

Figure 1 Integrated brightness of CdS:Cu EL powders against evaporated cadmium amount during CdS pre-treatment. Measurements carried out at room temperature, under 1200 V and ac 600 Hz voltage supply for EL cells.

It seems that the only factor causing such variation of EL brightness, is the non-stoichiometric change of CdS powders resulting from the pre-treatment operation. Since analyses of CdS stoichiometry are not yet fully completed nor are EL processes known in sufficient detail,

we are not in a position to offer an interpretation of the obtained result. However, as regards this result we would like to point out that according to the preliminary experiments of Vecht *et al* [10], the variation of non-stoichiometry of ZnS powders appears to have a great effect on EL processes.

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Field-Ion Microscopy of Aluminium and Plasma-Anodised Alumina Films

Field-ion microscopy has been used to study a wide range of materials [1-4], but neither aluminium nor alumina has been amenable to the technique. Aluminium presents difficulties because of its low evaporation field (Brandon [5] quotes a calculated value of 1.8 V/Å) and its ease of plastic deformation; however, low-field imaging and field-etching techniques offer some

hope of success. Alumina has an excessively high resistivity, and cannot therefore be imaged as a bulk specimen; however, a thin anodised film might be suitable, as has been shown by Southworth [4] for wet-anodised iridium. Recent work by the present author [6] and by Boyes *et al* [7] has shown that despite the experimental problems, both aluminium and alumina can be studied by field-ion microscopy.

A specimen of 99.99% pure aluminium wire was electro-polished into the required needle

shape in two stages:

1. Thin layer of dilute HCl on CCl_4 ; 2V AC; to form a waist.
2. 80% acetic acid – 20% perchloric acid; 10 V DC; until the lower end falls off.

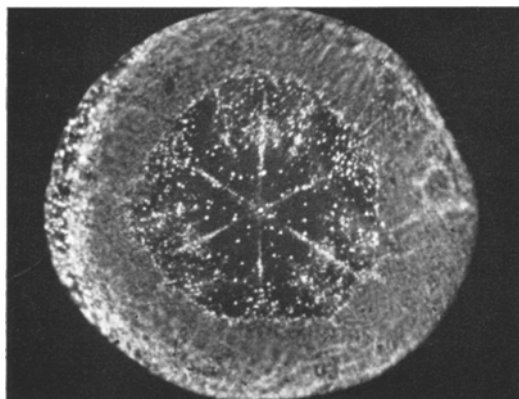


Figure 1 Argon-ion micrograph of aluminium.

After inserting into the microscope and baking overnight, the specimen was cooled with liquid nitrogen, field-etched with hydrogen to remove oxide and to develop a suitable end-form, and finally imaged in argon with a trace of hydrogen. The resulting micrograph is shown in fig. 1. The central plane can be indexed by symmetry as (111), but it is not possible to assign indices to the other regions of the micrograph because the field of view is restricted by what is thought to be a sheath of oxide.

The specimen holder was modified for plasma anodising as shown in fig. 2. A new specimen of aluminium was imaged as above, and was then plasma-anodised in an atmosphere of about 50 m torr of high-purity oxygen, with a discharge current of 1 mA at 1 kV, and a specimen current of 50 to 100 μA at 3 V bias, for 15 min. The specimen was cooled with liquid nitrogen during

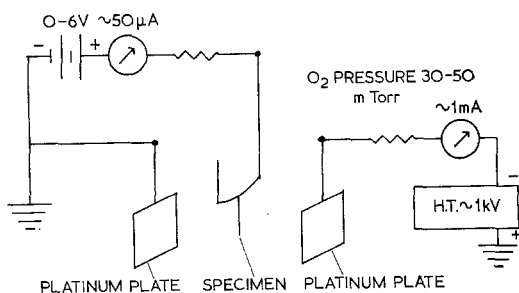


Figure 2 Plasma-anodising electrodes and circuit. Oxygen pressure 30 to 50 m torr.

this operation. After removing the oxygen, it proved necessary to leave the microscope chamber pumping for several hours before the background vacuum returned to a value suitable for argon ion microscopy ($\sim 10^{-10}$ torr).

A micrograph of the oxide imaged with argon

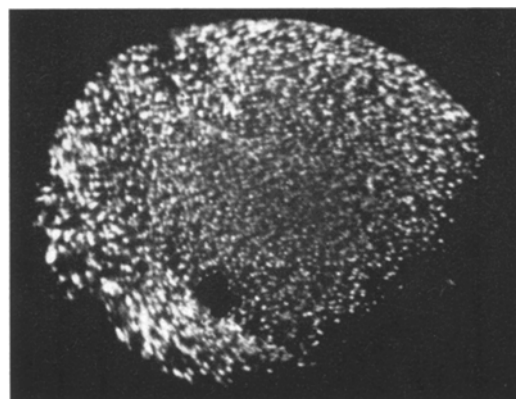


Figure 3 Argon-ion micrograph of anodised alumina film.

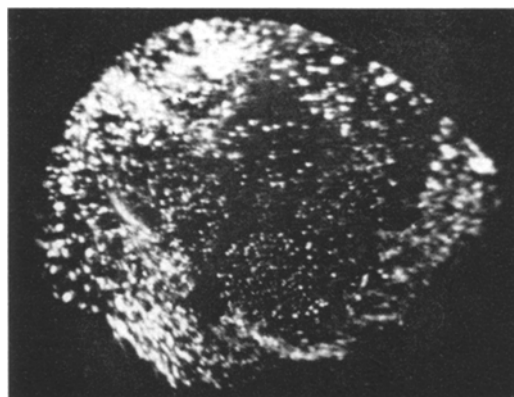


Figure 4 Image after partial removal of anodised oxide.

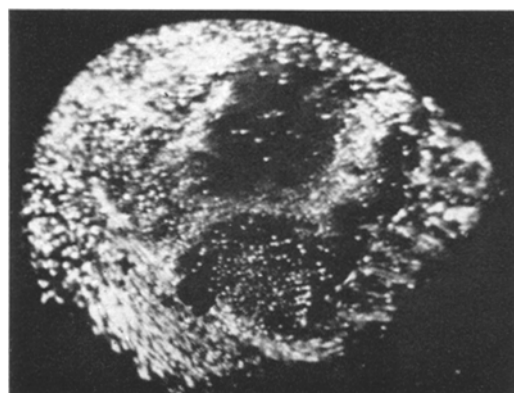


Figure 5 Image after complete removal of anodised oxide.

is shown in fig. 3. There is no evidence of any crystal structure. The oxide layer was field-etched with hydrogen in stages, imaging with argon between each stage of etching. It was possible to arrest the removal of oxide at a stage where both oxide and metal were visible, as in fig. 4, which should be compared with fig. 5 where the oxide has been removed completely.

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Diglycine sulphate – an interesting new dielectric crystal species

Experiments carried out on the growth of triglycine sulphate (TGS) [1] and its variation with the pH [2] led to the discovery of a new crystal, which has some interesting anomalies in its physical properties.

Solutions prepared with sulphuric acid and glycine in proportions of 1:1, 1:2, and 1:3, all yielded monocrystals of TGS. If, however, sufficient sulphuric acid was added to bring the solutions to a pH less than 1, a new species was obtained. If the pH was over 1.9, the crystals were TGS; if it was between 1 and 1.9, non-TGS crystals appeared.

The new crystal species had well-formed faces, good transparency and a more rapid growth than the TGS. Studies carried out with the use of X-ray techniques showed that it was a crystal belonging to the Space Group $P_{21/c}$, with parameters:

$$a = 9.62 \text{ \AA}, \quad b = 8.67 \text{ \AA}, \quad c = 6.75 \text{ \AA} \quad \text{and} \\ \beta = 106^\circ 30'.$$

A quantitative chemical analysis was made and the results showed that the substance was $\text{SO}_4\text{H}_2(\text{NH}_2\text{CH}_2\text{COOH})_2 \cdot \text{H}_2\text{O}$, i.e. diglycine sulphate with a molecule of water. Its density was 1.63 g/cm^3 which indicates that in each cell unit 2 molecules of said composition were present.

The crystal had a transition at 72°C . This result was obtained from differential thermal analysis and above the transition temperature it was found to change to a polycrystalline state, in which an opaline aspect was observed.

Measurements of the dielectric constant as a function of temperature were taken simultaneously on three plates of 1 to 2 mm thickness and 1 cm^2 area, which were cut in directions approximately perpendicular to crystallographic axes a , b and c . Colloidal silver was used as electrodes. The measuring device was a 1615-A, General Radio bridge; measuring operation – 0.5 V/cm . The results obtained are shown in fig. 1; these confirm the crystalline transition at 72°C . It was at first thought that the increase in the dielectric constant at this temperature was due to a loss of water, such as has been confirmed in other crystals, e.g. sodium rubidium tartrate [3], but thermal-balance analysis showed that most of the water was lost at temperatures above 150°C (fig. 2).

Because of this anomaly in the temperature dependence of the dielectric constant, it was thought that the crystals might be antiferroelectric; hence, sheets were cut in different directions and their possible hysteresis cycle studied. Nothing conclusive was found. If an antiferroelectric axis exists, it cannot be the twofold axis.