

**Chen, Gong, and Wei Reply:** Recently, Zhang, Sun, and Chen (ZSC) [1] studied the hardness of cubic (*c*) BC<sub>2</sub>N by examining the ideal strength (the minimum stress that causes the breakdown of the crystal) of seven BC<sub>2</sub>N-*m* (*m* = 1–7) structures and claimed that the hardness of the *optimal c*-BC<sub>2</sub>N is lower than that of *c*-BN. They further claimed that the measured [2,3] extreme hardness of BC<sub>2</sub>N nanocomposites is due to the nanocrystalline size effect and the bonding to the surrounding amorphous carbon matrix. Their results, therefore, do not agree with experimental findings [2,3] that *c*-BC<sub>2</sub>N, with high or low density, is harder than *c*-BN. Later, Pan, Sun, and Chen [4] modified their conclusion and proposed that a high-energy, low-density structure, BC<sub>2</sub>N-5, with broken N-N bonds and a very low ideal strength [1], can explain the extreme hardness of *c*-BC<sub>2</sub>N observed in Ref. [2], because the shear strength can be enhanced drastically if a compressive stress is applied along the N-N bond direction to cause a rebonding of the N-N bond. In this case, they used shear strength in a particular direction (not the weakest one) to infer the hardness of a material. However, it is difficult to understand why all the nanocomposites would line up in an amorphous carbon matrix and behave as a single crystal in the nanoindentation measurement [2]. Furthermore, there is no direct experimental evidence from x-ray measurement [2] that a single-crystal BC<sub>2</sub>N-5 superstructure actually exists.

In our Letter [5], we intended to address the question raised by ZSC as to whether or not *optimal* BC<sub>2</sub>N is harder than *c*-BN. We first performed an unconstrained search using the bond-counting rule and identified the low-energy structures of *c*-BN/C<sub>2</sub> alloys, which are *c*-BN/C<sub>2</sub> (111) superlattices (BC<sub>2</sub>N<sub>*n*×*n*</sub>). These superlattices are energetically more stable than any of the superstructures proposed by ZSC [1,6]. By calculating the ideal strength, as proposed by ZSC [1], we found that these low-energy structures could be harder than *c*-BN, and therefore consistent with experimental observations that *c*-BC<sub>2</sub>N is harder than *c*-BN [2,3]. From these calculations, we stated that the conclusion of ZSC [1]—that the hardness of the *optimal* BC<sub>2</sub>N structure is lower than that of *c*-BN—is not correct.

In the preceding Comment [7], Chen and Sun (CS) argued that the BC<sub>2</sub>N<sub>*n*×*n*</sub> superlattice has a higher density and bulk modulus compared to the experimental data in Ref. [2], and thus cannot be taken as the structure model of the synthesized sample. Their Comment, however, misunderstood the fact that the purpose of our Letter [5] was to identify low-energy small-unit-cell *c*-BC<sub>2</sub>N structures that could be harder than *c*-BN rather than to characterize a structure obtained in a particular experiment. In fact, samples with high density, high bulk modulus, and high hardness had also been synthesized [3].

We want to point out that part of the misconception of CS is that they interpreted *c*-BC<sub>2</sub>N as a structure with cubiclike lattice vectors. This is why they limited their

search of BC<sub>2</sub>N alloys to only a small 8-atom cubiclike supercell and found the seven BC<sub>2</sub>N-*m* structures to represent *c*-BC<sub>2</sub>N alloys [1,4,6]. In fact, a *c*-BC<sub>2</sub>N structure just means that the underlying lattice has the diamond *Fd3̄m* space group. Depending on the distribution of B, N, and C atoms on the lattice sites, different superstructures such as the BC<sub>2</sub>N-*m* and BC<sub>2</sub>N<sub>*n*×*n*</sub> can form and all can be characterized as *c*-BC<sub>2</sub>N structures. CS studied only properties of the seven BC<sub>2</sub>N-*m* structures by ignoring all other possible *c*-BC<sub>2</sub>N structures. This is not justified.

Another point CS addressed in the preceding Comment [7] is that it is difficult for the starting graphitic (*g*) BC<sub>2</sub>N used in the synthesis of *c*-BC<sub>2</sub>N to transform into the low-energy BC<sub>2</sub>N<sub>1×1</sub> structure because it first has to break bonds to form stacked graphite or *g*-BN layers. This is obviously incorrect, because BC<sub>2</sub>N<sub>1×1</sub> can be taken as a stack of low-energy *g*-BC<sub>2</sub>N [8] layers along the (1̄11) direction, as well as stacked graphite/*g*-BN layers along (111). Our calculations show that the energy barrier from the low-energy *g*-BC<sub>2</sub>N to BC<sub>2</sub>N<sub>1×1</sub> is lower than to BC<sub>2</sub>N-*m* [9]. Although Pan, Sun, and Chen proposed a high-energy *g*-BC<sub>2</sub>N as the precursor for the synthesis of *c*-BC<sub>2</sub>N, it is not clear how to prepare this high-energy precursor [9]. On the contrary, the low-energy *g*-BC<sub>2</sub>N and graphite/*g*-BN, which can be used as a precursor for synthesizing BC<sub>2</sub>N<sub>1×1</sub>, are much easier to prepare. As a superlattice structure, BC<sub>2</sub>N<sub>1×1</sub> should also be easier to grow by vapor phase epitaxial methods [5]. Finally, we have also calculated the cubic-to-graphitic energy barriers and find that, once synthesized, BC<sub>2</sub>N<sub>1×1</sub> is more stable than BC<sub>2</sub>N-*m* [9].

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