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Peculiarities of optical and structure characteristics of sapphire single crystals grown in Ar + CO atmosphere

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Presented are the results of optical and X-ray structure investigations of sapphire crystals grown by the method of HOC in the protective (reducing) medium Ar+CO under a pressure of 10...800 torr. The dependence of the crystals structure perfection on the pressure of the medium is established. It is shown that high-temperature annealing may raise the structure perfection up to the level characteristic of the crystals grown under the conditions of high vacuum (10^{-4} torr). Correlation of the parameters which characterize the structure perfection, with the concentration of anionic vacancies in the crystals, allows to assume that at the growth of sapphire crystals in reducing media, vacancy mechanism may play a noticeable role in the process of formation of dislocations and low-angle dislocation boundaries.

Представлены результаты оптических и рентгеноструктурных исследований кристаллов сапфира, выращенных методом ГНК в защитной (восстановительной) среде Ar + CO в интервале давлений 10...800 торр. Установлена зависимость структурного совершенства кристаллов от давления среды. Показано, что в результате высокотемпературного отжига совершенство структуры может быть повышено до уровня, характерного для кристаллов, выращенных в условиях высокого вакуума (10^{-4} торр). Корреляция параметров, характеризующих совершенство структуры, с концентрацией анионных вакансий в кристаллах позволяет предложить, что при выращивании кристаллов сапфира в восстановительных средах в процессе формирования дислокаций и малоугловых дислокационных границ заметную роль может играть вакансионный механизм.

The use of protective (containing the reducing components H_2, CO) gas media for the growth of sapphire single crystals by the method of horizontally oriented crystallization (HOC) [1] allowed to substitute expensive constructional materials (tungsten and molybdenum) by cheaper carbon graphite, to essentially raise the method's profitability and to bring it to a leading place on the world market of large sapphire elements for mass application [2]. Large-size sapphire crystals grown in CO gas atmosphere under a pressure of 0.1...0.3 torr have high optical quality and structure perfection which compare favorably with the said characteristics of the crystals obtained under the conditions of high vacuum [3].

However, high rate of Al_2O_3 evaporation under such conditions shortens the service life of carbon graphite screens located near the melt, and leads to changes in the heating regimes. This essentially reduces reproducibility of the crystal growth conditions and hinders optimization of the technological programs. Therefore, for further rise of the growth method profitability it is neces-

Table. Content of main impurities in the starting material

Element	Ca	Cr	Fe	Ga	Mg	Na	Si	Ti
Concentration, ppm	<5	<1	<4	<11	<3	7	<18	2...5

sary to decrease the rate of Al_2O_3 evaporation. This may be achieved with higher (>1 torr) pressures of a medium which main component is a gas neutral with respect to Al_2O_3 (e.g. Ar or He). Such a medium is not only protective for W and Mo (the crucible and heater materials), it also allows to essentially increase the service life of the carbon graphite screens. However, in this case the optical characteristics and the fine faulty structure of the crystals may be influenced by violations of the melt stoichiometry in the process of crystallization, due to the presence of the reducing component in the medium. The present paper is devoted to investigation of the mentioned characteristics of the sapphire single crystals grown in Ar + CO gas atmosphere under 10...800 torr pressure.

Experimental crystals measuring 70×35×10 mm^3 with the crystallographic orientation (0001) were grown in (Ar + CO) atmosphere under 10...800 torr pressure by the method of HOC using an apparatus with carbon graphite heating unit. For the obtaining of the crystals, there was used a starting material with low impurity content (Table1). The crystals were grown from the same starting material batch under identical technological conditions (growth rate, temperature gradient, etc.). The rectangular experimental samples measuring 20×10×6 mm^3 with the surface orientation (0001), $(11\bar{2}0)$ and $(10\bar{1}0)$ were cut out along the growth direction from the same tail parts of the grown crystals. The samples were oriented to an accuracy of ±0.5° and subjected to the following treatment: flat polishing by bound abrasive, precision grinding by boron carbide powders with different grain size, mechanical and chemico-mechanical finish polishing. The roughness R_A of the sample surfaces prepared for the measurements was ~15 E, and this fact did not exert essential influence on the contribution of the damaged surface-adjacent layer into the results of X-ray diffraction and optical measurements. The transmission spectra of the samples ($T(\lambda)$, %) were registered on "SPECORD-UV-VIS" spectrophotometer in 200...800 nm spectral region. The absorption spectra ($K(\lambda)$, cm^{-1}) were built after a correction for reflection and reduction to thickness units.

The concentration of F-centers in the samples was estimated from the Smakulla formula using the values of oscillator force obtained in [4]. To estimate the concentration of micro-particles in the samples, there was used MIC-4 optical microscope and the data on the crystals' absorption in the visible region of the spectrum. The degree of structure perfection of the grown sapphire crystals was studied on the multipurpose three-crystal X-ray diffractometer (TXD) in Cu Kα radiation. The use of TXD investigation methods allowed to exclude the contribution of instrumental broadening into the diffraction reflection curves (DRC), to achieve an angular DRC resolution of ~1 arcsec and the rocking curve halfwidth ~3...7 arcsec, the error of the determination of the integral reflection power $I^R \le 2$ %, the relative variation of crystal lattice parameter $\Delta d/d \sim 1 \cdot 10^{-7}$ [6]. The shape and angular position of DRC curve, the parameters β, I^R, $\Delta d/d$ allowed to estimate the degree of structure perfection of the investigated samples adequately enough. To estimate the structure perfection in the bulk of the crystals, there was realized linear scanning of the sample (at a step of 0.2...3 mm) with respect to incident monochromatic X-ray beam, and the characteristics $\beta(L)$, $I^R(L)$, $\Delta d/d(L)$ were obtained. The shape and angular DRC position were established at a temperature of 15 ± 0.5°C. The crystal lattice parameters (a, c) were determined using the Bond method and the method developed by the authors [6].

The performed optical investigations show that, in contrast to the optical spectra of sapphire crystals grown in CO gas medium under 0.1...0.3 torr pressure [2], those of the crystals grown in (Ar + CO) atmosphere under a pressure of 10...800 torr have no Ti^{4+} absorption bands, and this is caused by high degree of Ti reduction. Due to the same fact the latter crystals possess elevated resistance to UV-irradiation (color centers are not formed in them). The spectra of all the crystals contain only the absorption bands of F-centers (205 nm) which intensity increases as the protective medium pressure grows (Fig. 1).

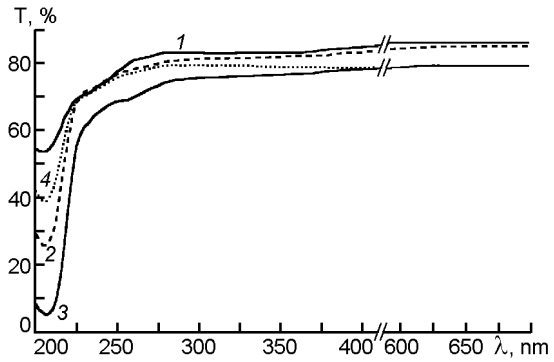

Fig. 1. $T(\lambda)$ spectra of sapphire crystals grown in Ar + CO medium. Curves *1*, *2*, *3* correspond to the crystals obtained at 10, 100 and 800 torr, respectively. Curve *4* is measured after high-temperature annealing of the crystals grown at 800 torr pressure. The samples thickness is 6 mm.

The concentration of *F*-centers in the samples estimated from the Smakulla formula increases from ~10^{16} cm^{-3} in the crystal grown under a pressure of 10 torr, up to ~$7...9 \cdot 10^{16}$ cm^{-1} in those grown at 400...800 torr (Fig. 4d).

There is also observed low transparency of the crystals grown under a pressure higher than 30 torr in the visible region of the spectrum. Such a fact is caused by the presence of micro-particles (light scattering centers) which formation is connected with violation of the melt stoichiometry [2, 7]. The micro-particle concentration also decreases when the pressure of the medium grows from ~10^4 cm^{-3} in the crystals grown under 30 torr pressure, up to $5...6 \cdot 10^6$ cm^{-3} in the crystal obtained under a pressure of 800 torr (Fig. 4d). The influence of these defects (which are not typical of the sapphire crystals grown in a medium neutral with respect to Al_2O_3 melt) on the formation of fine faulty structure of the crystals, is of considerable interest.

To study the crystals' structure perfection, there were used the reflexes of the reflection of the crystallographic planes (0001), $(22\bar{4}0)$, $(33\bar{6}0)$, $(30\bar{3}0)$. Presented in Fig. 2 are the structure perfection parameters β and $\overline{I^R}$ for the reflexes {00012} and $\{22\bar{4}0\}$ averaged over ten measurements (at scanning the samples along the growth direction) depending on the pressure of the growth medium Ar + CO (curves 1). As is seen, the grown crystals show tendency to an increase of the parameter β. DRC smearing is mainly caused by the presence of micro-blocks with low-angle dislocation boundaries and 1...20 arcsec disorientation angles. For the reflex $\{22\bar{4}0\}$ (Fig. 2b) the parameter values are higher than for the reflex {00012} (Fig.2a), and this is evidently bound up with the contribution of extension-compression stresses in the bulk of the crystal.

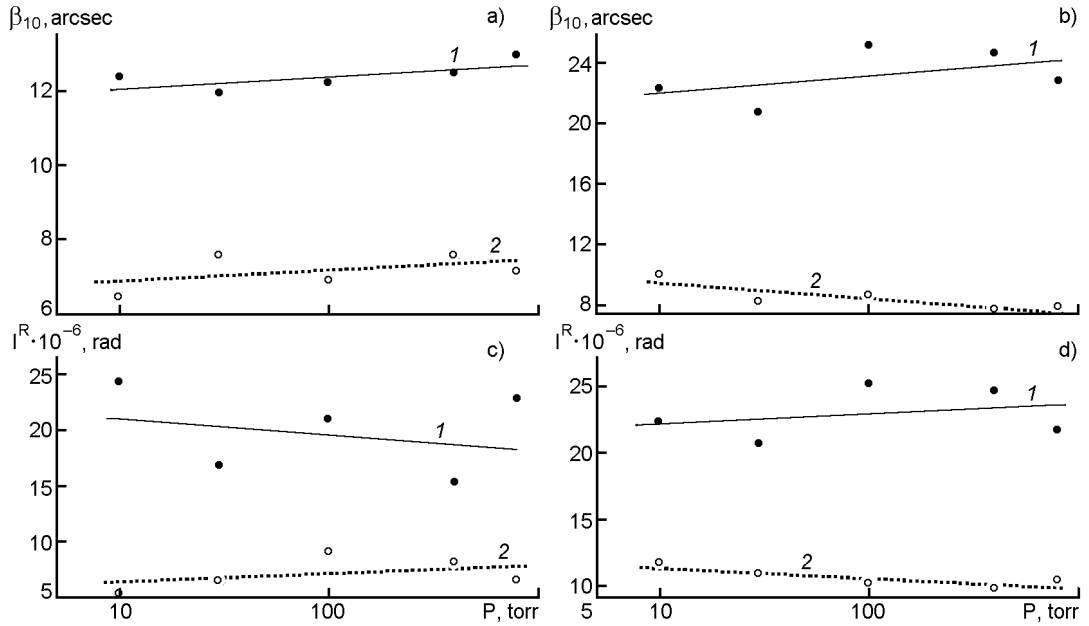

Fig. 2. Behavior of the rocking curve halfwidth β (a, b) and the integral reflection power I^R (c, d) depending on the growth medium pressure after the growth (curves *1*) and after additional high-temperature annealing (curves *2*).

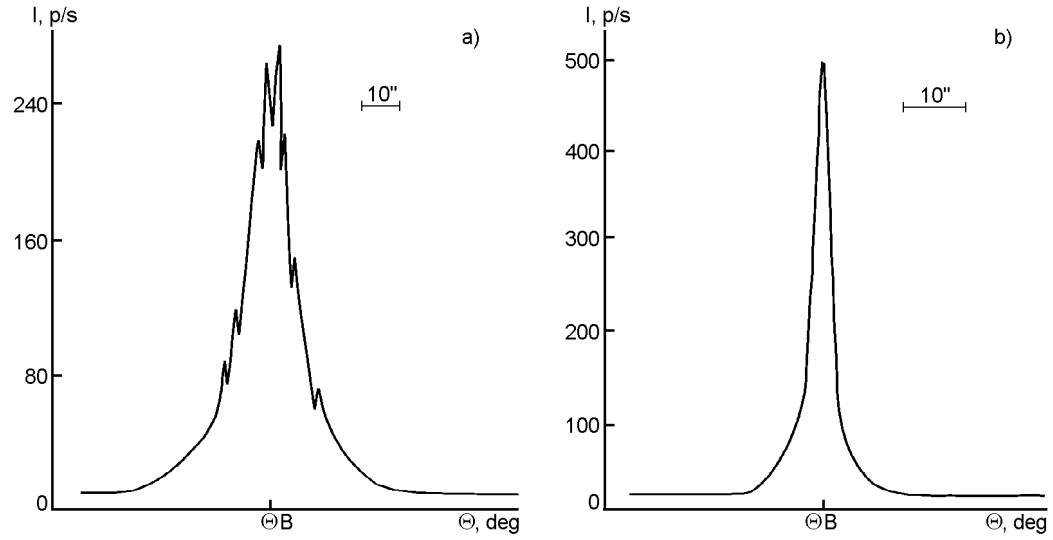

Fig. 3. Characteristic shapes of rocking curve for {22$\bar{4}$0} reflex: (a) — after the growth, (b) — after additional high-temperature annealing.

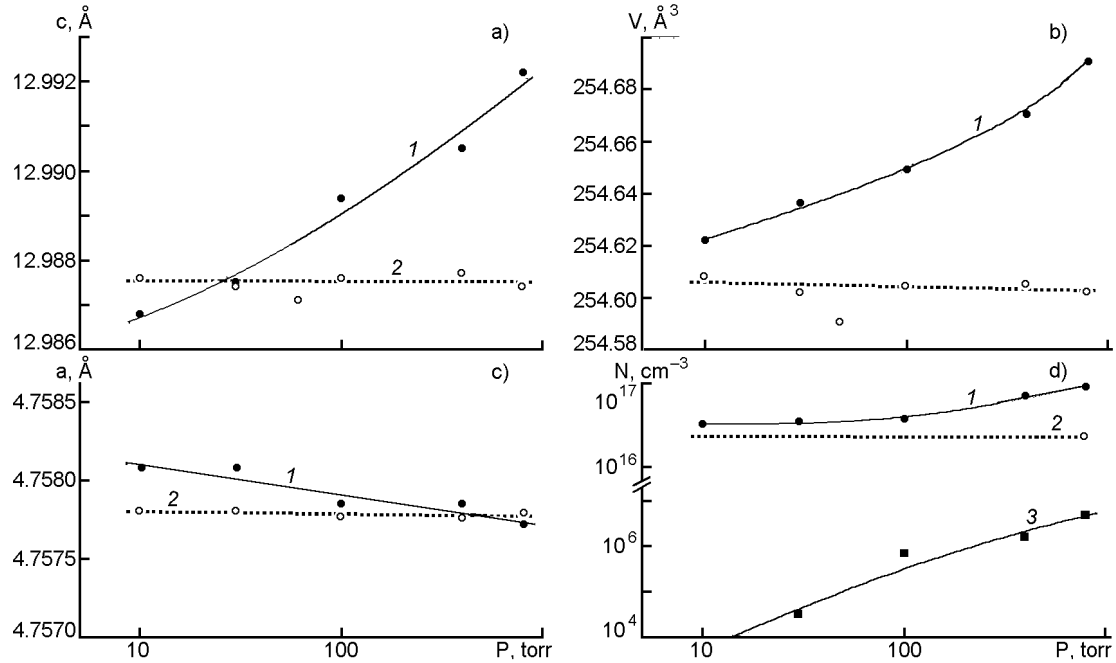

Fig. 4. Changes in the lattice parameters and the concentration of defects (vacancies and micro-particles) in the crystals depending on the growth medium pressure: (a) — the parameter c, (b) — the parameter a, (c) — the elementary cell volume V, curves *1* and *2* are measured before and after high-temperature annealing, respectively; (d) — the concentrations of F-centers before (curve *1*) and after (curve *2*) high-temperature annealing and the concentration of micro-particles (curve *3*).

The DRC splitting (Fig. 3) allows to estimate the cross-section of micro-blocks from the area of the irradiated part of the crystal, its cross-section, the quantity of the peaks and their intensity in the maximum. For instance, for the reflex of {22$\bar{4}$0} reflection the cross-section of monochromatic beam on the sample is ~80 μm and the DRC has not less than 8 separated reflexes of different intensity (Fig. 3a). The micro-block cross-section varies within the limits 4–15 μm. Rough micro-block structure with disorientation angles >0.1° was not observed in all the investigated samples.

The results of the measurements of the crystal lattice parameters c, E ($\pm 1 \cdot 10^{-4}$ E) and a, E ($\pm 3 \cdot 10^{-5}$ E) in the grown crystals are presented in Fig. 4 (a, b), curves 1. As is seen, the parameter

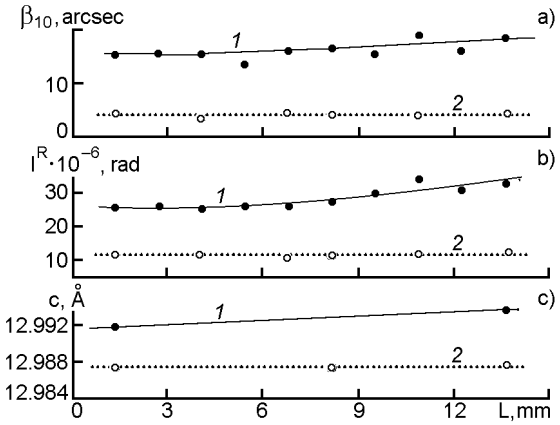

Fig. 5. Behavior of the rocking curve halfwidth β (a), the integral reflection power I^R (b) and the lattice parameter c at scanning the sample along the growth axis (at a distance of 15 mm from the center to the tail of the crystal grown at 800 torr pressure of Ar + CO medium) after the crystal growth (curve 1) and after additional high-temperature annealing (curve *2*).

c increases (~$5\cdot10^{-3}$ E) and the parameter a slightly diminishes (~$3.6\cdot10^{-4}$ E) when the pressure increases from 10 to 800 torr in the process of crystal growth. The dependence of the elementary cell volume V, E^3 ($\pm5\cdot10^{-3}$ E) presented in Fig. 3c (curve 1) was calculated from these parameters. The observed increase of V correlates with the dependence of the concentration of anionic vacancies and micro-particles in the crystals on the growth medium pressure (Fig. 4d, curves 1,3) obtained from optical measurements (Fig. 1).

As mentioned above, Fig. 2, 4 present the data averaged over ten measurements at scanning the samples along the growth direction. The dependences $\beta(L)$ and $I^R(L)$ for the reflex {00012} and $c(L)$ obtained while scanning the sample along the growth direction (for the crystal grown at 800 torr pressure of the medium Ar + CO) are shown in Fig. 5 (curves 1). Analogous dependences (more or less pronounced) are typical of all the investigated samples: at the crystal tail the amount of defects increases (there are observed DRC widening and growth of I^R), moreover, for all the crystals the lattice parameter c increases. It should be noted that rough micro-block structure is not revealed even in this part of the crystal. There only prevail low-angle (1...3 arcsec) rotations, though the increase of I^R up to 20 % testifies that the dislocation density and other defects (including possible impurities with $K < 1$) increase.

Thus, investigations of the structure of sapphire crystals grown in reducing Ar + CO gas media under pressures higher than 1 torr allowed to establish the influence of the pressure on the structure perfection of the crystals. The optical characteristics and structure perfection of the samples grown under a pressure of 10...30 torr are close to those observed for the crystals grown in vacuum or in CO medium under 0.1...0.3 torr pressure [3]. These characteristics worsen as the pressure increases. While analyzing these data, there must be taken into account not only obvious effects of dislocation density, stresses and non-uniform impurity distribution, but also specific defects characteristic of the crystals grown in reducing media. Comparison of the results of structure investigations with the data of optical measurements shows a correlation of the parameters characterizing the structure perfection with the concentration of defects which presence is caused by the interaction of Al_2O_3 melt with the reducing component of CO medium, i.e. anionic vacancies and micro-particles (Fig. 4c).

High-temperature annealing of the crystals changes both the concentration of anionic vacancies (increases or diminishes it, depending on the annealing medium potential) and the charge state of the impurities. As established earlier, specially chosen parameters of the annealing medium allow to equalize the optical characteristics connected with the presence of these defects, over the length and thickness even of large-size (215×215×30 mm^3) crystals [2]. In the present paper we investigated the influence of high-temperature annealing on their thin defect structure.

To diminish the concentration of anionic vacancies, annealing was realized in CO — the medium with a reducing potential lower than the one used for growing the crystals — under a pressure of about 0.2 torr at 1900°C during 10 hours. Typical changes in the optical characteristics of the samples caused by annealing are presented in Fig. 1. As is seen, for the crystal grown under 800 torr pressure of Ar + CO, annealing essentially diminishes the absorption in the region of F-centers, in the visible region of the spectrum noticeable changes are not observed (Fig. 1, curves 3,4). In all the samples the concentration of vacancies decreased down to the level of ~$2\cdot10^{16}$ cm^{-3} (in accordance with the value of the annealing medium potential), the concentration of micro-particles remaining unchanged (Fig.

4d, curves 1, 2, 3). The results of the performed structure investigations show that for all the crystals the halfwidth of the rocking curve diminishes, its shape changes (Fig. 2a, b, curves 2, Fig. 3b) and there also decrease the integral reflection power (Fig. 2c, d, curves 2) and the elementary cell volume (Fig. 4, curves 2). Within the limits of the measurement error, no noticeable changes of these parameters are established at scanning the annealed samples along the growth direction (Fig. 5, curves 2).

Analysis of the data presented above shows that the presence of micro-particles and non-uniform impurity distribution do not exert noticeable influence on the structure perfection of the crystals. Despite the fact that the concentration of micro-particles and the impurity distribution remain unchanged, high-temperature annealing leads to noticeable raise of the crystals' structure perfection (practically, up to the level characteristic of the conditions of high vacuum [3]) as well as to equalization of the structural characteristics over the crystal length. Thereat, there is observed a correlation of these characteristics with the concentration of anionic vacancies. Such a fact allows to assume that changes in both the structural and the optical characteristics of the crystals are closely connected with violation of the crystal lattice stoichiometry with respect to oxygen. Direct estimation shows, that if the vacancy concentrations is lower than 10^{17} cm^{-3}, less than $3 \cdot 10^{-5}$ vacancies correspond to one elementary cell. It is obvious that such an effect is beyond the limits of measurement sensitivity, therefore, the observed change in the elementary cell volume of the order of $7 \cdot 10^{-2}$ E^3 (Fig. 4c) cannot be defined by the presence of elevated vacancy concentration only.

Though in the process of growing the crystals by the method of HOC in vacuum the vacancy mechanism of formation of dislocations and low-angle dislocation boundaries is considered scarcely probable [8], one may assume that at the growth of the crystals in reducing media the action of the said mechanism becomes more essential, since these conditions require considerably higher vacancy concentrations. Taking into account such a mechanism allows to offer a plausible explanation for the obtained experimental results. From this point of view, the fact that while growing the crystals from the same raw material batch and under identical conditions (growth rate, temperature gradient etc.) the structure perfection parameters β, $\overline{I^R}$ and the elementary cell volume noticeably increase as the reducing medium pressure grows, can be attributed to the increase of vacancy concentration and to the formation of dislocation structure by the vacancy mechanism. Non-uniform distribution of vacancies in the crystal bulk caused by insufficient convection in the melt and by the duration of after-growth annealing insufficient for equalization of this non-uniformity, may be bound up with the fact that the values of β for the reflex $\{22\bar{4}0\}$ (Fig. 2b) are higher than for {00012} (Fig. 2a), i.e. with the presence of extension-compression stresses in the crystal bulk. Non-uniformity of the parameters β and I^R along the length of the crystals may also be explained by non-uniform vacancy distribution. When the concentration of vacancies in the crystals is reduced down to the same level under the influence of high-temperature annealing, similar decrease is observed for the structure-sensitive parameters.

The performed optical and X-ray structure investigations of sapphire crystals grown in Ar + CO protective medium under 10...800 torr pressures show that the crystals grown under 10...30 torr pressures have high optical characteristics and structure perfection, thus comparing favorably with the crystals grown in CO medium under 0.1... 0.3 torr. With the increase of the pressure the crystal perfection worsens, and the increase of the structure perfection parameters β, $\overline{I^R}$ the elementary cell volume testifies to this fact. High-temperature annealing in the medium with a reducing potential lower than the crystal growth potential leads to decrease of these parameters down to the same level, the crystals acquire the structure perfection comparing favorably with that of the crystals grown under the conditions of deep vacuum (~10^{-4} torr). Taking into account the vacancy mechanism of dislocation formation and low-angle dislocation boundaries allows to offer a plausible explanation for the obtained results.

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Особливості оптичних і структурних характеристик монокристалів сапфіра, вирощених у середовищі Ar + CO

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Представлено результати оптичних і рентгеноструктурних досліджень кристалів сапфіра, вирощених методом ГСК у захисному (відновному) середовищі Ar + CO в інтервалі тисків 10... 800 тор. Встановлено залежність структурної досконалості кристалів від тиску середовища. Показано, що в результаті високотемпературного відпалу досконаліть структури може бути підвищена до рівня, характерного для кристалів, вирощених в умовах високого вакууму (10^{-4} тор). Кореляція параметрів, що характеризують досконаліть структури, з концентрацією аніонних вакансій у кристалах дозволяє припустити, що при вирощуванні кристалів сапфіра у відбудовних середовищах у процесі формування дислокацій і малокутових дислокаційних границь помітну роль може грати вакансійний механізм.