# GROWTH TECHNOLOGY FOR ZnSe SINGLE CRYSTALS WITH LOW DISLOCATION DENSITY

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## Abstract

The influence of the growth temperature, undercooling, growth rate as well as growth chamber construction and furnace temperature profile on the structural perfection of the crystals grown by both physical and chemical vapors transport has been investigated. The conditions for growing of crystals free from subgrain boundaries and twins are suggested. The etch pits are not observed in the basic volume (up to 4 $cm^3$) of grown crystals. It is shown, that PL spectra of as-grown ZnSe crystals consist of the edge radiation only. The resistivity of ZnSe crystals annealed in a Zn melt is higher than $10^8$ Ohm·cm, whereas the electrical conductivity of ZnSe:I crystals grown by chemical vapor transport and annealed in a Zn melt is 10 $(Ohm \cdot cm)^{-1}$ at room temperature.

## 1. Introduction

The wide band gap (2.7 eV at room temperature) ZnSe semiconductor remains one of the most perspective materials for manufacturing optical devices operating in visible spectral region. ZnSe p-n junction manufacturing is a difficult technological problem. The degradation of light-emitting devices based on this p-n junction is the major factor limiting its use. It is suggested that the basic reason of p-ZnSe:N/n-ZnSe structure degradation is the exit of the nitrogen acceptor impurity from Se sublattice and the formation of compensating centers. The degradation rate depends on the dislocation density of used materials. The laser diodes can operate for 9 min when the dislocation density is about $10^5$ $cm^{-2}$ [1], 1 hour when the dislocation density does not exceed of $5 \cdot 10^4$ $cm^{-2}$ [2]. The most qualitative ZnSe crystals have a dislocation density of $10^4$ $cm^{-2}$. The preparation of stable light-emitting devices requires the use of more composite structures such as ZnMgBeSe [3]. Thus, manufacturing of the structurally perfect massive ZnSe crystals having the minimum dislocation density is an urgent problem. This paper is focused on this topic.

## 2. Experiment

The crystals growth was carried out by the method of seeded physical vapor transport in vacuum. The influence of the growth temperature, undercooling, growth rate as well as growth chamber construction and furnace temperature profile on the structural perfection of the grown crystals has been investigated. The growth temperature was varied in the 975÷1080°C range, undercooling was varied from 0.5 up to 10°C, the growth rate changed from 0.5 up to 10 mm / day.

The seeds were fragments of the crystals grown from a melt, having the dislocation density of $5 \cdot 10^5 \div 10^6$ cm$^{-2}$.

Zn annealed in Se vapors was used as a source. The synthesized material was purified by the sublimation in sealed ampoules.

The photoluminescence (PL) was excited by radiation of pulse nitric laser with a 337.1 nm. The PL spectra in the 430 ÷ 800 nm wavelengths region were investigated using a monochromator with a 1.4 nm/mm linear dispersion. The PL spectra investigations were carried out at 88 K. The PL spectra were decomposed on components by Alentsev method [4]. The peak localization accuracy is 0.5 nm for the edge PL components and 5 nm for long-wave (LW) luminescence components.

## 3. Experimental results

The use of growth temperature in the 975÷1080°C range at variation of undercooling from 4°C to 1°C allows reaching 1÷1.5 mm/day growth rates. It will be shown below that such growth rates and the use of seeds free from subgrain boundaries, having a dislocation density of $10^4$ cm$^{-3}$ and less, provide growth of crystals free from voids, having a volume up to 4 cm$^3$. The use of higher growth rates results in the growth of crystals containing voids with a volume of up to several mm$^3$. Voids are also present in the case of lower growth rates, at the use of seeds containing subgrain boundaries.

It is revealed that the application of classical parabola-like axial temperature profile of the furnace (Fig. 1a, above) results in the effect of grown crystal (seed) attachment to a flat ampoule bottom and crystal deformation during cooling. Thus, practically complete destruction of both the seed and the lower part of the crystal at a depth up to 5 mm happens. Fig. 1b (above) shows the fragments of the destroyed seed and the crystal part nearest to the seed. The use of the intact parts of similar crystals as seeds results in growth of crystals with high density of subgrain boundaries and twins (5÷40 cm$^{-1}$). The cut of such a crystal is shown in Fig. 1c (above). The dislocation density is $10^5 \div 10^6$ cm$^{-2}$ (Fig. 1d, above).

The influence of the technological parameters on the degree of the grown crystal attachment has been studied. The variation of distance between the seed and the flat ampoule bottom in an interval from 0 up to 2 mm results in parasitic crystal growth in this area. The change of total cooling time from 6 hours to 5 days does not reduce this destruction. Thus, the cooling was carried out at a reverse temperature profile that might promote the decrease of the attachment effect. The application of the growth chamber surface graphitization close to the seed liquidates this effect, but also results in prevailing secondary crystal growth on the ampoule walls due to temperature profile changing. The use of the growth chamber having a conical bottom, as well as growth on pedestals with their basic part located in the area of higher temperatures, allow reducing of the degree of crystals destruction, although this effect does not disappear completely.

It is revealed that the minimization of the temperature difference between the growth chamber bottom and growing crystal is the most suitable technological aspect for complete elimination of the grown crystals strain. This is carried out by means of temperature profile application, its minimum being located in the area of the seed and the ampoule bottom (Fig. 1a, below). Fig. 1b (below) demonstrates the transparence of the seed and crystal grown in the case of this temperature profile application.

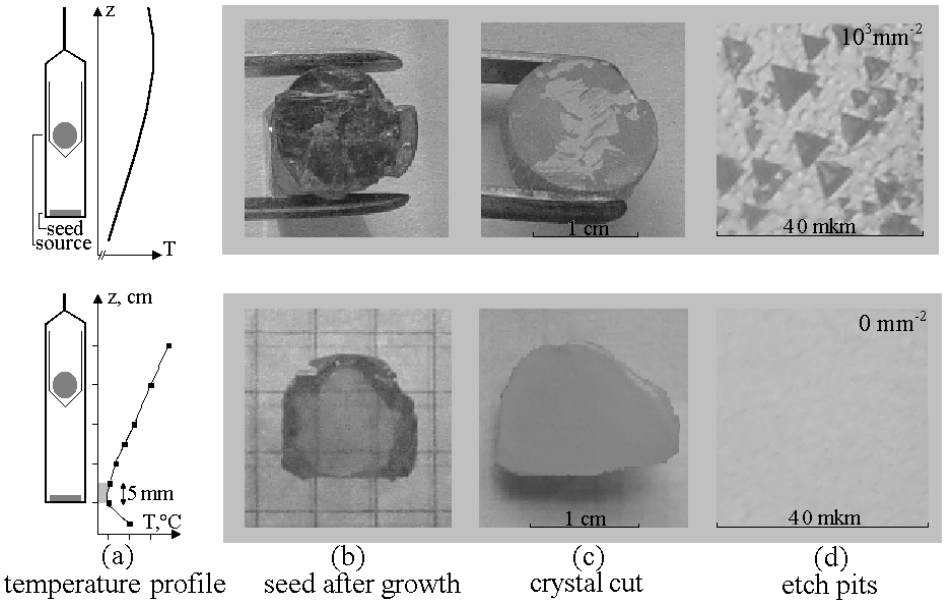


Fig. 1. The dependence of ZnSe crystal structural perfection on the furnace temperature profile.

The use of this temperature profile is not desirable due to high probability of the secondary crystal formation on the ampoule walls. It has been found that nearest to material source boundary of the secondary crystal growth area coincides with points corresponding to the requirement of $d^2T/dz^2 = 0$. It dictates necessity of minimization of distance between the temperature profile minimum and the point satisfying the requirement of $d^2T/dz^2 = 0$.

The growth under the suggested temperature profile condition, at the use of a seed with the dislocation density about $10^5 \div 10^6$ cm$^{-2}$, is accompanied by generation of subgrain boundaries. However, the top of crystals with a height no less than 1 cm has these defects only on periphery. Therefore, the fragments of the most qualitative parts of similar crystals might be used as seeds for obtaining of crystals free from twins and voids (Fig. 1c, below). The subgrain boundaries in these crystals are located only on periphery and have an area of not more than 2 mm$^2$. The etch pit density in the central part of similar crystals does not exceed $10^4$ cm$^{-2}$, and etch pits are not observed in the basic volume (90%) of crystals (Fig. 1d, below). As it follows from all the information available to us, the crystal manufacturing by the physical vapor transport method, which extended sites are "free from etch pits", is carried out for the first time.

The use of seeds oriented in the (100) and (110) direction does not allow obtaining of crystals with a high level of symmetry. The growth of the most symmetrical crystals is possible in the (111) direction. It is accordance with results of ZnSe crystal growth by the chemical transport at the use of I [5] and H [6] as transport agents. The lateral surface of the crystals grown in the (111) direction is limited by a hexagon with mirror grains. The diameter and height of largest crystals reaches 2 cm (Fig. 2a).

The edge radiation dominates in the PL spectrum of as-grown crystal. This spectrum consists of 5 components (Fig. 2b). The most high-energy component ($E_x$) is attributed to the free excitons, their binding energy being equal to 19 meV [7]. The $I_2^x$ radiation is attributed to the exciton complexes (EC) bound with shallow hydrogen-like donors. The behaviour of $I_2'$ component at an excitation level change appears practically identical with behaviour of $I_2^x$ component. This radiation ($I_2'$) might be also assigned to EC bound with deeper donor centers. The activation energy of these donors obtained from the Haynes' rule [7] is equal to

60±15 meV. The more LW component ($I_1^{Vzn}$) is caused by EC bound with deep acceptors of the Zn vacancy ($V_{Zn}$) or complexes on their basis, having an activation energy of 220 meV [8]. The binding energy of centers bound with acceptor EC responsible for the edge PL component located at 450.5 meV is 330±30 meV. It allows us to attribute the $I_1^{Cu\_g}$ band to centers of "a green luminescence of copper" ($Cu_{Zn}^{2+}$), having an activation energy of 350 meV [9]. The total intensity of more LW radiation does not exceed $10^{-4}$ share of total intensity of the edge luminescence.

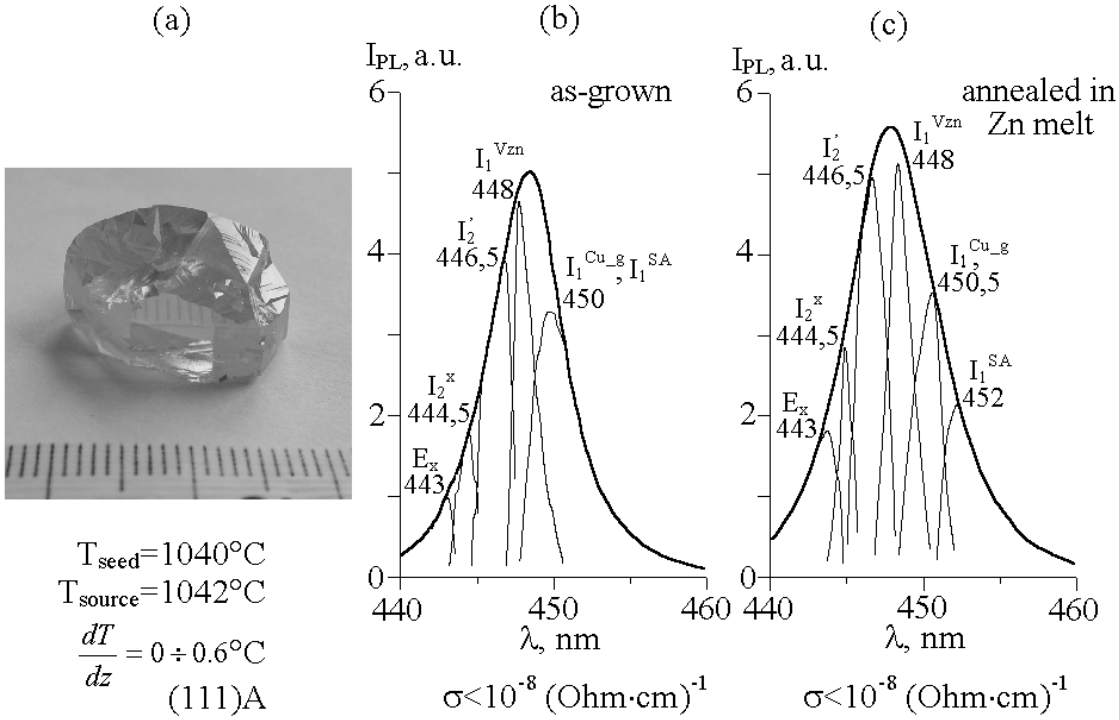


Fig. 2. The ZnSe crystal and the growth requirements (a). The photoluminescence spectra of as-grown (b) and annealed in a Zn melt (c) crystal.

The conductivity of these crystals does not exceed $10^{-8}$ (Ohm·cm)$^{-1}$.

The annealing in a Zn melt for 100 h at 900°C does not increase the conductivity above $10^{-8}$ (Ohm·cm)$^{-1}$. The PL spectrum of the annealed crystal consists of the edge radiation only (Fig. 2c), its composition appears to be close to the composition of the as-grown crystal relevant spectrum. The band located at 452 nm is attributed to EC bound with acceptors, having an activation energy of about 500 meV. This value coincides with the activation energy of self-activated PL centers [10].

Thus, the growth by means of the physical vapor transport in vacuum allows us to obtain highly pure ZnSe crystals. The growth by chemical transport at the use of I as a transport agent has been used for high conductance n-ZnSe crystal obtaining. The growth temperature was 860°C, undercooling was 20°C, seed crystallographic direction was (111), I concentration was equal to 1 mg/cm$^3$.

Presence of I impurity cardinally decreases total intensity of the edge radiation (Fig. 3a). This effect is assigned to high concentration of the ionized impurities reducing exciton radiation and contributing to radiation in the more LW spectrum region. There is an abnormal high-energy radiation extending down to 430 nm in this spectrum. The similar radiation, its nature remaining unknown, is in PL spectra of crystals grown in Cl and I media [11]. The in-

tensive LW luminescence contains the bands caused by the uncontrollable impurity of copper (located at 535 [9], 550 [12], 640 [9], and 670 [4] nm) and self-activated PL centers (605, 620 nm [7]).

The annealing in a Zn melt for 36 hour at 900°C, which decreases the $V_{Zn}$ concentration, reduces concentration of charged centers and, as a result, increases exciton radiation (Fig. 3b) and also liquidates centers responsible for the abnormal high-energy radiation. The composition of the edge PL spectrum of the annealed crystal (Fig. 3b) appears to be close to the composition of the as-grown crystal spectrum (see Fig. 2b).

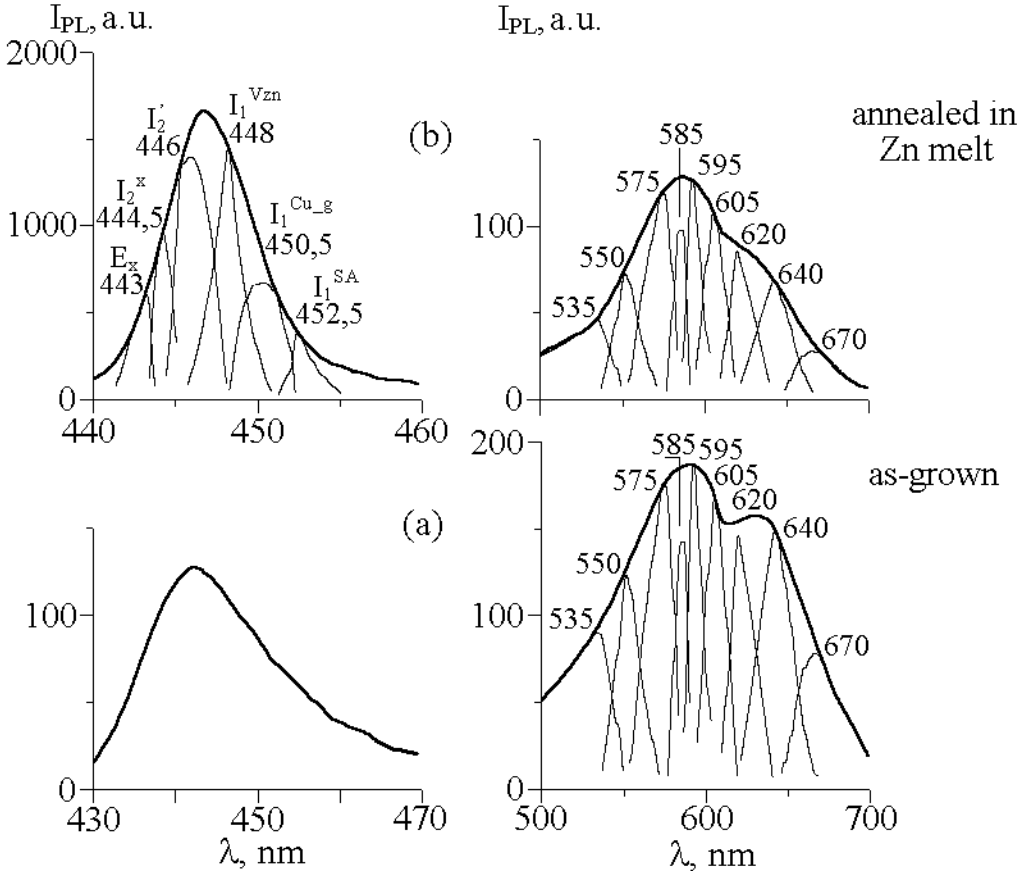


Fig. 3. The photoluminescence of ZnSe:I crystals before (a) and after (b) annealing in a Zn melt.

Similar short annealing provides obtaining of high conductance crystals, their conductivity achieves 10 $(Ohm \cdot cm)^{-1}$ at room temperature. The values of the electrical conductivity ($\sigma$), concentration of mobile electrons (n), and their Hall mobility ($\mu$) at various temperatures are shown in the table.

Table. The electrical parameters of ZnSe:I crystals annealed in a Zn melt.

| T, K | $\sigma$, $(Ohm \cdot cm)^{-1}$ | n, $cm^{-3}$ | $\mu$, $cm^2/(V \cdot s)$ |
|---|---|---|---|
| 300 | 10 | $5.0 \cdot 10^{17}$ | 125 |
| 77 | 7.8 | $6.3 \cdot 10^{16}$ | 770 |

## 4. Conclusions

The use of the parabola-like axial temperature profile of the furnace results in the seed attachment to the flat ampoule bottom. The crystal strain during cooling as a consequence happens. The minimization of a temperature difference between the seed and the growth chamber bottom eliminates this effect.

The use of the suggested temperature profile for physical vapor transport in vacuum and the application of low undercooling (2°C) and low temperature gradient (< 0.6°C/cm) in the crystallization area, at a growth temperature of about 1040°C allows growing of crystals free from subgrain boundaries and twins. The basic volume (up to 4 $cm^3$) of these crystals does not contain dislocations either.

The application of this growth method, at the use of the material synthesized by us, allows us to obtain ZnSe crystals with the PL spectra consisting of the edge radiation only. The radiation of excitons bound with natural defects of $V_{Zn}$ dominates in these spectra.

The annealing of similar crystals in a Zn melt for the decrease of $V_{Zn}$ concentration does not reduce resistivity below $10^8$ Ohm·cm. Such a high value of annealed crystal resistivity and absence of the PL radiation related to acceptor centers of uncontrollable impurities, testify to the low content of both donor and acceptor impurities in these crystals.

The I impurity introduction during growth favors formation of centers responsible for radiation corresponding to the energy exceeding ZnSe band gap and reduces total emissive properties of crystals in the edge spectrum region.

The annealing of ZnSe:I crystals in a Zn melt reduces the concentration of charged centers suppressing exciton radiation and centers responsible for the abnormal high-energy luminescence. The similar annealing increases the electrical conductivity up to 10 $(Ohm \cdot cm)^{-1}$ at room temperature.

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