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A structural and compositional analysis of interfaces in $ZnSe_{0.94}S_{0.06}$ layers grown on to GaAs by OMCVD

B. COCKAYNE, P. J. WRIGHT, G. W. BLACKMORE
RSRE, St Andrews Road, Malvern, Worcestershire, UK

J. O. WILLIAMS, T. L. NG
Edward Davies Chemical Laboratory, University of Wales, Aberystwyth, UK

High resolution transmission electron microscopy of lattice-matched $ZnSe_{0.94}S_{0.06}$ layers grown by organometallic chemical vapour deposition in the temperature range 275 to 350° C onto GaAs has shown that under specific growth conditions, layers of ZnS can form at the heterojunction interface. Chemical data from secondary ion mass spectrometry and energy dispersive X-ray analyses confirm the enhancement in sulphur content at the interface and also establish that gallium can diffuse into the II–VI layer from the III–V substrate. Growth conditions which eliminate the formation of the intermediate ZnS layer and the gallium diffusion have been identified.

1. Introduction

Thin epitaxial layers of the binary compounds ZnS and ZnSe can be grown readily onto a variety of substrates by chemical vapour deposition but generally with some lattice mismatch between the layer and the substrate. A combination of layer and substrate studied extensively has been ZnSe on GaAs [1–7] where the lattice mismatch is reduced to ~ 0.25%. Assuming Vegard's law, this mismatch can be reduced to zero by incorporating a small amount of sulphur onto the group VI sublattice to give the composition $ZnSe_{0.94}S_{0.06}$. This paper describes the growth by organometallic chemical vapour deposition (OMCVD) of lattice-matched $ZnSe_{0.94}S_{0.06}$/GaAs (100) heterojunctions and their subsequent characterization by high-resolution transmission electron microscopy (HRTEM), secondary-ion mass spectrometry (SIMS) and energy-dispersive X-ray analysis (EDAX).

2. Experimental details

The $ZnSe_{0.94}S_{0.06}$ layers were grown by OMCVD at temperatures of either 275 or 350° C onto polished (100) orientated GaAs substrates using the atmospheric-pressure cold wall reactor described previously [3]. The chemical reaction employed was that between dimethyl zinc (DMZ), hydrogen selenide and hydrogen sulphide; all the reactants were transported to the deposition zone of the reactor in a stream of purified hydrogen using conditions specified fully elsewhere [3] but which are summarized in Table I.

TABLE I

Substrate	n-type GaAs, polished, (1 0 0) orientation		
Growth temperatures	275 and 350° C		
Epitaxial layer composition	$ZnSe_{0.94}S_{0.06}$		
Layer thickness range	1 to 5 μm		
Gas phase ratio	$[H_2S]/[H_2S] + [H_2Se] = 0.65$		
Reactant gas flow rates	DMZ	5 cc min^{-1}	
	H_2Se	35 cc min^{-1}	5% mixtures in H_2
	H_2S	65 cc min^{-1}	
Carrier gas flow rate	H_2	4.5 l min^{-1}	

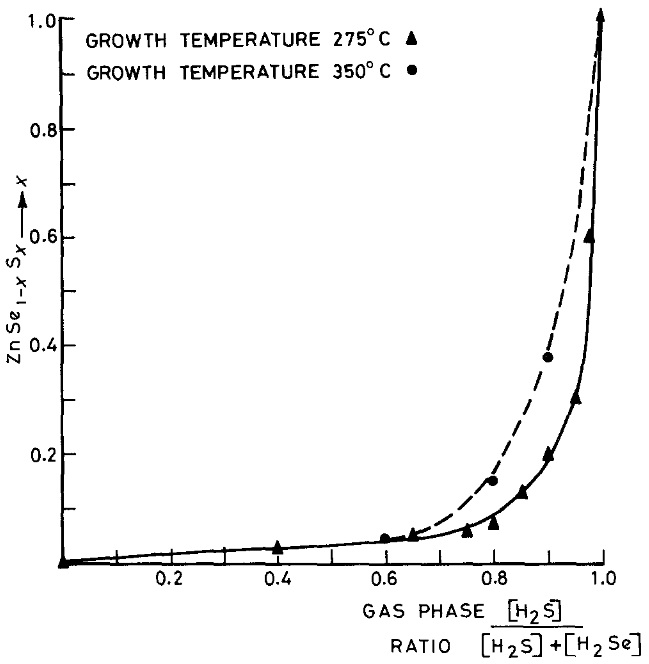

Figure 1 The relationships determined between the composition of $ZnSe_{1-x}S_x$ ($0 < x < 1$) layers and the gas phase ratio $[H_2S]/[H_2S] + [H_2Se]$ at temperatures of 275 and 350° C.

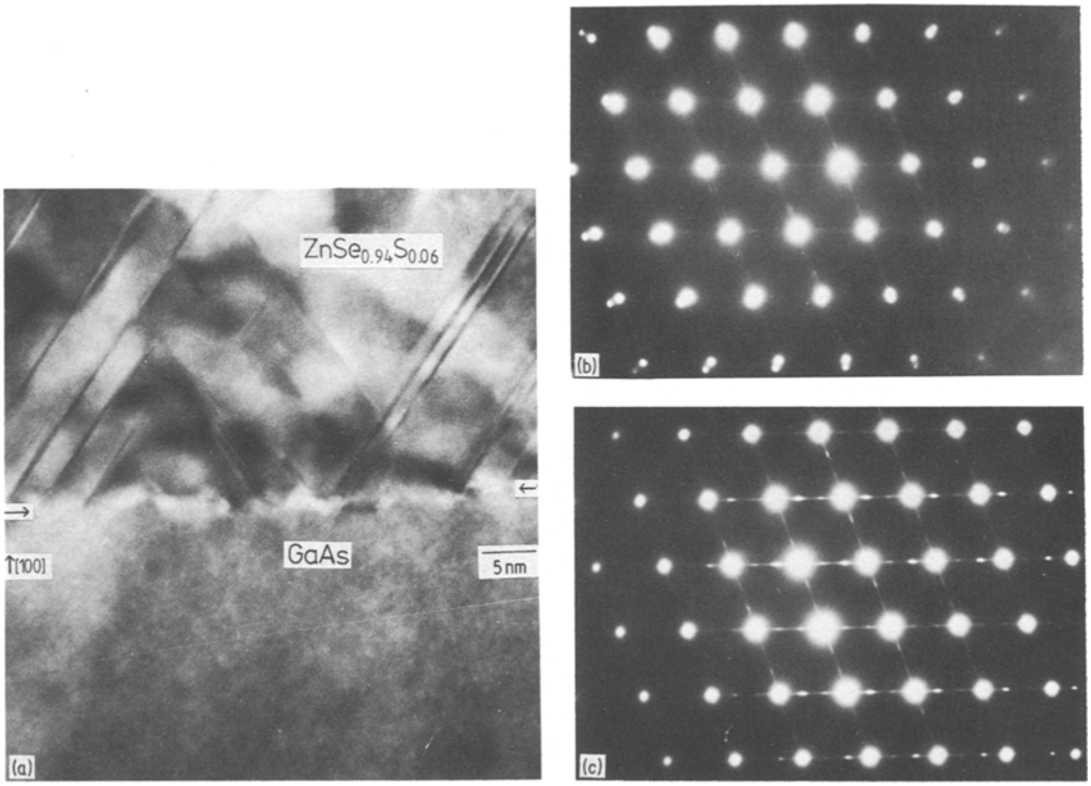

Figure 2 (a) High resolution transmission electron micrograph (n-beam; $n = 7$) of a $ZnSe_{0.94}S_{0.06}$/GaAs interface in (1 1 0) section grown under flow regime I. (b) Selected area diffraction (SAD) pattern corresponding to the interface region in Fig. 2a, in (1 1 0) section. (c) SAD pattern corresponding to the epitaxial layer region in Fig. 2a, in (1 1 0) section.

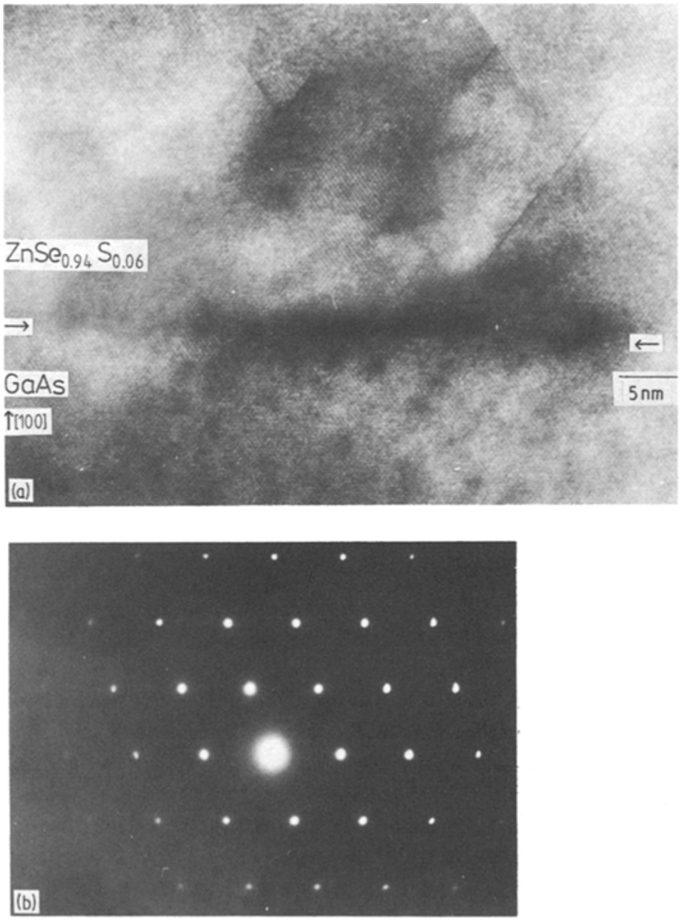

Figure 3 (a) High resolution transmission electron micrograph (n-beam; $n = 7$) of a $ZnSe_{0.94}S_{0.06}$/GaAs interface in (1 1 0) section grown under flow regime II. (b) SAD pattern corresponding to the interface region in Fig. 3a, in (1 1 0) section.

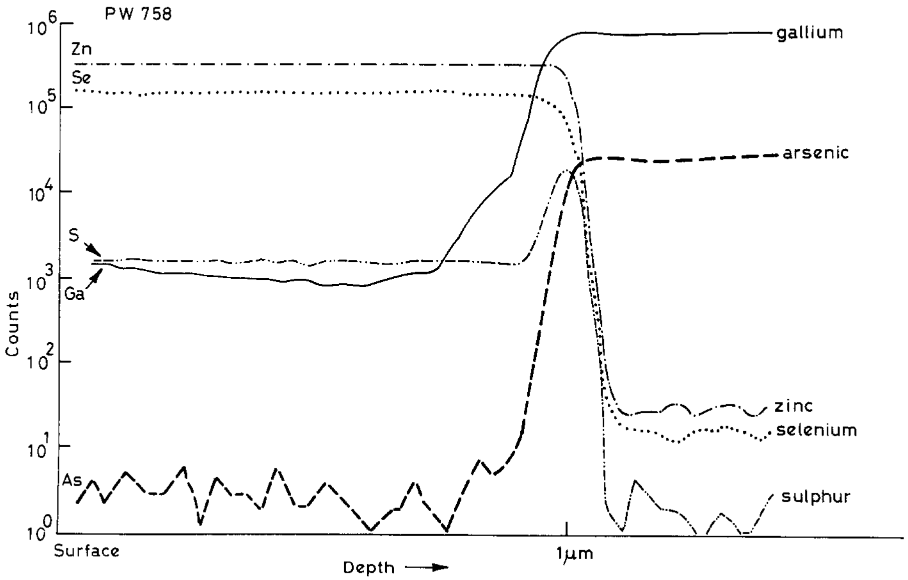

Figure 4 SIMS in-depth profiles for gallium, arsenic, zinc, selenium and sulphur taken through a $ZnSe_{0.94}S_{0.06}$/GaAs layer grown under flow regime I.

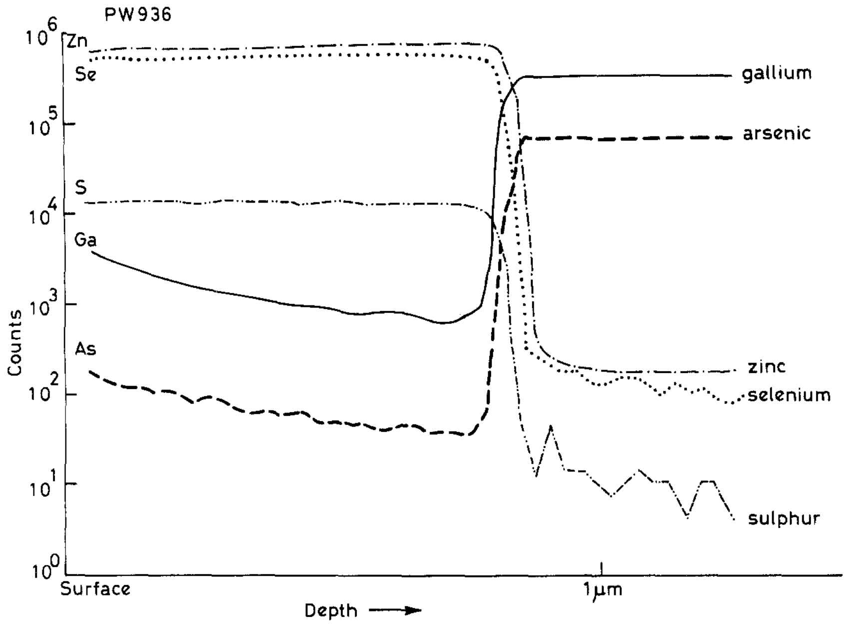

Figure 5 SIMS in-depth profiles for gallium, arsenic, zinc, selenium and sulphur taken through a $ZnSe_{0.94}S_{0.06}/GaAs$ layer grown under flow regime II.

A redetermination of the relationship between the solid composition, $ZnSe_{1-x}S_x$ $(0 < x < 1)$, and the gas-phase ratio, $[H_2S]/[H_2S] + [H_2Se]$, carried out as part of the present work is plotted in Fig. 1. This establishes that gas phase ratios within the range 0.6 to 0.65 lead to the deposition of the composition lattice matched to GaAs at temperatures within the limits used herein i.e. 275 to 350° C. For this redetermination, the solid composition was measured both by EDAX and from lattice-spacing data. Lattice matching for the $ZnSe_{0.94}S_{0.06}$ layers was confirmed by X-ray diffraction. The gas-phase ratios were deduced from mass flow rate measurements.

Structural studies were carried out on heterojunction cross-sections cut and thinned using methods developed for examination by HRTEM in a Siemens 102 instrument [8]. Compositional changes at the heterojunction interface and within the epitaxial layer were studied by EDAX in a JEOL 1200 EX electron microscope and by SIMS in a Cameca IM3-3F instrument again using conditions detailed in an earlier work [9].

3. Results

A basic problem which pertains to the growth of $ZnSe_{1-x}S_x$ layers by OMCVD under an excess of the group VI element is the nonlinearity between the gas-phase ratio and the solid composition (Fig. 1). Thus, for the growth of a specific solid composition, the gaseous mixture of reactants arriving in the reactor must have a uniform composition both at the start of and during growth. This point is illustrated in the present work by the growth of $ZnSe_{0.94}S_{0.06}$ under two different flow regimes. In the first regime (I), growth was induced by simultaneous switching of the DMZ, H_2Se and H_2S reactant gases into the main H_2 flow when the substrate had been stabilized at the growth temperature. In the second regime (II), the reactant flows were set up and stabilized prior to growth and simply vented away from the reactor until required; growth was then commenced by switching the total preset flow into the deposition zone. Examination by HRTEM of layers grown under these two types of flow regime shows very significant differences in the structures produced. For instance, Fig. 2a shows that under flow regime I a distinct interface layer is formed from which faults propagate into the epitaxial layer. The electron diffraction pattern of this interface region, Fig. 2b, is dominated by the [1 1 0] pattern attributable to $ZnSe_{0.94}S_{0.06}$ but shows extra spots arranged in an identical pattern which correspond to the ZnS lattice. The streaking in both patterns along ⟨1 1 1⟩ directions is characteristic of stacking fault formation and the double streaking demonstrates clearly the presence of such faults in both the ZnS and $ZnSe_{0.94}S_{0.06}$ lattices. Twin reflections from both lattices are also apparent and appear at the required

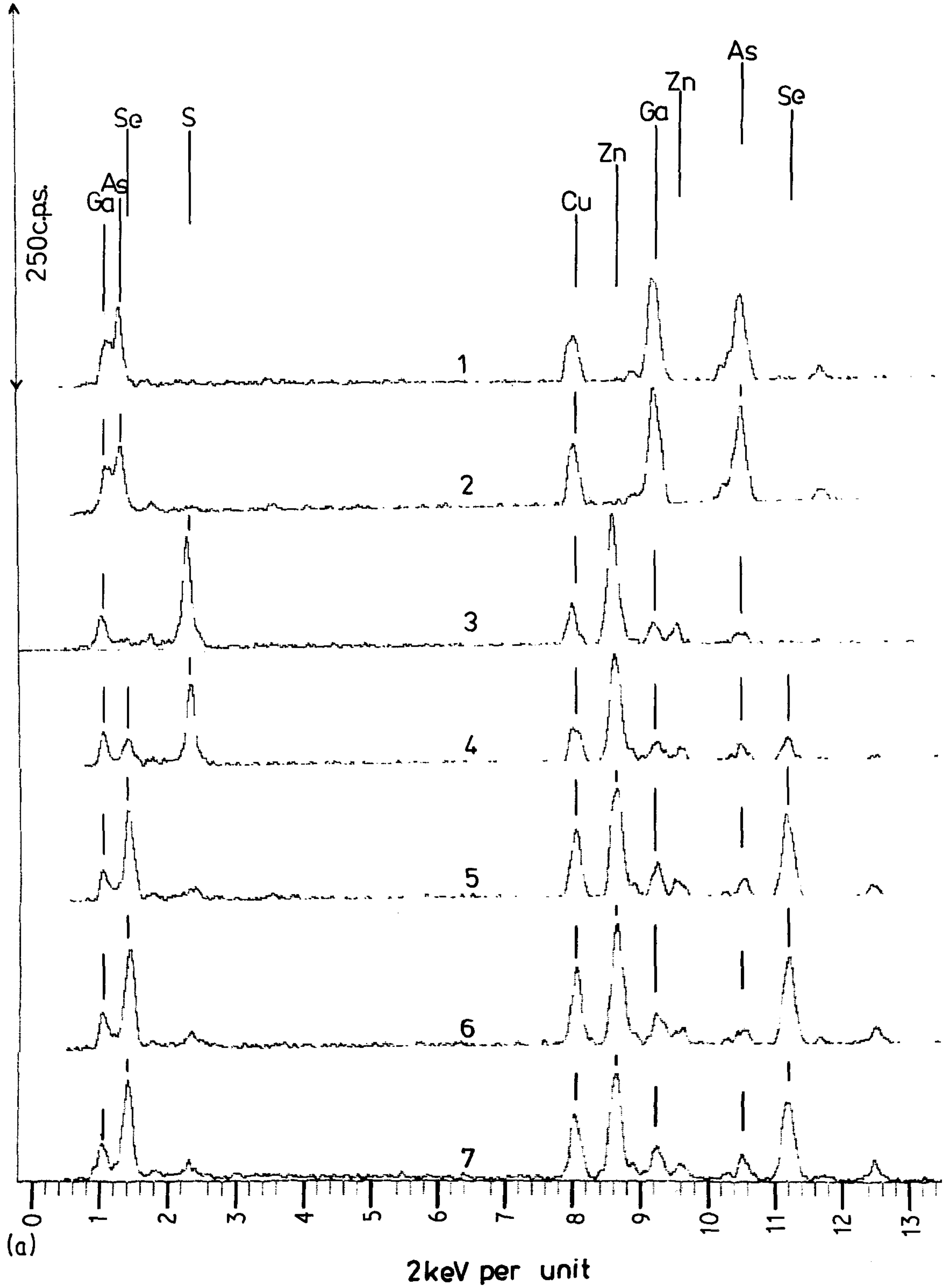

Figure 6 (a) EDAX profiles taken across the $ZnSe_{0.94}S_{0.06}$/GaAs interface shown in (b). The probe of *ca.* diameter 20 nm was positioned successively at points 1 to 7 and the spectra recorded. The peaks correspond to gallium, arsenic, zinc, selenium and sulphur from the sample and copper from the sample holder.

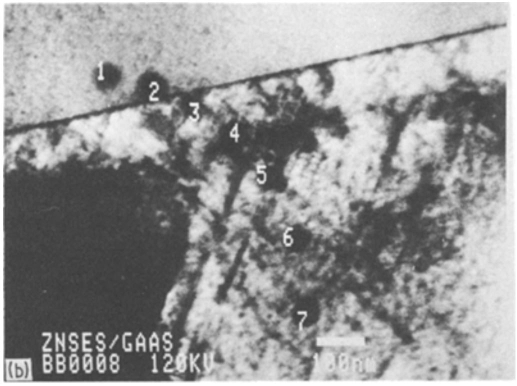

Figure 6 Continued.

distance of $a/3\langle 1\,1\,1\rangle$. Further into the layer, Fig. 2c, the extra spots and streaks associated with ZnS disappear leaving a pattern characteristic of $ZnSe_{0.94}S_{0.06}$ and associated stacking faults and twins. In marked contrast, Fig. 3a is typical of layers grown under flow regime II. In this case, the interface is barely discernible and very few faults are apparent. The corresponding [1 1 0] electron diffraction pattern (Fig. 3b) confirms the presence of only the $ZnSe_{0.94}S_{0.06}$ lattice and the lack of streaking is consistent with a very much lower number of stacking faults.

SIMS profiles taken through heterojunctions grown under flow regimes I and II are plotted in Figs. 4 and 5; these show an enhancement of S in the first part of the layer (~ 100 nm) grown under flow regime I but a uniform distribution of sulphur and selenium throughout the whole layer grown under flow regime II. The enhancement of sulphur at the interface has been further confirmed by EDAX (see Fig. 6).

Both the SIMS and EDAX experiments demonstrate the diffusion of Ga from the substrate into the layer grown under flow regime I (Figs. 4 and 6) whilst SIMS data for layers grown under flow regime II shows that no significant gallium diffusion occurs.

4. Discussion and conclusions

High resolution transmission electron microscopy has been used by others [10] and ourselves [8] to show that twins and faulted dislocations are present in ZnSe layers grown onto GaAs by OMCVD. The present work shows that in order to make abrupt heterojunctions of $ZnSe_{0.94}S_{0.06}$ lattice-matched onto GaAs, the growth of a substantially defect-free interface is essential as gallium is shown to diffuse from the substrate into the layer when twins and stacking faults are present. Furthermore, it is established that a defective interface can be associated with the formation of a thin layer of ZnS which is intermediate between the layer and the substrate and in which many twins and stacking faults are generated. This intermediate layer forms because the disparate flow rates of the gaseous hydrides used to grow the lattice-matched composition can be initially sulphur-rich, the H_2S flow rate being some 1.9 times that for H_2Se even though the solid composition is 15 times richer in selenium than sulphur. The formation of the defective layer and its associated enhancement of gallium diffusion can both be inhibited by using a continuous gas flow regime of preset composition which is vented away from the OMCVD reactor until required. This latter flow regime leads to the growth of abrupt and reproducible interfaces of $ZnSe_{0.94}S_{0.06}$ lattice-matched onto the (1 0 0) orientation of GaAs.

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References

1. W. STUTIUS, *Appl. Phys. Lett.* 33 (1978) 656.
2. *Idem*, *J. Cryst. Growth* 59 (1982) 1.
3. P. J. WRIGHT and B. COCKAYNE, *ibid.* 59 (1982) 148.
4. T. YAO, Y. MAKITA and S. MACKAWO, *Jpn. J. Appl. Phys.* 20 (1981) 747.
5. M. D. SCOTT, J. O. WILLIAMS and R. C. GOODFELLOW, *J. Cryst. Growth* 51 (1981) 267.
6. P. LILLEY, *ibid.* 44 (1978) 452.
7. P. BESOMI and B. WESSELS, *ibid.* 55 (1981) 477.
8. J. O. WILLIAMS, E. S. CRAWFORD, J. LL. JENKINS, A. M. PATTERSON, B. COCKAYNE and P. J. WRIGHT, *J. Mater. Sci. Lett.* 3 (1984) 189.
9. P. J. WRIGHT, B. COCKAYNE, A. F. CATTELL, P. J. DEAN, A. D. PITT and G. W. BLACKMORE, *J. Cryst. Growth* 59 (1982) 155.
10. F. A. PONCE, W. STUTIUS and J. G. WERTHEN, *Thin Solid Films* 104 (1983) 133.

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