Crystal Growth of Gallium Arsenide using Carbon Boats

GALLIUM arsenide is a semiconductor of great interest from the purely scientific point of view and as a device material. It is therefore desirable to be able to prepare single crystals of high purity. Because of the reactive nature of gallium liquid and arsenic vapour at high temperature, only a limited number of refractories may be used as boat materials for gallium arsenide (melting point, 1,511° K.). Among these are carbon, vitreous silica and alumina. In addition a sealed envelope of vitreous silica is generally employed to prevent the escape of arsenic vapour from the system.

It is observed that, in general, the use of carbon or carbonized silica boats facilitates single crystal growth, whereas ingots grown in silica boats exhibit various degrees of wetting and subsequent polycrystallinity. On the other hand, despite reduced wetting, material grown in carbon boats is the more strongly *n*-type. Typically, a crystal grown in a carbon boat yields an electron concentration of $1.3 \times 10^{18}/\text{cm}^3$ and Hall mobility, $\mu_n = 2,500 \text{ cm}^2/\text{V}.\text{sec.}$, compared with the usual $3 \times 10^{16}/\text{cm}^3$ and $5,000 \text{ cm}^2/\text{V}.\text{sec.}$ obtained for crystals grown in silica. It is worth adding that in all cases the observed mobility is less than that to be expected from the carrier concentration¹, implying a fair degree of compensation. There is, therefore, a considerable gain to be achieved by the removal of residual impurities.

Although the results above indicate that the presence of carbon increases the donor concentration in gallium arsenide, the absence of wetting suggests that this is not due to carbon being dissolved in the melt. It is suggested, therefore, that the prime effect of carbon is to bring about reduction of the silica envelope according to the equation:

Spectrographic examination indicates that silicon is present in fair amounts in gallium arsenide grown in carbon boats.

At the melting point of gallium arsenide, the standard free energy change for reaction (1) is $\Delta G^0 = 26,000 \text{ cal.}^2$. Using the relation:

$$\Delta G^0 = -RT \log_e Kp = -2RT \log_e p_{\text{CO}}$$

where p_{CO} is partial pressure of carbon monoxide, we obtain $p_{\text{CO}} = 1.3 \times 10^{-2}$ atmosphere. We can see, therefore, that starting with carbon and silica in a closed system, free silicon is produced until the pressure of carbon monoxide reaches the above value. In addition, the free silicon is able to dissolve in molten gallium arsenide to form a dilute solution; its activity is thereby reduced and the reaction can proceed further from left to right.

Since similar results are obtained for carbon as for carbonized silica boats, it seems that silicon must enter the melt from the vapour phase. The following reactions are reversible and provide mechanisms for the transport of carbon and silicon from one part of the system to another:

At 1,511° K., the partial pressure of silicon monoxide is 9.55×10^{-4} atmosphere.

In practice, the equilibrium vapour pressure of carbon monoxide is not attained. It seems likely that since the partial pressure of arsenic in the system is high (0.9 atmosphere), the rate at which silicon enters the melt is mainly limited by gaseous diffusion and convection.

Carbon should be a satisfactory crucible material for gallium arsenide under conditions where it is unable to react with reducible oxides such as silica. Recent chemical analysis of gallium arsenide grown in contact with carbon has shown the carbon content to be less than 2.7×10^{17} atoms/cm.³, which is the limit of detection of the method. One would expect the solubility of carbon in gallium arsenide to be comparable with that in germanium at the same temperature (about 10^{12} atoms/cm.³ at 1,511° K.).

This work is being carried out under Admiralty contract CP.4D(2) 5298/58/60.2.

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¹ Hilsam, C., *Proc. Phys. Soc.*, **76**, Part 3, 414 (1960).

² Richardson, F. D., and Jeffes, J. H. E., *J. Iron and Steel Inst.*, **160**, 261 (1948).

Methane Oxidation initiated by Electrical Discharge

AN apparatus for the mass-spectrometric study of free radicals occurring in gas-phase reactions has recently been completed in this Laboratory. While testing the equipment we have investigated the reactions in a methane-oxygen mixture, subsequent to electrical discharge in one of the gases.

The apparatus, which is illustrated in Fig. 1, is essentially similar to that of Foner and Hudson¹. A flow of gas is maintained through a silica discharge tube, the discharge products being swept into the 'Pyrex' reaction vessel, where they may mix with another gas entering down a side tube. The mixing zone is sampled by a pinhole in platinum foil leading to the ion source of a Metropolitan-Vickers M.S.2 mass spectrometer. The ion source was modified by the makers to provide a higher pumping speed, differential pumping from the filament region, and line-of-sight access from the pinhole leak to the ionization chamber.

The electrical discharges were maintained by a 200-watt radio transmitter, working at 13,560 kc./s., which supplied a coil wound around the discharge tube, 2 ft. above the sampling pinhole. Pressures of 500–750 μ and flow-rates of 500–700 ml./sec. were used in this work.

The detectable products from a discharge in methane were mainly ethane and hydrogen, with some acetylene and ethylene; approximately one-third of the methane was removed, but the C₂ hydrocarbons detected could only account for 60 per cent of this. When oxygen was added (through the side tube) to the products of a discharge in methane the detectable products were scarcely affected; there was a slight decrease in the amount of ethane formed, and some water and carbon dioxide were detected, but 40 per cent of the carbon was still unaccounted for.

If the oxygen is submitted to the electrical discharge and the products mixed with undissociated