Boron nitride (BN) is a III–V compound positioned in the upper row of the Periodic Table, and is used in a diverse range of applications. Hexagonal boron nitride (hBN) is known for practical applications such as heat insulation and heat-resistant materials. On the other hand, cubic boron nitride (cBN), which has a sphalerite crystal structure similar to diamond, can be obtained by converting hBN to a high density phase under high pressure and high temperature. Recent some activities studied on BN polymorphic phase transformation and synthesis of high purity cBN as well as hBN single crystals resulted in some new trends such as super-hard materials, wide-band gap materials with deep ultraviolet emission nature and substrate for 2D materials.

1. Introduction

One strong motivation for the application of high-pressure synthesis techniques in materials synthesis research is the supply of functional materials meeting engineering needs, such as diamond. At the same time, the uncovering of unknown properties of new materials would be significant for exploring new functional materials under high pressure. Extending the simple methodology of obtaining a recoverable high-pressure phase, and viewing it as a stage for chemical reaction processes that are difficult to achieve at standard pressure synthesis, is intriguing. For instance, high-pressure synthesis is conducted in a closed environment; hence, reactive reagents and volatile substances, which are challenging to use at normal pressure, can then be used as a solvent for crystal growth, for example.

The synthesis of an artificial diamond by GE in the USA in the early 1950s\(^1\) was a forerunner of engineering applications of high-pressure synthesis technologies. R. Wentorf, Jr., who led pioneering research at GE, established the basics of synthesizing sintered diamond and then synthesized cubic boron nitride (cBN), which is the second-hardest material after diamond and stable against ferrous metals, for the first time.\(^2\)\(^,\)\(^3\) The innovative high-pressure synthesis technologies that made these studies possible are of the utmost importance, and the development of belt-type high-pressure apparatus by T. Hall served as the foundation. The concept lives on in industry. Osamu Fukunaga at the former National Institute for Research in Inorganic Materials (NIRIM) introduced this belt-type high-pressure apparatus for the first time in Japan in 1975. Pressure and temperature generation technologies were developed further, first by conducting fundamental studies using small-scale equipment and then scaling up. In 1989, when present author started his tenure at NIRIM, the synthesis and evaluation of diamond, cBN single crystals, and sintered material were rigorously pursued in industries, universities, and national research institutes. Moreover, NIRIM was taking measures to enhance the belt-type apparatus such that achievements of high-pressure conditions of up to 7.7 GPa and 2300 °C could be attained.

This report is primarily on the efforts since NIRIM on the control of defects and impurities in ultrahigh-pressure synthesis of BN including high-pressure phase transitions of various BN polymorphs as well as the synthesis of cBN single crystals and sintered material\(^4\)\(^–\)\(^8\) together with the outlook and tasks for the future.

2. Structural phase transition of BN polymorphs

Hexagonal BN (hBN) and graphite are two-dimensional layered compounds, but their stacking sequences differ as hBN is A-A‘ type and graphite is A-B type (Fig. 1). Both undergo diffusionless transformations that result in wurtzite BN (wBN) and hexagonal diamond (lonsdalite), respectively, under high pressure where the interlayer distance is decreased. Heating under high pressure those result
in a diffusionless transformation to cBN and diamond, respectively. Although wBN can be frozen in a metastable phase after pressure is released, hexagonal diamond cannot. What is the reason? When the pressure is released after a diffusionless transformation at room temperature, the kinetic energy barrier before and after the phase transition is small. Consequently, reversible transformation to the original phase would typically occur. However, some mechanism that inhibits the reversible transition should exist in wBN. The wBN synthesized by a high-pressure phase transition from a hBN single crystal (discussed below) takes a highly oriented microcrystalline structure and its color turns black (Fig. 2).9)

A detailed observation of the fine structure of this wBN revealed an extremely large amount of inversion domain boundaries, the origin of which is attributed to stacking faults introduced during the initial stages of pressurization of hBN.10) The change in color reflects this change in fine structure. The inversion domain boundaries could be an inhibition factor (energy barrier) in a reversible transition from wBN to original hBN, and is characteristic of a binary system. Therefore, the barrier in a reversible transition from hexagonal diamond to graphite should be small because it consists of a single element, namely carbon. On the other hand, is it possible to freeze hexagonal diamond by introducing a factor in the fine structure that inhibits back phase transition? After much trial and error, no success has been reported so far but they should be important for the future work to realize function of hexagonal diamond.

Most of the many high-pressure phases convert to normal pressure phases or amorphous phases when pressure is released, but controlling the freezing of desired high-pressure phases by doping and other measures, as well as materials property evaluation, is an interesting topic in engineering.

The wurtzite structure is a common crystal structure in III–V compounds such as AlN and GaN, and there is recent interest in B–Al–Ga–N mixed crystals for power device development, using AlGaN compound semiconductors.11) From this viewpoint, evaluation of the fundamental materials properties of wBN is important. However, wBN is a thermodynamically metastable phase and a large single crystal cannot be obtained by a dissolution–reprecipitation process using a solvent, because the energetically favorable hBN or cBN always precipitates instead. Fundamental materials properties were measured, including hardness and Young’s modulus of wBN oriented crystals, which was mentioned above.9) The hardness of wBN crystals was about 90 % of that of cBN single crystals when evaluated under the same conditions (Fig. 3).12)

There is some confusion in recent literature about the hardness of ultrahard materials. There is a theoretical prediction that the hardness of wBN is larger than that of cBN and even diamond.13) There are fine stacking faults in wBN oriented crystals, as discussed previously, and a report claims that fine stacking faults increase hardness.14)
Although care should be required for precise measurements, nanoindentation technique\(^\text{12}\) seem useful as a method of assessing the hardness of ultrahard materials because the load–displacement curve can be obtained correctly in a hardness test and there is little effect of indenter deformation during hardness measurement. Although there is no evaluation comparing sintered materials with single crystals as predicted by theory, it seems that cBN is harder than wBN experimentally as shown in Fig. 3.

A known structural polytope of hBN and graphite is rhombohedral form with three-layer periodicity (A-B-C stacking). It has been said that hBN and rBN are subject to a diffusionless transformation to wBN and cBN, respectively, under high pressure when the gaps between layers are compressed.

The behavior of hBN was discussed earlier, while experimental verification of rBN is extremely difficult. Sample quenching tests using a belt-type high-pressure apparatus and high-pressure X-ray in-situ observations of rBN suggest that turbostratic disorder occurs due to shear stress at an early stage in the pressurizing process, and this inhibits the diffusionless transformation to cBN.\(^{15-17}\) Compared to hBN, where nitrogen atoms are positioned immediately above boron atoms and thus the degrees of freedom of displacements in the in-plane directions are limited, turbostratic disorder from shear stress can easily occur in rBN, where the periodicity of planes of boron and nitrogen atoms are shifted, as in graphite. Neither turbostratic disorder nor structural phase transitions were observed when rBN was pressurized to around 10 GPa under hydrostatic pressure.\(^{15}\) Diffusionless transformation from rBN to cBN requires higher pressure and is therefore unexplored.

The importance of the effect of shear stress on a high-pressure phase transformation process is not unique to BN systems. The establishment of control strategies and clear guiding principles that consider differences in the choice of pressure medium and pressurizing method (uniaxial belt-type apparatus or multi-anvil) continues to be an important issue.

On the other hand, what will happen under high pressure and high temperature when amorphous BN (aBN) is used as the precursor? Whether high-pressure synthesis conditions of cBN could be mitigated is an interesting topic. There are reports of many studies from this viewpoint, both in Japan and abroad, on the transformation of aBN to cBN through treatment at high pressure and high temperature. However, an integrated understanding is yet to be established of the pressure range of transformation and the transformation mechanism. An aBN sample with a halo pattern from X-ray diffraction (XRD) can be obtained by crushing hBN crystals for a long time using a vibrating ball milling, whereas aBN exposed to water in the atmosphere easily transforms into cBN at 4–8 GPa with belt-type high-pressure equipment. In contrast, anhydrous aBN prepared under careful atmosphere control during synthesis is less vulnerable to transformation to cBN when compared to hBN, even at around 8 GPa (Fig. 4).\(^{7,18}\)

An analogous verification study was subsequently carried out on aBN obtained by different synthesis routes, but the results were similar.\(^{19}\) A trace amount of water shows a significant catalytic role in the transformation of aBN to cBN under high pressure. A glove box with preparation equipment that can lower the water and oxygen concentration to less than 1 ppm was effective in the verification. This apparatus is commonly available today, but was state-of-the-art in the early 1990s.

3. Development of high-quality sintered cBN

Studies of cBN for cutting tools, where advances in functionality are becoming more and more important, is important considering actual deployment of applications. Synthesis of sintered cBN from direct transformation via hBN-wBN-cBN was reported by Corrigan and Bundy of GE in 1975.\(^{20}\) Transparent binderless sintered cBN was synthesized, using high-purity hBN as a starting material and processing conditions of 7.7 GPa and 2200 °C, by Akaishi et al. in 1990.\(^{21}\) Sintered cBN for tools currently being used in industry is produced in the 5 GPa region and contains a binder such as AlN, TiN, or Co. Binderless sintered cBN shows excellent characteristics in cutting tools because of its excellent hardness and heat resistance.\(^{22,23}\) Attempts to refine the grain size of sintered cBN have been made, to further enhance the performance of cutting tools. The grain size of sintered cBN obtained
by direct phase transition from hBN is determined by the temperature necessary to convert 100% of the starting material of hBN to cBN. Sintering at around 10 GPa reduces the transformation temperature from hBN to cBN to 1700 °C, which is approximately 500 °C lower than at about 7.7 GPa, and the grain size growth can be suppressed to less than 100 nm.\(^7\),\(^24\) This sintered material demonstrates excellent, precise cutting characteristics (Fig. 5; the cutting tests were performed by a Riken group\(^25\),\(^26\)). The reduction of transition temperature by treatment at a higher pressure was effective in suppressing grain growth in reaction sintering by direct transformation from a low density phase.

**Figure 6** is an example of binder-free sintered cBN prepared under high-temperature conditions of approximately 10 GPa and 2000 °C. The material is brittle from grain growth and therefore unsuitable for cutting tools, but is significantly transparent. Hence, windows are a potential application.

On the other hand, mass production for tool materials requires the synthesis of binder-free sintered material in a lower pressure range. Currently, the only method is direct sintering of cBN microparticles at high pressure instead of direct transformation. The outstanding issue is residual oxygen impurities at grain boundaries of the sintered material.\(^27\),\(^28\) The establishment of a procedure to remove the surface oxide layer of nitride nanoparticles is also an important research topic for mass production of high-quality sintered cBN.

Unlike the effect of the microstructure of sintered material, such as the constituent grain size and grain boundary structure, the manner in which the purity of individual particles affects mechanical properties remains unexplored. The main impurities in cBN are oxygen and carbon. Control of the carbon concentration in sintered cBN is now possible to some extent by changing the purity of the precursor hBN, as shown in **Fig. 7**. Investigating how the carbon impurity concentration in a conventional standard purity material ("Standard" in Fig. 7) influences the mechanical properties of cBN is a task for the future.

### 4. Wide band gap semiconductor development

#### 4.1 Creation and property evaluation of high-quality cBN single crystals and emergence of new functionalities by doping

In addition to its characteristics as an ultrahard material, cBN has been attracting attention as a wide band gap semiconductor material. Wentorf has already shown its potential as a semiconductor in 1962,\(^29\) and Mishima et al. at NIRIM succeeded in making an ultraviolet light-emitting diode and evaluated its rectification properties.\(^30\) However, assessment of fundamental material properties (such as Hall measurements) of a high-quality single crystal was unexplored in the 1990s, in contrast to other wide band gap materials.\(^31\)
gap semiconductors including diamond, GaN, and SiC. The synthesis of cBN single crystals using the temperature gradient method at high pressure has been carried out since the early 2000s, and conducted measurements on Hall properties of p- and n-type semiconductor single crystals (van der Pauw method). Although cBN is a wide band gap semiconductor (band gap $E_g = 6.2\,\text{eV}$), the acceptor (Be) and donor (S) levels were found to be relatively shallow, at around 0.22 and 0.32 eV, respectively.\(^{31,32}\) Evaluation of single crystals that were un-intentionally doped showed a clear n-type characteristic ($E_g = 0.4\,\text{eV}$).\(^{32}\) These single crystals exhibit an amber color that is typically found in commercial cBN abrasive grains. Figure 8 shows optical microscopy images of cBN single crystals synthesized at high pressure, using different solvents and dopants.\(^{33}\)

The yellow color of standard artificial diamond comes from nitrogen impurities, and its origin is contamination from starting material of graphite and the synthesis environment. The amber color of cBN similarly comes from carbon and oxygen impurities in starting material of BN and the synthesis environment. Independent control of carbon and oxygen impurity concentrations have not been accomplished yet, and the question of whether the origin of this donor level is carbon or oxygen has not been clarified. The purity of diamond can be enhanced by adding Ti to the synthesis solvent as a nitrogen getter, but no convenient additive element has been found for cBN. In spite of this, after much trial and error, an almost transparent single crystal could be obtained by a Ba-based solvent, and a band edge free exciton emission of wavelength 205 nm was observed.\(^{34}\) Li and various alkali earth metals were known to be solvents for cBN after a report by GE,\(^{35}\) but there was no prior study using Ba, perhaps because of its high reactivity.

Heteroepitaxial growth of cBN crystals under high pressure was conducted before studying the aforementioned high-purity crystal synthesis.\(^{4,36}\) Heteroepitaxial growth of cBN on a diamond crystal using Li$_3$BN$_2$ was reported by Sei et al. in 1994.\(^{37}\) The diamond surface orientation-dependent growth behavior of cBN crystals based on the growing method, the growth rates, and the structural stability of the surfaces was evaluated. The most important conclusion from these series of studies is that the growth rate of cBN crystals on a diamond seed crystal under conditions with no spontaneous nucleation is less than a few hundredths of the growth rate of diamond under similar pressure and temperature conditions. Therefore, obtaining a large single crystal on a seed crystal is not practical, and a reasonable growth rate must be secured at a certain level of high temperature, where spontaneous nucleation can occur. This is a significant difference in the growth behaviors between cBN and diamond, and this is exactly why the synthesis of large high-quality cBN single crystals is difficult. The rate of cBN crystal growth has an almost linear relationship with growth time, suggesting that the rate-controlling factor is reactions at the growth surface. In contrast, the rate-controlling factor of diamond growth is diffusion in the solvent. This difference is probably because BN is a compound.

The characteristics of the ultrafine structure of the diamond/cBN interface were clarified by the growth of cBN on diamond\(^{38,39}\) Microstructural analysis of the heterojunction interface through cross-section observation [high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) method with a scanning transmission electron microscope with an aberration corrector; University of Tokyo group] revealed that boron bonds first on the diamond (111) surface. [The cBN (111) surface is polar and there are nitrogen and boron layers.] The electronic properties of this interface are intriguing because, for instance, a high concentration of holes could accumulate on the diamond side of the diamond/cBN interface, but detailed evaluations have yet to be carried out.

The existence of a clear dislocation loop corresponding to the 1.35 % lattice mismatch between cBN and diamond was revealed for the first time by plain view STEM observations parallel to the interface. This is formed by a balance of dislocation or stacking fault energy and interface bonding strength, and thus is a unique characteristic of heterointerfaces of materials with strong covalent bonds, in this case diamond and cBN.

The introduction of color centers by doping rare earth elements was attempted, to add a new functionality to cBN.\(^{40,41}\) cBN crystals synthesized using a Ba-based solvent, where Eu, Tb, or Ce was added to the solvent, showed element-activated luminescence after exciting with ultraviolet light. First principles calculations predicted that rare earth elements with a large lattice mismatch in cBN substitute nitrogen sites and form vacancies at neighboring boron sites (Kyoto University group). Microstructure analysis (HAADF-STEM analysis, University of Tokyo group) strongly supported the predictions.\(^{39,42-44}\) Doping accompanied by a large lattice mismatch can be controlled by forming defect complexes, and the use of high-pressure environments would be useful in the emergence and control of new functionalities.

4.2 Synthesis of high-purity hBN single crystals and developments in applications

Techniques for the synthesis of high-purity cBN single
crystals using Ba-based solvents could be applied to the synthesis of high-purity hBN single crystals by controlling synthesis pressure and temperature conditions. hBN has been widely used in insulators and heat-resistant materials for a long time, but single crystals of sufficient quality for various evaluations have not been available. In particular, there has been no study of excited electronic states near the band edges. High-intensity deep ultraviolet luminescence has been achieved using hBN single crystals under normal pressure and high temperature. hBN is in a thermodynamically stable phase. Hence, crystal growth under normal pressure is possible if there is a suitable solvent. After much trial and error, increasing the nitrogen solubility in the alloy melt by adding, for example, (Cr, Mo) to (Ni, Co) has made possible the synthesis of hBN single crystals that show band edge emission properties. The evaluation of fundamental property characteristics and deployment to 2D devices is carried out using crystals synthesized with metal solvent under normal pressure. A search for more preferable solvents and optimization of gas phase synthesis methods is expected from the viewpoint of the increasing area of hBN single crystals.

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