

## Growing of sapphire for optics and optoelectronics by the HDC method in a protective atmosphere

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The gas environment process formation in the furnace for sapphire growth by horizontal directional crystallization equipped by a graphite heating assembly has been studied during the evacuation and the inert gas (Ar, He) bleeding. The effect of the furnace blowing by the inert gas on concentration of reducing components (CO, H<sub>2</sub>) and on optical properties of sapphire crystals grown in He atmosphere at 1 to 50 Torr pressure has been studied. The critical concentrations of the reducing components in the protective environment have been determined for growing of sapphire intended for standard optical and optoelectronic applications.

Изучен процесс формирования газовой среды в установке для выращивания сапфира методом горизонтальной направленной кристаллизации с углеграфитовым тепловым узлом в условиях форвакуумной откачки и в случае напуска инертного газа (Ar, He). Проведены исследования влияния продувки печи инертным газом на концентрацию восстановительных компонент и оптические свойства кристаллов сапфира, выращенных в атмосфере He при давлении 1–50 торр. Определены предельные концентрации восстановительных компонент (CO, H<sub>2</sub>) в защитной среде выращивания сапфира для стандартной оптики и оптоэлектроники.

To date, the gas technology has been mastered for growing high optical quality sapphire by the horizontal directional crystallization (HDC) method in CO atmosphere at about 1 Torr pressure [1]. The gas technology is more economical due to the use of graphite heating assembly instead of the tungsten-molybdenum one. This provides a higher borrowing power in the world-wide market of sapphire for optics and optoelectronics as compared to the traditional vacuum technology. The growing atmosphere in the graphite heating assembly is formed mainly due to CO and H<sub>2</sub> regeneration reactions, namely, CO<sub>2</sub> + C → 2CO and H<sub>2</sub>O + C → H<sub>2</sub> + CO. These processes, however, cause an appreciable consumption of graph-

ite, thus resulting in a reduced thermal insulation efficiency and a necessity for graphite shield replacement (every 5 or 7 crystallization runs). In this connection, one possible way to further economic improvement of the HDC method consists in elaboration of optical sapphire growing in Ar or He based protective gas media (50 to 800 Torr pressure) that make it possible to reduce considerably the melt evaporation rate and the intensity of the regeneration reactions of reducing components. To develop such a technology, it is necessary to determine the reducing component concentration being critical for growing optical crystals containing no light-scattering micro-inclusions [2] and to seek for ways to

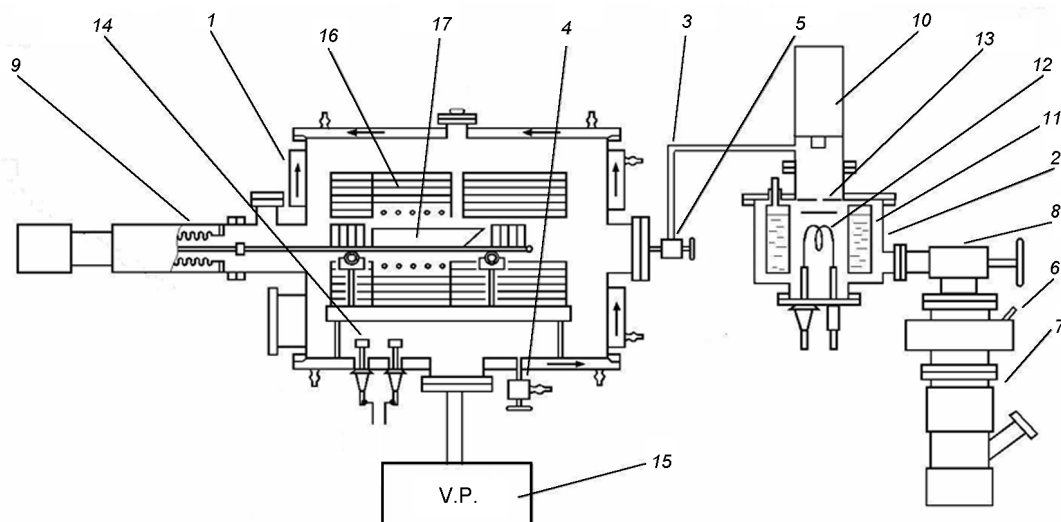


Fig. 1. Experimental setup: 1, growth chamber; 2, measuring chamber; 3, connecting tube; 4, gas bleed-in valve; 5, bleeder; 6, 11, nitrogen traps; 7, diffusion pump; 8, gate; 9, rod; 10, mass-spectrometer; 12, titanium atomizer; 13, diaphragm; 14, current bushings; 15, low-vacuum pump; 16, graphite heating assembly; 17, crucible.

control the preset atmosphere formation in the furnace.

To that end, we have studied in detail the gas medium composition using mass-spectroscopy. Studied have been the atmospheres formed spontaneously (under evacuation using a low vacuum pump) when growing sapphire crystals by the HDC method in a furnace equipped by a graphite heating assembly at the residual gas pressures of 0.05 to 1 Torr. These conditions make it possible to obtain the crystals having the highest attainable optical characteristics. Also, the growing under inert gas blowing into the furnace up to 800 Torr pressure was studied. The experiments were done using a modernized experimental growing unit [3] equipped by a ROMS-4 HF mass-spectrometer (see Fig. 1). To take the gas medium samples, a needle bleeder 5 was used connecting the growth chamber (GC) 1 with the measuring chamber (MC) 2 containing a low-temperature titanium pump (LTP) comprising a nitrogen trap 11 and titanium atomizer 12. After an appropriate vacuum preparation, the residual gas pressure in the closed MC volume may be as low as about  $10^{-9}$  Torr. In this investigation, the LTP was not used, so the residual pressure was  $5 \cdot 10^{-7}$  Torr. The measurements were done using the graphite heating assembly 16 with and without the crucible 17 containing granulated aluminum oxide powder.

Fig. 2 (curves 1-6) shows the characteristics of the medium composition (with-

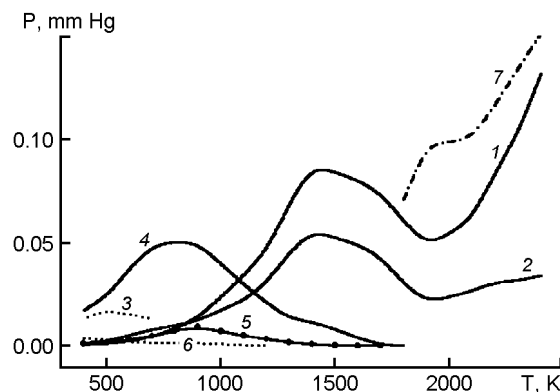
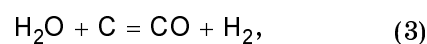
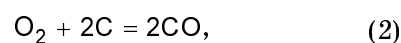
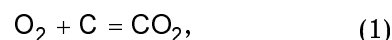


Fig. 2. Gas atmosphere composition in the furnace during its heating up to 2350 K. 1, CO; 2, H<sub>2</sub>; 3, N<sub>2</sub>; 4, H<sub>2</sub>O; 5, CO<sub>2</sub>; 6, O<sub>2</sub> without a crucible with Al<sub>2</sub>O<sub>3</sub> powder; 7, CO with a crucible with Al<sub>2</sub>O<sub>3</sub> powder.

out inert gas bleeding) in the furnace without the crucible as a function of temperature that was recorded in the heater zone using a tungsten-rhenium thermocouple. The temperature rise rate was about 400 K/h. The gas medium composition is seen to vary considerably at the furnace temperature elevation. The atmosphere composition is influenced mainly by the following reactions [4, 5]:



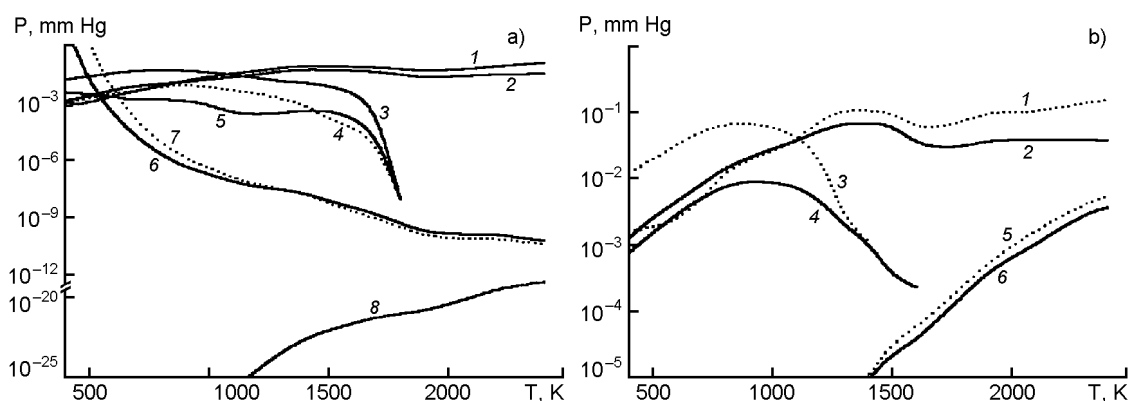
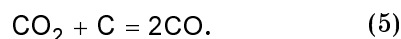
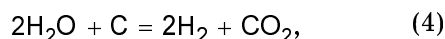


Fig. 3. Experimental partial gas pressures in the growth chamber as compared to the calculated equilibrium values: (a) without a crucible with  $\text{Al}_2\text{O}_3$  powder: 1, CO; 2,  $\text{H}_2$ ; 3,  $\text{H}_2\text{O}$ ; 4,  $\text{CO}_2$ ; 5,  $\text{O}_2$  (experimental data); 6,  $\text{H}_2\text{O}$ ; 7,  $\text{CO}_2$ ; 8,  $\text{O}_2$  (calculated equilibrium data over the graphite surface at experimental  $P_{\text{CO}}$  and  $P_{\text{H}_2}$  values). (b) with a crucible with  $\text{Al}_2\text{O}_3$  powder: 1, CO; 2,  $\text{H}_2$ ; 3,  $\text{H}_2\text{O}$ ; 4,  $\text{CO}_2$ ; (experimental data); 5,  $\text{H}_2\text{O}$ ; 6,  $\text{CO}_2$  (calculated equilibrium data over the  $\text{Al}_2\text{O}_3$  surface at experimental  $P_{\text{CO}}$  and  $P_{\text{H}_2}$  values).



According to the literature data [4, 5], the graphite oxidation reactions (1) and (2) start at  $t \sim 700$  to  $750$  K, while carbon dioxide is formed mainly at temperatures lower than  $900$  K and carbon monoxide being the major oxidation product at  $t > 1100$  K due to reaction (3). Intense interaction of water vapor with graphite (reactions (3) and (4)) takes place at  $t > 1100$  to  $1300$  K. Thus, the results obtained agree well with literature data.

A characteristic feature of the medium at low temperatures ( $<1300$  K) consists in a high water vapor content that is due to a rather high sorption ability of graphite. Above  $1200$  to  $1300$  K, the medium becomes a reductive one, with CO and  $\text{H}_2$  as the main atmosphere components, the relative CO content increases as the temperature rises. Perhaps it is caused by the fact that CO is formed not only from water vapor (reaction (3)) but also from chemisorbed oxygen that is desorbed mainly as CO (reaction (2)).

A comparison of the experimental data with thermodynamic consideration of processes running in the C-gas atmosphere- $\text{Al}_2\text{O}_3$  system has shown that the furnace gas medium is not equilibrium up to pre-melting temperatures and its composition is defined predominantly by gas desorption (Fig. 3). At low temperatures, the  $\text{O}_2$ ,  $\text{CO}_2$ , and water vapor exceed considerably the equilibrium values over graphite that would be observed for experimental  $P_{\text{CO}}$  and  $P_{\text{H}_2}$

values (Fig. 3a). At  $1440$ – $1500$  K, the partial pressures of those atmosphere components decrease gradually and at about  $1800$  K drop under the measurement sensitivity threshold and approach the equilibrium values over graphite. The presence of a crucible with  $\text{Al}_2\text{O}_3$  powder does not effect appreciably the atmosphere composition up to pre-melting temperatures (Fig. 3b). Only an increasing contribution from CO is observed at  $t > 1800$  K (Fig. 2, curve 7) when the influence of  $\text{Al}_2\text{O}_3$  evaporation and its vapor interaction with graphite becomes appreciable. The  $\text{CO}_2$  and water vapor pressures do not increase up to equilibrium values over  $\text{Al}_2\text{O}_3$  as the temperature increases up to  $2100$  K. At those temperatures, the  $P_{\text{CO}_2}$  and  $P_{\text{H}_2\text{O}}$  values are outside of the measurement sensitivity, both in the presence and in absence of a crucible with  $\text{Al}_2\text{O}_3$ . The melt exposure to a constant temperature of about  $2350$  K for 24 h results in a further furnace degassing and a decreased relative content of hydrogen down to about 4 vol %. The relative  $\text{H}_2$  content is reduced also when the low-vacuum pumping-out rate decreases.

Thus, the mass-spectrometric measurements and thermodynamic analysis of the data obtained have shown that the composition of gas medium being formed in a growth furnace during the temperature rise is defined mainly by water vapor and oxygen desorption and the interaction thereof with the graphite heating assembly elements. At high temperatures ( $>1800$  K), the interaction of  $\text{Al}_2\text{O}_3$  and its vapor with CO,  $\text{H}_2$ , and graphite is also of an impor-

Table 1. Composition of protective media formed in a graphite furnace (without inert gas blowing)

Growing medium formed in the growth furnace	CO+H <sub>2</sub> partial pressure, Torr	P <sub>H2</sub> /P <sub>CO</sub>
CO, H <sub>2</sub> (under low-vacuum pumping-out)	0.1	0.1
Ar, He + (COH <sub>2</sub> ), 50–100 Torr, no blowing	1–3	0.3
Ar, He + (COH <sub>2</sub> ), 800 Torr no blowing	7–10	0.5

tance. At a long-term exposure of melted aluminum oxide, it is just carbon monoxide that becomes the major component of the low-vacuum (0.1 to 1 Torr) gas medium. However, as hydrogen is a more active reducing agent than CO, its influence on the crystal optical characteristics may be considerable and thus requires a further study.

The studies of the medium compositions formed spontaneously in the working volume under inert gas bleeding have shown that in this case, the concentration of reducing components exceeds considerably (Table 1) the critical value that, at a first approximation, can be assumed to be of about 0.1 Torr, that is, the CO pressure under low-vacuum pumping-out. That value is confirmed also by the calculations carried out before [7]. Thus, it can be assumed that the growing of optical quality crystals using an inert gas to reduce the melt evaporation is possible only under forced decrease of the partial pressure of reducing components (CO, H<sub>2</sub>) below the critical level. This can be attained, under alia, by an intense blowing of the furnace by a pure inert gas [8]. In this work, the atmosphere formation under inert gas blowing has been studied and the admissible content of reducing components in the growth chamber has been determined in experiment.

The concentration of reducing components in the furnace depends on the accumulation rate thereof that is defined by the flow balance:

$$\frac{dN_r}{dt} = J_r - J_r^-, \quad (6)$$

where  $J_r$  is the formation rate of the reducing components and  $J_r^-$ , the removal rate thereof from the chamber. Assuming the gas in the chamber to be intermixed, we can write

$$J_r^- = J \cdot \frac{P_r}{P}, \quad (7)$$

where  $P_r$  is the partial pressure of the reducing components;  $P$ , total pressure in the growth chamber;  $J$ , total gas flow from the

chamber. If the total pressure is kept constant, the following equality is valid:

$$J = J_r + J_i, \quad (8)$$

where  $J_i$  is the inert gas inlet flow. Then, combining the Eqs.(6)–(8), and taking into account the relationship  $P_r = N_r kT/V$  ( $V$  is the growth chamber volume;  $T$ , gas temperature;  $k$ , the Boltzmann constant), we get an equation for the partial pressure of reducing components in the growth chamber:

$$\frac{dP_r}{dt} + (J_r + J_i) \frac{P_r kT}{P V} - J_r \frac{kT}{V} = 0. \quad (9)$$

Assuming the flows and temperature are constant and  $P_r \ll P$ , the Eq.(9) can be considered as a homogeneous linear differential equation. Let  $P_r^0$  be the initial content of reducing components; then the solution of (9) has the form

$$P_r = (P_r^0 - P_r^*) \cdot \exp\left(-\frac{t}{t^*}\right) + P_r^*, \quad (10)$$

$$P_r^* = \frac{P}{1 + \frac{J_i}{J_r}}, \quad (11)$$

$$t^* = \frac{PV}{(J_i + J_r)kT}. \quad (12)$$

It is seen from (10) that when the growth chamber is blown through with a pure inert gas, the content of reducing components after a time  $t^*$  attains a stationary value  $P_r^*$  that is defined by the flow ratio of the medium components and depends heavily on its pressure (see (6)). If  $P_{cr}$  is the critical content of reducing components, then, to grow the sapphire crystals containing no micro-inclusions, it is necessary to provide the flow rate

$$J_i \geq \left(\frac{P}{P_{cr}} - 1\right) \cdot J_r. \quad (13)$$

That is, using the blowing, it is more difficult to purify a medium of a higher pressure,

other conditions being the same. The time  $t^*$  to attain the stationary medium is defined by the gas flows, pressure, and volume.

Using (13), we have estimated the critical inert gas flow for various growth medium pressures (Fig. 4). The results obtained are in agreement with those reported before [2] where only a relatively intense blow-through at  $J_r > 200\text{--}300\text{ dm}^3/\text{h}$  provided a reduced micro-inclusion concentration when the Ar atmosphere at about 760 to 800 Torr pressure was used. It follows from Fig. 4 that at the medium pressure of  $\leq 100$  Torr, a substantially lower gas flow of about  $50\text{ dm}^3/\text{h}$  is required.

The melt evaporation rate is another parameter of importance that characterizes the gas atmosphere protective properties. The measurements of the evaporation rate as a functions of the protective medium (Ar, He) pressure have shown that an appreciable reduction (by a factor of 2 to 3) is observed already at pressures above 30 Torr. The inert gas pressure range of 50 to 100 Torr can be assumed to be optimum at the crystallization chamber blowing with inert gas and growing of optical sapphire.

We have studied the optical properties of sapphire crystals ( $90 \times 50 \times 300\text{ mm}^3$  size) grown in He atmosphere under 1 to 50 Torr pressure in a furnace with graphite heating assembly. Fig. 5 shows the transmission spectra for the initial and middle zones of the crystals grown under pure helium blowing ( $50\text{ dm}^3/\text{h}$ ) as compared to those obtained in low-pressure CO + H<sub>2</sub> medium (about 0.1 Torr). The spectra are seen to contain absorption bands at 205 and 230 nm wavelengths corresponding to  $F$  and  $F^+$  centers, respectively, the concentration and ratio thereof are known to be defined by the growth medium reducing potential,

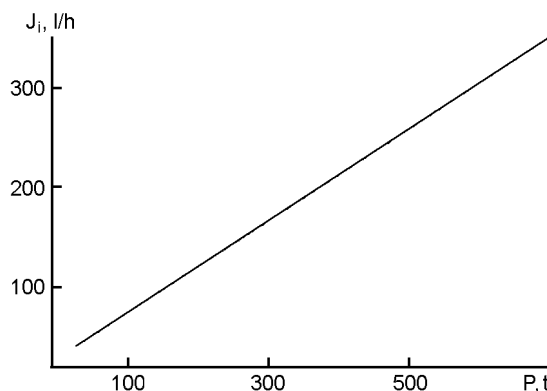


Fig. 4. Dependence of the inert gas critical flow rate on the growth atmosphere pressure ( $J_r = 0.1\text{ dm}^3/\text{s}$  at  $P_r = 0.5$  Torr).

as well as by the impurity content and charge state. The He blowing results in a decrease of the medium reducing potential (see Fig. 5b, He 1.2 Torr). To estimate qualitatively the growth medium reducing potential, the CO and H<sub>2</sub> concentrations were measured in the course of growing using a mass-spectrometer. To that end, the instrument was connected to an industrial crystal growth unit. The measured data (Table 2) show that the growth chamber blowing with helium provides the hydrogen concentration reduction and hinders the carbon monoxide accumulation ( $\leq 1$  Torr). The blowing efficiency drops as the medium pressure rises.

In crystals grown in He (50 Torr) under  $50\text{ dm}^3/\text{h}$  blowing, the micro-inclusions (1 to  $5\text{ }\mu\text{m}$ ) are contained at a concentration of  $\leq 10^4\text{ cm}^{-3}$  that is substantially lower than at growing in Ar (760–800 Torr) being  $\leq 10^6\text{ cm}^{-3}$  [2]. Since the formation thereof is due to the melt anionic non-stoichiometry [9],

Table 2. Composition of sapphire growth medium (under blowing)

Gas	Low-pressure reducing atmosphere (about 0.1 Torr), Torr ( vol %.)		He blowing, $50\text{ dm}^3/\text{h}$ (about 1.2 Torr), Torr ( vol %.)		He blowing, $50\text{ dm}^3/\text{h}$ (about 50 Torr), Torr ( vol %.)	
	1	2	1	2	1	2
H <sub>2</sub>	$1.51 \cdot 10^{-2}$ ( $22 \pm 4$ )	$3.12 \cdot 10^{-3}$ ( $5 \pm 1$ )	$5.95 \cdot 10^{-3}$ ( $0.5 \pm 0.2$ )	$1.7 \cdot 10^{-4}$ ( $0.05 \pm 0.05$ )	$1 \cdot 10^{-1}$ ( $0.2 \pm 0.2$ )	– ( $< 0.1$ )
He	0	0	1.1 ( $91.6 \pm 0.2$ )	1.05 (87.8 $\pm$ 0.2)	49.45 ( $98.9 \pm 0.2$ )	49.4 ( $98.8 \pm 0.2$ )
CO	$5.1 \cdot 10^{-2}$ ( $78 \pm 4$ )	$6.75 \cdot 10^{-2}$ ( $95 \pm 1$ )	$9.37 \cdot 10^{-2}$ ( $7.9 \pm 0.2$ )	$1.4 \cdot 10^{-1}$ ( $12.15 \pm 0.05$ )	$4.5 \cdot 10^{-1}$ ( $0.9 \pm 0.2$ )	$5.5 \cdot 10^{-1}$ ( $1.1 \pm 0.2$ )

Note: 1, at the growing onset; 2, at the growing middle stage (20 h later). The sum of other gases (CO<sub>2</sub>, N<sub>2</sub>, etc.) did not exceed 2 vol % in the low-pressure reducing atmosphere;  $\leq 0.2$  vol % under He blowing (about 50 Torr) and  $\leq 0.05$  vol % under He blowing (about 1.2 Torr).

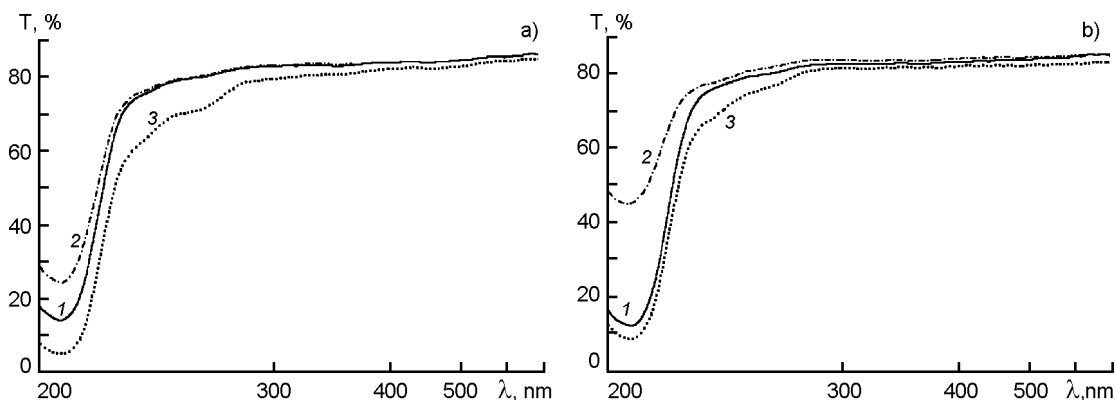


Fig. 5. Sapphire transmission spectra for the initial (a) and middle (b) parts of crystals grown under various gas media (the sample thickness 5 mm); 1 – low pressure CO+H<sub>2</sub> medium (0.1 Torr); 2 – He (1,2 Torr); 3 – He (50 Torr).

it is obvious that a reduction of the micro-inclusion concentration is possible at a further decrease of the reducing component (CO, H<sub>2</sub>) partial pressure in the growth atmosphere below the critical level. The comparative optical quality analysis of crystals and the growth medium composition shows that the critical concentrations are about 0.1 to 0.5 Torr for CO and about 0.01 Torr for H<sub>2</sub>.

Thus, it is possible to prepare sapphire for standard optical and optoelectronic applications in He atmosphere (1 to 50 Torr). The results obtained can be used also to develop a technique for growing of the optical quality crystals under protective gas atmospheres under 800 Torr pressure that is the most prospective for a considerable improvement in economic characteristics and borrowing power of the HDC method at the large-scale sapphire market.

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## Вирощування сапфіру для оптики і оптоелектроніки методом ГСК у захисній атмосфері

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Досліджено процес формування газового середовища в установці для вирощування сапфіру методом горизонтальної спрямованої кристалізації з вуглеграфітовим тепловим вузлом в умовах форвакуумної відкачки та у випадку напуску інертного газу (Ar, He). Проведено дослідження впливу продувки печі інертним газом на концентрацію відновних компонентів (CO, H<sub>2</sub>) та оптичні властивості кристалів сапфіру, що вирощені в атмосфері He при тиску 1–50 тор. Визначено граничні концентрації відновних компонентів у захисному середовищі вирощування сапфіру для стандартної оптики і оптоелектроніки.