

The Epitaxial Growth of Zinc Sulphide on Silicon by Forced Vapour Transport in Hydrogen Flow

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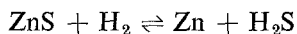
Epitaxial growth of zinc sulphide on silicon (111) substrates has been achieved by an open tube flow method in which hydrogen was used as the reactive transport agent. Epitaxy occurred for flow rates between 40 and 300 cc/min, and for substrate temperatures from 450 to 600°C, giving growth rates between 200 and 1300 Å/h. The crystal structure of the overgrowths was examined by electron and X-ray diffraction and was without exception single crystal. Both hexagonal and twinned cubic reflections were observed in the diffraction patterns from films grown from pure zinc sulphide powder, but films grown from photoluminescent material were entirely hexagonal.

1. Introduction

Thin films of zinc sulphide on silicon may provide useful electroluminescent devices for display systems compatible with modern electronic circuit techniques. The requirements for electroluminescence include the simultaneous existence of free electrons and holes in the zinc sulphide and these could be provided either by impact ionisation or carrier injection at the silicon-zinc sulphide heterojunction.

The choice of silicon as the substrate has previously been discussed [1]. Essentially the diamond cubic structure of silicon may accommodate on a (111) plane, with a very small lattice mismatch, an epitaxial layer of either cubic or hexagonal zinc sulphide.

The epitaxial layers described by Jones *et al* [1] were produced by vacuum evaporation. This report describes the epitaxial growth from the vapour phase of zinc sulphide on silicon (111) wafers. The reversible reaction



is employed, hydrogen acting as both reactant and carrier gas. It has been reported [2] that in vapour transport systems the use of a reactive atmosphere produces larger transport of source material, at low source temperatures, than is obtained using a non-reactive atmosphere. In addition, the use of forced transport by a reactive gas flow, rather than the diffusion of the re-

actants in a closed system, results in a large increase in the flux of growth material to the substrate. The reactive gas flow has been used by Frerichs [3] to grow large single crystals of II-VI compounds, and by Dijk and Goorissen [4] to produce epitaxial films of cadmium sulphide on germanium.

A necessary initial procedure for any epitaxial growth on a silicon slice is the removal of the oxide layer, and also the surface damage caused by lapping and polishing. The method adopted is a standard technique [5] used for silicon in which reduction of the oxide in a hydrogen flow at 1250°C is followed by a chemical etch at the same temperature in a flow of hydrogen and hydrogen chloride. This method has proved to be ideal for the production of the clean flat surface required for epitaxial growth.

Once a suitable surface has been produced, the substrate must be exposed to conditions in which epitaxial growth of zinc sulphide can occur. Vapour from a zinc sulphide powder source can be transported to a growth region using hydrogen as a reacting carrier gas. If epitaxy is to occur, contamination must be avoided and it is obviously an advantage if both the cleaning of the silicon and the vapour transport process can take place in rapid sequence within the same system.

2. The Growth Apparatus

A schematic diagram of the system is shown in

fig. 1. It is constructed mainly of quartz and care was taken that all other materials used did not react with the gases employed. The gas feed-tubes to the system are of stainless steel and are joined to the quartz by means of PTFE unions.

The apparatus provides two separate regions, one in which the silicon slice is cleaned and the other in which the epitaxial growth takes place. The slice is moved from the cleaning region to the growth region by means of a quartz push-rod.

The silicon slice is 9 mm diameter, 0.3 mm thick and is polished on both sides. It is heated on a graphite susceptor by a radio-frequency induction coil around the outside of the tube. The graphite is supported in the system by the hollow quartz push-rod which slides in a PTFE end plug. This hollow push-rod also contains a Pt/Pt. 13% Rh thermocouple used to monitor the temperature of the graphite block.

The quartz outer tube in the cleaning region is water-cooled to reduce attack by the cleaning gases and the graphite is protected in the usual way by a thin coating of silicon carbide.

The zinc sulphide source can be raised rapidly to the temperature needed for the transport process by means of a furnace, which can be moved into position when required.

All the gases used are of the high purity grade. The hydrogen is further purified by passing it through two molecular sieves. The first sieve operates at room temperature and reduces the oxygen content. The second is cooled to -77°C

to remove the final traces of carbon dioxide and water vapour.

3. The Growth Procedure

3.1. Preliminary Preparation

Before assembling the apparatus, any zinc sulphide deposits remaining in the tube from a previous growth cycle must be removed by soaking in hot concentrated hydrochloric acid for about 30 min. Any significant deposits on the tube in the region where the silicon is cleaned can affect unfavourably the cleaning process and must be removed by adding a small quantity of hydrofluoric acid to the hydrochloric acid. The same acid solution is used for cleaning the graphite susceptor and the quartz push-rod.

Following the acid treatment and a thorough rinse in distilled water, the apparatus is assembled and allowed to dry for about 5 h in a flow of 3 l/min of hydrogen, which enters the chamber at inlet C. During this time the flow is directed alternately to the outlets A and B. This method of drying the apparatus reduces the possibility of contamination and has proved to be very satisfactory.

When the apparatus is dry, the zinc sulphide powder charge (weighing approximately 2 g) is introduced into the far end of the chamber by means of a boat on the end of a long tube. However, before the silicon substrate can be introduced, the graphite susceptor must be subjected to further cleaning. The susceptor is therefore

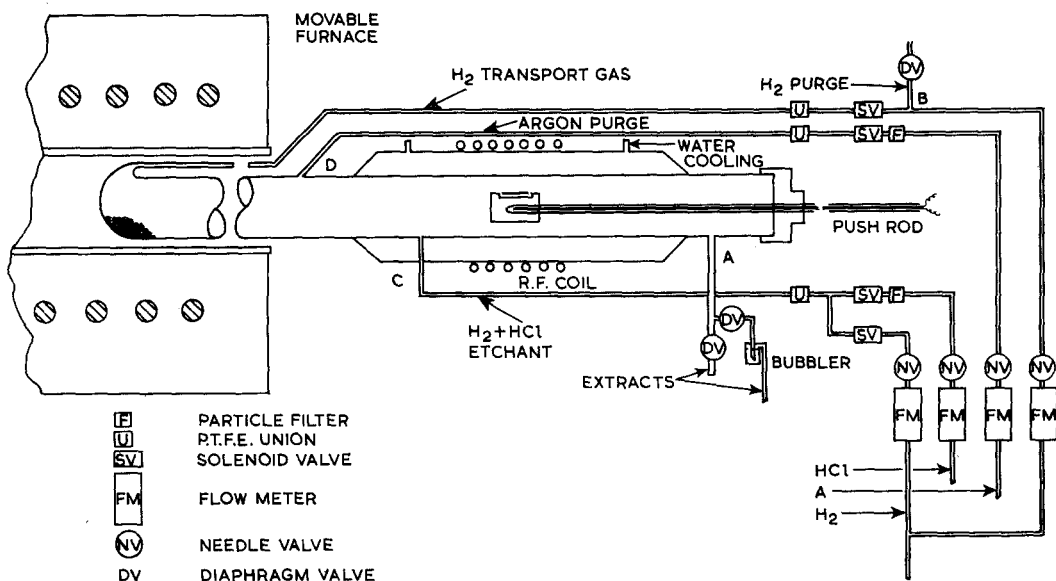


Figure 1 Apparatus for the growth of single crystal zinc sulphide on silicon wafers.

positioned near the outlet end of the silicon etching region.

A hydrogen flow entering at C at a rate of 3 l/min is now directed to outlet B for about 2 h to flush occluded gases from the region of the powder source. This flow is then directed to outlet A and the graphite susceptor heated to about 1250°C with about 10% hydrogen chloride mixed into the gas stream. This finally removes all contaminants from the surface of the graphite susceptor. After 5 min the hydrogen chloride flow is stopped and the susceptor allowed to cool in the hydrogen flow.

The silicon slice may now be placed on the susceptor and positioned in the etching zone, well clear and upstream of the region used for cleaning the susceptor. Hydrogen is passed over the slice to the outlet A for about 15 min to flush air from the system. The apparatus is now ready for use and a typical growth cycle proceeds as follows.

3.2. The Growth Cycle

A hydrogen flow of 3 l/min entering at C is directed to the outlet B and the furnace (hot zone 1050°C) is positioned over the zinc sulphide zone. In this manner any volatile contaminants present in the zinc sulphide powder are removed. It should be noted that if this stage is omitted, the attempt to grow epitaxial films inevitably fails.

To avoid substrate contamination it is desirable that the source region should be cool during the substrate etching process. Thus after 20 min the furnace is removed and the source allowed to cool to room temperature in the hydrogen flow.

The hydrogen is then directed to outlet A at 18 l/min and the silicon slice cleaned as follows.

The silicon is heated to 1260°C by means of the R.F. coil and a period of 5 min is allowed for the removal of the surface oxide layer. A flow of hydrogen chloride at 450 cc/min is then introduced into the gas stream for a period of 10 min during which time approximately 30 μm of silicon is removed from the surface of the slice. The slice is then allowed to cool to room temperature in the hydrogen flow.

The hydrogen is then directed to outlet B at 3 l/min and the furnace again positioned over the zinc sulphide source. Ten minutes is allowed for the temperature of the source to reach equilibrium, after which the silicon slice is positioned in the growth zone at a distance into the furnace

known to give the required growth temperature. The hydrogen flow is stopped and all inlets and outlets closed until the graphite temperature is stable. The required hydrogen transport flow rate is set up, entering at B, and directed to outlet A. To avoid back diffusion of air into the system with the low transport flow rates used (30 to 500 cc/min), the exhaust gases are passed through a bubbler.

After the required deposition period, which may be up to several hours, the growth is terminated in the following way. A flow of argon is introduced at D and directed over the slice to outlet B. The hydrogen flow is stopped, the furnace removed and the slice allowed to cool to room temperature in the argon flow.

4. Experimental Results

Deposits of zinc sulphide could be obtained in the substrate temperature range of 250 to 650°C. Below 250°C most of the zinc sulphide in the vapour stream had already been lost to the walls of the tube and so little would be expected to condense on the substrate. Between 650 and 800°C no deposit could be detected, and above 800°C severe etching of the substrate occurred.

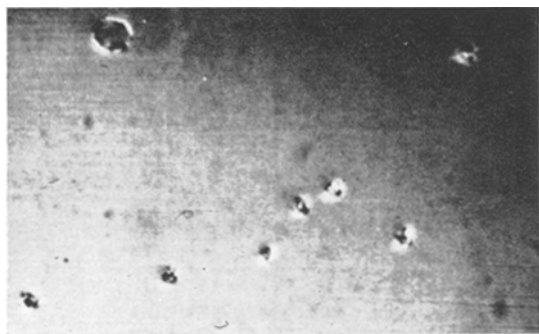
With a source temperature of 1050°C, the growth of deposits was investigated with hydrogen flow rates from 0.5 cc/min to 5 l/min. Flow rates greater than about 500 cc/min produced a rapid growth which was rough and dark in appearance. Such layers on exposure to air developed white spots which eventually spread over the entire film.

With flow rates below about 300 cc/min the deposits were completely transparent but their presence could be confirmed by the appearance of characteristic bands of interference colours related to the thickness of the layers.

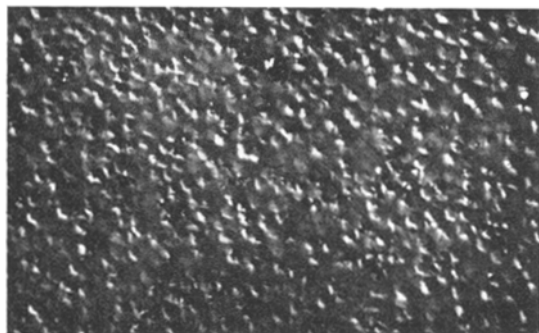
4.1. Observations with an Optical Microscope

The topography of the layers was examined using a Nomarski type Interference Contrast attachment. This revealed island growths for flow rates less than 5 cc/min (fig. 2a). For flow rates between 5 and 100 cc/min, the layers were continuous but matt in appearance and a typical micrograph is shown in fig. 2b. A further increase in flow rate to between 100 and 500 cc/min resulted in transparent layers but again fine detail was visible in the surface topography (fig. 2c).

Thickness measurements are made using a



(a)



(b)

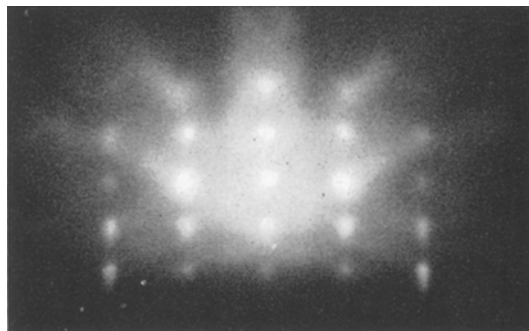


(c)

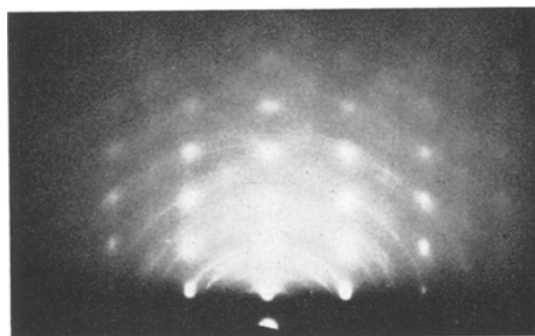
Figure 2 Interference contrast optical micrographs of layers grown on silicon substrates at 500°C with hydrogen flow rate (a) 0.5 cc/min; 1 cm = 25 μm (b) 40 cc/min; 1 cm = 25 μm (c) 250 cc/min. 1 cm = 100 μm.

Watson interference objective. As this device is basically a Michelson interferometer, white light fringes may be obtained from both the upper and lower surfaces of the zinc sulphide film. By measuring the separation between the central fringes the film thickness can be obtained non-destructively. This method requires films of at least 0.8 μm as otherwise the two fringe systems

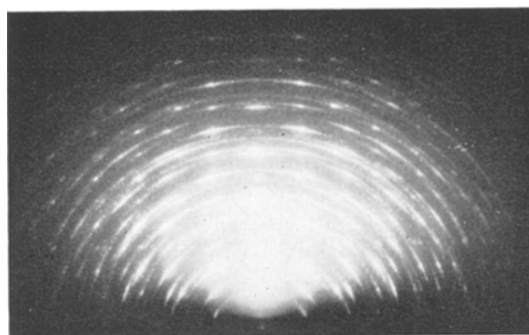
cannot be distinguished. For thinner layers a step height is measured after etching part of the film area in boiling concentrated hydrochloric acid. The thickness measurements showed that the growth rate is approximately proportional to flow rate, provided that the temperatures and flow rates are such that single crystal growth is taking place. Growth rates of 200 and 1300 Å/h were recorded for flow rates of 40 and 250 cc/min



(a)



(b)



(c)

Figure 3 Reflection electron diffraction patterns from layers grown on substrates at 500°C with hydrogen flow rate (a) 40 cc/min; (b) 250 cc/min; (c) 30 cc/min.

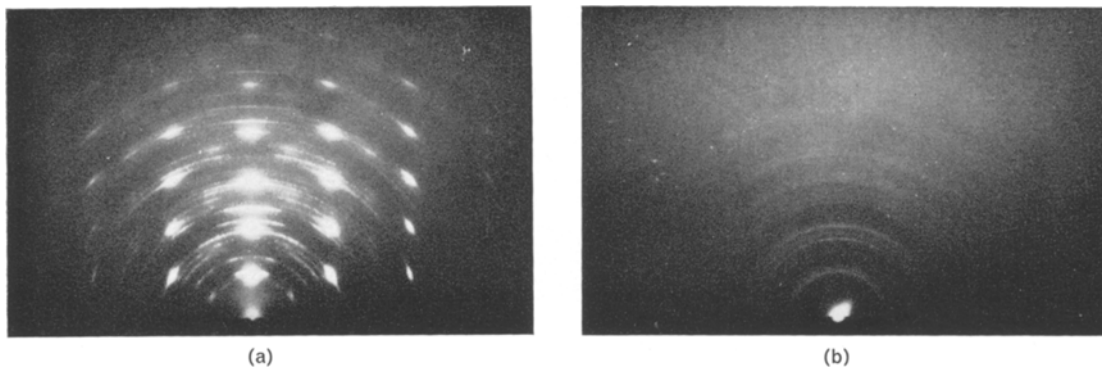


Figure 4 Reflection electron diffraction patterns from layers grown in a hydrogen flow of 40 cc/min on silicon substrates at (a) 450°C; (b) 360°C.

respectively, with a substrate temperature of 500°C.

4.2. Reflection Electron Diffraction

The specimens were mounted in the reflection electron diffraction stage of an EM6G electron microscope and the diffraction patterns observed. It was found that for specimens grown at 500°C, varying the flow rate in a range from 40 to 250 cc/min caused little change in the diffraction patterns. In every case the pattern (fig. 3a) indicates a good single crystal structure of the overgrowth.

With flow rates in the region of 250 cc/min, the appearance of ring patterns, superimposed on the characteristic single crystal diffraction pattern (fig. 3b), indicates the formation of some polycrystalline material on the surface. With much lower flow rates (< 40 cc/min) the heavily arced patterns (fig. 3c) clearly indicate a large amount of partly orientated material.

For a flow rate of 40 cc/min, reducing the

substrate temperature from 500 to 450°C caused arcing of the diffraction spots and the appearance of a faint ring pattern (fig. 4a). A further reduction in substrate temperature to 360°C produced only a ring pattern (fig. 4b), suggesting a completely polycrystalline deposition.

This general deterioration in the crystal structure of the film, which occurs when the growth temperature is lowered, may to some extent indicate that the higher temperatures are necessary for single crystal growth. However, it should be realised that the design of the apparatus is such that the concentration of vapour in the region of the substrate is lower for the lower substrate temperatures and this could well be a considerable factor in determining the type of crystal growth which occurs.

4.3. Transmission Electron Diffraction

In these investigations the microscope specimens were prepared by jet etching the silicon surface of a small chip until a suitably thin area was

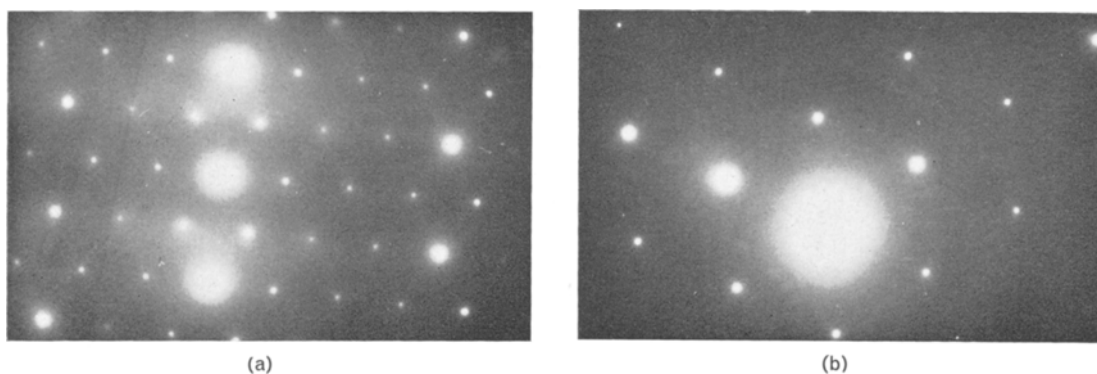
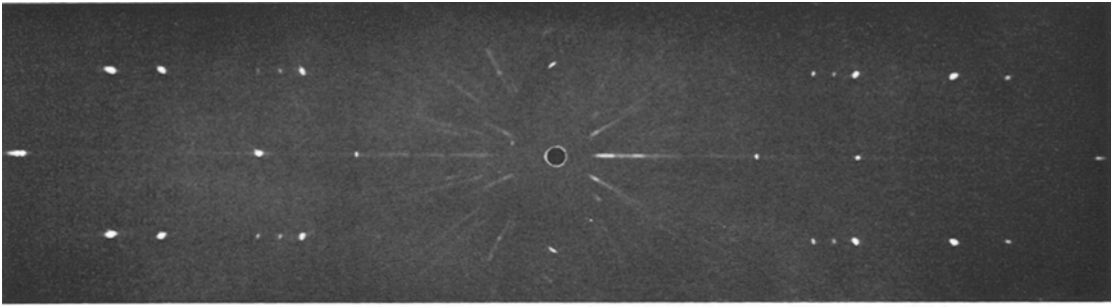
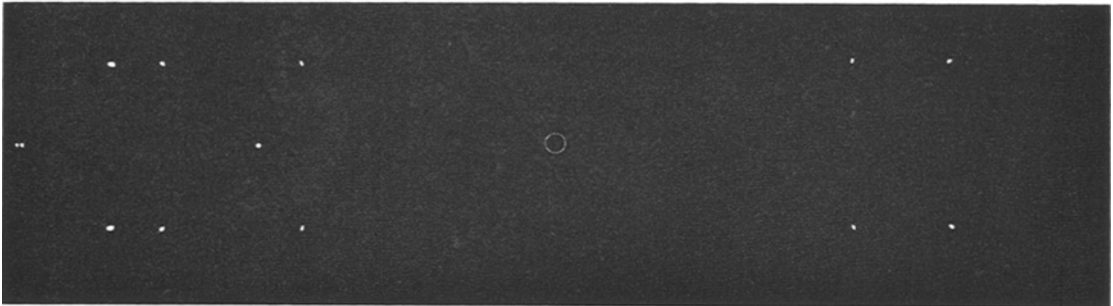


Figure 5 Transmission electron diffraction patterns from (a) epitaxial growth; (b) silicon substrate.



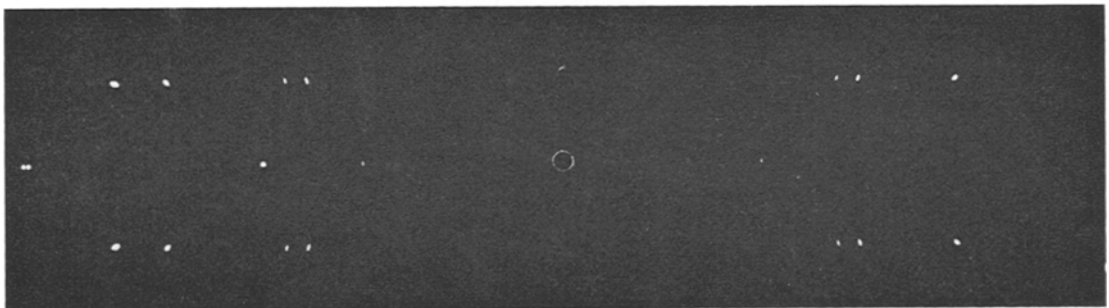
(a)



(b)



(c)



(d)

Figure 6 X-ray diffraction patterns. (a) layer grown from a pure zinc sulphide source; (b) silicon substrate; (c) index of (a); (d) layer grown from a photo-luminescent powder source.

- △ : Zns (hexagonal)
- : Zns (cubic and twinned cubic)
- : Si or Zns (cubic)

obtained [1], using a mixture of nitric and hydrofluoric acids.

The specimens were mounted in the microscope so that the beam was normal to the growth surface, a (111) plane. Fig. 5a shows a typical diffraction pattern from a specimen grown at 250 cc/min. For comparison, the spot pattern obtained for a clean silicon slice is shown in fig. 5b. It is evident from these patterns that hexagonal material is present in the zinc sulphide overgrowth. However, the presence of cubic material cannot be excluded since when viewed normal to a (111) plane, the diffraction patterns from silicon and epitaxial cubic zinc sulphide are indistinguishable.

4.4. Reflection X-ray Diffraction

The method described by Jones *et al* [1] was adopted, in which the main indication of cubic zinc sulphide is given by a strong 222 reflection (forbidden for silicon) with $\text{CuK}\alpha$ radiation. The method requires a layer of zinc sulphide which is relatively thick compared with layers investigated by electron diffraction. Accordingly, a layer 1.5 μm thick was grown using hydrogen flow rate of 250 cc/min, a substrate temperature of 500°C and a source temperature of 1050°C. The growth time was 13 h.

The diffraction pattern (fig. 6a) shows that the film is single crystal, perfectly aligned with the silicon substrate. The pattern from the overgrowth differs from that of the substrate (fig. 6b) in that it comprises a greater number of spots. These extra spots have been indexed and can be accounted for by the presence of twinned cubic and hexagonal zinc sulphide (fig. 6c).

A significantly different result was obtained when instead of pure material, zinc sulphide doped with 0.01% copper and aluminium was used as the source material. In this case under the same growth conditions, a faster rate of growth occurred. Typically, at a transport flow rate of 40 cc/min the growth rate was about 3300 Å/h compared with 200 Å/h using the pure source material. The diffraction pattern for such a specimen is shown in fig. 6d. In this case the overgrowth is still apparently single crystal and well aligned with the substrate, but the spot pattern indicates the structure to be purely hexagonal.

5. Conclusions

The source temperature, flow rate and substrate temperature are all interrelated in a system such

as the one described. Even so, it has been demonstrated experimentally that a certain amount of latitude is permitted in the choice of these variables without seriously affecting the quality of the film produced. Among the more crucial factors leading to the successful production of an epitaxial layer must be listed the pre-heating treatment given to the powder source and the careful control of the silicon cleaning process to give a clean flat surface.

Thus it appears that the method of chemical transport in a hydrogen flow is ideally suited to the growth of single crystal thin films of zinc sulphide on silicon. It is hoped in the future that the method described can be extended to the production of much thicker layers in which the bulk properties of the material can be more rigorously studied.

The X-ray diffraction spot patterns from the overgrowths are particularly sharp and compare favourably with the silicon diffraction spots. The zinc sulphide spots are much sharper than those obtained by Jones *et al* [1] indicating a higher degree of order in the epitaxial layer. In addition the previously reported layers all exhibited a mixed twinned cubic and hexagonal structure. It is of special interest that the layers grown from the photoluminescent source (fig. 6d) are of pure hexagonal structure.

Acknowledgements

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