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Dislocation Etching of GaS

The A^{III} B^{VI} compounds represent a new, interesting group of semiconductors of great photoconductivity. Their photo- and electroluminescence might usefully be studied at low temperatures. Most of them are *p*-type semiconductors whose charge carrier mobility is fairly low.

The *p*-type GaS is one of the most important compounds as well as the crystallographic basic model of the $A^{III}B^{VI}$ compounds. Its forbidden gap lies at 2.5 eV.

GaS crystallises in a hexagonal system. The crystals are built up of four-fold elementary layers of S-Ga-Ga-S [1, 2]. The Ga has a tetrahedral co-ordination in the layers, whereas the S atoms have a trigonal one. The presence of Ga-Ga metal bonds was proved by magnetic measurements [1].

The tetrahedral bonds of Ga sp^3 hybrids are formed by the s^2p and the *p* electrons of the sulphur. Within the four-fold layers the bonds are covalent, whereas the bonding between two adjacent layers is of van der Waals type.

Before it is possible to interpret the physical properties of the GaS its real crystal structure must be known. The lattice defects existing in GaS have not been studied in detail [3, 4]. The publications first of all dealt with the stacking faults since, due to the layer structure of the GaS crystal, many stacking faults might form by slipping and rotating. A defect structure similar to that of the graphite could be detected by transmission electron microscopy in GaS [5].

Since oxidising etching materials and hydrogen-halogenides had been successful for developing dislocations in II-VI compounds, hydrochloric acid, bromine-acetic acid mixture as well as aqueous chromous sulphuric acid were used as etchants for the GaS crystals.

The GaS crystals investigated were grown from Ga melt according to our previous publications [6]. Due to the high lateral solubility rate of the GaS treated with hydrochloric acid, only the lamellar crystal structure could be detected (fig. 1). Strong oxidising materials such as the acetic acid solution of bromine, which proved to be a good selective etchant for GaP [6] behaved in the same way as hydrochloric acid for GaS.

The etchant of medium oxidising effect described by Woods [7] (10 ml H_2SO_4, 10 g $K_2Cr_2O_7$, 70 ml H_2O) may also be used for GaS as a highly selective etching material. By applying it, two different kinds of etch pits could be observed on the (0001) planes of the GaS (fig. 2). One of them has a hexagonal pyramidal terraced shape, whereas the other shows conical character with indistinct hexagonal symmetry. The regular hexagonal etch pits occurred considerably more frequently than the other type. Etch pits appeared along low-angle grain boundaries that were perpendicular to the basal plane and parallel to $\langle 10\bar{1}0 \rangle$ and $\langle 1\bar{2}10 \rangle$ directions, respectively. Fig. 3 shows three low-angle grain boundaries running perpendicular to the basal plane.

Occasionally, evidence was seen of the movement of dislocations due to the low stresses that occurred during the etching process. This means that the dislocations have a considerable mobility at room temperature. Fig. 4 displays a dislocation shift of this kind. The great plane bottomed etch pit probably indicates the previous position of the dislocation marked by an arrow. Dislocations perpendicular to the lamellar structure form a new group of GaS crystal defects.

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A Simple Method for the Preparation of Wüstite Single Crystals

In recent years the electrical and magnetic properties of the transition metal oxides have received considerable attention. Much of the work has been aimed at the elucidation of the fundamental processes connected with the diffusion and the chemical reduction of these oxides. The use of single crystals in such experiments tends to simplify the analysis. The ready preparation of acceptable single crystals of the oxides has, however, proved to be a problem. The present letter describes a method for the preparation of wüstite single crystals which can also be used for certain other oxides.

Cech and Alessandrini [1] have described a technique for the preparation of single crystal films of wüstite. In this method evaporated $FeBr_2$ is oxidised to FeO in an atmosphere of H_2-H_2O. The oxide is allowed to condense on an MgO cleavage surface, where it is found to grow epitaxially when the substrate temperature is above 700°C. Since magnesium ions diffuse into the wüstite layer at this temperature it is difficult to remove a clean oxide layer from the substrate. The method is then, of limited use. Crystal growth from the melt is not advisable since crucible materials including platinum are heavily attacked by FeO melts. Crucible-free techniques for pulling oxide single crystals [2, 3, 4] are expensive and not always available.

During the course of an investigation into the early stages of the reduction of wüstite to iron [5], a very simple method for preparation of wüstite single crystals was developed. A strip of high purity iron was oxidised in a steep temperature gradient. The oxidising gas atmosphere contained 50% CO_2 and 50% CO. The lower part of the vertically suspended specimen was at 1450°C and the upper part at about 1250°C. The higher temperature exceeds the liquidus temperature of wüstite [6]. As a result of this, liquid oxide is formed which then drops into the lower part of the furnace tube. The specimen melts back until the temperature at its tip reaches the solidus temperature of wüstite. Grain growth takes place at the tip when the specimen is maintained at this temperature.

Fig. 1 shows large wüstite grains, prepared by this technique. The maximum grain diameter was found to be 20 mm after an annealing time of eight days. Plane surfaces formed at the tip of the oxide specimens as shown in fig. 2. Laue

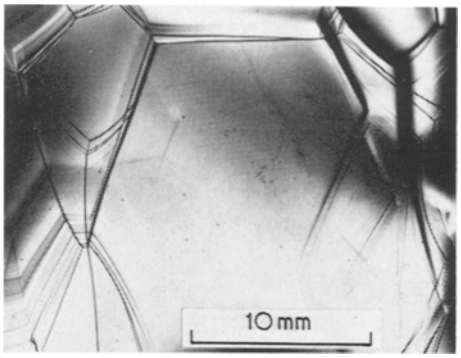

Figure 1 Polycrystalline wüstite (1390°C; 50% CO_2; 50% CO, 6 days). The large grain has a (230) surface orientation.

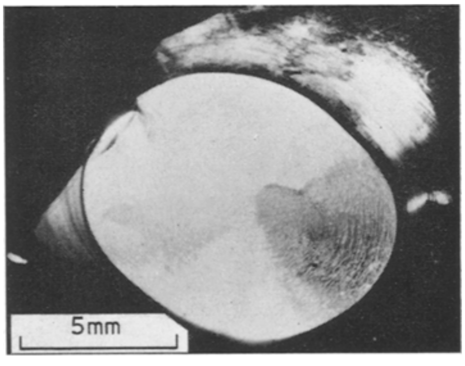

Figure 2 A surface with a (111) orientation at the tip of a wüstite specimen.