

ON THE PREPARATION, OPTICAL PROPERTIES AND ELECTRICAL BEHAVIOUR OF ALUMINIUM NITRIDE*

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Abstract—Methods are described for single crystal and film growth. The refractive index of crystals was found to be 2.16 ± 0.08 and the fundamental optical absorption edge 5.9 ± 0.2 eV. All crystals examined showed a weak absorption centred at 2.8 eV, which could be enhanced by the introduction of excess aluminium. The absorption edge of single crystals shifted to lower energies on heating in argon. Maximum photoconductivity occurred at 2.8 eV on illuminating the cathode. Thermal activation energies of 1.4 ± 0.1 eV and 0.5 ± 0.1 eV associated with electrical conductivity were observed. The log current-log voltage characteristics of crystals show an apparent Traps Filled Limit behaviour which is discussed in terms of a thin surface layer whose presence is indicated by experiments using current and potential probes. Thin films of AlN showed no apparent Traps Filled Limit behaviour.

1. INTRODUCTION

THE IMPORTANT properties of the 3-5 family of semiconductors are, with a few exceptions, now fairly well understood. The difficulties inherent in preparing certain of these materials in single crystal form has, however, left substantial gaps in our knowledge. In particular great difficulty has been experienced in the preparation of suitable specimens of aluminium nitride. Over the last few years we have developed the sublimation method originated by TAYLOR and LENIE,⁽¹⁾ to produce crystal plates of up to a few millimetres in length and have also been successful in growing thin films of the material by various techniques.

The morphology of the material has been the subject of considerable study by other workers⁽²⁻¹¹⁾ and numerous papers have appeared on the preparation of the material.^(1,12-20) In those cases where a reasonable degree of success

had been reported we attempted to reproduce the method described but found the TAYLOR and LENIE⁽¹⁾ method best. PASTRŇÁK and SOUCKOVA⁽²¹⁾ have produced thin layers of AlN by a plasma discharge technique. We have reproduced this method (see Section 3) but find in fact that much better layers may be grown by an epitaxial vapour phase growth technique using sapphire as a substrate. Results of experiments on luminescence^(22,23) have been reported, while LAGRENAUDIE⁽²⁴⁾ has published details of the electrical and optical properties of some rather impure samples. We have previously described⁽²⁵⁾ some of our preliminary electrical and optical work.

2. PREPARATION OF SINGLE CRYSTALS

Polycrystalline aluminium nitride may be produced by an electrical discharge between aluminium electrodes in an atmosphere of nitrogen. Our starting material was produced in this way by the United Kingdom Atomic Energy Authority and was of approximately 98 per cent purity. (The residual impurity was largely Al_2O_3). It was compacted in a die at a pressure of 10 ton/in² into a cylinder 3 cm long by 1 cm dia. The compacted charge was supported coaxially in a tubular

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graphite susceptor having an internal diameter of 17 mm, an external diameter of 20 mm and a length of 10 cm. The susceptor of Le Carbon No. 5501 graphite was mounted horizontally in the coil of a 10 kVA, 450 kc/s induction furnace and was supported at one end by a thin brass tube which also served as a nitrogen inlet. The coil was contained in a water cooled brass chamber which had a slow current of high purity nitrogen passing through it at approximately atmospheric pressure. A "Pyrex" window allowed the susceptor to be viewed through an optical pyrometer. Initially, the aluminium nitride charge was sintered by raising its temperature to about 1600° for 20 min. Thereafter the power input was increased until the temperature of the inside wall of the susceptor rose to the operating value of 1980°, measured at its centre by the optical pyrometer without correction for the emissivity of the carbon. The aluminium nitride sublimed from the hot region and recrystallized in the cooler zone. Crystals formed on both the carbon and the charge. The former were highly impure while the latter were clean flat plates having a very pale yellow colour and could be detached from the polycrystalline substrate.

Such crystals usually were about 0.1 mm thick and varied in length from 3 mm downwards. They were roughly square in shape. All crystals studied were oriented so that the large faces had the *c*-axis as a tangent and were normal to the 1210 direction.

3. PREPARATION OF THIN FILMS

PASTRŇÁK and SOUCKOVA⁽²¹⁾ described a method of producing thin films of aluminium nitride by a plasma discharge technique. We have found that, in order to obtain good films free from excessive oxide contamination, it is necessary to introduce a number of refinements not mentioned by these authors in their paper.

Nitrogen containing less than 20 parts per million of oxygen was passed through two columns containing MnO and one column containing Linde 5A molecular sieve in order to remove residual oxygen and water. Pressure was dropped to 1.0 torr by a needle valve giving admittance to a continuously pumped all glass system fabricated in one piece. This system had been previously baked at 10^{-6} torr to remove adsorbed gases. The

nitrogen flowed through a cold trap and a graded seal into a quartz tube passing through a tubular furnace maintained at 980°. The further end of the quartz tube was connected via a second graded seal to a cold trap which led to a 2 in. oil diffusion pump. An auxiliary system of furnaces allowed high purity AlCl₃ to be sublimed into the current of nitrogen. The chloride was prepared in the apparatus from "spec pure" aluminium and HCl gas formed by the dehydration of analar quality HCl by Analar H₂SO₄. Two aluminium electrodes placed at either end of the furnace, and 40 cm apart, were connected to a 1500 V d.c. supply. The negative electrode was at the outgoing end and a current of 10 mA was passed. Quartz microscope slides were placed between the electrodes and on some of these it was possible to form good films of AlN. The position of the region of optimum growth was very sensitive to the operating pressure. The films were clear and identifiable as AlN by reflection electron diffraction. Examination under an optical microscope revealed an irregular mosaic of polycrystalline islands having an average width of about 50 μ. Although in excess of 99 per cent of the surface was covered, it was not found possible to grow a continuous film. Far better films were grown by a simple extension of the technique used to grow single crystals. The substrate consisted of an optically polished "C" face of artificial sapphire. This was placed near the charge of AlN in the graphite susceptor. The operating temperature of the susceptor was 1780°. Over a period of half an hour it was possible to grow excellent epitaxial layers of AlN which were coherent over distances of the order of 2 mm.

4. ELECTRICAL AND OPTICAL PROPERTIES OF CRYSTALS

In our earlier work⁽²⁵⁾ we reported briefly on the properties of variously coloured crystals. We are now of the opinion that only the *very* pale yellow ones can be viewed as reasonably pure AlN and accordingly confine our remarks to these crystals. Crystals of other colours were occasionally obtained but their properties varied widely and they invariably nucleated on the graphite susceptor, not on the polycrystalline aluminium nitride. The orientation has already been discussed. We find for the refractive index

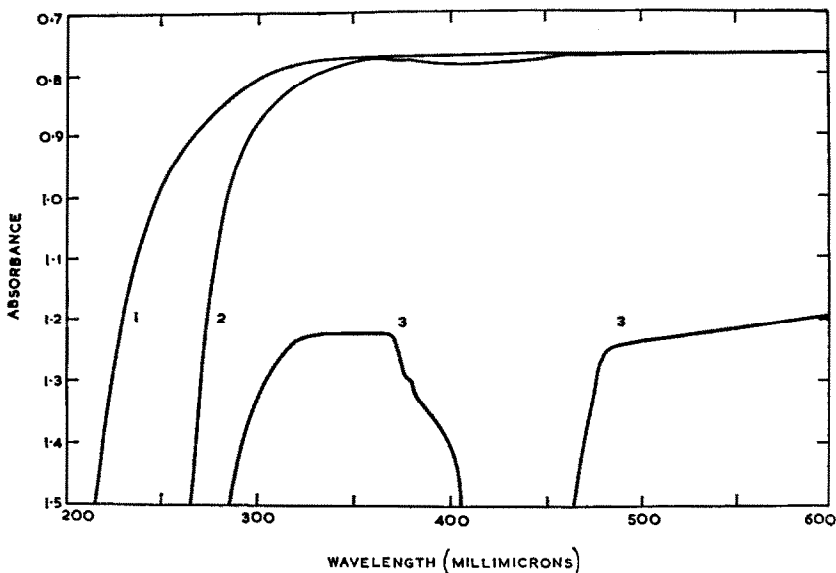


FIG. 1. Optical absorbance vs. wavelength for an AlN single crystal at 20°. Curve 1: as grown crystal. Curve 2: crystal heated at 1100° for 2 hr in argon. Curve 3: crystal plated with aluminium and heated at 1100° for 2 hr in argon. Aluminium then removed.

a value of 2.16 ± 0.08 in agreement with LAGRENAUDIE.⁽²⁴⁾ The apparent optical absorption edge is very sensitive to crystal defects as we show below. We thus choose the extreme short wavelength limit observed as being the true edge. We made repeated attempts to allow for reflectivity in our absorption studies but found that the small size of the crystals (1 mm \times 1 mm \times 0.1 mm) and interference effects made this very difficult. It is thus impossible to provide sufficient data to distinguish between direct and indirect transitions or to examine exciton effects. We conclude that the fundamental absorption edge is at 5.9 ± 0.2 eV. In addition to this edge all the crystals studied showed a weak absorption centred around 2.8 eV. This was thought to be due to excess aluminium and the following experiment was carried out to test this hypothesis. Crystals were plated with aluminium *in vacuo* and then baked for 2 hr at 1100° in argon at one atm. The aluminium layer was then removed using dilute nitric acid. Crystals so treated exhibited an apparent edge at 4.8 eV and a very strong absorption centred around 2.8 eV. Crystals baked in argon without aluminium plating showed the change of edge but no signifi-

cant increase in the absorption at 2.8 eV. These results are illustrated in Fig. 1. Our tentative conclusion is that the change of edge is associated with nitrogen vacancies and the 2.8 eV absorption with interstitial aluminium. It is possible that the change in edge is brought about by the FRANZ-KELDÝSH^(26,27) effect associated with large electric fields in the vicinity of the nitrogen vacancies.

A number of specimens had semitransparent electrodes evaporated on to opposite faces and were illuminated on each face in turn by monochromatic light while a potential was applied between the electrodes. In all cases photoconduction associated with the 2.8 eV absorption was observed. Experiments were carried out using a number of different combinations of electrode materials. The difficulty of measuring the optical absorption in the electrode made the interpretation of the results very difficult and only those obtained using gold electrodes on both faces are reported. In this case the absorption of light in gold in the region about 2.8 eV is so small that an accurate knowledge of the thickness of the electrode is not important. Results obtained are shown in Fig. 2. The large effect associated with

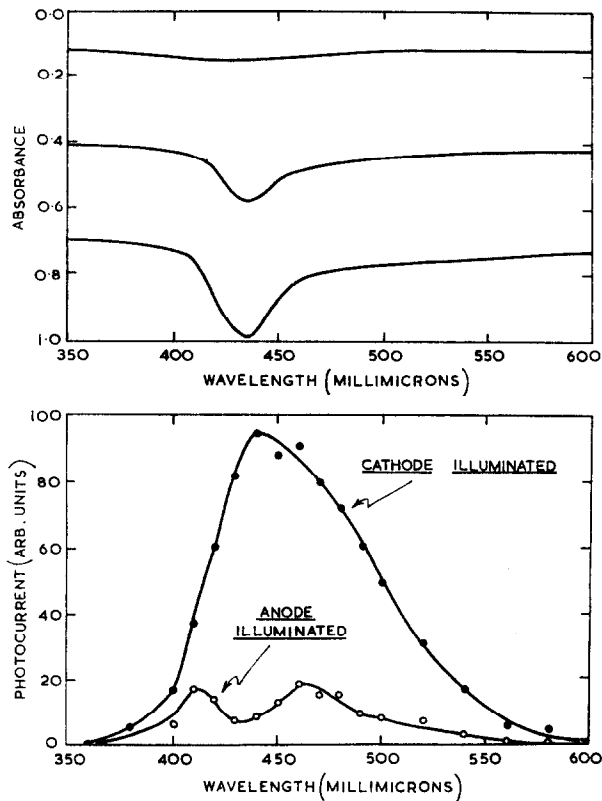


FIG. 2. Upper: Variation of optical absorbance with wavelength for three untreated specimens showing absorption at 2.8 eV. Lower: Photocurrent vs. wavelength showing increase in response at 2.8 eV on illuminating cathode.

illuminating the cathode leads to the surmise that the 2.8 eV absorption involves the excitation of electrons rather than holes.

When the anode is illuminated we believe that light corresponding to the peak of the absorption curve is virtually all absorbed before it reaches the cathode. Light having adjacent wavelengths is able to penetrate to the cathode and excite electrons.

In Fig. 3 we show a log of conductivity vs. $1/T$ plot for a typical specimen. All crystals studied yielded a slope corresponding to an energy of 1.4 ± 0.1 eV. Some crystals show a low temperature region in which the slope corresponds to an energy of 0.5 ± 0.1 eV. It seems at least possible that the 1.4 eV slope represents impurity conduction associated with the 2.8 eV level.

In Fig. 4 we show a log current vs. log voltage curve for a crystal bearing gold electrodes. As will be seen, it consists of an ohmic portion, a steep rise of current over several orders of magnitude and a region in which the current varies approximately as the square of the applied potential. It might be supposed that such behaviour corresponds to the Traps Filled Limit phenomenon predicted by LAMPERT⁽²⁸⁾ and discussed by various other authors.⁽²⁹⁾ However, subsequent studies have shown this point of view to be an oversimplification. Experiments which have been carried out, using current and potential probes on a crystal about 3 mm long indicate that the major part of the potential is dropped across a thin surface layer. This finding is supported by the results in Fig. 5,

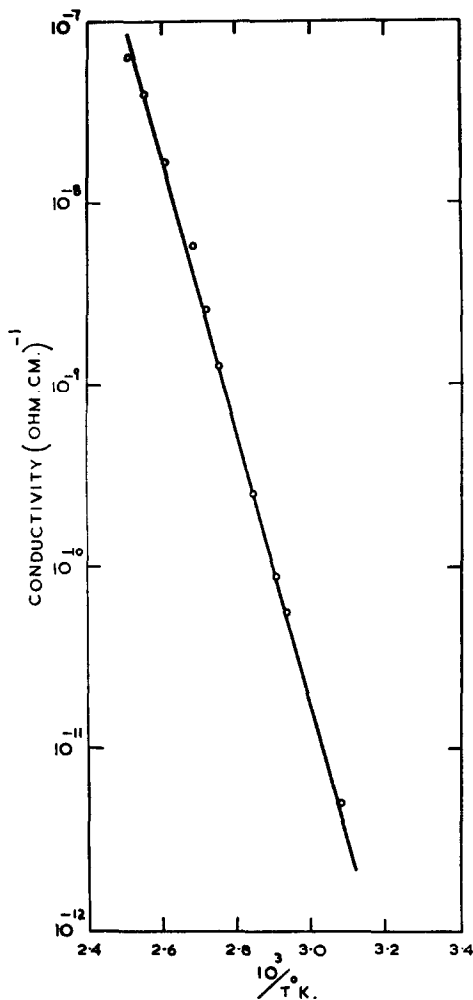


FIG. 3. Plot of conductivity vs. reciprocal temperature for a specimen bearing two gold electrodes.

where log current vs. log applied potential curves are shown for a crystal bearing indium electrodes on the same surface. Curve 1 indicates the behaviour of the virgin specimen. Subsequent application of a field gave the same result. On heating the crystal for seven hours at 150° *in vacuo*, the behaviour shown in curve 2 was obtained. Further application of a field gave high conductivity ohmic behaviour typified by curve 3. The sudden rise of current over a very short voltage range shown in Figs. 4 and 5 is, in both cases, brought about by the existence of the

surface layer. The process illustrated in Fig. 4 is reversible and is probably associated with the filling of traps in this layer. The process illustrated in Fig. 5 is irreversible and is obviously associated in some way with the diffusion of indium into this layer.

We believe that the layer consists of the mixed oxide-nitride which has been previously studied⁽²²⁾ and which could be formed by reaction with atmospheric water vapour thus:

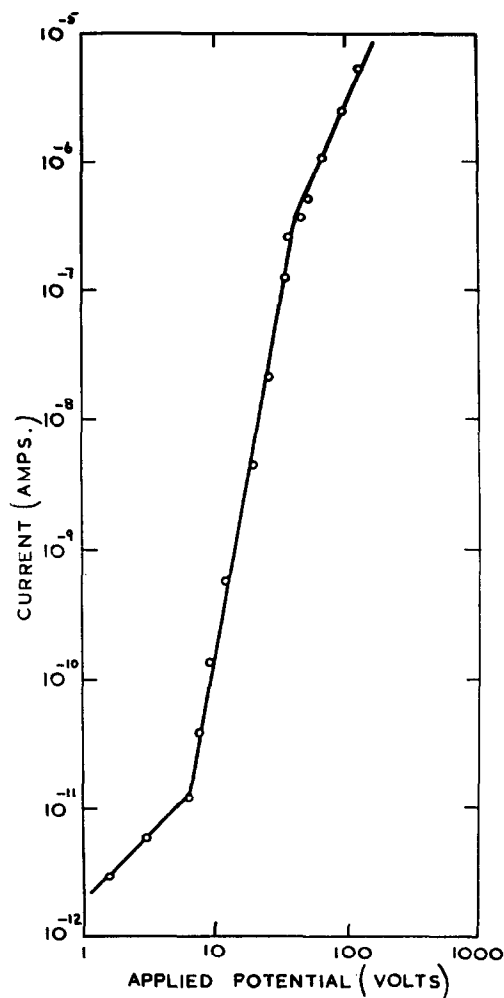
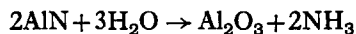


FIG. 4. Current vs. applied potential for a crystal bearing two gold electrodes on same surface.

5. PROPERTIES OF FILMS

The films discussed here were all identifiable as AlN by electron diffraction. However, attempts to measure the refractive index by reflection experiments always led to a value between those of AlN and Al₂O₃. If the layers are partially oxidized for an appreciable portion of their thickness, this result is not surprising. The plasma grown layers always showed ohmic conductivity but the epitaxial layers showed a behaviour such that the

value of dj/dU (j is current and U applied potential) is always positive. A typical low field specific resistivity using indium electrodes is of the order $10^{11} \Omega/\text{cm}$. When the film was baked at 150° in 12 hr *in vacuo* the resistivity decreased by two orders of magnitude. However, the resistivity returned to its original value over a period of 24 hr.

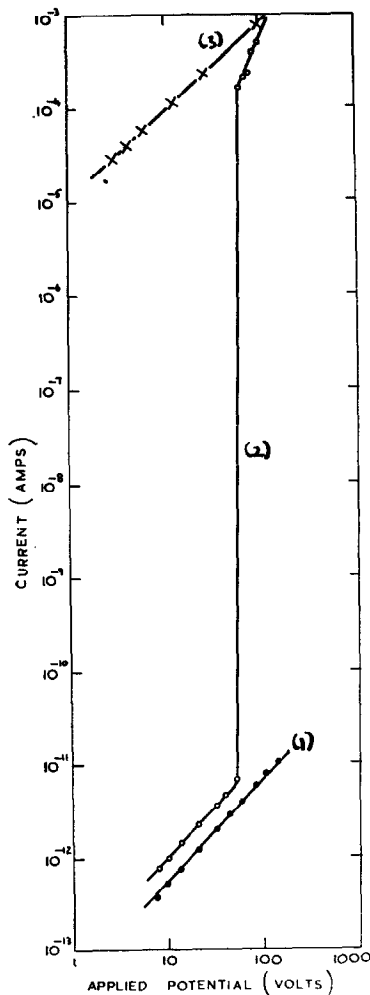


FIG. 5. Current vs. applied potential for a specimen bearing two indium electrodes on the same surface. Curve 1: Virgin crystal. Curve 2: after heating *in vacuo* at 10^{-5} torr for 7 hr at 150° . Curve 3: behaviour on second and subsequent application of a field after heating in vacuum as above.

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