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# Growth and annealing properties of Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> crystal

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#### 1. Introduction

Recently, GaN thin film has attracted considerable attention due to their potential applications in optoelectronic devices such as blue-, violet-, and ultraviolet (UV)-light emitting devices [1–3] as well as high-temperature, high-frequency and high-power electronic devices [4]. One of the major difficulties hindering the development of GaN-based devices is the lack of suitable substrate. To date, sapphire has been the most widely used substrate for GaN heteroepitaxy in industry. Although sapphire offers excellent crystal quality, surface finish and stable physico-chemical performance, its high thermal and lattice mismatch with GaN  $(3 \times 10^{-6} \text{ K}^{-1} \text{ and}$ 13.9%, respectively) result in high-dislocation densities and residual stress in the epitaxial layers, which affects both the electrical and optical properties of the devices. In order to further improve the quality of GaN epitaxial layers and therefore InGaN LEDs, SAINT-GOBAIN Crystals, a major supplier of substrates, has developed a new material, less mismatched with GaN but still chemically close to sapphire: an alumina-rich cubic spinel, MgAl<sub>6</sub>O<sub>10</sub> [5], also denoted MgO  $nAl_2O$  with n=3. This crystal has a lower thermal expansion mismatch with GaN:  $\Delta\alpha\approx 2.2\times 10^{-6}\,\text{K}^{-1}$  (measured at 800 °C), together with a lower lattice mismatch of -11.5% [6]. Compared with stoichiometric spinel (MgAl<sub>2</sub>O<sub>4</sub>), alumina-rich spinel benefits from compositional softening [7] and can easily be sliced and polished into large diameter wafers [5]. Excitingly, the GaN-

#### ABSTRACT

 $Mg_{0.4}Al_{2.4}O_4$  single crystals with good optical quality were successfully grown by the Czochralski method. The transmission spectrum indicated that the absorption edge of the crystal was at 220 nm, while no apparent absorption peaks were found. The X-ray diffraction and DSC curve analysis showed that Mg04Al24O4 crystal was stable at room temperature. While after annealing in the air and hydrogen atmosphere at about 1200 °C, Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> decomposed into Al<sub>2</sub>O<sub>3</sub> and (MgO)<sub>0.4</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>x</sub> (0.4 < x < 1.2). The reaction mainly occurred on the crystal surface, barely inside.

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based LEDs grown by MOCVD on MgAl<sub>6</sub>O<sub>10</sub>-(111) exhibit a higher EL-intensity and a narrower EL-linewidth than those grown on sapphire [8]. Therefore, Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> equivalent to MgAl<sub>6</sub>O<sub>10</sub> is a promising substrate material for GaN epitaxial growth. Herein, we report the Czochralski growth of Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> crystal in detail, and its annealing properties were studied.

#### 2. Crystal growth

Single-crystal growth of Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> was performed using a typical Czochralski method. High-purity MgO (>99.99%) and Al<sub>2</sub>O<sub>3</sub> (≥99.999%) compounds were weighted according to the following chemical reaction equation:  $MgO + 3Al_2O_3 = 2.5Mg_{0,4}Al_{2,4}O_4$ . The total weight of the initial charge was 220 g. After the starting materials were mixed, they were pressed into pieces and sintered in a resistance-heated furnace at 1200°C for 10 h. Before putting the charge pieces into the iridium crucible, we adjusted the position to make sure the radio-frequency coil, the crucible and the seed rod were accurately concentric. Then the charge was loaded into the iridium crucible (60 mm in diameter and 50 mm in height) and was heated to approximately 2100 °C to melt. The crystal growth was performed using a [111] MgAl<sub>2</sub>O<sub>4</sub> rod as a seed. The growth temperature was about 1950–2000 °C. The pulling and rotational speeds employed were 1–2 mm/h and approximately 20–25 rpm to even out the thermal field of the melt in the crucible. During the entire crystal-growing process, the growth boundary in solid-melt was convex towards the melt so that dislocations, faults, bubbles and impurities were reduced or eliminated from the crystal. Since the spinel may dissolve alumina at lower temperature [9], the

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crystal-cooling period was set within 20 h to maintain  $Mg_{0.4}Al_{2.4}O_4$  single phase. The as-grown crystal was colorless and transparent. The (1 1 1)-plane wafers were sliced perpendicular to the growth direction and were polished with mechanical method. Then the polished wafers were annealed in the air at 1200 °C for 15 h and in the hydrogen at 1250 °C for 10 h, respectively.

The phase identification of the obtained crystals and the annealed samples were investigated by X-ray diffraction, which were carried out on D/MAX-2550 diffractometer, using Cu K $\alpha$  radiation. Intensities for the diffraction peaks were recorded in the 10–90° (2 $\theta$ ) range, with a step of size of 0.02° and a scan speed of 8° min<sup>-1</sup>. The optical transmission spectrum was measured via a Model V-570 UV/VIS/NIR spectrophotometer (Japan JASCO) at room temperature. Differential thermal and thermogravimetry curves were measured by the differential scanning calorimeter (NETZSCH STA 409 PG/PC) under nitrogen atmosphere. The temperature was raised from 25° to 1400° at the heating rate of 100° min<sup>-1</sup>. The sample was a thin wafer weighted 26.000 mg.

#### 3. Result and discussion

The transparent and integral Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> single crystal with the dimension of Ø26 mm × 55 mm by the Czochralski technique is shown in Fig. 1. Green and red lasers were used to evaluate the crystal's overall quality. No light-scattering pellets were observed, indicating nearly no inclusions in the entire crystal. Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> has the space group of  $Fd\bar{3}m$  (227), classified as cubic. The X-ray powder diffraction pattern of the as-grown crystal is presented in Fig. 2. All the diffraction peaks can be indexed in cubic Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> (No. 87-0345). No other phase was found in the XRD patterns. It can be calculated that the unit-cell parameters of Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> crystal were a = 7.995 Å, and the lattice mismatch with GaN is -11.3%. The optical transmission spectrum of the Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> crystal wafer with the thickness of 1.0 mm is given in Fig. 3. The crystal has an absorption edge at about 220 nm and has no distinct absorption peaks from 190 nm to 1900 nm. The transmittance is about 87% in the wavelength range of 400-1900 nm, which demonstrates the crystal has good optical quality.

Fig. 4 is the TG and DSC curves of  $Mg_{0.4}Al_{2.4}O_4$  crystal. In the whole heating process, no mass change was observed. It is noticeable that there are four overlapping exothermic peaks in the temperature range of 25–1400 °C. The baseline below 950 °C is an increasing tendency, which means the sample is absorbing heat. According to the equilibrium phase diagram of the MgO–Al<sub>2</sub>O<sub>3</sub> system [10], Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> can decompose. The first step is from 950 °C to 1134 °C and there is an exother-

7 8 9 **10** 11 12 13 14 **15** 

Fig. 1. Photograph of as-grown  $Mg_{0.4}Al_{2.4}O_4$  crystal with the dimension of  $\rm @26~mm\times55~mm.$ 



Fig. 2. X-ray powder diffraction pattern of as-grown Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> crystal.



Fig. 3. Transmission spectrum of the Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> crystal wafer.

mic peak at 1112 °C. The corresponding reaction is given by 2.5Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub>  $\rightarrow$  MgAl<sub>2</sub>O<sub>4</sub>+2Al<sub>2</sub>O<sub>3</sub>. The second one extends up to 1262 °C, and Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> decomposes into Al<sub>2</sub>O<sub>3</sub> and (MgO)<sub>0.4</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>k</sub> (0.4 < k < 1.2). The exothermic peak at 1182 °C



Fig. 4. TG and DSC curves of Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> crystal.



Fig. 5. X-ray diffraction pattern of the as-grown (111)-Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> wafer.

corresponds with the process. The third one is from  $1262 \circ C$  to  $1337 \circ C$ , one exothermic peak at  $1317 \circ C$ . The decomposition products are  $Al_2O_3$  and  $(MgO)_{0,4}(Al_2O_3)_m$  (k < m < 1.2). The last one is till  $1400 \circ C$ . The decomposition reaction is described as  $Mg_{0,4}Al_{2,4}O_4 \rightarrow (MgO)_{0,4}(Al_2O_3)_n + Al_2O_3$ , and n satisfies the relation m < n < 1.2. The DSC curve shows that the decomposition of



**Fig. 6.** X-ray diffraction patterns of the annealed (111)-Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> wafer: (a) in the air atmosphere; (b) in the hydrogen atmosphere.



**Fig. 7.** X-ray diffraction pattern of the (111)-plane polished wafer after annealing in the air.

 $Mg_{0.4}Al_{2.4}O_4$  needs external heating to provide energy, and the decomposition products are different at different temperatures. To reduce and avoid these decomposition reactions mentioned above, the  $Mg_{0.4}Al_{2.4}O_4$  crystals should be taken a quick cooling speed in the later growth.

Besides, annealing experiments of the polished (111)-plane Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> wafers have been performed. Surface of the polished wafer is smooth. After annealing in the air and hydrogen at approximately 1200 °C, the wafers become milky and opaque. The surface becomes quite rough and appears grooves. Figs. 5 and 6(a) and (b) show the X-ray diffraction patterns of the as-grown, the air annealed and the hydrogen annealed (111)-Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> wafer, respectively. From Fig. 6, it can be clearly seen that after annealing in the air and hydrogen, the samples' XRD patterns are almost the same. Moreover, there are new diffraction peaks that can be indexed in hexagonal Al<sub>2</sub>O<sub>3</sub>. The experimental results demonstrate that the Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> wafers by the annealing treatment in the air and hydrogen are no longer Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> single phase, but become polycrystalline structure of  $Mg_{0.4}Al_{2.4}O_4$ ,  $Al_2O_3$  and  $(MgO)_{0.4}(Al_2O_3)_x$ (0.4 < x < 1.2). The amount of the  $(MgO)_{0.4}(Al_2O_3)_x$  compounds is possibly too trace to be detected in the XRD patterns. The result is in accordance with the DSC analysis. Then the annealed samples were polished with mechanical method, and they became colorless transparent again. In the X-ray diffraction pattern we can find  $Mg_{0.4}Al_{2.4}O_4$  peaks as well as (113)-plane and (223)-plane  $Al_2O_3$ peaks (see Fig. 7). The quantity of Al<sub>2</sub>O<sub>3</sub>'s diffraction peaks is less than that in Fig. 5. This shows that  $Mg_{0.4}Al_{2.4}O_4$  crystal is stable at room temperature. While after annealing in the air and hydrogen at about 1200 °C, Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> crystal decomposes. The reaction mainly occurs on the crystal surface, barely inside.

#### 4. Conclusion

In conclusion, we have successfully grown  $\emptyset 26 \text{ mm} \times 55 \text{ mm}$  cubic Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> crystals by the Czochralski method using a [1 1 1] MgAl<sub>2</sub>O<sub>4</sub> seed. The as-grown crystals are colorless transparent, and the transmittance is about 87% in the wavelength range of 400–1900 nm. The wafer surfaces by the annealing treatment in the air and hydrogen become quite rough. X-ray diffraction patterns have proved that Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> crystal is stable at room temperature. While after annealing at high temperature, Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> crystals decompose into Al<sub>2</sub>O<sub>3</sub> and (MgO)<sub>0.4</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>x</sub> (0.4 < x < 1.2). The reaction mainly occurs on the crystal surface, barely inside. In order to attain single crystal, Mg<sub>0.4</sub>Al<sub>2.4</sub>O<sub>4</sub> crystal should be cooled down to room temperature rapidly in the later growth.

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#### References

- J. Narayan, K. Dovidenko, A.K. Sharma, S. Oktyabrsky, J. Appl. Phys. 84 (1998) 2597.
- [2] Z.K. Tang, G.K.L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, Y. Segawa, Appl. Phys. Lett. 72 (1998) 3270.

- [3] D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, S. Koyama, M.Y. Shen, T. Goto, Appl. Phys. Lett. 70 (1997) 2230.
- [4] S. Nakamura, G. Fasol, The Blue Laser Diode: GaN Based Light Emitters and Lasers, Springer, Berlin, 1997.
- [5] M.R. Kokta, H.T. Ong, US Patent Application No. US 2003/0188678 A1, 2003.
- [6] F. Tinjod, P. de Mierry, D. Lancefield, Z. Bougrioua, S. Laügt, O. Tottereau, P. Lorenzini, S. Chenot, E. Virey, M.R. Kokta, J.L. Stone-Sundberg, D. Pauwel, J. Crystal Growth 285 (2005) 451.
- [7] T.E. Mitchell, J. Am. Ceram. Soc. 82 (1999) 3305.
- [8] F. Tinjod, P. de Mierry, D. Lancefield, S. Chenot, E. Virey, F J.L. Stone-Sundberg, F M.R. Kokta, D. Pauwels, Phys. Status Solidi (c) 3 (6) (2006) 2199.
- [9] A.D. Mazzoni, M.A. Sainz, A. Caballero, E.F. Aglietti, Mater. Chem. Phys. 78 (2002) 31.
- [10] D.M. Roy, R. Roy, E.F. Orborn, J. Am. Sci. 25 (1953) 337-361.