Comment on "Superhard Pseudocubic BC_2N Superlattices"

Recently, Chen *et al.* [1] reported a first-principles calculation on the ideal strength of short-period (111) $BC_2N_{n\times n}$ superlattices and claimed that the calculated results are "consistent with the experimental finding" reported in Ref. [2]. Here we point out that the proposed superlattice structures are incompatible with existing experimental data [2] and, therefore, cannot be used to explain the superhardness observed in the experiment.

A structural model for a new material phase must be scrutinized against a full set of experimental data. To interpret the results on BC_2N [2], a structure must be checked against available experiments and synthesis conditions.

The x-ray (XRD) measurement [2] indicates that the synthesized BC_2N is compatible with cubic symmetry with a lattice constant of 3.642 Å. The authors argued [1] that the weak (200) structure factor makes their result consistent with the experiment. The symmetry assignment based on XRD alone is sometimes arbitrary. It is therefore imperative that other physical properties and synthesis conditions be examined to corroborate the structural assignment. The proposed superlattice structures [1] have higher density and bulk modulus compared to the experimental data from the high-pressure XRD [2] and Brillouin scattering [3] measurements. Residual graphitic or amorphous phases and microscopic cracks likely present in the sample should not have significant effect that would change the results in a qualitative way given the measured superhardness. More important, these superlattices are composed of stacked graphite and graphitic (g-) BN layers that would require special growth conditions such as low-temperature vapor phase epitaxial methods [1]. Calculations [1] indicate that the total energy decreases as the superlattice period increases, which means that, under the experimental synthesis conditions (isotropic, high temperature, and high pressure) [2], long-period superlattices would be favored over the short-period ones, leading to phase separation. Consequently, the low (200) XRD peak cannot be selectively singled out to justify the use of the superlattice structures for interpreting the data on BC_2N [2]. We ruled them out in our previous work [4].

In their Letter, Chen *et al.* [1] attempted to justify the BC_2N superlattices by arguing that they are lower in energy than the cubic phases. However, since all the known BC_2N phases, including all the proposed superlattices, are metastable, the real issue here is how likely these metastable structures will move toward phase separation. As discussed above, the experimental synthesis conditions clearly would favor long-period superlattices, leading to phase separation. Moreover, the starting material used in the synthesis [2] is preformed g-BC_2N; its transformation into the proposed stacked graphite or g-BN superlattices would involve extensive breaking of the strong covalent bonds, which is energetically extremely costly and, therefore, unlikely to occur in the first place. The proposed superlattice structures should be regarded as hypothetical awaiting experimental confirmation.

Finally, we clarify two issues important to understanding the synthesized BC_2N phases. First, one must distinguish the high-density [5] and low-density [2] phases that have different properties [6–8]. An existing structural model [6,7] for the low-density phase produces the lattice constant and bulk modulus in very good agreement with the experimental data [2,3]. Furthermore, the starting preformed g-BC_2N can transform into this low-density cubic phase without breaking any preexisting bonds, making the process energetically feasible [7]. Once formed, it will not easily phase separate since the energy barrier for the required massive bond breaking is very high. Second, one must distinguish ideal strength from hardness. The former is well defined and can be obtained from first-principles calculations while the latter depends on many uncontrolled factors and must be carefully analyzed. An empirical positive correlation between them is useful for analyzing mechanical properties. Recent calculations [8] show that the low-density cubic BC_2N indeed has the high ideal shear strength above that of c-BN, consistent with the hardness testing data reported in Ref. [2], when the normal compression under the indentor is considered in the ideal shear strength calculations. Similar results have been recently obtained for the high-density phase.

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