good single crystals at 480° C between 650 and 750 bars. It is quite possible therefore that some of the other high-pressure phases reported in that paper [8] may also form under much milder conditions, particularly by the use of hydrothermal methods. Indeed, this has probably been done already in the case of $ZnMoO_4$ [9].

The parameters of the monoclinic unit cell of the hydrothermally grown $FeMoO_4$ were determined from precession films [7] as

$$a = 4.69 \pm 0.03 \text{ Å}$$
$$b = 5.69 \pm 0.03 \text{ Å}$$
$$c = 4.94 \pm 0.03 \text{ Å}$$
$$\beta = 90^\circ 15' \pm 10'$$

in reasonable agreement with the results of Young and Schwartz.

Acknowledgement

Thanks are due to S. C. Abrahams for drawing attention to the problem and for helpful discussion of the results.

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The Growth of Gallium Arsenide onto Single-Crystal Metallic Substrates

The attempts to deposit epitaxial layers of semiconductors onto single-crystal metallic substrates have been, in the main, limited to a study of the elemental semiconductors [1-4]. Amick [5, 6] has given details of an investigation to extend the study to compound semiconductors and has reported the growth of gallium arsenide onto single-crystal molybdenum and tungsten substrates. A conventional open-tube system, employing gallium, arsenic, and gallium trichloride as source materials, produced polycrystalline layers on molybdenum and highly oriented, but easily removable, deposits on tungsten. Two open-tube systems have been used in the present investigation [7]. The first system is similar to that of Amick, and the second system, using gallium and arsenic trichloride as source materials, is similar to that described by Knight [8] and Effer [9]. The furnace used in the second system is controlled by programmed cam-driven regulators which allow accurate control of temperature up to a maximum duration of 36 h. Both systems have been used to study the deposition of gallium arsenide onto electropolished (1 1 1) planes of molybdenum, tungsten, tantalum, and niobium.

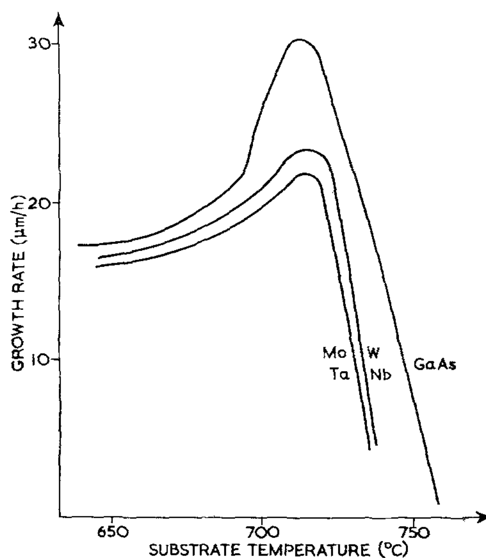
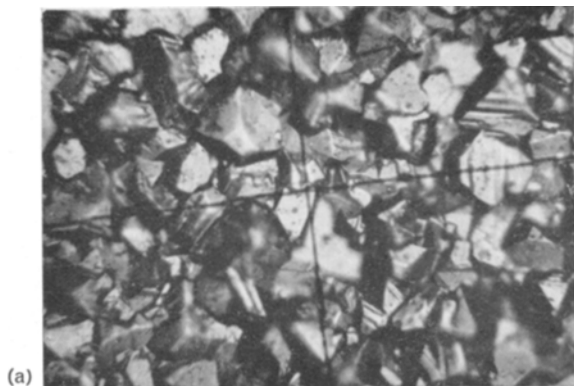
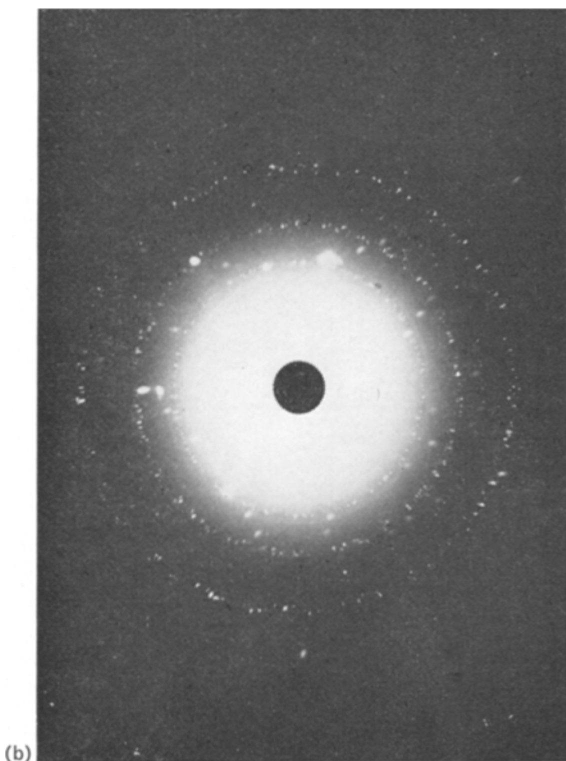


Figure 1 Rates of growth of GaAs on various substrates.



(a)



(b)

Figure 2 GaAs on Mo [111]: (a) polycrystal growth (×150); (b) Laue back-reflection.

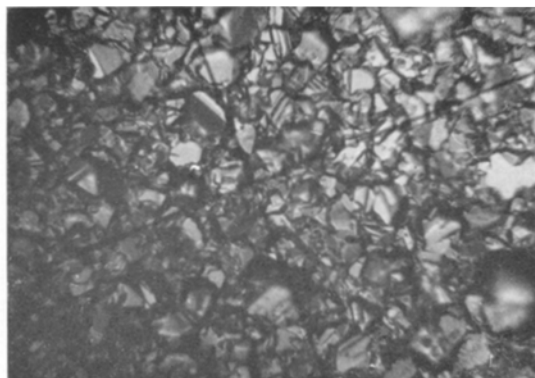


Figure 3 GaAs on Ta [111] polycrystal growth (×150).

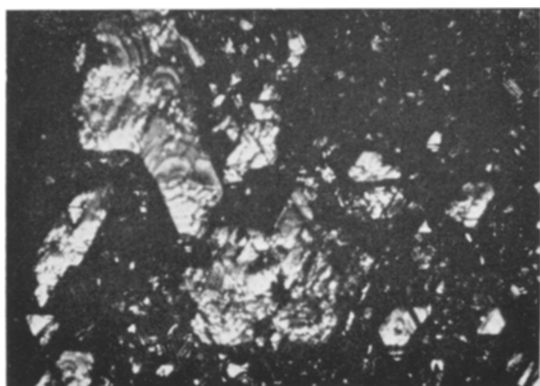
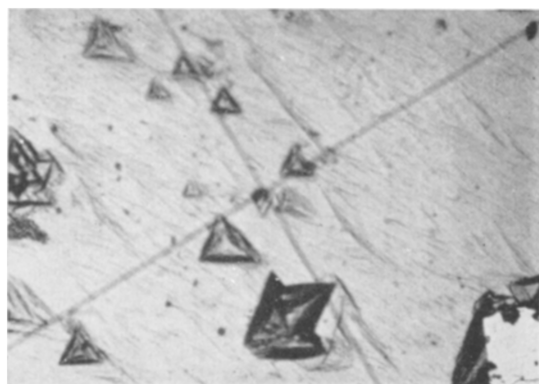
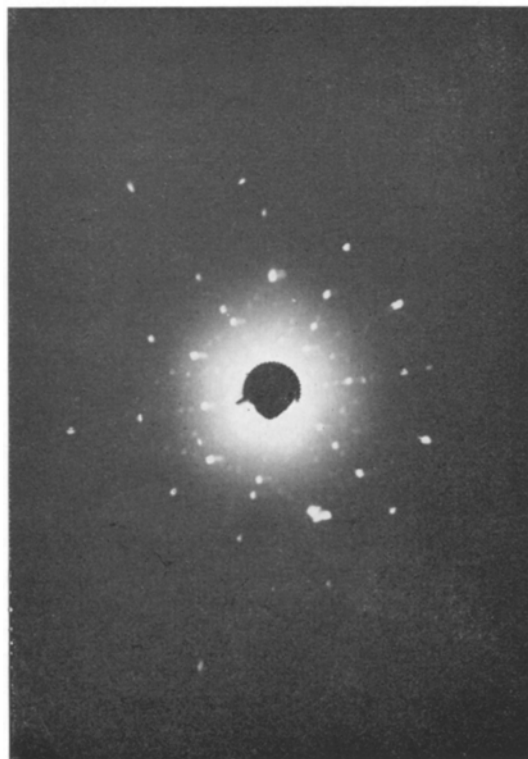


Figure 4 GaAs on Nb [111] single-crystal regions (×70).



(a)



(b)

Figure 5 GaAs on W [111]: (a) single-crystal growth (×70); (b) Laue back-reflection.

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.

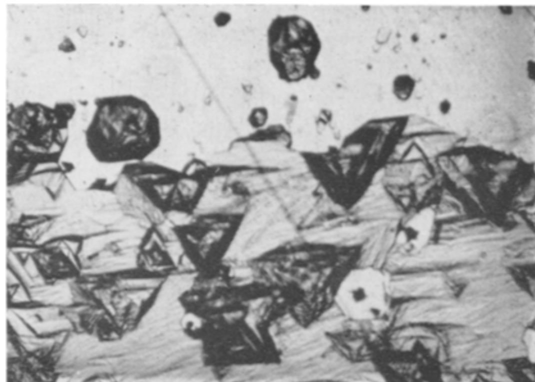


Figure 6 Edge of growth on [111] W (×70).

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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