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Dislocation Etching of GaSe Single Crystals

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Dislocation etching of GaSe single crystals was investigated by using a dilute chromic-sulphuric acid mixture, when conical etch pits were revealed on the (0001) surfaces. At the apices of spiral growth hills, bunches of spiral dislocations were revealed, proving that it is not a single screw dislocation of large Burgers vector, but a bunch of co-operating screw dislocations that were responsible for the spiral growth formations of large step-height. In the case of GaSe crystals, grown by vapour transport methods, dislocation densities of 10^2 to 10^6 cm^{-2} were found. The Bridgman crystals investigated were completely free from non-basal dislocations.

1. Introduction

$A^{III}B^{VI}$ crystals have gained increasing importance, often for general investigations as layer-structures, but principally for semiconducting, photoconducting and luminescent applications. Among these structures the compounds of Ga are of interest for their physical properties. GaSe is by far the most important Ga-chalkogenide compound. It shows strong photoconduction [1-3], interesting electrical properties [4-7] and low temperature photo- and electroluminescence [8-12].

GaSe exists in different crystal modifications. The lattice is either hexagonal (β and ϵ modifications), or rhombohedral (γ modification) [13-16]. All of the structures mentioned are built up of four-fold layers of Se–Ga–Ga–Se showing a sandwich-structure, in which Ga atoms have tetrahedral co-ordination, while Se has a trigonal one. There are van der Waals forces between the layers. Since the structures are very similar to those of mica and graphite, similar crystal defects can be expected. The dislocations and stacking faults lying in the basal plane determine most of the physical properties perpendicularly to the c-axis, but it is clear that the non-basal dislocations and faults also have an important influence on the properties of crystals.

In graphite, both non-basal screw and edge dislocations have been found [17, 18]. Etch pit counts made on cleaved surfaces were normally in the region of 10^5 cm^{-2}. The lattice defects in $A^{III}B^{VI}$ compounds have not been studied in detail, but some data on stacking faults have been published [13-15]. Boelsterli and Mooser [19] as well as Guseinov and Ramazanzade [20] investigated the non-basal GaSe defects, and growth spirals have been observed on the (0001) surface of the crystals. Using HF–HNO_3–HCl etchant, triangular etch pits also were observed [20]. More recently Williams [21] has shown that on GaSe crystals grown from vapour phase, using bromine dissolved in methanol as etchant [22], triangular etch pits having a mean density of 10^3 cm^{-2} can be revealed, in accordance with the result of Guseinov and Ramazanzade. In order to examine the dislocations and other non-basal defects in GaSe further etching experiments were carried out using different etchants. The work to be described is concerned with the application of an etchant for GaSe which had been successful for developing dislocations in $A^{II}B^{VI}$ compounds [23] and GaS [24]. This reagent, diluted chromic sulphuric acid, shows several advantages in comparison with the other etchants previously described for GaSe.

2. Experimental

The GaSe crystals selected for study were prepared by vapour phase transport methods or by the Bridgman method. In the first case plate-

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like crystals of surface up to 0.2 to 1.0 cm^2 were used. The hexagonal *c*-axis was perpendicular to the plane of the plates. The Bridgman crystals were large boules with a diameter of about 1 cm and length of 2 to 3 cm. For etching experiments, cleaved samples were used. The etchant was a solution containing 30 g $K_2Cr_2O_7$ and 25 ml concentrated H_2SO_4 in 180 ml distilled water. All the reagents used were analytical grade. In order to be able to compare the results obtained, the bromine etchant described by Williams in [21] was also used. The etching took place at room temperature either by dropping the etchant onto the surface, or by immersing the crystal in the etchant. Etching periods of 2 to 10 min were used. The crystals were washed in distilled water or with ethanol, and were dried in air. The washing must be done quickly as water itself reacts with the etched surface, forming a gallium oxidelayer. For long washing times ethanol has to be used as the reaction is a rather slow one.

For detailed investigation a Leitz microscope of Ortholux type was used.

3. Results

Previously published data [15, 16, 20, 21] were used for deciding the orientation of crystal edges and planes. Under the conditions described it was noticed that on the (0001) surfaces of GaSe conical etch pits appeared but no hexagonal or triangular pits were seen. Sometimes large, flat-bottomed pits were also found. On the pit walls "spikes" can be observed, either pointing to random orientations or aligned along lines running in $[1\bar{2}10]$ directions. A characteristic etch pattern is shown in fig. 1. Within the pits, multilayer terraces were found. It is apparent from these experiments that in the GaSe crystals grown from vapour phase, non-basal dislocations in a density of 10^2 to 10^6 cm^{-2} may be present. Examination of Bridgman crystals shows them to be free of non-basal dislocations and hence these crystals might be expected to be more perfect than the crystals grown by transport processes.

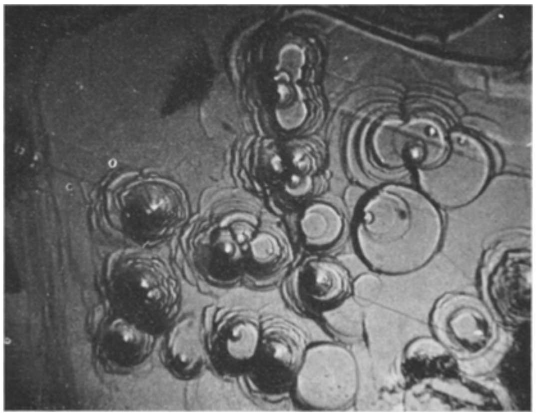

Figure 1 Characteristic etch pattern on GaSe (0001) surface using diluted chromic-sulphuric acid as etchant (× 140).

Figure 2 Pile up of non-basal screw dislocations along crystal ledges (× 140).

At medium dislocation densities (etch pit densities of about 10^4 to 10^5 cm^{-2}) the piling up of pits along crystal ledges can be observed. This kind of pit-arrangement is shown in fig. 2. It is interesting to note that many of the pits contain two peaks. At the bottom of such pits, two close spaced pits can sometimes be distinguished (see fig. 3), this is probably due either to the presence of dislocation half-loops or to dipole-interaction of dislocations, or both.

On the (0001) surfaces numerous spiral growth hills were observed. This may reflect the fact that these particular samples were grown partly by the dislocation mechanism, like the previously described samples [19-21]. Growth spirals on GaSe single crystals appeared in several forms. These were equilateral triangles or pyramids, truncated hills and non-polygonised forms showing curved spiral arms. This latter form is shown in fig. 4. The polygonised hills were generally bounded by three of the $[1\bar{2}10]$ directions, but sometimes the edges were truncated. As a result, on such hills all the $[1\bar{2}10]$ directions were apparent. This difference had been found already in the as-grown state.

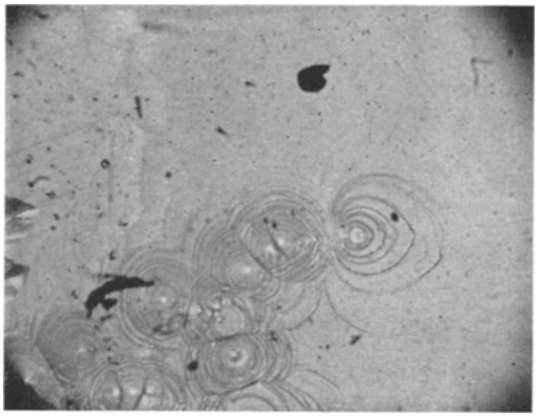

Figure 3 Double peaked etch pit (× 140).

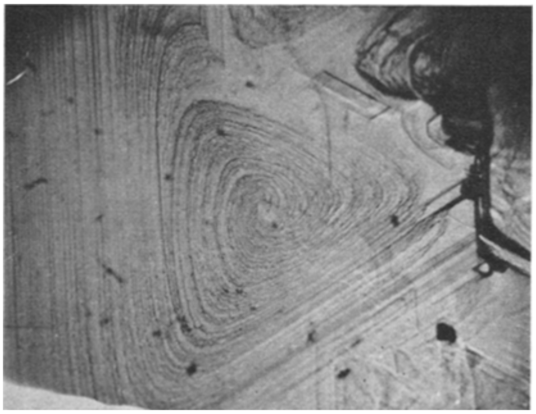

Figure 4 Growth hill showing curved spiral arms (× 140).

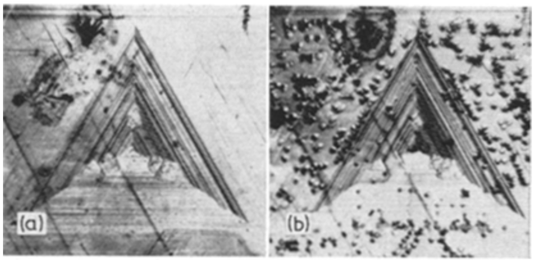

Figure 5 Truncated spiral growth hill on GaSe (0001) surface (a) before etching (× 35). (b) after etching (× 35).

Rotation of the sides of triangular hills during the etch process described previously [21] was never observed. Fig. 5 shows a truncated triangular hill of this type before and after etching, illustrating that during the process no rotation took place. A consequence of etching was that a number of etch pits formed at the apexes of growth spiral hills, as seen in figs. 5 and 6. In fig. 6 two growth hills are visible, one is rotated through 60° with respect to the other. Both hills contain many pits at the top, but on the edges no traces of the polar character supposed in [21] could be found.

On cleaved samples the extended deformation observed on graphite has not been detected.

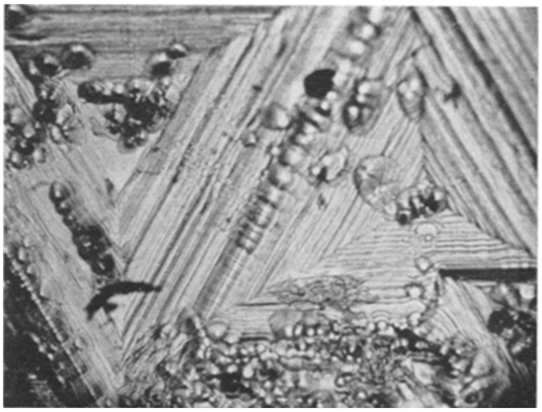

Figure 6 Two etched growth hills; one is rotated through 60° with respect, the other already in as-grown state (× 70).

4. Discussion

For the GaSe crystals examined there seems to be little doubt that the etch pits are nucleated at the emergence points of non-basal screw dislocations. Both etchants, chromic sulphuric acid and bromine, reveal the same dislocations; however, the symmetry of the pits is different. Since in the case of polar plane-pairs of the $A^{II}B^{VI}$ compounds the diluted chromic sulphuric-acid develops conical pits on the B side, the observed pit form on GaSe agrees well with the layer structure of the compound. It is interesting that although the mentioned etchant reveals both hexagonal and conical etch pits on GaS [24], on GaSe only the conical type was developed.

In order to confirm that these pits are due to non-basal screw dislocations, the bottom of the pits were investigated at high magnifications when spiral terraced formations were found. Further evidence that screw dislocations were revealed by the etchant is provided by the fact that at the apex of spiral hills – where screw dislocations are known to be present – a number of etch pits of the same kind were seen. It is, therefore, likely that the growth of these crystals, which are perpendicular to the basal plane, is promoted, partly or entirely, by the dislocation mechanism.

So far, many workers have studied the formation of spiral hills, but no definite answer has been reported about their exact nature. Since generally the step-height changes from some Ångström units to very large values, it was assumed, either that the Burgers vector of the screw dislocation has the same order of magnitude as the step-height, or that a bunch of screw dislocations was acting during the growth process. In the case of MoS_2 [18-25], graphite [17] as well as for GaSe [22] extremely large Burgers vectors (e.g. 1050 ± 50Å, see [19]) were assumed to be present. The observation of pit-groups at the GaSe hill apices containing sometimes more than forty distinguishable pits seems to support the supposition that no single screw dislocation of large Burgers vector, but rather a bunch of co-operating screw dislocations is responsible for the formation of spiral growth hills. This assumption is probably also valid for other cases where large step-heights were observed on spirals.

A large fraction of the hills developed only on one side of the thin GaSe plates. Etching the crystal on the other side, the bunch of screw dislocations can also be detected under the hill. Since the bunches lay perpendicularly to the main growth directions, no structural reason exists to explain this "polar" growth character. This point needs further investigation.

It is interesting to note that in the Bridgman crystals investigated, non-basal dislocations could not be revealed by etching at all although sometimes the traces of dislocations leaving the boules could be observed. On crystals grown by vapour transport the dislocation moving along the basal plane was also observed similar to the case of GaS [25].

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