



Phase transformation of boron nitride under hypothermal conditions

Gang Lian^{a,b}, Xiao Zhang^{a,b}, Lingling Zhu^a, Deliang Cui^{a,*}, Qilong Wang^{b,**}, Xutang Tao^a

^a State key Lab of Crystal Materials, Shandong University, Jinan 250100, PR China

^b School of Chemistry & Chemical Engineering, Shandong University, Jinan 250100, PR China

ARTICLE INFO

Article history:

Received 14 January 2009

Received in revised form

12 February 2009

Accepted 13 February 2009

Available online 26 February 2009

Keywords:

CBN

Phase transformation

Hydrothermal solution

Puckering mechanism

ABSTRACT

Phase transformation among different boron nitride (BN) phases in hydrothermal solution was investigated. It was found that hexagonal boron nitride (hBN) firstly formed in the solution at relatively low temperature (i.e., 220 °C). After that, a spot of hBN began to transform into wurtzite boron nitride (wBN) and cubic boron nitride (cBN) at 230 °C. More and more hBN converted into wBN and cBN with the increase in temperature, and this transformation process completed at 300 °C. In this paper, we have explained the mechanism of the above phase transformation by using a reported “puckering mechanism”.

© 2009 Elsevier Inc. All rights reserved.

1. Introduction

Cubic boron nitride (cBN), a valuable material with outstanding properties and important technological applications, has attracted much attention of the material researchers [1–5]. Up to now, cBN has been successfully synthesized by high temperature and high pressure (HTHP) method with the help of various catalysts [6–13]. Besides, the denser phases of BN, namely, wBN and cBN, can also be obtained from the transformation initiated by chemical shifts. On the other hand, many authors have also proposed some models for explaining the phase transformation of BN [14,15], which focuses on how the sp^2 -bonded hBN transformed into sp^3 -bonded cBN, but they are still in controversy. One opinion is that such a transformation proceeds directly via an amorphous phase [16], and the other one is that an intermediate phase exists between hBN and cBN [17–20]. In the latter case, a hybrid modification and stacking sequence alter process happened, namely, from the ABAB stacking order and sp^2 -hybrid form of hBN to the ABCABC stacking sequence and sp^3 -hybrid modification of cBN. Meanwhile, the intermediate metastable phase, such as wBN, usually exists.

On the basis of investigating the mechanism of BN phase transformation under HTHP conditions, some effective methods have been developed to synthesize cBN at milder conditions. Unfortunately, the temperature and pressure required for synthesizing cBN is still very high, which results in the high cost and poor yield of cBN. For overcoming this difficulty, a new

hydrothermal synthesis method has been developed for synthesizing cBN at much lower temperature and pressure. However, the as-prepared samples are usually mixtures of hBN, cBN and oBN etc., and it is very difficult to obtain single phase cBN [21–23]. On the other hand, in the experiment of in-situ monitoring the reaction process of synthesizing BN, we have found that there exist phase transformations among different BN phases in solvothermal solutions. It is reasonable to believe that the phase transformations should be the major reason for the coexistence of multi-phases in the samples prepared by hydrothermal method. So, investigating the phase transformations among different BN phases in hydrothermal solutions will provide us much useful information for developing new and effective methods, by which the reaction process can be controlled and single phase cBN will be easily synthesized.

2. Experimental

All the detailed preparation and characterization methods of the samples can be found in Ref. [23]. In order to investigate the phase transformation of BN within 220–300 °C, a series of BN samples have been prepared at different temperatures, and the correlation between samples and preparation temperature is presented in Table 1.

3. Results and discussion

In order to obtain an intuitionistic understanding of the phase transformation in hydrothermal solution, the phases of BN

* Corresponding author. Fax: +86 531 8361856.

** Also corresponding author.

E-mail addresses: cuidl@sdu.edu.cn, cuideliang@yahoo.com.cn (D. Cui).

Table 1
Correlation between the samples and preparation temperatures.

Samples no.	a	b	c	D	e	f
Temperature (°C)	220	230	240	260	280	300

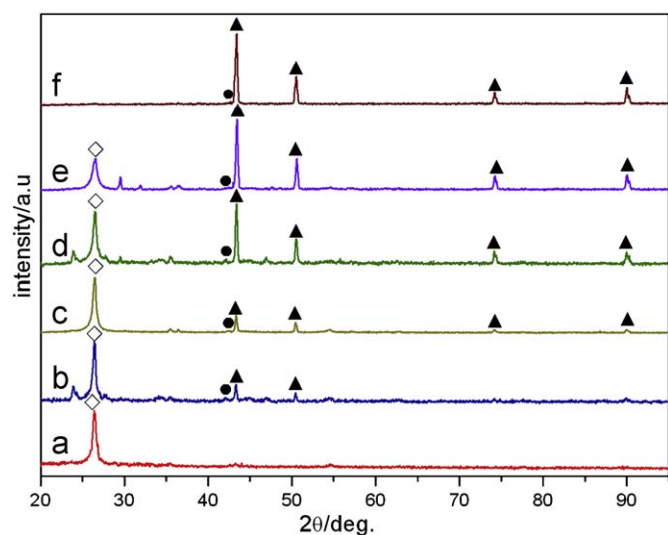


Fig. 1. XRD patterns of BN samples synthesized at different temperatures. (a) 220 °C; (b) 230 °C; (c) 240 °C; (d) 260 °C; (e) 280 °C; (f) 300 °C. cBN: $a = 3.615 \text{ \AA}$, marked with "▲" (JCPDS No. 89-1499); hBN: $a = 2.504 \text{ \AA}$, $c = 6.656 \text{ \AA}$, marked with "▲" (JCPDS No. 34-0421); wBN: $a = 2.550 \text{ \AA}$, $c = 4.215 \text{ \AA}$ (JCPDS No. 49-1327), marked with "●".

samples have been analyzed by using their XRD patterns. The corresponding XRD patterns of the samples prepared at 220, 230, 240, 260, 280 and 300 °C are shown in Fig. 1. In Fig. 1(a), the peaks of only hBN can be observed, which indicates that the sample prepared at 220 °C is composed of hBN. With the temperature increased to 230 °C, weak peaks of wBN and cBN can be found on the XRD pattern (Fig. 1(b)) of the corresponding sample, from which we know that some of the hBN converted into wBN and cBN at this temperature. Hereafter, with the temperature further increasing, the peaks of cBN became stronger and stronger, while that of hBN got weaker and weaker. This phenomenon clearly shows us that more and more hBN transformed into wBN and cBN when the temperature continuously increased. Finally, only wBN and cBN can be found in the sample prepared at 300 °C, which reveals that the phase conversion of hBN → wBN+cBN completed at 300 °C.

From the above analysis, it can be concluded that hBN formed at 220 °C in hydrothermal solution, and the transformation from hBN to wBN and cBN started at 230 °C and finished at 300 °C. During this process, the pressure in the autoclave was 12 MPa. These conditions are much milder than that required for the same transformation in conventional HTHP synthesis process (>1000 °C, >1000 MPa).

The above conclusion is also supported by the corresponding FTIR spectra. In Fig. 2, the peaks at 1017–1068 cm^{-1} are resulted from the absorption of TO phonons of cBN, while the shoulder-peaks at 1129–1148 cm^{-1} come from the absorption of wBN, and those at 1383–1387 cm^{-1} should be attributed to B–N stretch vibration mode of hBN. Obviously, when the sample was prepared at 220 °C, only the peak of hBN can be observed, and the peak at 1048 cm^{-1} just appeared if only the temperature increased to 230 °C. This phenomenon clearly indicates that a transformation

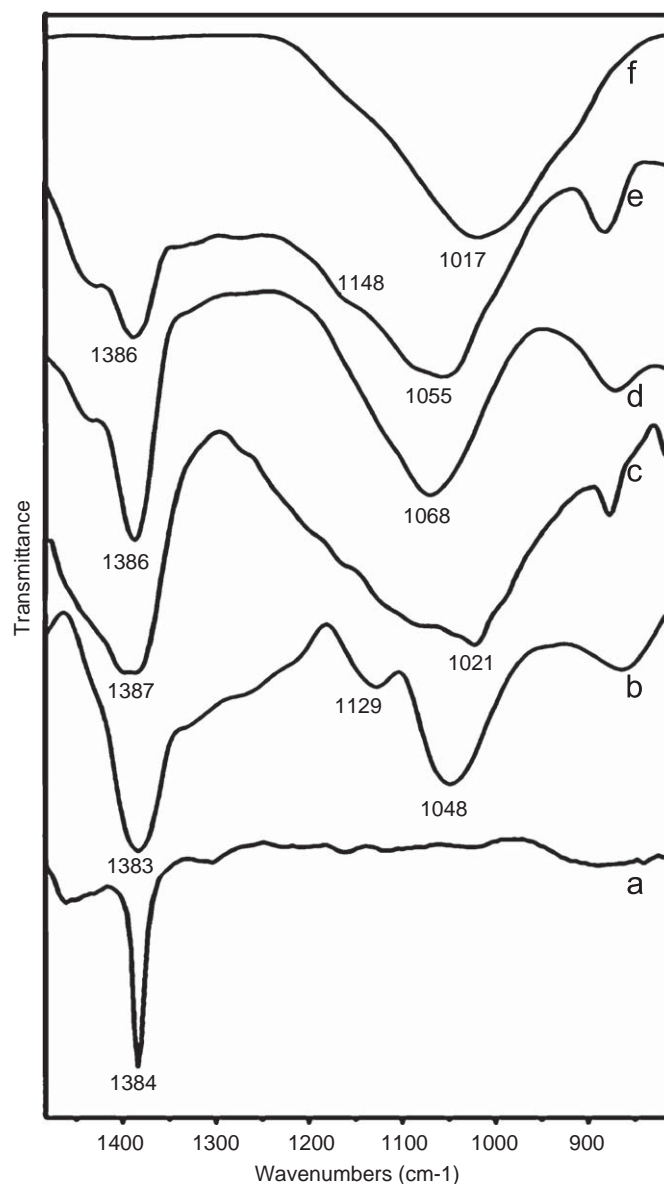


Fig. 2. FTIR spectra of BN obtained at different temperatures. (a) 220 °C; (b) 230 °C; (c) 240 °C; (d) 260 °C; (e) 280 °C; (f) 300 °C.

from hBN to wBN and cBN happened at 230 °C, thus part of hBN has been converted into wBN and cBN at this temperature. With the temperature further increasing, the characteristic absorption peak of wBN and cBN became stronger and stronger, and that of hBN became weaker and weaker and finally disappeared at 300 °C. This result proves again that the phase transformation hBN → wBN+cBN completed at 300 °C.

In order to quantitatively analyze the variation of contents of wBN and cBN with the increasing of temperature, FTIR peaks have been fitted by multi-Gaussian curves and the results are presented in Fig. 3. In this figure, the peaks at 1012–1067 cm^{-1} are attributed to cBN, and those at 1138–1157 cm^{-1} to wBN. Within 230–300 °C, it is found that the peaks of cBN are always dominating, and small peaks of wBN can also be observed. wBN, possessing the similar stacking sequence with hBN and the same sp^3 -hybrid form with cBN, is the intermediate phase between hBN and cBN. Thus, the existence of wBN should be regarded as an evidence of the phase transformation from hBN to cBN in hydrothermal solutions.

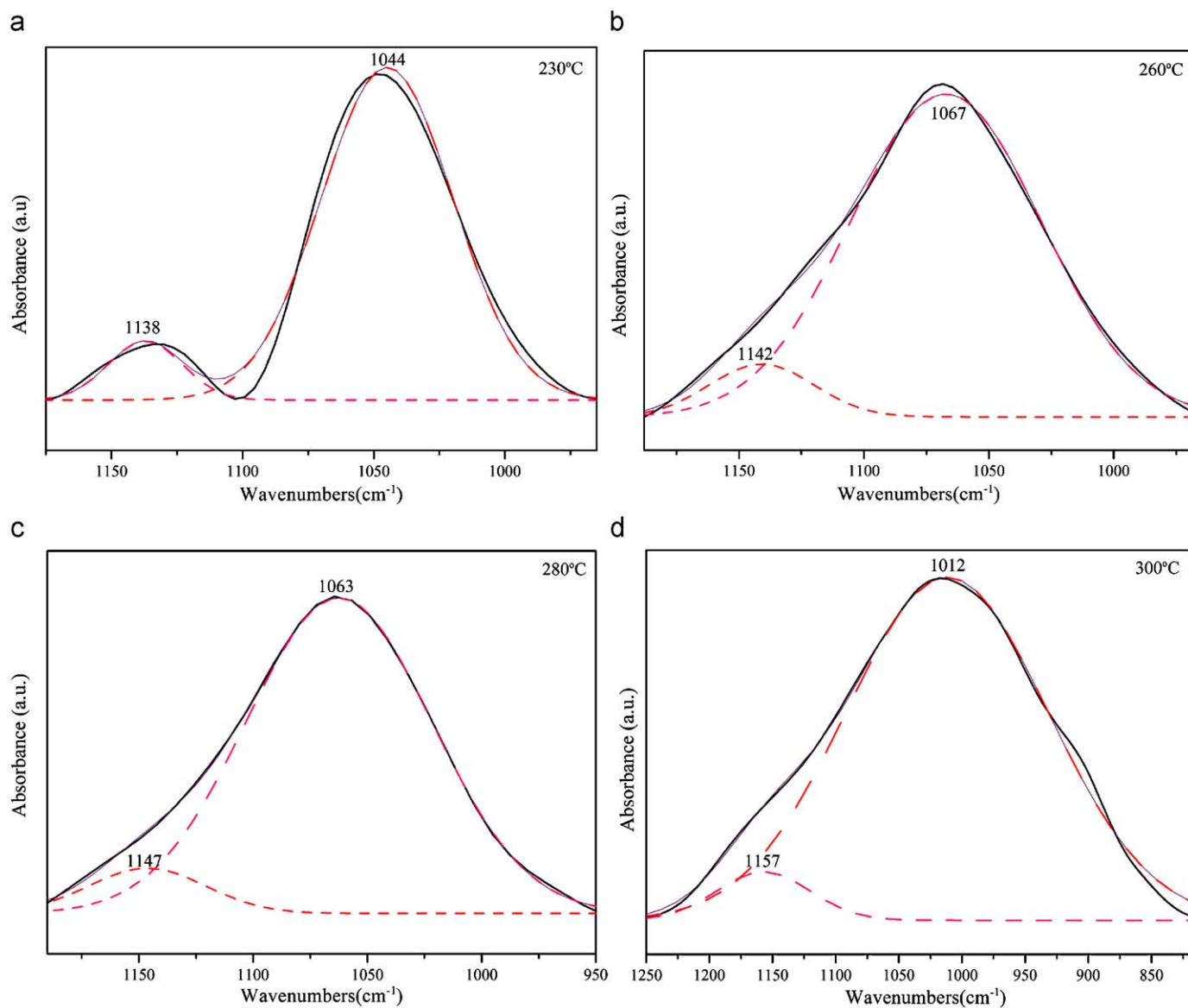


Fig. 3. Fitting results of the IR bands of BN samples. (a) 230°C; (b) 260°C; (c) 280°C; (d) 300°C. The peaks at 1012~1067 cm^{-1} are attributed to c-BN, those at 1138~1157 cm^{-1} to w-BN. (Origin Pro. 7.5 software was used in the analysis process).

Besides, the relative contents of hBN, cBN and wBN can be further estimated by using the similar method. Here, the intensities of corresponding FTIR peaks are denoted as I_{hBN} , I_{cBN} and I_{wBN} , and the contents of them are calculated using $X_{\text{hBN}} = I_{\text{hBN}} / (I_{\text{hBN}} + I_{\text{cBN}} + I_{\text{wBN}})$, $X_{\text{cBN}} = I_{\text{cBN}} / (I_{\text{hBN}} + I_{\text{cBN}} + I_{\text{wBN}})$ and $X_{\text{wBN}} = I_{\text{wBN}} / (I_{\text{hBN}} + I_{\text{cBN}} + I_{\text{wBN}})$. The result shown in Fig. 4 obviously indicates that the content of cBN monotonously increased with the increasing of temperature, and at the same time, the content of hBN decreased.

It is argued that during the synthesis of cBN by HTHP method, hBN was firstly compressed along the c-axis, then transformed into wBN by a “puckering mechanism” [20], followed by the conversion into cBN via a so-called “dislocation mechanism” [17,18], i.e. $\text{hBN} \rightarrow \text{wBN} \rightarrow \text{cBN}$ (Fig. 5). The definite orientation relationship $(0002)_{\text{h}} \parallel (0002)_{\text{w}} \parallel (111)_{\text{c}}$ directly verified such a mechanism [5,20]. For more clearly explaining such a mechanism, Table 2 and Fig. 5 present the crystal structure data and scheme for the transformation of hBN \rightarrow wBN \rightarrow cBN [5].

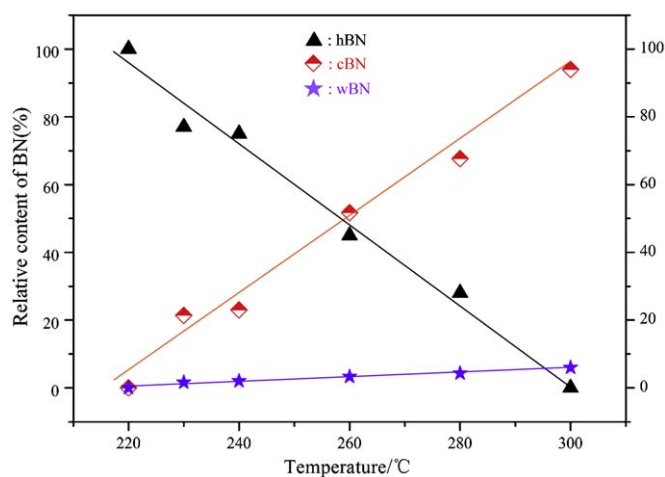


Fig. 4. Relative contents of hBN, cBN and wBN at different temperatures.

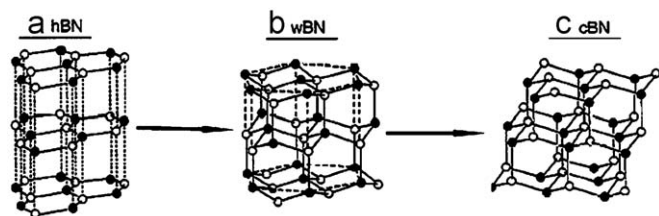


Fig. 5. Scheme of phase transformation from hBN to wBN and cBN.

Table 2

Structural data of different BN phases.

Phase	<i>a</i> (Å)	<i>c</i> (Å)	Space group	hybridized mode	Stacking sequence
hBN	2.5043	6.6562	$P6_3/mmc(194)$	sp^2	AA'A...[0001]
wBN	2.5505	4.210	$P6_3mc(186)$	sp^3	AA'A...[0001]
cBN	3.6153		$F\bar{4}3m(216)$	sp^3	ABC...[111]

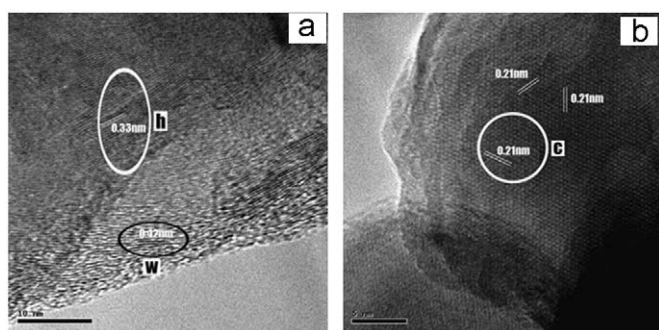


Fig. 6. HRTEM images of BN sample of mixed phases. h, w and c represent hBN, wBN and cBN, respectively. (a) small domain of wBN can be found at the edge of a hBN crystallite, the fringes with distances of 0.33 nm and 0.42 nm are indexed to the (002) plane of hBN and (001) plane of wBN, respectively. (b) cBN crystallite, fringes with distance of 0.21 nm corresponds to the (111) plane of cBN.

The above mechanism should also be valid for the BN in hydrothermal solution. In Fig. 6, we present the HRTEM images of hBN, wBN and cBN crystallites. In these crystallites, hBN (labeled with "h") are usually found at the inner part while some small wBN (labeled with "w") domains found at the surface region. Besides, cBN has also been identified on the basis of two-dimensional lattice fringes together with their corresponding angle (Fig. 6(b)). Considering this result, it should be reasonable to believe that wBN domains might nucleate at the surface region of hBN crystallites, then these domains became larger and larger. At higher temperature and pressure, wBN domains converted into cBN, and these newly formed cBN domains gradually developed into cBN nanocrystals.

On the other hand, the morphologies of hBN and cBN differ strikingly from each other. In Fig. 7, it is clear that hBN exhibits as nano-coshes while cBN appeared as small cubes. This difference in morphology reveals that besides the phase transformation of hBN→cBN, dissolving of hBN and re-growing process on the surface of cBN crystallites should also happened during the hydrothermal synthesis process, which is still under intensive investigations.

4. Conclusions

Phase transformations among different BN phases have happened at rather low temperature and pressure, namely, the

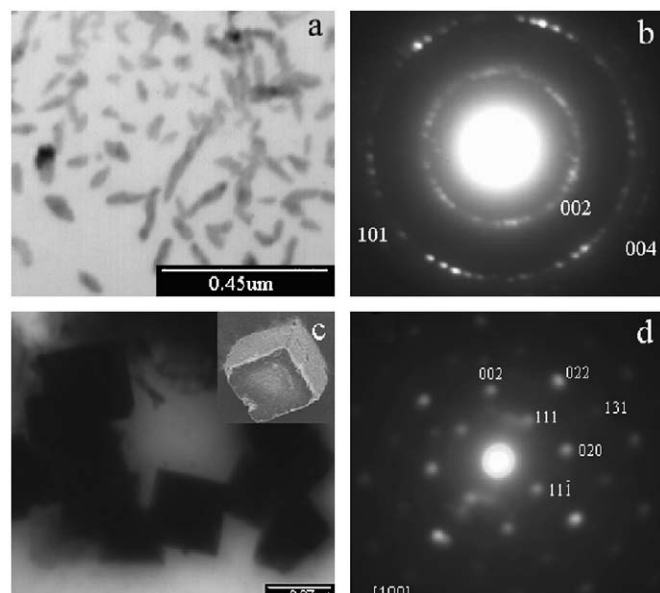


Fig. 7. TEM images and corresponding SAED patterns of hBN and cBN nanocrystals. (a) and (b) TEM image and SEAD pattern of hBN prepared at 220 °C; (c) and (d) that of cBN synthesized at 300 °C. The inset in (c) is the typical SEM image of a cBN single crystal.

transformation from hBN to cBN started at 230 °C and completed at 300 °C, and the pressure lower than 12 MPa, with wBN as the intermediate phase. This result should be very helpful for controlling the reaction process and synthesizing single-phase cBN microcrystals in a controllable way. Furthermore, the result reported in this paper also reveals that it should be possible to convert hBN microcrystals into cBN under much milder hydrothermal and solvothermal conditions.

Acknowledgments

This work is supported by the Natural Science Foundation of China (NSFC No. 50672048, 50721002), the Foundation of Chinese Ministry of Education (NCET-05-0585) and the Science & Technology Council of Shandong (No. 2005GG3203110, 2006GG2203039).

References

- [1] W.J. Zhang, I. Bello, Y. Lifshitz, K.M. Chan, X.M. Meng, Y. Wu, C.Y. Chan, S.T. Lee, *Adv. Mater.* 16 (2004) 1405.
- [2] M. Yeadon, M. Lin, K.P. Loh, C.B. Boothroyd, J. Fu, Z. Hu, *J. Mater. Chem.* 13 (2003) 2573.
- [3] W.J. Zhang, X.M. Meng, C.Y. Chan, K.M. Chan, Y. Wu, I. Bello, S.T. Lee, *J. Phys. Chem. B* 109 (2005) 16005.
- [4] W.J. Zhang, I. Bello, Y. Lifshitz, S.T. Lee, *MRS. Bull.* 28 (2003) 184.
- [5] P.B. Mirkarimi, K.F. Mccarty, D.L. Medlin, *Mater. Sci. Eng. R* 21 (1997) 47.
- [6] R.C. Devries, J.F. Fleischer, *Mater. Res. Bull.* 4 (1969) 433.
- [7] T. Endo, O. Fukunaga, M. Iwata, *J. Mater. Sci.* 14 (1979) 1375.
- [8] T. Sato, H. Hiraoka, T. Endo, O. Fukunaga, M. Iwata, *J. Mater. Sci.* 16 (1981) 1829.
- [9] T. Sato, T. Endo, S. Kashima, O. Fukunaga, M. Iwata, *J. Mater. Sci.* 18 (1983) 3054.
- [10] M. Kagamida, H. Kanda, M. Akaishi, A. Nukui, T. Osawa, S. Yamaoka, *J. Cryst. Growth* 94 (1989) 261.
- [11] V.L. Solozhenko, V.Z. Turkevich, *Mater. Lett.* 32 (1997) 179.
- [12] T. Kobayashi, *J. Chem. Phys.* 70 (1979) 5898.
- [13] K. Susa, T. Kobayashi, S. Taniguchi, *Mater. Res. Bull.* 9 (1974) 1443.
- [14] Al Douri, *Solid State Commun.* 132 (2004) 465.
- [15] H. Lorenz, I. Orgzall, *Scripta Mater* 52 (2005) 537.
- [16] M.I. Eremets, K. Takemura, H. Yusa, D. Goldberg, Y. Bando, V.D. Blank, *Phys. Rev. B* 57 (1998) 5655.

- [17] S. Horiuchi, J.Y. Huang, L.L. He, J.F. Mao, T. Taniguchi, *Philos. Mag. A* 78 (1998) 1065.
- [18] J. Huang, Y.T. Zhu, *Defect Diffus. Forum.* 186–187 (2000) 1–32.
- [19] S. Horiuchi, L.L. He, M. Onoda, M. Akaishi, *Appl. Phys. Lett.* 68 (1996) 182.
- [20] A.V. Kurdyumov, V.F. Britun, I.A. Petrusha, *Diam. Relat. Mater.* 5 (1996) 1229.
- [21] M.Y. Yu, D.L. Cui, K. Li, S.G. Chen, Q.L. Wang, Y.S. Yin, X. Wang, *Mater. Lett.* 61 (2007) 76.
- [22] K. Li, H.H. Jiang, G. Lian, Q.L. Wang, X. Zhao, D.L. Cui, X.T. Tao, *Chin. Sci. Bull.* 52 (2007) 1785.
- [23] K. Li, G. Lian, H.H. Jiang, X. Zhao, H.P. Jing, D.L. Cui, X.T. Tao, Q.L. Wang, *Diam. Relat. Mater.* 17 (2008) 989.