MICROSTRUCTURE OF CdS AND ZnS CRYSTALS OBTAINED FROM THE MELT UNDER PRESSURE

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The results of the investigation of the microstructure of CdS and ZnS crystals obtained from the melt under pressure by the Bridgman method are presented. The investigation confirms conclusions about the growth mechanism of ZnS crystals-layer by layer — which have been proposed. To explain the existence of optically inhomogeneous bands and lines in ZnS crystals, a model has been proposed. The CdS crystals showed some characteristic features of the "layer by layer" growth mechanism which was similar but not identical to that of ZnS crystals. The dislocation density has been estimated on the basis of the density of etch pits which was of the order of $10^5 - 5 \cdot 10^5$ cm^{-2}.

1. Introduction

In [1], characteristic defects like macroscopic inclusions and "negative crystals" were mentioned. They were grown during the crystallization of II—VI compounds (such as CdS and ZnS) from the melt by the Bridgman method under pressure [2]. Those defects can be disclosed by the microscopic observation of the crystals in transmitted light. Information on other defects in crystals grown by the Bridgman method, like grain boundaries, block boundaries and twin boundaries can also be obtained from the microscopic observation of the surface microstructure of a crystal, disclosed by selective chemical etching.

Our observations of etched crystals allow us to disclose these characteristic defects and moreover, to propose some conclusions about the growth mechanism.

2. Experimental

A specific compostion of chemical reagents and specific etching conditions were applied in the method of chemical etching, in order to disclose the crystal defects under study. Anyway, it is known that a small change in composition of the investigated crystals often requires considerable changes in etching conditions [3].

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In this paper several etchants known from the references [3–5] were investigated under variable conditions. The most effective reagents and etching conditions for the respective crystals are shown in Table I.

TABLE I

The etchants and etching conditions for CdS and ZnS crystals

No	Sample	Cristallographic orientation	Etchants	Etching conditions
1	CdS	(0001)	H_3PO_4 — 60%	40 min. at temp. 100°C (chemical polishing)
2	CdS	(0001) $(11\bar{2}0)$	1 HNO_3 + 2 CrO_3 + 3 H_2O	5 min. in hot solution
3	CdS	(0001) $(11\bar{2}0)$ and ⊥ to the growth direction	HCl	30 s in vapours
4	CdS	(0001)	35% H_3PO_4 saturation CrO_3 + 65% HCl	10—20 s at room temp.
5	ZnS	(0001) $(11\bar{2}0)$ and ⊥ to the growth direction	2p. CrO_3 + 1p. HNO_3 + 3p. H_2O	5 min. in hot solution

In most cases the microstructure of the crystals has been disclosed on cleaved planes. For the (0001) plane of CdS, the surface was prepared by mechanical — and next by chemical polishing in concentrated orthophosphoric acid for 40 min. at 100°C.

The results of observations

Figs 1–4 and 8–9 show pictures of the microstructure of the (0001) plane in CdS. crystals after etching for 5 min. in a hot solution of the composition given in Table I

As can be seen from Fig. 1, the etch pits on that plane generally show a terrace structure. The configuration of terraces inside the etch pits does not show the characteristic features of the "layer-spiral" growth mechanism which could be expected from the applied Bridgman technique for crystallization.

The presence of characteristic defects, called in [1] "negative crystals", and the shape of the etch figures on the different surfaces of the crystal (Figs 4—6) show that the growth mechanism is a succesive macrostep motion.

The configuration of the etch figures shows that the presence of defects like block boundaries, grain boundaries and twin boundaries can be observed mainly on the (0001) plane. On the $(11\bar{2}0)$ plane, one can observe mainly block boundaries.

In many cases we were able to observe a deep hexagonal figure from etching on the (0001) plane with a flat bottom without terrace structure. Sometimes on the flat bottom

one or a few typical dislocation etch-pits could be noticed (Fig. 2c). The presence of an etch figure like that arises from changes in the activity of the etchant on the bottom of the etch figure, where the density of dislocation is lower. Sometimes, we could observe a more perturbed structure on the bottom. Such a picture of the microstructure suggests that the growth of a perfect crystal on the more defective base is possible. On the (0001) plane, often the etch figures has been disclosed which prove the above mentioned layer structure of the crystals (Fig. 5).

The dislocation density has been estimated on the basis of the density of etch pits on the surfaces of the crystals. It was corroborated that the mean value of the dislocation density oscillates between $10^5 - 5 \cdot 10^5$ cm^{-2}. It is necessary to treat those values only approximately. It is known [5] that etch pits can be formed on the other imperfections of a crystal surface as well. Beside this, not all dislocations were disclosed. X-ray investigations of the density of dislocations show, as a rule, values about ten times higher than those values estimated on the basis of the density of etch pits. The CdS crystals, which have been obtained from the melt with the temperature increased by 30°C above the melting point, showed a mass loss of about 3%. In those crystals we have observed the presence of a micromosaic, like that shown in Fig. 7, and irregular loops of etch pits

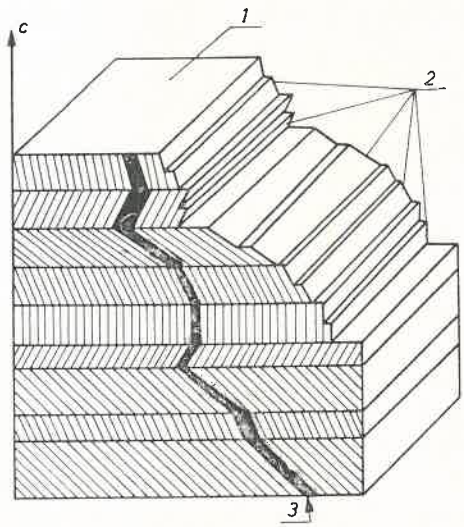

Fig. 12. The model of the growth mechanism of ZnS crystals from the melt; *1* — the macrostep, *2* — the layers in a head of the macrosteps, *3* — the mechanism of the passing on of growth defects during the formation of succesive layers as they were growing (see Fig. 11)

(Fig. 8) probably arising from the generation of dislocations in that area with a surplus of Cd and a higher concentration of impurities.

The observations of the microstructure of ZnS crystals tends to support the suggestion of crystal growth by succesive macrostep motion. We have presented this growth mechanism for the first time in [1] which explained the growth of "negative crystals" in ZnS crystals. Fig. 9 shows their appearance at the cross sections of a ZnS crystal per-

pendicular to the growth direction. Traces of macrosteps, which are going in front of crystallization can be clearly seen.

The pictures of a microstructure in the $(11\bar{2}0)$ and (0001) planes (Figs 10 and 11) after etching distinctly show that the crystal was grown by a mechanism of successive macrosteps. Some interesting picture of the microstructure in the $(11\bar{2}0)$ plane of a ZnS crystal are shown in Fig. 10. On that picture one can see the layers of inhomogeneous structure which we have observed previously [1] as optical inhomogeneous areas. Besides, we can see (Fig. 10) that the defect which reaches the front of crystallization, could pass on to successive layers in the course of their growth.

The oblique lines on the seperate layers can be explained by layer-growth on the forehead of macrosteps, like that shown on the model (Fig. 12). According to this model, layer inhomogeneities of ZnS crystal in the direction perpendicular to the *c* axis and inhomogeneous optical bands could be explained by the appearance of a transit-area with stacking faults among separate layers. These areas were very narrow, so that there was probably a reason, why Singer [7] in his X-ray investigations by means of 10 μm X-ray beam has not been able to disclose the dependence among the bands of optical inhomogeneities and changes of structure in the respective layers of a ZnS crystal [6]. Simultaneously, his report on the existence of structure changes in optically homogeneous bands, can be explained by the layer structure of respective layers perpendicular to the *c* axis as shown in Fig. 12.

3. Conclusions

The observations of the microstructure of ZnS crystals after etching, have disclosed and confirmed the growth mechanism which was proposed by us to explain the existence of "negative crystals" [1]. Besides, these observations allowed us to make some conclusions to explain the formation of inhomogeneous optical bands.

The microstructure of CdS crystals showed some characteristic features of the layer growth mechanism, similar but not identical as in the case of ZnS crystals. We have not found any traces of layers in the cross sections of macrosteps in CdS.

The defects of microstructure in CdS crystals are typical defects which we observed in crystals grown by the Bridgman method.

The density of dislocations in CdS crystals obtained from the melt is about 10 times higher than that in crystals obtained from the gaseous phase [5].

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Fig. 1

Fig. 2a

Fig. 2b

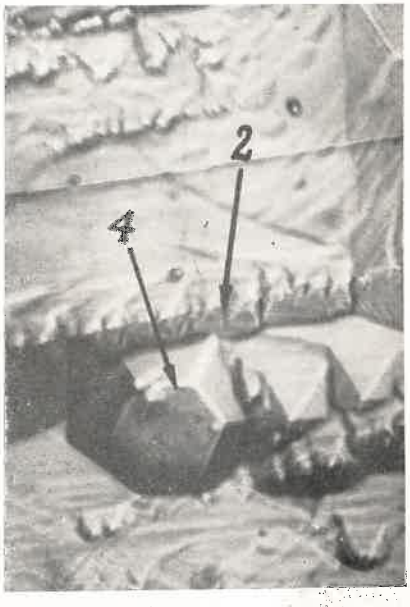

Fig. 2c

Fig. 1. The microstructure on the (001) plane of CdS crystal after etching in a solution consisting of 2 parts CrO_3 + 1 part HNO_3 + 3 parts H_2O with a typical configuration of terraces in the etched figure. The arrow-head shows the block boundary (×360)

Fig. 2. Typical defects, which we could observe on the (0001) plane of CdS crystals after etching, like in Fig. 1; *1* — the slip trace, *2* — the twin boundary, *3* — the block (Fig. 1) boundary, *4* — the etched figure with a flat bottom (×360)

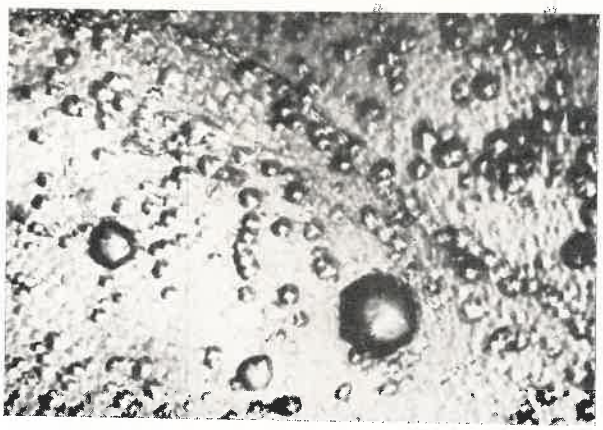

Fig. 3. The etch pits and tunnels of "negative crystals" on the (0001) plane of a CdS crystal after etching like in Fig. 1 (×360)

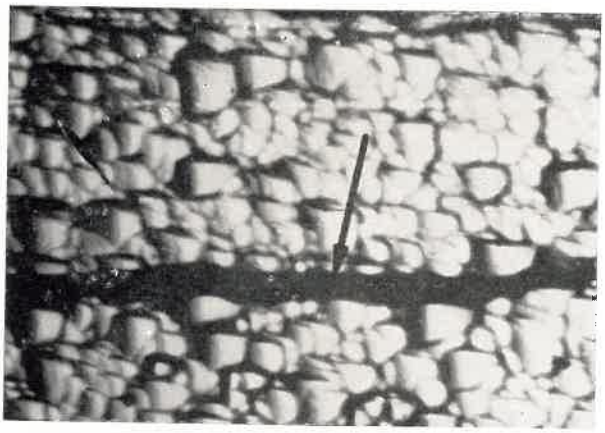

Fig. 4. The picture of the surface microstructure of a CdS crystal with $(11\bar{2}0)$ orientation with block boundary

Fig. 5. The layer structure on the 0001 surface of a CdS crystal (×360)

Fig. 6. The etch figures on the cross section of crystals perpendicular to the growth direction. The etching solution — like in Fig. 1 (×360)

Fig. 7. The picture of (0001) plane of a nonstoichiometric CdS crystal (×160)

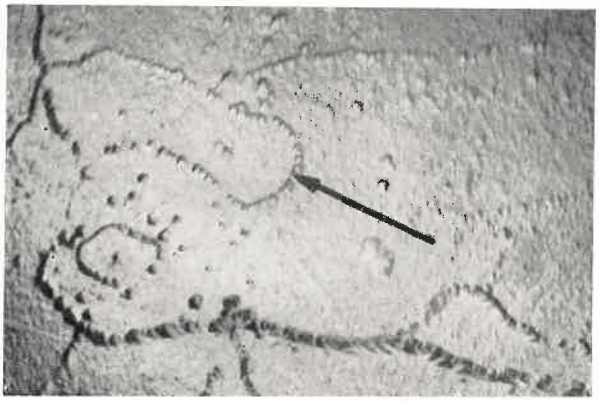

Fig. 8. The lines of the etch figures the surface with (0001) orientation of a CdS crystal, which could arise as a result of generation of dislocations by impurities (×160)

Fig. 9. The image of the microstructure of a ZnS crystal on the surface perpendicular to the growth direction after etching in a solution consisting of $2\,CrO_3+1\,HNO_3+3H_2O$ ($\times 360$)

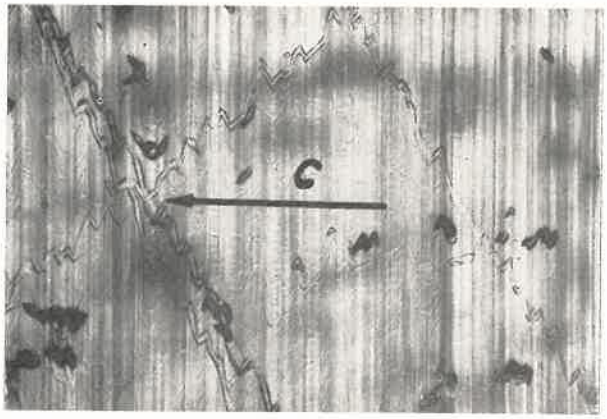

Fig. 10. The image of the surface microstructure of a ZnS crystal parallel to the c axis after etching, like in Fig. 1 ($\times 360$)

Fig. 11. The same sample like in Fig. 1. showing an image of microstructrue on the surface perpendicular to the c axis ($\times 360$)