Experimental

The gradient freezing method was chosen as the preferred method of crystallization. This technique simplifies the provision of the requisite equilibrium vapor pressure of arsenic by means of an arsenic reservoir in a secondary furnace. Possible interference with the crystallization process by vibration arising from a traveling furnace is also avoided. Polycrystalline GaAs and InAs were used as starting materials. Mass spectrographic examination of the final product showed that at that stage impurities were all at the part per million level, except for the presence of silicon, 50 p.p.m., and tin, 30 p.p.m. There was about 300 p.p.m. of tellurium derived from the GaAs, which was highly doped n-type. A ratio of 98 mole % GaAs, 2 mole % InAs was used. The crystallization was carried out in a fused quartz boat 6 in. long and about 0.75 in. wide contained in an evacuated fused quartz tube. A small amount of arsenic was contained in a separate quartz boat at one end of the tube. A main furnace was used to heat the arsenide boat and a secondary furnace was provided around the arsenic boat to maintain the lower temperature (610°) necessary to give the required arsenic pressure.[8] It was necessary to ensure, in the usual way, that no point in the quartz tube was at a temperature less than 610°, while obtaining a suitable symmetrical temperature profile along the arsenide boat. The polycrystalline arsenide starting materials were used without conversion to fine powders so as to minimize contamination. Intimate mixing of the components was therefore impracticable and it was found important to place the InAs on top of the GaAs rather than in contact with the quartz boat. Otherwise the lower melting InAs could form a separate liquid phase during heating and this tended to increase the chance of adherence to the quartz.

The main furnace temperature was raised by means of a program controller at a rate of 200–300°/hr. to 1300°, as measured by a Pt *vs.* Pt + 10%Rh thermocouple attached to the outside of the quartz tube above the middle of the arsenide boat. When the temperature reached 800° the secondary furnace was switched on so as to raise the arsenic reservoir temperature to 610°. The arsenide temperature was held at 1300° for 10 min., lowered to 1270° over a period of about 10 min., and then cooled at a rate of 20°/hr. to 800°. The main and secondary furnaces were then switched off and allowed to cool to near room temperature at their natural cooling rates.

Results

In general the above experimental procedure yielded ingots consisting of a number of single crystal regions, some of which were as large as 2 cm. × 1 cm.^{2}. Impact fracture of an ingot produced good cleavages, which often served to delineate crystal boundaries. Semiquantitative X-ray fluorescence measurements indicated that crystals near the ends of the boat contained <0.5 mole % InAs and that higher concentrations occurred nearer the middle of the boat. This type of distribution is to be expected from the higher freezing temperature of GaAs with respect to InAs and intermediate ratios.

A portion of an ingot about 2 cm. long and 1 cm.^{2} cross section and bounded by two parallel cleaved faces was studied in some detail in regard to crystallography and composition.

A series of X-ray Laue photographs was taken, with the beam incident at various points along the length of the specimen. Identical patterns were obtained in each case, consistent with the view that the sample was a single crystal. Laue photographs of an end face showed that this had cleaved in a [110] plane. Calculation of interplanar spacing from diffractometer measurements yielded a unit cell size of 5.6627 Å. A corresponding determination for a [110] plane sample of GaAs gave a unit cell size of 5.6567 Å., *i.e.*, 0.006 Å. smaller. According to Woolley and Smith[4] the lattice parameter varies linearly with molecular composition in the system GaAs–InAs and 1 mole % substitution of InAs increases the lattice parameter by 0.004 Å. The observed change of 0.006 Å. compared with GaAs thus corresponds to 1.5 mole % InAs.

Discussion

It has been shown that GaAs–InAs solid solutions near the GaAs end of the system can be prepared in the form of large single crystals by means of a gradient freezing technique. In contrast, prior work on binary III–V compounds appears to have been confined to powdered or polycrystalline specimens. Single crystal semiconductor materials of this kind are of interest in achieving energy band gaps intermediate between those available in the end members of the binary systems.

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Ethylmagnesium Ethoxide

By W. H. Birnkraut

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In the preparation of magnesium hydride by pyrolysis of diethylmagnesium at 200°, under high vacuum, Wiberg and Bauer[1] observed a small amount of a volatile organomagnesium compound. The authors formulated the product as ethylenemagnesium (MgC_2H_4) on the basis of the mass balance in the pyrolysis reaction and from the quantity of ethane evolved upon hydrolysis of the volatile material. We now have obtained evidence that this organomagnesium sublimate is essentially ethylmagnesium ethoxide. The results of elemental analysis were not in agreement with the values calculated for MgC_2H_4 but correspond closely to those for $C_2H_5MgOC_2H_5$.

Anal. Calcd. for MgC_2H_4: C, 45.9; H, 7.69; Mg, 46.4; ratio C:H, 2:4. Calcd. for $C_2H_5MgOC_2H_5$: C, 48.8; H, 10.2; Mg, 24.7; ratio C:H, 2:5. Found: C, 48.3; H, 10.0; Mg, 24.1; ratio C:H, 2:4.97.

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Hydrolysis of the organomagnesium compound with D_2O and mass spectroscopic analysis of the gaseous hydrocarbon generated in this reaction indicated that only monodeuterated ethane had been formed. No evidence was found for a dideuterated product which would be expected from the hydrolysis of ethylenemagnesium. Furthermore, gas chromatographic analysis of the hydrolysis solution showed that the other organic hydrolysis product was ethanol according to the equation

$$C_2H_5MgOC_2H_5 + 2H_2O \longrightarrow C_2H_6 + Mg(OH)_2 + C_2H_5OH$$

The formulation of the volatile organomagnesium compound as ethylmagnesium ethoxide does not conflict with Wiberg's hydrolysis experiments which showed that one mole of ethane is formed per g.-atom of magnesium.

Ethers can be strongly associated with diethylmagnesium; for example, diethylmagnesium dioxanate is reported to have no detectable vapor pressure below 110°.[2] Since in our work, as in Wiberg's, the diethylmagnesium was obtained from ether–dioxane solutions, formation of ethylmagnesium ethoxide can be rationalized as involving interaction of diethylmagnesium with solvate molecules.

Mixtures of ethylmagnesium ethoxide with transition element compounds, *e.g.*, $TiCl_4$, VCl_4, $VOCl_3$, were found to form coordination catalysts for homo- and copolymerizations of α-olefins in inert aliphatic and aromatic hydrocarbons. Such catalysts, however, are less active than standard coordination catalysts formed from the same transition metal compound and alkylaluminum compounds.

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Proton Magnetic Resonance Spectrum and Molecular Weight of Trimethylindium in Solution

BY NORBERT MULLER AND ARTHUR L. OTERMAT

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When trimethylindium was first prepared it was reported[1] that measurements of the freezing-point depression for benzene solutions showed that the compound was tetrameric in solution. This conclusion has been repeatedly quoted and seems still to be widely accepted[2] although at least one piece of conflicting evidence has been available for some time. This is the value of 13.8 kcal./mole for the heat of sublimation.[3] Since the vapor is monomeric[3] this implies that the intermolecular bonds responsible for the "pseudo-tetrameric" structure of the solid[4] can hardly be strong enough to hold together a tetrameric species in solution. In this note we present evidence that trimethylindium actually exists in solution in the monomeric form.

We originally attempted to confirm the tetrameric nature of dissolved trimethylindium by observing the hydrogen nuclear magnetic resonance (n.m.r.) spectrum at low temperatures. An earlier study[5] had shown that at −75° the n.m.r. spectrum of $Al_2(CH_3)_6$ in cyclopentane consisted of two well separated peaks attributable to terminal and to bridging methyl groups, and we expected analogous results for the supposed $In_4(CH_3)_{12}$.

To prepare trimethylindium, dimethylmercury and an excess of indium metal were sealed in a glass tube in the absence of air and heated at 100° for periods of up to 30 days.[1,6] After purification on the vacuum line the product (formed with yields better than 50%) consisted of white crystals whose melting point (88.0 to 88.5°) and vapor pressure (2.5 mm. at 25°) agreed with the values reported earlier.[3]

The n.m.r. spectrum of a saturated solution of trimethylindium in cyclopentane included only one solute peak, 1.56 p.p.m. upfield from the solvent signal. In a more dilute solution the solute peak occurred at 1.52 p.p.m. Since trimethylindium is only sparingly soluble in cyclopentane this small dilution shift was not studied quantitatively. Reducing the temperature produced an upfield shift of the methyl signal and a progressive loss of intensity as the solubility decreased. At −60°, the lowest temperature at which the signal could be detected, the peak was at 1.74 p.p.m. and was still sharp.

With dichloromethane as solvent a similar dependence of the chemical shift on concentration and temperature was found, and it was possible to reduce the temperature to −90° without losing the signal. For a solution containing 5 mole % trimethylindium the solute peak was at 1.55 p.p.m. (cyclopentane internal reference) at room temperature and at 1.83 p.p.m. at −90°. Again the peak remained sharp at the lowest temperature.

In benzene solution at room temperature the solute peak was at 1.70 p.p.m. and *independent* of concentration over the range 1 to 15 mole %. In toluene also the peak was concentration-independent, at 1.72 p.p.m. Lowering the temperature of the toluene solution to −90° produced no shift of the peak position, nor any broadening.

These results suggested that trimethylindium is monomeric in benzene and toluene and perhaps only slightly associated in the nonaromatic solvents. To test this we reinvestigated the apparent molecular weight by vapor pressure studies.

The isopiestic distillation method[7] was usable only if the equilibration was carried out at or below 0°. At higher temperatures the partial pressure of trimethylindium was sufficient to allow it to transfer from bulb to bulb and spoil the experiment. For a solution of 0.4 mole % of trimethylindium in cyclopentane, the ap-

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