Journal of Crystal Growth 360 (2012) 146–154

Contents lists available at SciVerse ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Problems and recent advances in melt crystal growth technology

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ARTICLE INFO

Available online 3 December 2011

Keywords:
A1. Heat transfer
A1. Mass transfer
A2. Growth from melt
A2. Scaling of crystal size
A2. Solid-state single crystal growth
B2. Dielectric materials

ABSTRACT

The present review deals with the novel developments in melt growth techniques which have arisen mostly within recent five-ten years and focuses on recent progress in growing bulk crystals of dielectrics, however, many developments could be easily applied to the semiconductor growth technology. The scaling of size and yield of crystals grown from the melt, and various ways and tricks to improve crystal perfection via homogenization of melt composition and governing the heat and mass transfer are under consideration. Particular developments such as low-thermal gradient and low-melt level growth techniques, governing by heat field rotation and applying of low-frequency vibration, as well as the use of double crucibles and submerged baffles are considering. The paper also discusses the current problems of bulk crystal growth due to the competition with arisen alternative technologies of manufacture the bulk crystalline or quasi-crystalline materials including transparent ceramics and glass-ceramics as well as the solid-state single crystal growth technology.

1. Introduction

Bulk crystal growth and, first of all, the growth of single crystals from the melt still remains one of the most important modern technologies of manufacture many high-tech products for electronics, photonics, communication systems, renewable energy technologies, etc. Key role play crystals in producing of new energy sources (light-emitting diodes, solar cells, laser fusion). Crystal growth, particularly its aspects related to the nucleation is the fundamental basis of many nanotechnological processes and creation of nanomaterials. So, the importance of crystal growth is hard to overestimate.

The remarkable progress and impressive achievements made in bulk crystal growth during the last 60 years are discussed in several review papers [1–4] and collected in the recent book [5] containing a series of articles written by a number of famous crystal growers. It could highlight two most important inventions in XX century which strongly influenced on the development of crystal growth technology and initiated its rapid progress. First of them was the invention of transistor in late forties that resulted in the development of semiconductor growth technology, and second was the invention of laser that caused very fast development of growth technology of dielectrics crystals starting from sixties. Today we observe one more impressive event, connected with just started unprecedented fast development of industrial production of large-scale sapphire crystals needed as the substrates for light-emitting diodes using for energy-saving illumination. The anticipated demand in sapphire substrates increases from 2010 to 2015 for 20 times [6].

The present review deals with the novel developments in melt growth techniques which have arisen mostly within recent five-ten years and focuses on recent progress in growing bulk crystals of dielectrics, however, many developments could be easily applied to the semiconductor growth technology. The production of single crystals is permanently increasing year by year. Unfortunately the information about commercial crystal growth is not widely available, and different output amounts could be found in the literature (see, for instance, [3,7,8,9]). The current estimations show that worldwide more than 50.000 t annually silicon crystals are produced for photovoltaics and electronics, 3000 t/a quartz single crystals for piezoelectricity, over 600 t/a GaAs for optoelectronics and high-frequency electronics, 500 t/a sapphire crystals for substrates for high brightness LEDs and silicon-on-sapphire RF devices, and even 10 t/a diamond micro crystals are produced.

At the same time the situation with bulk crystal growth today cannot be called the excellent. The situation essentially changed during last years and continues to change now. There is direct evidence of certain lowering of interest in crystal growth and in bulk crystal growth from melt, in particular [4,7]. This is accompanied by other negative tendencies like reducing activity, loss of knowledge and expertise in crystal growth, etc. However, these problems appeared not only due to the general crisis of science taking place now. There are also other reasons for that.

First, it is a progressive miniaturization of devices resulting in development of competing technologies of manufacture of thin films, glass and crystalline fibers, nanostructure technologies. Another

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doi:10.1016/j.jcrysgro.2011.11.049

competitive factor is the recent appearance of alternative technologies of fabrication the bulk crystalline or quasi-crystalline functional elements. These are technologies of high-quality transparent ceramics [10,11] and glass-ceramics [12,13], which allow manufacturing the optical and active elements for photonics besides the crystals. Their important advantages are the extended capabilities of the ceramic materials compared with the single crystals (larger size, increased compositional versatility, higher doping concentrations with controlled profile, etc). In particular, oxide transparent ceramics offers today the sizes of functional elements, which are beyond the reach of single crystals. Additional important advantage of ceramic technologies is a lower cost of production. This situation brings to the fore other than crystal growth technologies like sol-gel, co-precipitation, hot pressing, hot isostatic pressing, etc.

One more a promising development appeared recently. It is fabrication of single crystals by non-melting process, i.e. by solid-state synthesis or by so called solid-state single crystal growth (SSCG) [14,15]. This technology is a further development of old works devoted to recrystallization of metals [16,17]. In the SSCG process a small single crystal seed is diffusion-bonded to a polycrystalline body and grows by consuming fine matrix grains during a heat treatment process. This sintering method has many advantages. It permits the fabrication of single-crystalline materials with high melting point, with incongruent melting or with destructive phase transitions and it makes available the crystals with high level and uniform distribution of dopants. For instance, the authors of Ref. [14] fabricated by SSCG process a heavily doped by Nd^{3+} (4.8 at%) perfect YAG single crystal, which could not be produced by the conventional melt growth methods. The crystal growth rate obtained in this sintering method reached mm/h order.

It may be stated that the further development of these three novel alternative ceramic technologies could significantly change the situation with crystal growth in the nearest future. Nevertheless the reports of the death of melt crystal growth technologies are greatly exaggerated. It should be stressed that polycrystalline products don't have two important features of single crystals, namely, ordered structure and anisotropy. In this connection, the crystals with non-centrosymmetrical structure and polar crystals, in particular, are of specific interest. Today bulk single crystals have no alternative for a number of important applications (oriented substrates for fabrication of epilayers using in microelectronics and photonics; the piezoelectric resonators; nonlinear-optical, acousto-electronic, and magneto-optical devices, etc.)

In fact, during last five-ten years we observe a number of important inventions and improvements in bulk growth technology that allow expecting on its stable development and progress in the next decades. Since the goal of development of any crystal growth technology is the production of high quality and large size single crystals, two main subjects are under consideration in present review, namely, the scaling of size and yield of crystals grown from the melt, and various ways and tricks to improve a crystal perfection usually via homogenization of melt composition and governing the heat and mass transfer. There are many impressive developments in crystal growth, which have been made in recent years. Of course, it is impossible to overview all of them in a short journal paper. Some important developments of last years that reviewed in detail like ACRT [18], traveling magnetic field [19], detached Bridgman growth [20], micro-pulling-down technique [21] as well as numerical modeling of crystal growth [22] are omitted in this paper.

2. The scaling of crystal size

The scaling of crystal size and production yield of crystal growth technology one could consider on the example of sapphire crystals. Sapphire gives an example of the most imposing recent technological development among the dielectric crystals. The favorable combination of excellent optical, thermal, and mechanical properties of sapphire, together with high chemical durability, makes it an attractive structural material for high-technology applications. Sapphire crystals are used in optics, quantum electronics, and medicine as well as optical windows and substrates for the semiconductor industry. By now the commercial production of synthetic sapphire is more than 100 years old. However, the today booming in sapphire crystals production is connected with their using as substrates for GaN-based light emitting diodes (LEDs). To cover the existing huge demand in sapphire substrates the crystal producing companies make great efforts (for details see the analytical paper of E. Moersen [6] and review of M. Akselrod and F. Bruni [23]).

Several growth techniques allow today producing the large-size sapphire crystals, namely Kyropoulos, heat exchanger method (HEM), Stepanov (EFG) and horizontal directed crystallization (HDC, Bagdasarov technique). In addition, it should be also mentioned the using (in less extent) Czochralski [24], gradient solidification method (GSM) [25] and temperature gradient technique (TGT) [26]. The main difference between the HEM versus GSM and TGT is that the thermal field of the furnace in the GSM and TGT systems contains upward temperature gradients [27].

The largest and high-perfection crystals are producing now by Kyropoulos method. The "standard" sapphire crystal today has C-plane 6 in. diameter and 100 kg weight [6]. The adaptation of Kyropoulos method to growth of sapphire single crystals has been made by M.I. Musatov in 1970 s [28]. The special features of this technique with regard to sapphire growth are extremely low temperature gradients; in particular, typical radial gradients are 0.1–0.2 K/cm. Two leading companies Rubicon Technology Inc. (Illinois, USA) and the "Monocrystal" Co (Stavropol, Russia) are producing the sapphire by Kyropoulos technique and making the further development of this technology. Rubicon reported in April 2009 [29] on growth of big Kyropoulos sapphire boule of 200 kg weight. The "Monocrystal" Co introduced in December 2010 [30] ultra-large 10-inch C-plane epi-ready sapphire substrate cut from crystal grown by Kyropoulos technique.

GT Solar (formerly Crystal Systems Inc.), Salem, Massachusetts, USA is developing the HEM method as alternative technology for growth of large bulk sapphire crystals. GT Solar claims [31] that they grow by HEM the sapphire crystals with diameter up to 13.5 in. routinely and with diameter 26 in. as R&D production. Planned by GT Solar the significant extension of sapphire production could make HEM method a strong competitive technology in the sapphire market in the nearest future.

Two other bulk crystal growth technologies, namely EFG and horizontal directed crystallization (Bagdasarov technique) [32], producing sapphire plates for windows were also succeeded in recent years to increase the size and quality of crystals. Saint-Gobain presented [33] rectangular sapphire plates grown by EFG with thickness of 8 mm and size 12″ by 20″ (305×508 mm^2) and 9″ by 26″ (229×660 mm^2). Institute for single crystals (Kharkov, Ukraine) developed technology of large sapphire single crystals with size $350 \times 500 \times 50$ mm^3 grown by horizontal directed crystallization [34].

A few years ago it was presented one more technology aimed at fabrication of large-size sapphire crystals. Authors named it as "sapphire growth technique with micro-pulling and shoulder-expanding at cooled center" (SAPMAC) and explained that this technique was developed on the basis of Kyropoulos and Czochralski methods [35]. The crystal is growing by decreasing of temperature with velocity 10–30 K/h at simultaneous its pulling with rate 1–5 mm/h. The size of crystals reached by now is