ELSEVIER

Contents lists available at ScienceDirect

Journal of Alloys and Compounds



journal homepage: www.elsevier.com/locate/jallcom

Letter

GaN crystals prepared through solid-state metathesis reaction from NaGaO₂ and BN under high pressure and high temperature

Huan Ma^a, Duanwei He^{a,*}, Li Lei^b, Shanmin Wang^a, Ying Chen^a, Haikuo Wang^a

^a Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China

^b Geodynamics Research Center, Ehime University, Bunkyo-cho 2-5, Matsuyama 790-8577, Japan

ARTICLE INFO

Article history: Received 27 July 2010 Received in revised form 6 December 2010 Accepted 14 December 2010 Available online 22 December 2010

Keywords: Gallium nitride Solid-state metathesis reaction High pressure and high temperature

1. Introduction

GaN has attracted considerable attention as a semiconductor material for fabrication of optoelectronic devices, such as blue or green light emitting diodes (LEDs) and violet laser diodes (LDs) due to its wide band gap, high thermal stability, and high breakdown voltage [1–4]. Up to now, the growth of GaN crystals has been extensively investigated by several research groups using different preparation approaches mainly including flux growth [5,6], hydride vapor-phase epitaxy [7,8], pressure-controlled solution growth [9], high-pressure ammonothermal growth [10], mechanochemical reaction method [11] and so on. Because of the importance of application of GaN on optoelectronic industry, the pursuit of the optimal synthetic route to attain well-crystallized GaN crystals has not stopped so far. We are attempting to synthesize high quality crystals of GaN by using effective methods involving high pressure. Recently, a high-pressure solid-state metathesis (SSM) method [12,13] has been developed to synthesize GaN crystals from LiGaO₂ and BN [14]. In spite of its remarkable advantages, such as high growth rate, simple assembly and substrate free, there are still some inevitable disadvantages in this synthetic route. The precursor LiGaO₂ is usually unstable and may decompose into lithium-poor phase LiGa₅O₈ under high temperature [14-16]. The unreacted LiGaO₂ and the decomposition product LiGa₅O₈

ABSTRACT

GaN crystals are successfully obtained through solid-state metathesis (SSM) reaction between sodium gallium oxide (NaGaO₂) and boron nitride (BN) under high pressure and high temperature. X-ray diffraction (XRD) pattern indicates that the attained GaN crystals possess a hexagonal wurtzite-type structure. Scanning electron microscopy (SEM) is used to estimate the size and morphology of GaN crystals, and results show that GaN grains with the size over 100 μ m can be prepared at 5 GPa and 1600 °C. Moreover, pressure-temperature (*P*–*T*) formation region of GaN has been discussed. Our results suggest a promising novel route for synthesizing GaN crystals from SSM reactions under high pressure.

© 2010 Elsevier B.V. All rights reserved.

as impurities in the products cannot be easily removed. In the present work, NaGaO₂ and BN as the initial precursors for SSM reaction are used to synthesize GaN crystals under high pressure and high temperature (HPHT). Compared with LiGaO₂, NaGaO₂ will be a better choice to maintain the previous merits and overcome the aforementioned difficulties. It is because that NaGaO₂ does not decompose at our HPHT conditions and easily dissolves in water, implying that the purification process of GaN crystals will become simple. By optimizing the P-T conditions, the wellcrystallized GaN crystals with the size over 100 µm are prepared at 5 GPa and 1600 °C. Moreover, forming regions for GaN crystals are also discussed. Our results not only provide a new method for synthesizing GaN crystals from the SSM reaction of NaGaO₂ with BN under HPHT but also give us a better understanding of SSM reactions under high pressure. The method with respect to highpressure SSM reaction can also be extended to synthesize other materials.

2. Experimental procedure

The starting materials for synthesizing GaN crystals are NaGaO₂ (synthesized from Ga₂O₃ and Na₂CO₃ at 1100 °C for 12 h under ambient pressure, ~99.99% purity) and BN (hexagonal BN or cubic BN, ~99% purity) powders. Before high-pressure experiments, NaGaO₂ and BN powders were compacted into a disk shape of 8.0 mm in diameter and 6.0 mm in height, respectively. And the disk was placed in a capsule made of hexagonal BN (hBN) or Mo with a sandwich-like configuration, and then contained in a pyrophyllite high-pressure cell [14]. This cell assembly was put into a high pressure furnace chamber [17]. HPHT experiments were performed on a DS6×8 MN cubic press [17,18]. The experimental details were described elsewhere [14,19,20]. The samples were first pressurized to a certain pressure, and then heated to a desired temperature for 30 min. Before decompression, the samples were

^{*} Corresponding author. Fax: +86 28 85466676. *E-mail address:* duanweihe@scu.edu.cn (D. He).

^{0925-8388/\$ -} see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2010.12.087



Fig. 1. XRD pattern of the sample formed from SSM reaction between NaGaO_2 and hBN at 5.0 GPa and 1600 $^\circ C$ for 30 min.

quenched to room temperature with the cooling rate about $2 \circ C/s$. The recovered samples were cleaned in water and alcohol with an ultrasonic washer before examination by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray analysis (EDXA).

3. Results and discussion

At first, we tried to use NaGaO₂ and hBN as the starting materials to synthesize GaN crystals under HPHT. In this reaction, NaGaO₂ and hBN were as the precursors to provide gallium and nitrogen resources, respectively. When the reaction between the two compounds was occurred under HPHT, the massive yellowish crystals were found to grow on the interface of two precursors after sandwich-like precursor layers were separated and washed by the pure water and alcohol. Fig. 1 is the XRD pattern of the sample growth surface. The major diffraction peaks are well indexed based

on a hexagonal cell with a = 3.189 Å and c = 5.186 Å (ICCD-PDF NO.: 50-0792), implying the attained yellowish crystals are GaN crystals. Note that these GaN crystals exhibit a highly (0 0 2) preferred orientation, indicating the basal plane of crystals as c-plane. Besides the phase GaN, the other phase hBN is also found under the resolution of the X-ray diffractometer. XRD pattern contains only two phases (GaN and hBN) because the unreacted NaGaO₂ powder and the byproduct sodium metaborate (NaBO₂) were removed in washing process. Obviously, gallium and nitrogen of GaN come from NaGaO₂ and hBN, respectively. This also suggests that GaN is the product of the exchange reaction between NaGaO₂ and hBN. Therefore, the reaction should be a high-pressure SSM reaction and explained as the equation NaGaO₂ + BN = GaN + NaBO₂, which is similar to the reaction of LiGaO₂ with BN under HPHT [14].

SEM was used to investigate the size and morphology of GaN crystals. Prominent features observed are presence of well defined grains shown in Fig. 2(a)-(d). To get initial appearance of GaN crystals, fracture surface of the samples was observed directly by SEM without taking any further treatment. The fracture surface images of the sample formed from SSM reaction of NaGaO₂ and hBN are shown in Fig. 2(a) and (b). There mainly exist two strikingly different regions of the images which reflect morphologies of GaN and NaGaO₂. And the corresponding regions are marked as GaN or NaGaO₂ (confirmed by EDXA). The well-crystallized GaN crystals have a wurtzite-type structure, which is in good agreement with XRD measurement. Combined with XRD in Fig. 1, it indicates that the c axis is the preferential growth direction of GaN crystals under high pressure. As shown in Fig. 2(a), the biggest crystal dimension along the c axis direction can be over $100 \,\mu$ m, while the dimension along other crystallographic orientation is only \sim 50 μ m. Fig. 2(b) shows a closed image of the GaN crystals prepared at 5.0 GPa and 1600 °C for 30 min. Moreover, EDXA reveals that the main element components of the crystals are Ga and N, which further indicate that the obtained crystals are GaN. GaN crystals were also attained when cubic boron nitride (cBN) was used as the nitrogen precursor for



Fig. 2. SEM images of the samples prepared at 5.0 GPa and 1600 °C for 30 min. (a) and (b), the fracture surface of the sample prepared from SSM reaction of NaGaO₂ and hBN. (c) and (d), GaN crystals formed by the SSM reaction between NaGaO₂ and cBN in the cross-section.



Fig. 3. Forming region for GaN crystals by the SSM reaction of NaGaO₂ with BN under high pressures and temperatures. Inverse triangle indicates the experimental conditions at which GaN can be detected by XRD. Rhombus represents the pressure and temperature (P-T) conditions at which GaN crystal fails to form. The dashed line is the boundary line of synthesizing GaN crystal, and the solid line is the decomposition line for GaN from Ref. [21].

metathesis reaction under the same synthetic conditions. In order to get rid of unreacted NaGaO₂, the sample was washed by pure distilled water and alcohol. As shown in Fig. 2(c), these GaN crystals are different from those prepared from hBN precursor in morphology, and also possess a wurtzite-type structure and exhibit well-defined grains with the size range from several micron to 30 μ m. Fig. 2(d) presents a closer SEM picture of the GaN crystals synthesized from NaGaO₂ and cBN at 5.0 GPa and 1600 °C. It can be readily seen that these crystals have clearly visible grain boundaries. Compared with hBN and cBN situations described above, it suggests that GaN crystal growing rate may be related to the polytypism of BN under high pressure. It can be seen that hBN as nitrogen resource is more favorable for GaN crystal grain growth.

A series of experiments are conducted to investigate the possibility for the synthesis of GaN crystals through SSM reaction of NaGaO₂ with BN under different *P*–*T* conditions. Fig. 3 summarizes the P-T regions for GaN formation. Inverse triangle indicates the *P*-*T* conditions at which GaN crystals can be detected by XRD, and the rhombus represents that GaN crystals fail to form. GaN crystals can be synthesized at the *P*–*T* conditions above the dashed line (as shown in Fig. 3). The solid line is the decomposition line of GaN. At high temperature and low pressure, above the solid line, GaN will decompose into Ga and N₂ [21]. According to our experimental observation, under the pressure below 1.0 GPa and temperature above 1100 °C, the reaction cannot propagate and a mass of gallium metal will appear in the sample chamber, which may be caused by the decomposition of GaN [14]. As can be seen from Fig. 3, the synthesis temperature of GaN decreases as the pressure increases from 1.0 GPa to 2.0 GPa. We speculate that the pressure increases the contact between the two precursors, which speeds up the local reaction. So the synthesis temperature decreases under relatively low pressures (1.0–2.0 GPa) in our experiments. This has also been observed for some other materials, such as WB synthesis under HPHT [22]. The synthesis temperature of GaN increases when the pressure is elevated from 2.0 GPa to 5.0 GPa. In this case, a higher pressure may suppress the nucleation and growth of GaN crystals. However, high temperature usually prompts grain growth. Therefore, the dashed line at low pressure (<2 GPa) has a negative slope and the dashed line at high pressure (>2 GPa) has a positive slope. And the synthetic dashed line near the solid decomposition line may have some discrepancy with the normal synthesis model. Similar phenomena have also been observed by other researches [14,22-24].

High pressure served as an effective way can suppress GaN decomposition up to much higher temperature [21], which means that GaN crystal can grow up under high temperature and does not decompose when high pressure is applied. Previous studies show that the mobility of all species in the reaction is increased and subsequent reaction can rapidly occur if the temperature at this point is high enough to melt the byproduct salt [13], which has also proved in our study. Note that the melting point of the byproduct NaBO₂ is only 966 °C at ambient pressure [25], when the temperature is above the melting point, the mobility of NaGaO₂ with BN is enhanced and the SSM reaction of the two precursors under HPHT can unceasingly progress. Therefore, we suggest that GaN crystals are originally in the GaN-NaBO₂ solution at HPHT and precipitate from the melt during quenching [26]. NaBO₂ may also be a new solution of GaN for large single crystal growth. However, further investigation is still needed to optimize the synthetic conditions of GaN crystals from SSM reaction at HPHT.

4. Conclusion

In summary, GaN crystals are synthesized through SSM reaction of NaGaO₂ and BN at HPHT. hBN and cBN can all be as nitrogen source to synthesize GaN crystals and the bigger crystals over 100 μ m in size are attained at 5 GPa and 1600 °C by using hBN. The formation region of GaN is also described as the conditions of high pressure (1.0–5.0 GPa) and high temperature (1000–1600 °C). We suggest that GaN crystals are originally in the GaN–NaBO₂ solution and precipitate from the melt during quenching. NaBO₂ may also be a new solution of GaN for large single crystal growth. The results indicate a potential new route not only for preparing GaN crystals through SSM reaction under HPHT but also for other materials.

Acknowledgements

This work is supported by National Natural Science Foundation of China (Grant Nos. 10772126 & 11027405), National Natural Science Foundation of China – NSAF (Grant No. 10976018), and the China 973 Program (Grant No. 2011CB808200).

References

- [1] S. Nakamura, Science 281 (1998) 956-961.
- [2] F.A. Ponce, D.P. Bour, Nature 386 (1997) 351-359.
- [3] T. Miyajima, T. Tojyo, T. Asano, K. Yanashima, S. Kijima, T. Hino, M. Takeya, S. Uchida, S. Tomiya, K. Funato, T. Asatsuma, T. Kobayashi, M. Ikeda, J. Phys. Condens. Matter. 13 (2001) 7099–7114.
- [4] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, Y. Sugimoto, Jpn. J. Appl. Phys. 35 (1996) L74–L76.
- [5] X.L. Chen, Sci. Technol. Adv. Mater. 6 (2005) 766-771.
- [6] M. Aoki, H. Yamane, M. Shimada, S. Sarayama, F.J. DiSalvo, J. Cryst. Growth 242 (2002) 70–76.
- [7] S. Hontsu, N. Mukai, J. Ishii, T. Kawai, S. Kawai, Appl. Phys. Lett. 61 (1992) 2709–2711.
- [8] H. Morkoc, Mater. Sci. Eng. R 33 (2001) 135-207.
- [9] T. Inoue, Y. Seki, O. Oda, S. Kurai, Y. Yamada, T. Taguchi, J. Cryst. Growth 229 (2001) 35–40.
- [10] M.P. D'Evelyn, H.C. Hong, D.-S. Park, H. Lu, E. Kaminsky, R.R. Melkote, P. Perlin, M. Lesczynski, S. Porowski, R.J. Molnar, J. Cryst. Growth 300 (2007) 11–16.
- [11] J. Kano, E. Kobayashi, W. Tongamp, F. Saito, J. Alloys Compd. 464 (2008) 337–339.
- [12] A.M. Nartowski, I.P. Parkin, M. Mackenzie, A.J. Craven, J. Mater. Chem. 11 (2001) 3116–3119.
- [13] E.G. Gillan, R.B. Kaner, Chem. Mater. 8 (1996) 333-343.
- [14] L. Lei, D. He, Cryst. Growth Des. 9 (2009) 1264-1266.
- [15] M. Marezio, J.P. Remeika, J. Phys. Chem. Solid 26 (1965) 1277-1280.
- [16] C.J. Rawn, J. Chaudhuri, J. Cryst. Growth 225 (2001) 214–220.
- [17] S.M. Wang, D.W. He, W.D. Wang, L. Lei, High Pressure Res. 29 (2009) 806-814.
- [18] C.M. Sung, High Temp.-High Press. 29 (1997) 253-293.
- [19] D.W. He, M. Akaishi, T. Tanaka, Diamond Relat. Mater. 10 (2001) 1465–1469.
 [20] J. Qin, D. He, L. Lei, P. An, L. Fang, Y. Li, F. Wang, Z. Kou, J. Alloys Compd. 476
- (2009) L8-L10.
 [21] W. Utsumi, H. Saitoh, H. Kaneko, T. Watanuki, K. Aoki, O. Shimomura, Nat. Mater
- [21] W. Utsumi, H. Saitoh, H. Kaneko, T. Watanuki, K. Aoki, O. Shimomura, Nat. Mater. 2 (2003) 735–738.

- [22] Y. Chen, D. He, J. Qin, Z. Kou, S. Wang, J. Wang, J. Mater. Res. 25 (2010)
- 637.
 [23] H. Xiao, H. Ma, Z. Lin, J. Ma, F. Zong, X. Zhang, Mater. Chem. Phys. 106 (2007) 5–7.
- [24] H. Xiao, R. Liu, H. Ma, Z. Lin, J. Ma, F. Zong, L. Mei, J. Alloys Compd. 465 (2008) 340-343.
- [25] H.H. Nersisyan, J.H. Lee, C.W. Won, Mater. Chem. Phys. 89 (2005) 283–288.
 [26] D. He, M. Akaishi, B.L. Scott, Y. Zhao, J. Mater. Res. 17 (2002) 284–290.