Technical Note

EFFECT OF MASS TRANSPORT STABILITY AND UNDERCOOLING ON NUCLEATION OF ZNS CRYSTALS IN CLOSED AMPOULE CVT

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Abstract: *ZnS crystals were grown by CVT technique using iodine as a transporting agent under different mass transport stability conditions. Theoretically predicted optimum growth temperature and lower undercooling (ΔT) were applied for getting better control on mass transport and nucleation inside the quartz ampoule. ZnS crystals were grown at both optimum and non-optimum temperatures under different undercooling conditions and their characteristics were compared with each other. For 2 mg/cm³ concentration of transporting agent (C) and $\Delta T = 15\ °C$ growth at optimum temperature (1000 °C) yielded ZnS crystals with volume of 12x4x2 mm³ and proper quality. For C= 2 mg/cm³ and $\Delta T = 50\ °C$ growth at non optimum temperature (1050 °C) resulted to the formation of ZnS polycrystallites with faulty structures.*

Keywords: *ZnS, CVT, Nucleation.*

1. INTRODUCTION

ZnS, a II-IV wide band gap materials, has attracted considerable attention due to many potential applications in the field of short-wave length photoelectronic devices, especially for ultra-violet laser diodes and photodetectors [1,2]. ZnS crystals have been grown by variety of techniques [3-6]. Among these techniques, chemical vapor transport (CVT) has received grate interest due to several advantages such as lower growth temperatures than melting and sublimation points of materials [7]. It is difficult to grow ZnS crystals by sublimation because of the low vapor pressure at the temperatures where the cubic modification is stable. In addition, these compounds crystallize in a mixed zincblende-wurtzite structure with the presence of twinning and stacking faults when they are grown at high temperatures from melt. CVT has some disadvantages; as an example, controlling the nucleation and establishing optimum growth conditions to obtain high quality and large crystals is to some extend difficult. Experiments have shown that transport rate inside the closed CVT tube depends on the temperature difference between growth and deposition zones which is called undercooling. Literature survey shows that ZnS single crystals have been grown by CVT technique in broad range of temperature from 700 °C to 1150 °C using iodine with concentration of 1-7 mg/cm³ [8-15]. This survey also shows that these ZnS crystals have been grown in the wide range of 10-300 °C undercooling. 10 °C is the lowest undercooling for which the nucleation of zinc sulfide on the quartz has been reported [9]. For $\Delta T \geq 10$ °C the nucleation begins so vigorously that no control is possible inside the quartz ampoule and a number of crystals grow simultaneously. However, 10 °C undercooling results in the growth of ZnS crystals with bigger size and better quality when seeding procedure is performed. We have shown that in addition to undercooling the stability in flow of material inside the tube is another important factor which affects the nucleation and partially controls this process [7]. The flow of material is temperature dependent process and it has been shown that the exact temperature distribution inside the ampoule is different from that of the heating arrangement and temperature oscillations of up to ±25 °C under typical growth conditions have been measured [17]. In present work, we have grown ZnS crystals with different undercooling values and mass transport stability conditions. The quality of the crystals grown under different conditions has been compared with each other.

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2. EXPERIMENTAL

Ampoule with the length of 150 mm and inner diameter of 12mm was filled with 2 grams of heat-treated ZnS polycrystalline powder along with iodine at a concentration of 2 mg/cm^3. All compounds were purchased from Fluka with a purity of 99.999%. The ampoule was cooled by ice and evacuated to 2×10^{-6} torr and sealed off. The capsule was placed into a three-zone horizontal furnace controlled by Eurotheerm controllers. The growth runs were carried out at two temperatures 1000 °C and 1050 °C. The temperature of 1000 °C was the optimum temperature to grow ZnS crystals inside the CVT closed tube using iodine as the transporting agent at concentration of 2 mg/cm^3. This temperature was calculated based on a thermodynamic model for ZnS-I$_2$ system following the exact procedure which was applied to ZnSe-I$_2$ system [7]. For iodine concentration of 2 mg/cm^3, 1000 °C lies exactly at the peak of the curve in which transport rate is drawn versus temperature. At this temperature flow of material has more stability along the ampoule and growth interface is less sensitive to thermal fluctuations. However, for 50 °C above or below of the optimum temperature, the change in transport rate due to possible thermal fluctuation along the quartz ampoule is very high. For the growth temperature of 1000 °C the source temperature was kept at 1015 °C to provide ΔT=15 °C. This is the lowest undercooling that we experienced in our laboratory for starting nucleation of ZnS on quartz ampoule. Under these conditions, the growth process used the both advantages of lower undercooling and growth at optimum temperature. Meanwhile, the temperature of 1050 °C was selected as the non optimum growth temperature. For this growth temperature, the source temperature was kept at 1100 °C to provide a 50 °C undercooling. In this state, control of nucleation at 1050 °C not only suffered from higher undercooling, but also from non optimum growth temperature. At the end of each process, the furnace was slowly cooled to room temperature with a cooling rate of 50 °C/h to prevent thermal strains.

3. RESULTS AND DISCUSSION

ZnS crystals depending on growth condition exhibit sphalerite, wurtzite or intermediate structures. ZnS undergoes a phase transition at 1024 °C from low temperature stable phase sphalerite (cubic) to wurtzite (hexagonal) [14]. The results of growth runs showed that no crystal was grown in deposition zone when undrecooling was lower than 15 °C. Under such conditions, we had better control on nucleation at growth zone where limited numbers of crystals was grown. Fig.1 shows a ZnS crystal grown at 1000 °C with ΔT=15 °C. The crystal volume was determined as $\sim$12×4×2 mm^3. As is seen, this crystal is transparent and free from grain and twin boundaries over half the volume. Triangular etch pits revealed the large (111) upper face of this crystal. Growth of ZnS with similar morphology by CVT technique using seed crystal has been reported by Catano and Kun [12]. For the crystals which were grown at 1050 °C with high undercooling (ΔT=50 °C), controlling the transport of material from source zone to deposition zone was poor. Fig.2 depicts the coarse grained materials, which formed near the ampoule tip at 1050 °C. These aggregations

Fig.1. ZnS crystal grown at 1000 oC with ΔT=15 oC.
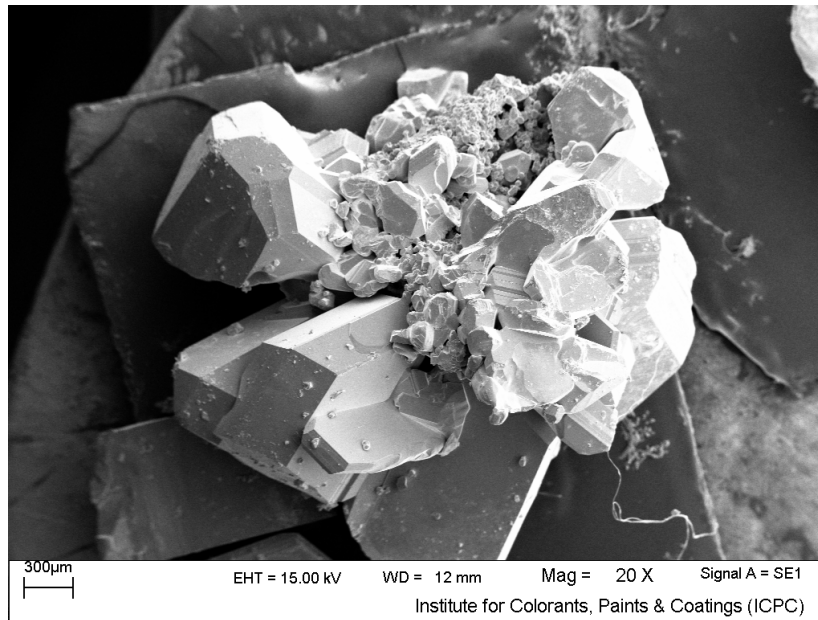
Fig.2. ZnS in the form of coarse grained material grown at 1050 °C with ΔT=50 °C.

develop into some isolated single crystals with relatively poor crystallographic perfection showing numerous defects and growth instabilities. Fig.3 shows many ZnS crystallites with different sizes and habits grown under poor control on nucleation. When growth is carried out at non optimum temperature, the growth zone experiences more change in supersaturation due to even small temperature fluctuation along the ampoule. Moreover 50 °C undercooling is big enough to change the supersaturation at the growth zone in favor of producing more number of nuclei at the same time. Always high supersaturation favors random nucleation and polycrystalline growth [9]. Fig. 4 shows that due to simultaneous growth of individual crystallites
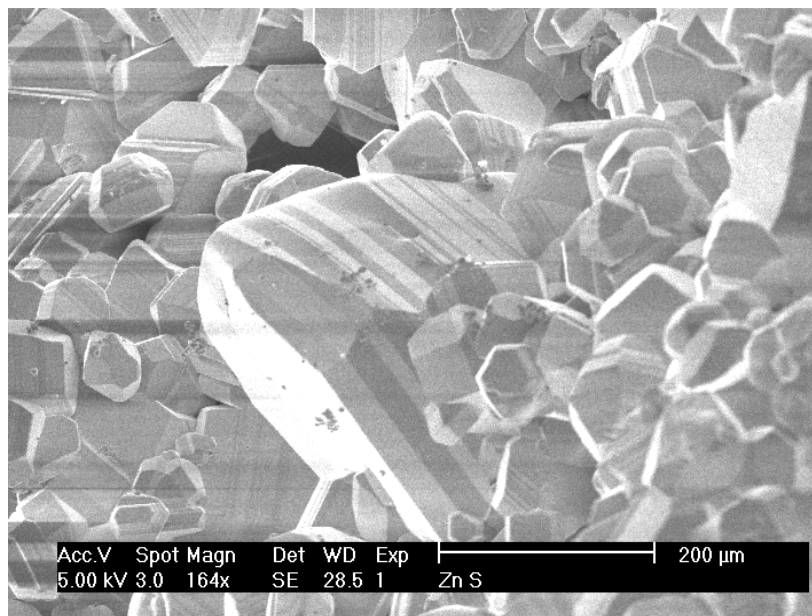

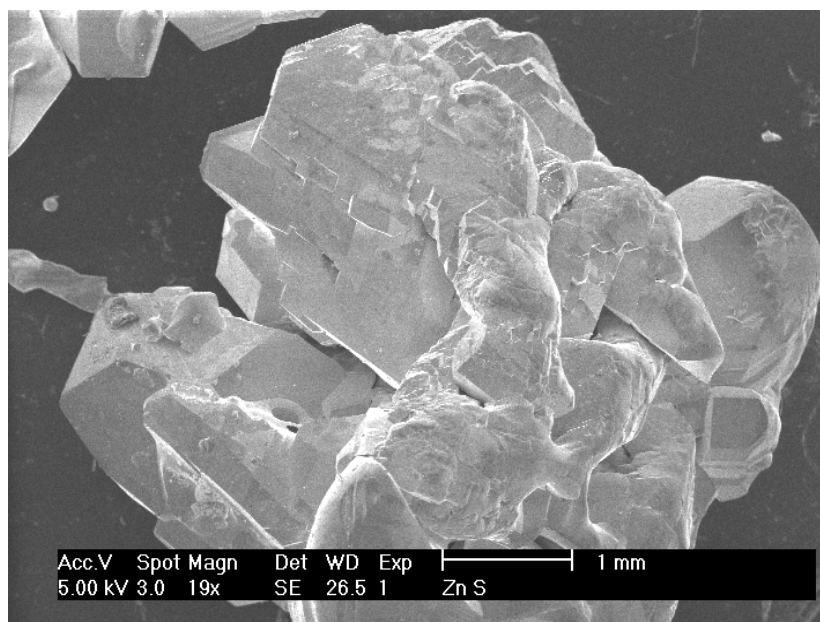**Fig.3.** ZnS Crystallites grown at 1050 oC with ΔT=50 oC.

Fig.4. Intergrowth of ZnS crystallites at 1050 °C.

closing to each other intergrowth has occurred. In some of the growth runs at $\Delta T=50$ °C, it was observed that the surfaces of the grown crystals have been contaminated by incorporation of iodine layers due to instability condition. To remove the iodine traces from surfaces, the as-grown crystals were immersed in $Na_2S_2O_3$ solution for few minutes. This treatment revealed some of the etch patterns on the surface of the crystals. Fig.5 shows the surface of the etched clusters in which the bright and dark stripes present the hexagonal and cubic structures, respectively. These stripes may have the hexagonal wurtzite structure, the cubic sphalerite
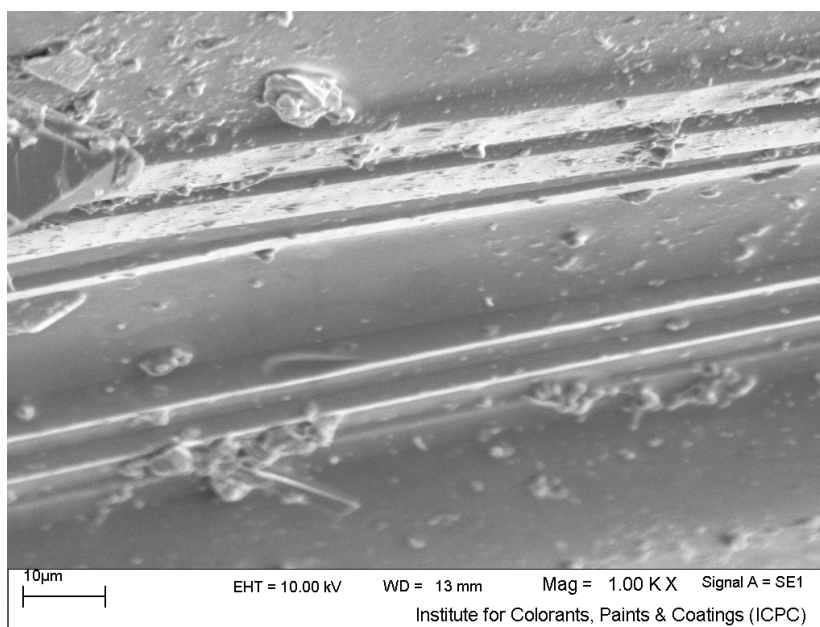

Fig.5. Surface of the etched ZnS clusters grown at 1050 °C.

structure, or a polytypic structure. These results were expected since 1050 °C lies at the temperature range where growth of ZnS crystals with faulty structure has been reported [14].

4. CONCLUSION

ZnS crystals were grown under different mass transport stability conditions. For an undercooling of 15 °C, ZnS crystal with apropriate quality and a size of ~12×4×2 mm³ was grown at theoretical predicted optimum temperature (1000 °C). For an undercooling of 50 °C, mostly polycrystalline aggregates with stacking faults were grown at a non optimum growth temperature (1050 °C).

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