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Titanium distribution in Ti-sapphire single crystals grown by Czochralski and Verneuil technique

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ABSTRACT

The distributions of Ti^{3+} and Ti^{4+} ions were evaluated by photoluminescence measurement in the wafers cut from different positions of the ingots grown by Czochralski and Verneuil techniques. Particular radial distributions of Ti^{4+} as function of the position in the ingot were observed in the crystals grown by Verneuil technique different than the crystals grown by Czochralski method.

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1. Introduction

Sapphire is one of the most significant tendencies in modern materials science. The raw material for sapphire production is readily available and cheap; the growth technology of sapphire production is less energy-intensive than alternative materials and allows the growth of large-size ingot; sapphire production does not pollute the environment, the growth of sapphire is less harmful than that of alternative materials.

Sapphire is a multifunctional material; it possesses high corrosion [1] and radiation resistance [2], high mechanical strength [3], good thermal conductivity [4], low thermal expansion coefficient [5], high hardness [5] and high biological compatibility [3], especially its perfection in the transmission from the ultraviolet 190 nm through the visible and into the midwave infrared [6–8]. The outstanding physical and chemical properties make sapphire widely applied in medical implants, epitaxial substrate material of new semiconductor GaN, optical window, excellent material of light emitting diodes (LED) [9], laser diodes (LD) and special light source tube, wearable parts of jewel bearing, watch bearing, instrument bearing and precision mechanism [1]. Many growth techniques such as Verneuil [10], Czochralski (Cz) [11], Kyropolous (Ky) [12], edge defined film fed growth (EFG) [13], heat exchange method (HEM) [14], micro-pulling down (μ-PD) [15] are employed to grow sapphire crystals.

Though great achievements have been obtained recently by the effort of researchers all over the world, there are still several technological challenges (increase sizes, eliminate defects, and improve optical performance) have to be faced. To increase the quality of the crystal, a better understanding of some growth parameters effects or some phenomena occurring during the growth process became key point.

Recently, we investigated the bubbles formation and their incorporation in sapphire crystal [11,15,16]. We study the influence of the pulling rate on color center [17,18]. In this paper we study particularly the effect of the growth technique on the distribution of titanium in sapphire crystal. The incorporation of titanium ions modified the optical and mechanical proprieties of the sapphire. The luminescence of the titanium in sapphire allows a very broad laser wavelength tunability extending from about 660 to 1180 nm, and the production of the shortest laser pulses, below 10 fs [19,20]. The distributions of Ti^{3+} and Ti^{4+} ions in the crystal are key factors for the performance of this laser material [21]. The incorporation of titanium increases the fracture strength and fracture toughness of sapphire [5]. However, these values increase differently in function of the valance of the titanium [5]. The knowledge of Ti^{3+} and Ti^{4+} repartition in sapphire could allow a better understanding of the mechanical properties of optical window and substrate. So, this paper presents the segregation and the distribution of titanium inside the crystal grown by Czochralski and Verneuil techniques.

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2. Materials and characterizations

2.1. Sample preparation

Ti-doped sapphire crystals were grown by Czochralski technique in Institute Light Matter. The starting raw materials were alumina and high purity TiO_2 (rutile) powders. Alumina (Al_2O_3-α) is produced by RSA Le Rubis company in good agreement with JSPDS file n° 46-1212 of at least 99.99% purity. A 60 mm-diameter iridium crucible was inductively heated and automatic controlled diameter based on the time derivative of the crystal weight is used for all the growth process. In addition, to control melt decomposition and material evaporating from the charge, the weight of the crucible including charge were followed during all the experimental procedure. To avoid oxidation or other damages of crucible and crystallization, high vacuum was carried out and appropriate pressure of argon (1 bar) is used during the whole growth process. The Ti-sapphire crystal using in this study (Fig. 1a) was grown along *a*-axis $[11\bar{2}0]$, the starting titanium concentration is 0.10 atom%. Its length was about 126 mm and diameter was around 30 mm. The grown Ti-sapphire crystal was transparent and pink, no cracks, bubbles, etc. defects were observed. To learn titanium distribution inside the crystal, it was cut into wafers with thickness 5 mm, 3 pieces of wafers (Fig. 1b) were chosen from top (beginning), middle and end part respectively then optically polished.

The Ti-sapphire crystals grown by Verneuil flame fusion technique are provided by RSA le Rubis Company [22]. The crystals are grown in a furnace from alumina powder that is fed through the H_2/O_2 flame onto a sapphire seed inserted at the bottom of the insulation. During the transit through the reacting flow, the raw material particles melt and these liquid alumina droplets deposits on the seed in the first stage and on the melt film of the crystal front after. All along the crystallization, flow rates of fuel and oxidant evolves allowing the shape control of the ingot. This method is able to produce sapphire crystal with maximal diameter of 40 mm and 130 mm of length. We studied a complete ingot (Fig. 2) cut into 27 wafers numbered from the top to the end.

2.2. Luminescence measurement

The laser excitation of the samples at 352 nm and 256 nm was performed with an Ekspla NT342 optical parametric oscillator (OPO) pumped with a pulsed frequency-tripled Nd:YAG laser. An iris followed by a beam expander system was used to shape the laser and obtain a good beam profile to gain spatial resolution. A laser power meter (Ophir) was placed in the beampath to monitor the laser energy in real time. The beam was introduced into a microscope (Zeiss, Axiotech) and focused on the sample surface through a $\times 50$ objective. The laser spot size is 5 μm in diameter and the energy is limited to some decades of μJ to avoid producing an increase of the temperature of the sapphire surface. Signal was collected through the same microscope system and transmit via an optical fiber to the spectrometer (Shamrock SR-303i; 1200-groves/mm grating with 303 mm focal length) and to the Intensified ICCD (IStar Andor).

3. Results and discussion

The radial distributions of Ti^{3+} and Ti^{4+} concentrations were evaluated using photoluminescence intensity.

The luminescence intensity of Ti^{3+} is evaluated at 730 nm after excitation at 532 nm. The maximum emission of F-centers in undoped sapphire is around 413 nm for excitation at 205 nm [23]. In titanium sapphire crystal, the blue luminescence is strongly exalted and the excitation band is shifted to low energy [17]. Different interpretations are proposed to explain this strong blue emission. In 1990, Blasse and Verweij [24] have reported that the blue emission at around 415 nm is due to a charge-transfer transition involving the Ti^{4+} ions. In 2010, Page et al. [25] explain: "transfer of electron–hole recombination energy to Ti^{4+}, which on de-excitation gives (410–430 nm) blue emission". In 2011, Mikhailik et al. [26] assignee this emission to luminescence of Ti^{4+}-F centers. Whatever the interpretation of the luminescence mechanism, this luminescence at 420 nm after excitation at 256 nm is induced by the amount of Ti^{4+}.

We assume that the variation of Ti^{3+} and Ti^{4+} is linear with the photoluminescence intensity on the same sample. Therefore, it is possible to compare the intensity profile between two samples but not their intensity values.

3.1. Photoluminescence of Ti^{3+} and Ti^{4+} in Czochralski sample

Fig. 3 shows the profiles of photoluminescence intensity of Ti^{3+} (Fig. 3a) and Ti^{4+} (Fig. 3b) of the samples grown by Czochralski technique. The curves indicated higher luminescence intensity at the periphery of the crystal which means higher Ti^{3+} and Ti^{4+} ions concentration in the edges. It is a typical effect of the segregation phenomena during growth process. At the same time, this titanium rejection also results in the destabilization of solid–liquid interface during growing process of Ti-doped sapphire crystal. From Fig. 3, we can find the concentration gradient is relatively small and increases gently from the center to the periphery, this homogeneous radial titanium concentration allow that a large part of the grown ingot can be used.

3.2. Photoluminescence of Ti^{3+} and Ti^{4+} in Verneuil sample

Fig. 4 presents the profile of photoluminescence intensity of Ti^{3+} (Fig. 4a) and Ti^{4+} (Fig. 4b) of 4 wafer samples, which were taken from different positions of the ingot: wafer number 2, number 6, number 18 and number 22. The photoluminescence measurement indicates that all the Verneuil samples, obtained from different positions of the ingot, present the same Ti^{3+} radial distribution.

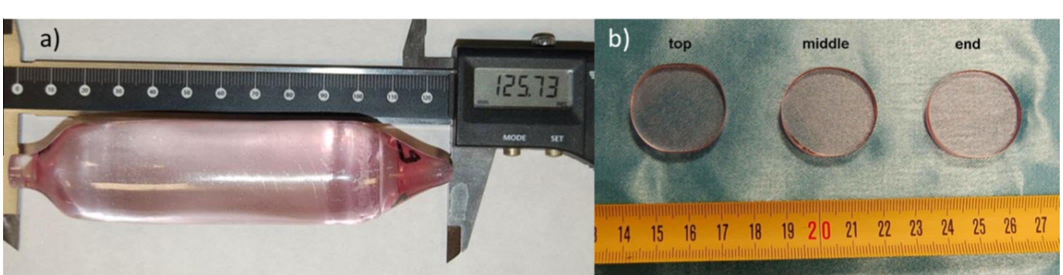

Fig. 1. (a) Ti-sapphire crystal grown by Czochralski technique in ILM. (b) The wafers taken from the different positions of the crystal.

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