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Investigation of the Process of Silicon Carbide Crystal Growth from Vapour Phase

The growth of SiC monocrystals from vapour phase by the sublimation method represents a superposition of several processes, namely evaporation of the source material, nucleation, diffusion or convection of the vapour to the growing crystals, and crystal growth under a specific mechanism of heat-exchange. The control of the process of growing of structurally perfect single crystals is impossible without studying each of these processes. The purpose of the present work is to determine the concentration distribution of SiC vapour in the crystal growth zone.

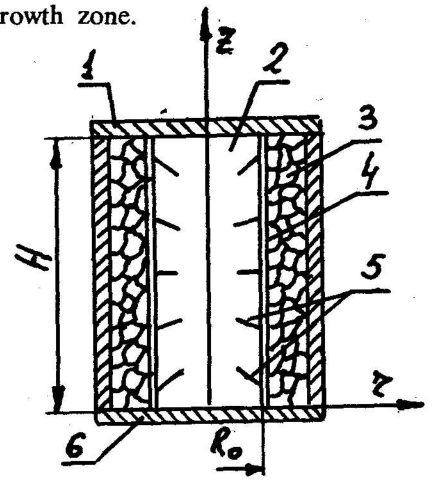

Fig.1 Construction of the graphite crucible for the growth of SiC monocrystals 1 - top lid; 2 - crystal growth zone; 3 - source poly-crystalline SiC; 4 - graphite crystallization sleeve; 5 - growing crystals; 6 - bottom lid.

The single crystals of SiC obtained in the crystal growth zone (Fig.1) are of various habits (flat-parallel platelets, stepped crystals with a single naturally smooth face, etc.). Furthermore it was established by experimental investigation of the growth rate along the c axis that the ratio of the growth rates of the natural face (0001) and that of the stepped-face of the crystals obtained in the middle part of the crucible amounts to 1. At the same time, for the crystals growing at the lids of the crucible, this ratio decreases to about 10^{-4}, i.e. the predominant growth occurs towards higher temperatures. This phenomenon is not satisfactorily explained until now.

For calculating the concentration distribution of SiC vapour in the crystal growth zone (Fig.1) one must know the mechanism of vapour propagation from the growth zone walls towards the lids (diffusion or convection). The investigation of the gas dynamics in such cases is carried out by a physical modelling or by using the similarity criteria. We profited by the second method as the simpler one. In order to determine the heat transfer mechanism in the closed cavity we have used the experimental dependence of convection factor ε_k on the product of the similarity criteria of Grashof (Gr.) and Prandtl (Pr.) [1]. Using the reference data for argon (this gas is used during SiC crystal growth) as well as the characteristics of the growth zone of the used crucible construction we obtain Gr.Pr = 67. From the relationship ε_k = f(Gr.Pr.) [1] one may conclude that the heat transfer in the growth zone is obtained through heat conduction and, hence, the SiC vapour transfer is by diffusion in argon (convection takes place when Gr.Pr >1000).

For the stationary case corresponding to the conditions of crystals growth, the distribution of vapour concentration in the growth zone was obtained by solving the Laplace equation in cylindrical coordinates, taking into account the axial symmetry of the system:

$$\partial^2 n/\partial r^2 + (1/r)\partial n/\partial r + \partial^2 n/\partial z^2 = 0 \tag{1}$$

The equilibrium concentrations of vapour on the growth zone walls were taken as boundary conditions. We assume that the temperature in the middle of the zone on the wall is equal to T_0. Then the temperature distribution on the wall in a linear approximation is:

$$T_z = T_0 - |z - H/2|\, \partial T/\partial z \tag{2}$$

$$T_0 = 2800\text{K}, \qquad \partial T/\partial z > 0$$

and the boundary condition on the wall of the growth zone is as follows :

$$n_z = \frac{A\exp\left[\dfrac{\Delta E}{R(T_0 - |z - H/2|\, \partial T/\partial z)}\right]}{k(T_0 - |z - H/2|\, \partial T/\partial z)}, \tag{3}$$

where $A = 4.3323\times10^{13}\, J/m^3$, ΔE = 135.6 kcal/mole is the activation energy of the sublimation process, **R** is the gas constant, **k** is Boltzmann's constant.

Analogously for the lid of the crucible:

(4) $$T_r = T_2 + r\,\partial T/\partial r,$$

where $\mathbf{T_2}$ is the temperature in the middle of the lid, $\partial T/\partial r > 0$.

Equations (2) and (4) are connected by the equation:

(5) $$T_2 + R_0\,\partial T/\partial r = T_0 - H/2\,\partial T/\partial z\,,$$

where R_0 and H are the radius and the height of the growth zone, respectively.

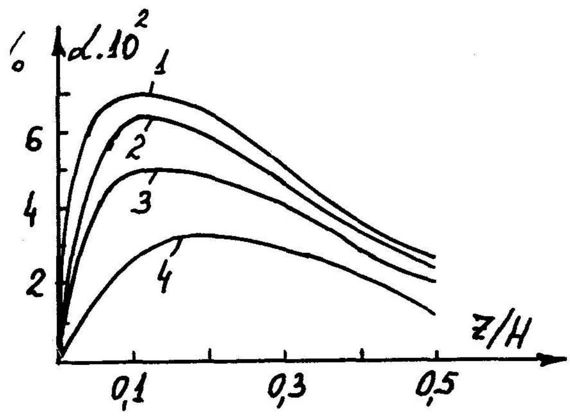

Fig.2. Dependence of the supersaturation α on the height z at different radii **r**:
1 - $r/R_0=0{,}1$; 2 - $r/R_0=0{,}3$;
3 - $r/R_0=0{,}5$; 4 - $r/R_0=0{,}7$;
($\partial T/\partial r=400K/m$, $\partial T/\partial z \doteq 400K/m$,
$R_0=0{,}015m$, $H=0{,}07m$)

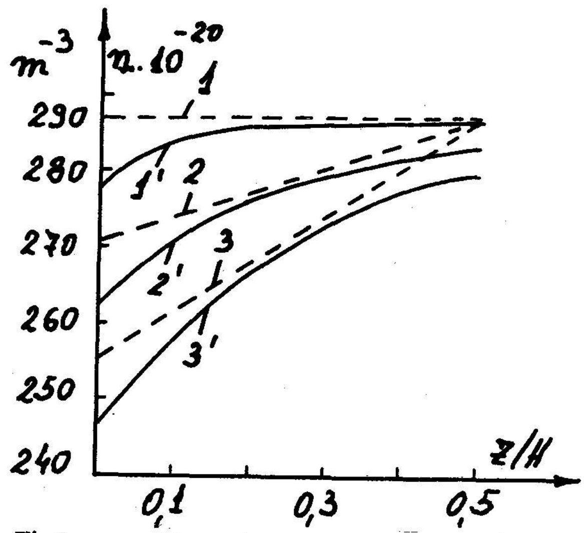

Fig.3. Dependence of the concentration **n** on the height z at different radii **r** and axial temperature gradients:
1 - $r/R_0=1$, $\partial T/\partial z=0K/m$;
1' - $r/R_0=0{,}3$, $\partial T/\partial z=0K/m$;
2 - $r/R_0=1$, $\partial T/\partial z=200K/m$;
2' - $r/R_0=0{,}3$, $\partial T/\partial z=200K/m$;
3 - $r/R_0=1$, $\partial T/\partial z=400K/m$;
3' - $r/R_0=0{,}3$, $\partial T/\partial z=400K/m$;
($\partial T/\partial r=400K/m$, $R_0=0{,}015m$, $H=0{,}07m$)

The concentration distribution of SiC vapour along the lid is of the kind:

$$(6)\qquad n_r = \frac{A \exp\left[-\dfrac{\Delta E}{R(T_2 + r\, \partial T/\partial r)}\right]}{k(T_2 + r\, \partial T/\partial r)}$$

Equation (1) at the boundary conditions (3) and (6) has been solved for a radial gradient $\partial T/\partial r = 400K/m$ and axial gradients $\partial T/\partial z = 0,200,400,800K/m$. The solution of the Laplace equation has been presented as a sum of three solutions, each one satisfying the boundary condition on one of the walls and being zero on the other two ones [2]. The solutions can be written in the form of Fourier-Bessel series. For the case considered, the solution satisfying the boundary condition on the cylinder wall can be approximated by the sum of the first eight terms of the corresponding series. The other two solutions satisfying the boundary conditions on the top and bottom walls are approximated by the sum of the first fifty terms of their corresponding series. The accuracy of the calculation for the concentration which was obtained in a quarter of the examined volume is better than 0.1% .

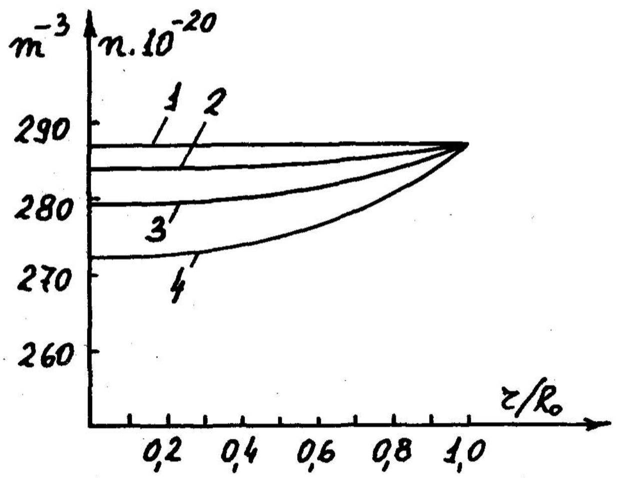

Fig.4. Dependence of the concentration n on the radius r at z/H=0,5 and different axial temperature gradients:
1 - $\partial T/\partial z = 0K/m$; 2 - $\partial T/\partial z = 200K/m$;
3 - $\partial T/\partial z = 400K/m$; 4 - $\partial T/\partial z = 800K/m$;
($\partial T/\partial r = 400K/m$, $R_0 = 0{,}015m$, $H = 0{,}07m$)

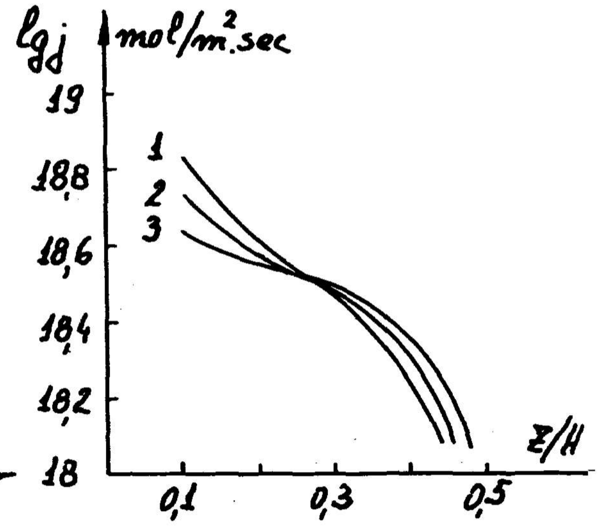

Fig.5. Dependence of the diffusion flows of SiC vapour on the height at different radii r:
1 - $r/R_0 = 0{,}1$; 2 - $r/R_0 = 0{,}5$;
3 - $r/R_0 = 0{,}7$;
($\partial T/\partial r = 400K/m$, $\partial T/\partial z = 200K/m$, $R_0 = 0{,}015m$, $H = 0{,}07m$)

For the calculation of the distribution of the supersaturation in the growth zone, it is necessary to know the equilibrium concentration, n_s, which can be calculated provided the temperature field in the zone is known. For the stationary process and a given temperature distribution along the boundary the temperature distribution in the zone is described by Laplace equation $\Delta T=0$ at boundary conditions (2) and (4). This equation was solved as equation (1). The distribution of the supersaturation $\alpha=[(n-n_s)/n_s].100\%$ in the vapour phase was obtained from the known temperature and concentration distribution in the zone and calculating n_s at each point. As an illustration, in Fig.2 the supersaturation distribution at $\partial T/\partial r=400K/m$ and $\partial T/\partial z=400K/m$ is shown.

The obtained data from our calculations permit to investigate the distribution of SiC vapour concentration in the growth zone as a function of the axial temperature gradient (Figs.3, 4). From Figs.3 and 4 it can be seen that the concentration of SiC vapour is the highest at zero temperature gradient and that maximum homogeneity in the distribution of SiC vapour along the axes **z** and **r** can be achieved at zero temperature gradient.

Our results agree very well with the experimental data from the literature [3, 4] according to which the best conditions for SiC growth can be achieved by decreasing to a minimum the temperature gradient. Furthermore the predominant crystal growth in [0001] direction, i.e. in the direction of higher temperatures, can be explained by means of the calculated distributions. Using the first Fick's law, the distribution of the diffusion flows of SiC vapour has been calculated. In Fig.5 the distributions of the diffusion flows are presented as a function of **z** for $\partial T/\partial r=400K/m$ and $\partial T/\partial z=200K/m$. It can be seen that at small values of **z**, the component of the flows of SiC vapour along the **z** axis increases, while at $z=H/2$ it tends to zero. Hence, it is clear that the crystals grow in the form of platelets in the places of the growth zone at $z \Rightarrow H/2$. With **z** decreasing the orientation of the crystal towards the vertical wall of the zone changes. As a result of this the diffusion flow of SiC vapour evidently is directed along the normal to the $(000\bar{1})$ plain which grows more quickly than the (0001) plain, against the flow of the vapour, i.e. in the direction of higher temperatures. Namely here stepped bulk crystals usually grow.

References

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