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CZOCHRALSKI GROWN $(Al_xGa_{1-x})_2O_3$ CRYSTALS WITH VARIABLE Al CONTENT

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Abstract. We propose a technuque of liquid-phase growth of $(Al_xGa_{1-x})_2O_3$ crystals with variable and controlled Al content in them. When using the Czochralski growth process Ga_2O_3 melt was dosed by sapphire seed. By applying of the special growth zone and the regulating the process parameters, a series of crystal samples with Al content varying from 0.51 to 4.68 % at. was obtained. In addition to the standard setting of the geometry and weight of the crystals using the process parameters, with an increase of the Al content in the melt, it is possible to control the color, transparency and crystallinity of the fabricated samples.

Keywords: Gallium oxide, sapphire seed, crystal growth, Czochralski process, growth zone, block structure, materials characterization

1. Introduction

Nowadays, wide-bandgap semiconductors are widely used in high-tech areas such as energy transfer, aircraft manufacturing, space technology, in fact, they are the basis of modern electronics and optoelectronics. Recently, the creation of semiconductor devices based on single-crystal gallium oxide (β-Ga_2O_3) became the subject of a special interest. This material has a number of advantages, such as high thermal and chemical stability, high breakdown electric field ($E_{br} = 8{\cdot}10^6$ V·cm^{-1}), UV transparency, etc. [1-3]. The scope of its application is already quite wide: photodetectors of deep UV of a different geometry [4], matrices of rare earth luminophores for chemically stable electroluminescent devices and displays [5,6], detection of hydrogen, oxygen and various organic spices [7] and much more [8].

However, despite the fact that Ga_2O_3 is an extremely promising wide-bandgap semiconductor, it also has some weaknesses. Thus, the mobility of carriers (electrons) is 300cm^2/(V·s), which is 4 times less than that of gallium nitride, the value of the bandgap is relatively small (4.9 eV), which is 2 times less than that of sapphire [9,10].

In order to improve the properties of this material for the last few years, active researches are carried out on a system of Ga_2O_3/Al_2O_3 solid solutions [11-13]. Single $(Al_xGa_{1-x})_2O_3$ crystals are promising wide-bandgap materials for the component base of power electronics, due to the high breakdown electric field (up to 10^7 V·cm^{-1} depending on the composition of the solid solution) and the large bandgap (depending on the Al content up to 5.5 eV) [14]. Therefore, the field of application of such materials will increase due to the improvement of their properties, such as high radiation resistance (nuclear industry and space), susceptibility in the wavelength range of 250 – 300nm (high-sensitive "sun-blind" (deep UV) optical detectors), high photocurrent, stable photoconductivity, and much more

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[15]. Thus, the variation of Al content implies achieving and controlling the required crystal properties.

One of the ways to fabricate bulk Ga_2O_3/Al_2O_3 single crystals is the applying of liquid-phase growth methods. The growth of high-quality single crystals of Ga_2O_3 and $(Al_xGa_{1-x})_2O_3$ is technically extremely difficult task, which still is not fully solved by any of the groups of researchers working in this area. One of the features of the process is the use of oxygen atmosphere at growth temperatures (about 1850°C) [16]. This requires using iridium equipment (crucible, shaper, fasteners), which is relatively resistant to oxidation at this temperature. Another problems arising in the process of growth are: the formation of twins and the stacking fault defects; chemical decomposition of gallium oxide melt, as a consequence, the formation of Ga-Ir intermetallides and the destruction of the crucible itself; the dependence of the Ga valence in the Ga-O compound on the oxygen balance and as a consequence, the instability of physical and chemical properties [17,18].

It is known that the following methods are the most suitable for growing Ga_2O_3 crystals: the Czochralski process (CZ), the Stepanov technique (also known as Edge Defined Film Fed Growth (EFG)) and the Bridgman method [19-21]. However, in the latter case, the crystals have a high degree of the blockiness. Thus, at the moment, the research groups in World studying this systems use only the first two methods. As is known, the EFG is an improvement of the CZ and has certain technological advantages. Nevertheless, CZ is much inexpensive at the stage of process organization, regimes modifying, more visual and variable, while allowing to obtain sufficiently high-quality single crystals. Based on these considerations, at this stage of research, we chose it.

The main purpose of this work was in improving the technology of growing Ga_2O_3/Al_2O_3 single crystals from the melt by the Chokhralsky process under conditions of a gradual increase of Al content.

2. Experimental

The liquid-phase growth of $(Al_xGa_{1-x})_2O_3$ samples was carried out with CZ process at NIKA-3 growth machine (production of EZAN, Chernogolovka) under the control of Aura computer program. Ga_2O_3 powder (99.99% purity) was used as the base growth material. The crucible had a cylindrical shape made of Ir by casting / welding. The growth zone consisted of ceramic (ZrO_2 stabilized by Y_2O_3) and mineral wool isolation. As a heater, a spiral Cu-based alloy inductor was used together with home designed re-heating elements. The heating process was first carried out in the absence of a protective atmosphere and then under overpressure in the Argon atmosphere. Adjustment of the power consumption, both during heating and cooling of the reactor working zone, was carried out smoothly in approx. 2 hours. Multiple loading of the crucible for compaction the working material with Ga_2O_3 powder occurred step-wise by sintering and melting the powder. We used W-Rh thermocouple (type A2) to control the temperature.

As a seed the rectangular plates and long cylindrical tubes made of Al_2O_3 (sapphire modification) single crystals were used. The increase of Al content in the Ga_2O_3 melt was controlled by the gradual transition of the sapphire seed material during its melting into the melt. Al content was checked directly by measuring the reduction of the seed length. After the seeding, we used a specified growth rate and rotation speed in CZ process. Thus, a series of Ga_2O_3/Al_2O_3 crystals with different aluminum content was grown.

The obtained crystal specimens were characterized by scanning electron microscopy (SEM), energy dispersion spectroscopy EDS and (X-ray) diffraction (XRD) methods. SEM (JEOL JSM-7001F) was used to study the crystal surface: morphology, inhomogeneities, defect and block structures. The chemical composition was analyzed at the same setup using the EDS method. The phase composition was studied with XRD technique (DRON-8) in the mode of Cu Kα (1,54 Å) radiation at U = 40kV, I = 30mA regime.

3. Results and discussion

Five crystal samples of similar shape but different sizes, weight and color were grown. The crucible was loaded with Ga_2O_3 powder in four stages. After each load, the content of the crucible was melted totally (the melting temperature was about 1800°C), as a result the melt level was lowered, respectively, after cooling, the next load was available. From the first to the last growth process, no loads were made, therefore, there was an increase of Al_2O_3 content in the initial melt by transferring the seed material into it. Finally, this led to an increase of Al content in the grown crystals. In Fig. 1 is shown one of the $(Al_xGa_{1-x})_2O_3$ grown crystal samples (sample no.1, Al = 0.51% at.), with a fragment of sapphire seed attached at the bottom. Visually, the sample has a spiral cylindrical shape. The color of this sample is light blue, transparency is high. Other four samples had similar look, however, they were differed in height, "turns of the spiral" number, weight and color. The geometric parameters and weight of the samples were not correlated with the Al content, but depend of technological process parameters, such as the seed temperature, the temperature of the growth process, the speed of forward and rotary movement of the upper shift during growth.

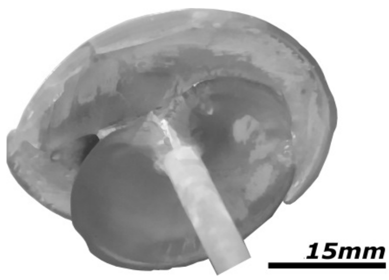

Fig. 1. Example of Czochralsi grown $(Al_xGa_{1-x})_2O_3$ crystal specimen with Al content 0.51% at.

The height of the samples was limited by the moment of the end of growth process, which occurred together with the detaching of the sample from the melt, which was controlled mainly by the temperature in the working zone and the speed of upper shift. The number of "turns of the spiral" depended in a complex way on the process parameters, the most essential factors were: the speed of the upper shift and the temperature field configuration inside the working zone. As the melt saturated with sapphire, the color of the samples became darker with a gray tint and a lower transparency degree. At the same time, the blockiness of crystals visually increased by reducing the block size, and the strength of the samples also decreased. Optical micrographs of the surface of fabricated $(Al_xGa_{1-x})_2O_3$ samples with varying Al content are given in Fig. 2.

SEM study showed that all sample surfaces have a different degree of crystallinity with block sizes from 0.5 to 300μm. The morphology and structure of the surface is rather complex and correlates indirectly with the Al content in the samples. Typical SEM images of sample surfaces of varying crystallinity degree are presented in Fig. 3.

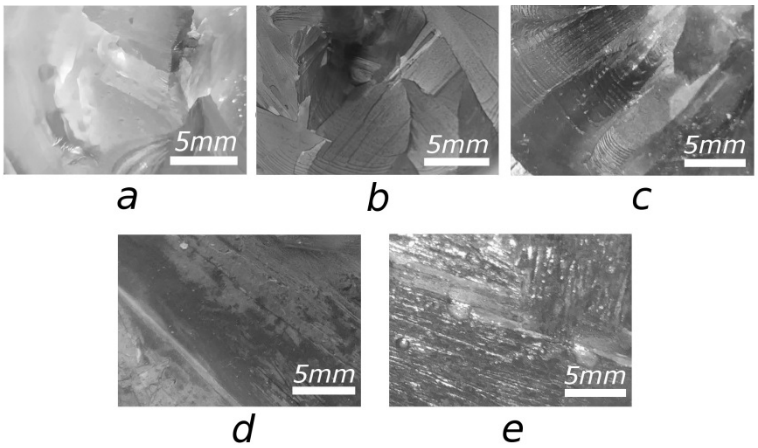

Fig. 2. Macro- images of the $(Al_xGa_{1-x})_2O_3$ crystal surface areas – a, b, c, d, e correspond to specimens 1 – 5 that fabricated at different Al content (see Table. 1 below)

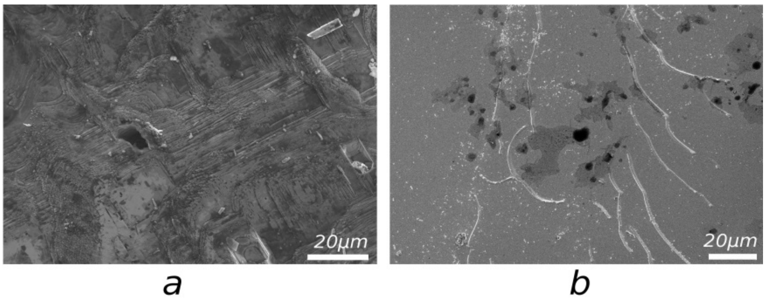

Fig. 3. SEM images of different surface areas of specimens no.1 (a) and no.2 (b). Both show different types of blocks, defects and surface homogenity at the same scales

In order to study the phase composition, the XRD analysis was used. According to the analysis, the main intensity peak in all samples was found at the angle of 2θ=30.06º that corresponds to (400) reflection of β-Ga_2O_3. There were also reflexes of metallic Ga (110) at 2θ = 45.54° and γ-Al_2O_3 (220) at 2θ=66.95°. At of the rocking curves (the sample no.1) several asymmetric peaks were recorded on the plane (200) and at the plane (400), with the angle of misorientation between the two satellite peaks being 2°25' and 2°30' respectively, which implies that the sample has a high degree of imperfection. Thus, all the obtained crystal compositions are qualitatively in accordance with the materials and process parameters, but the sample no. 1 itself is not a single crystal. Based on the SEM data and the (*macro*-) surface images of the remaining samples, it follows that all other samples (no. 2 – 5), having even higher block misorientations, and therefore are not real single crystals.

The chemical composition of the samples was detected by EDS. The Al content in the samples, varied within 0.5 – 5% at. In Table 1 the data on the chemical composition of the samples are provided. The Al content increases unevenly as the seed material (Al_2O_3) enters the Ga_2O_3 melt, which indicates the instability of the aluminum transfer process as a result of insufficient reproducibility of the initial growth process stage during seeding.

Additionally, there is a tendency of the gallium content reduction in the melt, since gallium oxide in a neutral atmosphere dissociates already at 400°C (and above) successively into the following compounds: $Ga_2O_3 \rightarrow GaO \rightarrow Ga_2O \rightarrow$ Ga plus O_2 [22]. Due to the appearance of free gallium, it is possible to form intermetallic Ir-Ga compositions, which bond the free gallium [23].

Table 1. Chemical composition of Czochralski grown specimens

Specimen no.	Al, % at.	Ga, % at.	O+C+Si, % at.	Al_2O_3 seed consumption, approx., mm
1	0.51	40.93	58.56	5
2	1.28	37.23	61.49	5
3	1.72	42.37	55.91	5
4	2.11	36.59	61.30	5
5	4.68	36.95	58.37	5

4. Conclusions

We have demonstrated the possibility of growing crystals $(Al_xGa_{1-x})_2O_3$ with Al content in the range of 0 – 5% by the Czochralski process. The input of Al into the solid phase was not controlled accurately enough, but this can be improved by aligning the process parameters at the initial growth stage during seeding. The entire crystal growth process requires the optimization, since, apparently, the process parameters must be set individually depending on the Al content, in order to improve the crystallinity of the specimens. In the future, we plan to explore the numerical modeling to optimize the growth process and crystal quality of CZ grown $(Al_xGa_{1-x})_2O_3$ crystals with variable al content.

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