Rubicon Technology
Evolving Science. Evolving Solutions.

# Improvements to Crystal Quality of Sapphire Grown by the Kyropoulos Method

By:
John P. Ciraldo,
Jonathan Levine
and Hasetha
Ganegoda

# Abstract

Strict process control, combined with proprietary process enhancements have enabled the production of large-scale single-crystal sapphire that demonstrates crystalline quality in excess of what has previously been possible. Extremely low defect densities, narrow rocking-curves, and very low stress gradients in the material are demonstrated through various X-ray diffraction techniques.
**Keywords:** Sapphire, X-ray diffraction, X-ray topography, optics, detectors, optical transmission, EPD, Kyropoulos

*jciraldo@rubicontechnology.com; phone 1 630 482-6009; fax 1 630 406-9273; rubicontechnology.com

# 1.1 Introduction

***The growth method utilized for sapphire synthesis greatly impacts the quality of sapphire produced.***

Due to its many unique properties, synthetic sapphire has been utilized in a wide array of products and applications where other materials are unable to satisfy requirements or are cost prohibitive. For example, the hardness of sapphire, nine on the Mohs scale, along with its high optical transparency across a broad range of wavelengths makes it a very appealing material for windows in harsh environments. Additionally, the lattice structure of sapphire is such that it can be used as a substrate for the epitaxial growth of gallium-nitride, a crucial semiconductor for the active layers of LEDs, lasers, and high-power devices. Another emerging application of sapphire is for the detectors and analyzers in X-ray experiments, where sapphire's crystal structure is advantageous. Notably, in each of the aforementioned applications, the crystal quality of sapphire is extremely important. Contaminants, voids, and point defects can all be highly detrimental to the optical performance of sapphire, and both stress gradients and linear defects have strong impacts on sapphire's efficacy as a substrate for epitaxy. The same problems that affect sapphire's usability as a substrate have a much stronger impact on the usefulness of sapphire for X-ray analyzers and detectors, where any crystal imperfections greatly exacerbate the energy resolution of the final device.

The growth method utilized for sapphire synthesis greatly impacts the quality of sapphire produced. With few drawbacks, the Kyropoulos method is known to produce higher quality crystals than can be achieved through any other method of synthesis[1]. As a result of the Kyropoulos method's tight control of thermal gradients during growth, the sapphire produced by this method demonstrates much lower stress gradients ensuring a significant reduction in linear defects within the bulk crystal. Nonetheless, even Kyropoulos grown material has historically suffered from defect densities that have been too high for the most stringent of applications. Moreover, Rubicon has observed an increasing demand for optical sapphire that is highly transmissive in the deep-UV. However, because sapphire demonstrates a sharp cutoff in transmission below ~200nm the material's transmission in deep UV is highly dependent on material quality.

# 1.2 Discussion

To address the increasingly stringent demands of these technical applications, Rubicon Technology has sought methods to improve the quality of our sapphire beyond what has previously been possible in industry. We primarily rely on a modified version of the Kyropoulos method, known as ES2, to produce our standard crystals material. The ES2 method has been highly optimized to produce very low crystal stress and crystal defects.

In addition to enhancements made to the Kyropoulos technique, Rubicon Technology also sought to improve the source material used to produce our sapphire crystals. Rather than relying on outside vendors to supply us with source material, as is the industry standard, Rubicon processes raw material internally[2]. By using a proprietary refinement method, Rubicon has been able to achieve better control over impurity concentrations in our material. Moreover, we have been able to ensure a greater consistency in our feedstock that has, in turn, allowed us to achieve a greater consistency in the quality of sapphire we produce.

***Rubicon's ES2 sapphire demonstrates transmission near or at the theoretical limits of sapphire.***

The consequence of our efforts is sapphire that is consistently higher in quality than what is otherwise available in the industry today. From UV through IR, Rubicon's ES2 sapphire demonstrates transmission near or at the theoretical limits of sapphire. Likewise, dislocation densities of the ES2 crystals are far lower than material obtainable through our competitors. Moreover, X-ray diffraction rocking curves reveal the narrowest full-width half-max (FWHM) of any known sapphire, with consistent values of 8.5-10.0 arcseconds.

In seeking to achieve that best possible crystal quality, Rubicon Technology sought to produce alumina feedstock with the highest possible purity. In order to achieve this, Rubicon began a dedicated effort to produce alumina powder containing fewer impurities than what is currently available. By ensuring extremely low levels of contamination, the ES2 material demonstrates fewer point defects and subsequent optical centers, allowing for the material to exhibit optical transmission that is consistently near or at the theoretical maximum. The success of our efforts was verified by two methods; optical transmission via a photospectrometer and glow discharge mass spectrometry (GDMS) elemental analysis of the as-grown sapphire. As can be seen in Table 1, the material produced via the ES2 process using Rubicon's proprietary powder refinement techniques yields crystals with extremely low levels of impurities. Amongst the benefits of this high purity is the reduction of optical centers in the crystal lattice, thereby reducing photon capture and subsequent loss of optical transmission through the sapphire. The evidence of this improvement in optical quality can be seen in figure 1, which depicts a comparison of transmission between material grown by the ES2 method and material grown by a competitor via the heat exchange method (HEM). As can be seen, the competitor material demonstrates strong absorption centered around ~210nm whereas the material grown by Rubicon's ES2 method does not demonstrate this optical defect.

***Table 1: GDMS elemental analysis results for Rubicon ES2 sapphire and HEM sapphire. ES2 sapphire contains fewer impurities and is of a higher quality.***

| | Impurity Concentration (ppm) | |
|---|---|---|
| | Element | HEM Sapphire |
| Li | <0.05 | <0.12 |
| Na | <0.10 | 0.66 |
| Si | 0.11 | 9.48 |
| Cl | <0.10 | 2.58 |
| K | <0.50 | 0.39 |
| Ti | 0.19 | 0.21 |
| Cr | <0.50 | 1.10 |
| Fe | <1.00 | 2.52 |

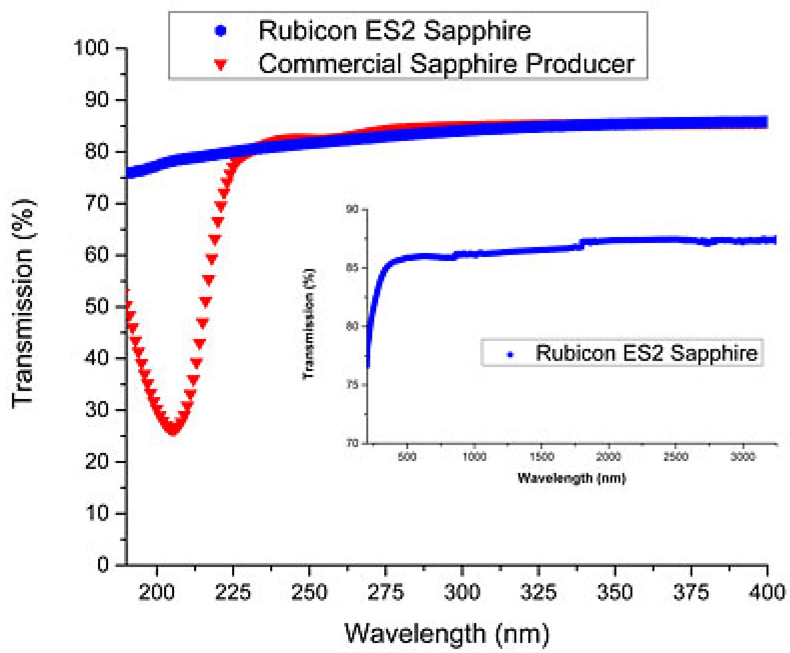


***Figure 1: A comparison of Rubicon ES2 sapphire's optical performance against another sapphire product available in the market. Inset: Broad-spectrum transmission of Rubicon's ES2 sapphire from 185 nm to 3300 nm.***

While impurity concentrations have a crucial impact on many applications of sapphire, and optical transmission can be revealing of overall crystal quality, the gold standard for evaluating crystals is X-ray rocking curves. This technique is highly sensitive to strain and can be utilized to provide highly detailed information about the crystal. Common causes of strain within the crystal include dislocations, vacancies, and bubbles (i.e. macro-scale vacancies within the bulk crystal), all of which contribute to broadening of the rocking curve.

***Material from Rubicon shows a greater overall intensity with a significantly narrower peak, both of which are indicators of superior crystal quality.***

In order to assess Rubicon's material, we collaborated with Dr. Albert Macrander and Dr. Naresh Kujala at Argonne National Lab. The unique capabilities of The Advanced Photon Source at Argonne enabled us to examine very large regions of the crystal, far larger than would otherwise be possible with conventional techniques. Typical beam sizes for this study were ~2cm x ~8.5cm, making the measurements much more characteristic of the entire wafer, whereas a typical XRD system would only allow for the evaluation of a small spot of ~0.25mm in diameter. The material used in this study included Rubicon sapphire, as well as commercially available sapphire material from three other vendors. The synchrotron X-ray beam had been preconditioned with a Si(111) x Si(111) double crystal monochromator, and intensity was recorded via a pin-diode. The results of the X-ray rocking curve analysis can be found in Figure 2. Material from Rubicon shows a greater overall intensity with a significantly narrower peak, both of which are indicators of superior crystal quality. Additionally, the full-width half-maximum (FWHM) of peaks from Rubicon's material show higher symmetry, which indicates a very low stress gradient within the material. FWHM values for each sample can be seen in Table 2 below.

***Figure 2: X-ray rocking curve of c-plane sapphire material. The Bragg reflection of the sapphire was for the (0006) reflection which occurred at a Bragg angle of 21 degrees. Data collected at The Advanced Photon Source at Argonne National Labs; Beamline 1-BM-C Beam Energy: 8keV***

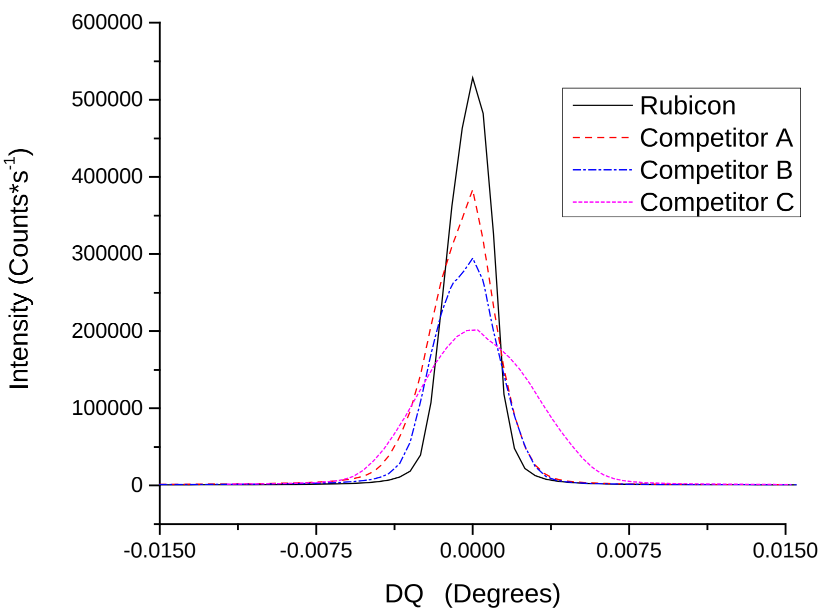

***Table 2: FWHM values for Gaussian fits of X-ray rocking curve data from Figure.***

| Sample | FWHM (arc-seconds) |
|---|---|
| Rubicon | 8.712 |
| Competitor A | 12.881 |
| Competitor B | 14.110 |
| Competitor C | 22.710 |

The information obtained from the rocking curve data indicates extremely high crystal quality, due to a low concentration of crystal defects. Nonetheless, it is worthwhile to evaluate the defect density of the crystals directly. Rubicon employed two distinct methods for examining linear crystal defects; etch-pit density (EPD) and X-ray topography. The former is a wet etch technique wherein the etchant is selected such that it anisotropically attacks lattice defects, leaving characteristic pits that can then be counted to reveal a 2-D defect density along the surface of the crystal. EPD is the industry standard for evaluating lattice defects. Figure 3 depicts a typical etch pit in sapphire after etching with potassium hydroxide (KOH).

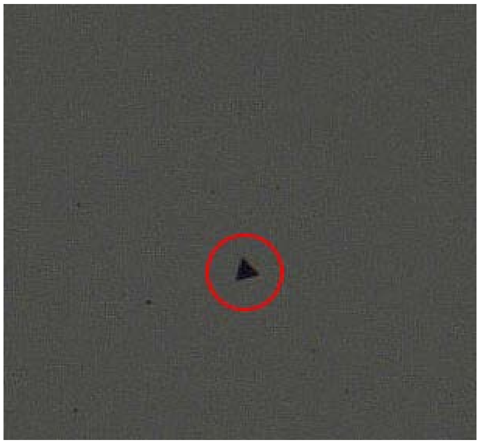

***Figure 3: Typical etch pit in sapphire after anisotropic etch in KOH.***

For the purpose of comparison, Rubicon acquired sapphire from leading competitors who use non-Kyropoulos methods for their sapphire synthesis and exposed them to the same EPD process used on our own material. The results of this study can be seen in figure 4. As results were similar, material produced by the heat exchange method and the Czochralski method (CZ) are presented as a single sample. Lastly, material produced by the edge defined film-fed growth (EFG) method is presented. In agreement with expectations, EFG material demonstrates the highest level of dislocations, followed by material grown by HEM and CZ methods. While it is expected that Kyropoulos sapphire will have the lowest density of etch pits, and therefore the lowest count of defects, it can be seen the reduction in defect density for Rubicon Technology's ES2 material is dramatically lower than for non-Kyropoulos based growth methods. Rubicon sapphire demonstrates a consistent etch pit density that is below 100 dislocations per $cm^2$, which is an order of magnitude better than industry standards for epitaxial wafers of 1000 pits per $cm^2$. This, in turn, indicates that ES2 sapphire is of a much higher quality, in agreement with the earlier rocking curve data.

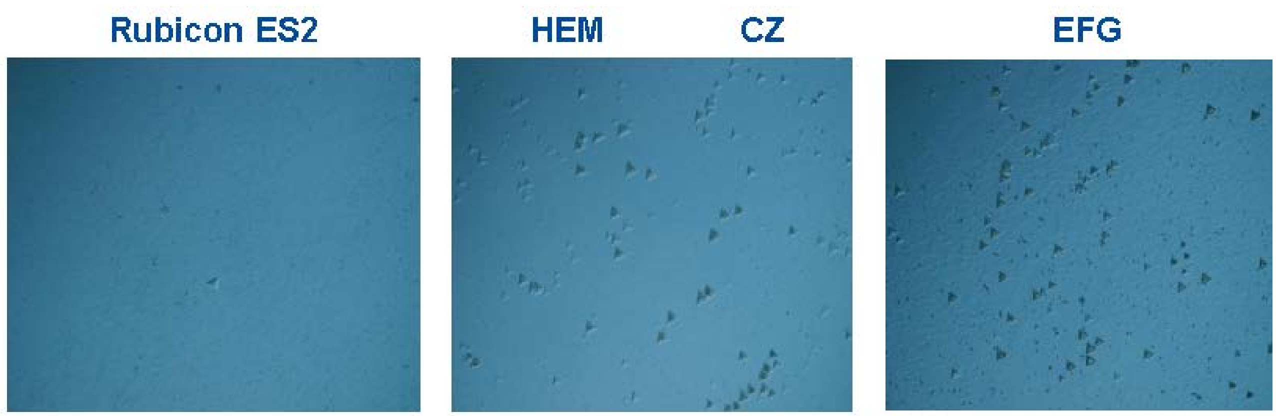


***Figure 4: Defect density of different sapphire materials. Rubicon's crystals have a significantly lower defect density.***

***The defect density of each material shows a strong correlation with the FWHM values.***

The second method that Rubicon employs to evaluate linear defects in crystals, X-ray topography, is a newer method that allows for imaging of defects within a volume of the crystal. By tuning the energy of the X-ray beam, one can move the region under examination from the surface at low energies to the bulk crystal at higher energies. Again, as with the rocking curve data, Rubicon Technology collaborated with The Advanced Photon Source at Argonne National Laboratory to perform topography studies. These studies were performed on the same samples used for the rocking curve data presented in figure 2 and the results of this study can be seen in figure 5. Each topographic image represents an area approximately 5.5mm wide x 3.5 mm high. Observable streaks in the topographic images represent lattice defects within the crystal. High densities of lattice defects (i.e. 'tangles') are represented by dark regions. Dark or light spots within the images are artifacts from the system setup and are not related to the samples themselves.  The sample from competitor C shows a very high density of lattice defects, including a large band of extremely high defect density. Competitor sample A is comparatively much better, but still demonstrates a significant amount of defects. Competitor sample B is similar in defect density to Competitor sample A. The final image is of the Rubicon material. While some lattice defects are present in the Rubicon sample, they are quite sparse and the defect density is clearly much lower than that of any of the competitor material (as indicated by the lack of obvious streaks). It is noteworthy that the defect density of each material shows a strong correlation with the FWHM values from Table 2. While this is not surprising, this correlation helps to validate each individual measurement. Lastly, it should be noted that, while only one Rubicon sapphire sample was presented for this study, several Rubicon samples, each randomly selected from stock, were studied with similar results.

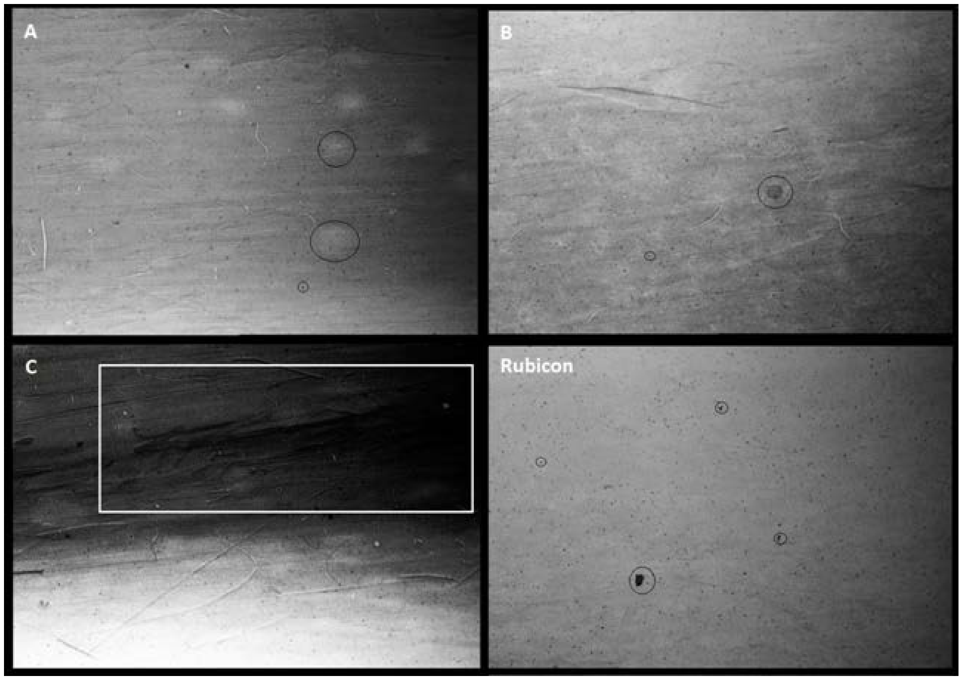


***Figure 5: X-ray topography images of c-plane sapphire. Light and dark spots, such as those that are circled, are artifacts from imaging and are unrelated to crystal structure. Boxed in region is an example of a tangle, or large band of defects.***

# 1.3 Conclusion

As sapphire continues to be adopted into use for a wide range of engineering and scientific applications, the industry must continue to improve crystal quality in order to keep up with market demands. Applications such as high-end optics, epitaxial substrates, and photonic energy analyzers have particularly tight tolerances. In order to satisfy these demands, Rubicon Technology continues to innovate and to optimize current processes in order to ensure that the quality of our sapphire material remains the industry standard. By maintaining fine control over the purity and consistency of our source material, combined with control over in-situ thermal conditions during crystal synthesis, Rubicon Technology has been able to produce sapphire boules as large as 200kg that demonstrate lower defects, lower strain, and superior optical products to those produced via any other method. X-ray diffraction confirms the industry-leading quality of our sapphire. Moreover, Rubicon's ES2 sapphire sets a new standard for low defect densities, making ES2 sapphire the superior choice for the vast majority of applications where sapphire can be utilized.

**Acknowledgements**

This work is supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357.

**References**

1. Dobrovinskaya, E., Lytvynov, L., and Pishchik, V., [Sapphire & Other Corundum Crystals], Folio Institute for Single Crystals, Kharkiv, Ukraine, 102-105 (2002)

2. Parvez, Raja, "Vertical integration streamlines sapphire production," Compound Semiconductor, 50-55 (March 2013).

Rubicon Technology

Evolving Science. Evolving Solutions.™

900 E. Green Street, Unit A
Bensenville, IL 60106
847.295.7000

www.rubicontechnology.com