EFFECT OF SURFACE DAMAGE ON THE TENDENCY FOR DARKENING OF ZnS SINGLE CRYSTALS

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(Presented by G. Szigeti — Received 13. X. 1964.)

The tendency for darkening of the mechanically abraded and polished, etched and cleaved surfaces of hexagonal ZnS single crystals has been examined simultaneously with electron diffraction studies. The obtained results showed that there is a strong connection between the quality of the crystal surface and the tendency for darkening.

1. Introduction

According to pictures published previously [1] the Zn precipitates produced during the photochemical decomposition of ZnS do not cover homogeneously the surface of the crystal. In the case of most of the crystals the Zn precipitates follow the stacking faults [2] perpendicular to the c-axis, as it was observed microscopically. In the case of a few other crystals not showing any oriented disorder and the surface of which seemed smooth before darkening, the orientation of the precipitated Zn could not be observed.

The question arises whether the orientation of the Zn remains if a layer is removed from such a crystal and the surface so obtained is irradiated. To decide this question a layer has been removed from the surface of crystals with mechanical abrading and polishing, and then they were irradiated in humid air. The study of the darkening of these crystals, however, gave surprising results: even after a 5 hours' irradiation no darkening observable with the naked eye could be seen on the abraded and polished surfaces, whereas if the surface was removed only by etching (without abrading and polishing) the darkening appeared in the same form as on the original crystals.

2. Experimental procedure

The single crystals used for our experiments have been grown from vapour phase in our laboratory [3]. They were prisms of a hexagonal structure. The length of the prisms was 5—6 mm, their diameter 3 mm. The crystals emitted the blue band characteristic for self-activated ZnS-s excited with 365 mm mercury line.

The electron diffraction study of the crystals was carried out with a 80 KV electron beam ($\lambda = 0{,}0417$ Å) in a JRM 6-A type electron microscope. Crystals were attached to the preparate-holder by a mixture of glue and silver colloide. For evaluation the patterns were compared with a transmission electron diffraction pattern of a gold foil made under the same conditions of operation.

The crystals were irradiated in humid air by a 250 W high-pressure mercury lamp fed from a stabilized source without filter. The intensity of the exciting light was approx. 100 mW/cm^2 on the crystal surface. Microphotos were taken by means of a MEF-type Reichert universal microscope.

3. Results

3.1. *Study of the darkening of mechanically abraded and polished and afterwards temperature-treated crystals*

The effect of abrading and polishing on the tendency for darkening of the crystals could be easily cleared. Single crystals suitable for polishing were available. After testing that the crystals chosen for the experiments could be darkened in a relatively short time they were abraded and polished mechanically. Abrading took place with a Naxos-type sand-cloth N^0 600. Polishing after the abrading was done with SiC or Al_2O_3. In the latter case the finest fraction was used. Both methods led to the same results.

The result was that the tendency for darkening of the crystals strongly decreased after such treatment. Fig. 1*a* shows an abraded and polished crystal surface. The same surface is given in Fig. 1*b* after a 5 hours' irradiation. In this figure larger and smaller Zn islands can be observed. It must be remarked that the covering of the treated surface with such particles is not a regular phenomenon. In case of the majority of the treated crystal surfaces no or hardly any metal precipitation could be observed after a 5 hours' irradiation.

The reason why we publish the rarely occurring surface picture is that this demostrates better the change of the surface picture after the heat treatment.

Heat treatment was carried out in purified N_2 atmosphere. The time of the heat treatment varied between 30 minutes and one and a half hour at a temperature of 900° C.

Fig. 1*c* shows the same crystal surface after a 1 hour heat treatment at 900° C. In the picture it can be well observed that the surface of the crystal clears after such heat treatment, i.e. a bleaching effect takes place.*

* With this phenomenon and with other forms of the bleaching effect we intend to deal in another paper.

The surface of this heat treated crystal after 10 minutes irradiation is shown in Fig. 1*d*. It can be seen clearly that after the heat treatment the tendency for darkening was noticed after a 10 minutes' irradiation, while a 5 hours' irradiation is not sufficient to produce such darkening (see Fig. 1*b*) after abrading and polishing.

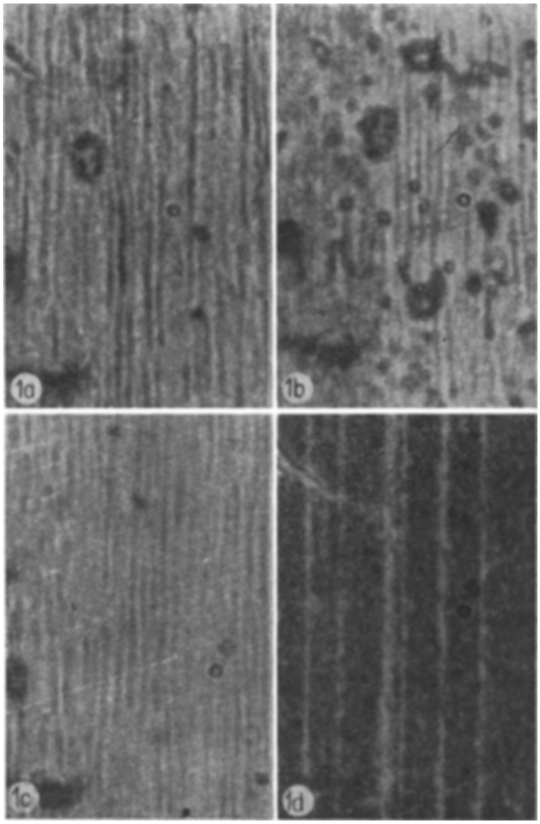
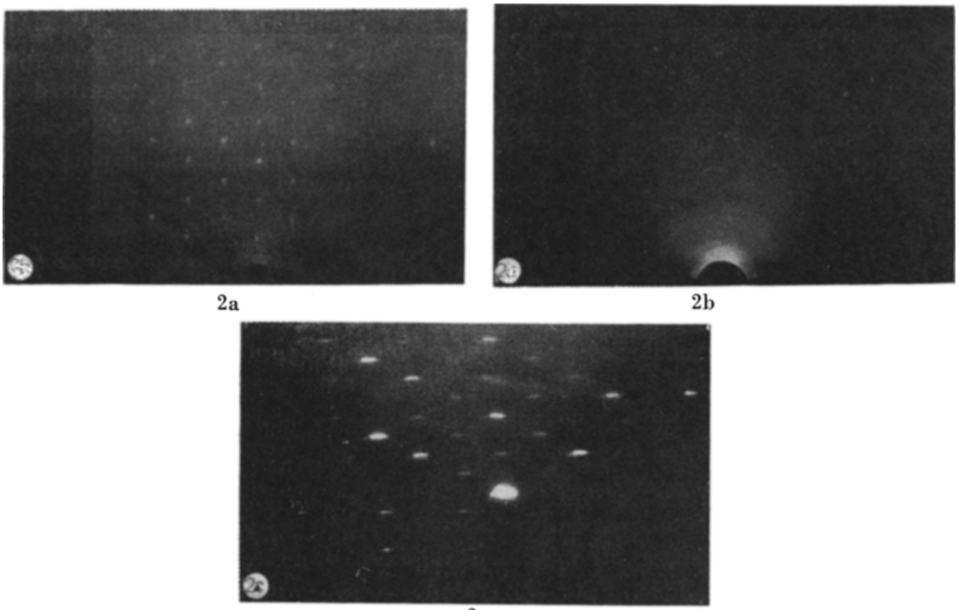


Fig. 1. Microphotograph of the surface of a ZnS single crystal (a) after abrading and polishing (b) after a 5 hours' irradiation, (c) after 1 hour's heat treatment at 900° C, (d) after 10 minutes' irradiation (128 fold magnification)

Parallel with the above experiments the electron diffraction study of the crystals took place too. The systematic examinations showed that the diffraction pattern along a crystal surface hardly changes. This seems very advantageous for the comparison of results as we were unable to make both a diffraction pattern and microscopic picture of the same part of the crystal surface because of technical reasons.

Single crystal spots and Kikuchi lines appeared on the electron diffraction pattern of untreated single crystals indicating that the chosen surfaces were single crystal faces. Fig. 2*a* shows such a picture. After mechanical abrading and polishing the electron diffraction patterns of the same surfaces showed diffuse Debye-Scherrer rings (Fig. 2*b*). This means that the surface consists of randomly oriented crystal fragments, produced by mechanical treatment.

After a 1 hour heat treatment at 900° C the crystal surface recrystallized and very good single crystal surfaces were formed. This is proved by the appearance of single crystal reflections. An example for this is given in Fig. 2*c*. Since



2a 2b 2c

Fig. 2. Electron diffraction pattern of the surface of a ZnS single crystal (a) before, (b) after abrading and polishing, (c) after 1 hour's heat treatment at 900° C

because of abrading and polishing the part of the lattice (directly beneath the fragmented zone) also became slightly deformed [4—5] and during recrystallization the very fine fragmented layer grew to this deformed matrix, so the recrystallized surface layer formed in the course of the heat treatment is also somewhat deformed. Consequently, the single crystal reflections are a little diffuse, too.

3.2. *Study of the darkening of crystals etched after abrading and polishing*

Fig. 3*a* shows the microscopic picture of an abraded and polished crystal surface after a 30 minutes' etching in $H_2SO_4 + H_2O_2$ solution. Irradiating the crystal surface obtained a strong darkening can be observed already after a 20 minutes' irradiation (Fig. 3*b*).

Fig. 4*a* gives the electron diffraction pattern of an abraded and polished crystal surface after etching for 10 minutes. In the photograph it can be easily observed that the single crystal reflections and in some cases even the Kikuchi lines reappear. Besides the single crystal reflections weak Debye-Scherrer rings can also be seen in the picture. This shows that the etching time in the present case was not sufficient for the total removal of the fragmented layer produced

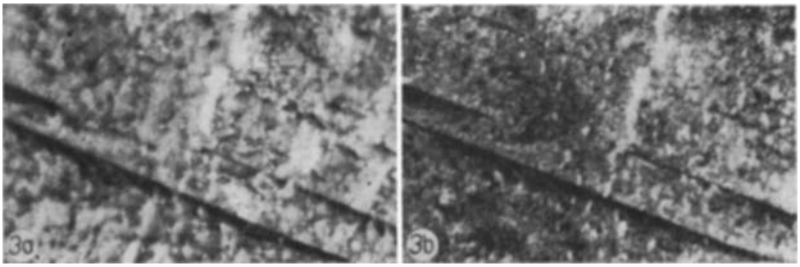


Fig. 3. Microphotograph of an abraded and polished ZnS crystal surface (a) after a 30 minutes' etching, (b) after 20 minutes' irradiation (128 fold magnification)

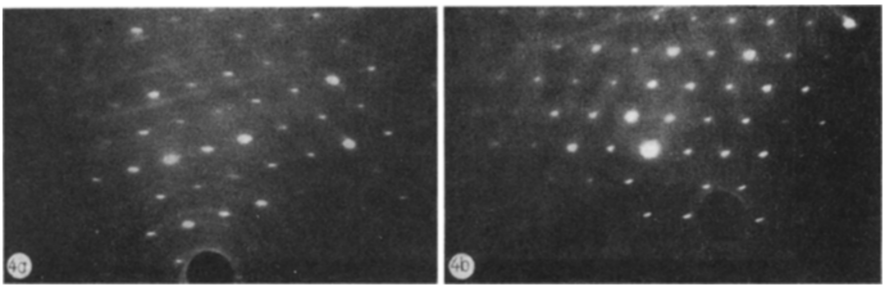


Fig. 4. Electron diffraction pattern of an abraded and polished ZnS single crystal surface (a) after 10 and (b) after 30 minutes' etching

by mechanical treatment. Increasing the time of etching (30 minutes) only single crystal reflections and Kikuchi lines appeared (Fig. 4*b*) i.e. the surface was already a fine single crystal face.

3.3. *Study of the darkening of crystal surfaces produced by cleavage*

As far as the authors know there is no literature concerning the cleavage of ZnS single crystals and the study of surfaces so obtained. This time our aim was not the study of this question either. We only endeavoured to obtain a new surface without greater damages as in the case of mechanical treatment. Hexagonal prisms were used for these experiments, too, the c-axis of which was parallel to the geometrical axis of the crystal. Cleavage took place in the plane of the c-axis. The surfaces obtained were of different qualities. Perfectly smooth surfaces were produced as well as such on which steps could be observed. These crack steps might be caused either by stresses causing that the cleavage does not work exactly along the respective crystal planes, or by imperfections in the crystal. E.g. it is well known that when an

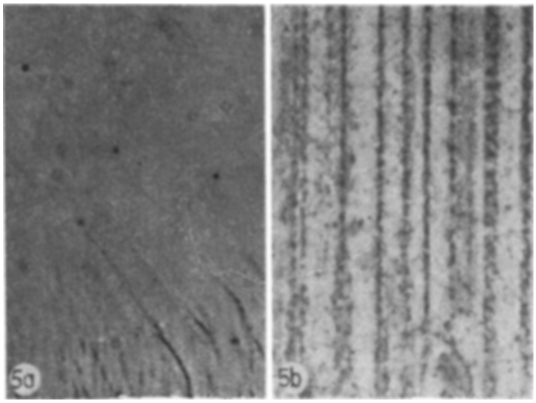


Fig. 5. Microphotograph of a cleavage surface of a ZnS single crystal (a) before irradiation, (b) after 2 minutes' irradiation (256 fold magnification)

Fig. 6. Electron diffraction pattern of a cleavage surface of a ZnS single crystal

otherwise perfect crystal contains screw dislocations intersecting the plane of cleavage a crack on passing along this plane leaves steps on the otherwise smooth cleavage surface [6].

Fig. 5*a* gives a cleavage surface of an average quality before irradiation. After a 2 minutes' irradiation the Zn precipitates are well observable. (Fig. 5*b*) A certain regularity in the position of the precipitates is remarkable. Obviously a decoration of the crystal defects is in question. [7]. In our case precipitation appeared both along the stacking faults, and the broken steps. The former are always parallel with each other, while the position of the latter relative to each other is different in each crystal.

On electron diffraction patterns of cleaved surfaces ZnS Debye-Scherrer rings were never observed. Only single crystal reflections and Kikuchi lines appeared (Fig. 6). This proves that the freshly cleaved surfaces are very good single crystal faces.

4. Discussion

It is well known that a mechanical treatment of the surface both in the case of metals and semiconductors may lead to an "amorphisation" of the surface layer, i.e. a formation of a layer consisting of extremely small crystallites [8]. As proved by our experiments, a similar layer appears on the surfaces of ZnS single crystals by mechanical treatment. ZnS single crystal faces showing good single crystal reflections in a natural state give no single crystal reflections after mechanical abrading and polishing. The upper layer of the surface is damaged. In this damaged layer there is an outer fragmented zone which consists of randomly oriented crystal fragments.

Since with the appearance of the damaged surface layer the tendency for darkening of the crystals considerably decreased, we have to suppose that the reason for this is just the "amorphisation" of the surface. If a crystal with a damaged layer was heat-treated at 900° C for an hour, i.e. the very fine fragmented outer zone was subjected to recrystallization, the tendency for darkening grew parallel with the appearance of single crystal reflections on the electron diffraction pattern. If the fragmented layer is removed by etching i.e. a new crystalline surface is produced, we again obtain the increase of the tendency for darkening. The new surface appearing by cleavage of the crystals is a very good single crystal surface. In this case no decrease of the tendency for darkening was observed.

Accordingly, the results of our experiments unambiguously led to the conclusion that there is a strong connection between the quality of the ZnS crystal surface and the tendency for darkening.

In the first place one can suppose that the reason for the strong decrease of the tendency for darkening after mechanical treatment is that after polishing abrasive particles remain embedded in the surface. It was recently established conclusively by a radiometric technique [4] that such particles are really present in lapped steel surfaces. But in our case this is not the reason for the decrease of tendency for darkening. This is also justified by the following experiment.

As was seen above (point 3.1), the tendency for darkening which existed before mechanical treatment can be practically restored by 1 hour heat treatment at 900° C. This obviously means that the causes of the decrease of the tendency for darkening — produced during the mechanical treatment — cease to exist. If we suppose that these causes would be associated with the embedding of the abrasive particles in the surface, then these causes should act after the heat treatment, too, because at the temperature mentioned the Al_2O_3 or SiC does not evaporate from the surface. The following experiment was carried out. A very fine dispersed Al_2O_3 or SiC powder was settled on the original (untreated) as well as the abraded and polished crystal surface, respectively. The quantity of the settled material was so little that its presence was hardly detectable by electron diffraction investigations. After a 1 hour heat treatment in N_2 atmosphere at 900° C, the rings characteristic for Al_2O_3 resp. SiC could be similarly observed on the electron diffraction pattern as before. This shows that the particles settled on the surface before the heat treatment remained really on it after the heat treatment too. In such a way these cannot be responsible for the strong decrease of the tendency for darkening after polishing and the intensive increase of it after heat treatment.

GOBRECHT and KUNZ [9] noticed a slight decrease of the tendency for darkening of ZnS-Cu luminophores when milling them. Unfortunately, these authors did not make parallel structural studies. From other works [10], however, it is known that on the Debye-Scherrer diagram of milled ZnS luminophores the diffraction lines widen and their intensity decreases. At the same time background grows also. All this indicates that after milling strong inner deformations appear in the surface layers of the crystal, i.e. the first step towards the formation of the very fine fragmented surface layer has taken place. Consequently, the tendency for darkening must have decreased also, which has been observed by the authors of [9].

Naturally the above described connection between surface damage and tendency for darkening gives no ansver to the question of why the tendency for darkening decreases with damaging. Further studies are required to clarify this question.

Acknowledgement

The authors are indebted to Dr. G. SZIGETI, for his constant interest in the present work.

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ВЛИЯНИЕ ПОВРЕЖДЕНИЯ ПОВЕРХНОСТИ МОНОКРИСТАЛЛОВ ZnS НА ИХ СКЛОННОСТЬ К ПОЧЕРНЕНИЮ

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Резюме

Исследовалась склонность к почернению гексагональных монокристаллов ZnS с механически шлифованной и поливоранной, расколотой, а также травленной поверхностью. Параллельно было также произведено электроннодифракционное изучение этих поверхностей. Полученные экспериментальные результаты показывают, что имеется тесная связь между качеством поверхности кристаллов и их склонностью к почернению.