9. J. S. HAGGERTY and A. R. COOPER, "Physics of non-Crystalline Solids" (ed. J. A. Prins, North-Holland Publishing, Amsterdam) (1965) p. 436.

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Non-Basal Dislocations in GaS Crystals

A detailed study of the nature of non-basal dislocations in GaSe crystals has recently been reported [1, 2] and it is therefore of interest to compare the properties of dislocations and fracture in the crystallographically similar material GaS. GaS is composed of four-fold layers, each layer consisting of two sheets of gallium atoms sandwiched between sheets of sulphur atoms [3]. In view of its layered structure non-basal dislocations may have a significant influence on the anisotropy of the physical and chemical properties of the material [4].

Large single crystals of GaS were grown from the melt by the gradient freeze technique, and thin platelets were also grown from the vapour phase using the iodine transport method [5]. Non-basal dislocations were revealed by etching, for some minutes, in a solution consisting of approximately 5 % bromine dissolved in methanol at room temperature. The good one to one correspondence of etch pits on matching cleaved surfaces is taken as evidence that the pits are of dislocation origin. On vapour grown crystals, pits are also formed at the apex of growth spirals, where screw dislocations are known to be present.

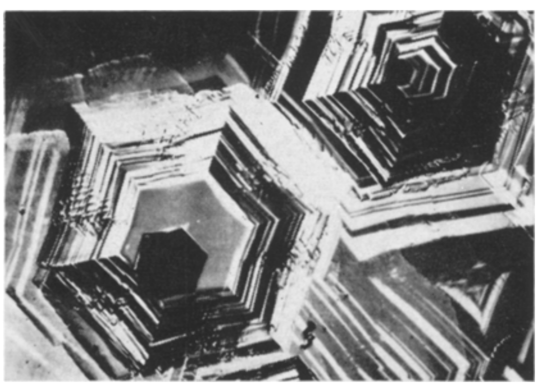

Figure 1 Etch pits in a GaS crystal.

Optical microscopy of etched surfaces reveal well defined hexagonal etch pits (fig. 1). These pits are always bounded by $[11\bar{2}0]$ directions, and are to be contrasted with the triangular pits observed in GaSe [1, 2]. This difference is caused by the fact that the etch pit shapes reflect the stacking sequence of the layers in the two materials. In the ϵ and γ modifications of GaSe a layer may be transformed into its neighbouring layer by translational movements alone, while for GaS a rotation of 60° as well as a translation is required. If oxidation produces triangular depressions in each layer (fig. 2), then triangular etch pits are to be expected in GaSe and hexagonal pits in GaS. The situation is analogous to that in the hexagonal and rhombohedral modifications of MoS_2 [6, 7]. It is also apparent that most of the pits are composed of closed hexagonal terraces, and in fact some pits become flat bottomed on prolonged etching. This situation is fairly common in layered structures [2, 8] and may be taken as evidence of the bending of non-basal dislocations within the solid.

The existence of non-basal screw dislocations, of large Burgers vectors, is revealed on cleaved

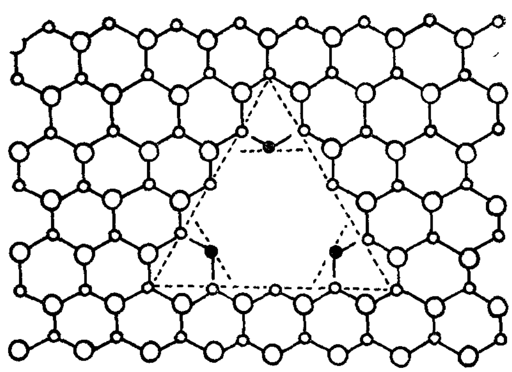

Figure 2 Schematic illustration of the production of hexagonal etch pits in GaS, by the formation of triangular depressions in successive layers. The small circles represent gallium atoms, the large ones denote sulphur. Open circles represent atoms in the top layer and the closed ones atoms in the second year.

faces by steps which terminate within the surface. Etch pits are always found at the termination of such steps (fig. 3). The existence of such dislocations are of considerable interest in layered solids [9].

Arrays of etch pits are occasionally observed in melt grown crystals. Of these, the most common are linear arrays extending along $\langle 11\bar{2}0\rangle$ directions (fig. 4). These pits denote slip traces formed at temperatures close to the melting point of the solid, during crystal growth. These arrays are rarely seen in vapour grown crystals, which grow at lower temperatures and in conditions which involve much smaller thermal strains. The average dislocation density is approximately 10^3 per cm^2 in melt grown crystals and around 10^2 per cm^2 in vapour grown GaS.

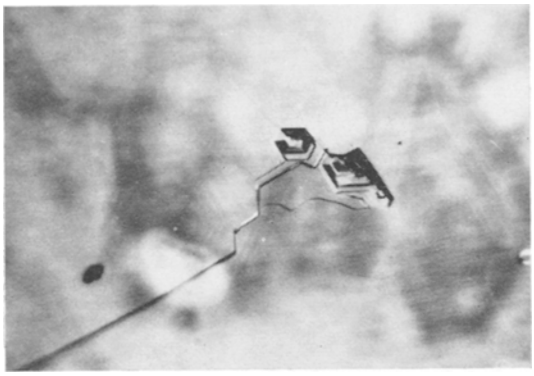

Figure 3 Etch pits at the termination of cleavage steps in GaS.

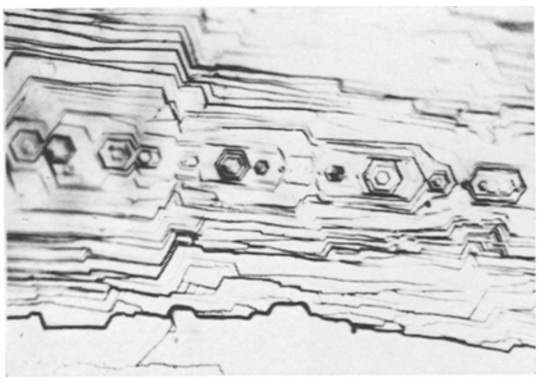

Figure 4 Array of etch pits denoting a slip trace in GaS. The array runs along a $\langle 11\bar{2}0\rangle$ direction.

Well defined dislocation etch pits, of the type described above, are only observed on crystals that have been kept free of water vapour. Exposure of a surface to humid air, or the addition of a few drops of water to the etching solution, leads to a high density of shallow background pits whose origin are not related to dislocations. These pits are believed to be due to vacancies or vacancy clusters formed by the reaction of the water vapour with the surface.

Examination of micrographs such as fig. 3 also shows that on cleaved faces of GaS there is a pronounced preference for cleavage steps to run along $[10\bar{1}0]$ directions, exposing $\{11\bar{2}l)\}$ planes. The steps appear close to the vertical, in which case l is zero. It is of interest to note that this same direction is preferred in GaSe [1], but not in the similarly layered structure MoS_2 [6]. Current theories of the nature of the bonding in GaS and GaSe assume an ionic contribution due to electron transfer from sulphur (or selenium), to gallium atoms. A strong preference for cleavage to expose $\{11\bar{2}0\}$ planes, rather than $\{10\bar{1}l\}$ planes, is in accordance with this model since in this case each parted surface is left neutral. A significant difference in the chemical properties of $\{10\bar{1}l\}$ faces compared with $\{11\bar{2}l\}$ planes is indicated by the fact that the oxidation rate in the $\langle 10\bar{1}0\rangle$ direction (as measured by the rate of recession of surface steps, at room temperature) is approximately half that in the $\langle 11\bar{2}0\rangle$ direction.

References

1. R. H. WILLIAMS, *Trans. Faraday Soc.* **66** (1970) 1113.
2. *Idem, J. Mater. Sci.* **5** (1970) 566.
3. Z. S. BASINSKI, D. B. DOVE, and E. MOOSER, *Helv. Phys. Acta.* **34** (1961) 373.
4. JEROME ROTHSTEIN, *Phys. Rev.* **95** (1954) 370.
5. H. SCHAFER, "Chemical Transport Reactions" (Academic Press, London and New York, 1964).
6. O. P. BAHL, E. L. EVANS, and J. M. THOMAS, *Proc. Roy. Soc.* **A306** (1968) 53.
7. *Idem, Trans. Faraday Soc.* **64** (1968) 3354.
8. A. SAGAR and J. W. FAUST, JR., *J. Appl. Phys.* **38** (1967) 2240.
9. J. M. THOMAS and E. L. EVANS, *Nature* **214** (1967) 167.

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