Nanoindentation measurements of a highly oriented wurtzite-type boron nitride bulk crystal

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We succeeded in synthesizing a bulk crystal of wurtzite-type boron nitride (w-BN) by the direct conversion method. The synthesized crystal was approximately 2 mm wide and 350 µm thick, and highly oriented to the c-axis. We performed nanoindentation measurements on the c-plane of the w-BN crystal at room temperature to evaluate the mechanical properties of w-BN. The hardness and Young’s modulus of w-BN from the obtained curves were simultaneously determined to be 54 ± 2 and 860 ± 40 GPa, respectively. The underlying physical mechanism that dominates the mechanical properties of group-III nitride semiconductors is also examined. © 2017 The Japan Society of Applied Physics

Boron nitride (BN) has attracted attention as a group-III nitride semiconductor material for various optical and electronic devices.1–4 Furthermore, BN has been the focus of attention as a substrate for two-dimensional materials such as graphene5,6 and as a hard material utilized for machining process such as cutting instruments for ferrous metals.7–9

For optoelectronic devices using BN, it is heterostructured and/or alloyed with other group-III nitrides, such as AlN, GaN, and InN. Because the stable structure of these conventional group-III nitrides is wurtzite, it is essential to elucidate the fundamental characteristics for wurtzite-type BN (w-BN). However, the stable structure of BN at ordinary temperatures and pressures is of the hexagonal type (h-BN) and that at high temperatures and pressures is of the cubic type (c-BN), that is, wurtzite is a metastable phase of BN at all pressures and temperatures. Therefore, a w-BN crystal is difficult to fabricate using common growth methods. In previous studies, only w-BN particles have been obtained10–13 while the other phases easily mix through phase transformation during additional thermal and/or pressurized treatment or fabrication of sintered compacts.14,15 Accordingly, there have been few studies of the physical properties of w-BN.16 To accurately evaluate characteristics of w-BN, it is crucial to obtain a crystal with high phase purity and crystal coherency.

In this study, we successfully synthesized a highly oriented single-phase w-BN bulk crystal from a h-BN bulk crystal by the direct conversion method. Using this crystal, we evaluated the mechanical properties, in particular, the hardness and Young’s modulus of w-BN, by nanoindentation experiments. The mechanical properties are fundamental and thus important parameters for semiconductor materials, as are the optical and electric properties because they influence the generation, multiplication, and motion of dislocations in crystals.17

As the source material to fabricate w-BN, h-BN bulk crystals were grown for 50–100 h at 1500 °C and 4 GPa by the temperature gradient method using commercial h-BN sintered bodies or powder in Ba3B2N4 solvent.18 The obtained hexagonal truncated pyramidal h-BN crystals were almost single crystals. The h-BN crystals were contained in CsCl powder and compressed at a pressure of 10 GPa uniaxial to the c-axis at 850 °C using a belt-type high-pressure apparatus. During this process, h-BN was directly converted to w-BN by diffusionless transformation. Because high temperatures above 1300 °C result in conversion to c-BN, a moderately high temperature is necessary to synthesize w-BN crystals.10,19 As shown in Fig. 1, the crystal retains its hexagonal truncated pyramidal feature with the c-plane surface. The width and thickness of the crystal are approximately 2 mm and 350 µm, respectively.

We evaluated the phase purity of the crystal by X-ray powder diffraction (XRPD) after crushing the entire crystal. The 2θ–ω XRPD profile in Fig. 2(a) indicates that w-BN was successfully synthesized, which is distinguished by the presence of several characteristic peaks. The coexisting peak from h-BN indicates that h-BN sections remained in the crystal. The phase purity of w-BN in the crystal is over 98%, which was calculated from the integrated intensity of the peaks calibrated by measurement of w-BN (shock-synthesized w-BN powder, Nippon Oil and Fats) and h-BN powder samples with known mixture proportions. Part of h-BN was unsuccessfully compressed to w-BN owing to initial stacking faults (i.e., displacement among planes) because of their weak bonding. The h-BN sections mainly existed in the back surface and/or the edge of the crystal, and only a w-BN(0002) single peak is present in the symmetric reflection 2θ–ω profile obtained by high-resolution X-ray diffraction (HR-XRD), as shown in Fig. 2(b). Therefore, the pure w-BN front surface free from h-BN sections is suitable for quantitative nanoindentation measurements. Furthermore,
sixfold peaks are observed in the $\phi$ scan on the asymmetric (1012) plane (data not shown). The full-width at half maximum (FWHM) of the X-ray rocking curve (XRC) on the (0002) plane was $\sim$8°. The crystal coherency is much higher than that of conventional sintered compacts, although it is inadequate compared with other group-III nitrides [XRC-FWHM (0002) $\leq$ 1°] probably owing to the mosaic structure. Therefore, the BN crystal used in this study was of the high-purity wurtzite-type and highly oriented to the c-axis.

Nanoindentation measurements were performed on the c-plane at room temperature. Both the front and back surfaces were mechanically polished for 20–30 µm using a 1-µm-diameter diamond adhesive sheet before the nanoindentation measurements. The average surface roughness ($R_z$) for a 5 x 5 µm² area was 2 nm after the polishing, as evaluated by atomic force microscopy (AFM). A commercial nanoindenter (Elionix ENT-1100a) equipped with a triangular pyramidal (Berkovich type) diamond indenter was used in the continuous depth-sensing mode. The curvature radius of the apex of the indenter is less than 100 nm. Therefore, the effect of the surface roughness of the sample on the nanoindentation measurements was negligible. The temperature and humidity were kept constant during the measurements. The maximum applied load was in the range of 10–300 mN, and ten indentations were performed for each maximum load. The relationship between the load and the penetration depth was continuously recorded throughout the loading–unloading cycle. Figure 3 shows the load–penetration depth ($F$–$h$) curves for different maximum loads ($F_{\text{max}}$). The three curves that give the maximum, average, and minimum values of the maximum penetration depth ($h_{\text{max}}$) are shown for each maximum load. The variation among the curves becomes larger above a maximum load of 150 mN, which may result from the dependence on the indentation location and/or maximum penetration depth because of different mosaics. A scanning electron microscopy (SEM) image of the impression after a measurement is also shown in the inset of Fig. 3. There are no cracks from the edge of the impression, while the sides of the impression slightly deform toward the inner side of the triangle owing to elastic recovery.

From the obtained $F$–$h$ curves, the hardness ($H$) and Young’s modulus ($E$) were calculated for all of the measurement points. $H$ and $E$ represent the resistances against plastic deformation and elastic deformation, respectively. They are expressed as

\[
H = \frac{F_{\text{max}}}{A_p(h_c)},
\]

\[
E = \frac{1 - \nu_{\text{BN}}^2}{\frac{1}{E_t} - \frac{1}{E_{\text{tip}}}},
\]

\[
h_c = h_{\text{max}} - \epsilon(h_{\text{max}} - h_0),
\]

\[
A_p(h_c) = 3\sqrt{3}\tan^2\alpha + \sum_n C_n h_c^{1/2n} \quad (n = 0–7),
\]

\[
E_t = \frac{S\sqrt{\pi}}{2\sqrt{A_p(h_c)}},
\]

\[
S = \left.\frac{dF}{dh}\right|_{h_{\text{max}}},
\]

where $h_c$ is the actual penetration depth and $A_p(h_c)$ is the corrected projected contact area. $S$ is the unloading stiffness, that is, the slope of the tangent line of the unloading curve at $h_{\text{max}}$, which was obtained by power-law fitting of the

![Figure 3. (Color online) Load–penetration depth ($F$–$h$) curves with different maximum loads ($F_{\text{max}}$). The three curves that give the maximum, average, and minimum value of the maximum penetration depth ($h_{\text{max}}$) are shown for each $F_{\text{max}}$. The inset shows a SEM image of the impression after the measurement for $F_{\text{max}} = 300$ mN.](image)
The evaluated properties of the w-BN crystal. Moreover, because of the use of $F$–$h$ curves, the nanoindentation analysis is not affected by elastic recovery. Therefore, our results are presently the most reliable.

We also performed nanoindentation measurements of c-BN sintered compacts to confirm the validity of our results for w-BN because numerous reports of the mechanical properties of c-BN have been published. The obtained $H$ and $E$ were $59 \pm 1$ and $960 \pm 30$ GPa, respectively. Our results agree reasonably well with previous reports, although the values differ among the studies. Therefore, our results for w-BN are also valid. Although it has been reported that w-BN could be harder than diamond, our results show that the hardness of w-BN is lower than that of diamond.

Figure 5 shows $H$ and $E$ of all of the wurtzite-type group-III nitrides as functions of the $a$ lattice constant. The results for AlN, GaN, and InN are for epitaxial thin films on $c$-plane sapphire substrates. AlN and GaN were grown by metal–organic vapor phase epitaxy, and InN was grown by molecular beam epitaxy. Compared with the other group-III nitrides, $H$ and $E$ of w-BN are much larger, which indicates that w-BN is a much harder material because of its smaller lattice constant, that is, the mechanical properties are governed by the atomic bonding. Sher et al. predicted that the hardness of cubic-type semiconductors is dependent on the bond length $d$ as $d^{-5.6}$ and $a^{-4.7}$, respectively. Because $a$ corresponds to $d$ in the wurtzite structure, the relationship between the mechanical properties and bond length of the wurtzite-type group-III nitrides is almost the same as that of cubic-type semiconductors.

Table 1. Reported hardness ($H$) and Young’s modulus ($E$) of w-BN determined from experiments and calculations. NI, V, and K indicate nanoindentation, and the Vickers and Knoop hardnesses, respectively. The values marked with an asterisk were calculated with the elastic constants reported in each study.

| Ref. | $H$ (GPa) | $E$ (GPa) | Exp. or calc. | Crystal |
|------|-----------|-----------|---------------|---------|
| This study | $54 \pm 2$ (NI) | $860 \pm 40$ | Exp. | Bulk |
| 26 | $57.8$ (V) | | Exp. | Sintered |
| 27 | $39.2$ (K) | | Exp. | Sintered |
| 28 | $24.5$ (V) | | Exp. | Sintered |
| 24 | $831$ | Calc. | — | — |
| 25 | $1011^*$ | Calc. | — | — |
| 33 | $1067^*$ | Calc. | — | — |

Fig. 4. (Color online) Dependence of the (a) hardness ($H$) and (b) Young’s modulus ($E$) on $h_{\text{max}}$ for the w-BN crystal. The line indicates the average values and data range used for calculation of the average.

unloading curve, $h_i$ is the intersection of this tangent line with the horizontal axis, $e$ and $\alpha$ are the shape factor and apex angle of the indenter, which are 0.75 and 65.03° for the Berkovich indenter. $C_n$ is the apex correction coefficient. $E_{\text{tip}}$ and $E_{\text{tip}}$ are Poisson’s ratio and the Young’s modulus of the diamond indenter, which are 0.07 and 1140 GPa, respectively. $E_{\text{BN}}$ is Poisson’s ratio of w-BN, which can be calculated from the elastic stiffness constants. In this study, 0.664 was used as the average of the stiffness constants from previous reports. Figures 4(a) and 4(b) show the dependences of $H$ and $E$ on $h_{\text{max}}$, respectively. $H$ for w-BN was determined as the average of the data points at higher $h_{\text{max}}$, while $E$ was the average of all of the data points. The evaluated $H$ and $E$ are $54 \pm 2$ and $860 \pm 40$ GPa, respectively. Using the isotropic approximation, the bulk modulus $B$ and the shear modulus $G$ are expressed as

$$B = \frac{E}{3(1 - 2\nu_{\text{BN}})},$$

$$G = \frac{E}{2(1 + \nu_{\text{BN}})}.$$
In summary, we succeeded in synthesizing a high-purity w-BN bulk crystal from a h-BN bulk crystal by the direct conversion method. The obtained crystal was highly oriented to the c-axis and the XRC-FWHM (0002) was much smaller than that of conventional sintered compacts. We performed nanoindentation measurement of this w-BN crystal to evaluate its mechanical properties. The hardness and Young’s modulus were simultaneously determined to be 54 ± 2 and 860 ± 40 GPa with sufficient accuracy. The relationship between the mechanical properties and a lattice constant of group-III nitrides is equivalent to that of cubic-type semiconductors.

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