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The Identification of Non-basal Dislocations in GaSe by the Etch-Pit Technique

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A detailed study has been made of the etch-pits produced on GaSe crystals, grown by various methods, using etchants consisting of bromine or iodine in methanol. Non-basal dislocations of both screw and edge types, sometimes aligned to form low-angle boundaries, are revealed. Detailed observations of the pit shapes indicate that the dislocations bend and dissociate within the solid. The reorientation of etch-pits within existing pits is discussed in terms of stacking faults. Networks of etch grooves have been observed and are believed to be due to dislocations lying in the basal plane.

1. Introduction

During the last decade a number of materials which crystallise with the layered structure have been subjected to intensive investigation both in relation to the anisotropy of their physical and chemical properties and as possible device materials. GaSe crystallises with a layered structure in which each four-fold layer consists of two sheets of Ga atoms sandwiched between sheets of Se atoms. Within a four-fold layer the bonding is predominantly covalent but between layers the bonding is mainly of the van der Waals type [1]. Three modifications of the crystal structure, which differ from each other only by the way in which layers are stacked, are known to exist [2, 3]. In the ϵ- and γ-modifications (figs. 1b and c) each layer may be transformed into its neighbouring layer by translational movements alone, while for the β-modification (fig. 1d) a rotation of 60° as well as a translation is required.

The recent observations of negative resistance [4], stimulated emission [5], and switching behaviour [6] in single crystals of GaSe, coupled with their known photoconductive [7, 8] and electroluminescent [9, 10] properties, underline the need for a thorough study of the basic properties of this material. Investigations of some of the optical [11-13] and electrical [14-16] properties have been reported, but as yet there exists little information concerning the nature of the electrical conductivity in the direction of the c-axis. In view of its structure GaSe may be readily deformed and dislocations lying in the basal plane may be introduced with ease. These may be conveniently studied using transmission electron microscopy on samples prepared by cleavage [17, 18]. Little information exists, however, concerning the detection and nature of dislocations which traverse across the basal planes. These may play a rôle in the determination of the anisotropy of the electrical properties since non-basal screw dislocations, for example, introduce a continuation of layer planes in the direction of the c-axis.

In an earlier communication [19] the use of a chemical etchant for revealing non-basal dislocations in single crystals of GaSe, grown from the vapour phase, was described. The studies have now been extended to include crystals grown by other methods from which information concerning the nature of the dislocations may be derived. In addition to revealing the emergence points of non-basal dislocations the technique may also be used to reveal stacking faults in the crystal lattice. Etch-grooves, which sometimes take the form of extended networks, are believed to be due to dislocations lying in the basal plane.

2. Experimental

Polycrystalline GaSe was prepared by heating

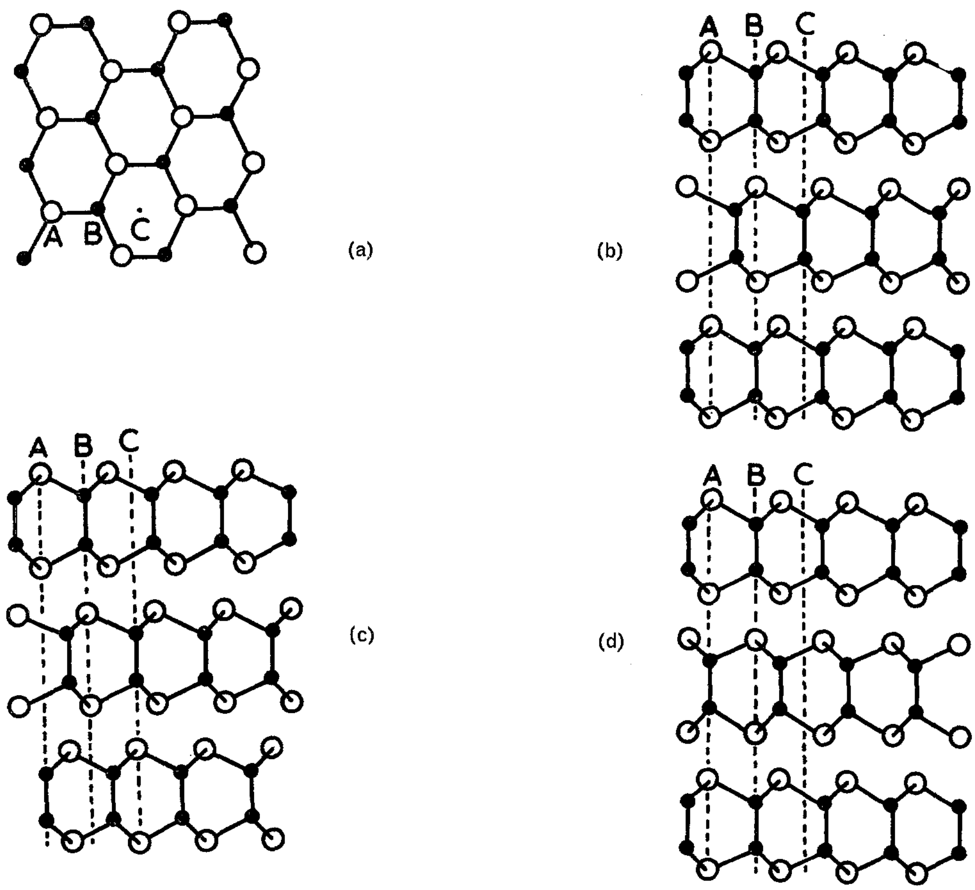


Figure 1 The structure of GaSe. Dark circles represent gallium atoms, open circles selenium atoms: (a) c-axis view of a layer with selenium atoms in position A and gallium atoms in B; (b) stacking sequence of ϵ-modifications; (c) stacking sequence of γ-modification; (d) stacking sequence of β-modification.

together stoichiometric amounts of 5N gallium and 3N selenium in a two-zone, evacuated, sealed tube. The zone containing the gallium was kept at a temperature of 1000° C while the other zone, containing selenium was at 650° C. Single crystals were grown by four methods: (i) from the melt by a vertical Bridgeman technique; (ii) from the melt by a gradient freeze technique; (iii) from the melt by pulling using a boric oxide encapsulant and under a pressure of 50 lb in.$^{-2}$* of nitrogen; (iv) from the vapour phase by the iodine vapour transport technique [20]. The first three methods yielded crystals a few cm in length and about 1 cm diameter, from which thin platelets could easily be cleaved. Method (iv) yielded thin flat plates, about 1 cm^2 in area, with the c-axis perpendicular to the plane of the plates. A full report of the growth of crystals by these techniques will be given elsewhere [21]. Crystals were cleaved using a stainless steel blade or adhesive tape.

In order to reveal the emergence points of non-basal dislocations two etchants were developed. The first consisted of bromine in methanol, in concentrations similar to those described previously [19]. The second consisted of analytical grade iodine, also dissolved in methanol and at a temperature of approximately 50° C. In general, about 1 g iodine dissolved in 50 cc methanol gave well-defined etch-pits. Etching periods were of the order of 45 min. After etching the crystals were washed in methanol and dried in warm air. Washing in water must be avoided due to effects already described [19].

All observations were made on (0001) faces by optical microscopy, using the Nomarski interference contrast technique.

* 1 lb in.$^{-2}$ = 6894.76 N m^{-2}.

3. Results and Discussion

3.1. Reliability of the Etchants

In order to check the reliability of the etchants for revealing dislocations in any particular crystal it is customary to compare etch-pit patterns on surfaces parted by cleavage. For GaSe crystals, grown by all the techniques described, approximately 95% of the pits could be correlated from one such face to another, for both bromine and iodine etchants. This test is even more convincing if corresponding pits are produced on matching surfaces using different etchants for each parted face. Figs. 2a and b show etch patterns on two such surfaces, one of which has been etched using bromine in methanol (fig. 2a) and the other using iodine in methanol (fig. 2b). The good one to one correspondence is apparent. It is of interest to note that the pits produced by the iodine etch are rotated through 60° with respect to those produced by bromine. This difference is undoubtedly related to different adsorption properties of the bromine and iodine species on gallium and selenium sites [19]. Apart from the large difference in etching rates, this was the only significant difference observed in the behaviour of the two etchants.

3.2. Etch-Pit Shapes

For relatively low etching rates all pits on a given surface are triangular and bounded by [11$\bar{2}$0] directions. Careful observations of pits on a large number of crystals, however, indicate that a full description of the pit shapes involves roughly four categories:

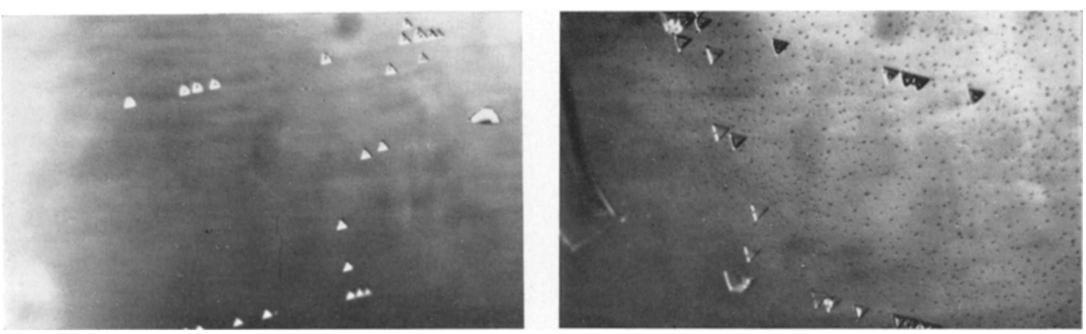
(i) A large percentage are nearly symmetrical, having pointed bottoms, and in almost all cases the side of the pit is composed of closed hexagonal terraces (figs. 3a and b).

(ii) Other pits are observed in which the terraces are unsymmetrically arranged, as if the centre of attack has shifted in a plane parallel to the surface as etching proceeds in the *c*-direction (figs. 3c and d).

(iii) A number of pits have flat bottoms (fig. 3e). On further etching most of these continue to deepen and eventually assume the shapes described in (i) and (ii) above. A number, however, do not deepen further with continued etching. It should be emphasised that nearly all these pits possess corresponding pits on matching cleaved faces. The matching pits generally belong to categories (i) and (ii).

(iv) A small number of pits (around 1%) develop around small inclusions in the crystal lattice (fig. 3f). These do not have corresponding pits on a matching face parted by cleavage. These pits are probably nucleated at impurity precipitates or clusters in the lattice and it is highly unlikely that they correspond to the points of emergence of non-basal dislocations.

Flat bottomed etch-pits, of the type described in (iii) above, are a regular feature in the etching of other layered structures, such as mica [22], graphite [23] and Bi_2Te_3 [24, 25]. In the case of graphite their existence has been interpreted in terms of non-basal dislocations which terminate at voids and intercrystallite boundaries lying in or close to the basal plane. For Bi_2Te_3, on the other hand, the appearance of etch-grooves, which mark dislocations lying in the basal plane, accompanying some flat-bottomed pits, provide a strong indication that their origin is due to non-



(a) (b)

Figure 2 Etch patterns on matching cleaved faces: (a) etched using bromine in methanol; (b) etched using iodine in methanol (× 108).

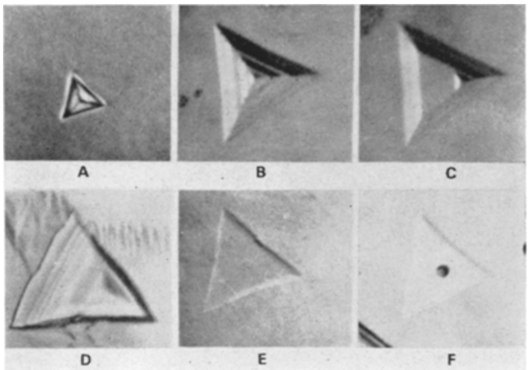


Figure 3 Different etch-pit shapes observed on GaSe.

basal dislocations which bend within the crystal and subsequently assume arbitrary directions lying close to the *c*-plane. As the etch reaches the point at which the dislocation bends, the etching rate in a non-basal direction is no longer enhanced and the etch-pit appears flat-bottomed. The great similarity between the etching characteristics of Bi_2Te_3 and GaSe leads us to believe that this latter mechanism is responsible for the flat-bottomed pits in GaSe. In fact, grooves associated with flat-bottomed pits have often been observed in our studies (see section 3.7), but it is difficult to prove conclusively that these are due to basal dislocations. This interpretation also accounts for some of the non-matching etch-pits observed on faces parted by cleavage since a dislocation which changes from a non-basal to a basal direction at, or near, the cleavage plane leads to an etch-pit on only one surface. The appearance of new pits, occasionally observed with continued etching, is similarly explained.

Although it is difficult to rule out the fact that some of these flat bottomed pits may be due to microprecipitates or chemical inhomogenity, the general appearance of deep pits on one surface, corresponding to flat-bottomed pits on a matching cleaved surface, supports their interpretation in terms of dislocations.

The terracing of etch-pits, and the continued deepening of pits which appear flat-bottomed, with continued etching, have been observed on a number of materials [26-28]. These may be explained in terms of non-basal dislocations which bend to a basal one, and then bend back again to a *c*-axis direction [25]. Alternatively they may be due to kinks or jogs in the dislocation line which shift the centre of oxidation in a direction normal to the *c*-axis.

The bending and dissociation of dislocations as they traverse across the basal planes also account for a lack of correspondence of etch patterns on opposite faces of a relatively thick crystal. On a crystal approximately 100 μm thick there is only a 5 to 10% correspondence. On opposite sides of a thin sliver, however, the correspondence is approximately 80%.

3.3. Screw Dislocations

Non-basal screw dislocations are present to a greater or lesser extent in crystals grown by all methods. The growth of crystals from the vapour phase is catalysed by such dislocations and their presence is denoted by triangular growth spirals [19]. On cleaved surfaces their existence may easily be detected by the presence of cleavage steps which terminate within the surface. As a consequence of etching, pits are always formed at the termination of such steps. In common with graphite and MoS_2 [29, 30] the Burgers vectors of these dislocations, as indicated by the height of the steps issuing from their cores, may be extremely large. In GaSe these dislocations are often aligned [19] to form twist boundaries lying mainly in $[11\bar{2}0]$ directions (fig. 4).

On crystals grown from the vapour phase, steps are sometimes observed emanating from the centres of growth spirals. These steps always run in $[11\bar{2}0]$ directions and indicate the glide direction of the non-basal screw dislocation associated with the spiral, at temperatures close to the melting point of the solid.

3.4. Slip Traces and Low-Angle Boundaries

On crystals grown by the gradient freeze and Bridgeman techniques, and to a lesser extent, on crystals pulled from the melt, extended arrays of

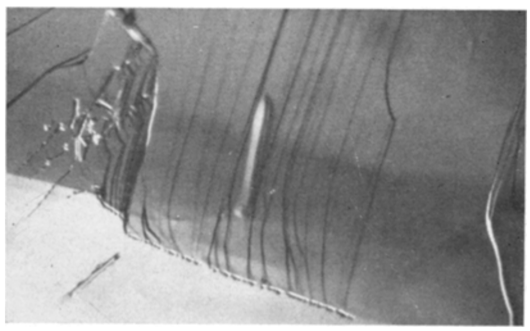


Figure 4 Array of screw dislocations forming a twist boundary. The array lies in a $\langle 1120 \rangle$ direction ($\times$ 108).

etch-pits are commonly observed. Fig. 5 shows linear arrays that extend in [11$\bar{2}$0] directions across the surface. These arrays are particularly apparent on crystals cleaved from near the edge of a boule and denote the emergence points of non-basal dislocations lying in their slip planes. It is believed that these arrays are produced by thermal strains at temperatures close to the melting point of GaSe. Since crystals grown by the gradient freeze and Bridgeman techniques are enclosed in quartz ampoules, thermal strains due to the different coefficients of expansion of the crystals and containing vessels are inevitable as the crystals cool. The fact that similar arrays have not been observed on crystals grown from the vapour, where such strains are far less severe, lends further support to this interpretation. Thermal strains are also less severe for crystals pulled from the melt, where the crystal is enclosed only by a thin layer of the boric oxide encapsulant.

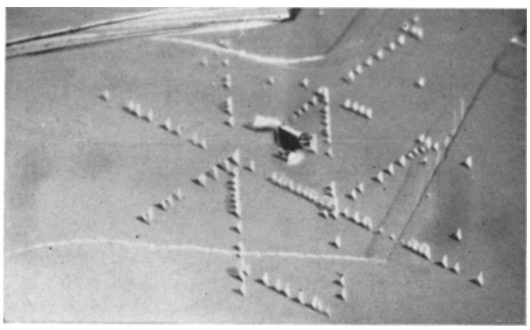


Figure 5 Etch-pits revealing dislocations lying in their slip planes (× 108).

Large surface steps, of the type described in the previous section have not been observed issuing from the cores of these dislocations. Scanning electron microscopy was used unsuccessfully in an attempt to detect such steps. These arrays, therefore, probably represent edge dislocations of the {10$\bar{1}l$} ⟨11$\bar{2}$0⟩ type. Unsuccessful attempts were also made to produce these arrays at room temperature by deformation and indentation of the samples. Hence it appears that non-basal slip in GaSe occurs only at elevated temperatures.

Arrays of dislocation etch-pits denoting the emergence points of non-basal dislocations lying in low-angle boundaries are occasionally observed on crystals grown by methods (i) and (ii). One of the most common consists of an array of closely-spaced pits running in [10$\bar{1}$0] directions. Such a boundary, together with a slip trace is shown in fig. 6. This boundary is in all probability a symmetrical tilt boundary made up of non-basal edge dislocations of the type {10$\bar{1}l$} ⟨11$\bar{2}$0⟩. Similar dislocations in MoS_2 have been schematised by Bahl *et al* [30].

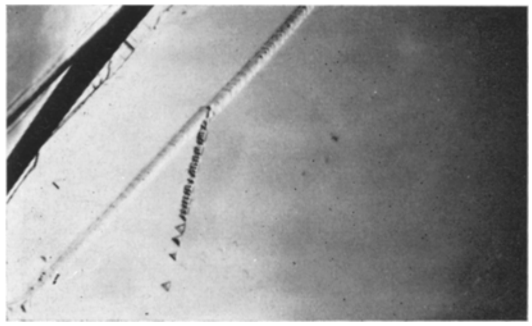


Figure 6 Array of etch-pits forming a tilt boundary in GaSe. The short array of pits denotes a slip trace (× 108)

3.5. Twin Boundaries and Stacking Faults

A phenomenon which occurs fairly rarely, but one which has been observed in crystals grown by all four methods, is shown in fig. 7. It may be seen that a groove has been etched in well-defined crystallographic directions, namely [11$\bar{2}$0], and the etch-pits on either side of the boundary are rotated through 60° with respect to each other. The sections of crystals on each side of the boundary are therefore rotated through 60° with respect to each other and the etch-groove demarcates a non-basal twin boundary.

In some cases further etching led to another interesting phenomenon. With continued etching the pits on one side of the boundary retain their shape and deepen in the normal way, the groove becomes flat-bottomed, and reorientation of the pits on the other side of the boundary occurs within existing pits. This reorientation is shown in fig. 8.

This effect may be explained by considering the stacking faults which may exist in GaSe single crystals. X-ray techniques indicate that crystals grown by the methods described consist of a mixture of the ϵ- and γ-modifications. The stacking sequence in the former may be written A_B, B_C, A_B, B_C, . . . , and in the latter A_B, B_C,

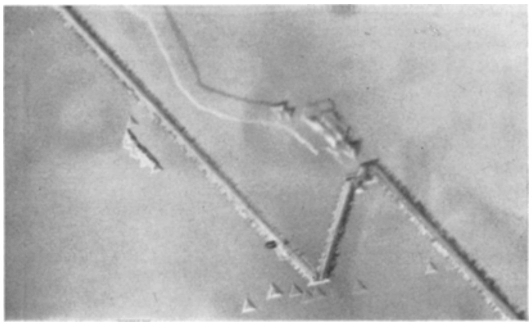


Figure 7 Etch-pits rotated through 60° with respect to each other, on opposite sides of a twin boundary (× 108).

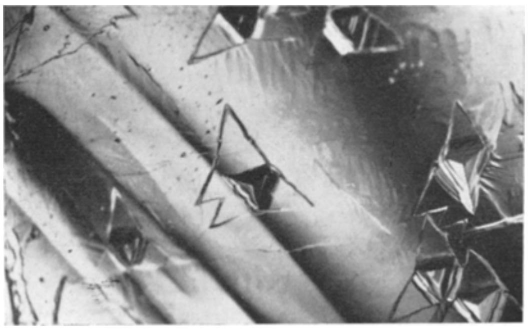


Figure 8 Reorientation of etch-pits within existing pits (× 216).

C_A, . . . , where the capital and subscript letters denote the position of the selenium and gallium atoms respectively in each multiple layer (see fig. 1). For the β-modification of GaSe the stacking sequence is A_B, B_A, A_B, B_A . . . .

If a crystal is composed entirely of the ϵ- and γ-modifications then all etch-pits in that crystal will have the same orientation [19]. If, however, part of this crystal is rotated through 60° with respect to the other half, thus creating a basal plane boundary between the two halves, then as etching follows a dislocation line across this boundary, a reorientation of the pit within the existing pit will occur. Tables I and II show the possible stacking faults that may exist at such a boundary for crystals composed of the ϵ- and γ-modifications of GaSe respectively. In both cases types II and III are associated with relatively high stacking fault energies since in one case gallium atoms in adjacent layers across the boundary lie above one another, and in the other case selenium atoms lie above each other. Type I is much more likely to occur and in this case the two adjacent layers across the boundary would occupy the β-configuration. This approach has been used by Evans *et al* [31] to interpret a similar phenomena in synthetic MoS_2.

TABLE I Possible stacking faults, leading to reorientation of etch pits, in the ϵ-modification of GaSe

Stacking sequence of ϵ-modification	Stacking faults I	II	III
A_B	A_B	A_B	A_B
B_C	B_C	B_C	B_C
A_B	A_B	A_B	A_B
B_C	B_A	A_C	C_B
A_B	A_C	C_B	B_A
B_C	B_A	A_C	C_B

TABLE II Possible stacking faults, leading to reorientation of etch-pits, in the γ-modification of GaSe

Stacking sequence of γ-modification	Stacking faults I	II	III
A_B	A_B	A_B	A_B
B_C	B_C	B_C	B_C
C_A	C_A	C_A	C_A
A_B	A_C	C_B	B_A
B_C	B_A	A_C	C_B
C_A	C_B	B_A	A_C

3.6. Etch-Pit Densities

A comparison of the densities of non-basal dislocations in crystals grown by the various techniques was made by counting etch-pits. The results indicate an approximate average density of 10^3 per cm^2 in crystals grown from the vapour, 4×10^3 per cm^2 in crystals grown by pulling from melt, and 10^4 per cm^2 in crystals grown by the gradient freeze and Bridgeman techniques. The higher density of dislocations in melt grown crystals is understandable in view of the higher temperatures and more severe strains involved in their growth processes.

3.7. Etch-Grooves

Sagar and Faust [24, 25, 32] have presented reasonably conclusive evidence showing that dislocations lying in the *c*-plane may be revealed by weak chemical etchants in the layered material Bi_2Te_3. These are revealed on the *c*-plane as etch-grooves, and sometimes form extended networks due to twisting and dissociation of basal dislocations. Grooves resulting from basal dislocations have also been observed on Si [33].

As mentioned in a previous section, etch-grooves are often seen on the *c*-face of GaSe, as a consequence of etching. Occasionally these grooves are associated with flat-bottomed pits, and on a few occasions extended networks of shallow grooves have been observed. The general behaviour of these etch-grooves in GaSe strongly resemble their behaviour in Bi_2Te_3.

In view of the layered nature of its structure the basal plane is the easy slip plane in GaSe, and dislocation networks extending over long distances would be produced in this plane [18]. It is difficult to interpret these grooves in terms of phenomena other than basal dislocations, and the similarity of their behaviour with that in Bi_2Te_3 is a strong indication that this is the case in GaSe. The appearance of etch-grooves leading from flat-bottomed etch-pits may then be taken as strong evidence for the bending of non-basal dislocations, to basal directions, within the solid.

4. Conclusion

Non-basal dislocations of both screw and edge type may be revealed in GaSe using etchants composed of bromine or iodine in methanol. The frequent occurrence of flat-bottomed pits, sometimes associated with etch-grooves, coupled with the lack of correspondence of etch-pit patterns on opposite sides of a relatively thick crystal, indicate that these dislocations bend and dissociate within the solid. On melt grown crystals non-basal dislocations are often aligned to form low-angle boundaries, and at elevated temperatures non-basal slip is produced by thermal strains. In common with other materials having the layered structure screw dislocations of large Burgers vectors are often observed in GaSe. The etch-pit method is also capable of revealing non-basal twin boundaries and basal plane stacking faults. Etch-grooves, which are commonly observed, are believed to be nucleated at dislocations lying in the basal plane.

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