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PROGRESS REPORT ON THE GROWTH  
OF ZnTe BY ATMOSPHERIC PRESSURE  
METAL-ORGANIC VAPOUR PHASE  
EPITAXY (APMOCVD)

By

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19 ABSTRACT

- (i) The growth temperature and the V/II gas phase ratio have been optimised for ZnTe epitaxy on GaAs by APMOCVD. These are: a  $T_g = 430^{\circ}\text{C}$  and a  $V/II = 4$ . Material prepared under these conditions was found to be of high crystalline quality, comparable to the one obtained by MBE, and of high purity as demonstrated by the presence of the free exciton transition in low temperature PL spectra.
- (ii) Assuming the PL assignment is correct, the GaAs substrate and the organometallics are the main origins of layer contamination.
- (iii) Electrical properties are yet to be investigated and cannot be measured until reliable ohmic contacts can be made.
- (iv) The growth of ZnTe on GaSb substrates was not successful due to difficulties with pre-growth surface treatment of the substrate. A satisfying way of removing the oxide layer is being investigated.

This report has been reviewed and is releasable to the National Technical Information Service (NTIS).  
At NTIS it will be releasable to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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**PROGRESS REPORT ON THE GROWTH OF ZnTe BY ATMOSPHERIC  
PRESSURE METAL-ORGANIC CHEMICAL VAPOUR DEPOSITION (APMOCVD)**

**1. INTRODUCTION**

The aim of the first phase of the present project was to optimize the APMOCVD growth conditions for ZnTe on (100) GaAs. using DMZn and DiPTe as precursors. These conditions will subsequently be used for the growth on the closely matched GaSb (0.15%) substrate. The assessment of the prepared layers was by optical microscopy (morphology), x-ray double crystal diffraction (crystalline quality), photoluminescence (purity) and Vader Paw technique for electrical properties.

**2. GROWTH AND CHARACTERISATION OF ZnTe ON GaAs:**

**2.1 Growth**

The layers were deposited on (100) GaAs (MCP Electronics) using DMZn (Epichem, CVD) and DiPTe (St Andrews). Two parameters were investigated: the growth temperature and the VI/II gas phase ratio. The adopted growth conditions are shown below:

|                                      |   |                                             |
|--------------------------------------|---|---------------------------------------------|
| Total hydrogen dilution flow (l/min) | = | 1.6                                         |
| Temperature of DMZn bubbler (°C)     | = | -18                                         |
| Flow rate of DMZn (mole/min)         | = | $1.1 \times 10^{-5}$ - $1.1 \times 10^{-4}$ |
| Temperature of DiPTe bubbler (°C)    | = | 40                                          |
| Flow rate of DiPTe (mole/min)        | = | $2.7 \times 10^{-5}$ - $1.1 \times 10^{-4}$ |

|                                           |   |           |
|-------------------------------------------|---|-----------|
| Growth temperature ( $^{\circ}\text{C}$ ) | = | 370 - 510 |
| VI/II gas phase ratio                     | = | 0.25 - 8  |
| Thickness ( $\mu\text{m}$ )               | = | 0.75 - 8  |

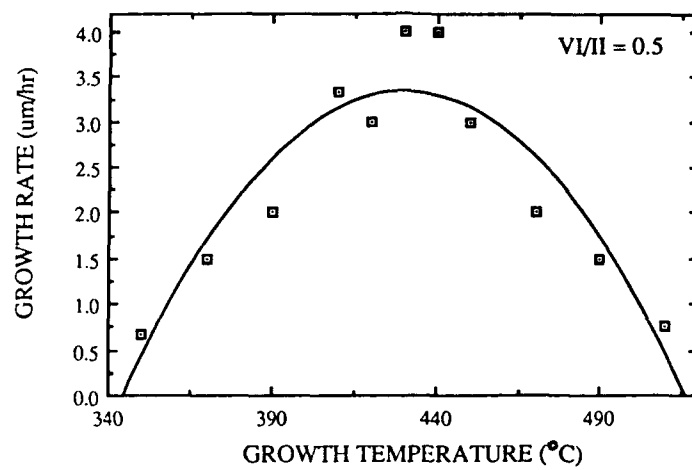
The nozzle, conventionally used in the growth of II-VI materials to suppress premature gas phase reaction between the metal alkyl and the group VI hydride, was not used here since DMZn and DiPTe can be mixed without prereaction. This has the additional benefit of allowing good mixing of the precursors before reaching the heated substrate.

### 3. RESULTS AND DISCUSSION

#### 3.1 Optimization of the Growth Temperature

Figure 1 shows the variation of the growth rate (Gr) vs the growth temperature ( $T_g$ ). The usual dependence is seen whereby the three regimes can be distinguished. An increase in the Gr with increasing  $T_g$  up to around  $420^{\circ}\text{C}$  is brought about by the cracking efficiency of the DiPTe precursor. This is the so-called kinetic regime. The curve then levels off in the region between  $420^{\circ}\text{C}$  and  $450^{\circ}\text{C}$  with a maximum at about  $430^{\circ}\text{C}$ . In this region (diffusion controlled regime) the Gr is only a little dependent on  $T_g$  and is controlled by the rate of diffusion through the boundary layer. A third region where the curve falls off with a further increase in temperature beyond  $450^{\circ}\text{C}$  possibly results from re-evaporation of the absorbed species.

From the behaviour of the growth rate with respect to temperature,  $430^{\circ}\text{C}$  can be inferred as the optimum temperature where the growth rate is at its maximum. Investigation of the crystalline quality by x-ray rocking curves yielded a lowest FWHM



**Figure 1:**

Variations of the growth rate Vs  
the VI/II ratio

value of 369 arcsec at 420°C suggesting therefore that this temperature to be the optimum. However, this temperature lies on the edge of the diffusion controlled regime which is sought for obtaining high quality layers.

Therefore, 430°C was selected as the optimum temperature for the rest of the growth experiments. The x-ray FWHM value of 369 arcsec is high. Nevertheless, this can be related to the low VI/II ratio (0.5) employed when investigating the effects of the substrate temperature. Much lower values, comparable to the best MBE material [1], were obtained when optimizing the VI/II ratio.

High growth temperatures are undesirable since they are known to induce high densities of structural defects which affect the electrical and optical properties. The temperature of 430°C is regarded as high when compared with temperatures used in MBE growths: typically in the region of 300°C - 325°C [1]. In MOCVD however; temperatures are generally higher, with the lowest of 350°C obtained by H P Wagner et al [2] for the growth of ZnTe at atmospheric pressure using DiPTe in conjunction with DEZn. The majority of the MOCVD ZnTe has been grown at low pressures using a combination of diethyl or dimethyl tellurium in conjunction with diethyl or dimethyl zinc [3,4,5]. Good layers were generally obtained at temperatures higher than 400°C. Other workers [6,7] have used precracked tellurium source to bring down the temperature to 350°C. Although in the present work the same tellurium precursor and pressure were used, a different temperature is obtained possibly because of the different zinc sources employed in the two projects. To reduce the growth temperature, alternative Te source could be used. Such source would be Diteritary-butyl tellurium ( $t\text{Bu}_2\text{Te}$ ) which has been employed to grow CdTe [8] and HgTe [9] at 250°C.



The surfaces of the deposited layers as studied by optical microscopy using the Normaski interference contrast, are characterised by two kinds of morphologies. The "orange peel" morphology for layers grown at temperatures below 400°C as shown in figure 2, and "ridged" morphology above 400°C as illustrated in figure 3. The last kind of surfaces show superior crystalline quality.

### 3.2 Optimization of the VI/II Ratio

Figure 4 illustrates the dependence of the crystalline quality as judged by the x-ray rocking curve FWHM, on the gas phase VI/II ratio. It can be seen that the x-ray FWHM decreases with increasing the VI/II ratio until reaching the lowest value of 210 arcsec at VI/II ratio of 4. There is then a further increase in FWHM with further increase in the VI/II ratio. A typical double crystal x-ray diffraction profile is shown in figure 5. The low value of ca 230 arcsec demonstrates the excellent crystalline quality which can be achieved by optimizing the preparation conditions. This value is comparable to the best of both MBE and LPMOCVD materials reported by Fiedman et al [1], where 200 - 225 arcsec was reported and by Shtrikman et al [4] who reported a value of 200 arcsec respectively. One of our layers, which was very thick (14  $\mu\text{m}$ ), has shown an unprecedented low value of only 102 arcsec suggesting the superb crystalline quality that can be grown away from the interface with the substrate.

With regard to the morphology of layers the surfaces have the "orange peel" texture for the VI/II ratios of 0.25 and 8 whilst for intermediate VI/II values ridged morphologies with tetragonal hillocks are obtained. The size of the hillocks was found to increase as the thickness of the layer increases resulting in rougher surfaces. Figure 6 illustrates such hillocks for a 14  $\mu\text{m}$  thick sample. These features are not characteristic of ZnTe. They do appear in other materials grown on (100) GaAs eg: ZnSe [10]. Other types of

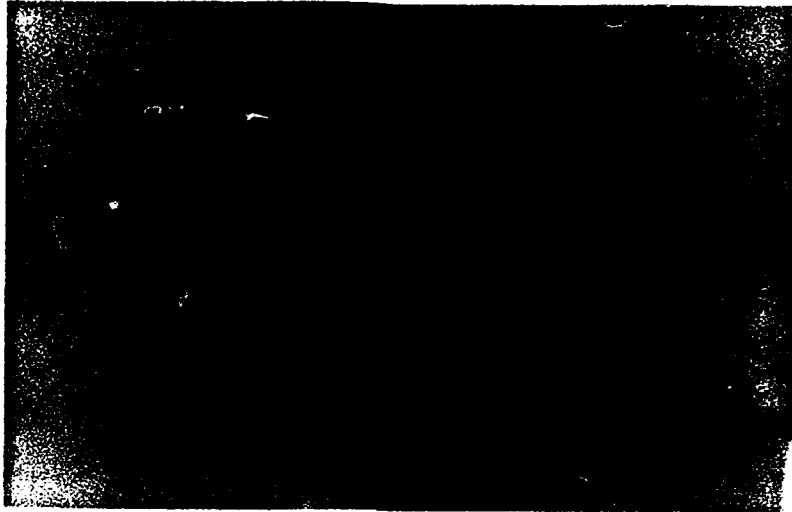


Figure 2:

"Orange Peel" morphology of samples  
grown at low temperature.

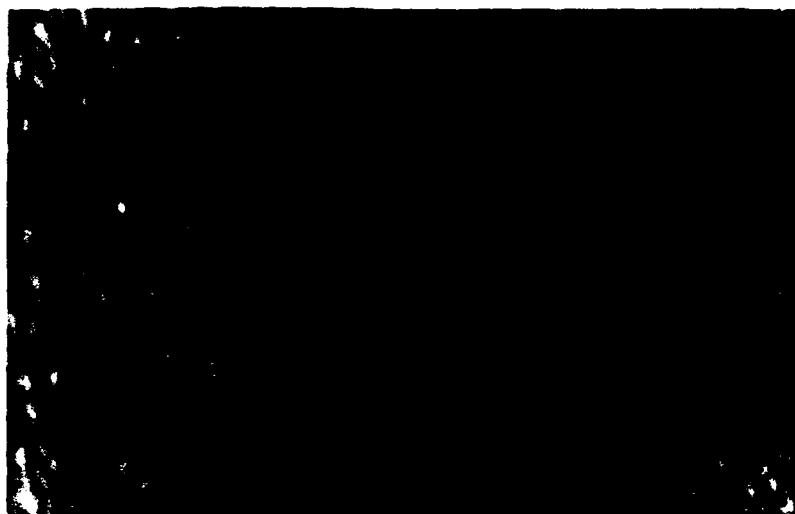
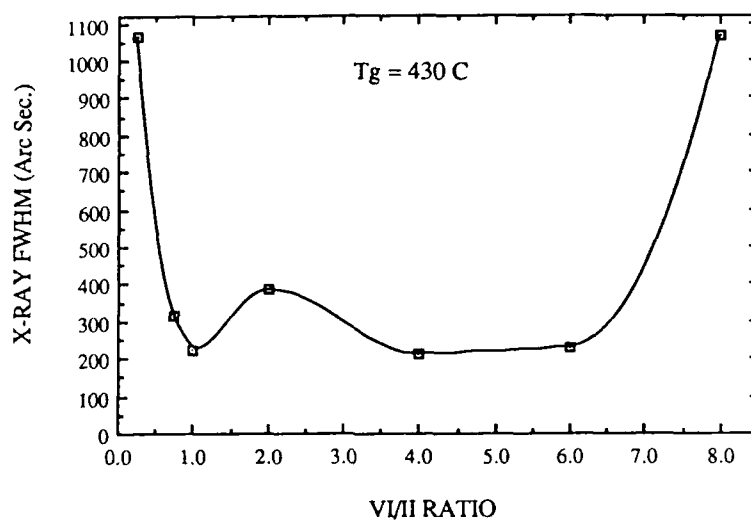
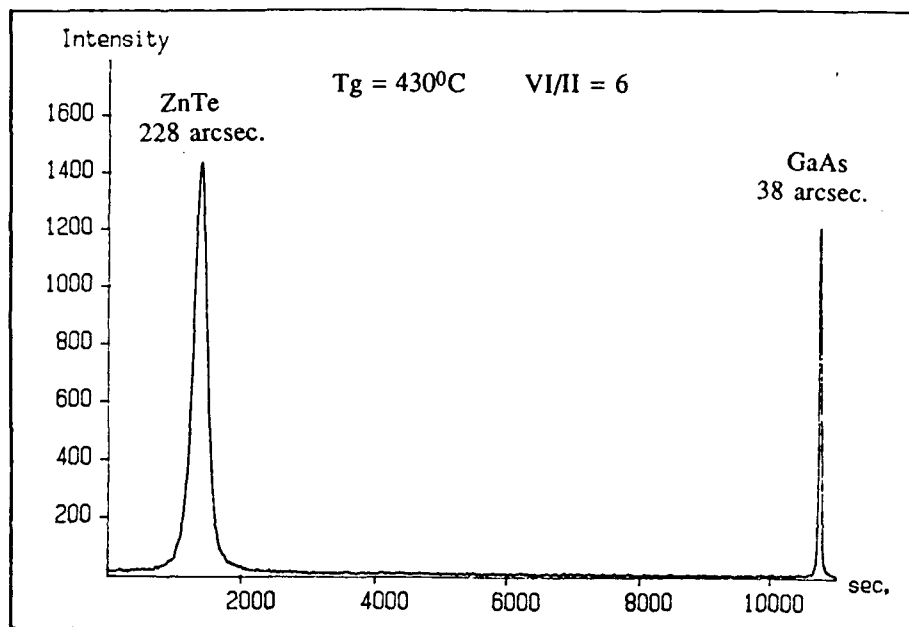


Figure 3:  
Typical morphology for samples  
grown at high temperature



**Figure 4:**  
Variations of the x-ray FWHM Vs  
the VI/II ratio



**Figure 5:**  
Typical x-ray rocking curve profile  
for samples grown on GaAs



**Figure 6:**

**Micrograph showing the hillocks type  
seen for samples grown at high temperature**

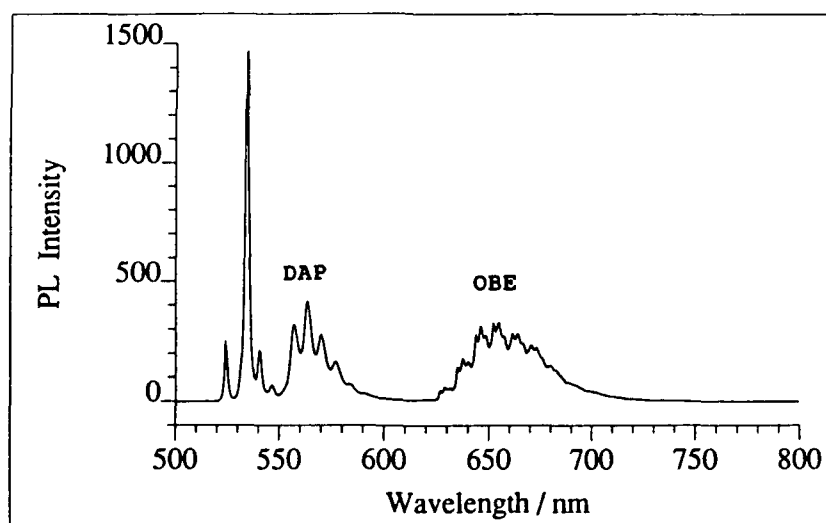
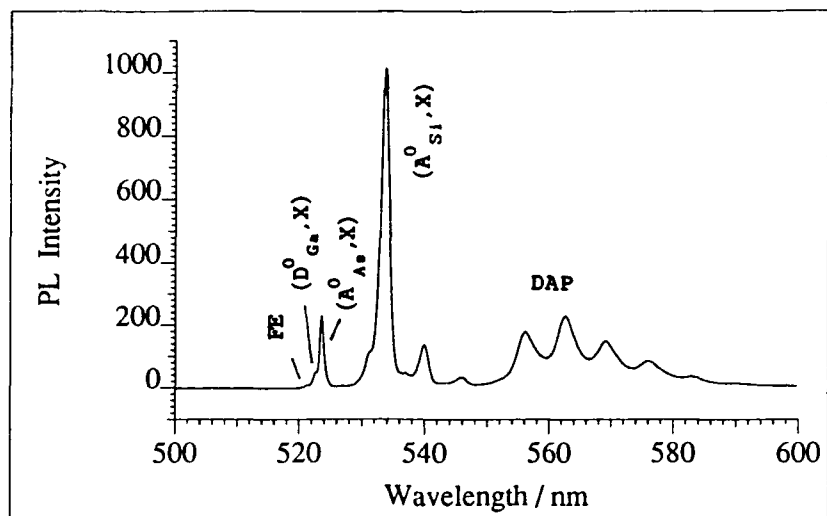
hillocks were also occasionally seen in some samples which are hexagonal in shape. From what has been mentioned above, it can be clearly established that the gas phase VI/II ratio of 4 is the optimum.

### 3.3 Photoluminescence

In this section the different emission peaks seen in low temperature PL will be discussed. The relation between growth parameters and the changes in PL features have been studied. To illustrate the changes, spectra recorded for different growth conditions are shown in figures 7, 8, 9, 10 and 11. The main PL features seen are:

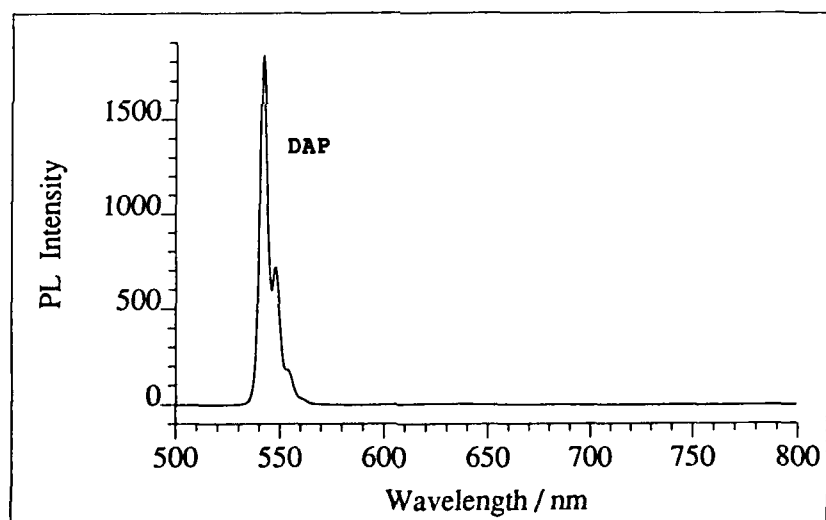
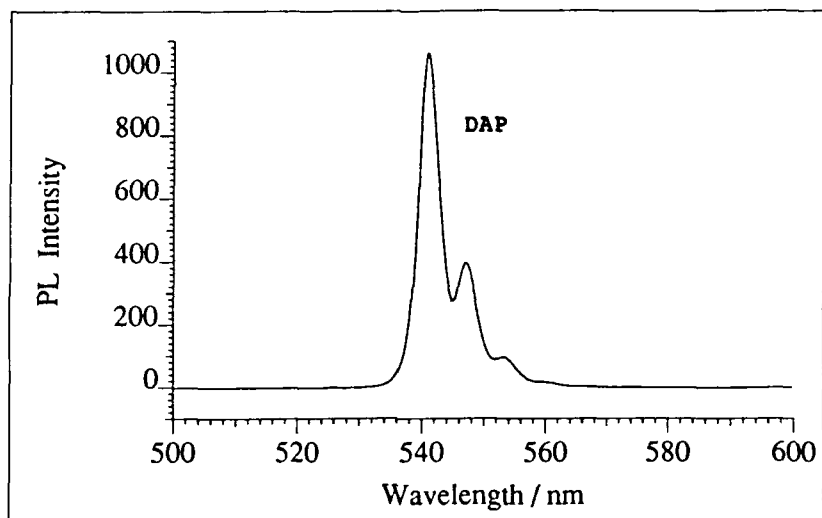
- A peak in the region of 2.379 eV is believed, as judged by its position, to be due to recombination of free excitons. Wagner et al [2] have reported the splitting of this excitonic peak into two peaks resulting from the strain induced by the mismatch in lattice parameters and linear expansion coefficients between the layer and the GaAs substrate. The other effect of the induced strain is the lowering of the band gap, with regards to the value for the bulk material, by a few meVs. Ekawa et al [6] estimated the shift to lower energy of the free exciton (FE) to be 4.4 meV.

The FE appears only in samples grown at temperatures in the region of 370°C to 450°C at a VI/II ratio of 0.5. At extreme values of VI/II ratio the emission is seen only as a shoulder to a lower energy peak. Similarly when keeping the growth temperature at 430°C and changing the VI/II ratio this feature was found to be present only for VI/II ratios ranging from 0.5 to 6, though it appears as a shoulder in some cases.

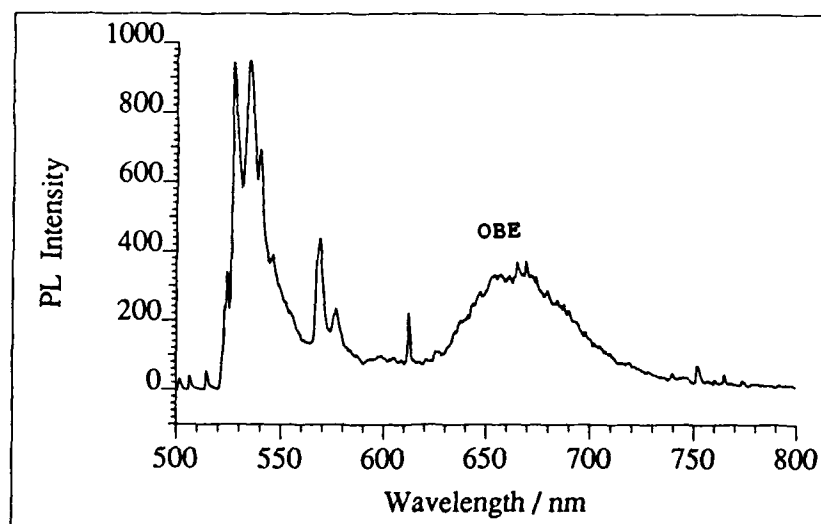
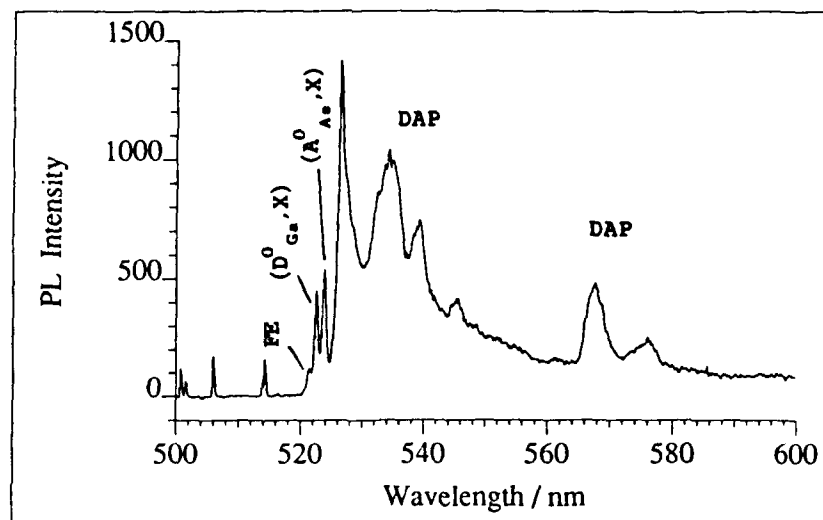


**Figure 7:**  
PL Spectra of a sample grown at  
370°C and a VI/II = 0.5



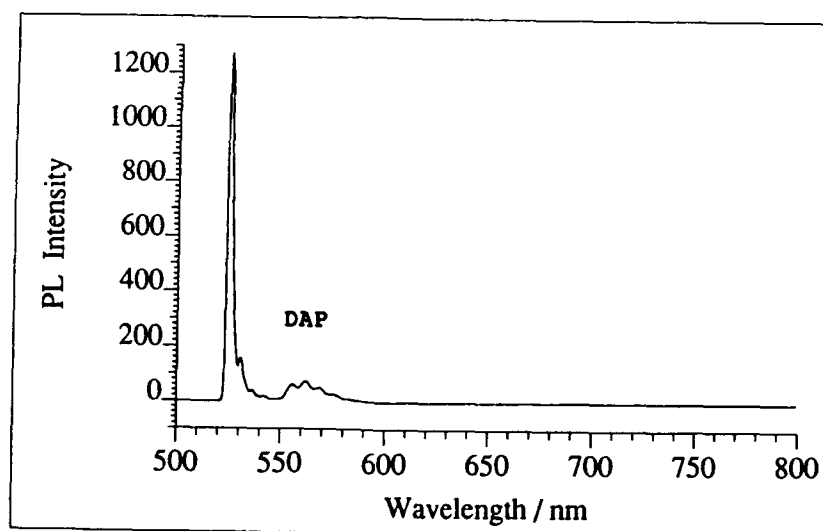
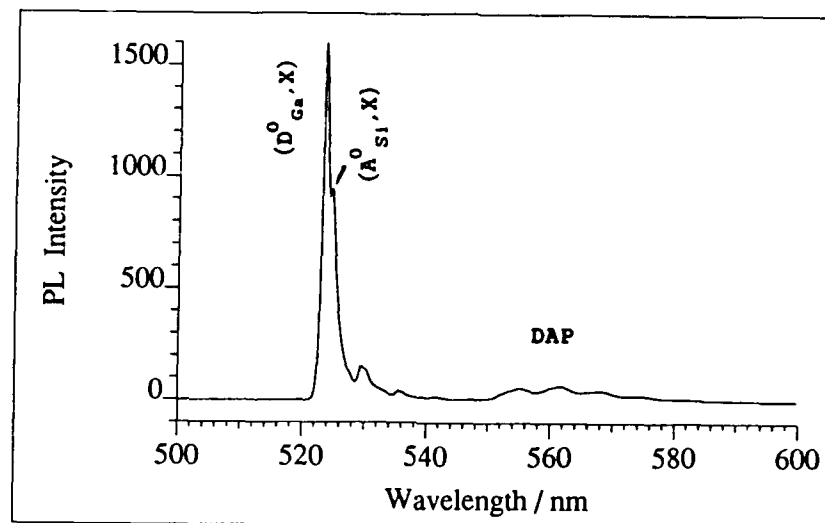


**Figure 8:**  
PL Spectra of a sample grown at  
470°C and a VI/II = 0.5



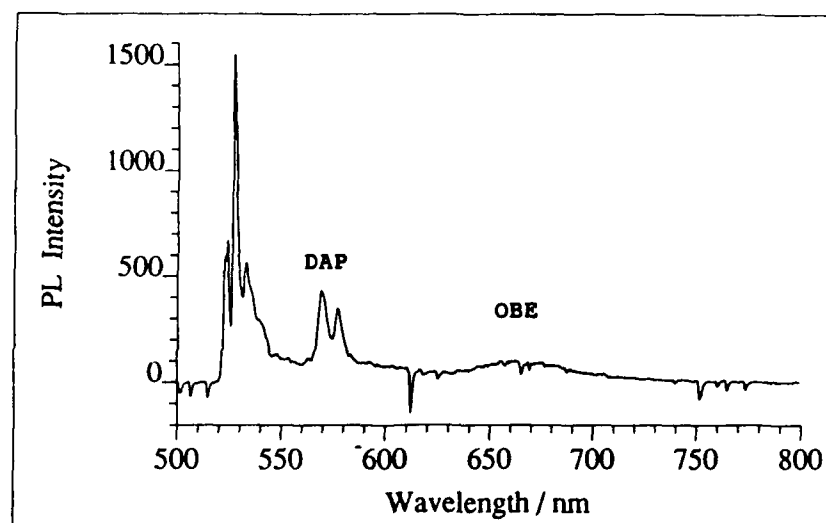
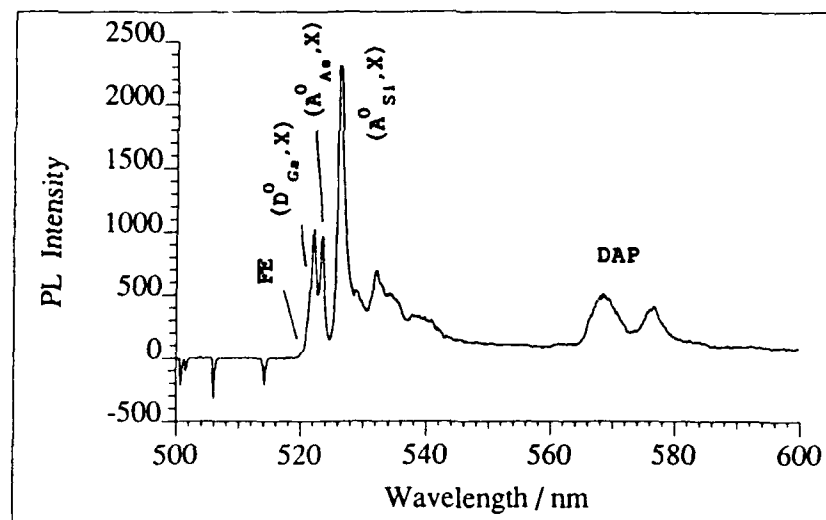
**Figure 9:**

PL Spectra of a sample grown at 430°C and a VI/II = 4



**Figure 10:**

PL Spectra of a sample grown at  
430°C and a VI/II = 4, heat treated substrate



**Figure 11:**

PL Spectra of a sample grown at  
430°C and a VI/II = 4, thick layer (14  $\mu\text{m}$ )

- At slightly lower energy than the free exciton emission there appears a peak in the vicinity of 2.3723 eV. It is possibly an exciton bound to a neutral donor (DBE) and could correspond to Ga outdiffusing from the substrate. This emission has been reported by Wagner et al [2] and ascribed to gallium. This was suggested from its clear increase in intensity when the material was doped with Ga. In our experiments, it was found that the intensity ratio of this peak to the free exciton increases as the growth temperature is increased from 420°C to 450°C. Such an increase would be expected if the impurity is coming from the substrate. The diffusion process is known to be enhanced by higher temperatures. Also samples grown on substrates which were heated to temperatures above 500°C for more than 15 minutes before initiating the epitaxy, had spectra dominated by this peak. Such dominance can be predicted since heat treatment leads to a Ga rich GaAs surface as As is much more volatile than Ga. Subsequently, the latter element will find its way into the depositing layer. However, this assignment is far from conclusive. The sudden disappearance of the peak at high temperature together with its undoubted appearance for a thick layer (14  $\mu\text{m}$ ) clearly mitigates against the previous assignment. Other plausible sources of contamination are the organometallics. It has been shown in recent years [11], that the  $I_2$  line seen in the PL of MOCVD ZnSe resulted from halogen species such as Cl and I. These impurities remain from the preparation procedure of these organometallics despite the rigorous purification processes applied.
- In the region of 2.3682 eV appears another, generally sharp, line. This, has been interpreted by Wagner et al [2] as an exciton bound to a neutral acceptor believed to be As originating from the substrate. Ekawa et al [7] has also reported it to be an acceptor-bound exciton (ABE), while Wilson et al [12] attributed it to a zinc vacancy complex. In the present experiments, the line was found to be

persistent in most of the layers (even in the thick layer) and heat treated substrate samples. However, it is absent in some samples grown at temperatures above 450°C.

- Another sharp emission also appears at around 2.356 eV. It has been suggested by Wagner et al [2], based on the assignment given by Dean et al [13], to be an acceptor bound exciton associated with silicon on Te site. The source of the silicon is likely to be the DiPTe source. Inductively Coupled Plasma Emission Spectroscopy (ICPES) shows Si (0.05 ppm) to be the only element detected in our DiPTe. The behaviour of this peak with the VI/II ratio makes this assignment plausible. It increases in its intensity relative to the free exciton as the VI/II ratio is increased and becomes dominant at ratios of 2, 4 and 6. This however, could also mean that the involved impurity substitutes for zinc rather than tellurium which is still consistent with the above assignment. With respect to the substrate temperature, the peak appears only in samples grown in the region of 420°C to 450°C owing possibly to the low VI/II ratio of 0.5 and the relatively high temperatures at which the DiPTe is fully cracked.
- At around 2.298 eV appears a band followed by replications with decreasing intensity. Their positions are separated by a gap of about 26 meV corresponding to the optical phonon in ZnTe [12]. These bands are persistent in all layers and dominant at temperatures higher than 420°C and for the VI/II ratios of 0.25 and 8. Their dominance seems to be at conditions where the emission at 2.3723 eV is weak or undetected suggesting, therefore, that the same impurity is involved in both transitions. Depending on the surrounding medium, the latter impurity contributes to the DAP emission and/or to the BE emission. Wagner et al [2] has

attributed these bands (in this case it is at a slightly higher energy viz ? 3058 eV) to DAP transitions between the Ga donor and the As acceptor.

- Another series of bands is also seen in the region of 2.254 eV to 2.137 eV. Ekawa et al [6] has reported such series and attributed it to a DAP emission. It is believed to be due to recombination between the Cu acceptor and the Cl donor [Ogawa 1989 + ref therein]. This emission is found to be weak in intensity for samples grown at high temperatures (450°C and above) but persistent in all the other samples.
- At low energies a broad emission band is seen around 2 eV for thin layers of about 1  $\mu\text{m}$  and centred around 1.88 eV for thicker layers. This band is known to be due to the isoelectronic Oxygen substituting for Te [14, 15]. In the present experiments it is found to be relatively intense when the specimens are grown at relatively lower temperatures and weak or unseen when the VI/II ratio is 6 or 8. It can be explained by the occupancy of  $V_{\text{Te}}$  by oxygen. At lower temperatures, the cracking efficiency of DiPTe is low leading to a material deficient in Te while at higher temperatures enough Te is available to reduce the vacancy concentration.

As regard the origin of oxygen, two plausible sources are possible viz the oxide layer at the interface and the organometallic precursors where diethylether was used in its preparation. The former source is the very likely origin since it has been found that the oxygen band is virtually unseen in heat treated substrate samples, and weak in thick ZnTe layers. This last specimen is too thick (14  $\mu\text{m}$ ) to expect any diffusion from the interface.

An additional source is also worth mentioning, though it is unlikely. This is the susceptor. The current susceptor is made of carbon and completely coated with silicon carbide except for a hole reserved for housing the thermocouple tube. This uncoated region may behave like a sponge in holding water left from the cleaning procedure and then slowly releasing it during the growth. It has been confirmed by mass spectrometry that water remains even after backing the susceptor for half a day [16] at elevated temperatures.

### 3.4 Electrical Properties

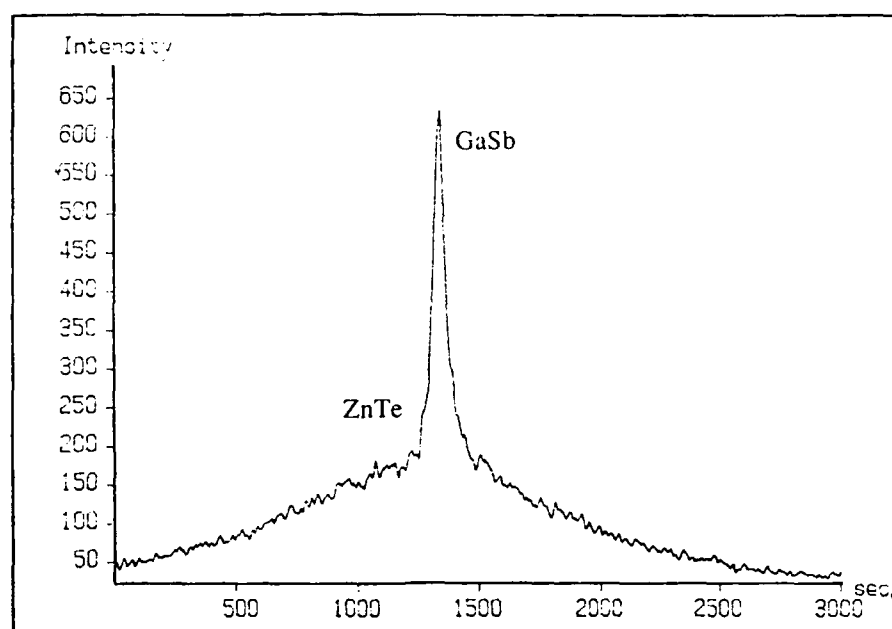
Electrical measurements were attempted on a few layers. The gold contacts were deposited by vacuum evaporation, then annealed at 310°C for 30 minutes. They were found to be either highly resistive or rectifying in most cases. However, one of the samples was found to be of relatively low resistance with nearly ohmic contacts. Measurements performed at room temperature on this latter sample has yielded a p-type material with a resistivity of 2.41  $\Omega\text{-Cm}$ , a mobility of 68  $\text{Cm}^2/\text{Vs}$  and a carrier concentration of  $3.82 \times 10^{16} \text{ Cm}^{-3}$ .

Judging from our experiences, the electrical properties are difficult to measure. This can only be ultimately achieved through success in finding a reliable way of routinely making ohmic contacts. Gold seems to offer such possibility providing the contacts are annealed at higher temperatures than those used in this work.



## 5. GROWTH ON GALLIUM ANTIMONIDE (GaSb)

Growth on the closely matched GaSb (0.15% mismatch) is expected to improve the crystal quality, the surface morphology and the abruptness of the interface; as well as reducing the substrate contamination. To seek such improvements, deposition on this substrate has been initiated. The adopted growth conditions are the ones optimized for the growth on GaAs. These are: a substrate temperature of 430°C and a gas phase VI/II ratio of 4. Although some of the conditions were optimized, the deposited material was not as good as the one obtained on GaAs owing to other conditions which were not optimized. In particular the pre-growth surface treatment of the substrate aimed at removing the oxide layer and hence starting the nucleation on a fresh surface is not yet satisfactory. GaSb has been known to oxidize readily [16]. Two different approaches have been used. By heat treatment at rather high temperatures > 500°C without chemical etching, and by heat treatment at lower temperatures after chemical etching and surface passivation. In both cases the surfaces obtained were very rough and the ZnTe crystal quality characterised by high values of the x-ray FWHM (>500 arcsec). A typical x-ray profile is shown in figure 12. The two peaks appear at nearly the same angle due to the small lattice mismatch in the ZnTe/GaSb system. The PL spectrum of a layer grown on heat treated surface without etching is shown in figure 13. The NBE spectrum (figure 13) is dominated by two broad features appearing in the region of 2.2907 eV and 2.151 eV. The latter feature is split into two peaks. The features are yet unidentified though Wagner et al [2] speculates that they are related to carbon impurities. The other emissions are a DAP series in the region of 2.238 eV, a peak at 2.3718 eV and another at a slightly lower energy of 2.358 eV. According to Wagner et al [2], the former peak is a DBE associated with Sb while the latter is associated with Si.



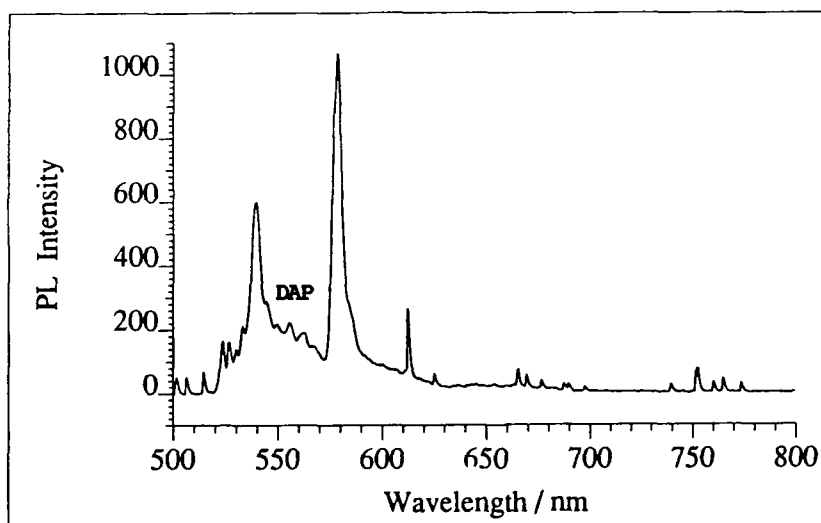
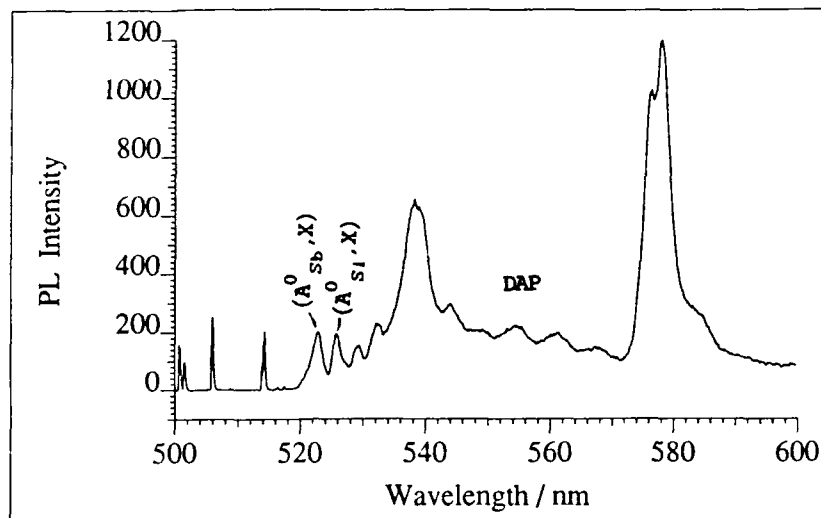
**Figure 12:**  
**X-Ray Profile of a sample grown on GaSb**

The large scan spectrum does not reveal any deep level emission associated with oxygen impurity.

## 5. CONCLUSIONS

The following conclusions can be drawn:

- (i) The growth temperature and the V/II gas phase ratio have been optimised for ZnTe epitaxy on GaAs by APMOCVD. These are: a  $T_g = 430^\circ\text{C}$  and a  $V/II = 4$ . Material prepared under these conditions was found to be of high crystalline quality, comparable to the one obtained by MBE, and of high purity as demonstrated by the presence of the free exciton transition in low temperature PL spectra.
- (ii) Assuming the PL assignment is correct, the GaAs substrate and the organometallics are the main origins of layer contamination.
- (iii) Electrical properties are yet to be investigated and cannot be measured until reliable ohmic contacts can be made.
- (iv) The growth of ZnTe on GaSb substrates was not successful due to difficulties with pre-growth surface treatment of the substrate. A satisfying way of removing the oxide layer is being investigated.



**Figure 13:**

PL Spectra of a sample grown at  
430°C and a VI/II = 4, on GaSb

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## APPENDIX I

In addition to work on the growth of ZnTe we have investigated the improvements in the quality of DEZn as an alternative precursor by growing ZnSe on Ga As substrates using H<sub>2</sub>Se as a source of selenium. The following abstract summarises our work in this area. It is our intention to employ improved DMZn and DEZn precursors in our future work on ZnTe.



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**Atmospheric Pressure Metal-Organic Chemical Vapour Deposition (APMOCVD) for the growth of ZnSe epilayers on (100)-GaAs substrates using diethyl zinc (DEZn) and hydrogen selenide ( $H_2Se$ ). A Study Involving Photoluminescence (PL).**

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#### Abstract

The preparation and purification of DEZn for the APMOCVD growth of zinc selenide will be described. Crystal growth data for epitaxial ZnSe where we have investigated the role of growth temperature ( $T_G$ ), VI/II ratio and growth rate ( $G_R$ ) will be presented. The role of these variables in modifying the photoluminescence (PL) spectra will be discussed.

PL spectra at 10 K have been analyzed in terms of assigned transitions for ZnSe as follows:  $E_x$  (free exciton (FE) at 2.8016 eV),  $I_2$ ,  $D^+X$  or DBE (donor bound exciton at 2.7976 eV),  $I_1^D$  or  $A^+X$  (acceptor bound exciton associated with an impurity at 2.7840 eV),  $I_v$  (acceptor bound exciton associated with intrinsic point or structural defects at 2.7777 eV),  $Y_0$  (emission related to an extended defect at 2.6050 eV). The relative ratios of certain emissions eg  $I_2/E_x$ ,  $Y_0/E_x$  have been determined and used to confirm assignments for  $I_2$  and  $Y_0$  in terms of donor (halogen) impurities and structural defects, respectively. Purification of DEZn leads to less contamination of ZnSe by halogen impurities. Impurity incorporation reduces both with increasing  $T_G$  and VI/II ratio indicating that it is controlled by the sticking coefficient in the former case and by occupancy of selenium vacancies in the latter instance. Additional supporting evidence will be presented.