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Heteroepitaxial Overgrowth of ZnS on GaS Single Crystals

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The heteroepitaxial overgrowth of ZnS on the basal plane of GaS single crystals was observed during the simultaneous synthesis of GaS and ZnS. The morphology and orientation of ZnS nuclei were investigated in the initial stage of overgrowth. It was found that the ZnS nuclei might be either regular forms such as triangles and hexagons, or dendritic formations with definite orientation relations. The system investigated proves the possibility of heteroepitaxy between compounds with different lattice parameters if these fulfil some special conditions.

1. Introduction

Crystallisation from metal melt is a well-known procedure for obtaining single crystals of elementary semiconductors such as Ge, Si and semiconductor compounds, especially of III-V and II-VI materials [1-4].

The Ga and In chalcogenides have increased in importance in recent years and form a new group of single crystals obtained by the above method. Gallium selenide and indium selenide crystallised from metal solution show dendritic growth, whereas, GaS single crystals grown from metallic gallium behave differently. These crystals are similar to those grown by transport reactions, forming large hexagonal plate-like crystals with mica-like properties due to their layer structure [5, 6].

The solubilities of the above mentioned compounds in the metal used as solvent differ. Therefore by choosing suitable pairs of compounds the production of heterojunctions in a single step is in principle possible.

The ZnS–GaS system was chosen for investigation of this phenomenon, since according to our experiments the temperature-dependence of the solubilities of these materials in metallic gallium differed considerably.

2. Experimental

The synthesis of the materials and their subsequent crystallisation was carried out in vacuum-sealed quartz ampoules of 20 mm diameter. 5 N gallium (product of the Aluminium Works, Ajka), 5 N sulphur and zinc (Koch Light Co.) were used as source material. 5 at. % sulphur and varying amounts of zinc (0.5 to 4.5 at. %) were added to 20 g samples of gallium. Each ampoule was placed in the homogeneous temperature zone of a vertical electrical furnace. The synthesis of the compounds takes place

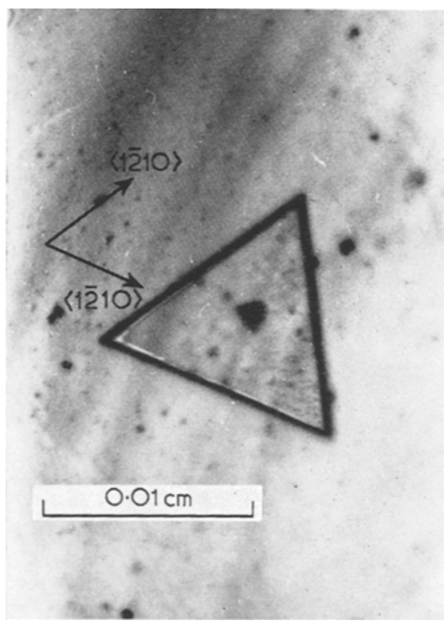

Figure 1 Triangle-like ZnS nucleus on the (0001) plane of GaS. The marked directions correspond to the GaS orientation.

during 2 h at a temperature of 450 to 500° C. When the temperature was raised to 1180° C and the ampoule vigorously vibrated, a homogeneous solution was obtained. Crystal growth was performed at a cooling rate of 12° C/h. The separation of the crystals from the metallic gallium was performed by filtration and subsequent washing with metallic mercury and 2% NaOH solution [6].

3. Results

3.1. Morphology of the ZnS Overgrowth

Under the above conditions GaS developed as a plate-like crystal whose plane is of (0001) orientation and the ZnS overgrowth is practically limited to the basal plane of GaS. The orientations of the GaS crystal edges were identified by X-ray methods. At low zinc concentration, large GaS plates are formed on the surfaces of which ZnS nucleation can be observed. By increasing the Zn concentration the ZnS coverage of the GaS surface is increased and the morphology of the overgrown ZnS changes as well. At high zinc concentration (ZnS > 0.5) the formation of individual dendritic ZnS crystals can be observed. According to their morphological features the ZnS nuclei grown on the (0001) GaS surface can be classified into three groups: equilateral triangles, hexagons and dendritic formations.

3.1.1. Triangle-like ZnS Nucleus

In the minority of cases, but especially at low zinc concentrations, the formation and growth of

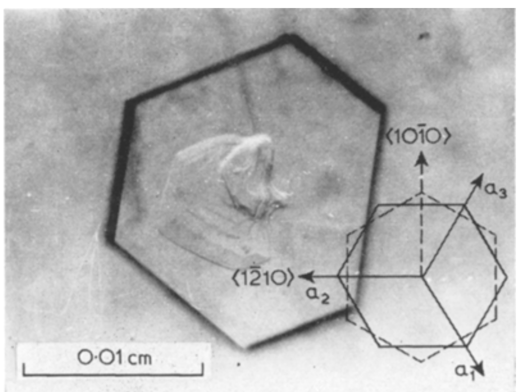

Figure 2 ZnS nucleus with hexagonal morphology on the (0001) plane of GaS single crystal. The marked directions correspond to the GaS orientation. The solid and dotted lines represent the two observed types of hexagonal nuclei.

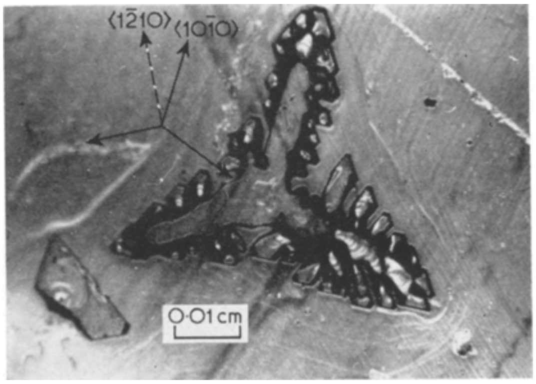

Figure 3 Dendritic ZnS nucleus on the GaS basal plane. The marked directions correspond to the GaS orientation.

perfect triangular nuclei can be observed on the GaS surfaces (fig. 1). The triangles show an exact orientation related to the GaS substrate. Their sides are parallel to ⟨1$\bar{2}$10⟩. The triangles occupy one or other of two orientations, in mirror symmetry to each other.

At higher nucleation densities the growth of truncated ZnS triangles could be observed while in some limiting cases the development of hexagons was also detected.

3.1.2. ZnS Nucleus with Hexagonal Morphology

The formation of ZnS nuclei with hexagonal morphology is considerably more frequent than that of triangular ones.

Two kinds of orientation were observed for hexagonal nuclei. One of them is defined by sides parallel to ⟨1$\bar{2}$10⟩, as in triangular growth, whereas the other nucleus is rotated by an angle of 30°: thus their sides have ⟨10$\bar{1}$0⟩ orientations. These relations are shown in fig. 2.

3.1.3. Dendritic ZnS Nuclei

At high zinc concentration the dendritic growth of ZnS on the basal plane of GaS can often be observed. Several forms of dendritic growth exist. The most simple of these show a three-fold symmetry according to fig. 3.

The main growth directions in the dendritic islands in fig. 3 nearly correspond to the ⟨10$\bar{1}$0⟩ directions. The secondary dendritic branches form an angle of 90° or 30° with the main growth directions, that is, they represent ⟨1$\bar{2}$10⟩ directions.

Another dendritic growth formation is shown in fig. 4. One part of the (0001) plane of the GaS single crystal is covered by ZnS dendrites with main growth directions of $\langle 10\bar{1}0\rangle$ or $\langle 1\bar{2}10\rangle$. The secondary branches also correspond to these directions but in some cases dendritic branches of $\langle 21\bar{3}0\rangle$ directions could also be observed.

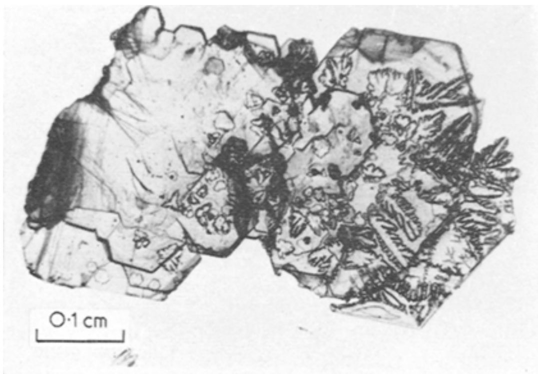

Figure 4 Solution-grown GaS–ZnS system. On the GaS surface numerous dendritic, overgrown ZnS nuclei are observable.

The orientation relations can be especially well observed at the GaS edges overgrown by ZnS.

Fig. 5 shows the orientation of ZnS nuclei on two GaS edges. There is a 30° rotation similar to the above-mentioned cases of hexagons. In fig. 5a a ZnS crystallite has the same orientation as the GaS side and emits fast growing dendritic branches of $\langle 10\bar{1}0\rangle$ orientation towards the GaS plane centre. The sides of the triangular apices at the end of the dendritic branches correspond with the orientations $\langle 1\bar{2}10\rangle$.

The ZnS crystallite shown in fig. 5b was grown in a position rotated through 30° compared to the previous case. In this figure one corner of the hexagonal GaS substrate onto which a hexagonal ZnS nucleus formed is well observable. In this case the orientation of the dendritic branch is contrary to the previous one, being of the $\langle 1\bar{2}10\rangle$ type. Near the mentioned nucleus, a nucleus of threefold symmetry can be observed corresponding to the previous type of orientation, demonstrating thus the simultaneous appearance of two differently oriented ZnS islands.

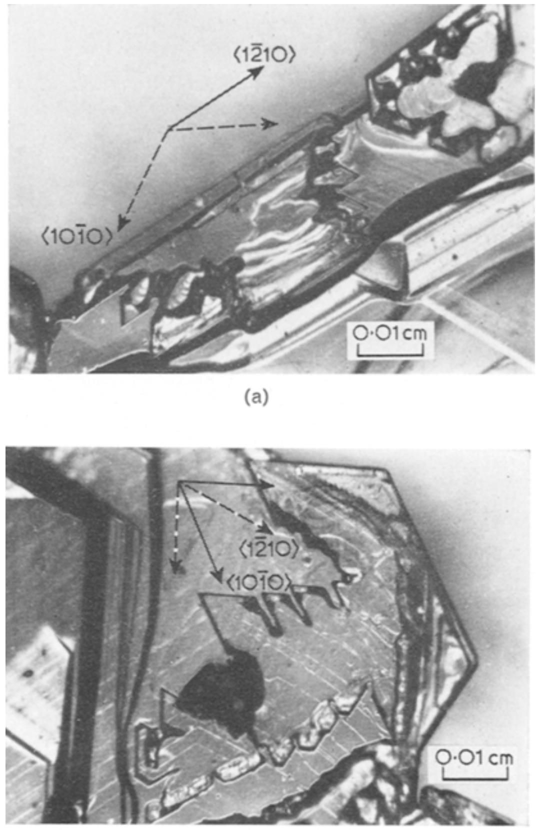

Figure 5 (a) ZnS overgrowth on the edge of a GaS substrate. The nucleus follows the substrate orientation. (b) ZnS overgrowth on the edge of GaS substrate. The nucleus is rotated through 30° compared to the previous case and to the CaS lattice. The marked directions correspond to the GaS orientation.

4. Discussion

Heteroepitaxy occurs between ZnS and GaS notwithstanding the great difference between their lattice parameters ($a_{ZnS} = 5.402$ Å, $a_{GaS} = 3.585$ Å) in fact, comparing the (0001) plane of the GaS lattice with the closed-packed (0001) or (111) ZnS planes one can observe that $d_{(111)\,ZnS} \approx d_{(0001)\,GaS}$. The two lattices can be fitted best along the $\langle 1\bar{2}10\rangle$ directions. This immediately explains the appearance of the hexagonal and triangular morphology of ZnS nuclei of same orientation. X-ray examinations prove that ZnS nuclei grown on the basal plane of GaS single crystals show the same orientation on the whole surface; thus a perfect epitaxy exists.

From these results it seems probable that the growth of ZnS nuclei is in both cases of similar orientation but the sides limiting the nuclei are in one case $\langle 10\bar{1}0\rangle$ and in the other $\langle 1\bar{2}10\rangle$.

The epitaxial relation remains even for dendritic overgrowth. It is remarkable that the structure of the ZnS on the hexagonal GaS surface is cubic and the lateral planes of the islands are of {111} type, according to fig. 5.

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