## References

- 1. M. F. ASHBY and R. A. VERRALL, Acta Met. 21 (1973) 149.
- P. M. HAZZLEDINE and D. E. NEWBURY, Proceedings of the III International Conference on Strength of Metals and Alloys, Cambridge, 20-25 August 1973, Vol. I, p. 202.

## The initial growth of GaAs layers

The Ga/AsCl<sub>3</sub> technique has now become widely used for the production of high-quality layers of GaAs [1]. In this method, AsCl<sub>3</sub> vapour is used as the transporting agent in a system in which layers of the semiconductor are grown on some substrate. It is generally assumed that the rate of growth of the GaAs on the substrate does not change during the growth cycle. Shaw [2], for instance, states that in his experiments the rate was uniform up to a growth time of 90 min. He does not give his evidence for this however. Seki et al. [3] show results indicating that growth was linear with time on their apparatus over a period of 2 h, but their measurements were taken only at 30 min intervals. In this note we present evidence that although the growth rate is uniform for longtime growths, the rate during the first few minutes is very much higher.

All of the substrates were  $(1\ 1\ 1)$  slices of GaAs, and the growths were carried out using the gallium face. The growth surface was polished using a 10% solution of NaOCl on a polishing pad [4]. About  $20\,\mu\text{m}$  was removed, and a high quality polished surface was obtained. Before mounting in the specimen holder, the substrates were washed in distilled water and a degreasing agent.

A simplified diagram of the apparatus is shown in Fig. 1. The growth technique employs two stages. The gallium in the boat is first saturated. Pure hydrogen is passed through the  $AsCl_3$ bubbler where the reaction takes place:

$$2 \operatorname{AsCl}_3 + 3\operatorname{H}_2 = 6\operatorname{HCl} + \frac{1}{2}\operatorname{As}_4.$$

The gallium is held at  $850^{\circ}$  C and it dissolves the arsenic, forming a crust of solid GaAs in the boat on top of a Ga/As liquid. The substrate can now be introduced. The reaction

$$2\text{GaAs} + 2\text{HCl} = 2\text{GaCl} + \frac{1}{2}\text{As}_4 + \text{H}_2$$

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then takes place at the boat. The vapours flow to the substrate end of the reaction tube where the  $As_4$  and GaCl react to deposit GaAs. In the experiments described here, the substrates were held at 750° C. In order to time the growths accurately, a specimen holder fitted with a shutter was used. When the shutter was closed, the specimen was cut off from the gas flow. It was operated from outside the apparatus.

The first stage of the experiment was carried out separately, i.e. a ready-saturated boat was put into a clean reaction tube, together with a specimen holder containing a substrate. The furnaces were brought up to temperature with a flow of pure hydrogen passing through the apparatus, and with the shutter open, so that the specimen was in the hydrogen flow. Some time after reaching operating temperature, the shutter was closed and the hydrogen was diverted through the AsCl<sub>3</sub>. The gallium source had become slightly undersaturated during the initial flushing and it generally took about 4 min to become re-saturated. The shutter was then removed, and growth commenced. At the end of the pre-determined growth time, the shutter was replaced. Growths were carried out for times in the range 1 to 60 min.

Growth rates were determined by weighing the sample before and after growth. The average rate for twelve samples for a growth time of 1 h was  $27 \,\mu m h^{-1}$ . It is difficult to compare this with





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Figure 2 Average growth rates for short growths.

results of previous workers because growth rates are extremely sensitive to the vapour pressures in the apparatus [5]. The order of magnitude seems reasonable, however. Seki et al. [3], for instance, quote a mean rate of  $27 \,\mu m h^{-1}$  for (111) Ga slices at 760° C and Hollan and Schiller [6] give  $80 \,\mu m h^{-1}$  for a temperature of 755° C. A curve giving the average growth rate for different growth times is given in Fig. 2. It can be seen that the very short growths show a greater average rate. The effect is partly masked in a plot such as Fig. 2, however, because of the averaging effect. It is a simple matter to use the graph of Fig. 2 to calculate a curve of true growth rate against time. This is presented in Fig. 3 which also shows, dotted, the long-term growth rate of  $27 \,\mu m \, h^{-1}$ .

Fig. 3 indicates that the true growth rate settles down to its long-term value after about 2 min. Observation of the grown layers by optical and scanning-electron microscopy indicated that this time corresponded approximately to the time taken to form a complete layer on the substrate. The likely explanation for the effect is therefore that

Figure 3 Growth rate versus time for GaAs on a  $(1 \ 1)$  Ga face. The dotted line represents the long-term rate.

growth is much more rapid on the chemically polished surface of the substrate than on a completed layer. The two types of surface would be expected to be quite different on the atomic scale, so it is perhaps not surprising that they gave rise to different growth rates.

## References

- 1. D. EFFER, J. Electrochem. Soc. 112 (1965) 1020.
- 2. D. W. SHAW, *ibid* **115** (1968), 405.
- H. SEKI, I. ASAKAWA and S. HORIE, Jap. J. Appl. Phys. 7 (1968) 1324.
- 4. A. REISMAN and R. ROHR, J. Electrochem. Soc. 111 (1964) 1425.
- 5. D. W. SHAW, *ibid* **117** (1970) 683.
- 6. L. HOLLAN and C. SCHILLER, J. Crystal Growth 13/14 (1972) 319.

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## The growth and characterization of strontium fluoro chloride crystals

A variation of the normal flux method, in which growth is accomplished as a result of a chemical reaction taking place in the molten state and subsequent cooling of the molten mass, has been

successfully used over the past few years to grow crystals of specific interest [1-4]. This method, sometimes referred to as the reacted flux technique, has been employed by us to grow single crystals of SrFCl and an account of the growth and related studies made on them is reported here.

The production of SrFCl can be materialized by