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EUGENIO SCANDALE *, FERNANDO SCORDARI *

DISLOCATION STUDIES IN GaSe BY ETCHING AND X-RAY TOPOGRAPHY TECHNIQUES

RIASSUNTO. — Le superfici parallele ai piani (0001) di cristalli di GaSe cresciuti da fase vapore, sono state sottoposte ad attacco chimico per mezzo di una soluzione diluita contenente acido solforico e bicromato di potassio. Gli effetti prodotti provano che le dislocazioni basali esaltano l'azione del reattivo. A conferma di ciò vengono confrontate topografie a Raggi X e figure di corrosione.

ABSTRACT. — (0001) planes of GaSe crystals grown from vapour phase have been etched by a dilute chromic-sulphuric acid mixture. Our observations provide direct evidence that glissile basal dislocations lead to enhanced reactivity. In order to confirm that, X-ray diffraction topography patterns have been compared with etch pictures.

Introduction

GaSe single crystals were grown from the vapour phase by iodine vapour transport technique in closed quartz ampoules (TERHELL and LIETH, 1972; CARDETTA et al., 1972). Large plates of hexagonal ε-modification (BASINSKI et al., 1961) were obtained, having the (0001) plane as the basal plane. GaSe crystallizes in a layered structure: each layer is made by four monoatomic sheets in the sequence Se-Ga-Ga-Se. Between adyacent layers weak Van der Waals forces exist, within each layer the bonding is essentially covalent. Since the structure is similar to that of graphite, similar crystal defects are expected. The basal GaSe defects were investigated by electron microscopic techniques (BASINSKI et al., 1961 and 1963). Dislocation grids were observed which arise from elastic interaction between partial dislocations lying in closely (0001) planes.

Non-basal defects were investigated mostly by BOELSTERLI and MOOSER (1962), GUSEINOV and RAMAZANZADE (1967), WILLIAMS (1970), LENDVAY et al. (1971).

In particular WILLIAMS (1970) used as etchant a solution of analytical grade bromine dissolved in methanol: triangular etch pits were observed at the apex of growth spirals, and a number of shallow etch pits were easily distinguishable from deeper dislocation etch pits. The background pits were attributed to the action of the water vapour on surface defects such as vacancies and vacancy clusters.

* Istituto di Mineralogia e Petrografia dell'Università, Piazza Umberto I, Bari (Italia).

LENDVAY et al. (1971) used a dilute chromic-sulphuric acid mixture: conical etch pits were observed at sites which correspond to the sites of emergence of screw-dislocations.

For revealing basal and non-basal defects of GaSe we have used as etchant either bromine-methanol solution or chromic-sulphuric acid mixture. More reliable results we have obtained with this second etchant: essentially to those we refer in this paper.

Dislocation etching

As in the paper of LENDVAY et al. (1971) the etchant consists of a solution in 180 ml distilled water of 30 g $K_2Cr_2O_7$ and 25 ml concentrated H_2SO_4. The etching

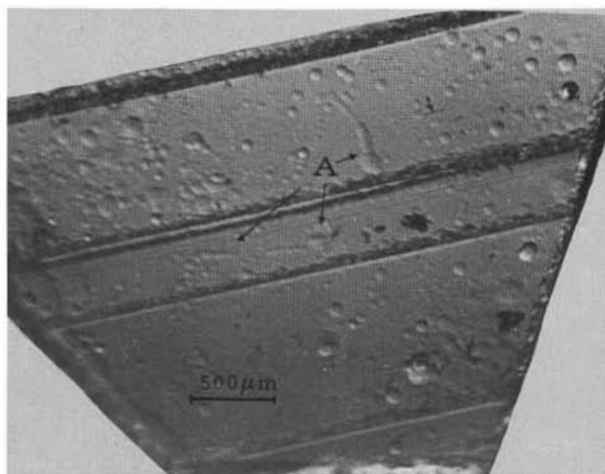

Fig. 1. — Characteristic bubbles on GaSe (0001) surface produced by dilute chromic-sulphuric acid mixture in a specimen containing dense tangles of basal dislocations (compare with figure 5).

was performed at room temperature by immersing the crystal in the solutions: etching periods of 2, 4, 10 minutes were spent.

After two minutes of etching, pits of non-basal screw dislocations were clearly visible while some random distributed shallow « bubbles » could be poorly seen. In accordance with LENDVAY et al. (1971) bunches of cooperating screw-dislocations were observed: neverthless, in order to explain the step-heigth changes in spiral growth, multiple strength dislocations, as in graphite, must be assumed. In the subsequent etching two distinct types of effects on the basal surfaces can be shown: in the former only « bubbles » continue to appear, on the contrary in the latter also grooves appear.

Fig. 1 shows an example of the first type of GaSe crystal in which, after an etching period of 4 minutes, only « bubbles » are observed.

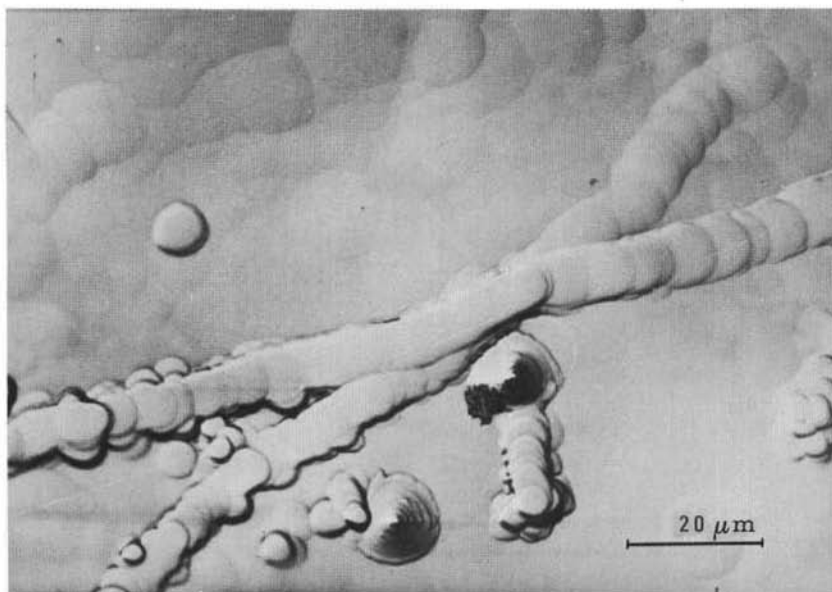

Fig. 2. — Characteristic grooves on GaSe (0001) surface in a specimen with basal dislocations in bunch (compare with fig. 7).

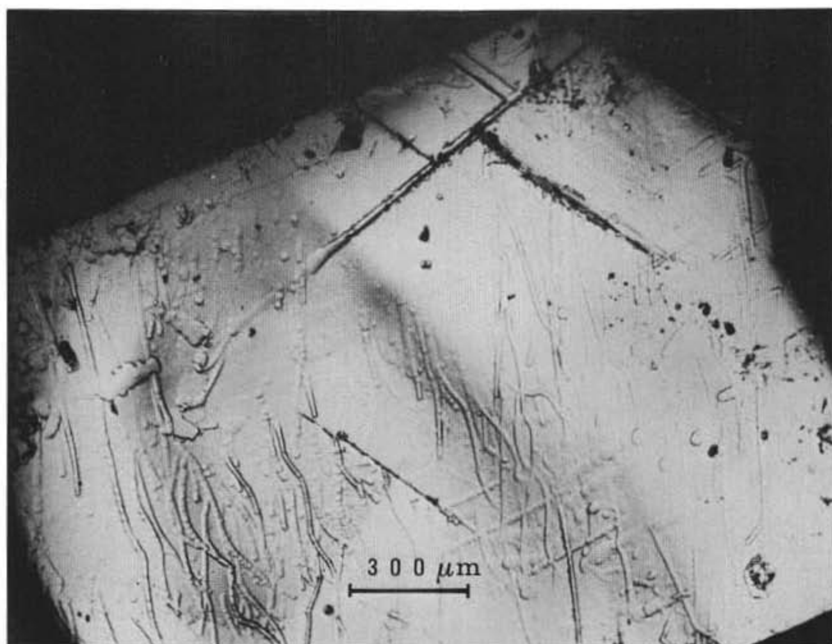

Fig. 3. — Large crystal region of a GaSe specimen after 10 minutes of etching.

Fig. 2 shows a region of the second type of GaSe crystal after a etching period of 4 minutes. Background broadened « bubbles » and two large etch pits at the sites of emergence of screw-dislocations are recognizable.

Yet the non-basal dislocations are not the only centres of enhanced reactivity: one pair of irregular grooves, nearly 10 μm wide, is the site of preferential etching. For higher etching rates these two grooves disappeared and other irregular grooves become visible (here not shown).

In fig. 3 a large crystal surface is shown after an etching period of 10 minutes. A very complex system of grooves is clearly recognizable in the picture: the large number of grooves seems to indicate their significance in the process of the crystal decomposition.

In the literature there is no indication that basal dislocations in layer structures as mica, graphite and molybdenum sulphide are responsible for enhanced reactivities of the solids (THOMAS, 1965; THOMAS and EVANS, 1967). Neverthless, by comparing etching figures with X-ray diffraction topographs, we can show that when a basal dislocation is very closed to the etched (0001) surface, preferential etching occurs on the strained region. Surface decomposition moreover is quicker in this region: further etching can reveal progressively the forms of the basal dislocations and their train in the z-direction.

Fig. 3 is a significant example of etch patterns in which some basal dislocations are clearly recognizable: we will compare this picture with diffraction topograph (fig. 8).

It can be useful to speculate on the general reasons for these results. Screw dislocations, owing to their multiple strength, have large hollow core (FRANK, 1951) and constitute higly active centres for the crystal decomposition. Basal dislocations do not involve, as screw dislocations, the breaking of intra-layer covalent bonds, but necessitate deformation of these bonds causing so an energy increase in the surrounding region. The etchant, moreover, behaves differently in screw dislocations cores, near the basal dislocations, and in unfaulted regions. Still, if the basal dislocation density is high and the dislocations are entangled, it is clearly impossible to distinguish individual dislocations by means of a etching technique. In fact, in these cited conditions, the etching cannot show resolved grooves, but only the « bubbles » thate should have composed the individual grooves, if resolved (see fig. 2).

Topographical observations

A number of GaSe specimens, each about 50 μm thick, was investigated by X-ray topographical technique (LANG, 1958). Traverse topographs were taken with MoKα radiation and recorded on Ilford L4 plates. In order to avoid a too heavy mechanical damage any GaSe specimen was suitably mounted by four needles at the center of a plexiglas hoop and this was fixed to a goniometer head. The

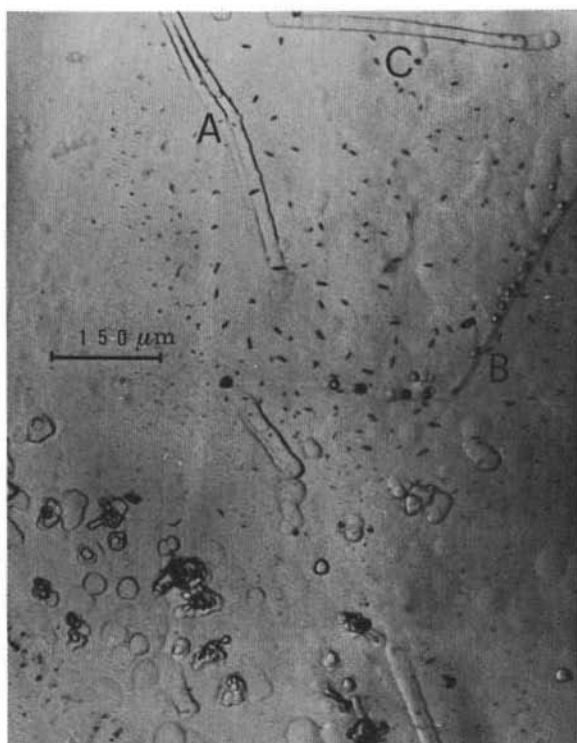

Fig. 4. — Etch figures on the plane (0001) of the GaSe single crystal. Grooves are lebelled in A and C; etch pits nucleated at the emergence points of the screw dislocations are shown in B.

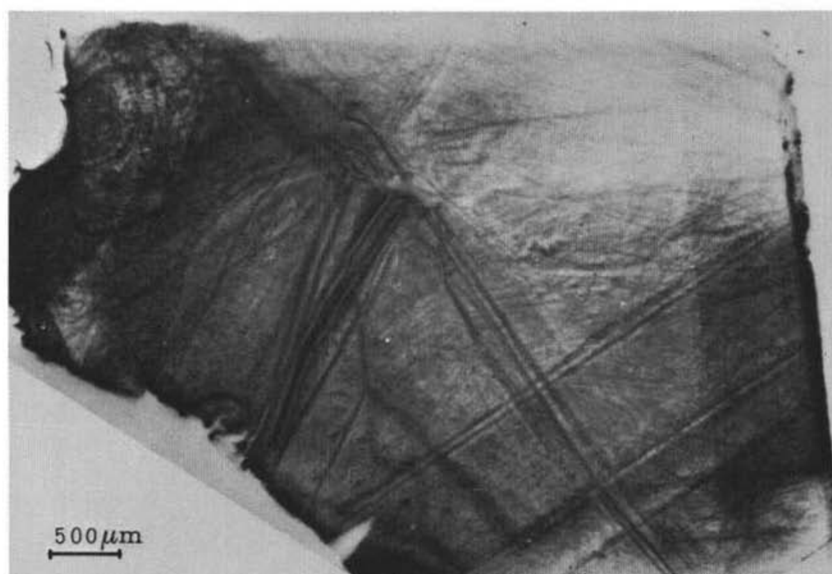

Fig. 5. — X-ray traverse-topograph (reflexion $11\bar{2}0$). We can note a dense mesh of basal dislocations.

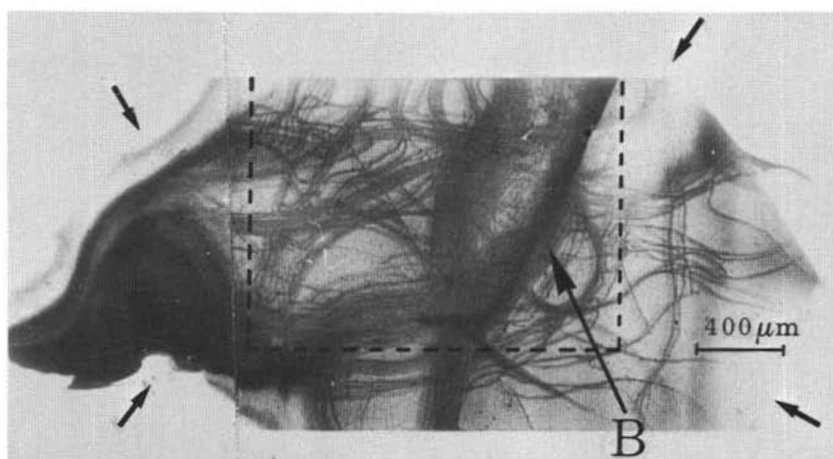

Fig. 6. — X-ray traverse-topograph: (reflexion $(11\bar{2}0)$). The framed region is reproduced in figure 8 at a higher magnification. The arrow marked B a low angle twist-boundary.

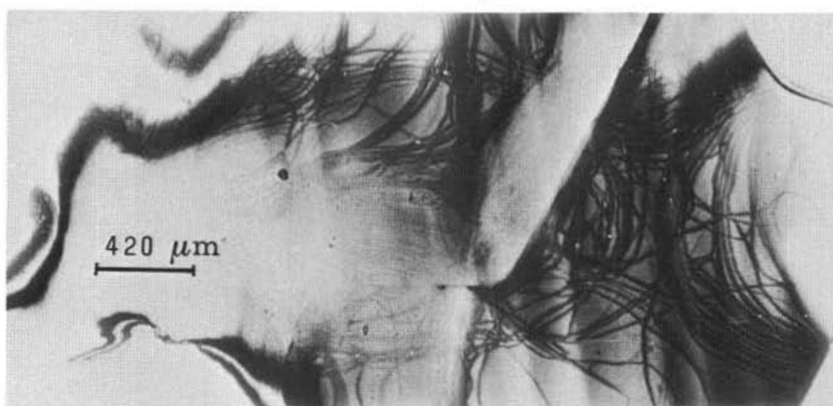

Fig. 7. — X-ray traverse-topograph: (reflexion $(11\bar{2}0)$). Evidence is seen of the large production of basal dislocation and of their movement due to the low stresses that occurred during the handling of the specimen (compare with figure 6).

advantage of this assembly is that the alignment of the crystal at various Bragg-angles is performed only handling the hoop.

It is a known result (Basinski, 1963) the splitting in GaSe of perfect basal dislocations into Shockley partials according to the reaction:

$$AB \quad \rightarrow \quad A\sigma + \sigma B .$$

In order to select important Bragg-reflecting planes, we have used a result of the kinematical theory for plane-wawe diffraction developed by Gevers (1963) for interpreting the electron microscope image of partial dislocations parallel to the crystal surface.

In accordance with GEVERS (1963) a negligible disilocation-line contrast is found for $|n| = |\mathbf{g} \cdot \mathbf{b}| = \frac{1}{3}$ ($\mathbf{g}$: diffraction vector, $\mathbf{b}$: Burgers vector): for $|n| = \frac{2}{3}$ a strong line image is recognizable, superposed on stacking fault contrast. In this paper topographs of reflexions from $(11\bar{2}0)$ planes only will be shown.

The stacking fault resulting from the displacement on a partial vector has a low energy: BASINSKI (1963) found experimentally stacking-fault ribbons whose width ranges from 0,25 μm to 1 μm. Owing to the poor resolution of lang-technique

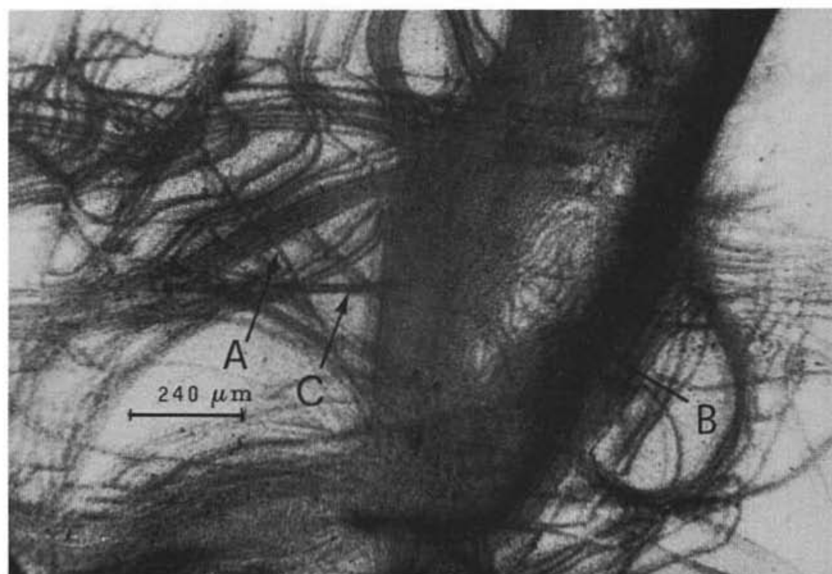

Fig. 8. — Magnification of the rectangular region marked in figure 6. The arrows marked A and C indicate the diffraction images of the two basal dislocations whose etch pattern is shown in figure 4. The diffraction contrast in corrispondence of the twist-boundary is due to the pile-up of the basal dislocations.

($\sim$ 2 μm) we have not been able to separate the contrast of two partials rising from the same perfect dislocation. Neverthless X-ray topographical technique can clearly record the generation of basal dislocations and their propagation in large crystal volumes.

The majority of basal dislocations seems to have been generated at local stress concentrations due to the handling of the specimens. Figs. 6 and 7 are $(11\bar{2}0)$ traverse topographs of the same GaSe specimen; fig. 8 is a magnification of the rectangular region marked in fig. 6. A period of one week intervenes between two topographical records. Owing to the layered structure and to a very small stacking-fault energy, basal dislocations are readily introduced by the plastyc action of the adhesive: in fig. 6 we denote by arrows the crystal regions in contact with this one.

These gripped regions behave as many dislocation sources: if we compare fig. 6

and 7, we can observe in fig. 7 new dislocations arrays, which, nucleated on parallel planes as half loops, move across the crystal in bunches.

It can be useful to note in figs. 6, 7 and 8 the resistance to the dislocation motion offered by a low-angle twist boundary (labelled B in figs. 4, 6 and 8): a non ideal pile-up configuration is clearly visible in X-ray topographical patterns. The arrangement of the dislocations around the boundary seems to suggest that this one can act also as secondary source of basal dislocations. Large deviations from the Bragg conditions, indeed, are recognizable in the topographs around the twist-boundary as well as the crystal regions gripped by the adhesive.

Enhancement of the diffraction contrast around some screw-dislocations belonging to the twist boundary may be observed in the topographical paterns. This contrast does not represent the « direct image » of the screw dislocations (in fact $\mathbf{g} \cdot \mathbf{b} = 0$), but is due to the lare strain produced by the crowding of the entraped basal dislocations.

Owing to the great mobility of the basal dislocations, some differences we must expect between the configuration of the dislocation lines as revealed by etching and that one displayed topographically by diffraction contrast. Moreover, it is necessary to keep in mind that topographical pictures refer to the whole specimen before etching, while any etch pattern shows basal dislocations very close to the actual free surface during the etching process. Neverthless some undoubted connections are evident between etch and topographical pictures: for example, we have labelled by A, C some basal dislocations which are recognizable in etch figure 4, and in topography (fig. 8).

By different etching rates we have been able to relate a considerable number of grooves on the etched surface with the dislocations arrays visible in diffraction patterns. These observations provide direct evidence of enhanced reactivity in regions surrounding basal dislocations.

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