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INVESTIGATION OF GROWTH PROCESSES OF INGOTS OF SILICON CARBIDE SINGLE CRYSTALS

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As a result of investigation performed, the possibility of producing silicon carbide single-crystalline ingots grown from seeds in the 1800 to 2600°C range has been established. Silicon carbide single crystal growth in vacuum has been shown to be very promising at low temperatures.

1. Introduction

At present silicon carbide single crystals are mainly produced from the vapour phase by the sublimation technique suggested by Lely in 1955 [1]. Although this method has been considerably modified in the last twenty years, the essential drawbacks inherent in this technique have not been overcome. They include, first of all, uncontrolled nucleation of crystals and dendrite-like growth. For controlling the nucleation process we, as in [2], have proposed growing single crystals on SiC single-crystalline seeds which are placed in the holes of a graphite crystallization cylinder [3] in a certain way. This results in a considerable increase in the size and quantity of perfect SiC single crystals. However, to grow structurally perfect bulky single crystals of the various polytypes of silicon carbide, new methods of growing SiC crystals need to be investigated.

2. Experiment

The investigations of mass transfer and growth kinetics of silicon carbide single crystals from the vapour phase [3–5], which have been carried out, resulted in the successful solution of the problem of producing silicon carbide single-crystalline ingots [6]. The method proposed, unlike [7], is based upon the classical scheme of supersaturated vapour condensation on a single-crystalline seed in a quasi-closed volume (fig. 1), which was first utilized for producing ZnS ingots [8]. Single-crystalline platelets of SiC with {0001} faces are used as seeds (4). The seeds of polycrystalline silicon carbide synthesized from silicon and carbon of semiconductor purity [3] are used as vapour source (2) and are placed either around a thinwalled graphite cylinder (3) or inside it. Good results have been obtained when a solid graphite cylindrical block was used as a crucible, having a hole bored in place of a thin-walled graphite cylinder. In this case a single-crystalline seed of SiC was also placed on top, as in fig. 1, and the starting polycrystalline silicon carbide material was inserted into the bored hole. The shape of ingot grown is determined

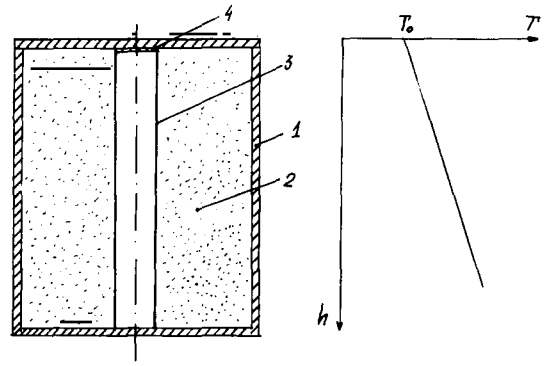

Fig. 1. Diagram of producing silicon carbide single-crystal ingots in a quasi-closed volume: (1) graphite crucible; (2) starting polycrystalline silicon carbide; (3) thin-wall shaping graphite cylinder; (4) single-crystalline SiC seed.

either by the shape of a graphite thin-walled cylinder (3), or by the shape of the hole inside the graphite block. The investigation of the growth process of ingots was carried out in the 1800 to 2600°C temperature range (T_0) at partial argon pressures from 10^{-4} to 760 Torr in the setups described in ref. [9].

Silicon carbide ingots as well as plates cut out of ingots were studied by X-ray structural analysis. X-ray topograms from thin platelets were taken by the Lang method [10]. The ingots were studied by a modified Schultz method [11]. To obtain the reflection from the ingot top the reflection (00.12) was used.

3. Experimental results and their discussion

As our investigations have shown, the utilization of single-crystalline seeds results in growing ingots of single-crystalline silicon carbide in the 1800 to 2600°C temperature (T_0) range. The growth rate of ingots was determined in this case by the growth temperature, axial temperature gradient and the pressure of the inert gas – argon. The dependence of the ingot growth rate on these parameters is similar in shape to the one obtained in the growth of SiC epitaxial layers [5]. The diameters of the ingots grown depended on the seed areas and on the diameters of the graphite cylinders (3) (or on the diameters of the holes in the graphite blocks). The length of the ingots was dependent on the time of the complete decomposition of the silicon carbide starting material.

Some investigations have been carried out with a view to reducing the growth temperature of the silicon carbide ingots. In order to obtain extra-pure ingots it is advisable to grow crystals in vacuum.

The advisability of lowering at silicon carbide single-crystal growth temperatures (including the growth of epitaxial layers) can be based on the following three requirements:

(1) The improvement of the purity of material produced. The main uncontrolled impurity in silicon carbide is boron, whose source is graphite. (It is assumed that when growing in vacuum, one can achieve the required purity with respect to nitrogen.) Let boron concentration in graphite be C_B. The solubility of boron in SiC, N_B^0, depending on temperature, obeys the following relation [12]

$$N_B^0 = 10^{23} \exp(-1.6\ \mathrm{eV}/kT) \tag{1}$$

at boron vapour pressure in the vapour phase equal to saturated P_0. At boron concentration in graphite C_B the boron vapour pressure over graphite will be (assuming the validity of Henry's law):

$$P = C_B P_0 , \tag{2}$$

and its solubility in SiC will be, respectively,

$$N_B = C_B \times 10^{23} \exp(-1.6\ \mathrm{eV}/kT) . \tag{3}$$

The decrease in the growth temperature to 2000 K resulted in a lower boron content in SiC by the factor of 25, as compared to the crystals produced at 3000 K;

(2) The raising of efficiency of single-crystal production. The rate of graphite diffusion mass transfer from the heater as a result of its evaporation, to the adjacent screen is dependent on the equation

$$J_C \simeq (D_{C-Ar} Q_C P_C / R^2 T^3)(\mathrm{d}T/\mathrm{d}x)_C . \tag{4}$$

The rate of silicon carbide ingot growth under conditions limited by the diffusion mass transfer is equal to

$$J_{SiC} \simeq (D_{SiC-Ar} Q_{SiC} P_{SiC} / R^2 T^3)(\mathrm{d}T/\mathrm{d}x)_{SiC} , \tag{5}$$

where J_C determines the heater life which is proportional to $1/J_C$; J_{SiC} determines the productivity of the SiC ingot growth method; D_{C-Ar} and D_{SiC-Ar} are C and SiC diffusion coefficients in argon; Q_C and Q_{SiC} are activation energies of C and SiC evaporation respectively; P_C and P_{SiC} are carbon – and SiC – vapour pressure at temperature T; $(\mathrm{d}T/\mathrm{d}x)_C$ and $(\mathrm{d}T/\mathrm{d}x)_{SiC}$ are temperature gradients near the heater and in the growth zone of SiC ingots; R is the universal gas constant.

The efficiency of the whole process can be characterized as the ratio

$$G = J_{SiC}/J_C = D_{SiC-Ar} Q_{SiC} P_{SiC} (\mathrm{d}T/\mathrm{d}x)_{SiC} \times [D_{C-Ar} Q_C P_C (\mathrm{d}T/\mathrm{d}x)_C]^{-1} . \tag{6}$$

Apart from the vapour pressures, all other parameters are slightly dependent on temperature, and as a result (6) can be rewritten

$$G \simeq C^1 P_{SiC}/P_C \,, \tag{7}$$

where

$$P_{SiC} = A_1 \exp(-150 \text{ kcal mol}^{-1}/RT) \,,$$

$$P_C = A_2 \exp(-170 \text{ kcal mol}^{-1}/RT).$$

In its final form eq. (7) can be given as

$$G = C \exp(20 \text{ kcal mol}^{-1} RT). \tag{8}$$

As follows from (8) the amount of silicon carbide grown per unit mass of the graphite heater evaporated is increased 4.5 times when the growth temperature is reduced from 3000 to 2000 K.

(3) The decreased concentration of silicon and carbon vacancies and the resulting decrease of deflection from stoichiometry, since, as our calculations have shown, point defects in SiC, as well as in GaP, greatly affect the efficiency of luminescence.

Because of this the growth of ingots was subsequently produced at about 1800°C in 10^{-3} to 10^{-4} Torr vacuum, the axial temperature gradient amounting to about 30 deg/cm. It was established that under such conditions the growth of silicon carbide single-crystalline ingots was accomplished with the rate of up to 1.6–2 mm/h. Fig. 2 shows the X-ray diffraction topogram from the top of the silicon carbide ingot which confirms its single-crystalline structure. The ingot was grown in the [0001] direction, in 10^{-3} Torr vacuum at about 1800°C, the growth time being 5 h; the ingot has a 8 mm diameter and is 8 mm long. The ingots grown had always the same polytype structure. Most of them were of 6H structure, but we obtained ingots of 15R polytype and 4H polytype as well. The ingots did not contain disordered D-layers which are typical for SiC crystals grown by the Lely technique [13], and interlayers of other polytypes different from the ingot polytype structure. For obtaining ingots of different polytypes, growth can be

Fig. 2. X-ray diffraction topogram from the ingot top of single-crystalline silicon carbide ingot. Reflection from (00.12) plane.

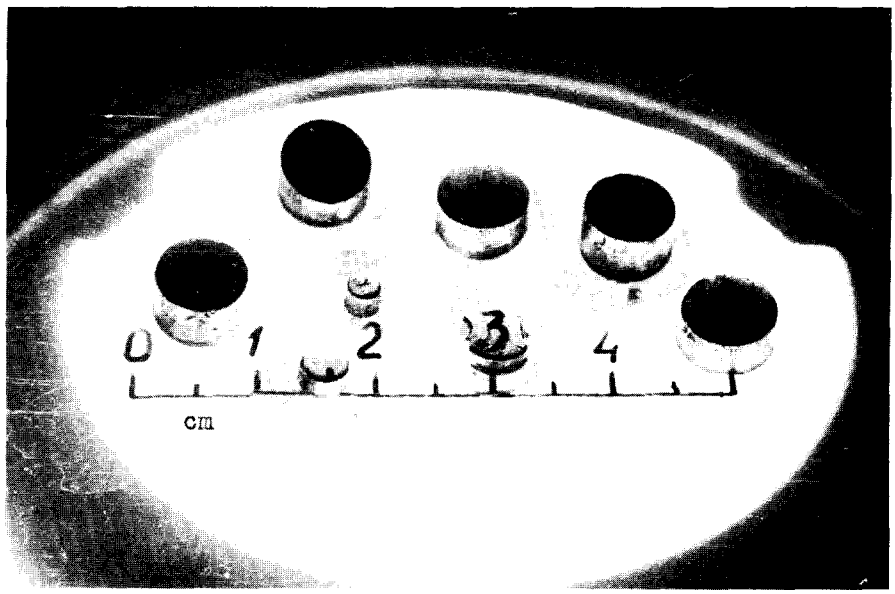

Fig. 3. Photograph of SiC ingots grown at ~1800°C.

produced on the planes of respective seeds deflected from the (0001) plane by the angle of α, as was described by us in [5].

In fig. 3, a photograph of ingots grown under the same conditions and doped with nitrogen is given. In pure ingots the (Nd–Na) concentration was at the level of 1×10^{16} cm^{-3}.

After boron diffusion the ingots acquired the effective yellow luminescence at room temperature, the luminescence efficiency in ingots with a starting concentration of (Nd–Na) equal to 1×10^{16} to 5×10^{17} cm^{-3}, being several times higher than in crystals grown by the Lely technique with (Nd–Na) equal to 2×10^{18} cm^{-3}.

3. Conclusion

As a result of investigations performed, the possibility of producing silicon carbide single-crystalline ingots grown from seeds in the 1800 to 2600°C range has been established. Silicon carbide single crystal growth in vacuum has been shown to be very promising at low temperatures.

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