered diamond, we studied indentations at 19.6 N load and found a peak hardness for the composition C2-BN (Fig. 5b).

The compressibility of C2-BN was studied under quasi-hydrostatic pressures up to 40 GPa at 300 K in a diamond-anvil cell using synchrotron X-ray diffraction at Sector 16 (HPCAT) of the Advanced Photon Source (APS). Figure S10 shows the compression data of diamond and cBN domains in the bulk C2-BN sample, together with the previously reported equations of state of single-crystal diamond \( \nu \) and ultrahard nanopolycrystalline (NP) cBN\(^{17} \). The \( P-V \) data (Table S2) were fitted to a third-order Vinet equation of state, finding for diamond \( V_0 = 44.18 \) (±0.8) Å\(^3\) and \( K_T = 442.5 \) (±0.5) GPa for NP-diamond\(^{17} \). For the cBN domains, we obtained \( V_0 = 47.33 \) (±0.01) Å\(^3\) and \( K_T = 398.6 \) (±2.5) GPa when \( K_0' = 3.6 \) is fixed to the value of a previous study\(^{38} \). When \( K_0' \) is allowed to refine, we obtain \( V_0 = 47.33 \) (±0.01) Å\(^3\), \( K_T = 377.4 \) (±7.1) GPa, and \( K_0' = 3.6 \) (±0.4) (Fig. S10). Using \( K_T = 398.6 \) (±2.5) GPa for the cBN domains, we obtain a theoretical nanopolycrystalline average \( K_T \) value of the C2-BN composite of 417.5 (±2.4) GPa.

We also determined the thermal stability (in air) of the Cx-BN samples by thermoanalytical analysis (TG/DTG) from 400 K to 1620 K (Fig. 5c). The synthetic C2-BN sample shows remarkably higher stability than either single-crystal boron-doped diamond (≈1000 ppm) with the onset temperature of oxidation in air, \( T_{OX} \approx 1027 \) K, or nanopolycrystalline diamond (\( T_{OX} \approx 950 \) K)\(^{17} \). The synthetic nanocomposite of C2-BN remains stable up to 1183 K. Moreover, the oxidation rate for C2-BN composite decreases substantially between 1183 K and 1425 K.
To investigate the electrical properties of our synthetic Cₓ-BN nanocomposites, Hall measurements were performed with four electrodes at room temperatures (Table 1). The sintered diamond (sample S6) and Cₓ-BN materials with high carbon concentration (sample S5) show good n-type conductivity with a low resistivity that can be due to the graphitization under HPHT treatment. Both Cₓ-BN and Cₓ-BN nanocomposites synthesized at 2273 K and 7.5 GPa exhibit p-type semiconductivity. Resistivity of the p-type Cₓ-BN is observed to decrease and the carrier concentration of the Cₓ-BN composite can reach 1.4387×10¹⁹ cm⁻³ at 300 K. This value is comparable with that of B-doped diamond. These results suggest that we can control the electrical properties of our Cₓ-BN materials from insulator to highly conducting by adjusting synthetic P-T or tuning the ratio between the C and BN with high flexibility and applications in electronics.

Temperature-dependent electrical measurements on our Cₓ-BN nanocomposite (Fig. 5d) show a significant increase in resistance by more than 7-fold on cooling from room temperature (ρ = 21Ω) to 1.8 K, a typical semiconducting behavior. The value of the activation energy is calculated on the basis of a linear Arrhenius plot of the logarithm of the resistance ln (R) versus the inverse temperature T⁻¹ in the temperature range from 50 to 100 K. The linear fit (solid line) shows that the data are well described by R(T) ∝ exp(Eg/kBT), where Eg is the activation energy and kB is Boltzmann’s constant.

Figure 5. Mechanical and electrical properties of Cₓ-BN nanocomposite. (a) Hv of Cₓ-BN as a function of applied load. Left inset: Optical micrograph of an indentation in Cₓ-BN produced by a load of 19.6 N. Right inset images in (a) show profiles across d₁ and d₂ measured using a 3D microscope. (b) Hv as a function of composition for Cₓ-BN materials. For comparison, we measured the Vickers hardness of Cₓ-BN with higher diamond:CₓBN ratios at only the highest load of 19.6N. The measured indentation hardness of Cₓ-BN ranged from 40 GPa to 85 GPa. (c) Thermogravimetric data (in air) for Cₓ-BN (the onset temperature of oxidation Tox is 1183 K) and boron-doped diamond single crystals (Tox=1027 K). (d) A resistance-versus-temperature curve for Cₓ-BN measuring 2×2 mm and 1 mm thick. The inset in (d) shows ln (R) as a function of T⁻¹ in the temperature range from 50 to 100 K. The linear fit (solid line) shows that the data are well described by R(T) ∝ exp(Eg/kBT), where Eg is the activation energy and kB is Boltzmann’s constant.
diamond. However, it is difficult to synthesize high-quality diamond crystals with heavy B-doping because boron is typically heterogeneous distributed within the crystal and it is difficult to avoid graphitic defects\(^1,2\). The current synthesis and characterization of \(p\)-type bulk nanopolycrystalline \(C_xBN\) with low activation energy suggests that stable and uniform diamond-based semiconductors can be formed in large quantities and in a reproducible way. In addition, the well-sintered nanopolycrystalline bulk pieces possess no cleavage, which will allow \(C_xBN\) composite materials to be fabricated into arbitrary shapes for industrial applications such as machine parts. Combining the high thermal conductivity and radiation resistance of diamond with the toughness of diamond at high temperatures, the ultrahard \(C_xBN\) bulk nanocomposites have potential applications in electronics under extreme thermal and pressure conditions.

In summary, we synthesized \(C_xBN\) composites with dimensions up to 10 mm × 5 mm at 7.5 GPa and 2273 K. The composite of nanotwinned diamond and cBN in a 2:1 ratio (\(C_xBN\)) shows ultrahard properties by Vickers indentation tests, low compressibility, high thermal stability, and \(p\)-type semiconductivity - a combination of features that have not previously been found together in pure diamond-like B-C-N materials. Subsequent annealing at 15–18 GPa and 2100 K improves its transparency. The nanotwinned domains of diamond and cBN are stitched by \(sp^3\) hybridized C-B and C-N bonds with dislocations near the grain boundaries to accommodate the rigid lattice mismatch of diamond and cBN, thus combining the features of a variety of recently reported ultrahard materials\(^3,18,23–24\). The moderate synthesis \(P\)-\(T\) conditions and rapid annealing time (2 hours) to form ultrahard nanopolycrystalline \(C_xBN\) composite make it a promising material for machine tooling with other practical benefits. The unique combination of properties in \(C_xBN\) provides a pathway for fabrication of diamond-based electronics applicable to multifunctional devices operating in extreme environments.

**Methods**

**Sample synthesis and characterization.** HP-HT synthesis experiments were carried out using a China-type cubic high-pressure apparatus (SPD-6 × 1200) at the State Key Laboratory of Superhard Materials, Jilin University. High-purity mixtures were prepared of nanodiamond (50 nm) and cBN (250 nm) with varying ratios (\(x\)) of diamond to cBN (i.e. \(C_xBN\)), including BN, \(C_xBN\), \(C_2BN\), \(C_3BN\), \(C_4BN\), \(C_6BN\), \(C_8BN\), \(C_{16}BN\), \(C_{25}BN\) and C. The starting materials were prepared by mechanically mixing for five hours at ambient conditions and treated by hot sulfuric acid/diluted hydrochloric acid to remove impurities introduced during the milling progress. Synthesis temperatures were measured using a Pt-30% Rh/Pt-6%Rh thermocouple junction placed within 0.5 mm of the sample. Pressure was pre-calibrated at high temperatures by the graphite-diamond transition with different catalysts. Samples were first subjected to pressures of 7.5 GPa, heated to temperatures of 1500–2273 K with holding times of 2 hours before rapidly cooling to room temperature in 2 minutes. The \(C_xBN\) cylinders (10-mm diameter × 5-mm height) are black in color. One sample of \(C_xBN\) was re-annealed at 15–18 GPa and 2100 K for 2 hours using the 1000-ton multi-anvil press at GSECARS (Sector 13) of the APS, Argonne National Laboratory (ANL), producing a transparent and colorless run product (Fig. S3). Run products were initially studied using an optical microscope, SEM, a powder XRD diffractometer, and Raman spectroscopy. Then we employed HRTEM, EELS, IXS, and XPS measurements on the produced \(C_xBN\) composites to determine their chemical compositions and crystal structures.

**Hardness and thermal stability measurement.** Vickers Hardness measurements were performed in the Optical Microscopy & Metallography (OMM) Facility at Northwestern University. A microhardness tester (KB 5 BVZ) was used to measure \(H_v\) with a diamond Vickers indenter. \(H_v\) was determined from \(H_v = 1.854AF/d^2\), where \(F\) (in Newtons) is the applied load and \(d\) (in \(\mu\)m) is the arithmetic mean of the two diagonals (\(d_1\) and \(d_2\)) of the Vickers indentation (Fig. 5a). For \(C_xBN\), the average of at least seven hardness data points for each load value was used to determine the \(H_v\) from the asymptotic intercept. To study the effect of cracking around the projected area on the inferred indentation dimensions, we used a combination of optical microscopy, SEM, and a high-resolution 3D microscope (Bruker, ContourGT Optical Profiler) to analyze the indented surface. The dynamic TG/DTG studies were performed in air using the NETZSCH STA 449 C thermoanalyzer operating at a heating rate of 10 K min\(^{-1}\) in the temperature range from 200 to 1650 K. These bulk samples were crushed into powders of micron sizes before the thermoanalytical studies.

**Compressibility.** The compressibility measurement was carried out in diamond-anvil cell using neon as the pressure medium. High-pressure X-ray diffraction patterns were collected up to 40 GPa, with exposure times of 5–10 min, at room temperature at beamline 16BM-D (HPCAT) of the APS. The beam size was ∼5 × 10\(\mu\)m at FWHM. Pressure was measured using the ruby fluorescence method\(^45\). A fragment of \(C_xBN\) (50-\(\mu\)m diameter, 8–10\(\mu\)m thick) was placed into the 160-\(\mu\)m diameter hole of a rhenium gasket, pre-indented to 25\(\mu\)m thickness.

**Electrical measurement.** The van der Pauw method was used for electrical transport measurements, in which four electrodes were used in the resistivity measurements. The electrical characteristics were measured with a transport properties measuring system (East Changing ET 9000 Series). The resistivity measurements were carried out at room temperature (300 K) and normal humidity level (40% RH). The temperature dependence of the resistance was measured using a standard four-probe method (PPMS, Quantum Design).

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Author Contributions
X.L. designed the study. X.L., X.C., S.D.J., Y.W. and C.R.B. wrote the manuscript. X.L., X.C., H.-A.M. and X.J. synthesized the samples and performed the thermoanalytical measurements. J.G. performed the electrical measurements. X.L., T.Y. and Y.W. conducted HPHT annealing experiments. X.L. performed the high-pressure X-ray diffraction experiments. S.D.J. and S.P. conducted FIB preparation, X.L. and J.W. conducted SEM and HRTEM measurements. All authors contributed to data analysis, interpretation, and revision of the manuscript.

Additional Information
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