In each case, the results have been similar, but the arsenic trichloride system has consistently produced layers of better crystallinity, and it is these results which are described. The arsenic trichloride system also produces higher-purity layers on gallium arsenide substrates, consistent with other investigations [8, 9].

The mass deposited onto the metals is, for similar conditions, less than the mass deposited onto single-crystal semi-insulating gallium arsenide substrates (see fig. 1). The heavier deposits in the auto-epitaxial growth may be ascribed to greater surface-catalysis effects. Typical growths on the various metallic substrates are shown in figs. 2 to 5. In each case, the layer is n-type, judged by the direction of rectification in the resulting metal-semiconductor diode. The source of impurity is thought to be copper or silicon, both of which act as donors in gallium arsenide [10]. The layers grown on molybdenum and tantalum are polycrystalline, and those grown on niobium and tungsten show a high degree of orientation when studied by Laue back-reflection X-ray photography. The best orientation is achieved on tungsten, agreeing in part with the results of Amick [5, 6]. These layers have not, however, proved easy to remove, and the best-oriented layer may only be removed by mechanical grinding. This is probably due to the increased purity of the deposits obtained in the arsenic trichloride process. The greater part of the deposit formed on tungsten is smooth, but, in fig. 6, the edge of a deposit with typical single-crystal gallium arsenide facets is shown. A striking feature of the deposits is that they are least ordered for those substrates whose expansion coefficient is nearest to that of gallium arsenide. Mismatches in expansion coefficient may cause strains which disturb the layers upon cooling to room temperature, but it is difficult to explain the large difference in degree of orientation between the gallium arsenide layers grown on different substrates. It is hoped that an investigation of the surface chemistry of the metals during the growth will help to explain this difference. Further useful information should be obtained when single-crystal alloys of these metals, with expansion coefficients almost equal to that of gallium arsenide, are available.

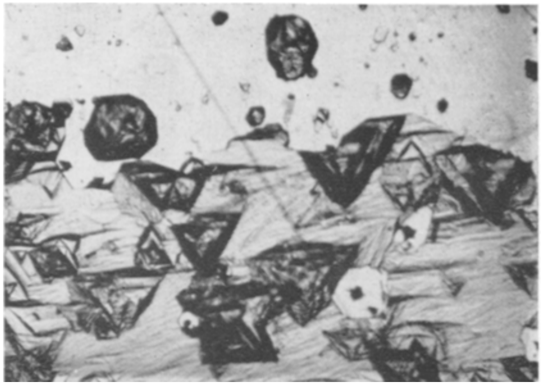

Figure 6 Edge of growth on [111] W (×70).

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The Determination of Crystallisation Temperatures in Fluxed Melts by a Thermogravimetric Method

The determination of the stability field of a crystalline refractory material in a fluxed melt is an essential preliminary to the growth of single crystals, and the phase equilibrium data required are usually obtained by relatively tedious methods involving quenching or exploratory crystal-growth experiments [1]. For fluxes of low volatility, the temperature of formation of a crystalline phase may be determined by the simple thermogravimetric method described. A platinum wire is partly immersed in the melt to provide a nucleation centre for the growth of crystals by slow cooling. For refractory materials of different density to that of the melt, the formation of crystals on the wire, when the melt becomes supersaturated, is indicated by a discontinuity in the rate of change of weight of the wire with temperature.

The apparatus is shown schematically in fig. 1.

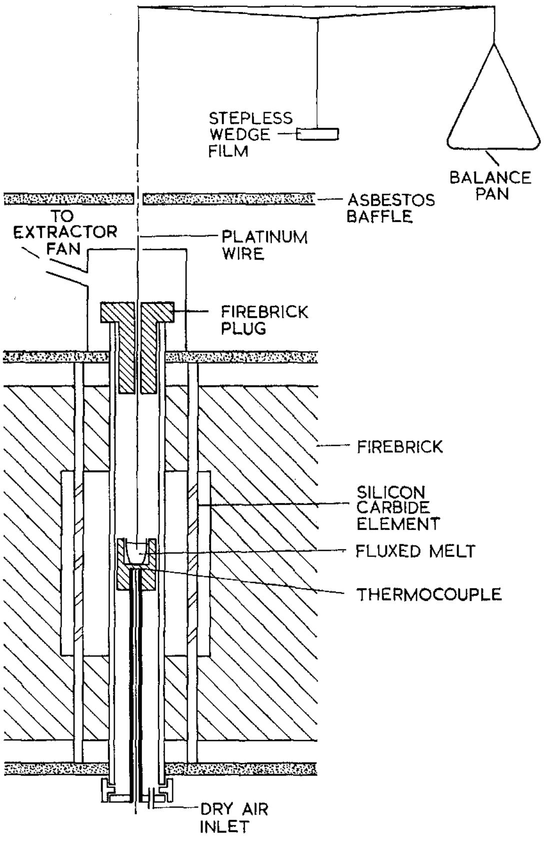

Figure 1

A vertical tube furnace is situated directly below a Baird and Tatlock chemical balance of 0.1 mg sensitivity, which is thermally shielded by an asbestos baffle. The fluxed melt is contained in a 15 ml platinum crucible supported on an adjustable pedestal within the furnace so that the temperature of the surface of the melt is 5 to 10° C below that of the base of the crucible. A platinum wire, 0.5 mm in diameter, is suspended from the balance so that the free end is immersed in the melt to a depth of about 5 mm.

A steady stream of dry air is passed upwards through the furnace tube at a rate of about 1 l/min. The air flow reduces the fluctuation in the balance reading, owing to convection currents, to within 0.5 mg at 1300° C, and the absence of water vapour in the atmosphere reduces the volatility of the solvent in the case of the borate fluxes used [2].

The platinum wire is automatically weighed for a 30 sec period at 10 min intervals. At the end of this period, a solenoid-operated mechanism arrests the balance to reduce wear on the knife-edges. The balance pointer carries a stepless wedge film which controls the intensity of a beam of light incident on a photoconductive cell. This cell forms part of a bridge circuit, and the out-of-balance current, which depends on the deflection of the pointer, is displayed on a chart recorder.

The experimental procedure is as follows. The fluxed melt is maintained for 12 h at a sufficiently high temperature to ensure complete solution of the crystal constituents prior to immersion of the free end of the platinum wire. The furnace controller is programmed to reduce the temperature at a linear rate of 2 to 5° C/h, until an increase in weight of the wire is observed in addition to the apparent gain caused by the increase in surface tension with decreasing temperature.

The corresponding temperature is noted and the wire removed for microscopic examination. Small crystallites are observed on that part of the wire which has been immersed and the nature of the material deposited can often be inferred from the external morphology. When necessary, the wire is replaced in the melt, and larger crystals are obtained by further cooling for examination by X-ray methods. If the melt is slowly heated after crystals have been formed, the temperature at which the last traces of crystalline material disappear is found to agree with the measured crystallisation temperature to within 1° C at 1200° C.

Further discontinuities in the rate of change of weight of the wire with temperature during continued cooling can be correlated with termination of crystal growth, the appearance of a new phase, or solidification of the melt.

The apparatus is currently being used to investigate the growth of nickel ferrite from a barium borate flux.

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A Method of Epitaxial Gallium Phosphide Growth

The interesting characteristics of the semiconductor gallium phosphide are now well known. It may be of practical importance for electroluminescent diodes and solar cells, but it is difficult to obtain single crystals of this compound of a useful size. Because of its high melting point (≃1450° C) and the high partial pressure of phosphorus over the melt (>30 atm), solution- or vapour-phase growth are the preferred techniques [1-6]. Indeed, these give good results, but they require sharply defined, experimental conditions. We describe here a technique of epitaxial growth, which is among the easiest of present methods of preparation.

Our method differs from the one described by Flicker *et al* [6] in the fact that we use, in an open tube system, pure dried hydrogen (fig. 1). The quality of purification has been tested by heating a chromium steel slab, in this hydrogen flow, at a temperature higher than 1000° C: no alteration of the polished surface appeared.

In this tube, we place two, thin wafers (each about 500 μm thick) – a polycrystalline gallium phosphide source (provided by Monsanto) and, 500 μm away, a monocrystalline gallium *arsenide* substrate. These wafers are heated by radiation above 900° C.

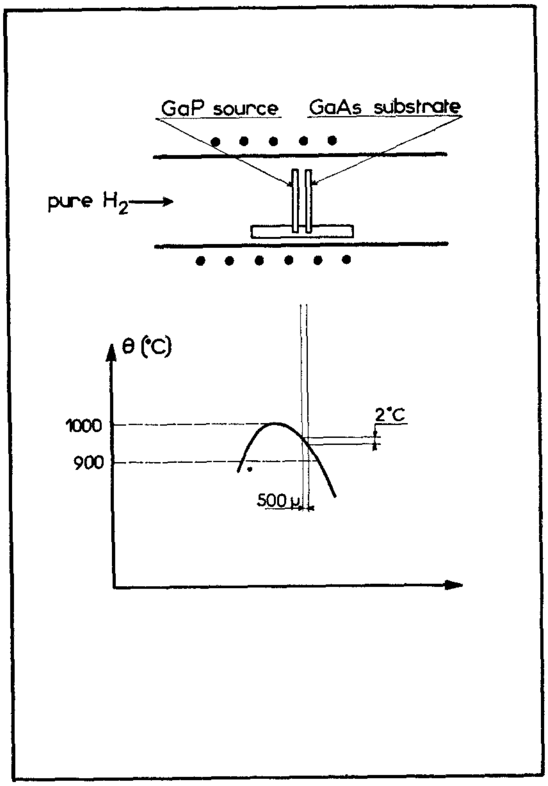

Figure 1 Apparatus used for growth of GaP.

At this temperature, the gallium phosphide is evaporated and transported to the gallium arsenide by the gas stream. This effect is enhanced by a steep temperature gradient (40° C/cm), so that a small temperature difference of 2° C exists between the slices (source at the upper temperature). When the gallium phosphide reaches the substrate surface, it forms an epitaxial deposit at a relatively slow rate (about 7 μm/h).

With the conditions briefly described above, we have obtained several layers of gallium phosphide on (111) and (110) substrates. X-ray studies have demonstrated that the deposits have the same orientations as the substrates. The diffraction spots are well defined, indicating a good crystalline quality. X-ray