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# GaN GROWTH ON β-$Ga_2O_3$ SUBSTRATES BY HVPE

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**Abstract.** Gallium oxide β-$Ga_2O_3$ crystals were grown by a seedless crystallization from a $Ga_2O_3$-$Al_2O_3$ melt. Platelets with (100) orientation were produced by cleaving of the β-$Ga_2O_3$ ingot. These platelets were employed as substrates for GaN deposition by HVPE. Properties of the β-$Ga_2O_3$ crystals and GaN epitaxial layers on β-$Ga_2O_3$ substrates were studied.

## 1. Introduction

Gallium oxide (β-$Ga_2O_3$) is a promising wide-band-gap semiconductor material for applications in optoelectronics and power semiconductor technology. The band gap energy of β-$Ga_2O_3$ is about 4.8-4.9 eV which is the largest value amongst other semiconducting oxides. Because of the extremely wide band gap, the material is transparent from the visible to the UV-C (260 nm) range of the spectrum. Gallium oxide is essentially insulating, however it can also exhibit n-type conductivity when synthesized under reducing conditions. Such unintentional conductivity is commonly attributed to oxygen vacancies [1] or hydrogen shallow donors [2]. Also, n-type β-$Ga_2O_3$ can be produced by doping with silicon [3] and tin [4, 5].

High quality single crystals of β-$Ga_2O_3$ can be grown from melt by Czochralski [6, 7], edge-defined film-fed growth (EFG) [5] and floating zone (FZ) [8] methods. This is an important advantage of β-$Ga_2O_3$ over conventional wide bandgap semiconductors such as gallium nitride and silicon carbide which are mainly produced by crystallization from the gas phase. When compared to other methods, melt growth techniques offer the benefits of lower energy consumption, higher throughput and superior material quality. In the case of mass production, the price of β-$Ga_2O_3$ substrates is expected to be significantly lower than those for GaN and SiC substrates.

Various semiconductor devices made of β-$Ga_2O_3$ have been reported, for example, UV photodetectors [9] and field effect transistors [10, 11]. Another promising application of β-$Ga_2O_3$ is its use as a substrate for epitaxial growth of GaN and related III-nitrides. Ultimately, native GaN substrate would be the best choice for III-nitride devices as only homoepitaxial growth can provide the lowest defect density, zero lattice mismatch and no thermal coefficient difference. However, the cost of bulk GaN remains prohibitively high for the majority of device applications. So far, the use of GaN substrates is economically viable only in niche applications such as manufacturing of violet laser diodes for blu-ray DVD drives. Sapphire is generally used as a substrate material for GaN growth. Although the technology of GaN on sapphire is well established and mature, it has fundamental limitations such as poor lattice match (13.9 %) and insulating nature of sapphire. By contrast, the lattice mismatch between β-$Ga_2O_3$ and GaN is significantly lower. For GaN films grown on *a* plane β-$Ga_2O_3$ the epitaxial relationship is (011) β-$Ga_2O_3$ ∥ $(10\bar{1}0)$ GaN and the lattice mismatch is only 2.6 % [12]. Muhammed *et al* [13] reported on GaN growth on $(\bar{2}01)$ β-$Ga_2O_3$ substrates. In this case the epitaxial relationship is (010) β-$Ga_2O_3$ ∥ $(11\bar{2}0)$ GaN leading to a lattice mismatch of 4.7 %. N-type β-$Ga_2O_3$ is a reasonable conductor which makes it possible to produce devices with a vertical geometry. Several other research groups also published results on GaN growth on β-$Ga_2O_3$ substrates using various methods [14–17]. The growth of GaN-based light emitting diode structures on β-$Ga_2O_3$ substrates has been demonstrated by Zi-Li *et al.* [18].

Earlier, we reported on the feasibility of growing β-$Ga_2O_3$ crystals in non-metallic crucibles [19], and it was demonstrated that the most suitable crucible material is sapphire, $Al_2O_3$. Sapphire does not chemically interact with the $Ga_2O_3$ melt, however dissolution of the crucible walls was observed. Consequently, the produced ingot was an alloy of $Ga_2O_3$ and $Al_2O_3$. More detailed study of crystal growth in the $Ga_2O_3$-$Al_2O_3$ system can be found in [20].

In this work we present our initial results on GaN epitaxial growth on β-$Ga_2O_3$ substrates by hydride vapour phase epitaxy (HVPE).

## 2. Experiment

β-$Ga_2O_3$ crystals were grown in a growth chamber equipped with a graphite resistive heater. Gallium oxide powder (99.5 %) was used as a starting substance. The diameter of sapphire crucible was 25 mm and the wall thickness was about 3 mm. $Ga_2O_3$ charge was loaded into the crucible, heated up to 1850 $^oC$ and soaked at this temperature for 30-60 minutes in order to homogenize the melt. The growth chamber was filled with argon to a pressure of 0.5 bar. The melt was cooled to room temperature during 5 hours. $Ga_2O_3$ crystals were formed by free crystallization of the melt. The produced ingot was cleaved into platelets having (100) orientation. Cleaved single crystals have been studied by X-ray, optical and scanning electron microscopy.

GaN deposition on β-$Ga_2O_3$ platelets was performed in a home-made horizontal hot wall HVPE reactor. High-purity metallic gallium (Ga) (99.9999 %) and gaseous ammonia ($NH_3$) (99.9995 %) were used as gallium and nitrogen precursors, respectively. Hydrogen chloride (HCl) gas was passed over Ga at 600°C to form GaCl vapour, which was transported to the growth zone of the reactor and reacted with $NH_3$ at 1050 $^oC$ to produce GaN. Argon (Ar) was used as a carrier gas. The growth was performed at atmospheric pressure. Typical growth rates were in the range from 30 to 100 μm/h.

## 3. Results and discussion

**The structure and properties of β-$Ga_2O_3$ crystals.** The produced β-$Ga_2O_3$ ingots were aggregates composed of several single crystals of various size. Some crystals measure over 10 mm across but because of high fragility of crystals along cleavage planes it was extremely difficult to separate larger plates. The maximal size of the successfully separated single crystal was about 8 mm across. As confirmed by electron microprobe analysis, crystals contained up to 10 at.% of aluminium because the sapphire crucible was partially dissolved by the $Ga_2O_3$ melt.

Some of the single crystals (Fig. 1) were of good optical quality, colourless and transparent. The transmission spectrum measured using Specord UV-VIS spectrophotometer shows an absorption edge at wavelength around 260 nm (Fig. 2). The X-ray diffraction spectrum confirms that the obtained β-$Ga_2O_3$ single crystals are of good structural quality. The ω-scan rocking curve had a half width at half maximum of about 70 arcsec.

The smallest lattice mismatch (2.6 %) of β-$Ga_2O_3$ to GaN is achieved for (100) oriented substrates. This orientation is particularly interesting for substrate preparation because (100) is the strongest cleavage plane (100) in β-$Ga_2O_3$. Therefore thin platelets of (100) orientation can be relatively easy produced by cleaving. Another advantage is that as-cleaved surface is already smooth and does not require any additional grinding or polishing before epitaxial growth.

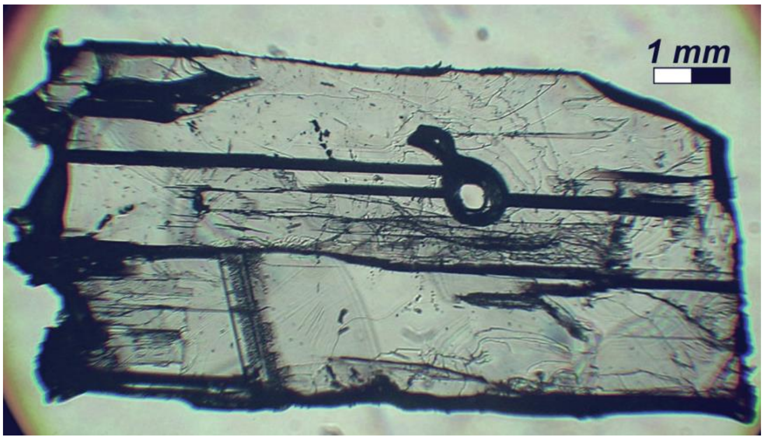

**Fig. 1.** Single crystal β-$Ga_2O_3$ plate.

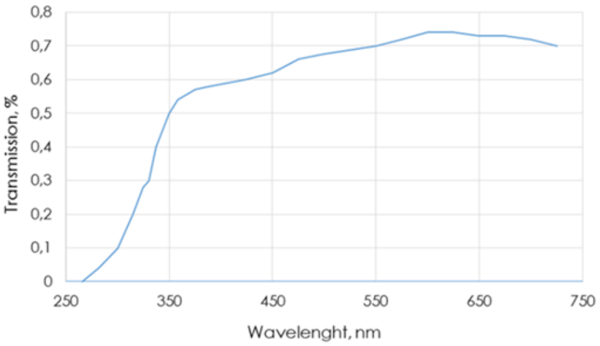

**Fig. 2.** Optical transmission spectrum of β-$Ga_2O_3$ crystals.

**GaN epitaxial layers on β-$Ga_2O_3$.** The morphology of the GaN films on β-$Ga_2O_3$ substrates was characterised by electron microscopy (see Fig. 3). The surface of GaN layers is full of three-dimensional features such as faceted pyramids and pits. This is possibly related to non-optimised growth conditions and defects in the β-$Ga_2O_3$ substrate which were replicated in GaN film.

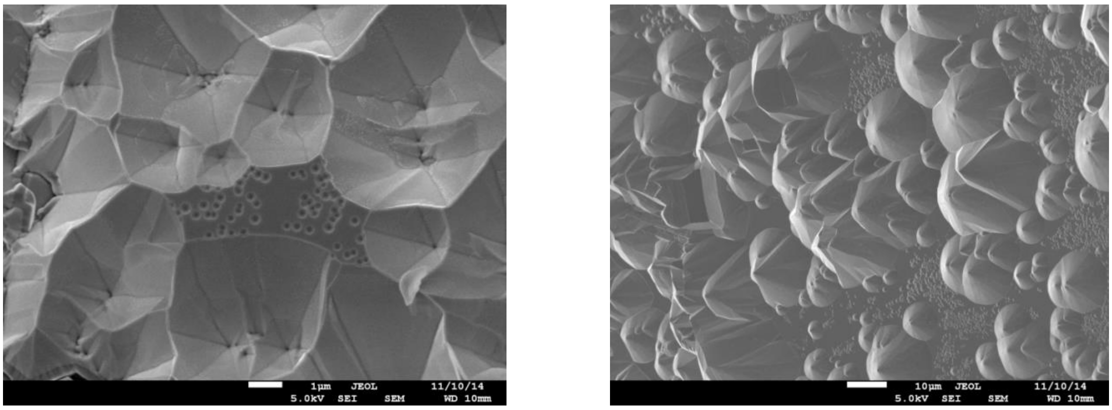

**Fig. 3.** Plan view SEM image of the HVPE GaN layer on β-$Ga_2O_3$ single crystal.

Orientation and structural quality of the deposited GaN layers were assessed by means of x-ray diffraction measurements. It was found that the GaN film grows along [0001] direction. Figure 4 shows an omega x-ray diffraction rocking curve of (0002) GaN reflection. The full width at half maximum (FWHM) of the x-ray rocking curve is 546 arcsec. It should be noted that this value is more than twofold larger than typical FWHM values for GaN layers grown on sapphire substrates. Rather broad XRD rocking curve indicates that optimum growth conditions have not been achieved yet.

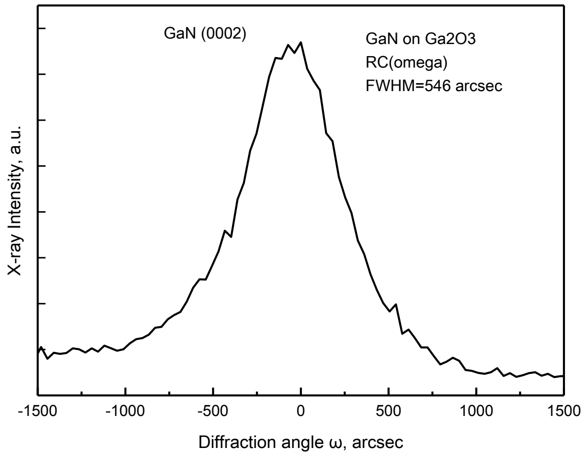

**Fig. 4.** X-ray diffraction ω-scan of GaN epitaxial film on β-$Ga_2O_3$ substrate.

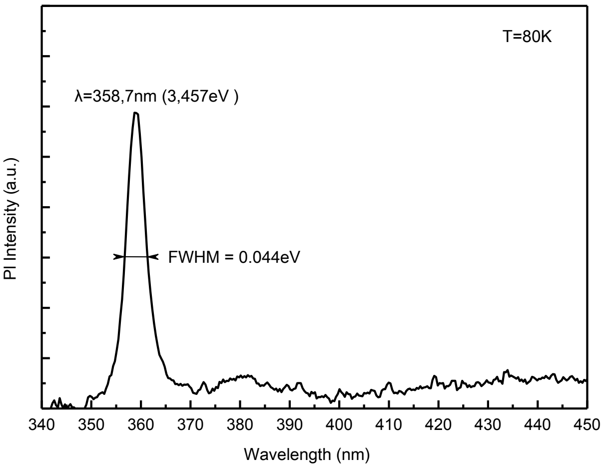

**Fig. 5.** Low temperature (80K) photoluminescence spectrum of the GaN epitaxial film on β-$Ga_2O_3$.

Optical quality of the GaN films was analysed by photoluminescence (PL) measurements. PL spectra were obtained at liquid nitrogen temperature (80K) using pulsed nitrogen laser excitation (337 nm). Typical PL spectrum for the GaN film on β-$Ga_2O_3$ substrate is shown in Figure 5. A strong bandedge emission peak centred at 358.7 nm was observed. A low intensity bump at 385 nm (3.2 eV) is possibly related to donor-acceptor pair recombination. The FWHM of the dominant peak is 44 meV, which is comparable to that for GaN layers grown on sapphire. The intense and narrow band-to-band transition indicates high optical quality of the GaN layer.

## 4. Conclusions

In conclusion, β-$Ga_2O_3$ crystals were grown from melt by seedless crystallisation. The crystals were cleaved into (100) platelets which were used as substrates for GaN epitaxial growth. To the best of our knowledge this is the first report on GaN growth on β-$Ga_2O_3$ substrates by HVPE technique. Although the quality GaN epitaxial films was somewhat inferior when compared to that of GaN films grown on sapphire under optimised conditions, the initial results provide a compelling proof of concept of β-$Ga_2O_3$ as a new substrate material for GaN growth.

***Acknowledgements***

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## References

[1] Z. Hajnal, J. Miró, G. Kiss, F. Réti, P. Deák, R.C. Herndon, J.M. Kuperberg // *Journal of Applied Physics* **86** (1999) 3792.

[2] P.D.C. King, I. McKenzie, T.D. Veal // *Applied Physics Letters* **96** (2010) 062110.

[3] E.G. Víllora, K. Shimamura, Y. Yoshikawa, T. Ujiie, K. Aoki // *Applied Physics Letters* **92**. (2008) 202120.

[4] S. Ohira, N. Suzuki, N. Arai, M. Tanaka, T. Sugawara, K. Nakajima, T. Shishido // *Thin Solid Films* **516** (2008) 5763.

[5] H. Aida, K. Nishiguchi, H. Takeda, N. Aota, K. Sunakawa, Y. Yaguchi // *Japanese Journal of Applied Physics* **47** (2008) 8506.

[6] Y. Tomm, P. Reiche, D. Klimm, T. Fukuda // *Journal of Crystal Growth* **220** (2000) 510.

[7] Z. Galazka, R. Uecker, K. Irmscher, M. Albrecht, D. Klimm, M. Pietsch, M. Brützam, R. Bertram, S. Ganschow, R. Fornari // *Crystal Research and Technology* **45** (2010) 1229.

[8] Y. Tomm, J.M. Ko, A. Yoshikawa, T. Fukuda // *Solar Energy Materials & Solar Cells* **66** (2001) 369.

[9] T. Oshima, T. Okuno, S. Fujita // *Japanese Journal of Applied Physics* **46**. (2007) 7217.

[10] W.S. Hwang, A. Verma, H. Peelaers, V. Protasenko, S. Rouvimov, Huili (Grace) Xing, A. Seabaugh, W. Haensch, C. Van de Walle, Z. Galazka, M. Albrecht, R. Forrnari, D. Jena // *arXiv:1310.6824* (2013).

[11] M. Higashiwaki, K. Sasaki, A. Kuramata, T. Masui, S. Yamakoshi // *Applied Physics Letters* **100** (2012) 013504.

[12] E.G. Víllora, K. Shimamura, K. Kitamura, K. Aoki, T. Ujiie // *Applied Physics Letters* **90** (2007) 234102.

[13] M.M. Muhammed, M. Peres, Y. Yamashita, Y. Morishima, S. Sato, N. Franco, K. Lorenz, A. Kuramata, I.S. Roqan // *Applied Physics Letters* **105**. (2014) 042112.

[14] K. Shimamura, E.G. Víllora, K. Domen, K. Yui, K. Aoki, N. Ichinose // *Japanese Journal of Applied Physics* **44** (2005) L7.

[15] S. Ito, K. Takeda, K. Nagata, H. Aoshima, K. Takehara, M. Iwaya, T. Takeuchi, S. Kamiyama, I. Akasaki, H. Amano // *Physica Status Solidi C* **9(3-4)** (2012) 519.

[16] H.J. Lee, T.I. Shin, D.H. Yoon // *Surface and Coatings Technology* **202** (2008) 5497.

[17] K. Kachel, M. Korytov, D. Gogova, Z. Galazka, M. Albrecht, R. Zwierz, D. Siche, S. Golka, A. Kwasniewski, M. Schmidbauer, R. Fornari // *CrystEngComm* **14** (2012) 8536.

[18] X. Zi-Li, Z. Rong, X. Chang-Tai // *Chinese Physics Letters* **25(6)** (2008) 2185.

[19] V.N. Maslov, V.M. Krymov, M.N. Blashenkov, A.A. Golovatenko, V.I. Nikolaev // *Technical Physics Letters* **40** (2014) 303.

[20] V.N. Maslov, V.M. Krymov, E.V. Kalashnikov, V.I. Nikolaev // *Materials Physics and Mechanics* **21(2)** (2014) 194.