Growth of sapphire shaped crystals with continuously modulated dopants

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Abstract

Dopant-modulated sapphire crystals with combinations of various structures in one sample have been prepared in situ by the growth from an element of shape (GES) method. Ti$^{3+}$ is the primary dopant element used. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

By now the actual problem in the field of optoelectronics is the development of new materials which can combine various functions. One way to solve this problem is the growth of crystals with modulations in dopant concentrations, and a combination of continuous structural variations in one sample.

Recently, alongside with conventional methods of heterostructures production, there appears to be significant interest in obtaining, in situ, crystals with a variable structure via melt growth [1–6]. At the same time, the larger place in research is allocated to growth and application in laser engineering of sapphire single crystals, activated by titanium and chromium ions. In Ref. [7], it has been shown that the availability in crystals of Al$_2$O$_3$·Ti$^{3+}$ of spatial resonant structures, i.e. periodical structures of variable composition, sharply reduces threshold of the laser oscillation and makes it weakly dependent on the characteristics of an external resonator. The characteristics of the laser medium are influenced by the contrast of the spatial resonant structures according to the parameter $a$, for example, refractive index. The contrast is determined as

$$K = \frac{a_{\text{max}} - a_{\text{min}}}{a_{\text{max}} + a_{\text{min}}}$$
The contrast is a function of many variables (matrix–activator pair, concentration of the activator, conditions of growth).

The main purpose of the present work is to discuss preparation of, in situ, shaped crystals with spatially modulated properties by the growth from an element of shape (GES) method.

2. Experimental procedure

For preparing, in situ, various structures of variable composition as a model material, we have used sapphire doped by active laser ions Ti$^{3+}$. The crystal growth is carried out with standard equipment using inductive heating. For the shaped crystal growth, we use a crucible combined with reservoirs for doped and undoped melts, and dies feeding these melts simultaneously to the crystallization front. An initial charge was crushed sapphire Verneuil crystals, containing Ti$^{3+}$ at less than $10^{-4}$ wt% in undoped raw material and up to 0.5 wt% in doped raw material. The crystals have been grown parallel and perpendicular to the crystallographic $c$-axis.

The doping concentrations in the grown crystals have been measured by an X-ray microanalyzer “Camebax” provided with a semiconductive detector and “Link AN 10000” system. The observation of dopant modulation in the grown crystals has been made with the help of the cathodoluminescence (scanning electron microscope DSN-960 (“Opton”)), the image contrast being dependent on the contents of the luminescent impurity Ti$^{3+}$ in the matrix–activator couple.
3. Results and discussion

For growth of the shaped crystals with spatially modulated properties we have used GES method. The main principles of the GES method were described in Ref. [3]. The dies are placed at some distance from the rotation axis, the menisci are small elements of the melt form. The crystal growth occurs in layers by means of simultaneous rotation and pulling. The period of the layer nonuniformity $l$ is defined by the equation $l = V/\omega$, where $V$ is the pulling rate and $\omega$ the frequency of rotation.
A transitional region between doped and undoped layers is determined by the depth of partial melting of the earlier grown layer in contact with the meniscus melt. Depth of repeated melting and character of dopant distribution between layers depend on thermal conditions in the crystallization zone and pulling and rotation velocities of the crystal. In particular, high-contrast modulated structures with a small transitional region were obtained under conditions close to supercooling, i.e. with a small height of the meniscus.

Dopant-modulated sapphire crystals have been grown at the pulling rates of 3–25 mm/h and at the rotation frequencies 0.5–20 rpm. In grown crystals, the structures Al$_2$O$_3$–Al$_2$O$_3$:Ti$^{3+}$ with period 5–100 µm, have been produced (Fig. 1). The concentration of Ti$^{3+}$ ions in undoped parts of crystal was less than $10^{-4}$ wt% and in doped parts of crystal was up to 0.2 wt%.

The use of the GES method allows one to considerably expand possibilities in preparing in situ various types of spatial structures. Transition from the periodical structures to the uniformly doped or undoped crystal was carried out by disconnection of melt feeding in one die during the growth process. The variation of period was realized by changing the ratio $V/\omega$ during the growth process. Fig. 2 shows various variants of the distribution of cathodoluminescence intensity along the samples in the direction of crystal pulling.

Location of the dies with various areas of the work surfaces and/or various distances of dies from the rotation axis and/or combinations of the die’s arrangement makes it possible to obtain the various types of doping structures in crystals, which cross-sections are shown in Fig. 3.

The GES technique demonstrates broad possibilities of obtaining in situ various types of dopant-modulated structures. The dopant-modulated bulk crystals can become a new class of materials. Such crystals will be very promising for applications in nonlinear optics.

4. Conclusions

The periodical structures and structures with modulated period were obtained in situ in Ti$^{3+}$ activated shaped sapphire crystals grown by the GES method. The concentration of Ti$^{3+}$ in the crystals is about $10^{-4}$ wt% in the undoped part and up to 0.2 wt% in the doped part of the crystal.

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