Crystal growth of large sapphire and its optical properties

Shuichi KAWAMINAMI,*,**,† Keisuke MOCHIZUKI,*** Nobuyasu ADACHI* and Toshitaka OTA*

*Advanced Ceramics Research Center, Nagoya Institute of Technology, 10–6–29 Asahigaoka, Tajimi, Gifu 507–0071, Japan
**Shinkosha Co., Ltd., 2–4–1 Kosugaya, Sakae-ku, Yokohama 247–0007, Japan

Large sapphire crystals for 200-mm LED wafers were successfully grown by the top seeded melt growth (TSMG) method. The sapphire had excellent crystallinity as LED substrates. However, in the as-grown crystal, there was remarkable absorption in UV region caused by the F-center (V02). To reduce the absorption, we studied several heat treatment methods using oxidized atmospheres. In air or O2 atmospheres, the absorption was difficult to reduce because oxygen diffusion was slow and new absorption occurred. We found that heat treatment in an H2–O2 combustion flame was highly effective in reducing the absorption in the UV region. After the combustion flame heat treatment, the sample had an absorption coefficient less than 0.5 cm−1 at 200 nm, and no photoluminescent emissions were caused by color centers. Consequently, sapphire crystals grown by the TSMG method had good crystallinity and low absorption in the UV region.

Key-words : Sapphire, α-Al2O3 single crystal, Crystal growth, Color center, Transmittance in VUV

1. Introduction

Sapphire (α-Al2O3 single crystal) is intrinsically transparent with no absorption from the ultraviolet (UV) to the near infrared (NIR) region. Because of its advantages such as thermal and chemical stability and easy access to raw materials, it is used for a wide variety of applications.1 In the 1990s, sapphire substrates were used to develop blue light emitting diodes (LEDs), and since then, the demand for sapphire has increased. Recently, sapphire-based LEDs are widely used for backlighting of liquid crystal displays (LCD) and lighting. Furthermore, the wafer size is increasing to meet production needs. In the early stages, 50.8-mm (2-in.) wafers were used. Currently, 100-mm wafers are primarily used, and 150-mm wafers have been introduced in some production areas. In the near future, production demands will require 200-mm wafers.

Simultaneously, UV LEDs and their applications have been industriously investigated.2–4 As a result, the demand for sapphire has increased for substrates as well as transparent materials in the UV region. However, sapphire may have problems in the UV regions, such as absorption, which are caused by impurities or color centers attributed to oxygen vacancies.5–10

Metals with high melting points such as Ir, Mo, and W are indispensable crucible materials for the crystal growth of sapphire because sapphire has a high melting point of 2050°C. Furthermore, sapphire is usually grown in an inert gas or a reducing gas, which may generate some oxygen vacancy defects. The sapphire band gap is approximately 9 eV, and therefore it transmits light with wavelength greater than 140 nm.11–13 Realistically, some absorption exists around 200 nm,14,15 increasing the desire for transparent materials in the vacuum UV (VUV). While there are some reports of absorbance and luminescence of sapphire in the VUV region,16–19 these properties depend on the growing methods and impurities, which are still open problems.

Several sapphire growth methods exist, such as the Kyropoulous (KY) method, the Czochralski (CZ) method, the edge defined film-fed growth (EFG) method, the heat exchange method (HEM), and the Bridgman method. However, these methods are not ideal for large crystal growth. Though the KY method and the HEM realize to grow large ingots, contact with crucible and limitation of growing direction are not desirable. We developed the top-seeded melt growth (TSMG) method for growing large sapphire crystals.20 Figure 1 shows a schematic of the TSMG method.

The TSMG method combines the advantages both the CZ method and the KY method. Generally speaking, while the CZ method allows arbitrary growth direction and provides good control over the shape, the crystallinity is not ideal. In particular, the temperature gradient of the crystallization area is relatively large because the crystal grows on the surface of the melt. Furthermore, to obtain a large crystal with the CZ method, larger equipment must be used. In contrast, crystals grown with the KY method are grown in the melt, and the crystallinity is comparatively good. Furthermore, since the solidification ratio of the KY method is high, a small furnace can be constructed. In the TSMG method, the crystal grows inside the melt in the same way as the KY method, so the temperature gradient is small. Consequently, the crystallinity obtained with the TSMG method

1 Corresponding author: S. Kawaminami; E-mail: kawaminami@shinkosha.com

Fig. 1. Schematic illustration of the TSMG method.
3. Results and discussion

3.1 Crystal growth

Figure 2 shows sapphire crystals grown with three different methods and the corresponding XRCs. For the crystal grown by FFM, we observed a split in the peak attributed to the sub-grain boundary which resulted from the relatively high growing speed and the large temperature gradient at the point of crystal growth. The crystal grown by the CZ method had no split and the full-width at half maximum (FWHM) of the XRC was 12 arcsec. In contrast, the FWHM of the sapphire grown by TSMG method was less than 5 arcsec, which was near the resolution of the equipment. Furthermore the etch pit density (EPD) was 600–1100 cm², In our measurements of commercially available sapphire substrates, the FWHM and EPD of sapphire grown with the KY method were 5–10 arcsec and about 800 cm², respectively, and the FWHM and EPD for substrates grown with the EFG method were 7–11 arcsec and 2000–4000 cm², respectively. These results demonstrate that the crystallinity of crystals grown with the TSMG method had similar quality to those grown with the KY method, which is sufficient for LED substrates.

3.2 Transmittance of sapphire grown by different methods

Figure 3 shows the transmittance of the as-grown crystals grown by different methods, where the dotted curve shows the ideal transmittance calculated from the refractive index using the Sellmeier dispersion formula for a perfect sapphire crystal without absorption. The TSMG sapphire had significant absorp-

\[\text{Transmittance of as-grown crystals grown by various methods in UV region. (Specimens: c-plane, KY has no data below 190 nm)}\]
nation near 200 nm. This 205-nm peak was a color center (F-center) that caused an oxygen defect (\(V_{O}^{+}\)). The F-center formation is described as follows:

\[
\text{Al}_2\text{O}_3 \rightarrow 2\text{Al}^3_2 + 3\text{O}^+ + 3/2\text{O}_2 \quad (g)
\]

Furthermore, an absorption near 255 nm, which is attributed to the F\(^{\text{2+}}\)-center (\(V_{O}^{+}\)) was sometimes observed in the TSMG sapphire. These F-center and F\(^{\text{2+}}\)-center absorption were similarly observed in KY crystals.

The crystal grown by the CZ method had no clear absorption peak at 205 nm by the F-center, but there were absorption peaks at 160, 180, and 260 nm, which could possibly be attributed to the F\(^{\text{2+}}\)-center (\(V_{O}^{+}\)) or other color centers. In the crystal grown by the FFM, there were weak absorption peaks at 160, 180, and 260 nm, but the transmittance in the VUV range was much larger than that of the CZ method, where the crystal was grown in an \(\text{N}_2\)-O\(_2\) (2\% \(\text{O}_2\)) atmosphere. In the FFM, on the other hand, the crystal was grown in an \(\text{H}_2\)-O\(_2\) combustion flame. Consequently, the \(\text{H}_2\) atmosphere may affect the decrease of F\(^{\text{2+}}\)-centers.

3.3 Transmittance change after heat treatment

Figure 4 shows the transmittance of the as-grown sapphire with different thicknesses. As the specimen thickness increased, the absorption caused by F-center was very conspicuous, and the absorption caused by F\(^{\text{2+}}\)-center was broader than that of the TSMG sapphire, while the absorption caused by F\(^{\text{2+}}\)-center was remarkable. On the other hand, for the transmittance of the SR-TSMG sapphire, the F-center absorption was broader than that of the TSMG sapphire, while the absorption of the F\(^{\text{2+}}\)-center was remarkable.

In order to reduce these absorptions, heat treatment methods were examined. Figure 5 shows the transmittance after heat treatment in air at 1400°C for 10 h. The difference in thickness was remarkable, and the notable F-center absorption was not observed in the 1-mm specimen. In contrast, the heat treatment was insufficient for decreasing the F-center absorption in samples with a thickness of more than 2 mm. Furthermore, the transmittance recovery of the c-plane, where the transmission direction was parallel to the c-axis (0001), was faster than that of the a-plane, which had a transmittance direction parallel to a-axis (11–20). Consequently, the diffusion coefficient of oxygen parallel to the c-axis was larger than that perpendicular to the c-axis. Namely, the asymmetry in the oxygen diffusion coefficients can be attributed to the crystal structure. Along the c-axis, oxygen and aluminum are stacked in layers, and aluminum ions only occupy two-thirds of the sites. Therefore, oxygen ions could easily jump to the next layer.\(^{22,23}\)

Because the heat treatment at 1400°C for 10 h did not sufficiently reduce the absorption, the heat treatment was repeated. Figure 6 shows the transmittance of the 2-mm thick sample after repeated heat treatments in air at 1400°C. Contrary to our expectations, the maximum transmittance at 200 nm was reached after two heat treatments (10 + 10 h), but, any subsequent heat treatments decreased the transmittance at 200 nm. Moreover, after two heat treatment (10 + 10 h), the F-center (205 nm) absorption disappeared, but with subsequent heat treatment, new absorption peaks appeared at 170, 195, and 260 nm.

As mentioned before, while the size and crystallinity of the FFM-sapphire were limited, it had high transmittance in the UV region. We believe that \(\text{H}_2\)-O\(_2\) combustion flame atmosphere was responsible for the high transmittance, so we investigated heat treatment in different atmospheres. Figure 7 shows the transmittance after the heat treatment in \(\text{O}_2\), \(\text{H}_2\)-H\(_2\)O/N\(_2\), and \(\text{H}_2\)-O\(_2\) flame. In the \(\text{O}_2\) atmosphere, the heat treatment was more effective at 1400°C than at 1500°C, and the transmittance at 205 nm recovered to 60%. In the heat treatment at 1500°C in \(\text{O}_2\) for 10 h, the transmittance degradation was similar to that of long-term heat treatment in air at 1400°C, and new absorption peaks

![Fig. 4. Transmittance of as-grown crystals with various thickness, (a) c (0001) plane, (b) a (11–20) plane. SR-TSMG means TSMG-sapphire grown in strongly reduced atmosphere.](Image)

![Fig. 5. Transmittance after heat treatment at 1400°C for 10 h, in the air, (a) c (0001) plane (b) a (11–20) plane.](Image)
Kawaminami et al.: Crystal growth of large sapphire and its optical properties

In H₂ gas, the F-center absorption is stronger than in air. In the as-grown sapphire, there is no absorption peak attributed to the OH bond. After heat treatment at 1750°C in H₂–O₂ flame, the transmittance of 10-mm thickness sample increased more than 60% at 200 nm. In addition, F-center and F⁻-center absorption disappeared in the SR-TSMG sapphire. Therefore, heat treatment in H₂–O₂ flame could be very effective for thick sapphire samples.

These results were considered as follows. After the heat treatment in O₂ gas, the F-center (V⁰) should be oxidized to O²⁻:

\[ V^0 + 1/2O_2 (g) \rightarrow O^2⁻ \]  

(2)

This oxidation should reduce the F-center absorption. However, other absorptions appeared at 195 and 260 nm, and the total absorption in the VUV region increased. If the absorptions at 170, 195, and 260 nm were attributed to the F⁻-center, additional reactions may occur.

In a sapphire crystal, the Schottky-type defects \( 2V^0 \rightarrow \) \( V^0 \) + hole, which are thermodynamically the most stable defect, always occur. Although \( V^0 \) does not act as a color center, it is oxidized to form \( O^2⁻ \) and a hole:

\[ V^0 + 1/2O_2 (g) \rightarrow O^2⁻ + 2h^+ \]  

(3)

Then, the hole might be trapped in \( V^0 \) to form \( V^*_0 \) (F⁻-center) as follows:

\[ V^0 + h^+ \rightarrow V^*_0 \]  

(4)

On the other hand, in the heat treatment in the H₂–H₂O/N₂ atmosphere, the additional absorption peaks (170, 195, and 260 nm) could hardly be observed, and the transmittance was high. Then, the hole formed from \( V^*_0 \) [Eq. (3)] may have reacted with \( H_2 \) in the atmosphere to form an interstitial hydrogen ion \( (H^+_i) \) as follows:

\[ H_2 + 2h^+ \rightarrow 2H^+_i \]  

(5)

Furthermore, it is well-known that H₂O decomposes to H₂ and O₂ at higher temperatures. Therefore, for heat treatment under an oxidizing atmosphere containing H₂ or H₂O, the formation of \( V^*_0 \) shown in Eq. (4) should rarely occur because the hole was consumed as shown in Eq. (5).

### 3.4 Study of absorption by FT-IR and PL

Figure 8 shows the transmittance in the infrared region. After heat treatment in an H₂–O₂ atmosphere at 1750°C, an absorption peak appeared at 3050 nm (3278 cm⁻¹). In the FFM sapphire, there were peaks at 2923, 3050 and 3066 nm. These may be attributed to the OH bond such that the hydrogen was located on the oxide ion triangle parallel to the basal plane.\(^{27,28}\) In addition, hydrogen ions can dissolve at interstitial sites in the sapphire crystal.\(^{27,28}\) Consequently, these facts are supported by the hydrogen ions incorporated in the crystal during heat treatment.

It is thought that hydrogen is incorporated in the sapphire crystal with relative ease, simultaneously promoting the diffusion of oxygen. In contrast, the incorporated hydrogen may be released during heat treatments without a hydrogen atmosphere such as those with air or O₂ atmospheres. In the as-grown sapphire, there is no absorption peak attributed to the OH bond.
Hydrogen may exist as interstitial ions because hydrogen is included in the crackle. The new absorptions may be formed by the release of interstitial hydrogen during the heat treatment. Unfortunately, we are not able to fully explain these phenomena, but we plan to address these phenomena in a future study.

Both the non-photoluminescence and non-absorption were important phenomena in the UV transmittance. Namely, the emission caused by both the F-center and F\(^+\)-center was unfavorable for UV light transmittance.

**Figure 9** shows the PL spectrum of sapphire crystals grown by the TSMG method. When the excitation wavelength of 205 nm, which was the wavelength of F-center, was irradiated, the emission was observed at 410 nm. We found no difference between the TSMG and SR-TSMG samples. On the other hand, excitation at 254 nm, which is the bright line of a low-pressure mercury lamp and which was near the absorption of F\(^+\)-center, produced another emission at 330 nm. At 330 nm, the emission intensity of the SR-TSMG sapphire was much stronger than that of the TSMG sapphire. This corresponds to stronger F\(^+\)-center absorption in the SR-TSMG sapphire than that in the TSMG sapphire. After heat treatment at 1750°C in an H\(_2\)-O\(_2\) combustion flame furnace, PL was not observed. These results demonstrate that the color centers are diminished by heat treatment, resulting in materials without emission or absorption in the UV region.

**Figure 10** shows the absorption coefficient of the TSMG-sapphire after heat treatment compared to the as-grown FFM-sapphire. Though there were absorption peaks at 195 and 260 nm in the specimen heat treated in air, the absorption after heat treatment in H\(_2\)-H\(_2\)O/N\(_2\) or H\(_2\)-O\(_2\) was scarce. The absorption coefficient of specimens heat treated in H\(_2\)-H\(_2\)O/N\(_2\) and H\(_2\)-O\(_2\) atmospheres were less than 0.5 cm\(^{-1}\) at 200 nm. Therefore, we successfully obtained a TSMG-sapphire with small absorption.

4. Conclusion

We utilized the TSMG method to obtain large sapphire crystals that can be used to make 200-mm wafers. The as-grown crystals had sufficient crystallinity to be used as LED substrates; the FWHM of XRC was 5 arcsec, and the EPD was 600-1100 cm\(^{-2}\). However, in the as-grown crystal, we found remarkable absorption near 200 nm caused by the F-center because the sapphire was grown in a reducing atmosphere. After heat treatment in an oxidized atmosphere such as air and O\(_2\) gas, this color center decreased, and the transmittance increased. The transmittance at 200 nm was improved more than 60% in a 1-mm thick specimen after heat treatment at 1400°C for 10 h in air, but thicker specimens did not improve after the same treatment. In addition, it was confirmed that the diffusion of oxygen along the c-axis was faster than that along the a-axis. While the absorption of the F-center decreased after the oxidation heat treatment, other absorption peaks at 195 and 260 nm increased. Though it was thought that this absorption was attributed to an increase of F\(^+\)-center or other color centers, it was not clarified in this study. To decrease the absorption, heat treatment in an H\(_2\)-H\(_2\)O/N\(_2\) atmosphere was effective. In particular, heat treatment in an H\(_2\)-O\(_2\) combustion flame furnace was advantageous for the resulting high temperature and increased supply of oxygen and hydrogen. After heat treatment at 1750°C using this furnace, the absorption coefficient at 200 nm in a 10-mm thick specimen was less than 0.5 cm\(^{-1}\), and this had no PL emission due to oxygen defect based color centers. Consequently, this TSMG specimen can be used in the UV region.
References

1) E. R. Dobrovinskaya, L. A. Lytvynov and V. Pishchik, “Sapphire Material, Manufacturing, Applications”, Springer Science+Business Media, New York (2009).

2) Tokyo University of Agriculture and Technology, and Tokuyama corporation, http://www.tuat.ac.jp/~koukai/gakuhou/2012/529/news2.siryou.pdf (2013) [in Japanese].

3) T. Oto, R. G. Banal, K. Kataoka, M. Funato and Y. Kawakami, Nat. Photonics, 4, 767–770 (2010).

4) A. Ren, Q. Sun, S. Y. Kwon, J. Han, K. Davitt, Y. K. Song, A. V. Nurmikko, W. Liu, J. Smart and L. Schowalter, Phys. Status Solidi, 4[c], 2482–2485 (2007).

5) A. I. Surdo, V. S. Kortov and V. A. Pustovarov, Radiat. Meas., 33, 587–591 (2001).

6) S. V. Solov’ev, I. I. Milman and A. I. Syurdo, Phys. Solid State, 54, 726–734 (2012).

7) B. Li, S. L. Oliveria, S. C. Rand, J. A. Azurdia, T. R. Hinklin, J. C. Marchal and R. M. Laine, J. Appl. Phys., 101, 053534 (2007).

8) K. H. Lee and J. H. Crawford, Jr., Phys. Rev., 19, 3217–3221 (1979).

9) V. S. Kortov, I. A. Vainshtein, A. S. Vokhmintsev and N. V. Gavriliu, J. Appl. Spectrosc., 75, 452–455 (2008).

10) B. D. Evans, G. I. Pogtashnik and Y. Chen, Nucl. Instrum. Methods Phys. Res. B, 91, 258–262 (1994).

11) T. Tomiki, Y. Gamaha, T. Shikenbaru, T. Futemma, M. Yuri, Y. Aiura, S. Sato, H. Fukutani, H. Kato, T. Miyahara, A. Yonesu and J. Tamashiro, J. Phys. Soc. Jpn., 62, 573–584 (1993).

12) M. E. Thomas, W. J. Tropf and S. L. Gilbert, Opt. Eng., 32, 1340–1343 (1993).

13) V. N. Abramov, B. G. Ivanov, A. I. Kuznetsov, I. A. Merilco and M. I. Musatov, Phys. Status Solidi, 48, 287–292 (1978) (a).

14) Y. M. Puzikov, A. Y. Dan’ko, G. T. Adonkin, N. S. Sidel’nikova, V. F. Tkachenko and A. T. Budnikov, Semiconductor Physics, Quantum Electronics & Optoelectronics, 3, 185–190 (2000).

15) G. Zhou, Y. Dong, J. Xu, H. Li, J. Si, X. Qian and X. Li, Mater. Lett., 60, 901–904 (2006).

16) R. H. French, H. Mullejans and D. J. Jones, J. Am. Ceram. Soc., 81, 2549–2557 (1998).

17) V. A. Arutyunyan, A. K. Bahayan, A. N. Belskil, V. A. Gevorkyan, V. N. Makhov and U. M. Martirosyan, J. Appl. Spectrosc., 62, 585–588 (1995).

18) V. V. Harutunyan, V. A. Gevorkyan and N. E. Grigoryan, Nucl. Instrum. Methods Phys. Res. A, 308, 200–202 (1991).

19) V. I. Baryshnikov, E. F. Martynovich, L. I. Shchepina and T. A. Kolesnikova, Opt. Spectrosc., 64, 455–457 (1988).

20) K. Mochizuki, H. Shimura and S. Kawaminami, Japan patent, P4810346 (2011) [in Japanese].

21) I. H. Malitson, J. Opt. Soc. Am., 52, 1377 (1962).

22) N. D. Hine, K. Frensch, W. M. C. Foulkes, M. W. Finnis and A. H. Heuer, www.tcm.phy.cam.ac.uk/~mdt26/esdg_slides/hine030609.pdf (2009).

23) J. H. Harding, K. W. Atkinson and R. W. Grimes, J. Am. Ceram. Soc., 86, 554–559 (2003).

24) V. I. Baryshnikov, T. A. Kolesnikova, E. F. Martynovich and L. I. Shchepina, Opt. Spectrosc., 66, 930–932 (1989).

25) N. A. Kulagin, Opt. Spectrosc., 101, 402–409 (2006).

26) W. Chen, H. Tang, C. Shi, J. Deng, J. Shi, Y. Zhou, S. Xia, Y. Wang and S. Yin, Appl. Phys. Lett., 87, 317–319 (1995).

27) N. Fukatsu, N. Kurita, Y. Oka and S. Yamamoto, Solid State Ionics, 162–163, 147–159 (2003).

28) A. K. Kronenberg, J. Casting, T. E. Mitchell and S. H. Kirby, Acta Mater., 48, 1481–1494 (2000).