# ZnSe Single Crystals Grown by Vapor Growth Methods and Their Applications

Yasuo NAMIKAWA

ZnSe-based white LED (light emitting diode) can be fabricated by homoepitaxial growth on ZnSe conductive substrate. This LED emits white light by mixing the blue-green emission from the ZnCdSe active layer and the deep level yellow emission from the ZnSe substrate excited by the active layer emission. Large conductive ZnSe substrates with high quality are required for this device application. The vapor growth techniques, such as PVT (physical vapor transport) method and CVT (chemical vapor transport) method, were applied to the growth of the ZnSe single crystals. The most important problem to be solved in the PVT growth of the ZnSe single crystal is voids formation during the crystal growth. The voids formation was eliminated by the semi-open free-growth method in which the growing crystal could be kept at the local minimum temperature position during the crystal growth. ZnSe single crystals of 45 mm diameter and 35 mm length with dislocation density of about 5 x $10^3$ $cm^{-2}$ could be grown by this PVT method. For CVT method, on the other hand, the suppression of the influence of the convection during the crystal growth is the problem. This subject was solved by the rotational CVT method. ZnSe-based white LED could be operated the low applied voltage of 2.75 V and demonstrated that the optical output power was 4.25 mW at forward current of 20 mA. The life time of the LED showed longer than 10,000 hours at room temperature. This paper reviews mainly ZnSe single crystal growth techniques and shows some application results.

Keywords: ZnSe, crystal growth, PVT, CVT, white LED

## 1. Introduction

ZnSe (Zinc Selenide) is a II-VI compound semiconductor with band-gap energy of about 2.58 eV. It has attracted a great attention as a material for the blue light emitting devices because of its band-gap energy. Especially after the report of 3M Company in USA in 1991, in which they reported the blue-green light laser diode by using the ZnSe thin film hetero-epitaxially grown on GaAs substrate, many companies and universities around the world accelerated the development of the ZnSe devices[(1),(2)]. Improvement of the intensity of the emitting light and the life time was important for the realization of the ZnSe-based blue light emitting devices as the product. In order to perform this improvement, the crystal quality of the epitaxially grown active layer was a key issue. The hetero-epitaxial film, however, has the essential problem that the crystal defects are easy to increase due to the difference of the lattice constants and the thermal expansion coefficients between the substrate and the epitaxial layer. Therefore, in 1993 we started the development focused on the fabrication of the ZnSe single crystal substrates by applying our long experience for the compound semiconductor crystal growth technique. High quality blue light emitting devices should be realized by using the homo-epitaxial growth active layer.

Al or I doped ZnSe substrates are necessary, since substrates for the light emitting devices should be conductive. Through the development of the blue light emitting devices, we found that the impurity doped ZnSe substrate emitted the yellow light by absorbing the blue light from the active layer. This emission was the SA (self-activation) emission from the complex defect of doped impurity and Zn vacancy[(3)]. This phenomenon was a problem for the blue light emitting device, because the intensity of the blue light from the active layer was decreased due to the absorption of the substrate and because the pure blue emission was disturbed by the yellow emission from the substrate. But this difficulty gave us a new idea. We discovered that the white light emitting device could be fabricated by mixing the blue light from the active layer and the yellow SA emission from the ZnSe substrate. Then we started the development of the white LED (light emitting diode) by using the ZnSe substrate, considering the rapid advance of the performance of the GaN-based blue light emitting devices[(4)]. ZnSe-based white LED has advantages such as lower operating voltage, higher controllability of color attributed to the fluorescent material free process and simpler structure due to the conductive substrate compared with the GaN-based white LED.

This paper introduces mainly the development of the ZnSe substrates for the while LEDs in Sumitomo Electric Industries, Ltd., including some results about the white LEDs using these ZnSe substrates.

## 2. ZnSe Crystal Growth

ZnSe does not melt under the normal pressure. As a result, it is difficult to grow ZnSe crystal by the melt growth such as the pulling method or Bridgman method which are generally used for Si or GaAs crystals. Hence, various growth methods, including vapor growth methods, solid growth methods and high pressure melt growth methods, have been attempted for ZnSe crystal growth[(5)-(9)].

Among these methods, PVT (physical vapor transport) method and CVT (chemical vapor transport) method are the promising candidates to grow large and high quality crystals. The PVT method is a simple sublimation method and has an advantage to obtain relatively large crystals. But the crystal quality grown by the PVT method was inferior. In addition, the growing crystals were undoped and high resistive. It is necessary for fabricating the LED substrates to add the conductivity by introducing Al as impurity into the growing crystal. On the other hand, the CVT method uses iodine as a growth agent. The agent is introduced into the crystal during the growth and this result in the merit of the formation of the conductive crystal. Subjects of the CVT method are the low growth rate and the difficulty of large crystal growth. Both methods have strong points and shortcomings; therefore, we employed the both two methods to develop the ZnSe crystal growth technique.

## 3. ZnSe Crystal Growth by the PVT Method

ZnSe crystal growth of the PVT method is performed as follows: As shown in **Fig. 1**, ZnSe seed crystal and ZnSe polycrystalline source is sealed in a quartz ampoule, ZnSe crystal is grown in the low pressure of inert gas at about 1100 ˚C. The seed crystal is settled at lower temperature position and the poly crystalline source material is settled at higher temperature position. Source gas sublimated from the solid source material is transported to the seed crystal attributed to the temperature dependence of the equilibrium constant, and the crystal is grown on the seed crystal according to the following equations (1) and (2). $Kp(T)$ is the equilibrium constant at temperature $T$, $P(\mathrm{Zn}(T))$ and $P(\mathrm{Se_2}(T))$ are the equilibrium vapor pressure of Zn and $Se_2$ at temperature $T$, respectively.

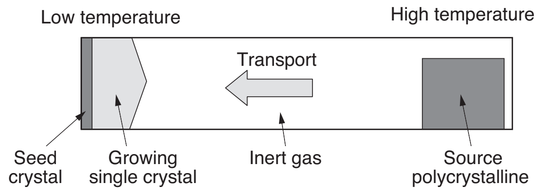


**Fig. 1.** Schematic diagram of ZnSe single crystal growth by PVT method

$$2\mathrm{ZnSe}\,(s) \leftrightarrows 2\mathrm{Zn}\,(g) + \mathrm{Se_2}\,(g) \quad \cdots\cdots(1)$$

$$Kp\,(T) = P\,(\mathrm{Zn}\,(T))^2 * P\,(\mathrm{Se_2}\,(T)) \quad \cdots\cdots(2)$$

This process utilizes equilibrium state, so that ZnSe crystal can be obtained easily. At the beginning of the development, however, the stability of the crystal growth was low and the crystal quality was poor. In order to realize the large and high quality single crystal growth, it was necessary to solve three problems; (1) stabilization of the growth rate, (2) prevention of the voids formation and (3) reduction of the dislocation density.

### 3-1 Stabilization of the growth rate

The first problem of ZnSe crystal growth by the PVT method was low reproducibility of the growth rate. Generally, the crystal quality largely depends on the crystal growth rate, in other words, on the supersaturation at the growth interface. Reproducibility of the desirable growth rate is indispensable for the constant fabrication of the high quality single crystal. The fluctuation of the growth rate impedes the investigation of the other growth parameters.

The cause of the growth rate fluctuation in the PVT method was the fluctuation of the source material composition. ZnSe polycrystalline made by CVD (chemical vapor deposition) method was used as the source for ZnSe crystal growth. The polycrystalline material has not perfect stoichiometry but some variation of the composition due to its synthesizing process. If the source material composition is different from the stoichiometry, the surplus component remains in the growth zone and accumulates with growth time, because the single crystal grows in almost stoichiometry. This component accumulation leads to the decrease of the growth rate according to Equations (1) and (2).

In order to solve this problem, the semi-open ampoule method was developed. As shown in **Fig. 2**, the quartz ampoule was divided in two areas of the growth zone and the leakage zone, and these two zones were connected by the orifice. The end of the leakage zone was settled at the sufficiently low temperature. The equilibrium vapor pressure at the low temperature leakage zone was nearly zero, so that ZnSe was solidified and deposited at the low temperature region. Accordingly, the difference of the partial pressure between the growth zone and the leakage zone was generated, which resulted in the continuous material transportation through the orifice from the growth zone to the leakage zone by diffusion. The surplus component in the growth zone was exhausted by this process and the composition ratio in the growth zone was controlled automatically at the composition defined by the conductance of the orifice. This semi-open ampoule method could realize the stable crystal growth and development of the improvement of the crystal quality.

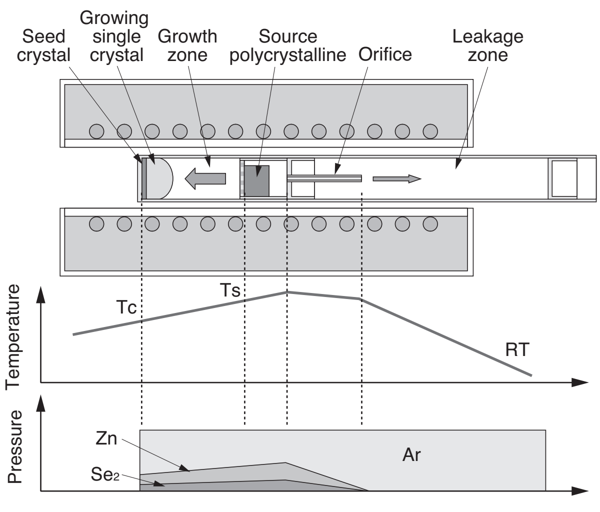


**Fig. 2.** Schematic diagram of semi-open PVT method

### 3-2 Suppression of the voids formation

Generally speaking, the crystal growth from the dilute system, such as vapor or solution, easily forms various kinds of hollow defects, namely voids, in the growing crystals. The void formation is more serious in the vapor growth than in the solution growth, because vapor is not stored in a vessel by gravity. Therefore, the suppression of the voids formation is one of the important subjects for making high quality crystals by the vapor growth.

Hence, the suppression of the voids formation was large problem in the ZnSe crystal growth by the PVT method. We investigated these voids on the basis of the relationship between their structures and their growth conditions, and classified them into three kinds of voids, as shown in **Photo 1**. The voids in **Photo 1 (a)** are attributed to the cellular growth in the compositional supersaturation. The voids in **Photo 1 (b)** are due to the over lateral growth in the facet surface. These voids of **Photo 1 (a) and (b)** could be suppressed by optimization of the thermal condition with the improvement of the furnace heater structure and by the purity control of the source material.

The voids in **Photo 1 (c)** are caused by the sublimation from the back surface of the seed crystal. These kinds of voids might be formed from the roughing of the seed crystal back surface due to the sublimation of ZnSe from the seed back surface to the lower temperature position. The temperature difference in the void itself can become the driving force for the sublimation and the recrystallization, so that the voids continue to invade into the crystal. If the seed crystal is set tightly at the lowest temperature position in the growth ampoule, these voids cannot be generated. But the tight fixing of the seed crystal leads to the increase of the dislocation density because of the low critical shear stress of ZnSe.

Hence, a new crystal growth technique, the free-growth method, illustrated in **Fig. 3 (a)** was developed[(10)-(12)]. In this method, the temperature of the seed crystal can be the local minimum temperature by using the heat radiation, and the sublimation from the seed back surface and the voids formation can be suppressed. The sapphire rod pedestal with both edge surfaces polished was settled at the lower end of the quartz ampoule, and the seed crystal was set on the pedestal. The sapphire rod was selected as the pedestal, because it has the thermal stability, no impurity out-gas, no reaction with ZnSe and high transmittance at infrared radiation at the ZnSe crystal growth temperature of about 1100 ˚C. The seed crystal was only settled on the pedestal with no mechanical fixing or sticking, so that it received no physical stress. There was the clearance of about 0.5 mm between the inner surface of the quartz ampoule and the side surface of the sapphire pedestal. The lower end of the growth furnace was fully opened and the quartz ampoule was set on the cylindrical support. The seed crystal was faced directly to the low temperature region outside of the furnace through the sapphire pedestal and the cylindrical support. As a result, the seed crystal was expected to be locally cooled by the heat radiation.

The four zone heater shown in **Fig. 3 (a)** was used in order to obtain the temperature profile that could settle the growing crystal at the local minimum temperature position. The pedestal was heated intensely by the lowest position heater (H4) for keeping it high temperature. On the other hand, the heater surrounding the growing crystal (H3) gave a little power. **Figure 4 (b)** shows the temperature profile measurement result that was obtained by moving the thermocouple along the central axis of the furnace without quartz ampoule. It was confirmed that the temperature profile showed the local minimum point at the growing crystal position.

This furnace structure had the small clearance be-

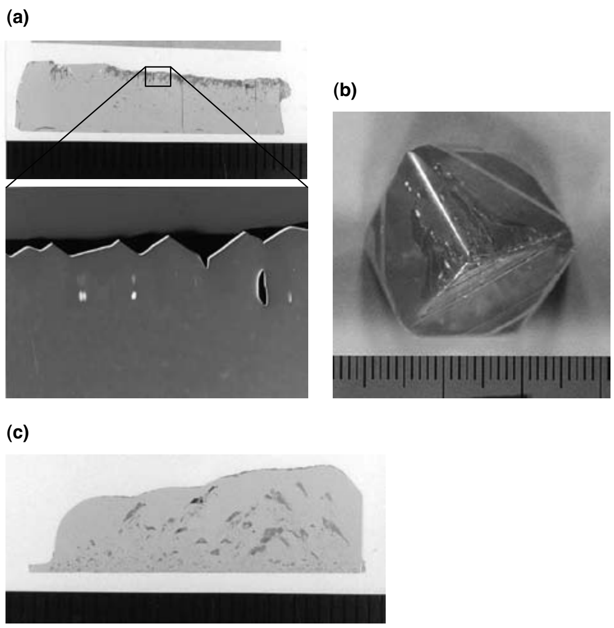


**Photo 1.** Voids in the as-grown ZnSe crystals
(a) Voids attributed to the constitutional supersaturation
(b) Voids attributed to the faceted growth
(c) Voids attributed to the sublimation from the back surface of the seed crystal

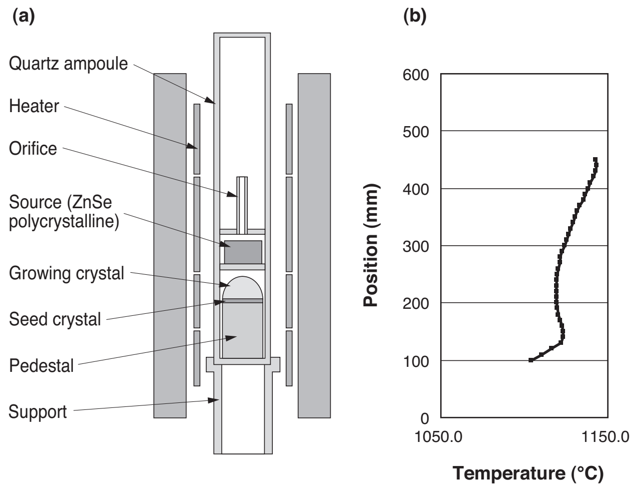


**Fig. 3.** Schematic diagram of the free-growth method
(a) Structure of the furnace
(b) Temperature measurement result in the furnace

tween the quartz ampoule and the sapphire pedestal, which resulted in continuous mass transport by diffusion through the clearance from the source material to the lowest temperature position at the low end of the ampoule. As a consequence, the growing crystal did not expand larger than the pedestal diameter and did not contact with the ampoule surface, so that the crystal quality deterioration due to the thermal stress by the adhesion to the ampoule could be suppressed. The development of the free-growth method could realize the crystal growth condition that kept the growing crystal at the local minimum temperature position and that fabricated the void-free ZnSe single crystal reproducibly.

**3-3 Decrease of the dislocation density**

As described above, the adhesion between the ampoule inner surface and the growing crystal could be avoided, and the voids formation due to the sublimation from the seed crystal back surface could be suppressed, so that the crystal quality could be improved. But the crystal back surface was adhered to the pedestal after the crystal growth, and the increase of the dislocation density from the adhesion area could not be restricted. This adhesion might be caused by the temperature profile change during the cooling process after the crystal growth. The temperature of the pedestal was considered to become lower than the temperature of the seed crystal in the cooling process due to the decrease of the radiation effect.

In order to prevent the growing crystal from adhering to the pedestal during the cooling process, the ampoule was elevated to the upper position so as to locate the growing crystal at the middle of the furnace, and the temperature profile was changed to the reversed profile that the lower part of the furnace high temperature and the upper part of the furnace low temperature. Consequently, the adhesion of the seed crystal to the pedestal could be avoided. **Photo 2** shows the back surface of the as-grown crystals. **Photo 2 (a)** shows the roughing surface before the improvement and indicates the sublimation from the back surface. On the other hand, **Photo 2 (b)** shows the clear surface after the improvement and indicates the suppression of the sublimation from the back surface. **Photo 3** shows the dislocation distribution near the crystal back surface. These

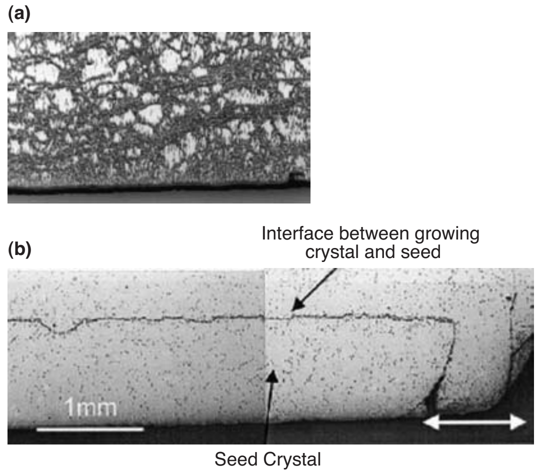


**Photo 3.** Dislocation distributions in the vicinities of the seed crystals of as-grown crystals
(a) Before improvement of the cooling process
(b) After improvement of the cooling process

are the etching pit distribution obtained by NaOH etching of the vertical sliced wafers. The improvement of the cooling process could prevent the increase of the dislocation density. It indicates that the thermal stress attributed to the adhesion of the crystal to the pedestal can be suppressed effectively.

**Table 1.** ZnSe crystal growth conditions by PVT method

| | |
|---|---|
| Growth direction | <111> |
| Growth temperature | ~1100 ˚C |
| Growth atmosphere | Ar |
| Crystal diameter | 2 inch |
| Crystal length | 30〜40 mm |
| Growth rate | ~1 mm/day |
| Growth period | 30 days |

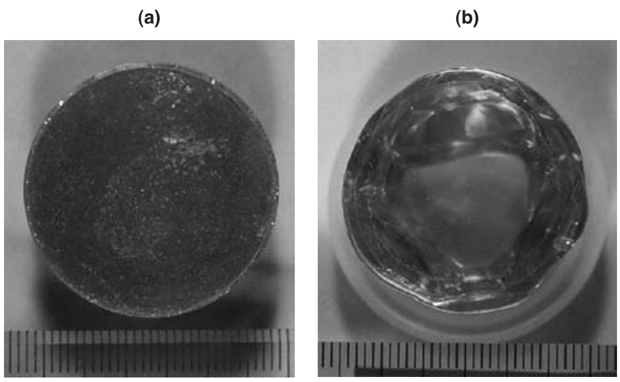


**Photo 2.** Back surfaces of seed crystals after crystal growth
(a) Before improvement of the cooling process
(b) After improvement of the cooling process

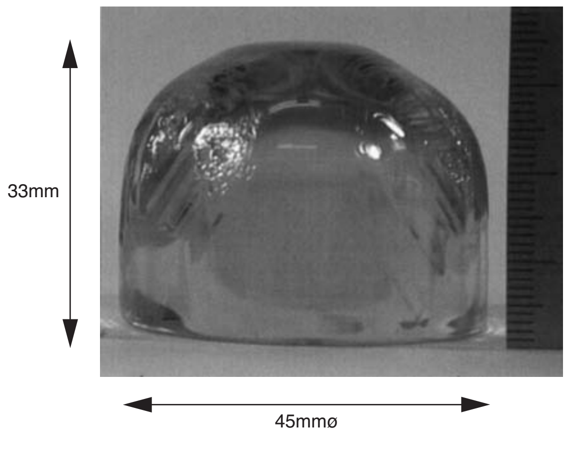


**Photo 4.** ZnSe single crystal grown by PVT method

ZnSe single crystals with high quality suitable for the LED substrates could be fabricated reproducibly by means of the techniques described above. **Table 1** indicates the crystal growth condition and **Photo 4** shows the ZnSe single crystal with the crystal diameter of about 45 mm and the crystal height of about 35 mm. The average dislocation density in the wafer was about 5 x $10^3$ $cm^{-2}$, which was satisfied the requirement of the LED substrates.

## 4. Al Thermal Diffusion

ZnSe crystals grown by the PVT method were undoped and had high-resistivity. In order to fabricate the substrates for the white LED, it is necessary to dope the impurity for adding the conductivity and emission characteristics. Al thin film was deposited on the surface of the sliced ZnSe wafer by the vacuum evaporation, and then Al was diffused into the ZnSe crystals by the thermal annealing in Zn atmosphere in the quartz ampoule. Si vapor from the quartz ampoule was the problem in this method. $Al_2SiO_5$ particles generated by the reaction of Al and Si vapor adhered to surface of the ZnSe wafers and caused the increase of the dislocation density.

The double wall annealing vessel that the pBN inner ampoule was settled in the quartz ampoule was used, so that the reaction between the Si vapor from the quartz ampoule and the Al on the ZnSe wafers was eliminated. In addition, Al was deposited not on the front surface of the wafer, namely the surface constructing the device structure, but on the back surface to prevent the front surface from deteriorating. Al concentration of higher than 2 x $10^{18}$ $cm^{-3}$ in the region from the substrate surface to about 500 um depth could be obtained by the thermal annealing of 950 ˚C and 168 h[12]. **Figure 4** indicates the substrate emission depth profile of ZnSe substrate of 720 um thickness measured by using the laser scattering tomography. **Figure 4** shows that the substrate emission intensity has almost symmetric profile at the front surface and the back surface. The surface diffusion coefficient is generally several orders higher than the bulk diffusion coefficient. Therefore, Al deposited on the back surface of the wafer should diffuse along the surface to the front surface and diffuse into the substrate not only from the back surface but from the front surface. While the dislocation density increases due to the generation of $Al_2SiO_5$ occurred only on the back surface, the high Al concentration ZnSe substrate could be obtained without increase of the dislocation density on the front surface of the substrate. **Figure 5** indicates the measurement result of the X-ray rocking curve of the ZnSe substrate after Al diffusion treatment. FWHM of about 9.0 arcsec shows that high crystal quality can be maintained after Al diffusion.

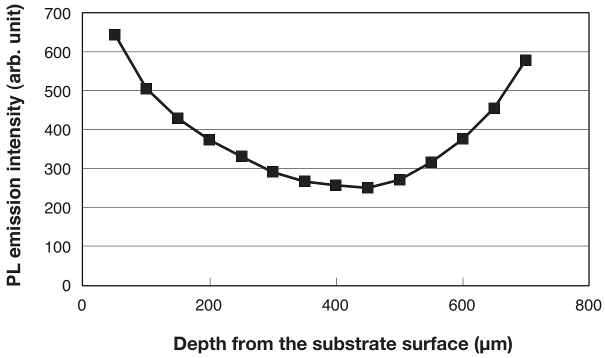


**Fig. 4.** Depth profile of the intensity of substrate emission measured by light scattering tomography

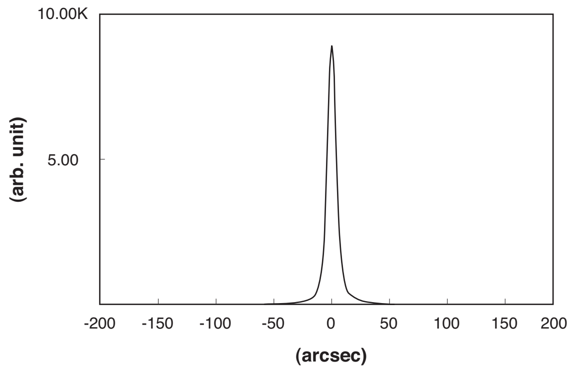


**Fig. 5.** X-ray rocking curve of ZnSe substrate after Al diffusion

## 5. ZnSe Crystal Growth by the CVT Method

ZnSe crystal growth by the CVT method uses Iodine as an agent for the crystal growth and the growth pressure is relatively high (about 1 atom). This high pressure leads to the problem it is difficult to get a large size crystal. The driving force for the natural convection can be expressed by Grashof number which is the dimensionless number defined by equation (3).

$$Gr = g\beta\Delta TL^3\rho^2/\mu^2 \quad \cdots\cdots\cdots\cdots(3)$$

Where, $g$: gravitational acceleration, $\beta$: coefficient of cubical expansion, $\Delta T$: temperature difference in the ampoule, $L$: representative length of the ampoule, $\rho$: density of the gas and $\mu$: coefficient of viscosity of the gas. The ampoule inner diameter is smaller than the ampoule length in the usual ampoule structure, so the representative length $L$ of the ampoule is the ampoule inner diameter. Equation (3) indicates that the natural convection becomes stronger proportional to the 3rd power of the ampoule inner diameter, namely the growing crystal diameter. Accordingly, the transport of the source gas is controlled not by the diffusion but by the convection, so that the supersaturation near the growth interface becomes larger and it causes the instability of the growth interface.

Therefore, the reduction of Gr number is necessary for stabilizing the crystal growth condition. $\beta$ and $\mu$ are the physical properties and cannot be changed, while decrease of $\Delta T$ and $\rho$ causes the decrease of the growth rate and it is not desirable for practical application. For these reasons, we developed the new methods to reduce $L$ or $g$.

**5-1 Reduction of the representative length of the ampoule**

In order to decrease the ampoule representative length $L$, the distance between the growing crystal and the source material should be reduced. But the reduction of the distance results in the problems that the temperature difference between the crystal and the source cannot be maintained and that long length crystal cannot be obtained.

**Figure 6** shows the ampoule structure having the quartz mesh convection suppression plate[13]. With the decrease of the volume of the ZnSe source material by the sublimation, the position of the convection suppression plate lowers and the distance between the growing crystal and the convection suppression plate can be kept almost constant during the crystal growth. The representative length $L$ becomes the distance between the growing crystal and the convection suppression plate by keeping this distance sufficiently smaller than the ampoule inner diameter. Accordingly, the natural convection can be suppressed and the stable crystal growth can be realized in spite of the enlargement of the crystal diameter. **Photo 5** shows the ZnSe crystals grown (a) without and (b) with the convection suppression plate. They indicate that the convection suppression plate can stabilize the crystal growth condition.

**5-2 Decrease of the effective gravitational acceleration**

If the gravitational acceleration can be reduced, the natural convection can be suppressed according to eq. (3). Use of the micro gravity in the space is not actual solution. The rotational CVT method shown in **Fig. 7** was developed as a technique to reduce the gravitational acceleration effectively[14],[15]. The growth ampoule was settled horizontally and rotated around the central axis of the ampoule at uniform rate. When the ampoule is rotated at a rotation rate higher than the gas rotation rate induced by the natural convection in the ampoule, the direction of the gravity should rotate higher than the natural convection. As a consequence, gas in the ampoule does not rotate in the ampoule but oscillates at the position. In this method, the gas transport was controlled not by the convection but by the diffusion, so that the increase of the supersaturation at the growth interface could be suppressed and the stable crystal growth could be expected.

**Photo 6** shows the growing ZnSe crystals. The growth conditions are as follows: ampoule inner diameter 25 mm, distance between the seed crystal and the quartz mesh 40 mm, source temperature 890 ˚C, seed temperature 850 ˚C, Iodine concentration 1.7 mg/cm$^3$ and seed crystal (111)B face ZnSe single crystal. The ampoule rotation rates are **Photo 6 (a)** 0 rpm and (b) 60 rpm. The ZnSe crystal with

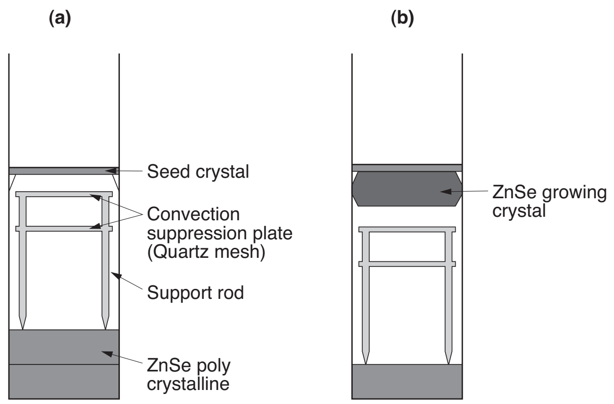


**Fig. 6.** Schematic diagram of ZnSe crystal growth with convection suppression plate
(a) Initial stage of the growth
(b) Final stage of the growth

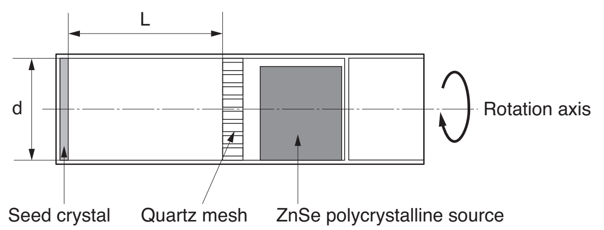


**Fig. 7.** Schematic diagram of ZnSe crystal growth by the rotational CVT method

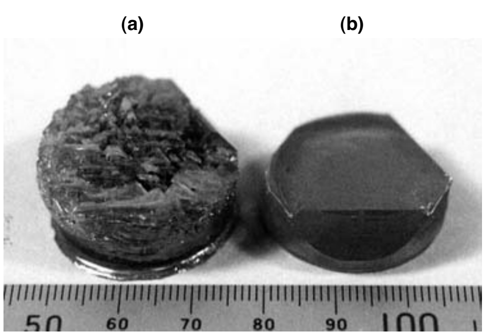


**Photo 5.** ZnSe crystals grown by CVT method
(a) Crystal grown without convection suppression plate
(b) Crystal grown with convection suppression plate

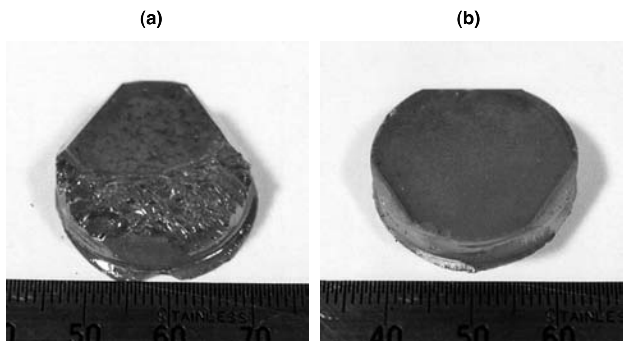


**Photo 6.** ZnSe crystals grown by the rotational CVT method
(a) Crystal grown at 0 rpm
(b) Crystal grown at 60 rpm

flat growth interface could be obtained by rotating the ampoule, and it is confirmed that the rotational CVT method is effective to stabilize the crystal growth condition.

## 6. Application to the ZnSe White LED

The fabrication of the large-sized ZnSe substrates with high quality could become possible through the techniques described above, and the ZnSe white LED with homoepitaxial growth on these ZnSe substrates was developed[(16),(17)].

**Figure 8** indicates the schematic diagram of the cross section of the epitaxial structure. The epitaxial layer was grown by the MBE (molecular beam epitaxy) method, and chlorine and nitrogen were used as the n-type dopant and the p-type dopant, respectively. The active layer was ZnCdSe/ZnSe multi-quantum well structure. The p-type electrode at the front surface was semi-transparent Au electrode for increasing the light emission efficiency. The n-type electrode at the back surface of the substrate was Au/Ti electrode.

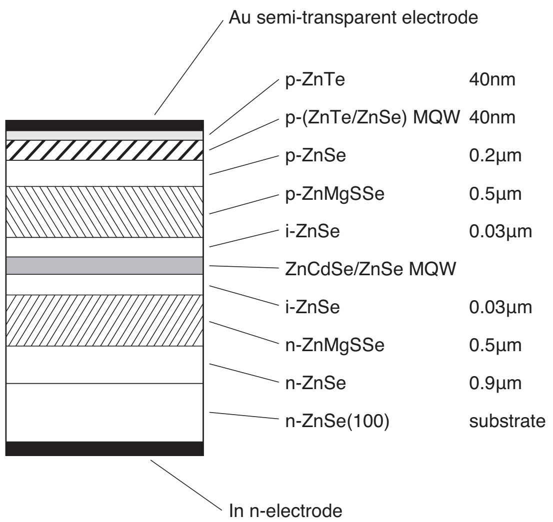


**Fig. 8.** Schematic cross section of the epitaxial structure of ZnSe-based white LED

**Figure 9** shows the emission spectrum of the ZnSe white LED. It consists of the sharp 485 nm blue emission from the epitaxial active layer and the substrate SA emission centered at about 585 nm which expands from green to red region. White light can be obtained by mixing the blue emission from the active layer and the yellow emission from the substrate. The white color temperature can be controlled intentionally by controlling the intensity ratio of the active layer emission and the substrate emission. The intensity of the substrate emission can be controlled by the substrate thickness which can be determined by lapping the back surface of the substrate after making device structure on the front surface. In terms of the color temperature, the white color of approximately 3400 K to infinite can be realized.

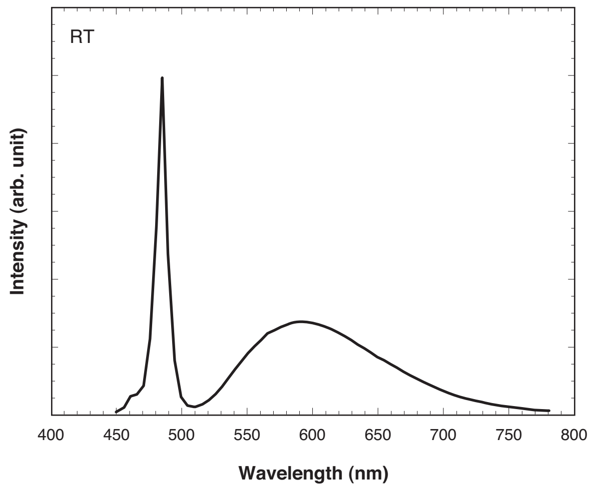


**Fig. 9.** Emission spectrum of ZnSe-based white LED

**Figure 10** indicates (a) the current - voltage characteristics and (b) the light output power - current characteristics of the epoxy resin molded device[(18)]. It shows the linear relationship between the applied current and the output

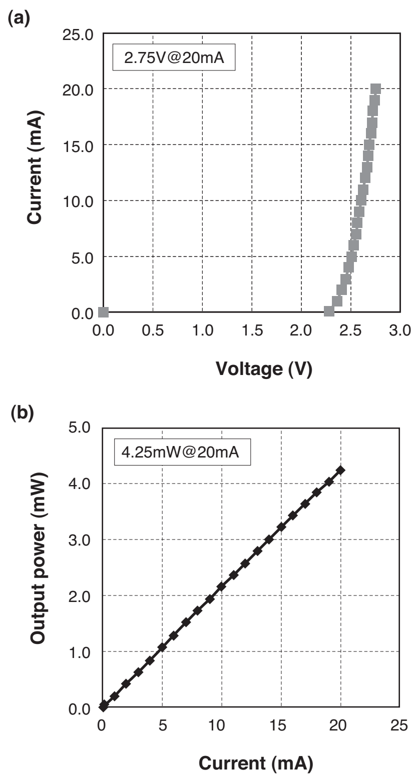


**Fig. 10.** Characteristics of epoxy resin molded ZnSe-based white LED
(a) Current – voltage characteristics
(b) Light output power – current characteristics

light power and shows the light power of 4.25 mW at the current of 20 mA. The external quantum efficiency of the LED is 8.7 %, the luminous flux and the luminous efficiency at the operating current of 20 mA are 1.1 lm and 20 lm/W, respectively. The operating voltage of this LED is 2.75 V at 20 mA, which is lower than the operating voltage of GaN-based white LED of 3.6 V. The output voltage of the lithium-ion rechargeable battery that is usually used for the mobile devices is about 3.6 V. Therefore the step up circuit for stabilization is not necessary for the ZnSe-based white LEDs, while it is necessary for the GaN-based white LEDs. The low voltage operation is suitable characteristics for the mobile devices. **Photo 7** shows the ZnSe-based white LEDs actually emitting white light.

The ZnSe-based white LED demonstrated the high performance for the light emission as described above. But the device efficiency was easy to deteriorate due to the extension of the crystal defects in the material, and hence the life of the device was the problem to be solved. The deterioration mechanism of the device was investigated and the life of the device was extended by the various improvements, such as the decrease of the defect density in the ZnSe substrate, the epitaxial structure, the device process, the packaging process and the material used. **Figure 11** shows the relationship between the half-life of the output light power and the current density[19]. The half-life of the output light power above 10,000 hr was obtained and it displayed the sufficient ability for mobile device application.

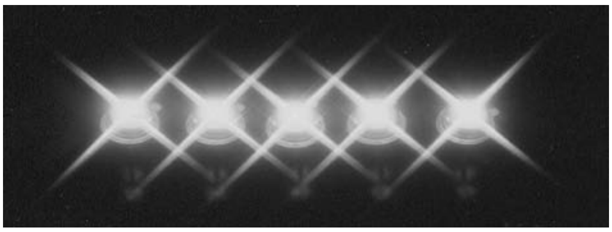

**Photo 7.** ZnSe-based white LED actually emitting white light

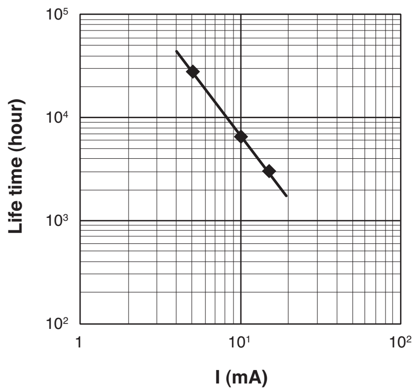


**Fig. 11.** Relationship between the half-life of the output light power and the current density

## 7. Conclusion

The development of ZnSe substrates by the vapor growth and their application for white LEDs are described. In the early stage of the development, ZnSe-based light emitting devices were developed vigorously all over the world. As the GaN-based light emitting devices had made rapid progress in their performance, the main stream of the development of the white light emitting devices were shifting to GaN-based material, and finally almost only Sumitomo Electric continued the development of ZnSe-based material. Under such circumstances of little useful information from the outside, engineers in the company taking charge of substrates, epitaxy, devices and packages struggled to solve various problems and achieved the production technique for the large-sized ZnSe substrates with high quality and for the ZnSe-based white LED with practical use performance.

The development of new technology, especially new material, depends mainly on the abilities of engineers for watching the fact, understanding the problems, investigating the mechanisms and originating the new concepts without restricted by the fixed ideas. I thought that it was exactly true when I looked back upon the various breakthroughs that were devised in the development of ZnSe-based white LEDs. The experiences about the measures against the difficulties might be shared with the colleagues of the ZnSe white LED development. These experiences should be the valuable assets in the innovative manufacturer, and they would be spread with the engineers over the organization and be connected to the next new activities for the development. I believe that the new innovative technologies, products and businesses will be created in the persistent endeavor for the development in the activated company.

**References**


(1) M .A. Haase, J. Qui, J. M. Depuydt and H. Cheng, "Blue-Green laser diodes." App. Phys. Lett. 59, p.1272 (1991)

(2) E. Kato, H. Noguchi, M. Nagai, H. Okuyama, S.Kijima and A. Ishibashi, "Significant progress in II-VI blue-green laser diode lifetime." Electon. Lett., 34, p.282 (1998)

(3) H. Wenisch, M. Fehere, K. Ohkawa, D. Hommel, M. Prokesch, U. Rinas and H. Hartmann, "Internal photoluminescence and lifetime of light-emitting diodes on conductive ZnSe substrates." J. Appl. Phys. 82, p.4690 (1997)

(4) S. Nakamura, "High-power InGaN-based blue laser diodes with a long lifetime." J. Crystal Growth 195, p.242 (1998)

(5) S. Fujita, H. Mimoto, H. Takebe and T. Noguchi, "Growth of cubic ZnS, ZnSe and ZnSxSe1-x single crystals by iodine transport." J. Crystal Growth 47, p.326 (1979)

(6) G. Cantwell, W. C. Harsch, B. G. Markey, S. W. S. McKeever and J. E. Thomas, "Growth and characterization of substrate-quality ZnSe single crystals using seeded physical vapor transport." J. Appl. Phys. 71, p.2931 (1992)

(7) H. Hartmann and D. Siche, "ZnSe single crystal growth by the method of dissociative sublimation." J. Crystal Growth 138, p.260 (1994)

(8) K. Kurisu, H. Iwamoto, T. Shirakawa, F. Higuchi and H. Namba, "Characteristics of ZnSe single-crystal wafer grown via the solid-growth method." SEI Techinical Review 151, p.128 (1997)

(9) Yu. Y. Korostelin, V. I. Kozlovsky, A. S. Nasibov, P. V. Shapkin, S. K. Lee, S. S. Park, J. Y. Han and S. H. Lee, "Seeded vapour-phase free growth of ZnSe single crystals in the <100> direction." J. Crystal Growth 184/185, p.1010 (1998)
(10) E. V. Markov, A. A. Davydov, Neorg. Mater. 11, p.1755 (1975)
(11) Yu. Y. Korostelin, V. I. Kozlovsky, A. S. Nasibov and P. V. Shapkin, "Vapour growth and characterization of bulk ZnSe single crystals." J. Crystal Growth 161, p.51 (1996)
(12) Y. Namikawa, S. Fujiwara and T. Kotani, "Al diffused conductive ZnSe substrates grown by physical vapor transport method." J. Crystal Growth 229, p.92 (2001)
(13) T. Kotani, S. Fujiwara, R. Hirota, M. Irikura and T. Matsuoka, "Development of conductive ZnSe single-crystal substrate with low dislocation density using the vapor transport method." SEI Technical Review 48, p.56 (1999)
(14) S. Fujiwara, Y. Watanabe, Y. Namikawa, T. Keishi, K. Matsumoto and T. Kotani, "Numerical simulation on dumping of convection by rotating a horizontal cylinder during crystal growth from vapor." J. Crystal Growth 192, p.328 (1998)
(15) S. Fujiwara, Y. Namikawa and T. Kotani, "Growth of 1" diameter ZnSe single crystal by a rotational chemical vapor transport method." J. Crystal Growth 205, p.43 (1999)
(16) H. Matsubara, F. Nakanishi, H. Doi, K. Katayama, A. Saegusa, T. Mitsui, T. Takebe and S. Nishine, "Development of homo-epitaxial ZnSe-based white light emitting diodes." SEI Technical Review 49, p.123 (2000)
(17) K. Katayama, H. Matsubara, F. Nakanishi, T. Nakamura, H. Doi, A. Saegusa, T. Mitsui, T. Matsuoka, M. Irikura, T. Takebe, S. Nishine and T. Shirakawa, "ZnSe-based white LEDs." J. Crystal Growth 214/215, p.1064 (2000)
(18) T. Takebe, "ZnSe-based white light emitting diode." Oyo Butsuri 70, p.554 (2000)
(19) T. Nakamura and T. Takebe, "ZnSe-based white light emitting diode and its application." OPTRONICS (2000) No.12, p.126

## Contributor

Y. NAMIKAWA

- Senior Specialist
  Doctor of Engineering
  General Manager
  Technologies Department
  Power Device Development Division
  He is engaged in the research and development of crystal growth of compound semiconductors and oxides and the development of power devices.