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Hexagonal Boron Nitride Single Crystal Growth at Atmospheric Pressure Using Ni−Cr Solvent

Yoichi Kubota,* Kenji Watanabe, Osamu Tsuda, and
Takashi Taniguchi

*National Institute for Materials Science (NIMS), 1-1 Namiki,
Tsukuba, Ibaraki 305-0044, Japan*

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Hexagonal boron nitride (hBN), with a layered structure similar to that of graphite, is the simplest III−V nitride compound. High-purity hBN emits intense 215-nm band-edge luminescence, which is attributed to free excitons and which may have potential wide band gap semiconductor characteristics.[1] It is a promising material for the production of deep ultraviolet light-emitting devices. However, the synthesis routes for high-purity hBN single crystal have thus far all been high-pressure, high-temperature (HP-HT) ones.[1–3] Since products of HP-HT synthesis are generally limited in size, development of an alternative synthesis process that can fabricate hBN fine crystal on a large scale is an important step in realizing hBN's potential.

We recently found a new way of obtaining hBN crystals at atmospheric pressure using Ni−Mo alloy as a solvent.[4] The obtained crystals exhibit the band-edge optical nature of deep ultraviolet luminescence at 215 nm at room temperature, which indicates high crystallinity of our crystals. Although the Ni−Mo is a useful solvent for growing high-quality hBN crystals, the obtained crystals formed aggregates and each crystalline size was several hundred micrometers wide and 10-μm thick. This dimension of the crystals is not adequate for the characterization of single crystal's physical properties, because the small thickness requires careful handling of the crystal owing to the softness attributable to the layered structure of hBN. To cite one example, the stress-induced defects dramatically change the optical properties near the band edge.[5] Therefore, obtaining a larger size of a self-standing single crystal at atmospheric pressure is the next important step toward practical development of deep ultraviolet light emitting hBN.

Previously, we showed ability of Ni solvent to grow high-quality hBN crystal.[4,6] However, owing to small nitrogen dissolution into the Ni solvent, the growth rates are too low at atmospheric pressure. The key issue to enhance the growth rate of hBN crystals was the addition of Mo in the Ni solvent for crystal growth,[4] because nitrogen solubility in Ni solvent was enhanced by the addition of Mo, as suggested by Kowanda and Speidel.[7] We have therefore deduced that increasing the nitrogen concentration in Ni solvent is essential for growth of hBN crystal at atmospheric pressure. According to Kowanda and Speidel,[7] the effect of Cr on nitrogen solubility in the Ni melt is much stronger than that of Mo. The binary phase diagram of the Ni−Cr system shows a simple eutectic crystallization of Ni and Cr at 1345 °C,[8] which is nearly the same as that of the Ni−Mo system (the

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* Corresponding author. E-mail: kubota.yoichi@nims.go.jp.

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eutectic temperature, 1317 °C).[9] Consequently, when using Ni−Cr solvent, the synthesis of hBN crystal can be carried out in a similar condition as in the case of using Ni−Mo solvent system.[4] In the present study, we applied Ni−Cr alloy as a solvent for use in hBN synthesis at atmospheric pressure and obtained fine hBN single crystals that exhibit intense free exciton luminescence.

The starting material, hBN powder (Denka, type GP), was heated at 2100 °C for 2 h in a flow of nitrogen gas to remove oxygen impurities. The eutectic composition of the Ni−Cr alloy lump (56 atom % Cr, Rare Metallic, 99.9%) was used as a solvent. Attention to keep the freshness of the Ni−Cr alloy is important for the reproducible crystal growth study. Surface oxidization of the solvent is harmful for the crystal growth. The starting hBN and solvent were in an approximate weight ratio of 1:10. In the sample assembly, the hBN powder was put into the hBN crucible, and the metal solvent was placed on the powder. The hBN crucible was then put into an alumina crucible with a cap and placed in a horizontal electric furnace. The furnace was purged by nitrogen after being evacuated to 27 Pa. During the growth, nitrogen gas flowed into the furnace at approximately 2 L/min. The sample was heated at a rate of 300 °C/h and held at 1350–1500 °C for 12 h followed by slow cooling to 1200 °C at a rate of 4 °C/h. Then the sample was cooled by turning off the electrical power to the furnace.

We characterized the crystals grown on the solidified solvents by using optical microscopy, Raman spectroscopy, and cathodoluminescence (CL) spectroscopy. The CL measurement was carried out at room temperature. The CL equipment and methods are the same as described in a previous paper by some members of the current team.[2] After the synthesis, some of the solidified solvents were polished on the surface, and then the structures of those were examined by X-ray diffraction and electron microprobe analysis (EPMA).

The solubility of solute of boron and nitrogen to the Ni−Cr solvent is controlled by temperature. By the slow cooling process from high temperature, the saturated B−N solute was precipitated as hBN crystals on the surface of the solidified solvent. Figure 1a shows an optical micrograph of the hBN crystals synthesized at 1500 °C. The solidified solvent was covered by the recrystallized hBN. The crystal size was relatively small owing to the formation of many crystal nuclei at higher temperatures. At lower temperatures around 1350 °C, extremely small quantities of hBN crystals were precipitated, presumably due to small solubilities of boron and nitrogen in the solution for crystal nucleation and growth. In the middle of the two temperatures, the highly facetted hBN single crystals with typical hexagonal morphology were obtained on the surface of the recovered solvent. Figure 1b shows an optical micrograph of the hBN crystals removed from the solvent, which were synthesized at 1430 °C. They were colorless and transparent and had a plate-like habit and smooth surface. The largest crystal obtained so far was about 500-μm wide and 60-μm thick.

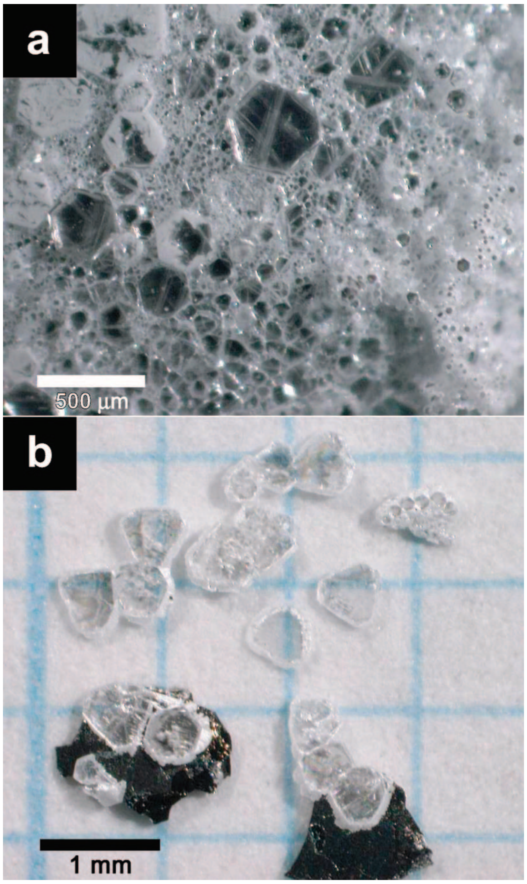

Figure 1. Optical micrograph of hBN single crystals (a) on the solidified solvent (as grown, synthesized at 1500 °C) and (b) removed from the solvent (synthesized at 1430 °C).

As previously reported, when using Ni−Mo solvent, the grown crystals formed aggregates with a dimension of several hundred micrometers wide and about 10-μm thick. Using Cr in the growth system obviously increases crystal size, especially the crystalline thickness, of recrystallized hBN. The thickness of hBN crystal obtained using Ni−Cr solvent was nearly 10 times greater than that obtained using Ni−Mo solvent with almost the same growth condition. The reported results of the nitrogen solubility in Ni−Cr alloy appear to be more than 10 times as high as that in the Ni−Mo alloy at 1550 °C.[7] According to the reference,[7] solubility of nitrogen into Ni40Cr alloy (Ni alloy contain 40 wt % chromium) at 1550 °C was approximately 0.6 wt % whereas that into Ni40Mo alloy was less than 0.04 wt %. Therefore, we conclude that an increase in nitrogen solubility increases the size of hBN crystals.

X-ray diffraction studies on the polished surface of the recovered solidified Ni−Cr solvent revealed the presence of some unknown phases in addition to the main phase of Ni−Cr. From the results of EPMA studies, the formation of a small amount of chromium nitride as well as chromium boride was found within the Ni−Cr matrix. By studying the recovered specimens only, we could not clarify the formation process of such the chromium boride and nitride. This may, however, indicate large chemical reactivity between chromium and B−N, suggesting the ability to dissolve some amount of nitrogen in Ni−Cr solvent. Although the phase diagram of the Ni−Cr−B−N system is not known yet, the

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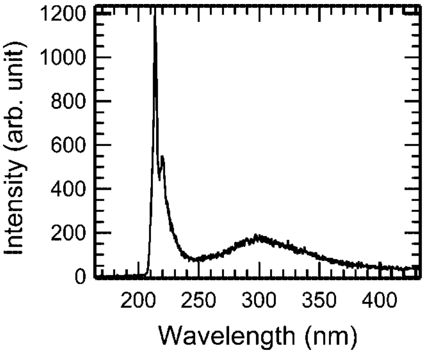

Figure 2. CL spectrum of hBN single crystal (measured at room temperature).

important result is the fact that the yield of recrystallized hBN was significantly enhanced by the addition of chromium in the Ni−B−N system.

Figure 2 shows the CL spectrum of the obtained hBN crystal measured at room temperature. An intense peak near 215 nm, which is attributed to the free exciton luminescence of hBN crystal, was observed. The intense intrinsic band-edge luminescence is characteristic of a high-purity, high-quality hBN crystal.[3]

A second highest peak at 220 nm was often observed in hBN crystals grown by HP-HT[1,3,5] and deposited by the thermal chemical vapor phase deposition.[10] Although the detail of the origin of the 220-nm band has not been completely defined yet, this may be attributed to the bound excitons caused by crystalline imperfection, such as stacking fault in layered hBN structure.[5]

The weak broadband observed at around 300 nm can be attributed to defects caused by trace residual impurities such as carbon and/or oxygen.[3]

The recovered crystals exhibit a typical Raman spectrum of hBN with an intense peak at 1367 cm^{-1} that corresponds to the in-plane vibrational mode of hBN.[11] A full width at half-maximum value of this Raman peak is about 9 cm^{-1}, which is comparable to that for our high-quality hBN crystal obtained by HP-HT synthesis.[4]

In conclusion, high-quality bulk hBN single crystals were successfully grown from Ni−Cr solvents at atmospheric pressure. The obtained crystals had a fine hexagonal platelet shape and were colorless and transparent. The crystalline thickness (∼60 μm) was several times greater than that of the crystal obtained using Ni−Mo solvent. They showed an intense CL peak near 215 nm related to free exciton luminescence near the band edge of hBN. Using Ni−Cr solvent is beneficial for the growth of a large single crystal of deep ultraviolet light emitting hBN. The addition of an element such as Cr, which has the ability to enhance nitrogen solubility, probably leads to an increase in crystal size.

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