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Growth Modes of GaAs on Tungsten

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An account is given of the various types of crystal growth observed when GaAs is grown by a conventional vapour transport process on to a tungsten substrate. Three main types of growth are described:
(*i*) three-dimensional nucleations which eventually grow together to form polycrystalline layers,
(*ii*) thin single-crystal layers,
(*iii*) dendrites.

The thin layers appear to grow by steps sweeping across the surface, and evidence is presented to suggest that adjacent steps are twinned with respect to one another. Some of the dendrites have a relatively large mass of material at the growing end: it is suggested that this is due to a vapour-liquid-solid mode of growth. The regular hexagonal shape of some of the dendrites is noted and a growth mechanism is suggested to account for their shape.

1. Introduction

The technique of preparing high quality GaAs from the vapour phase, by passing $AsCl_3$ over a heated boat containing gallium is now well established. In general the material is deposited on a carefully prepared single crystal slice of GaAs and a single crystal layer of the same orientation results, i.e. the growth is epitaxial. More recently work has been carried out investigating the possibility of depositing device-quality GaAs on to foreign substrates [1, 2] because GaAs is not the most suitable substrate material for all devices. For instance, some high-power devices would be better served by a heat-conducting substrate which would minimise rise in temperature. This paper describes nucleation and early growth modes of GaAs when grown on to tungsten substrates using the $AsCl_3$ process.

2. Experimental

The tungsten substrates used were in the form of circular discs, about 6 mm in diameter and 2 mm thick. They were prepared from zone-refined material and were single crystals with the circular faces within $\pm 2°$ of (111). Before insertion in the growth apparatus the growth faces were first mechanically polished and then electropolished in a solution of sulphuric and hydrofluoric acids in methanol to remove the polishing damage. This resulted in bright shiny faces which were optically flat.

The vapour transport apparatus is shown in fig. 1 [3]. This particular process uses $AsCl_3$, gallium and hydrogen. The gallium in the boat is first saturated to form a crust of GaAs on the surface. Pure hydrogen is passed through the $AsCl_3$ bubbler where the following reaction occurs

$$2AsCl_3 + 3H_2 = 6HCl + \tfrac{1}{2}As_4$$

The gallium is held at 850°C and the reaction

$$2Ga + \tfrac{1}{2}As_4 = 2GaAs$$

takes place at the gallium surface. When

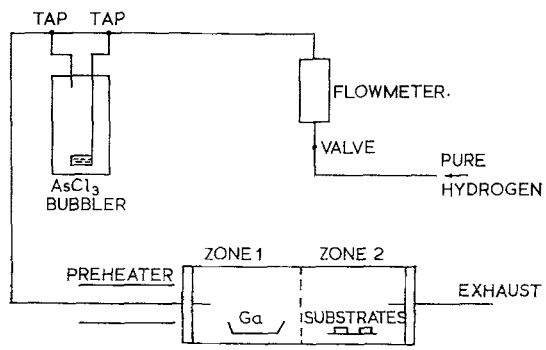

Figure 1 The $AsCl_3$ system.

saturation is complete free arsenic appears at the tube exhaust.

The substrate is now introduced and may be heat treated *in situ* at 900°C in the hydrogen stream prior to growth, which starts when the temperature of the substrate is reduced to between 730 and 750°C. The reaction

$$2GaAs + 2HCl = 2GaCl + \tfrac{1}{2}As_4 + H_2$$

takes place in the boat, whilst

$$3GaCl + \tfrac{1}{2}As_4 = 2GaAs + GaCl_3$$

occurs at the substrate. The $GaCl_3$ is deposited in the cool region at the exhaust.

In this work the rate of hydrogen flow through the reaction tube was 300 cc/min. Growth times in the range 2 min to 4 h were used. For the shorter growth times a problem arose because of the length of time taken to reach steady-state conditions in the reaction tube; this was likely to be of the order of several minutes. A shutter system was therefore employed which prevented the vapour stream coming into contact with the substrate. After about 10 mins, thermal equilibrium was established, the shutter was removed and growth commenced. The growth period was ended finally by withdrawing the specimen holder from the furnace.

At the end of a growth run the substrate was removed from the apparatus and inspected, using a scanning electron microscope. All photographs in the paper were taken with this instrument. It is possible with the microscope to have any view of the specimen which may be required by changing its orientation with respect to the electron beam. Angles between planes and between directions can therefore be measured with reasonable accuracy and it is known that GaAs has the zincblende structure. A large number of these angles were measured and attempts were made to identify crystallographically the various growth modes observed.

3. Results

The growth features observed were of three main types which will be discussed separately.

3.1. Discrete Nucleations

This was the most common type of initial growth observed, and presumably corresponds to the "three-dimensional nucleation" observed by Joyce *et al* [4] in their work on the growth of silicon on silicon. Fig. 2 shows a very early stage in the development of these nucleations when they are only about one micron in size. They do not appear faceted at this stage,

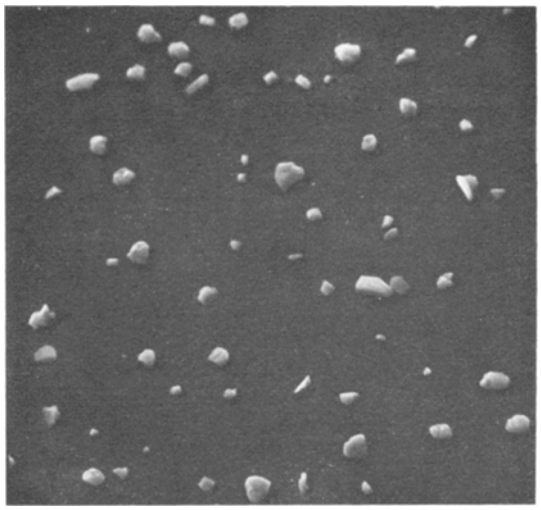

Figure 2 Nucleations after 7 min at 750°C (× 2300).

presumably because the initial growth is too fast for different growth rates along different axes to be important. It seems likely, however, that at this point each individual nucleation is a single crystal. A saturation number of nuclei becomes established within a time which is short when compared to the shortest growth periods. Thereafter the number does not increase and the nucleations become larger with growth time. For the higher growth temperatures the saturation number is smaller but the nucleations are, on the average, larger.

With increasing deposition time the nucleations become faceted. They also tend to become polycrystalline and to grow together as shown by fig. 3. Some of them remain monocrystals, however; an example is shown in fig. 4. The facets on these single crystals have been observed to be composed mainly of {111}, {110} and {100}-type faces.

Most theories of growth from the vapour on to a solid substrate assume a mechanism in which individual atoms are adsorbed on to the surface. They then diffuse to join a nucleus [5]. Nucleations would be expected to be approximately pyramid-shaped therefore, i.e. to have the surface in contact with the substrate as the largest cross-sectional area. This shape is often observed in practice [4]. Most of the nucleations observed in this work were equi-axed, however, suggesting the possibility of some of the growth occurring directly from the vapour. After about one hour's growth the nucleations grow together to form a continuous layer over the substrate, 25

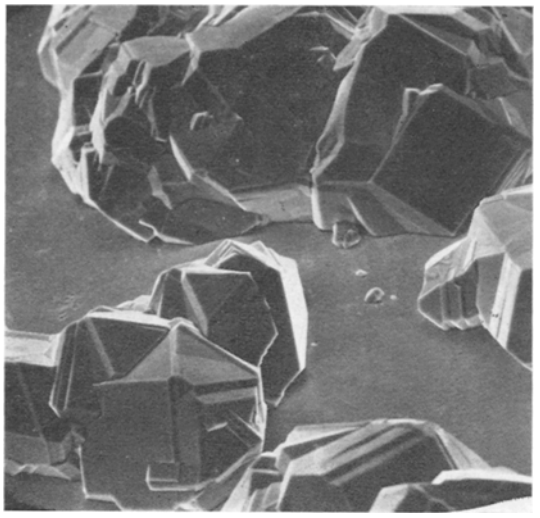

Figure 3 Faceted polycrystalline deposit grown at 750°C (× 500).

to 40 μm in thickness. As a consequence of the equi-axed nature of the nucleations, gaps are left in some places between the top of the substrate and the bottom of the layer. This can easily be demonstrated by chipping off part of a layer from the tungsten: cavities are seen on the under-side of the layer.

Layers grown in this way are in general polycrystalline, therefore, although sometimes small, single-crystal areas exist where nucleations of the type shown in fig. 4 have grown together in the same orientation.

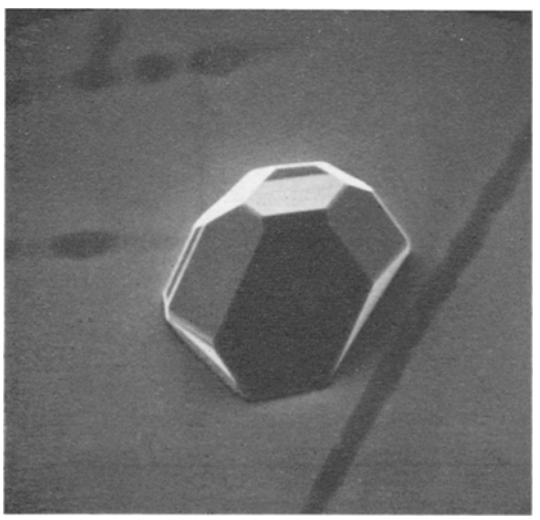

Figure 4 Faceted single-crystal nucleation grown at 742°C (× 650).

3.2. Layer Growth

Occasionally a deposit was grown which covered the whole of the substrate in a few minutes. The thickness of the layer at this stage was only a few microns and in this case it was a single crystal. This is similar to the "two-dimensional growth" reported for silicon [6]. Fig. 5 shows a layer about 2 μm thick just before complete cover of the substrate was achieved, while fig. 6 shows a later stage in which a complete single crystal layer has grown. Part of the layer has been removed to reveal the substrate in fig. 6. All of these layers showed regular triangular etch pits. When pieces were chipped off the substrate they cleaved in

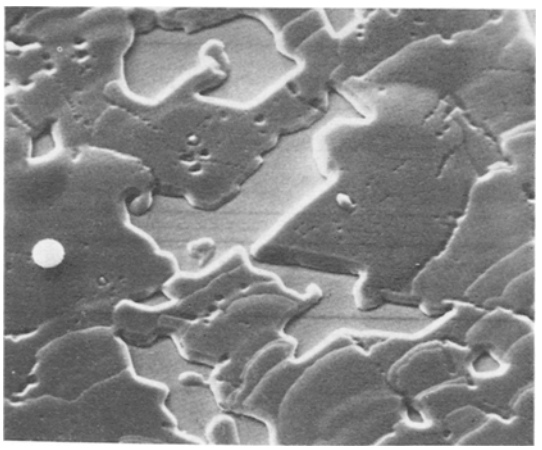

Figure 5 Early stage in the growth of a single-crystal layer at 735°C (× 1100).

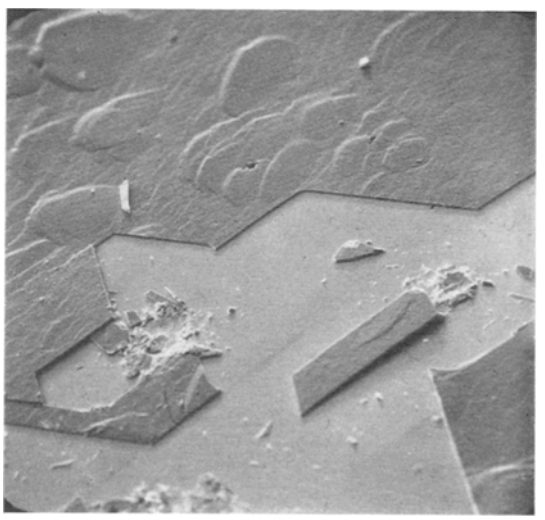

Figure 6 Later stage for a single-crystal layer grown at 749°C. Part of the layer has been chipped away, revealing the substrate (× 48).

straight lines making angles of 60° and 120° with each other. It seems reasonable, therefore, to assume that the layers were single crystals of (1 1 1) orientation.

Steps appeared on all the surfaces giving the layers a scaly appearance (see fig. 6). They were about 0.2 μm in height: presumably the layers grow by the steps sweeping across the surface. An interesting feature shown by the etch pits is demonstrated in fig. 7. It may be seen that etch

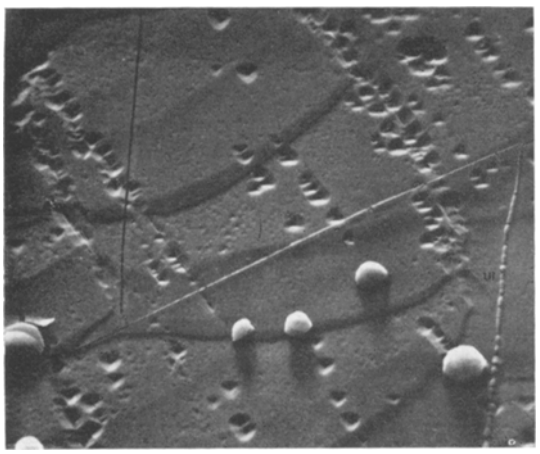

Figure 7 Layer grown at 750° C, showing etch pits (× 500).

pits on adjacent steps are mirror-images. There are two possible explanations for this effect. The first is due to the fact that a (1 1 1) surface is likely to produce two types of triangular etch pits; the more usual one in which the sloping sides are the three remaining {1 1 1} planes and another in which the sloping sides of the pit are {3 1 1}-planes. These two types of pit both have triangular traces in the (1 1 1) surface and the traces are mirror-images. However there is no apparent reason why the crystal should favour first one type then another type of pit on consecutive steps. A more likely explanation is that adjacent steps are twinned with respect to each other. Twinning can only take place about a ⟨1 1 1⟩ direction in GaAs, as demonstrated in fig. 8. The twinning amounts to a 60° rotation of the upper (1 1 1) plane with respect to the lower so that they are mirror-images of each other, with a gallium atom "reflecting" an arsenic atom. As a consequence, the ⟨1 1 0⟩ directions which define the etch pit on a (1 1 1) plane are rotated by 60° and any etch pit will be a mirror-image of one in an untwinned layer of material.

If one of these layers is replaced in the

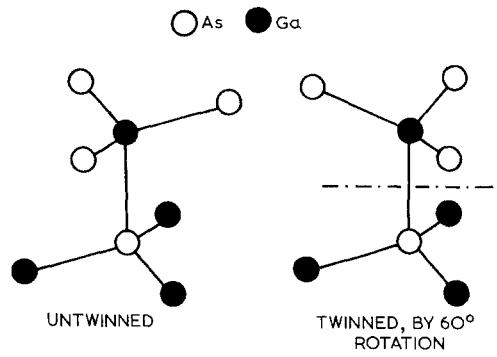

Figure 8 Twinning mechanism in GaAs.

apparatus for further growth to take place, the layer continues to grow as a single crystal.

3.3. Dendritic Growth

Dendritic growth was observed on a number of specimens, often when part of a run had taken place at an unusually low growth temperature. The dendrites took the form of hexagonal whiskers or of flat platelets and ribbons.

An example of whisker growth is shown in fig. 9. The whiskers are hexagonal with sym-

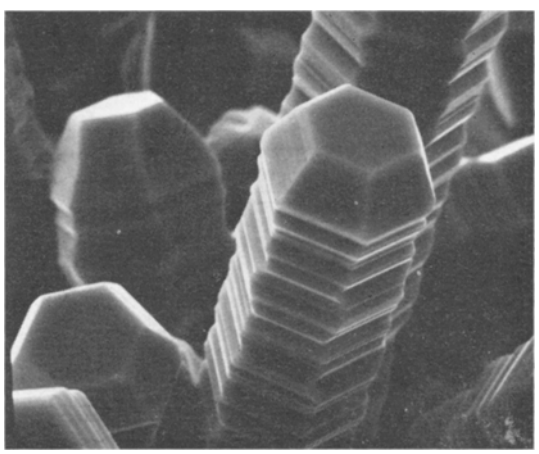

Figure 9 Hexagonal whiskers on tungsten (× 2400).

symmetrical caps and concertina-like edges. There are two simple ways in which a hexagonal shape of the general type exhibited by a whisker cap can be obtained in a cubic crystal. These are shown in fig. 10. They both have a (1 1 1) plane for the top surface. One has alternately {1 0 0} and {1 1 1} planes for the six side faces and the other has {1 0 0} and {1 1 0} types alternating. Comparison of figs. 9 and 10 shows that neither

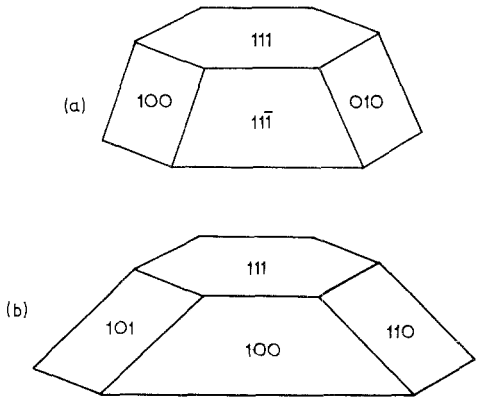

Figure 10 Simple hexagonal features in a cubic lattice.

of these models alone will do to explain the whiskers, however, since they both require the edges of adjacent sides to be alternately parallel and converging. If both of these mechanisms occurred, however, so that the whisker rapidly changed from one to the other, then a growth form would be observed that was the average of the two. This would give rise to a hexagonal feature with the top hexagonal face a (1 1 1) plane and the six side faces alternately {1 0 0}- and {2 2 1}-type faces. The shape formed by these faces is shown in fig. 11 and compares well with the shape seen in fig. 9. Close observation of the side faces on the cap of a whisker reveals a series

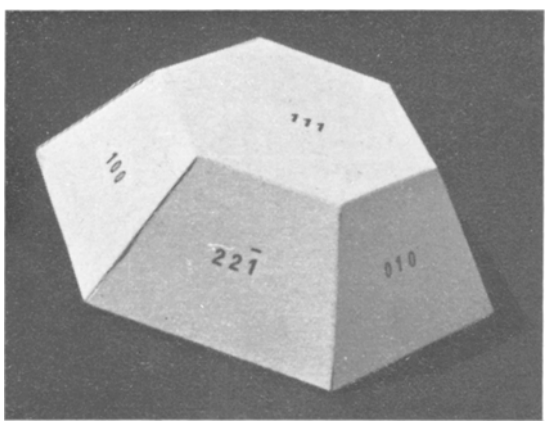

Figure 11 Model showing shape of hexagonal cap predicted by suggested growth mechanism.

of fine parallel lines. This is especially apparent for the whisker in the foreground of fig. 9. It seems likely that these are steps at which the change-over between the growth modes occurs. Further evidence is shown by the whisker in the left background of fig. 9. This growth cap appears to have changed its mode of growth just once, in the middle of the cap, rather than continually.

The concertina-shape is also of interest. One possible explanation is that the whiskers are twinned at regular intervals along the growth axes. This would require the top hexagonal face to be a (1 1 1) plane, in agreement with the growth mode proposed.

Ribbon growth normally takes place with the two flat faces parallel to the twinning plane, which is (1 1 1) in GaAs [7]. This was found to be the case for all the ribbons and platelets studied in this work. In fig. 12 is shown an example of a large platelet with a characteristic hexagonal

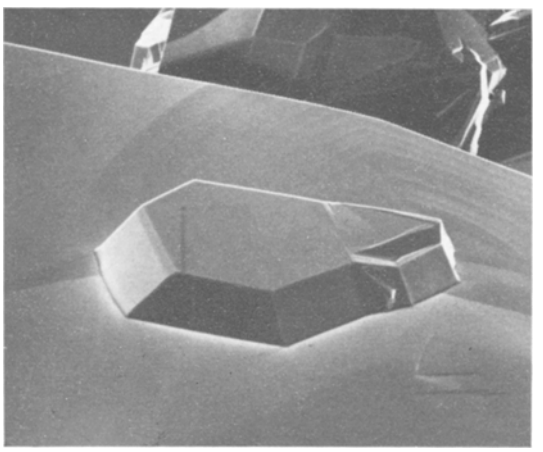

Figure 12 Growth feature on platelet (× 48).

feature on one side. Measurement of the angles of this feature show it to be of the type drawn in fig. 10a and confirm that the platlet is (1 1 1). A (1 1 1) plate of GaAs has one face composed entirely of gallium atoms and one of arsenic atoms. The effect of nitric acid on such a plate is to polish the arsenic face, and stain the gallium face a dark brown colour. Many of the flat dendrites were large enough to handle and they all showed this characteristic behaviour with nitric acid.

Many of the ribbon growths showed a relatively large mass of material at the growing end. An example of this is shown in fig. 13, a side view of a ribbon. It is possible that a variation of the vapour-liquid-solid mechanism, originally postulated for whisker growth in silicon [8], may be the mode of growth for the dendrites observed in this work. Such a mechanism would work as

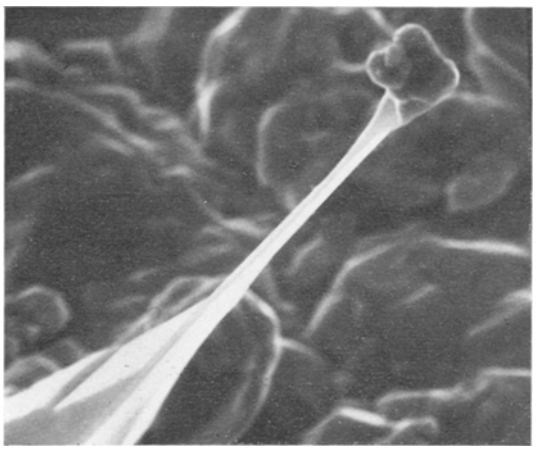

Figure 13 Side view of ribbon growth (× 740).

follows. First a liquid gallium droplet forms on the substrate surface; this can happen if there is a temporary deficiency of arsenic vapour. This droplet can dissolve arsenic vapour until it becomes saturated, when it will deposit GaAs on the substrate. The remaining gallium liquid is left sitting on top of the deposited material, i.e. it has moved off the substrate into the vapour. The droplet can continue moving off the surface and creating a dendrite until all the gallium has been used up. If the growth is interrupted a dendrite will be seen with a mass of a Ga-As solution on the end, as seen in fig. 13.

A slightly more complex version of this mechanism would allow the Ga-As liquid to dissolve gallium as well as arsenic. The growth mechanism would then not be arrested by the gallium present in the original droplet being used up.

4. Conclusions

The work has shown that when GaAs is grown on to electropolished tungsten using the $AsCl_3$ process, the usual mode of growth is that of nucleations growing together to form a polycrystalline layer. However, it has been seen that, occasionally, thin single crystal layers can be grown. It seems likely that if this mode of growth can be made more reproducible then it will become feasible to prepare devices on heat-conducting substrates. The state of the work resembles in many respects the early work of Joyce *et al* who grew silicon on silicon substrates using the molecular beam technique [4, 6]. They also found three-dimensional and two-dimensional nucleation. By removing impurities from their substrates they managed to achieve two-dimensional nucleation in a reproducible way. Further work on the GaAs-tungsten system in which substrate preparation is studied more carefully may bring about similar progress. However, the molecular beam growth of silicon is carried out in high vacuum and it is therefore possible to achieve a much higher standard of cleanliness than in a continuous flow system.

Dendritic growth has also been studied and suggestions have been made concerning growth mechanisms. A vapour-liquid-solid mechanism has been suggested for at least some of the dendrite growth and posibly all of it. The predominant growth direction is $\langle 1\,1\,1 \rangle$, and in two of the growth mechanisms twinning seems to occur.

Acknowledgements

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