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The vapour phase deposition of thick epitaxial (100) ZnS layers on elemental and compound substrates in H_2 gas flow

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An investigation of the epitaxial growth of (100) ZnS on GaAs, GaP, Si, Ge and sapphire substrates in H_2 gas flow is described. The objective of the work was to establish the most suitable substrate material and growth conditions for the deposition of highly ordered films of ZnS, about 80 μm thick, at growth rates > 20 μm h^{-1}. Substrate temperatures > 550° C were found to be necessary and GaAs was the most stuitable substrate material. It would appear that in the temperature range used for these experiments a close thermal expansion match is an important factor.

1. Introduction

Single crystal cubic (100) ZnS films, about 80 μm thick and with an area of at least 6 cm^2 are required for electro-optic devices [1, 2]. ZnS crystals can be grown in a closed capsule [3] by sublimation from a powder source, but this method cannot be used to produce large area slices. Recent work by the authors [4] has shown that thick cubic layers can be grown from the vapour phase by homo-epitaxial deposition on ZnS–Si substrates using H_2:HCl transport gas in an open tube system. The cubic ZnS substrates used for these experiments were prepared by vacuum evaporation on to Si wafers [5]. Although thick (> 50 μm) single crystal cubic layers could be grown at high growth rates by this method, the films were found to have twinned structures and to contain microcracks. The cracks were considered to be due to excessive stress at the ZnS–Si interface generated during the after-growth cooling period.

Yim and Stofko [6] have produced highly ordered ZnS films about 20 μm thick [7] by reacting H_2S with zinc vapour on GaAs and GaP substrates in an open tube system. One of the growth conditions found to be necessary for epitaxy was a non-stoichiometric composition of the H_2S and zinc in the vapour stream. Vohl *et al.* [8] used GaAs substrates in a close-space system, but were unable to grow layers greater than 25 μm thick in a reproducible manner.

This report describes the hetero-epitaxial deposition of ZnS from the vapour phase on various single crystal substrates using Derby Luminescents Limited ZnS powder source (Grade LN/123/5 lot 16346), H_2 as the transport gas and a 22.0 mm diameter growth tube. The apparatus, described in previous publications [9, 10] consists of a quartz growth tube (i.d. 22.0 mm) and a moveable furnace (Fig. 1). Separate regions are provided for the cleaning of the graphite substrate holder and the deposition of ZnS.

The tube is loaded with ZnS powder and, by means of a moveable quartz push-rod, the substrate is located in the deposition region of the tube. The tube and its contents are then outgassed by heating the system to the growth temperature in a reverse flow of H_2. Deposition is commenced by directing the transport gas to the source material where chemical reaction occurs. The reactants are transported in the gas stream to cooler regions of the tube where the reaction reverses and ZnS is deposited on to the substrate. HCl was not used in the transport gas to avoid problems associated with substrate etching by the reactants in the vapour phase.

The objective of the work was to establish experimentally the most suitable substrate material for the growth of thick highly ordered cubic films at growth rates exceeding 20 μm h^{-1}. The lattice constants and thermal expansion coefficients of the materials used are shown in Table I [6]. It can be seen that no substrate

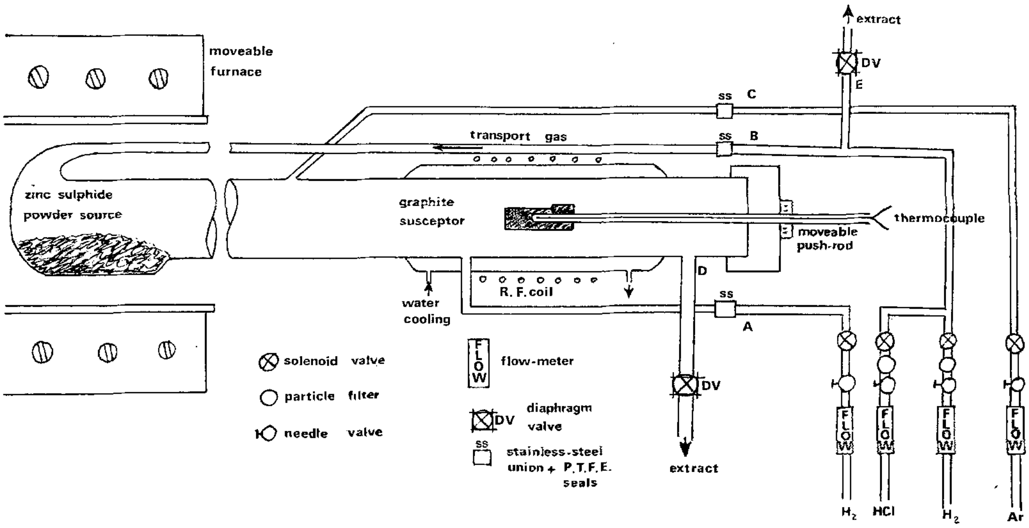

Figure 1 Apparatus for the epitaxial growth of zinc sulphide.

TABLE I Lattice constants and thermal expansion coefficients

Material	Lattice constant (Å) *	Linear thermal expansion coefficient (10^{-6} °C^{-1})†
ZnS	5.41	6.5–8.5
GaAs	5.65	6.7
GaP	5.45	5.8
Si	5.43	4
Ge	5.66	6.2

*Lattice constant (room temperature).
†Average value up to 800°C.

material provides both lattice and thermal expansion match with ZnS.

2. Substrate preparation

After a thorough preclean, the GaAs and GaP substrates were etched at room temperature in a 2% bromine : methanol solution, producing suitable optically-flat surfaces. The germanium substrates were also etched in a room temperature bromine : methanol solution, and heated *in situ* at 600°C in a low H_2 flow for 20 min before growth to ensure the removal of the oxide layer. The sapphire substrates were prepared for growth by heating *in situ* to 1150°C in a low H_2 flow, and the silicon substrates were etched in an iodine saturated solution of 4 ml 40% HF, 25 ml acetic acid and 25 ml 70% HNO_3 at 40 to 50°C. The Si wafers were heated *in situ* to 1100°C in H_2 flow prior to growth to remove any further oxide.

3. Preliminary experiments

Initial tests were carried out to establish growth conditions suitable for the deposition of highly ordered cubic layers (5 to 15 μm thick) at growth rates in the region of 20 μm h^{-1}. Table II summarizes the best structures obtained on each substrate and corresponding growth rates. It can be seen that GaAs, GaP and Ge substrates produced highly ordered layers. Fig. 2a shows a reflection electron diffraction pattern from a good deposition on GaAs, and similar patterns were obtained from layers grown on GaP and Ge.

TABLE II A summary of the characteristics of the "best" growths (< 15 μm thick) on each substrate material

Substrate	Growth rate (μm h^{-1})	Structure
GaAs	10–40	Highly ordered cubic
GaP	10–40	Highly ordered cubic
Ge	1–5	Highly ordered cubic
Si	1–3	Partially orientated
Al_2O_3	> 5	Highly ordered hexagonal

The strong Kikuchi lines suggest the presence of a highly ordered structure, which was confirmed by the sharp spots of the reflection

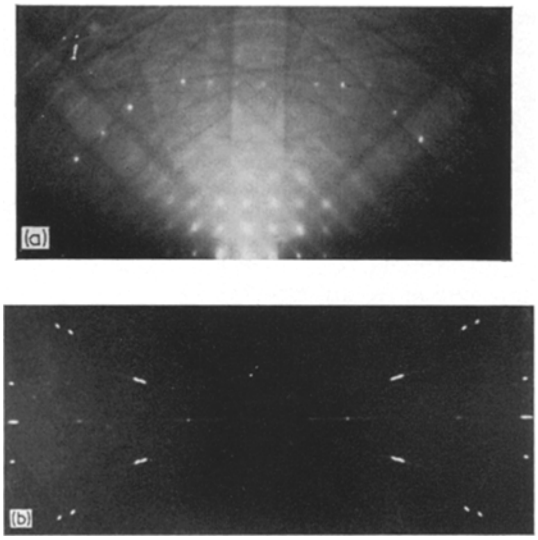

Figure 2 (a) Reflection electron, and (b) X-ray diffraction patterns from a thin layer of ZnS on GaAs.

X-ray diffraction pattern (Fig. 2b). It was found necessary to use lower substrate temperatures for the deposition on Ge (compared with GaAs and GaP) to avoid substrate etching and consequently the growth rates on Ge substrates were comparatively slow.

Silicon and sapphire were found to be unsuitable substrate materials. Deposition on Si, under growth conditions suitable for epitaxy on Ge, resulted in partially oriented structures (thin epitaxial films of ZnS have been grown on Si at very low rates in this apparatus [9] but the layers were not cubic.) Growth on $(1\bar{1}02)$ sapphire substrates (successfully used for the deposition of silicon [11])at temperatures above 700° C produced highly ordered hexagonal layers of ZnS, while depositions between 600 and 700° C were of mixed structure and layers grown at lower temperatures were polycrystalline.

Table III shows in detail the results of the preliminary experiments on GaAs. Using a low H_2 flow rate of 0.75 l min^{-1} and a source temperature of 1120° C, highly ordered cubic structures were obtained at substrate temperatures between 500 and 650° C. Optical micrographs of surfaces grown at 500 and 650° C are shown in Fig. 3 and it can be seen that smooth surfaces were not obtained. Deposits grown above 650° C had twinned cubic structures, highly faceted surfaces (Fig. 3c) and numerous microcracks.

Using a substrate temperature of 600° C, the H_2 flow rate could be increased to about 1.5 l min^{-1} before the structure deteriorated, with growth rate approximately proportional to flow rate. Fig. 4, an X-ray pattern of a layer grown in an H_2 flow of 1.6 l min^{-1}, shows arced spots due to some partially orientated material, and streaks caused by {1 1 1}-twinning [4].

Comparatively few depositions were carried out on GaP substrates. However, it was clear that the results were similar to those obtained on GaAs.

4. Structural characteristics of thick layers

The preliminary experiments had shown that suitable growth conditions for the deposition of

TABLE III Preliminary growths of ZnS on (100) GaAs (indicating deposition time t, H_2 flow rate, substrate temperature T, thickness d and structure

Specimen	t (h)	H_2 (l min^{-1})	T (°C)	d (μm)	Structure	Figure
G13	1	0.75	500	0.8	Highly ordered cubic	3a
G14	1	0.75	600	3.0	Highly ordered cubic	2a and b
G113	1	0.75	650	8.0	Highly ordered cubic	3b
G114	1	0.75	700	13.5	Twinned cubic	
G48	0.5	0.75	750	20.0	Twinned cubic	
G49	0.25	0.75	800	25.0	Twinned cubic	3c
G22	0.25	1.0	600	4.3	Highly ordered cubic	
G21	0.25	1.25	600	9.6	Highly ordered cubic	
G23	0.25	1.4	600	11.4	Highly ordered cubic	
G24	0.25	1.6	600	15.5	Slightly disordered	4
G25*	0.25	1.25	600	3.3	Highly ordered cubic	
G26*	0.25	1.25	700	15.1	Slightly disordered	

*The source temperature was increased from 1120 to 1220° C for these depositions.

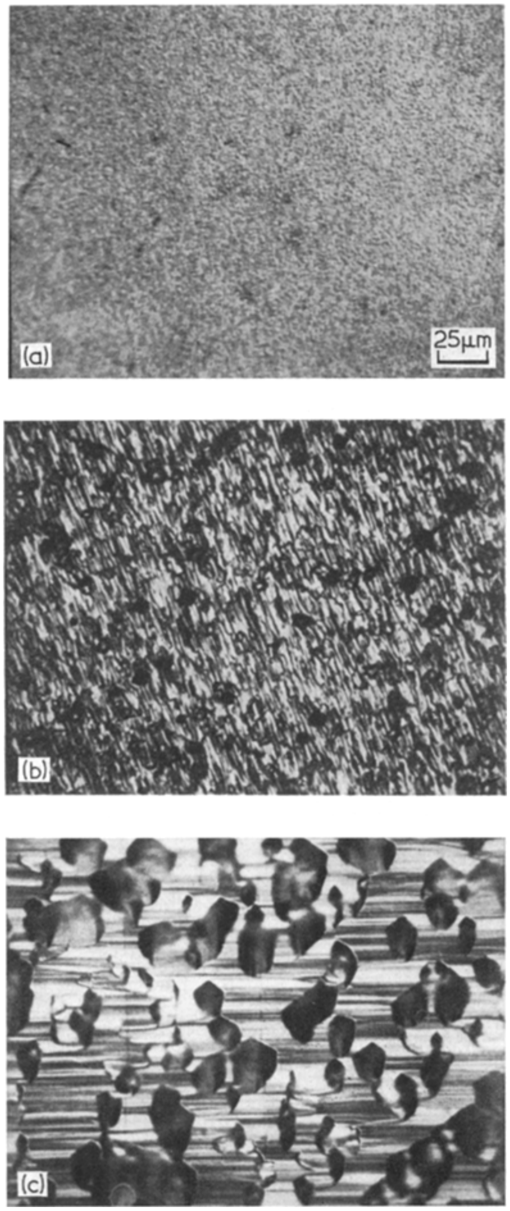

Figure 3 Optical surface micrographs of thin layers grown at (a) 500°C, (b) 650°C and (c) 800°C using an H_2 flow of 0.75 l min^{-1} and a source temperature of 1120°C.

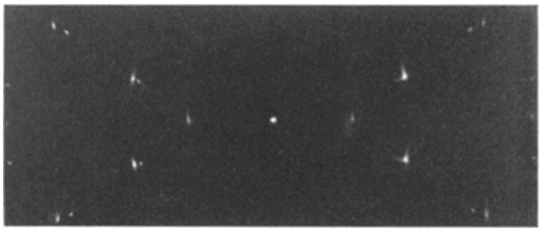

Figure 4 Reflection X-ray diffraction pattern from a thin layer grown in an H_2 flow of 1.6 l min^{-1} at 600°C using a source temperature of 1120°C.

thick ZnS layers on GaAs or GaP are an H_2 flow rate of about 1.15 l min^{-1} and a substrate temperature of 600°C. Table IV summarizes the crystal structures of thick films of ZnS on GaAs, showing the effects of various growth conditions. Also included are details of one growth on GaP. However, this layer shattered into several pieces on cooling. Some fragments were large enough to be examined by reflection electron diffraction, and their structures found to be highly ordered cubic.

The above growth conditions produced thick layers on GaAs containing a small percentage of polycrystalline material. However, after polishing about 1 μm off the growth surfaces with alumina powder, the structures were found to be highly ordered.

Attempts at achieving growth rates $\simeq$ 50 μm h^{-1} by raising the H_2 flow rate or substrate temperature resulted in imperfect structures. For example, an H_2 flow of 1.5 l min^{-1} produced a polycrystalline layer of 108 μm thick in 2 h, whilst a substrate temperature of 760°C resulted in a twinned cubic layer of 95 μm thick in 2 h.

5. Surface features of thick layers

The "as-grown" surfaces of all depositions were very rough and Fig. 5 shows typical features of (a) an ordered structure, and (b) structures with surface disorder. Fig. 5 shows characteristic tetragonal-shaped pits similar to surfaces of layers grown by Vohl *et al.* [8]. It has been suggested [8, 12] that these pits are caused by cleavage defects originating from the GaAs and from polycrystalline pockets which flare with thickness until the entire surface film becomes polycrystalline. We have observed this effect in thick layers (> 50 μm) although it has been minimized by reducing the H_2 flow rate and the source temperature.

Fig. 6 shows cleavage edge views of (a) a highly ordered cubic deposition and (b) an apparently polycrystalline layer. The latter layer was grown in an H_2 flow of 1.5 l min^{-1} and it can be seen that the deposition was single crystal to a well-defined thickness, followed by polycrystalline material.

TABLE IV A summary of the growth of thick ZnS layers on (100) GaAs substrates

Specimen no.	t (h)	H_2 (l min^{-1})	T† (°C)	T (°C)	d (µm)	Structure	Figure
G27	3	1.15	1120	600	45	Slightly disordered	5a, 6a, 7a
G27†	3	1.15	1120	600	44	Highly ordered cubic	
G210‡	2	1.5	1040	645	108	Polycrystalline	7b
G211	2.5	1.25	1040	600	70	Highly ordered cubic	5b, 6b
G212	5	1.15	1040	600	118	Slightly disordered	
G410	2	0.75	1120	760	95	Twinned cubic	
P12*	4	1.15	1040	600	80	Highly ordered cubic	

*(100) GaP substrate.
†Source temperature.
‡Polished.

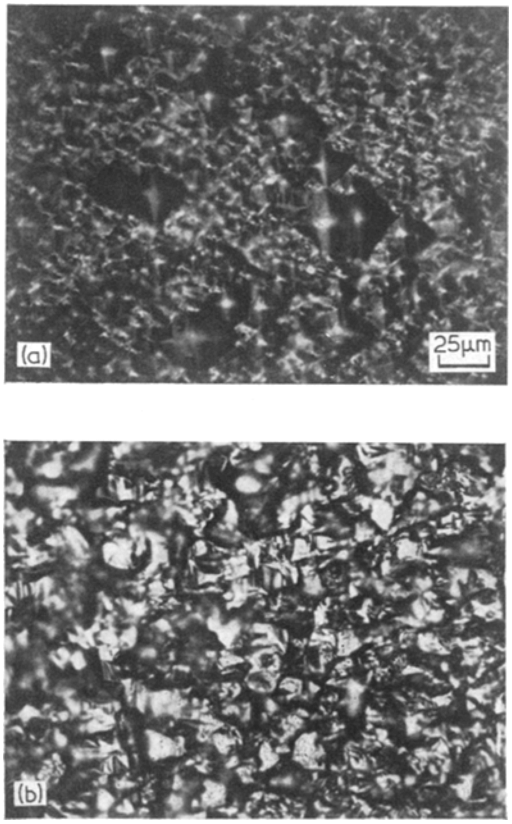

Figure 5 Optical surface micrographs of thick layers with (a) a highly ordered cubic structure and (b) a structure with surface disorder.

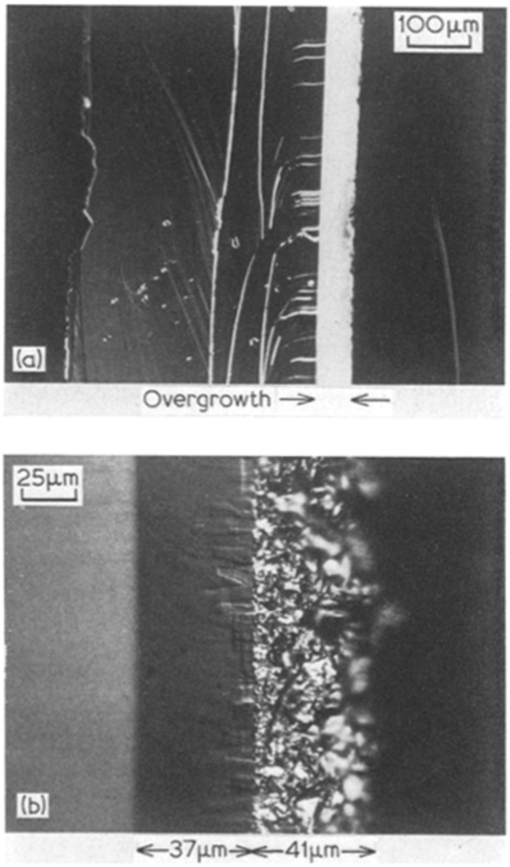

Figure 6 Cleavage edge views of (a) a highly ordered cubic deposition and (b) an apparently polycrystalline layer.

6. Discussion

This work has shown that highly ordered 80 µm thick layers of ZnS can be grown by vapour transport in H_2 flow on GaAs substrates. A substrate temperature of 600°C and 1.5 l min^{-1} H_2 flow rate (for a 22.0 mm diameter tube) seem to be ideal conditions for growth, but these are not critical. The growth rate was found to be proportional to exp $\{E_a/kT\}$, where E_a is an activation energy ($\simeq 0.8$ eV) similar to deposition in H_2 : HCl [4].

Highly orientated films were grown on GaP under similar conditions but were found to crack on cooling. Table I shows that although ZnS is a close lattice match to GaP, it is a poor thermal expansion match, which may account for the cracking.

Deposition on Si and Ge substrates was restricted to lower growth temperatures and consequently lower growth rates. This was necessary to overcome substrate etching by the vapour species particularly in the case of silicon. Growth of cubic ZnS on sapphire substrates in the temperature range likely to yield reasonable growth rates (> 500° C) was not achieved.

This films of ZnS have been grown on ZnS–Si substrates [4] at high substrate temperatures (> 700° C) and were twinned cubic containing microcracks. In this case the lattice match was within 0.5%, and again the reasons for cracking may be associated with the large thermal expansion coefficient mismatch (Table I). A comparison of surfaces of films grown by H_2 and H_2 : HCl transport gives a clear indication that smoother surfaces are obtained by using H_2 : HCl transport gas. It is possible that by using lower substrate temperatures ($\simeq$ 600° C), at the expense of growth rate, twin-free smooth layers may be grown on GaAs in H_2 : HCl gas flow.

7. Conclusions

GaAs appears to be the most suitable substrate material for the growth of thick ($\simeq$ 80 μm) layers of highly ordered (100) ZnS in an open tube vapour phase system. This work has shown that to obtain crack-free films a close match between the linear expansion coefficient is possibly a more important factor than a lattice constant match.

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