Micromorphological studies on the ZnSe single crystals grown by chemical vapour transport technique

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Single crystals of ZnSe have been grown by chemical vapour transport technique. Microscopic observation of crystal surfaces has been carried out using optical microscope and scanning electron microscope (SEM). Different micromorphological patterns such as microsteps, spirals and kinks were observed on the surface of the grown crystals in different growth conditions. Present studies show that the formation of these microstructures on the surface of the grown crystals depends on the growth parameters such as undercooling and stability of the growth interface. The morphology and lattice parameters of the grown crystals have also been determined by X-ray analysis.

1. Introduction

Zinc selenide and related compound semiconductors are promising materials for blue-light emitting diodes and laser diodes [1]. Bulk crystals of ZnSe are mostly grown by melt, solution and vapour methods [2]. The melt technique, in spite of its potential for high production efficiency [3], suffers from many drawbacks such as the defects which are produced by thermal strains, pollution from the crucible and use of expensive and complex furnaces [4]. Growth of ZnSe by solution method is limited because of its relatively low liquidus solubility in molten metals at high dissociation pressures [5]. To reduce the disadvantages of growth from the melt, ZnSe single crystals have been grown in low temperature range, below 1000 °C by chemical vapour transport (CVT). Literature survey shows that the habit of the ZnSe single crystals grown by CVT technique is affected by change in growth parameters such as growth temperature, undercooling and change in stoichiometry of the constituent elements [6–13]. It has also been discussed by Kaldis [14] that the morphology of the crystals grown from vapour phase depends on the mechanism which is a rate-determining step. By changing the experimental conditions such as pressure, temperature and supersaturation, there will be an interplay between the mass transport, kinetics of the chemical reaction and/or surface reactions on the growth interface and one of these processes will become the rate determining step. Very recently it has been shown that the change in experimental variables such as system pressure, temperature conditions and concentration of the transport agent will affect the contributions of mass transport through the convection and diffusion mechanisms and affect the crystallographic perfection and morphological stability of the ZnSe single crystals grown by the CVT method [15]. In the present investigation ZnSe single crystals have been grown by chemical vapour transport with more attention to the formation of different microstructural patterns on the surface of the grown crystals in different growth conditions. Crystals have been grown in different experimental conditions including various undercooling (ΔT) values and stability of the growth interface. The microscopic examination on the surface of the as-grown crystals has been carried out using optical microscope and scanning electron microscope (SEM). Morphology and lattice parameters of the grown crystals have been determined by single crystal X-ray diffraction measurements.

2. Experimental procedure

Quartz ampoules having the length of 23 cm and diameter of 1 cm were filled with 3 g of heat-treated ZnSe polycrystalline powder along with iodine at a concentration of 3 mg cm^{-3} of the empty space of the ampoule. The ampoules, cooled by ice, were evacuated to 2.66×10^{-4} Pa and sealed off. The capsules were placed into double-zone horizontal furnace controlled by Eurotherm controllers with the accuracy of ± 0.1 °C. Proportional Integral Differential (PID) controllers with the accuracy of ± 5 °C were also used in one of the growth runs. A reverse temperature profile was developed across the ampoule with growth zone in higher temperature for 24 h to remove the sticking powders from deposition zone of the ampoule and diminish the active sites. Different growth runs were carried out for different undercooling (ΔT) values using the same composition of starting materials and ampoule geometry and keeping the temperature of growth zone constant at 890 °C. Each growth run was carried out for 1 week. At the end of each growth process, the furnace was slowly cooled to

TABLE I Crystal habit and microstructural patterns observed for ZnSe crystals, grown at 890 °C with iodine concentration of 3 mg cm^{-3}, and tube dimensions ($l = 23$ cm, $d = 1$ cm) as a function of undercooling (ΔT)

No. of growth runs carried out	Undercooling (ΔT °C)	Crystal habit and dimensions (mm^3)	Microstructures observed (shown in)
2	15	Cubic platelets and pyramidal $2 \times 3 \times 1$	Microsteps (Fig. 3)
2	60	Cubic, tetragonal and hexagonal platelets $2 \times 2.5 \times 1$	kinks (Figs 4, 5) Microsteps (Fig 6)
1[a]	60	Thin platelets $2 \times 3 \times 0.2$	Spirals (Fig 7) bunch of steps (Fig 8)

[a] Poor control on temperature at growth interface because of PID controllers.

room temperature at a cooling rate of 50 °C h^{-1} to prevent thermal strains. The stoichiometry of the grown crystals were examined by atomic absorption spectroscopic (AAS) measurements. The structure and morphology of the grown crystals were studied using a computer–aided single crystal X-ray diffractometer (Enraf minus, FR 590) attached with rotating goniometer. The microscopic observation of the as-grown crystal surfaces was carried out using optical microscope and scanning electron microscope (SEM). Gold coating was made on all the samples before they were analysed by SEM.

3. Results and discussion

3.1. Morphological and structural analysis

Many individual crystals of different sizes were observed at the deposition zone of the ampoules in all the growth runs. The crystals observed at the tip of the ampoule were smaller in size compared to those grown far from the tip position. Intergrowths were observed mostly in the case of growth runs when the furnace was controlled by PID controllers in both zones. The crystals grown with lower undercooling were light brown and the crystals grown with higher undercooling were yellowish brown in colour. The habit and average dimension of the grown ZnSe crystals along with applied growth conditions have been summarized in Table I. The results of structural analysis showed that crystals grown in all the growth runs are a combination of both cubic and hexagonal structures. X-ray analysis showed that the crystals grown with cubic structures are having lattice parameter of $a = 0.566$ nm with large (1 1 1), small (1 1 0) and (2 1 1) faces. The result of AAS measurements of the grown crystals shows that there is 5% deviation in stoichiometry of the grown crystals due to the deficiency of the zinc atoms. It has been reported that deviation from stoichiometry causes well-developed (1 1 1), and small (1 1 0) and (2 1 1) faces in ZnSe single crystals with cubic structures [11]. Therefore deviation from stoichiometry has caused more development of (1 1 1) face compared to the other faces in our case. Fig. 1 shows the cubic ZnSe single crystal with (1 1 1) as the upper face. The layers grown in the form of triangles are showing the three-fold symmetry of the (1 1 1) face. Fig. 2 shows the hexagonal ZnSe single crystal with hexagonal structure. It is seen that in hexagonal modification the (0 0 1) face is the prominent face.

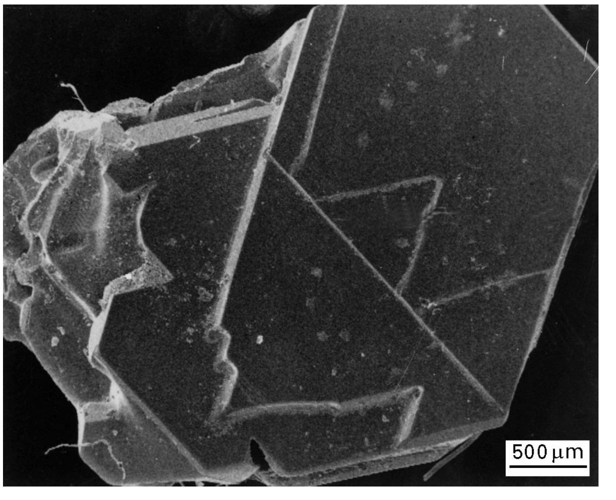

Figure 1 ZnSe single crystal with cubic structure and (1 1 1) as the upper face.

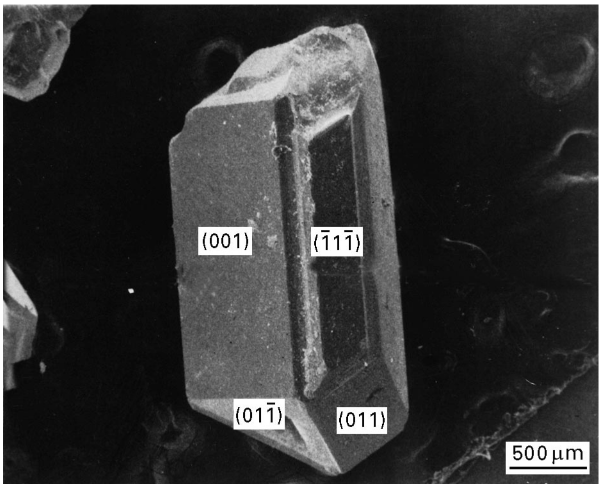

Figure 2 ZnSe single crystal with hexagonal structure (crystal faces are marked).

3.2. Micromorphological studies

The microscopic observation of the surface of the as-grown crystal showed the formation of different

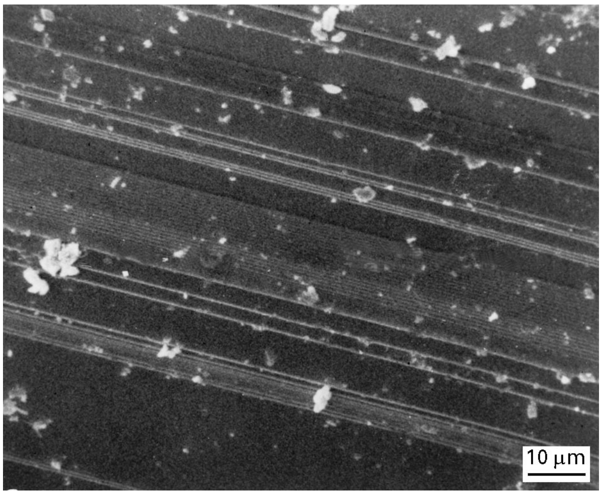

Figure 3 Microsteps on the surface of the ZnSe crystals grown with lower undercooling.

microstructural patterns such as microsteps, spirals and kinks. Table I shows the different types of microstructures which have been observed in each growth condition. In addition to the microstructural patterns, it was observed that the surface of the as-grown crystals have been covered by fine crystals and flecks left by the transport agent. Removing these particles which have been attached to the surface by chemical agents can damage the microstructural features on the crystal surfaces.

The crystals grown with lower undercooling ($\Delta T = 15\,^{\circ}\mathrm{C}$) showed mostly smooth and flat faces without microstructures up to a SEM magnification of $3000\times$. Microsteps were also observed on the surface of some of the crystalline pieces. Fig. 3 shows microsteps on the surface of the ZnSe crystals grown with lower undercooling. Microsteps are in the form of parallel and straight lines with the thickness of the order of micrometres. Steps have not distributed uniformly on the surface and they appear to be more dense and bunched in some of the surface portions. This can be due to the non-uniformity in the supersaturation caused by slight local thermal fluctuation on the surface of the crystal during the growth process. Two mechanisms have been suggested for the generation of these microsteps [16]. First, they can be generated at the emergence points of dislocations and expand over the surface. Second, in addition to dislocations, crystal edges and corners frequently favour the nucleation of new layers and therefore are able to spontaneously generate microsteps. Since no sign of screw dislocation is observed on the surface of the crystal shown in Fig. 3 and, moreover, the microscopic observation showed that the microsteps are continued on the surface up to the surface edges, it is more probable that microsteps originate from crystal edges.

The microscopic examination of the crystal surfaces grown in higher undercooling condition ($\Delta T = 60\,^{\circ}\mathrm{C}$) showed that surfaces of the grown crystals were rougher compared to the surface of the crystals grown with lower undercooling ($\Delta T = 15\,^{\circ}\mathrm{C}$). The smooth faces free from microstructures were also observed in limited number of crystalline pieces grown in higher undercooling conditions. Figs 4, 5 and 6 show different types of features observed on the surface of the crystals grown with higher undercooling. Fig. 4 shows kinks with well-resolved structure. As the separation of these kinks is very small, it is not possible to resolve them under an optical microscope. Fig. 5 shows a similar structure which has been formed on the rough surface of the grown crystals. Fig. 6 shows the formation of microsteps with irregular shapes formed between two flat faces.

Microscopic examination of the surface of the crystals grown with higher undercooling value ($\Delta T = 60\,^{\circ}\mathrm{C}$), but poor control on temperature of the growth interface, showed the formation of spirals and structures with a bunch of steps. Because of oscillation in temperature of the growth zone, there will be a change in flow of the material and its stability at the interface of growing crystal. Hence, it will lead to the formation of microstructures with incompleted faces. Figs 7 and 8 show the formation of spirals and structures with bunch of steps on the surface of the crystals respectively. Fig. 7 shows the spirals which have

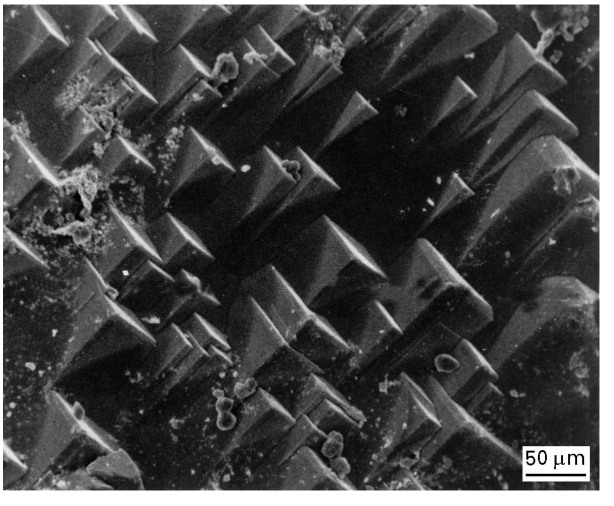

Figure 4 Kinks with well-resolved structure grown with higher undercooling.

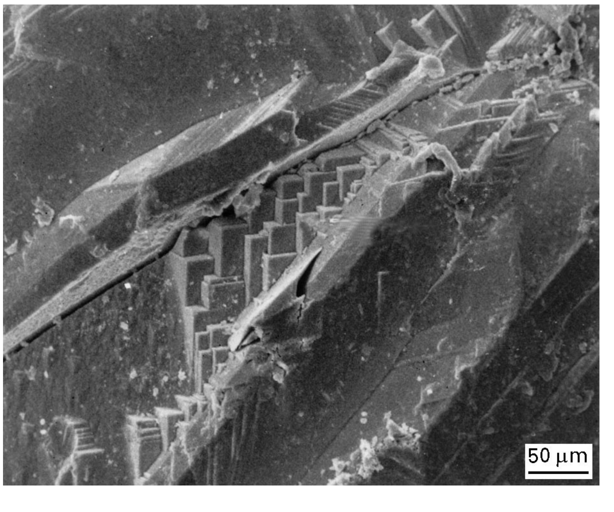

Figure 5 Kinks formed on the rough surface of the ZnSe single crystals grown with higher undercooling.

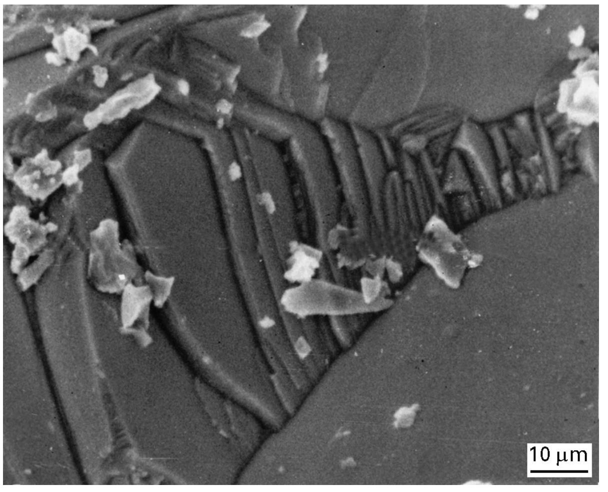

Figure 6 Growth layers in the form of steps with irregular shapes on the surface of the ZnSe single crystals grown with higher undercooling.

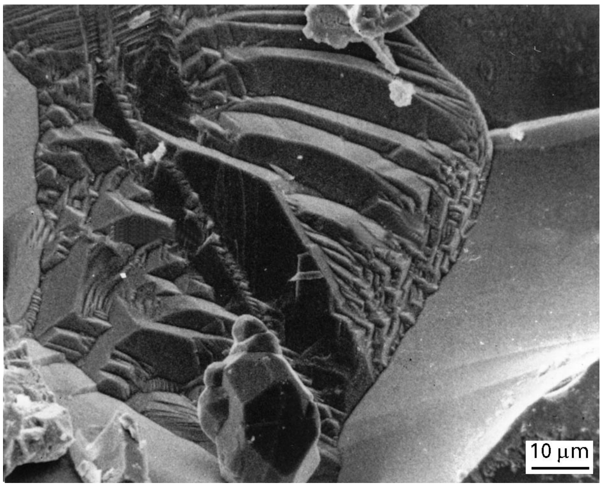

Figure 8 Microstructure, including bunch of steps and microcrystals grown with higher undercooling and instability of growth interface.

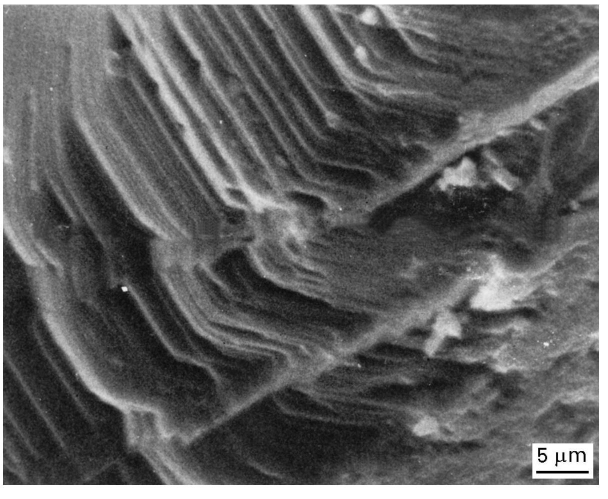

Figure 7 Growth of layers in the form of spirals with irregular bunching on the surface of the ZnSe crystals grown with higher undercooling and poor control of temperature at the growth interface.

bunched in an irregular manner. It has been suggested by Hottenhuis and Lucasius [17] that the shape, number and thickness of marcrospirals will change because of the effect of different parameters, such as supersaturation and temperature. Fig. 8 shows a structure in which some of the layers have been bunched together and they lead to a rough surface on the right side of the figure. Formation of microcrystals with irregular and regular habit can also be seen in the lower part of this figure. The structure with a bunch of steps shown in Fig. 8 is an unusual combination of two fundamental morphological features which are separately treated by the main theories of crystal growth: train and bunches of steps (Burton-Cabrera-Frank, BCF, theory, two-dimensional nucleation) and wave-like morphological perturbations (morphological stability theory). The active coexistence of these features has been confirmed in several micrographs of crystals growing at high temperatures from the vapour. Similar features have been observed on rare earth phosphides which have been grown at high temperatures ($T \sim 2100\,^{\circ}$C) from vapour [14]. Our observation shows that this type of structure can also be formed on the surface of the crystals which are grown in low temperatures (below 1000 °C) by chemical vapour transport technique.

4. Conclusion

Single crystals of ZnSe have been grown in different growth conditions. The grown crystals were found to have both cubic and hexagonal structures. Microscopic analysis of the surface of ZnSe crystals grown in different experimental conditions showed formation of different types of microstructures. The crystal surfaces became rougher with increasing density of kinks, as the degree of undercooling increased. The results also showed that the instability of the growth interface will result in the formation of structures with a bunch of steps.

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