

This is the author's final, peer-reviewed manuscript as accepted for publication. The publisher-formatted version may be available through the publisher's web site or your institution's library.

Optimization of Ni–Cr flux growth for hexagonal boron nitride single crystals

T. B. Hoffman, B. Clubine, Y. Zhang, K. Snow, and J. H. Edgar

How to cite this manuscript

If you make reference to this version of the manuscript, use the following information:

Hoffman, T. B., Clubine, B., Zhang, Y., Snow, K., & Edgar, J. H. (2014). Optimization of Ni-Cr flux growth for hexagonal boron nitride single crystals. Retrieved from <http://krex.ksu.edu>

Published Version Information

Citation: Hoffman, T. B., Clubine, B., Zhang, Y., Snow, K., & Edgar, J. H. (2014). Optimization of Ni-Cr flux growth for hexagonal boron nitride single crystals. *Journal of Crystal Growth*, 393, 114-118.

Copyright: © 2013 Elsevier B.V.

Digital Object Identifier (DOI): doi:10.1016/j.jcrysgro.2013.09.030

Publisher's Link: <http://www.sciencedirect.com/science/article/pii/S0022024813006313>

This item was retrieved from the K-State Research Exchange (K-REx), the institutional repository of Kansas State University. K-REx is available at <http://krex.ksu.edu>

Optimization of Ni-Cr Flux Growth for Hexagonal Boron Nitride Single Crystals

T.B. Hoffman¹, B. Clubine, Y. Zhang, K. Snow, and J.H. Edgar

Kansas State University, Department of Chemical Engineering, Durland Hall, Manhattan, KS 66506

Abstract

Hexagonal boron nitride (hBN) single crystals were grown using a Ni-Cr flux growth method. The crystallization cooling rate, soak temperature and soak time were controlled to determine their effect on crystal size and quality. A cooling rate of 2°C/hr produced the best quality hBN crystals. The maximum crystal width increased with soak temperature from 1 mm at 1450°C to 5 mm at 1700°C. The crystal thickness decreased with soak temperature from 500 µm at 1500°C to 40 µm at 1700°C. A soak time of 24 to 48 hours produced the maximum crystal thickness. X-ray diffraction and Raman spectroscopy confirmed that the crystals were highly ordered and of high purity.

Keywords: *B1. Nitrides, B2. Semiconducting III-V materials, A2. Single crystal growth, A2. Growth from solutions, A1. Crystal morphology*

I. Introduction

Hexagonal boron nitride (hBN) is of interest for several electronic and optoelectronic devices including neutron detectors [1, 2], ultraviolet light emitters [3, 4], and deep ultraviolet light detectors [5], and as a substrate for graphene and other two dimensional atomically thin materials, such as MoS₂ [6, 7]. ¹⁰B is one of the few isotopes of any elements that has a strong interaction with thermal neutrons, thus hBN is suitable for use as a solid state neutron detector. The photoluminescence intensity of hBN is 100 times higher than aluminum nitride for the same input light stimulation, thus it is attractive as a deep ultraviolet (215-230 nm) emitter [4]. For example, Watanabe *et al* [8] successfully demonstrated a deep UV hBN field emission device that generated a wavelength of 225 nm. The charge mobility of graphene on hBN is significantly higher than graphene on silica [6]. This is attributed to hBN's near atomic scale flatness, the absences of dangling surface bonds, and low phonon interactions between materials.

For all of these applications, hBN single crystals are preferred to achieve the best possible properties. In general, single crystals have the highest charge carrier mobilities, as they lack grain boundaries to cause scattering. Similarly, grain boundaries and other defects can create charge recombination centers that degrade luminescence efficiency. For substrate applications of hBN, a single crystal orientation is best, since the layer's properties change with its crystallographic orientation relative to the substrate; grain boundaries in the hBN substrate may affect the electrical properties of the graphene it supports [9].

Because of hBN's high melting temperature (>2950 °C) [10] and the low vapor pressure of boron even at high temperature [11], the growth of single crystals from a melt or by sublimation would be quite difficult. Instead, crystal growth from a flux (*i.e.* from solution) is preferred. Solvent choices that have been tested for hBN crystal growth have included silicon [12], sodium [13], lithium bromide (LiBr) [14], copper [15], and BaF₂-Li₃N [16]. The process employing a

¹ Corresponding Author: T.B. Hoffman, thoffman@ksu.edu, (785) 531-1639, Kansas State University, 1005 Durland Hall, Manhattan, KS 66506

nickel-chromium flux developed by Kubota *et al* [17] has perhaps been the most successful in its ability to produce good sized crystals ($>500\text{ }\mu\text{m}$) at modest temperature ($1500\text{ }^{\circ}\text{C}$) with excellent optical properties. For this reason, the Ni-Cr flux growth method was employed in this study.

In this paper, we report on the impact of temperature and time on the quality, size and habit of crystals formed. We show that the relative growth rates in the *c*- and *a*-directions are influenced by temperature. These results will be helpful in determining the best process conditions for producing high quality hBN crystals of the necessary dimensions for specific applications.

II. Experimental

Bulk hBN crystals were grown using two different resistance-heated furnaces: a vertical graphite furnace ($T_{\text{max}} > 2000\text{ }^{\circ}\text{C}$) and a horizontal MoSi_2 furnace ($T_{\text{max}} < 1600\text{ }^{\circ}\text{C}$). Source materials were Ni and Cr powders, mixed to a composition near 53 wt.% Cr, plus boron nitride powder, loaded at a 1:20 weight ratio to the Ni and Cr powders. These powders were loaded into boron nitride crucibles and placed within the respective furnaces.

Experiments were initiated by evacuating the furnace chambers and then backfilling with N_2 gas to near atmospheric pressures (850 torr). Next, the heating cycle was started, which consisted of four steps. First, furnace temperature was increased from room temperature to the maximum or soak temperature. Then the soak temperature was maintained for several hours so the Ni-Cr flux could saturate with boron and nitrogen. Following the soak step, samples were cooled at a controlled rate to $1200\text{ }^{\circ}\text{C}$, causing the hBN to precipitate and crystallize on the surface of the flux. After cooling to $1200\text{ }^{\circ}\text{C}$, the furnace was turned off, allowing it to cool to room temperature for analysis.

Three parameters were controlled throughout these experiments to determine the conditions necessary to produce optimal hBN crystal size and quality: soak temperature, soak time, and cooling rate. Soak temperature was varied from 1450 to $1700\text{ }^{\circ}\text{C}$, soak time from 6 to 72 hours, and cooling rate from 2 to $10\text{ }^{\circ}\text{C/hr}$. The cooling rate experiments were performed in the horizontal MoSi_2 -heated furnace, with growth occurring at constant soak time and temperature of 24 hours and $1500\text{ }^{\circ}\text{C}$, respectively. The soak time and soak temperature experiments were performed in the vertical graphite-heated furnace, with cooling rate maintained at $2\text{ }^{\circ}\text{C/hr}$ for both sets of experiments, soak temperature held between 1500 and $1550\text{ }^{\circ}\text{C}$ for the soak time experiments and soak time held at 24 hours for all soak temperatures except for $1700\text{ }^{\circ}\text{C}$, which was instead held only for 6 hours to limit vaporization of the metal flux.

Analysis of the hBN samples began with examination by optical microscopy to determine the crystal morphology and size. X-ray diffraction (XRD) and Raman spectroscopy were performed to analyze the quality, phase and strain of crystals. Raman spectroscopy was performed using a HeNe ion laser with a spot size of 1 micron upon the *c*-plane of hBN crystal samples. XRD was performed using a Cu K-alpha source (wavelength of 1.54 angstroms) on hBN crystals which had been transferred to a glass substrate.

III. Results and Discussion

Following the procedure described above, the hBN crystals formed on the top of metal flux surface. The quality of the hBN was highly dependent on the cooling rate, as illustrated in Fig. 1. A major shift in crystalline quality was observed, from a fine grain, grey-white layer formed at $10\text{ }^{\circ}\text{C/hr}$, shown in Fig. 1 (a), to a sheet of clear crystals formed at a $2\text{ }^{\circ}\text{C/hr}$, shown in Fig. 1 (c).

4 °C/hr, shown in Fig. 1 (b) appeared to mark the transition cooling rate for the formation of large ($>500\text{ }\mu\text{m}$) crystal grains, which tended to be surrounded by white fine gray powder-like hBN. Crystals grown at 2 °C/hr were the highest quality grown in this study. They were clear and colorless. Some cracking was observed within crystalline grains, presumably due to strain from the difference in the coefficients of thermal expansion of the metal and hBN. Subsequent experiments were pursued with the cooling rate fixed at 2°C/hr to investigate the effects of soak temperature and time on crystal size.

The maximum apparent crystal width formed increased with temperature from 0.75 mm across at 1450 °C to 5.0 mm across at 1700 °C, as shown in Fig. 2 (a). Crystal thickness showed an opposite trend, with crystal thickness as large as 500 μm at 1500 °C and decreasing to 40 μm at 1700 °C. Images of the crystal width and thickness of samples grown at (a) 1500 and (b) 1700 °C are shown in Fig 3. The habit of crystals formed also changed with the temperature. At lower temperatures, the crystals exhibited a thicker, more regular hexagonal shape, with growth rates roughly equal in the *a* and *c* directions. At higher temperatures, the crystals exhibited a more triangular habit and preferred to grow wider and thinner. This difference in shape may be due to preferential termination of the crystal edge with either N or B atoms, maximizing exposure of one set of dangling bonds and increasing crystal stability [18, 19]. Schematics of these two crystal habits and a diagram of an atomic layer of hBN preferentially terminating with N atoms are shown in Fig. 4 (a) and (b), respectively.

Unlike the trend in soak temperature, the crystal width and thickness both appeared to produce the maximum values for soak times between 24 and 48 hours. Crystals grown within this soak time window produced maximum widths. Crystals grown with soak times outside of this window had poor crystal width ($< 500\text{ }\mu\text{m}$), as shown in Fig 5 (a). Crystal thickness showed a similar trend, with thicknesses up to 200 μm for soak times between 24 and 48 hours, but only 100 μm or less outside of this window, as shown in Fig 5 (b). Twenty-four hours may be the minimum time needed for the Ni and Cr powder to fully melt and for boron and nitrogen to dissolve to the maximum extent possible in the melt. It is unclear at this time why crystal size decreases with increasing soak time beyond 48 hours.

A comparison of the X-ray diffraction pattern for crystals grown at 1550°C and 1700°C is shown in Fig. 6. These samples consisted of sheets of hBN, consisting of multiple crystalline domains, which were carefully removed from the surface of the metal flux using forceps and transferred onto glass substrates. Both hBN crystals exhibited strong, narrow peaks for the (002), (004), and (006) planes, corresponding to stacked planes in the *c*-direction. The FWHM for the (002) peak decreased with increasing soak temperature, from 0.60° at 1550°C to 0.31° at 1700°C. Both of these values confirm that crystals grown consist of well-ordered stacked crystal planes, as is expected of single crystal hBN, although some peaks consistent with disordered hBN, such as the (121), (101) and (102) peaks, were present in the spectra. These peaks are likely the result of hBN powder trapped within the crystalline layers as well as inter-crystalline grain boundaries. The higher FWHM for the 1550°C and the increase in intensity of these disordered peaks was likely caused by the increased thickness of the crystal, which increased the likelihood for misoriented planes as well as the inclusion of undissolved hBN powder.

Raman spectroscopy was performed on an hBN crystal layer grown at 1450°C, which had been transferred onto a glass substrate, similar the XRD samples. The sample exhibited a single peak at 1366 cm^{-1} , as shown in Fig. 7. This peak corresponds to the E_{2g} vibration mode of hBN and its measured FWHM, 8.0 cm^{-1} , is one of the narrowest peaks observed for hBN, compared to

values of 9.1 cm^{-1} reported by Watanabe *et al* [20]. That there is only a single narrow peak confirms that these crystals exhibit low stress and high purity (*i.e.* no cubic BN) and is indicative of the quality of the crystals grown by this metal flux growth process.

IV. Conclusions

Bulk hBN single crystals have been, up to this point, difficult to grow in large quantities. However, hBN appears to have great potential for several different applications, notably as neutron detectors, deep UV light sources, and as substrates for graphene and other two dimensional materials. Flux growth of hBN in Ni-Cr is a flexible process, and its growth parameters, notably soak temperature can be adjusted to optimize crystals for each application. For example, for neutron detectors, thick crystals (exceeding 1 mm) are needed to completely capture all the thermal neutrons, and thereby greatly boost the device efficiency. This suggests crystals for these devices should be grown at lower temperatures to promote a greater thickness. On the other hand, hBN substrates for 2D materials require large areas, but can be quite thin; therefore crystals can be grown at higher temperatures to promote wider, thinner crystals. Further developments of hBN crystal growth techniques, such as lowering the cooling rate below 2°C/hr or adapting a seeded-crystal growth method may yield even larger hBN crystals and allow for the large scale development of hBN devices.

Acknowledgments

Special thanks to the University of Kansas Bioengineering Research Center for the use of their LabRAM ARAMIS Raman spectrometer for the measurement of our samples.

Funding for this project was made possible thanks to the National Science Foundation and Department of Homeland Security through funding of the Academic Research Initiative (ARI) program, ARI-MA grant number *1038890*.

Original Article Statement

This manuscript is the original work of the authors and has not been previously or simultaneously submitted elsewhere. All authors have reviewed the content of this manuscript and have consented to its contents.

References

- [1] D.S. McGregor, T.C. Unruh, and W.J. McNeil, *Thermal neutron detection with pyrolytic boron nitride*, Nucl Instrum Meth A **591** 530 (2008).
- [2] J. Li, R. Dahal, S. Majety, J.Y. Lin, and H.X. Jiang, *Hexagonal boron nitride epitaxial layers as neutron detector materials*, Nucl Instrum Meth A **654** 417 (2011).
- [3] K. Watanabe, T. Taniguchi, and H. Kanda, *Direct-bandgap properties and evidence for ultraviolet lasing of hexagonal boron nitride single crystal*, Nat Mater. **3** 404 (2004).
- [4] S. Majety, X.K. Cao, J. Li, R. Dahal, J.Y. Lin, and H.X. Jiang, *Band-edge transitions in hexagonal boron nitride epilayers*, Appl. Phys. Lett. **101** 051110 (2012).
- [5] J. Li, S. Majety, R. Dahal, W.P. Zhao, J.Y. Lin, and H.X. Jiang, *Dielectric strength, optical absorption, and deep ultraviolet detectors of hexagonal boron nitride epilayers*, Appl. Phys. Lett. **101** 171112 (2012).
- [6] C.R. Dean, A.F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei K. Watanabe, T. Taniguchi, P. Kim, K.L. Shepard, and J. Hone, *Boron nitride substrates for high-quality graphene electronics*, Nat Nanotechnol **5** 722 (2010).
- [7] H. Wang, T. Taychatanapat, A. Hsu, K. Watanabe, T. Taniguchi, P. Jarillo-Herrero, and T. Palacios, *BN/graphene/BN transistors for RF applications*, IEEE Electron Dev. Lett. **32** 1209 (2011).
- [8] K. Watanabe, T. Taniguchi, T. Niiyama, K. Miya, and M. Taniguchi, *Far-ultraviolet plane-emission handheld device based on hexagonal boron nitride*, Nat Photonics **3** 591 (2009).
- [9] M. Kalbac, O. Frank, J. Kong, J. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, P. Jarillo-Herrero, and M.S. Dresselhaus, *Large variations of the Raman Signal in the spectra of twisted bilayer graphene on a BN substrate*, J. Phys. Chem. Lett. **3** 796-799 (2012).
- [10] V.L. Vinogradov and A.V. Kostanovskii, *Determination of the melting parameters of boron-nitride*, High Temperature **29** 901 (1991).
- [11] L.H. Dreger, V.V. Dadape, and J.L. Margrave, *Sublimation and decomposition studies on boron nitride and aluminum nitride*, J. Phys. Chem. **66** 1556 (1962).
- [12] T. Iishi and T. Sato, *Growth of single-crystals of hexagonal boron-nitride*, J. Cryst. Growth **61** 689 (1983).
- [13] M. Hubáček and T. Sato, *The effect of copper on the crystallization of hexagonal boron nitride*, J. Mater. Sci. **32** 3293 (1997).
- [14] M. Yano, Y.K. Yap, M. Okamoto, M. Onda, M. Yoshimura, Y. Mori, and T. Sasaki, *Na: A new flux for growing hexagonal boron nitride crystals at low temperature*, Jpn. J. Appl. Phys. Pt. 2 Lett. **39** L300 (2000).
- [15] Y. Gu, M. Zheng, Y. Liu, and Z. Xu, *Low-temperature synthesis and growth of hexagonal boron-nitride in a lithium melt*, J. Am. Ceram. Soc. **90** 1589 (2007).
- [16] B.N. Feigelson, R.M. Frazier, M. Twigg, *III-nitride crystal growth from nitride-salt solution*, J. Cryst. Growth **305** 399 (2007).
- [17] Y. Kubota, K. Watanabe, O. Tsuda, and T. Taniguchi, *Hexagonal boron nitride single crystal growth at atmospheric pressure using Ni-Cr solvent*, Chem. Mater. **20** 1661-163 (2008).
- [18] K. K. Kim, A. Hsu, X. Jia, S. M. Kim, Y. Shi, M. Hofmann, D. Nezich, J. F. Rodriguez-nieva, M. Dresselhaus, T. Palacios, J. Kong, *Synthesis of Monolayer Hexagonal Boron Nitride Thin Film by Chemical Vapor Deposition*, Nano Lett. **12** 161-163 (2012).

- [19] Y. Liu, S. Bhowmick, B. I. Yakobson, *BN White Graphene and “Colorful” Edges: The Energies and Morphology*, Nano Lett. **11**, 3113-3116 (2011)
- [20] Y. Kubota, K. Watanabe, O. Tsuda, and T. Taniguchi, *Deep ultraviolet light-emitting hexagonal boron nitride synthesized at atmospheric pressure*, Science. **317** 932-934 (2007).

Figures

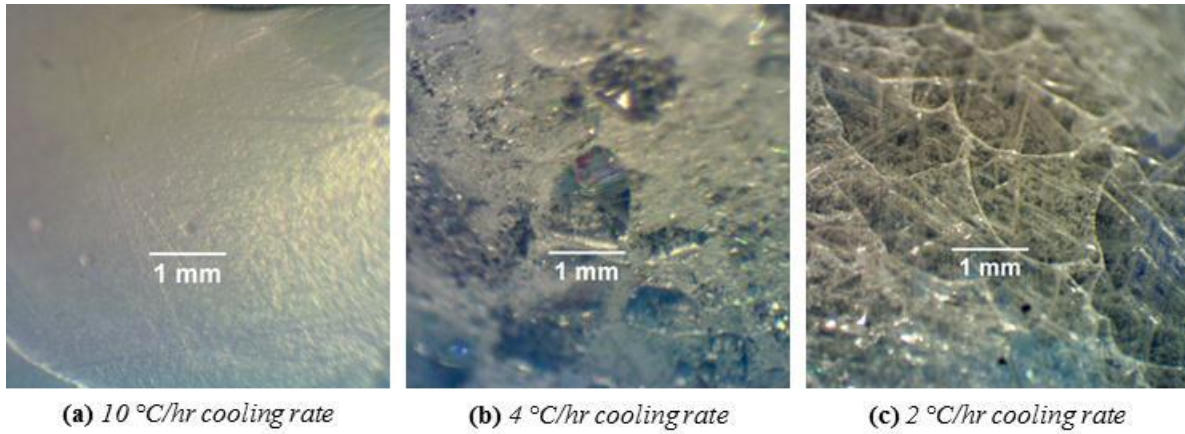


Figure 1: Comparison of hBN grown at cooling rates of (a) 10°C/hr , (b) 4°C/hr and (c) 2°C/hr , after having soaked at $1500\text{ }^{\circ}\text{C}$ for 24 hours. hBN quality transitions from white-grey in color and very small grain size (10°C/hr) to clear crystals with macroscopically visible grain size (2°C/hr) with decreasing cooling rate.

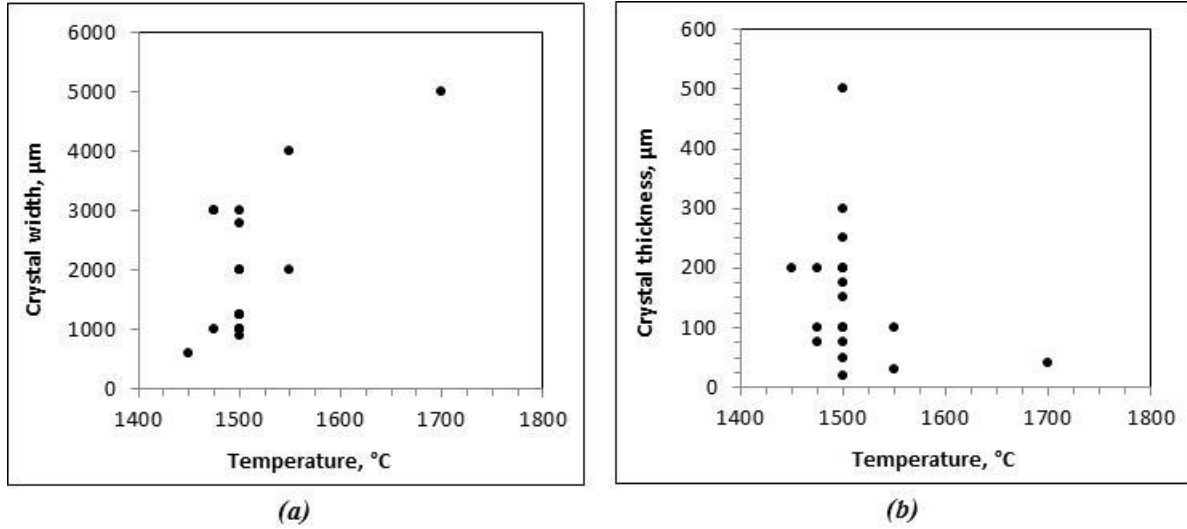


Figure 2: Dependence of maximum hBN (a) crystal width and (b) crystal thickness on soak temperature. The crystal width increases with increasing soak temperature across the temperature range considered (1450-1700°C) while crystal thickness decreases sharply with increasing soak temperature. Cooling rate for these samples was held at 2 °C/hr and soak time was maintained at 24 hours for all samples except for that grown at 1700 °C, which was soaked for 6 hours.

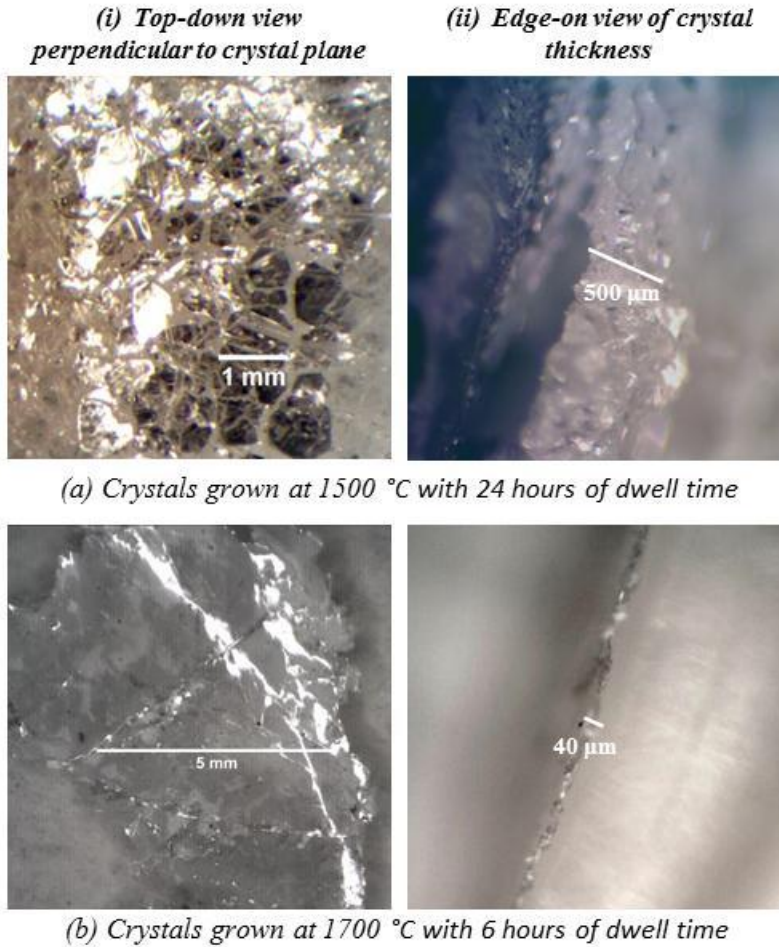


Figure 3: Optical image of crystals grown at (a) 1500 °C and (b) 1700 °C from both the (i) top-down perspective showing crystal width and (ii) edge-on view showing crystal thickness. These samples were both grown in the graphite furnace, with the 1500 °C sample grown with a soak time of 24 hours and the 1700 °C with a soak time of 6 hours. Maximum crystal width and thickness were estimated to be 1.25 mm and 500 μm , respectively, for the 1500 °C sample and 5 mm and 40 μm for the 1700 °C sample

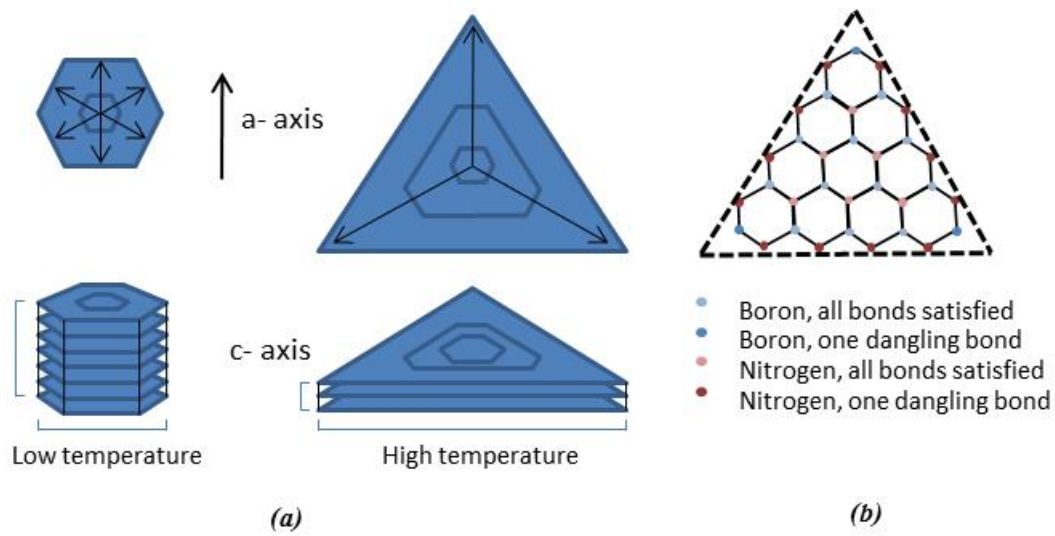


Figure 4: Diagram of (a) differences in crystal habit for hBN grown at low and high temperatures and (b) theoretical atomic arrangement for the high temperature, triangular hBN habit, as adapted from Kim et al [18] and Liu et al [19].

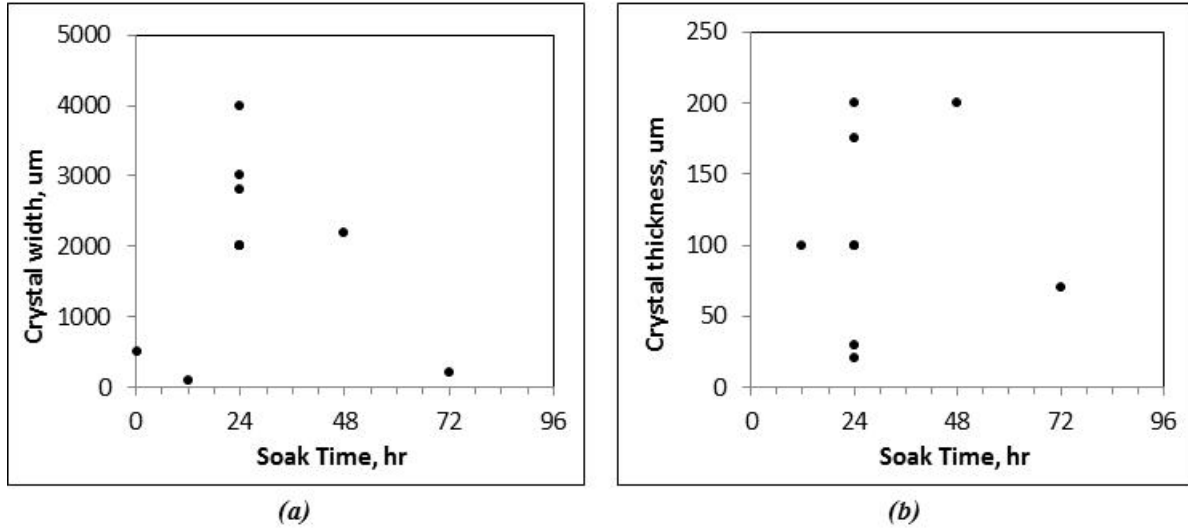


Figure 5: Dependence of maximum hBN (a) crystal width and (b) crystal thickness on soak time. Both the width and thickness appear to have maximum values for soak times between 24 and 48 hours, with both width and thickness sharply declining for longer and shorter soak times. Cooling rate and soak temperature for these samples was 2 °C/hr and between 1500-1550 °C, respectively.

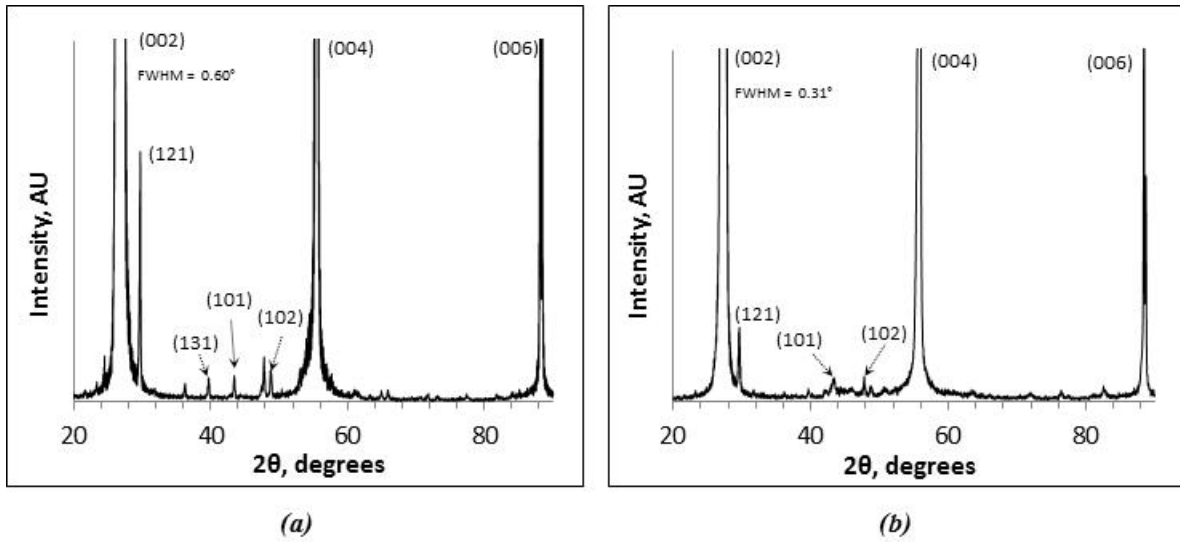


Figure 6: X-ray diffraction spectra for hBN crystals growth with soak temperature of (a) 1550°C and (b) 1700°C. FWHM for the (002) peak decreases from 0.60° at 1550°C to 0.31° at 1700°C. Peaks not corresponding to stacked planes [(121), (101), and (102)] also decrease with increasing soak temperature.

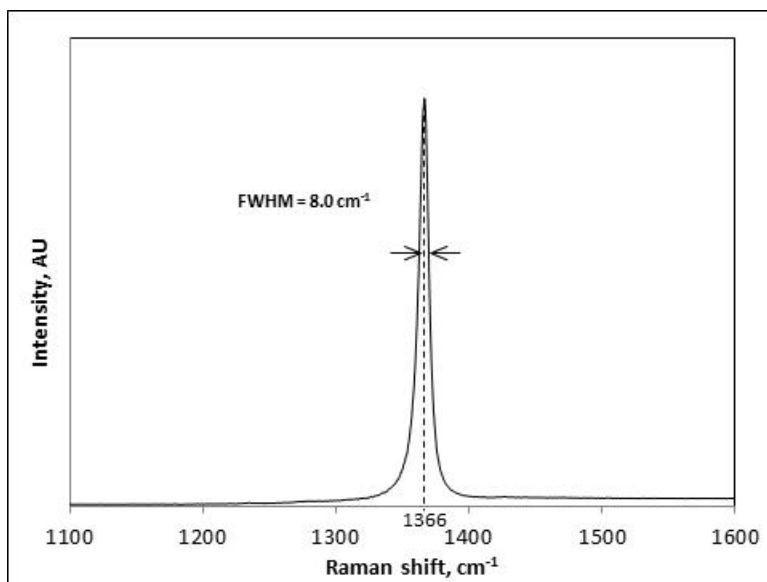


Figure 7: Raman spectrum for crystalline hBN sample grown at a soak temperature of 1450°C. Peak observed at 1366 cm⁻¹ with FWHM of 8.0 cm⁻¹ corresponds to the E_{2g} vibration mode for hBN and is indicative of the high purity and order of the single crystals grown by this process.