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Blocks and residual stresses in shaped sapphire single crystals

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ABSTRACT

The formation of blocks and residual stresses in shaped sapphire crystals grown from the melt by the Stepanov method (EFG) has been studied. The probability of block formation is higher for the growth along the *c* axis compared to that grown in the *a*-axis direction. The distribution of residual stress in sapphire crystals of tubular, rectangular and round cross section was measured by the conoscopy method. It was found that the magnitude of the residual stress increases from the center to the periphery of the crystal and reaches up to about 20 MPa. Residual stress tensor components for solid round rod and tubular single crystals were determined by numerical integration.

1. Introduction

Sapphire is one of the most widely used single crystal material for optical, electronic and semiconductor applications for its high hardness, thermal stability, chemical resistance, wide transmission range from *ultraviolet* to *infrared*, and biocompatibility [1]. Nowadays, bulk sapphire crystals are industrially produced using various methods such as Czochralski process, Kyropoulos process, heat exchange method (HEM) etc. Sapphire wafers produced by slicing from bulk crystals are widely used for the manufacturing of high-brightness Light Emitting Diodes (LED) and as an active luminescent medium [2].

Edge-defined film-fed growth (EFG) and related Stepanov method were developed at the same time with bulk sapphire growth techniques. These methods allow to produce shaped crystals of the most various forms, e.g. plates, rods, tubes, etc. EFG technique is widely used to produce sapphire protective glasses for watches, scanners and phones. Sapphire rods of a rectangular or round cross section can be efficiently used as seeds for bulk crystal growth. The essential requirement for seed crystals is the absence of block boundaries because the growing ingot inherits defects from the seed.

Single-crystal sapphire tubes of different size are widely used as laboratory chemical glassware (crucibles, boats and beakers), thermocouple jackets, multichannel thermocouple tubes, high-pressure sodium lamp bulbs, needle capillaries for laser medicine, and sheaths of ultraviolet water treatment systems [1]. Mechanical strength and durability of sapphire parts are almost always affected by the presence of block structure and residual stresses.

It should be noted that the formation of various kinds of defects is a common phenomenon and is typical of all grown crystals. For example, the most common defects in semiconductor crystals affecting their properties are point defects, dislocations, micro- and macro- segregation of impurities, twinning, etc. [3–5]. These defects are also found in sapphire crystals. However, the mechanical strength is largely determined by the existence of block boundaries, dislocations and residual stresses. Optical properties are strongly affected by gas inclusions (pores) and other inclusions [6].

Residual stresses arising due-to complex geometry of crystals, high temperature gradients and high growth rates are commonly found in shaped crystals. A number of publications report on the measurements of residual stresses by polarization-optical method in lithium fluoride ribbon crystals [7], silicon [8–10], sapphire [11].

By block structure we mean that sapphire crystal has regions which are misoriented by a small angle but have the same preferred orientation in respect of the growth axis. Most often the block structure is classified by the angle of misorientation and the size of blocks [1].

The first-order substructure consists of the blocks stretched along the growth axis with the misorientation angles of 0.5–3°. The size of the blocks varies from a fraction of one to few centimeters. Sometimes this structure is referred to as "striated', or "columnar". Such substructure significantly reduces the mechanical strength of crystals and makes them unfit for many applications.

The second-order substructure is formed by blocks with sizes from 100 μm to 1 mm and misorientation angles from 0.5 to 30 arcmin. Usually these microblocks diverge in the crystal like a fan.

The third-order substructure consists of small angle dislocation boundaries with block sizes of 10–100 μm and misorientation angles less than 30′. Crystals with this substructure are suitable for

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some mechanical and optical applications.

The growth process is strongly influenced by the anisotropy of physical and mechanical properties of sapphire. As a result, the formation and the development of structural defects in sapphire crystals largely depend on the growth direction. Perfect sapphire crystals can be readily grown in the ⟨a⟩ direction while growth along the ⟨*c*⟩ axis is more difficult and generally results in crystals with high defect densities. The standard approach to produce ⟨*c*⟩-plane substrates widely used for LED manufacturing is to core rods from the as-grown crystal perpendicularly to the growth axis. An obvious drawback of such process is low material utilization.

There were several attempts to grow bulk sapphire crystals along the c-axis direction to improve volumetric yield of wafers of the target ⟨*c*⟩ orientation. A so-called CHES (Combined Heat Exchanger Solidification) process by ARC Energy Corp allows to grow crystals in the ⟨*c*⟩ axis direction by careful selection of thermal conditions [2]. Czochralski growth of 4″ and larger diameter boules along the c-axis direction has also been reported [2]. Similarly to the bulk sapphire growth, high quality sapphire plates are typically grown by EFG (Stepanov) method in the ⟨*a*⟩ axis direction, so the ⟨*c*⟩ axis is perpendicular to the narrow face of the plate. The block structure is easily formed in sapphire ribbons when crystallographic ⟨*c*⟩ face coincides with its main surface. The nature of this phenomenon was studied in [12,13] and it was found that the difference in crystal growth behavior is related to the features of high-temperature plastic deformation on the two possible slip systems. It was shown that block-free ribbons of the demanded ⟨*c*⟩ orientation can be grown by controlling thermal field distribution in the crystallization zone [14–16]. Such ribbons for LED and silicon on sapphire (SoS) applications are industrially produced by Saint-Gobain and Kyocera firms [2].

The key factors of production of high quality and defect less crystals are careful optimization of the thermal field distribution, seeding conditions and the judicious choice of the growth direction. In the present work we studied the block structure and residual stresses in shaped sapphire crystals.

2. Experiment

2.1. Crystal growth

For this study, sapphire rods of round, rectangular and tubular cross sections were grown by the Stepanov method. The cross-sectional dimensions of the rods were as follows: 8, 12, and 23 mm in diameter for the round rods; 9 × 9 mm and 17 × 14 mm for the rectangular rods; and 27 × 10 mm and 16 × 9 mm for the tubular crystals. Seeds of ⟨*c*⟩[0001] and ⟨*a*⟩[$2\bar{1}\bar{1}0$] orientations were used. The crystallization conditions were identical in all cases.

The hot zone consisted of a graphite heater with a diameter of 120 mm, graphite thermal shields, molybdenum crucible and die. The growth was conducted under argon gas ambient. The crystallization rate was 1 mm/min. Grown ingots of both orientations were sliced perpendicular to the pulling direction into 4-mm-thick specimens, which were then ground and polished to optical transparency.

2.2. Block structure

The block structure of crystals was studied by the polarization-optical method (PO) and X-ray diffraction topography (XDT). X-ray topography images were obtained by back reflection of unfiltered CuKα radiation using a DTS camera. The results of that study for round rod and tubular crystals were reported in detail in publications [17,18], respectively. Below we present a brief summary of the main findings.

It was revealed that the defect structure essentially depended on crystallographic orientation and structural perfection of the seed crystal. Annular development of the block structure from the periphery to the center was observed in rod crystals grown along ⟨*c*⟩-axis on a seed containing block boundaries. This was accompanied with increasing of number of blocks and decreasing of block size. In contrast, growth on a block-free seed under the same conditions resulted in block-free rod crystals with a diameter up to 20 mm.

Growth along the ⟨*a*⟩-axis presented quite the opposite picture. None of the samples exhibited any developed block structure. A few of the ⟨*a*⟩-axis grown crystals had sporadic blocks on one of basal ⟨*c*⟩(0001) faces. Such blocks were visible to the naked eye and penetrated into the bulk by no more than 2 mm.

It was observed that when a tube of 16 × 9 mm cross-section was grown along ⟨*c*⟩-axis direction on a rod seed, blocks were formed at the seeding site within the first few millimeters of crystal growth. In the process of growth blocks penetrated into other parts of the crystal until they occupied the entire cross-section of the tube.

Next we studied the development of block structure in a single-crystal tube of 27 × 10 mm, grown along ⟨*c*⟩-axis direction. In contrast to the previous experiment, a tubular seed was used instead of a rod seed. After the growth, three specimens were cut out from the tube, the first one directly adjacent to the seed and the other two at distances of 5 and 30 mm from the seed. Despite the sharp transition from the tubular seed to the final dimension of the tube under study, no blocks are detected in the region adjacent to the seed. The block structure starts to appear only in the second wafer and develops in the third one. Fig. 1 shows the block

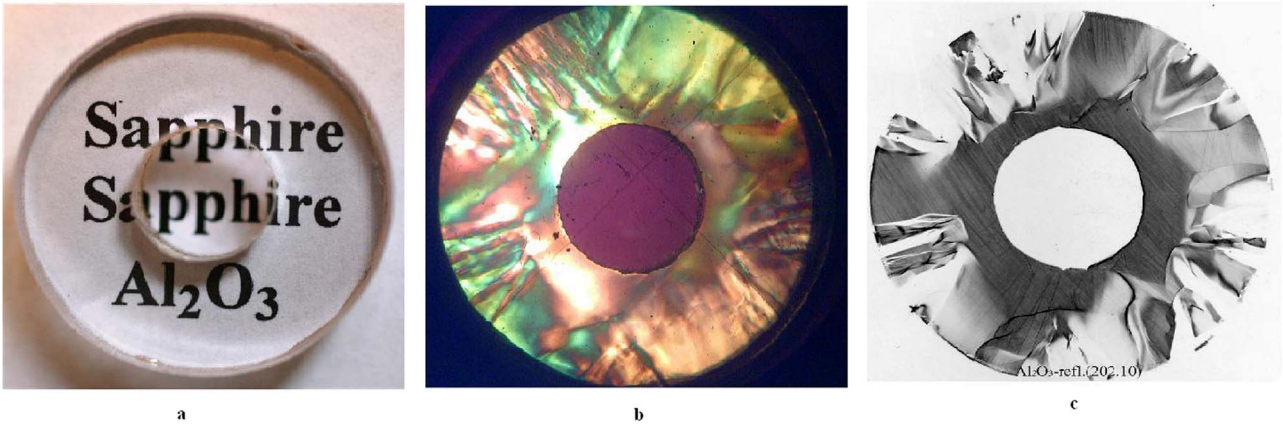

Fig. 1. Sample cut out from a tubular sapphire single crystal (27 × 10) mm: a – unpolarized light view, b – cross-polarized light view, c – X-ray topography image.

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