First-Principles Predictions and Synthesis of $B_{50}C_2$ by Chemical Vapor Deposition

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Density functional theory predictions have been combined with the microwave-plasma chemical vapor deposition technique to explore metastable synthesis of boron-rich boron-carbide materials. A thin film synthesis of high-hardness (up to 37 GPa) $B_{50}C_2$ via chemical vapor deposition was achieved. Characterization of the experimental crystal structure matches well with a new theoretical model structure, with carbon atoms inserted into the boron icosahedra and 2b sites in a $\alpha$-tetragonal $B_{52}$ base structure. Previously reported metallic $B_{50}C_2$ structures with carbons inserted only into the 2b or 4c sites are found to be dynamically unstable. The newly predicted structure is insulating and dynamically stable, with a computed hardness value and electrical properties in excellent agreement with the experiment. The present study thus validates the density functional theory calculations of stable crystal structures in boron-rich boron-carbide system and provides a pathway for large-area synthesis of novel materials by the chemical vapor deposition method.

Boron-rich boron-carbide materials are of interest because of their thermal stability, high mechanical strength and their ability to function in extreme conditions of pressure, temperature, and corrosive environments. In general, materials for extreme environments typically contain at least one of the light elements C, N, O, and B, such as diamond and cubic boron nitride (c-BN). The short bond lengths of these light elements and the tendency to form directional covalent bonds make the structures difficult to compress or distort. Due to the high hardness of diamond, much research has been done on the synthesis of carbon-rich compounds with additions of boron and nitrogen, including the finding that the limit of solubility of boron in the diamond lattice is approximately 7.7 at%\(^1\). Boron-rich compounds are more difficult to categorize due to their tendency to form clusters of $B_{12}$ icosahedra with interconnecting boron atoms in complex unit cells. Other elements typically insert into regions between icosahedra and can substantially change the mechanical and electronic properties of the materials. Boron-rich boron-carbide materials synthesis by chemical vapor deposition methods continues to be relatively unexplored and a challenging endeavor. In fact, even though boron was originally discovered in 1808, it was not produced in reasonably pure (99%) form until 1909. The pure phase is difficult to form due to impurities incorporating the lattice. The stable ambient pure form is still under contention, as there are $\alpha$-tetragonal and $\beta$-rhombohedral phases that are thermodynamically stable under various conditions\(^2\)–\(^6\). First-principles predictions have led to solutions for some of the pure and boron-rich phases\(^7\)–\(^11\).

Researchers have found two difficulties when synthesizing boride compounds: achieving stoichiometric ratios uniformly throughout the material and keeping impurities from reacting with the boron during the synthesis process. Most of the novel high boron compounds are formed in high pressure high temperature (HPHT) cells, which produce very small volumes of material for analysis. Boron-rich boron-carbide in varying stoichiometric ratios has been made by HPHT methods\(^12\), but these methods are not scalable for producing large area coatings and can be difficult in controlling the impurities. On the other hand, microwave-plasma chemical vapor deposition (CVD) methods are better for controlling impurities in the material and can be used for large-area synthesis. The challenge is to find the correct set of conditions that are favorable for growth of the desired phase. In this study, we report the growth of high-hardness $B_{50}C_2$ thin films via CVD and experimentally characterize their properties by comparing to the predicted behaviors of a new theoretical stable and insulating $B_{50}C_2$ structure by first-principles calculations.

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Methods

Film growth and characterization. The sample substrates were all sourced from a 550 nm silicon wafer (University Wafer ID: 1095) and cleaned in acetone, methanol, and DI water. The samples were all grown in a 2.45 GHz microwave-plasma chemical vapor deposition system (Vawemat MPDR 313EHPI) using hydrogen as the carrier gas and diborane (90% H₂, 10% B₂H₆, and ppm carbon) as the reactive gas. Low level of residual carbon has been found to appear consistently in the high-boron deposited films. The gas flow rates were: H₂ = 500 Standard Cubic Centimeters per Minute SCCM, B₂H₆ (10%) = 1 SCCM. Samples were grown at ~750 °C substrate temperature. The growth was performed at a pressure of 15 Torr using 1 kW of microwave power, and the deposition time per sample was 4 hours.

Characterization of the films was performed with X-ray photoelectron spectroscopy (XPS) using a Phi Electronics, Inc. Versaprobe 5000 equipped with a monochromatic Al X-ray source with a 100 um spot size at 25 W. The system has dual charge neutralization so no corrections were done to the peak positions. Survey scans were taken with 0.8 eV step size and a pass energy of 187.85 eV. High resolution scans were taken with 0.1 eV step size and a pass energy of 23.5 eV. Scanning Electron Microscopy (SEM) was performed with a FEI Quanta 650 FEG system. X-ray diffraction (XRD) analysis was performed using a Panalytical Empyrean system with a Cu anode (λ = 1.54187 Å) and Cu K-beta reducing incident optic with 1/8° divergence slit and 1/16° anti-scatter slits (quasi-parallel beam setup). On the diffracted optics side a parallel plate collimator (0.027° acceptance) with a proportional detector was used. The incident beam was fixed at 1° omega and the detector scanned from 10–100° 2θ. A Rietveld refinement was performed using the various structures and compared for weighted profile R-value (wrP). Hardness and Young’s modulus were measured using an MTS Nanoindenteter XP having a Berkovich diamond tip with nominal radius of 50 nm. Calibration of the indenter area function before and after hardness measurements was tested on the fused silica standard (accepted Young’s modulus of 72 GPa) to confirm that the tip geometry did not change during testing of the B₅₀C₂ film. All indents, including those on silica, were made to a maximum depth of 150 nm. The measured Young’s modulus and hardness values were determined at maximum load. Young’s modulus of the silica before and after testing the CVD-grown B₅₀C₂ film was 72.4 ± 4.9 GPa and 72.8 ± 3.0 GPa, respectively. Therefore, the indenter tip area function was determined not to have changed significantly as a result of testing the film.

First-principles predictions by density functional theory. The density functional theory (DFT) calculations are performed with VASP (the Vienna ab initio simulation package) in which a plane-wave basis set and pseudopotential method are adopted. In our calculations, we employ the projector augmented wave (PAW) method and Perdew-Burke-Ernzerhof (PBE-GGA) exchange correlation functional with a plane-wave kinetic cutoff energy of 600 eV. The Monkhorst-Pack k-point sampling of the Brillouin zone is chosen for a Γ-centered mesh with resolution \( = 0.02 \times 2\pi/Å \) (6 × 6 × 10). The convergence criteria for self-consistent field and structure relaxation are set to \( 10^{-6} \) eV/unit cell and \( 10^{-6} \) eV/Å, respectively. We have made convergence tests with respect to k-points and cutoff energy. With a 6 × 6 × 10 k-grid and 600 eV cutoff energy, our calculations are able to achieve a total energy difference within 1 meV/atom. For electronic density of states, we adopt the tetrahedron method with a k-point sampling resolution = 0.01 × 2π/Å (12 × 12 × 20). In the phonon calculations, the interatomic force constants are obtained by density functional perturbation theory implemented in VASP, and the vibrational properties are computed by PHONOPY. The magnitude of the displacement (d) in our B₅₀C₂ phonon calculations is 0.1 Å. To justify this value, we have first computed the phonon dispersions of α-Boron and cubic-diamond with d = 0.01 Å, and obtained good agreements with those in the literature. Moreover, for B₅₀C₂, we have further tested d = 0.008 Å and 0.012 Å in the phonon calculations, and the results are basically identical to that with d = 0.01 Å. Therefore, using d = 0.01 Å is appropriate in our study. The theoretical XRD patterns and structural visualization are plotted by the VESTA software. In our calculations, we started with the tetragonal B₂C₂ structure reported in ref. 31, and then created a series of B₅₀C₂ structures by replacing 2 borons with 2 carbons. We have tried to put the 4 interstitial atoms in different symmetry sites as initial structures, and then fully relaxed the lattices and atomic positions before any further phonon and electronic structure calculations. Each B₅₀C₂ structure contains a unit cell of 52 atoms with a volume ~385 Å³. The lattice parameters for different B₅₀C₂ structures under study are summarized in Table 1.

Results

Characterization of films via XRD, XPS, raman, and nanoindentation. Samples grown at 750 °C were found to contain only the B₅₀C₂ crystalline phase. The elemental analysis was confirmed by XPS and the phase determination was made using XRD analysis. No graphitic carbon or B₄C were present as determined by XRD data (see Fig. 1). A Rietveld refinement was performed for B₅₀C₂ phase along with our newly-proposed insulating B₅₀C₂ phase. The most stable α-tetragonal B₂C₂ consists of four tetrahedrally coordinated B₂C₂icosahedra, with four additional boron atoms occupying the interstitial 2b (0, 0, 0.5) and 4c (0, 0.5, 0) Wyckoff sites of the P₄/nmm space group. A B₅₀C₂ structure can be formed by replacing boron with carbon in the B₂C₂ structure, or by inserting carbon into different interstitial sites. For example, previously reported B₅₀C₂ structures have carbons and interstitial boron inserted into the 8h (0, 0.5, z), 8i (x, 0.5, 0.5), or 4c sites. These reported B₅₀C₂ structures are metallic and found to be dynamically unstable in our phonon calculations. In contrast, the new B₅₀C₂ stoichiometric structure proposed here has carbon atoms inserted in both the B₂C₂icosahedron and the 2b sites, and it is made convergent with respect to k-points and cutoff energy. With a 6 × 6 × 10 k-grid and 600 eV cutoff energy, our calculations are able to achieve a total energy difference within 1 meV/atom. For electronic density of states, we adopt the tetrahedron method with a k-point sampling resolution = 0.01 × 2π/Å (12 × 12 × 20). In the phonon calculations, the interatomic force constants are obtained by density functional perturbation theory implemented in VASP, and the vibrational properties are computed by PHONOPY. The magnitude of the displacement (d) in our B₅₀C₂ phonon calculations is 0.1 Å. To justify this value, we have first computed the phonon dispersions of α-Boron and cubic-diamond with d = 0.01 Å, and obtained good agreements with those in the literature. Moreover, for B₅₀C₂, we have further tested d = 0.008 Å and 0.012 Å in the phonon calculations, and the results are basically identical to that with d = 0.01 Å. Therefore, using d = 0.01 Å is appropriate in our study. The theoretical XRD patterns and structural visualization are plotted by the VESTA software. In our calculations, we started with the tetragonal B₂C₂ structure reported in ref. 31, and then created a series of B₅₀C₂ structures by replacing 2 borons with 2 carbons. We have tried to put the 4 interstitial atoms in different symmetry sites as initial structures, and then fully relaxed the lattices and atomic positions before any further phonon and electronic structure calculations. Each B₅₀C₂ structure contains a unit cell of 52 atoms with a volume ~385 Å³. The lattice parameters for different B₅₀C₂ structures under study are summarized in Table 1.
for compounds with only C, N, O, and B as possible elements yielded the phases B$_{50}$C$_2$ and pure Boron (B$_{52}$) as the most likely candidates. The new B$_{50}$C$_2$ phase was also added to the database by creating a line pattern in the software. A Rietveld fit was performed using each of these phases and the best fit to the experimental data was the new B$_{50}$C$_2$ phase with a weighted profile R-value (wRp) of 15 and the fit is shown in Fig. 1.

XPS of a B$_{50}$C$_2$ sample showed that the surface is composed of 89.3% B, 7.8% C, and 3.0% O (rel. at %) with no other elements present, as shown in Fig. 2. A small amount of surface contamination due to adventitious carbon is generally present in samples which have been exposed to air. Our high resolution scans in Fig. 2 inset shows that 40% of the carbon is C-C bonded (binding energy of 284.5 eV) and the remaining 60% is B-C bonded (binding energy of 282.9 eV). Using this information our XPS measured carbon content in the B-C bonded sample is 4.7%. The stoichiometric ratio for B$_{50}$C$_2$ should be 96% B: 4% C, and is close to our XPS measured value of 4.7%.

SEM imaging of the surface showed well-formed crystallites between 5 and 10 micrometers in size, as can be seen in Fig. 3. There does not appear to be any preferred orientation for the crystal growth. A large number of crystals appear to be twinned and many have stacking faults. These are likely due to the rapid growth (~2 μm/hour) of the crystals from the vapor phase.
Nanoindentation measurements were taken to a depth of 150 nm at several locations (N = 17 indents) on the film. The average hardness of all indents is 14 GPa, however, well faceted surfaces yield hardness as high as 37 GPa. The large spread in these hardness data can be attributed to the surface roughness causing the tip to make less than ideal initial surface contact during the load segment. It is interesting to note that the indent with the highest Young's modulus Y did not have the highest hardness H (Y = 500 GPa and H = 25 GPa, respectively). This is not atypical of nanocomposite materials which have been reported with a non-linear modulus vs. hardness trend, and may be related to grain boundary deformation mechanisms\textsuperscript{23–25}.

Figure 4 shows the load-displacement data for the 37 GPa indent, also labeled with measured Young's modulus of 436 GPa. Although the indent depth was set to 150 nm, the maximum depth can be seen to be about 15 nm higher than this. This is due to a small correction made to the surface find segment to ensure a sharp increase in stiffness (corresponding to a displacement set at 0 nm) when indenter contact was made. The nanoindentation hardness of B\textsubscript{50}C\textsubscript{2} is 37% of the hardness value for cubic diamond and Young's modulus is about 41% of the value for the cubic diamond.

Figure 5 shows the DFT calculations of phonon spectra for two different B\textsubscript{50}C\textsubscript{2} structures. The structure in Fig. 5(a) has been considered previously in the literature\textsuperscript{11}. This B\textsubscript{50}C\textsubscript{2} structure is metallic, and it can be obtained...
by inserting carbon atoms into the 2b sites in a B\textsubscript{52} \(\alpha\)-tetragonal base structure (or equivalently into two of the 4c sites after a lattice translation and mirror reflection). However, our phonon calculation [Fig. 5(a), right panel] indicates negative phonon modes, showing that the corresponding crystal structure is actually dynamically unstable. By examining the phonon eigenvector at the \(\Gamma\) point, we found that the unstable mode has a predominant contribution from the two interstitial borons. This result suggests that relaxing the boron positions away from the 4c sites could potentially lead to a lower energy structure. On the contrary, in the structure shown in Fig. 5(b), the corresponding phonon modes are all non-negative, and thereby the newly predicted B\textsubscript{50}C\textsubscript{2} structure is dynamically stable. This new B\textsubscript{50}C\textsubscript{2} structure has one carbon replacing boron in the B\textsubscript{12} icosahedron\textsuperscript{26} and the other carbon inserted in one of the 2b sites (or equivalently one of the 4c sites after a lattice translation and mirror reflection). We note that in the new B\textsubscript{50}C\textsubscript{2} structure, one interstitial boron atom relaxes to a Wyckoff position (0.488, 0.915, 0.575), and the other one to a site near 8h (0, 0.5, \(z\)) with \(z\) \~ 0.189. This agrees with previous finding that the 8h site is occupied in B\textsubscript{50}C\textsubscript{2}\textsuperscript{2}, but not in B\textsubscript{52}\textsuperscript{2}. We also note that since B\textsubscript{50}C\textsubscript{2} is a 3D material with strong covalent bonding, we do not expect much difference in the structure relaxation by employing a DFT-D3 correction\textsuperscript{27}, which is relevant for layered materials or large molecules with van der Waals interaction. For the tetragonal B\textsubscript{50}C\textsubscript{2}, for example, we have checked that the lattice parameter \(a\) shows a difference of only \~0.023 Å (~0.26%) by applying a DFT-D3 correction, which is consistent with our expectation that such effect will not cause an appreciable difference in our study.

The Cu K-\(\alpha\) XRD pattern computed for the new theoretically stable B\textsubscript{50}C\textsubscript{2} structure is shown in Fig. 6(a), which also matches well the experimental XRD pattern in Fig. 1, where the computed phase is fit to the experimental data. Moreover, it is noted the previously reported (unstable) B\textsubscript{50}C\textsubscript{2} structure [Fig. 5(a)] is metallic, while the stable B\textsubscript{52} and B\textsubscript{50}N\textsubscript{2} structures are both insulating\textsuperscript{7}. Indeed, a corresponding calculation of the electronic density of states (DOS) shown in Fig. 6(b) demonstrates that the new theoretically stable B\textsubscript{50}C\textsubscript{2} is also insulating, which potentially helps its structure stability. We note that the carbon position plays the most important role in changing the electrical property. In particular, when a carbon atom is placed within one of the four B\textsubscript{12} icosahedra, the Fermi level will move to the valence band top, and a gap \~0.7 eV will appear. This behavior also occurs in other superhard B-C system. For example, it is known that B\textsubscript{12}C\textsubscript{3} has two different structures B\textsubscript{12}(CCC) and B\textsubscript{12}C(CBC). The lower symmetry structure B\textsubscript{11}C(CBC) consists of B\textsubscript{11}C icosahedra and C-B-C chains, and it also has a lower total energy with a bandgap \~1.4 eV larger than that of B\textsubscript{12}(CCC), which has carbon atoms placed outside the B\textsubscript{12} icosahedron. Our results on B\textsubscript{50}C\textsubscript{2} thereby agree with previous findings on B\textsubscript{12}C\textsubscript{3}\textsuperscript{28}. Finally, additional DFT calculation using Chen’s model\textsuperscript{29} finds a Vickers hardness around 36 GPa for our newly reported B\textsubscript{50}C\textsubscript{2} structure, also in excellent agreement with the hardness measurement.

Figure 5. Crystal structures and phonon spectra for B\textsubscript{50}C\textsubscript{2} with (a) carbon atoms inserted only into the 2b sites of a base B\textsubscript{52} \(\alpha\)-tetragonal phase, and (b) carbon atoms inserted into both the B\textsubscript{12} icosahedron and 2b sites. The negative phonon modes for the structure shown in (a) indicates its dynamical instability.
conclusions

We have produced a boron-rich boron-carbide phase B_{50}C_{2} by microwave-plasma chemical vapor deposition over an area of 25 mm², and have shown that it more closely resembles a crystal structure which includes carbon atoms inserted in the icosahedra of boron as well as in sites between icosahedra. This is opposed to previously proposed structures that are found to be dynamically unstable in our phonon calculations. The new phase has a high hardness value in excellent agreement with the experimentally measured value of 37 GPa. The new phase is predicted to be insulating by electronic band structure calculations in agreement with our measured resistivity value of MΩ-cm. Our present studies thus provide validation of the density functional theory in predicting stable crystal structure and providing a metastable synthesis pathway for boron-rich boron-carbide materials for applications under extreme conditions of pressure, temperature, and corrosive environments.

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**Author contributions**

P.B. and Y.V. conceived the idea of synthesis of high-boron boron-carbide material by chemical vapor deposition. P.B. performed the XRD. and XPS. characterization of B50C2 this film. W.C.C. and C.C.C. carried out the density functional calculations on stable crystal structures for B50C2 and its electronic band structure. S.C. performed the nanoindentation hardness measurements on B50C2 sample and carried out analysis of the mechanical properties of the sample.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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