Semiconductor Physics, Quantum Electronics & Optoelectronics. 1999. V. 2, N 1. P. 76-79.

PACS 81.05. C, D, E, G, H

Investigation of structural perfection of SiC ingots grown by a sublimation method

S. F. Avramenko, V. S. Kiselev
Special Design Office of the Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kyiv, 252028, Ukraine, fax: 380(44) 265-19-57, e-mail: kisvs@usa.net

M. Ya. Valakh, V. G. Visotski
Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kyiv, 252028, Ukraine, fax: 380(44) 265-83-42, e-mail: valakh@isp-div6.kiev.ua

Abstract. Monocrystalline SiC ingots were grown by a modified Lely method using 6H-SiC seed crystals with (0001) base plane. The crystal growth was carried out in the temperature range 2200-2500 °C at Ar pressure from 2 to 40 mbar. The rate of growth varied between 0.3 and 1.5 mm/hour in the C-axis direction. At growth time of about 15 hours we obtained the ingots with 35 mm useful diameter. To determine the polytype composition of SiC ingots the Raman scattering technique was used. The structural defects were investigated by means of reflection and transmission light microscopy and by selective etching. In the best ingots the dislocation density did not exceed 10^2 cm^{-2}, the micropipe density – 10-20 cm^{-2}, and blocks were absent.

Keywords: silicon carbide, modified Lely method, Raman scattering, defects.

Paper received 19.03.99; revised manuscript received 30.03.99; accepted for publication 31.03.99.

1. Introduction

Silicon carbide has a unique combination of electronic and physical properties for application in various fields of modern engineering such as high power devices which operate at high temperature, and devices for microwave electronics. The modified sublimation Lely method is the only growth technique providing large bulk SiC crystals [1-3]. The most serious drawback of this method is low structural perfection of crystals. Commercially available 6H- and 4H-SiC substrates contain different types of defects, namely: dislocations, dislocation loops, misoriented domains (a mosaic structure), inclusions, blocks and, especially, micropipes [4]. The crystal defects do not allow to realize completely advantages of silicon carbide. This is currently important for progress in the development of new semiconductor devices of the next generation. The concentration of these defects depends mainly on the growth conditions. Therefore, the aim of the present paper is to study the influence of the initial stage growth on the structure of SiC crystals.

2. Equipment and method of growth

We have used the resistively heated industrial furnace "Redmet-30". The sublimation vapor transport system we designed for SiC ingot growth is shown in Fig. 1. The growth system consists of concentric graphite heater, crucible made from vacuum-tight graphite with 180 mm in diameter and 200-mm long, and two heat screens for thermal insulation made of graphite, rigid carbon foam and carbon foil. We used a double wall or coaxial arranged cylinder type crucible [5]. A porous carbon membrane separated the growth cavity in the crucible. At high temperature the source material diffused through the membrane to the seed crystal which has lower temperature in comparison with the source material. As a seed we used 6H-SiC Lely [5] crystals with (0001) base plane. The diameters of the seeds lay between 8 and 10 mm.

The seeds were etched in KOH melt (T = 600 °C, t = = 3-5 min). The orientation of (0001) Si and (0001) C type plane was determined by this process. The source material used was the polycrystalline SiC powder of p-

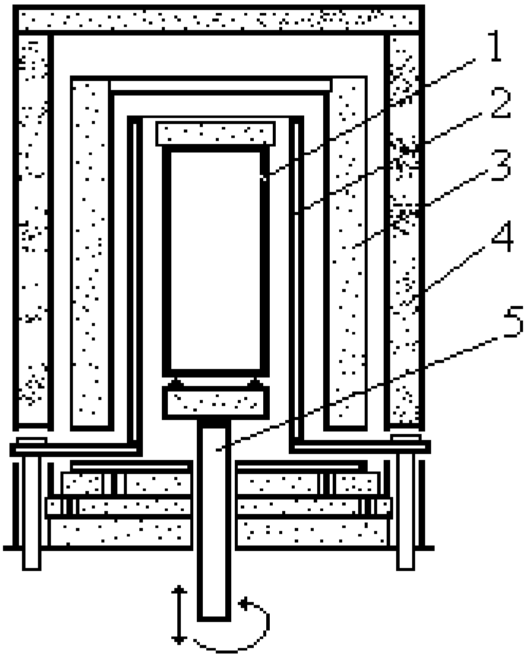

Fig. 1. Design of the equipment: 1 – crucible of vacuum-tight graphite, 2 – heater, 3 – first screen, 4 – second screen, 5 – rotated rod.

or n-type conductivity, which was synthesized by us from Si and C powders. The crystal growth was carried out in the temperature range 2200-2500 ^{o}C and at the Ar pressure ranging from 2 to 40 mbar. The average rate growth varied from 0.3 to 1.5 mm/hour in the C-axis direction. When the growth time was as long as 15 hours we obtained the ingots with 35 mm useful diameter.

3. Results and discussion

To determine SiC ingots polytype composition we used the Raman scattering technique [6-9]. Structural defects were investigated by means of reflection and transmission light microscopy. In order to study crystal parameters, ingots were cut into plates in two directions: parallel and perpendicular to the C axis. The thickness of the plates varied from 0.5 to 1.0 mm. The facets of these plates were the crystallographic planes {0001}, {1120}, {1100}. It enabled to study not only the basis plane {0001}, parallel to the surface of the seed, but also facets {1120} and {1100}. The plates were polished with diamond pastes and etched in KOH melt. Thermoelectric power measurements were used to determine the conductivity type. The etching in KOH melt is polishing for a plane {0001} C and selective for a plane {0001} Si. In the latter case, the etch pits are seen on the surface. Their shape depends on the tilt of dislocations and on the type of defects. The shape of dislocation etch pits is the inverted hexagonal pyramid, and the etch pits for tilted dislocations are the deformed hexagonal pyramid. The deformation is dependent on the angle between the dislocation and {0001} Si plane. The etch pits of closed dislocation loops have the same shape but are smaller and often situated in pairs. Other microdefects and the inclusions of other phases have etch pits with flat bottom (inverted truncated pyramid). Dislocations or their parts located in a subsurface layer, microtwin lamellas and block boundaries are seen as grooves. Dislocations, dislocation loops, blocks and pipes were found to be the main defects in ingots. The concentration of these defects depends mainly on the structural quality of seed, its preparation and growth conditions. Our results have shown that the main reasons of these defects formation are:

1) *Conditions of growing*. Defects of crystalline structure can appear at different stages of crystal growth. But the majority of defects are generated at the initial growth stage due to the formation of 3C-SiC. This modification of SiC is of low stability; it transforms to a-SiC at high temperature. This transformation leads to the emergence of pores, inclusions and pipes in growing crystals. Correct selection of Ar pressure at the initial growth stage allows one to avoid the formation of 3C-SiC. Moreover, the stability of growth conditions (temperature of growth, pressure and vapor equilibrium) also essentially influences the structural perfection of crystals.
2) *Fixation of the seed*. Pipes can be caused by defects in the graphite seed-holder and incorrect fixation of a seed.
3) *Quality of the seed*. The largest part of defects can originate from the defects of the seed crystal and its surface. Therefore, to obtain high-quality crystals one should carefully choose seed crystals.

Shown in Fig. 2 is the appearance of the typical SiC crystals obtained by the Lely method and used as a seeds

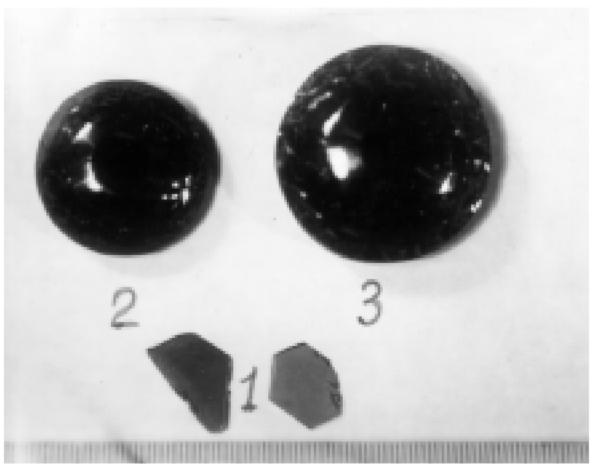

Fig. 2. The appearance of the typical SiC crystals obtained by Lely method (1) and ingots (2,3) grown in this work. Time of growing: 2 – 5 hours, 3 – 10 hours.

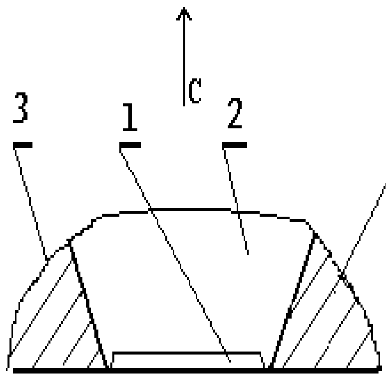

Fig. 3. The shape of the crystal: 1 – seed, 2 – monocrystalline part, 3 – peripheral part.

(1) and ingots (2,3) grown in this work. Fig. 3 shows the schematic cross-section of the ingot along the C axis. It can be conventionally divided into three parts taking into account a content of defects: the seed (1), the monocrystalline part (2), the outer part (3). The blocks in the area (3) frequently consist of various polytypes (15R, 6H, or 4H) differing from the polytypes of the seed (6H-SiC) and of the growing crystal (6H- or 4H). Significant elastic deformations arise at the part (3), these sometimes extend into the area (2).

Fig. 4 represents the Raman spectra for various parts of the ingot. As the absorption coefficient for Ar laser radiation is small, the Raman spectra give information about a polytype structure averaged by the entire light path inside the ingot. The spectra show that the peripheral, polycrystalline part and the bulk of the ingot consist of 15R and 6H polytypes, respectively, while the seed-ingot interface contains the inclusions of the 4H polytype.

The shape of the ingots is determined by the configuration of a thermal field used. The main structural defects (dislocations and micropipes) originating from the seed surface propagate along the vector grad T; they are normal to the ingot surface.

The polarity of SiC seed (Si-type or C-type plane) influences the polytype structure of growing crystals. The difference of the binding energy values for the (0001) C and (0001) Si surfaces of SiC allows one to control a polytype structure of growing crystals [10,11]. Using the charge caused by doping with boron on the surface of 6H-SiC seed (0001) C, we obtained the 4H-SiC ingots, while on the (0001) Si surface we always got the 6H polytype. This result was obtained in several dozens of experiments at the growth temperature T < 2400 °C. However, rising the temperature up to 2500 °C, we obtained only 6H-SiC polytype ingots on the (0001) C surface. Thus, one can control the polytype structure using (0001) C surface by varying the technological conditions of growth (temperature, impurity and so on) [11]. In Fig. 5 the Raman spectra of plates cut from two different ingots are represented. In the first case, the growth was carried out on a surface (0001) Si of the seed and, in the second one, on a surface (0001) C of 6H-SiC seed.

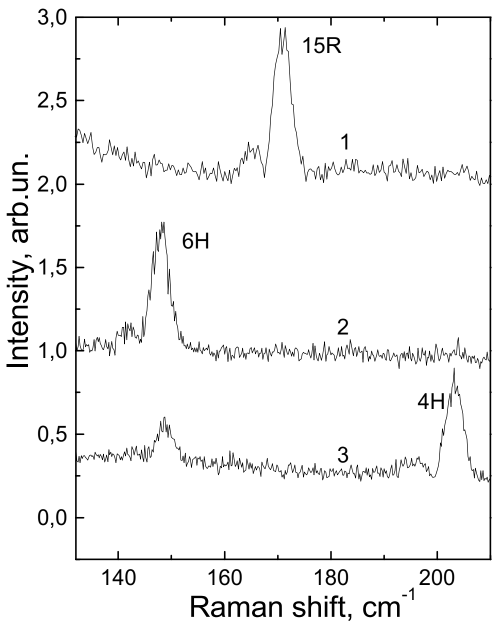

Fig. 4. Raman spectra for various sites of the same ingot: 1 – interface seed/ingot, 2 – mono-crystalline part, 3 – peripheral part.

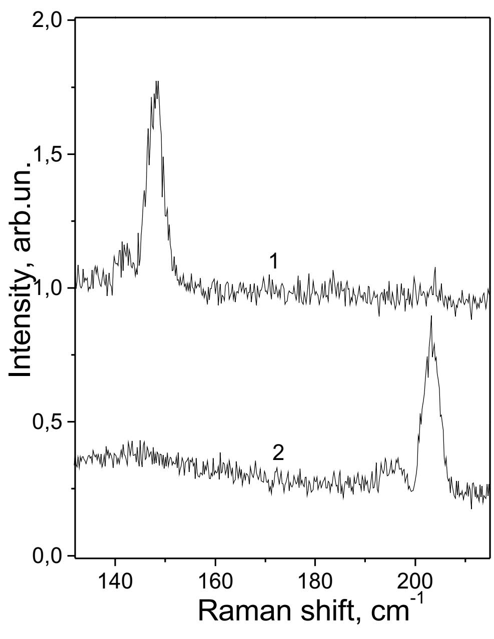

Fig. 5. Raman spectra of ingots grown on 6H-SiC seed: 1 – 6H-SiC grown on a surface (0001) Si, 2 – 4H-SiC grown on a surface (0001) C.

3. Conclusions

The construction of the crucible designed by us, with a thermal field of a hemispherical configuration, allows to conduct effective growth of SiC crystals of large sizes. Using seeds of 8 to 10 mm in diameter, we received the plates with the diameter up to 35 mm.

The investigation of structural defects in silicon carbide ingots obtained by the modified Lely method has been carried out. It has been shown that there are three characteristic parts in the grown crystals that differ by the defect composition. The main defects are dislocations, screw dislocations, dislocation loops, blocks and pipes. The seed/ingot junction area plays the main role of a dislocation source. The pipes mainly originate from the boundaries of the seed in peripheral parts of ingots. These parts of ingots consists of misoriented blocks. The causes of structural defect formation are analyzed. It is shown that the modified Lely method developed allows to produce SiC substrates of fairly high quality. In the best ingots the concentration of dislocations did not exceed 10^2-10^3 cm^{-2}, micropipes – 10-20 cm^{-2}, and blocks were absent.

References

1. Yu. M.Tairov, V. F. Tsvetkov, General principles of growing large-size single crystals of various silicon carbide polytypes // *J.Cryst.Growth*, **52**, pp.146-150 (1981).
2. Yu. M. Tairov, V. F. Tsvetkov, *Crystal growth and characterization of polytype structures*, p.111, Pergamon Press, London (1983).
3. G. Ziegler, P. Lang, D. Theis, C. Weyrich, Single crystal growth of SiC substrate material for blue light emitting diodes // *IEEE Transactions on ED*, **ED-30**(4), pp.277-281 (1983).
4. S. F. Avramenko, M. Ya. Valakh, V. S. Kiselev, O. T. Sergeev and M. Ya. Skorokhod, Study of structural perfection of a-Silicon Carbide crystals //*Met.Phys.Adv.Tech.*, **15**, pp.729-735 (1996).
5. S. Nishino, Bulk growth of SiC, Chap.8 *in Properties of Silicon Carbide*, Ed. G.L. Harris, pp.163-169, INSPEC, Washington DC, USA (1995).
6. D. F. Feldman, J. H. Parker Jr, W. Choyke, L. Patrick Raman scattering in 6H-SiC //*Phys.Rev.*, **170**(3), pp.698-704 (1968); D.F.Feldman, J.H.Parker Jr,W.Choyke, L.Patrick Phonon dispersion curves by Raman scattering in SiC. Polytypes 3C, 4H, 6H, 15R and 21R. //*Phys.Rev.* **173**(3) pp.787-793 (1968).
7. V.V. Artamonov, M.Ya.Valakh, M.P.Lisitsa, V.Ye.Nizkova, Determination of a polytycal composition of SiC joints (in Russian) //*Ukr.fiz.zhurn.,* **32**(6), p.848-851 (1987).
8. V. V. Artamonov, A. V. Pogorelov, M. Renucci, M. Ya. Valakh, Micro-Raman characterization of SiC polytype natural heterostructures //*Proc. SPIE*, **2543**, pp.46-51 (1995).
9. S. Nakashima and H. Harima, Raman investigation of SiC polytypes //*Phys.Stat.Sol.*, **162**(1), pp.39-66 (1997).
10. R. A. Stein, P. lanig, S. Leibenzeder, Influence of surface energy on the growth of 6H- and 4H-SiC //*Materials Science and Engineering*, **B11**, pp.69-71 (1992).
11. Yu. A. Vodakov, E. N. Mokhov, A. D. Roenkov, D. T. Saidbekov, Effect of crystallographic orientation on the polytype stabilization and transformation of silicon carbide //*Phys.Stat.Sol.*, **51**(1), pp.209-215 (1979).