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On the Preparation, Growth and Properties of Cd_3As_2

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A new general method for the preparation of compounds having volatile components, and its application to the preparation of Cd_3As_2, is described. The pulling of Cd_3As_2 by liquid encapsulation, using firstly a new encapsulant to clean the melt, and secondly a modified B_2O_3 encapsulant for pulling, is reported. Electrical properties of pulled Cd_3As_2 are given.
The effects of annealing on the optical transmission of evaporated Cd_3As_2 films are described, and the energy gap suggested by optical transmission and photoconduction are briefly discussed.

1. Introduction

Cadmium arsenide, Cd_3As_2, is a semiconductor which has received sporadic attention for some years [1–10]. The true value of its energy gap has not, to our knowledge, been finally settled, but the balance of the evidence, including our own, favours a value in the range 0.5 to 0.6 eV. Cd_3As_2 melts at 716° C and shows a phase change at approximately 615° C. The vapour pressure above the melt at the melting point is approximately 0.8 atmospheres. Reported carrier concentrations in Cd_3As_2 have generally been in the 1 to 4×10^{18} electrons/cm^3 range. Despite these high carrier concentrations electron mobilities are very high – up to 100 000 cm^2/Vs – and Cd_3As_2 thus shows the highest mobility of any known semiconductor for a given temperature and the reported carrier concentrations.

Zone-refining of Cd_3As_2 has been achieved using an adaptation of the liquid encapsulation technique [11] and it was found that, even after 35 zone passes, the carrier concentration in the resulting material was still 1×10^{18} cm^{-3}, half that of the starting material. While this could, in principle, be due to an impurity with a segregation coefficient of near unity, the fact that almost all workers, including ourselves, have reached similar lowest carrier concentrations regardless of starting materials and means of growth (including vapour growth), suggests strongly that it is due to a non-stoichiometry or equilibrium defect concentration in the pure compound.

2. Preparation of Cd_3As_2

Cadmium metal was of 6 N quoted purity supplied by Koch-Light Laboratories Ltd, and arsenic was supplied in the β (non-oxidising) form by Hoboken with a quoted purity of 99.999%.

Cadmium arsenide, Cd_3As_2, was prepared by heating together stoichiometric proportions of the elements. It was found that there was a tendency for ingots cooled in silica ampoules to stick to the silica and break up, necessitating a lengthy and difficult separation procedure to remove the silica. The technique of liquid encapsulated Stockbarger growth and preparation was therefore developed, and this is shown diagrammatically in fig. 1.

The liquid encapsulation technique has been described several times [12–14] with reference to the pulling (Czochralski growth) of crystals from volatile melts. In this technique the melt is covered by a layer of an inert liquid, usually B_2O_3, and there is applied a pressure of an inert gas, greater than the equilibrium vapour pressure which would exist above a free melt at that temperature. Evaporation from the melt is thus virtually eliminated and seeding and pulling can take place through the B_2O_3 layer.

In the liquid encapsulated Stockbarger tech-

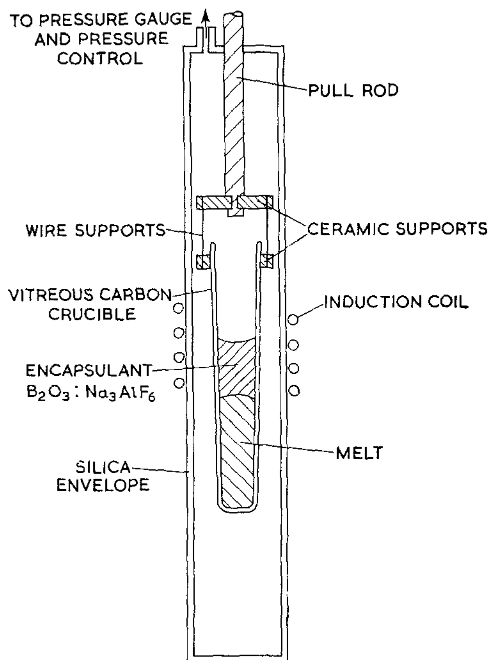

Figure 1 Schematic representation of the liquid encapsulated Stockbarger technique showing the final stage as the melt emerges from the heating coil.

nique a crystal puller with inductive heating was used, for convenience, as a high pressure, hot zone furnace. For the preparation of Cd_3As_2 a vitreous carbon 2° tapered tube, 20 cm long, 18 mm ID at the mouth, and hemispherically closed at the lower (smaller) end, was used as shown in fig. 1. Weighed quantities of Cd and As, totalling 60 to 70 g, were placed in the tube, with the As at the bottom, and 25 to 30 g of dried B_2O_3, containing $\sim 0.3\%$ Na_3AlF_6 (cryolite), was placed on top.

The tube was then suspended from the pull rod in the crystal puller with only the top of the tube (containing only encapsulant) within the induction coil. The system was evacuated, flushed with N_2 three times, and then pressurised to 2 to 3 atm. The heater was switched on and the temperature of the top of the tube raised to about 750° C. The puller drive was now used to raise the tube through the fixed coil at about 20 cm/h. The encapsulant first melted and became effective before the Cd melted and ran down to mix and subsequently react with the As. When the bottom of the tube was in the hot zone the drive was reversed and the tube lowered out of the coil at 5 to 10 cm/h such that solidification of the Cd_3As_2 took place from the bottom. When the system had cooled and been opened, the encapsulant was removed with a stream of hot water and the ingot would then drop free from the tube. Impurities and departures from stoichiometry were concentrated at the top of the ingot which could be cut off and discarded. In general, this preparative method proved to be rapid, easy, and safe, and to involve virtually no losses providing a careful check was kept on the temperature of the tube by optical pyrometry so that the pressure of the Cd_3As_2 did not exceed the ambient pressure.

This technique can equally well be used for the Stockbarger single crystal growth of those materials in which the suppression of volatility at the melting point is required, and has been used in the growth of Cd_3As_2–NiAs eutectic ingots [16]. For single crystal growth, the round bottomed tube used in the preparation of Cd_3As_2 is replaced with a tapered crucible with a pointed or constricted bottom.

3. Growth of Cd_3As_2

Crystals of Cd_3As_2 were grown by the liquid encapsulated Czochralski (pulling) technique [14]. Initial experiments showed that the viscosity of pure B_2O_3 is too high for liquid encapsulated pulling at the melting point of Cd_3As_2, and research, to be reported elsewhere [15], on the modification of the viscosity of B_2O_3 by additives was undertaken.

B_2O_3 with additions of 0.3 to 0.6 mole % Na_3AlF_6 proved to be the most suitable encapsulant for use with Cd_3As_2. This works out, conveniently, as ~ 1 wt %. It was found, however, that, while B_2O_3/Na_3AlF_6 was a satisfactory encapsulant in most respects, it would not dissolve a thin skin which sometimes formed on the melt surface of the Cd_3As_2. This skin interfered with seeding on, and therefore had to be removed. Pure B_2O_3 was equally ineffective and a number of possible encapsulants were attempted before it was found that $K_2B_2O_7$:B_2O_3:KHF_2 (55 : 15 : 30 wt %) was completely effective in removing the scum layer and leaving a clean, bright melt surface. Unfortunately, the $K_2B_2O_7$:B_2O_3:KHF_2 flux is a simple liquid rather than a semi-viscous glass. It cannot therefore be used for crystal pulling because it does not coat the crystal as it emerges above the encapsulant surface and most of the crystal is consequently lost by sublimation.

The procedure finally adopted therefore was

to take material produced by the liquid encapsulated Stockbarger technique and melt this in a silica crucible contained in a close fitting graphite susceptor, under $K_2B_2O_7$:B_2O_3:KHF_2, in the crystal puller to provide a clean melt. This was then cooled and the flux was washed away and replaced by B_2O_3/Na_3AlF_5 which had previously been baked dry in a Pt crucible at $\sim$ 1000° C under vacuum. Liquid encapsulated pulling now proceeded in the usual way using a Ta capillary seed [17]. During all heating an ambient of 1.5 to 2 atm was maintained, since the dissociation pressure of Cd_3As_2 at its melting point had been found, again by liquid encapsulation, to be about 0.8 atm [18]. A crystal grown in this way is shown before and after the removal of its B_2O_3 coating in figs. 2a and b. This Cd_2As_2 crystal apparently grew as a single crystal, with threefold symmetry, but became polycrystalline on passing through the phase change at 615° C. The phase change also introduces small cracks and it appears that these can be avoided only by growing from the vapour below the phase change temperature. Specimens could be cut so as to avoid these cracks to a large extent.

4. Electrical Measurements

Hall effect and conductivity measurements have been made over the temperature range from 4.2 to 300° K. The carrier concentration was constant throughout the range at 2.10^{18} electrons/cc. The Hall mobility (given by the product of the Hall coefficient and the conductivity) is shown as a function of temperature in fig. 3. The flat peak at low temperatures is consistent with ionised impurity scattering in a heavily degenerate material and Zdanowicz [19] has shown that acoustic mode lattice scattering dominates at high temperatures.

5. Thin Films of Cd_3As_2

Mention should finally be made of some experiments carried out on thin films of Cd_3As_2 with a view to determining the energy gap and photoconductive response. Films were prepared in a standard bell jar evaporation system

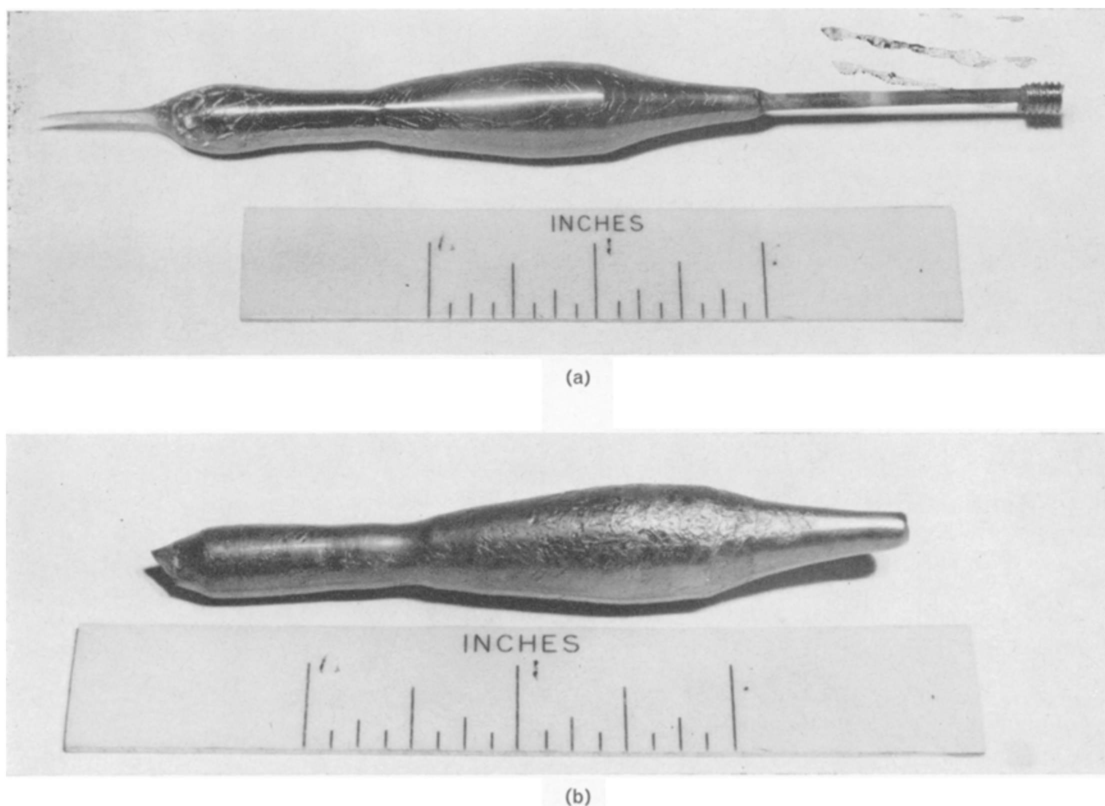

Figure 2 (a) A pulled crystal of Cd_3As_2 on a Ta capillary seed before removal of the encapsulant layer which has protected it against losses after growth. (b) The same Cd_3As_2 crystal after the removal of the encapsulant.

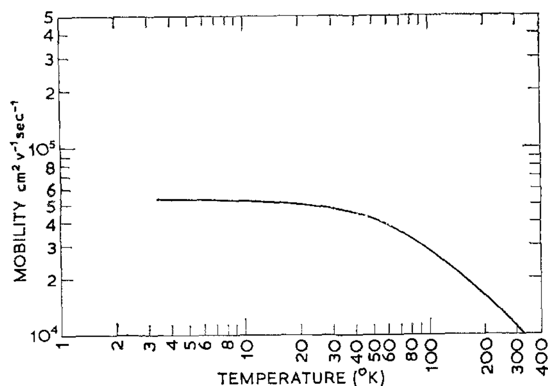

Figure 3 The variation of Hall mobility, μ, with temperature in a Cd_3As_2 crystal containing 2×10^{18} electrons/cc.

operating at 10^{-6} to 10^{-5} torr. Charges were evaporated from a Ta boat at 800 to 1000° C onto Si or SiO_2 substrates held at room temperature. Films were 2 to 6 μm thick, clean, bright, and perfectly stable, although adhesion to substrates, especially to Si, was poor.

Transmission measurements between 1 and 15 μm gave sharp transmission edges and high transmission but an extreme variability of transmission edge position similar to that reported by Zdanowicz [8]. Edge positions tended however to be at longer wavelengths than those shown in [8] and corresponded to energy gaps of 0.35 to 0.7 eV. The influence of annealing on films was briefly examined and it was found that the transmission edge shifted markedly to shorter wavelengths with both increasing time of anneal at a given temperature, and increasing temperature for a given time.This result again agrees with [8] in that all the transmission curves shown in [8] were put down at a substrate temperature of 160° C and were thus effectively annealed. Percentage transmission dropped on annealing.

To ensure that the films were not $CdAs_2$, rather than Cd_3As_2, some $CdAs_2$ was also prepared and films grown. These gave strong and reasonably reproducible transmission edges corresponding to an energy gap of 0.89 ± 0.03 eV. The annealing of a $CdAs_2$ film altered the shape of the transmission edge, and increased the per cent transmission slightly, but had no significant effect on the energy gap.

A single film of Cd_3As_2 was examined for photoconductive response at 77° K with radiation from a Nernst filament chopped at 800 c/s. Filters of Si, Ge, and InSb were used. A very strong response was observed with Si alone and no response was observed through InSb and Si. A weakened response was observed through Ge and Si implying an energy gap, for that film, of between 0.17 and 0.65 eV.

6. Discussion

Research into the growth and properties of Cd_3As_2 was undertaken with a view to its possible use as an intrinsic detector material in the 10 μm region of the infra-red on the basis of reports suggesting an energy gap of 0.13 to 0.14 eV. It now seems certain that the true energy gap of Cd_3As is in the 0.5 eV region and that reports of gaps in the 0.13 range have been due either to an impurity level or to a direct to indirect transition in the conduction band. While it would be of great interest to know more about the situation, no work was undertaken in this direction.

The two major problems remaining from the materials viewpoint are the carrier concentration and the cracking of crystals on cooling due to the phase change. Swiggard [11] has extensively zone-refined Cd_3As_2 without reducing the carrier concentration below 10^{18} electrons/cc and it seems unlikely therefore that the problem is one of impurities, unless something has a distribution coefficient of unity. This seems unlikely since similar carrier concentrations are obtained in vapour grown material. The most likely cause is therefore an equilibrium departure from stoichiometry similar to that found in PbTe or in ZnSe. The effects of prolonged annealing in atmospheres of Cd and As_4 at various temperatures have not apparently been investigated and would be of great interest.

The problem of cracking due to the phase change is more straightforward and has already been solved by vapour growth below 575° C [1, 3, 5, 8]. Our own work has shown that a single crystal of the high temperature phase grown from the melt will not convert to a single crystal of the low temperature phase on cooling and one must therefore grow below the phase change temperature. In addition to vapour bulk growth and vapour epitaxy, which have been used, growth from Cd solution, either by liquid epitaxy or in bulk, should be simple. The solubility of Cd_3As_2 in Cd at 550° C is about 30 mole % [20].

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