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Dislocation Etch Pits in Zinc Selenide

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It is shown that triangular etch pits are produced at the points of emergence of dislocation lines on the (1 1 1) zinc faces of single crystals of zinc selenide. Conical etch pits can be produced on the ($\bar{1}\bar{1}\bar{1}$) selenium faces with a solution of one part HCl to three parts HNO_3. Etch patterns produced following indentation confirm the identity of the etch pits. Triangular etch figures which are associated with stacking fault tetrahedra have also been observed.

1. Introduction

In a recent publication, Burr and Woods [1] described an X-ray photographic method of determining the polarity of {1 1 1} slices of single crystals of ZnSe. That work was almost exclusively concerned with a discussion of the anomalous dispersion of X-rays but it was observed that etching in concentrated HCl produced triangular etch figures on the (1 1 1) zinc faces whereas the ($\bar{1}\bar{1}\bar{1}$) selenium faces were merely roughened. The triangular etch figures bore no relation to the points of emergence of dislocation lines. Sagar, Lehmann, and Faust [2] reported that a dilute solution of bromine in methanol produced well defined dislocation etch pits on one (1 1 1) face of a ZnSe crystal while the opposite face showed no observable features following the etch. They made no comment on the polarity of the faces. We have used the bromine in methanol etch to demonstrate that dislocation etch pits which are triangular in shape are formed on the (1 1 1) zinc faces, and have also found that conical dislocation etch pits can be formed on the ($\bar{1}\bar{1}\bar{1}$) selenium faces if a solution of one part by volume of HCl to three parts by HNO_3 is used.

During the course of this work, etching studies of indented crystals have been made, and characteristic "rosette" patterns have been observed. Some large triangular etch patterns can also be produced on many (1 1 1) faces of the crystals and it is suggested that these are associated with stacking-fault tetrahedra similar to those observed in epitaxial layers of silicon [3, 4].

2. Experimental

2.1. Crystal Growth

The ZnSe crystals used in this work were grown from the vapour phase in a continuous flow of argon. Prior to the growth process ZnSe powder supplied by Derby Luminescents Ltd was subjected to a vacuum sublimation process to remove volatile materials and zinc oxide impurity. During sublimation the zinc oxide remained with the charge. Some 80 g of the sublimate was then crushed, placed in a silica boat, and loaded into a long silica growth tube. A stream of high purity argon (350 ml/min) was then passed over the ZnSe which was held at a temperature of 1150° C. ZnSe vapour was transported in the stream of argon to a cooler part of the growth tube where it condensed and crystals grew on a silica liner at about 1050° C. The flow was maintained for six days during which time some 50 g of the charge sublimed. The crystals produced were pale yellow in colour and grew in the form of rods and irregularly-shaped plates containing various low index faces. X-ray back reflection and powder photographs, together with examination under the polarising microscope, showed that the majority of crystals possessed the cubic zinc blende structure. Occasionally a rod would be found with a mixed cubic-hexagonal structure. The etching studies reported here, however, were made on samples with the cubic structure.

2.2. Chemical Etching

Although a number of as-grown, low index faces have been studied, dislocation etch pits have been produced successfully on (1 1 1) zinc faces and ($\bar{1}\bar{1}\bar{1}$) selenium faces only. The etchant which produced triangular pits (fig. 1) on the zinc faces of all the crystals studied was that recommended by Sagar, Lehmann, and Faust [2]. This consists of a dilute solution of bromine in methanol. The exact concentration was not critical, but in general

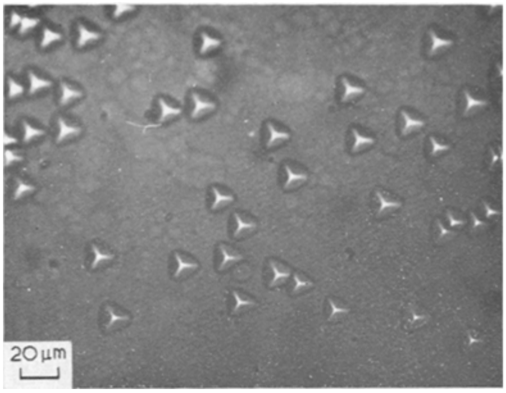

Figure 1 Etch pits on a (111) face of ZnSe following etching in bromine in methanol.

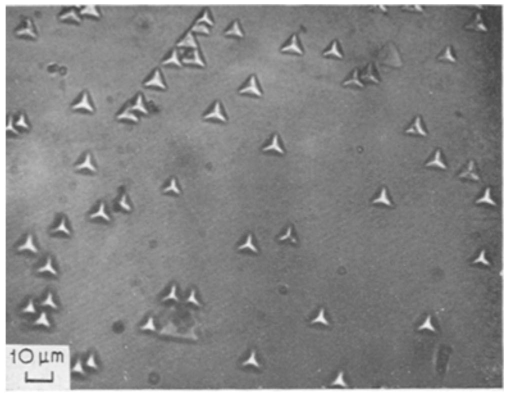

Figure 2 A (111) face of ZnSe following etching in concentrated HCl.

a quantity of bromine ranging from a few drops to about 0.5 ml added to 100 ml of methanol produced well-defined triangular pits. The crystals were immersed in the etchant for 45 sec. After etching, the crystals were washed in methanol and then left in CS_2 for 45 min to remove the dark red liquid which was usually visible on the surfaces of the samples. This liquid is either Br_2Se_2 or Br_4Se_2. Finally the crystals were rinsed in chloroform and dried in warm air.

Since we were interested to determine the polarity of the face on which the bromine in methanol produced triangular pits, we have also used concentrated HCl as an etchant, in order to compare our results with those of Burr and Woods [1]. After crystals had been immersed in hot (60° C) concentrated HCl for 75 sec triangular etch patterns apparently unrelated to dislocations were observed on the zinc faces whereas light was diffusely reflected from the whole of the selenium faces. For some reason which is not understood it was possible with some crystals to obtain triangular etch pits on zinc faces provided that the etching in HCl was not prolonged beyond 1 min. These pits do appear to be associated with dislocations. An example of some of these pits is shown in fig. 2.

Warekois, Lavine, Mariano, and Gatos [5] have also studied the effects of crystallographic polarity on the etching characteristics of a number of II-VI compounds which did not, however, include ZnSe. They recommended the use of a one to one solution of HCl and HNO_3. We have found that a solution of one part by volume of HCl to three parts by volume of HNO_3 provides a superior etchant for ZnSe, when conical pits (fig. 3), are produced on $(\bar{1}\bar{1}\bar{1})$

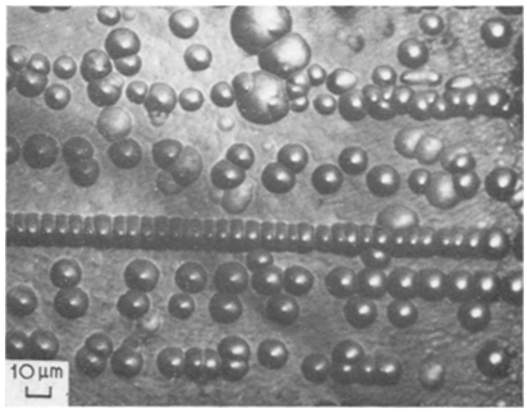

Figure 3 A $(\bar{1}\bar{1}\bar{1})$ face of ZnSe following etching in HCl and $3HNO_3$.

selenium faces. Once again, best results were obtained by using the etchant at room temperature and an immersion time of some 45 sec. Washing in CS_2 was again required to clean the crystal surface following etching.

3. Experimental Results

3.1. Etch Pits on (111) Zinc Faces

The etch pits produced by immersion in bromine in methanol (fig. 1) were usually very uniform in size. The sides of the equilateral triangles lay in $\langle 110 \rangle$ directions while the vertices of the triangles were all oriented in the same $\langle 2\bar{1}\bar{1} \rangle$ direction. Nearly all the pits converged to a point at the bottom but occasionally some flat bottomed pits were observed. The triangular shape of these latter was not usually so well defined as that of the pointed pits.

The appointed pits exhibited many phenomena associated with dislocation etch pits. For example, on prolonged etching, most pits, while retaining their shape, became larger. The density of the pits remained constant between 2 and 5×10^3 cm^{-2}. Very occasionally a pit developed a flat bottom as the dislocation line branched. Closely associated pairs of pits were often observed which suggests that they were formed at the points of emergence of dislocation half-loops. Lines of pits in $\langle 110 \rangle$ traces of the $\{111\}$ slip planes have been observed in heavily slipped regions and rows of pits delineating low angle grain boundaries have also been found.

3.2. Indentation of (111) Faces

In an attempt to verify that the triangular etch pits are associated with dislocations the etch pit pattern which can be obtained round points of indentation on (111) faces has been studied. Controlled indentation was performed using a microhardness tester in which the indenter was a fine steel needle to which loads from 1 to 5 g could be applied. Some ten indentations were made on the (111) faces of each of the crystals studied and after etching in bromine in methanol "rosette" patterns of etch pits centred on each indentation were readily observable. With the smallest loads the etch pits were arranged in a triangular pattern with rows of pits aligned along the $\langle 110 \rangle$ traces of the $\{111\}$ slip planes (see fig. 4). With increasing loads the patterns became more complex with a tendency to form a "star of David" arrangement, fig. 5. In such patterns the density of the etch pits was so high that it was impossible to determine their size. After weak indentation, however, it was possible to verify that the pits associated with the new dislocations produced during slip on the $\{111\}$ inclined planes were comparable in size to the pits associated with the dislocations which were present in the as-grown crystal. This experiment suggests, therefore, that the pits formed at the points of emergence of the dislocation half loops, which lie in the $\{111\}$ inclined planes following indentation, are identical in size and shape to those which are formed at the points of emergence of pre-existing dislocations. Incidentally, with most crystals, no etch pit pattern was produced by etching with concentrated HCl following indentation.

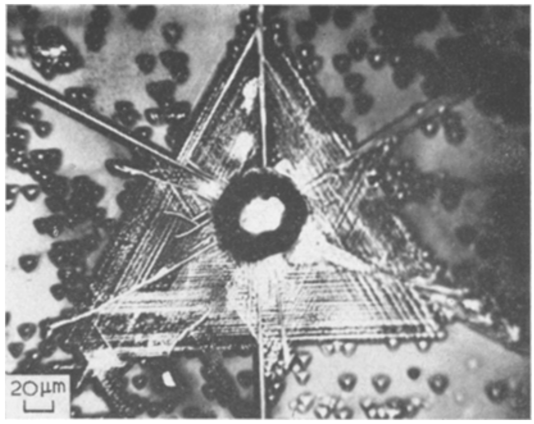

Figure 5 Etch pattern on a (111) face after strong indentation.

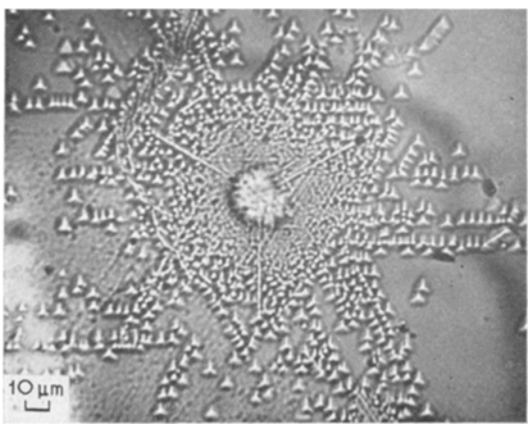

Figure 4 Etch pattern on a (111) face after weak indentation.

Another feature of the "rosette" patterns is that following indentation with moderate to high loads, the etch pattern displayed a number of radial channels, emanating from the point of indentation and running in $\langle \bar{1}\bar{1}2 \rangle$ directions, see fig. 5. These directions are the traces of the cleavage planes on the (111) face (In ZnSe cleavage occurs on $\{110\}$ planes), and the radial lines are the result of etching small cleavage cracks. The etched crack lines were usually perfectly straight and terminated in triangular etch pits. Following heavier indentation, additional but shorter cracks appeared which were at first nearly straight and ran approximately parallel to the $\langle \bar{1}\bar{1}2 \rangle$ directions. After using the largest loads however, short, irregular cracks following no particular crystallographic direction appeared.

The identification of the straight, radial channels as the etch figures found at small cracks was confirmed by observing indented crystals between crossed polaroids prior to etching. Under these conditions cracks in $\langle \bar{1}\bar{1}2 \rangle$ directions were visible with 90% of the indentations

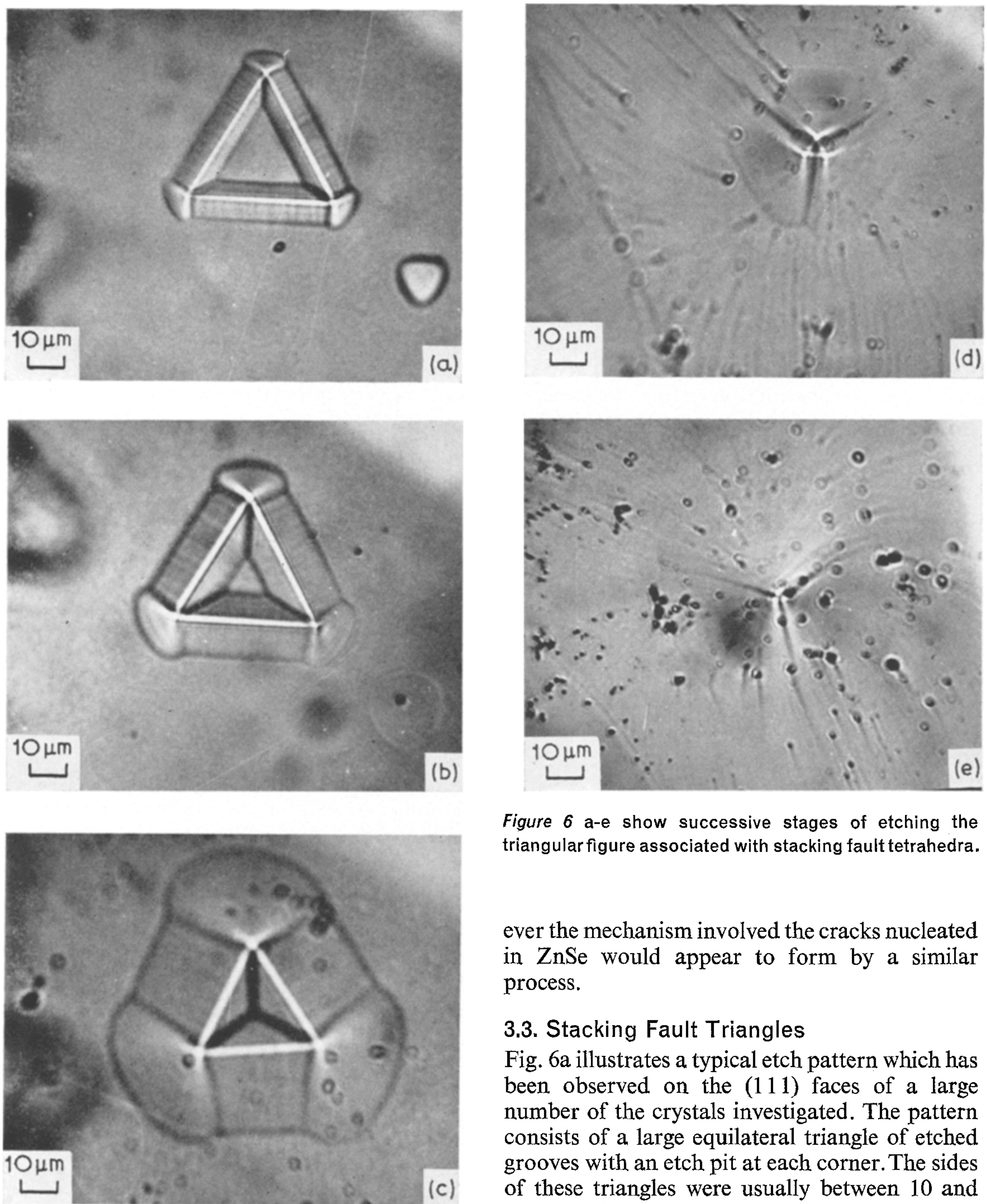

Figure 6 a-e show successive stages of etching the triangular figure associated with stacking fault tetrahedra.

studied. Cracks have frequently been observed in ionic crystals at the intersection to two sets of slip bands, see, for example, Stokes, Johnston and Li [6], who explained the nucleation of cracks in MgO in terms of the stress concentration at the head of piled-up dislocations. Whatever the mechanism involved the cracks nucleated in ZnSe would appear to form by a similar process.

3.3. Stacking Fault Triangles

Fig. 6a illustrates a typical etch pattern which has been observed on the (1 1 1) faces of a large number of the crystals investigated. The pattern consists of a large equilateral triangle of etched grooves with an etch pit at each corner. The sides of these triangles were usually between 10 and 50 μm in length. The sides of the triangles again lay in $\langle 1 1 0 \rangle$ directions but the triangles were oriented in the opposite direction to the etch pits. The effect of successively etching a crystal displaying one of these large triangular patterns is shown in figs. 6a-e. It is clear that as the surface of the crystal was etched away the triangle was

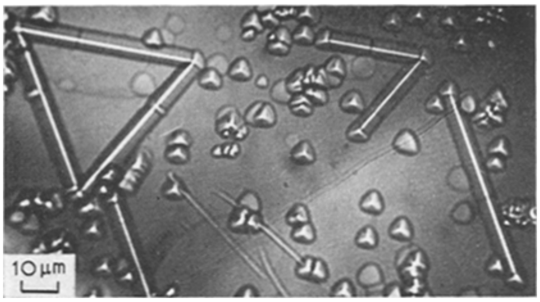

Figure 7 A triangular, single line and V-shaped defect on a (1 1 1) face.

reduced in size but retained its equilateral shape, with etch pits in each corner and a high point at the centre, until it completely disappeared. It is clear, therefore, that the etch pattern is associated with a three-dimensional defect the section of which parallel to (1 1 1) is an equilateral triangle. It is tempting to assume that the defect is a stacking fault tetrahedron such as has been observed in epitaxial layers of silicon [3,4]. In addition to the triangular defects, single line and V-shaped figures have been observed, fig. 7, which again are similar to stacking fault defects observed by Booker and Stickler [3] in epitaxial layers of silicon. The line defects terminate in etch pits as do the V-shaped defects which also have an etch pit at their apexes. We have not been able to determine the depth to which the triangular defects descend but it seems very probable that the defect is indeed a tetrahedron of stacking faults which grows in the manner postulated by Booker and Stickler. Their argument predicts that the triangles will be oriented with one apex pointing along the [$\bar{2}$1 1] direction, which is the orientation observed. If this assignation is correct the etch pits at the corners of the triangular defects are associated with stair-rod dislocations. Those at the ends of the line defects are presumably formed at Shockley partials.

3.4. Etch Pits on ($\bar{1}\bar{1}\bar{1}$) Faces

Although the HCl and $3HNO_3$ etchant produces excellent conical pits on the ($\bar{1}\bar{1}\bar{1}$) selenium faces, fig. 3, we have been unable to make extensive studies of such faces because our platelet crystals were asymmetric. Usually they contained perfect zinc faces, but the opposite faces were irregular. Only one or two good plane selenium faces were found and these occurred in regular platelets which also contained a perfect zinc face. In consequence we have been unable to make indentation studies on selenium faces. Further we have not observed triangular defects on these faces either, but this may be because insufficient crystals of the appropriate habit were examined. However, we have observed a number of etch grooves on ($\bar{1}\bar{1}\bar{1}$) selenium faces, one example of which is shown in fig. 8, and is attributable to a helical dislocation. Other patterns illustrating the presence of helical dislocations have also been observed.

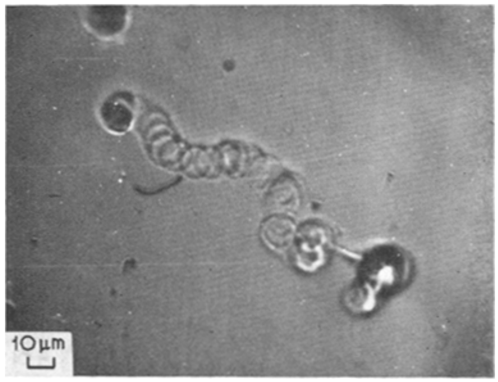

Figure 8 Etch patterns of a helical dislocation lying close to a ($\bar{1}\bar{1}\bar{1}$) surface.

4. Conclusions

The work reported here clearly indicates that the polarity of ZnSe crystals can be determined by etching in a solution of bromine in methanol when triangular etch pits are formed on the zinc faces. Etching following identation produces patterns which are characteristic of large numbers of dislocation half loops moving in the inclined {1 1 1} slip planes, and confirms the identity of the individual etch pits. The nucleation of cracks when two sets of edge dislocations moving in two different slip systems intersect has also been observed.

It is suggested that the large triangular etch figures with an etch pit at each corner are associated with stacking fault tetrahedra. According to the mechanism postulated by Booker and Stickler to explain the growth of such tetrahedra in epitaxial layers of silicon, the triangles observed should increase in size as the crystal grows in thickness, and the triangles should be oriented with their apexes laying in the ⟨$\bar{2}$11⟩ directions. The triangles reported here have the same characteristics, although in contrast with silicon their orientation is opposite to that of the etch pits. Which of the two possible triangular orientations on zinc faces corresponds to normal layer growth is uncertain, since as-grown crystals exhibit triangular growth features with both orientations.

The failure to observe triangular etch patterns on selenium faces may well indicate that platelets of ZnSe grow preferentially in the [111] direction although it may be that too few selenium faces have been examined to justify such a conclusion.

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