Heterostructure of binaries II-VI semiconductors ZnTe and ZnSe / III-V (GaAs, InP, GaSb)

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Abstract - Epitaxial ZnSe, ZnTe and multilayers have been grown on III-V (InP, GaAs and GaSb) substrates by organometallic vapor phase epitaxy. First, the OMVPE growth technique used is described. The microstructural quality of the epilayers was determined by SEM (EDX) and X-Ray diffraction. Mechanical strain, due firstly to a mismatch between II-VI layers and III-V substrates and secondly to different thermal expansion coefficients is studied. Reflectivity and photoluminescence spectra are presented for one type of material. Growth parameters are identified and problems associated to experimental conditions are discussed.

Introduction

Zinc selenide and zinc telluride have been considered as promising materials for application in diodes emitting devices because of their direct band gap at room temperature (1). In conjunction with other semiconductors visible lasers, high speed devices and tunable visible detectors could be produced. The main interest now in this research is to obtain low resistivity p-type materials. Low temperature processes to produce II-VI epilayers have been recently investigated : Molecular Beam Epitaxy (2-5), Hot Wall Epitaxy (4) and Organometallic Vapor Phase Epitaxy (6,7). OMVPE is an attractive technique because it is the most suitable for large scale applications (production as well as high quality epilayer).

For this reason the growth and doping of zinc chalcogenide by OMVPE method should be considered. Moreover, in order to obtain information on the stresses (and associated strains) it is of interest to study the misfit dislocations in the layers. Up to now, gallium arsenide substrates have been the mainly used substrate for the growth of these semiconductors (8). However epilayer quality is dependent of the lattice-matching and the thermal expansion coefficient difference of the two materials.

This paper presents some results regarding the growth of ZnSe and ZnTe on InP(001), GaSb(001), GaAs (001) and alternative ZnSe / ZnTe / InP (001) structures. State of strain is studied by means of X-Ray diffraction and optical methods such reflectivity and photoluminescence.

Experiments

ZnSe and ZnTe is grown by OMVPE at atmospheric pressure in horizontal reactor with graphite susceptor heated by a high frequency heater. The reactant carrier gas flow is controlled by an idle / vent / run switching manifold. The flows are switched under pressure balanced conditions. Reactants are transported through the injector tube inside the reactor and gas flows are tangential to the substrate. Dimethylzinc (DMZn), Diethylselenium (DESe) and Diisopropyltelluride (DiPTe) are used as organometallic sources in hydrogen gas flow. Exhaust fluxes are completely destroyed by a chemical process. The DMZn, DESe and DiPTe sources are maintained at -7, 15 and 40°C respectively. The hydrogen gas flux carries

precursors through bubblers, it is controlled in order to obtain the appropriate partial pressure, given by the relation : $P_{r,i} = P_i^0 / P_T \cdot d_{T,i} / D_T$; where $P_{r,i}$ is the partial pressure of the i -precursor, $d_{T,i}$ hydrogen flow that carries the precursor i through the i -bubbler, P_i^0 is the vapor pressure of the i precursor at T_i and P_T, D_T are the total pressure and flows in the reactor.

Table I : Growth conditions

	T_G (°C)	P_1^0 (10^{-4} atm)	P_2^0 (10^{-4} atm)	P_3^0 (10^{-4} atm)	D_T (l/mm)	V_G ($\mu\text{m/h}$)	LM (%)
ZnSe/InP(100)	530	11		5.7	2	12	+3.8
ZnTe/InP(100)	340-400		10.7	5.7	2	0.6-2.5	+4
ZnTe/GaSb(100)	340-400		10.7	5.7	2	0.6-5	+0.1
ZnTe/GaAs(100)	350-400		10.7	5.7	2	0.6-3.3	+7

where T_{Gi} is the growth temperature, P_1^0 the partial pressure of DESe, P_2^0 the partial pressure of DiPte, P_3^0 the partial pressure of DMzn, D_T the hydrogen flux, V_G the growth rate and LM is the theoretical lattice mismatch between substrate and layer.

The InP(001), GaSb(001) and GaAs(001) substrates were cleaned by bromine methanol solution 1.5%, rinsed with methanol, deionised water, and dried with nitrogen. Before running the process, the substrates are then loaded inside the reactor and thermally etched at 550°C for ten minutes ; thermal etching is not suitable for InP substrates. Experimental conditions used for growth process of zinc selenide and zinc telluride thin films are listed in table I : ZnSe films are made at 530°C and ZnTe films in the temperature range 340°-400°C. In order to improve the crystalline quality of ZnTe layers, some of them are prepared on ZnTe buffer.

X-Ray characterization was performed using Cu K α radiation. ZnSe epilayers are characterized by a Philips simple diffractometer PW1380 type, with Ni filter or by double crystal X-Ray measurements. ZnTe epilayers are characterized by Siemens diffractometer U 8-006 type, with back monochromator. This study is performed in the Θ range corresponding to (004) crystallographic planes, at room temperature. It enables us to calculate with good precision the lattice parameter. As evidence of the crystalline quality we used the Full Width Half Maximum of the (004) line obtained with back the monochromator and by double crystal X-Ray experiments.

Results

Microstructural investigations

Simple X-ray diffraction pattern for two samples of ZnSe/InP of 2.2 μm and 0.5 μm thicknesses are presented in figure 1(a) and 1(b) respectively. In spite of large lattice mismatch ($\epsilon=+0.035$ for tensile), samples appear to be single layers oriented along the <001> axis. Figure 2 shows an example of good quality of ZnSe epilayers on InP(100) by double crystal X-Ray diffractions and the FWHM is found to be 195 arc sec. This result is in agreement with the other works concerning ZnSe epilayers on GaAs (8,9). Figure 3 shows the lattice constant versus layer thickness. Below the value of 0.5 μm , the lattice constant is smaller than the bulk. As the thickness increases, misfit dislocations appear, the strain is released and the layer is relaxed.

Fig.1(a) and 1(b). - X-ray diffraction pattern of ZnSe epilayer of a 2.2 μm and 0.5 μm thick respectively grown on InP(001)

Fig. 2.- DCXD pattern of a 2.0 μm thick ZnSe epilayer grown on InP(001)

X-Ray diffraction pattern of a ZnTe/InP(001) sample is presented in fig.4(a). The layer was grown at 400°C with buffer and arises as single crystalline and oriented along the $\langle 001 \rangle$ axis. The FWHM of the ZnTe line is found to be 104 arc sec suggesting a good crystallinity. The lattice parameter is found to be independent of the layer thickness and not far from the bulk value (fig. 5). This observation indicates the absence of strain in the layer.

Fig. 3.- Lattice constant vs thickness for ZnSe epilayer grown on InP(001).

Fig. 4 - X-ray diffraction pattern of ZnTe epilayers grown on InP substrate (a), GaSb substrate (b), GaAs substrate (c).

Fig. 5.- lattice constant of ZnTe epilayer on InP(001) vs thickness.

The growth of ZnTe epilayers on GaSb(100) is proved to be more difficult than on InP substrates and needed a good substrate preparation before deposition. Fig. 4(b) shows the diffractogram of one sample performed at 350°C. This result is in agreement with previous work (10). The lattice constants is measured and is independent of the thickness. This is in contradiction with some work indicating that relaxation of strains in ZnTe on GaSb is obtained for 4 μm thick layers (11).

The same experiment is realized with GaAs(001). Fig. 4(c) shows the diffractogram of a sample obtained at 350°C. Single crystalline layers oriented along (001) planes are successfully grown despite the large mismatch in lattice parameter. The ZnTe diffraction peak has a FWHM of about 150 arcsec.

By SEM observations on zinc telluride epilayers grown on InP, one can observe diamond shaped hillocks with few growth pits in places (Fig. 6). We present the surface of ZnTe/GaSb in which is possible to observe a rough surface with numerous features oriented along the same direction (fig. 7). This typical morphology of ZnTe layer grown on III-V substrates has already been observed by different authors (11,12).

Finally a multilayer structure ZnSe/ZnTe/InP(001) is prepared. The fig. 8 shows the X-Ray diffraction pattern corresponding to this structure. Both layers look oriented along the <001> axis with same quality as it has been shown previously.

Fig.6.- SEM observation of ZnTe surface of one sample grown on InP without buffer at 380°C.

Fig.7.- SEM observation of ZnTe surface of one sample grown on GaSb without buffer at 340°C.

Fig. 8.- X-Ray diffraction pattern of ZnSe/ZnTe alternative epilayer on InP(100) using the same deposition conditions.

Reflectivity and Photoluminescence measurements

Among the prepared samples we focused our physical work in a first step on ZnSe/InP layers. In the zinc blende structure, it is well known the strain due to lattice mismatch is given by equation (1) :

$$(1) \epsilon = \epsilon_{xx} = \epsilon_{yy} = (a - a_{\text{ZnSe}}) / a_{\text{ZnSe}}$$

where ϵ is defined as negative (or positive) for compressive (or tensile) strain, a_{ZnSe} and a are lattice constant of bulk ZnSe and that of epilayer along the layer surface, respectively. The energy splitting between the heavily and light hole bands is given by

$$(2) \Delta E_s = \Delta E_{hh} - \Delta E_{lh} = 5.117 \epsilon \text{ (meV)} \quad (13,14).$$

The experimental values of splitting of excitonic transitions ΔE_s and the calculated values of strain from (1) are listed in table II as a function of thickness. For an hypothetical pseudomorphic epilayer (one or few epilayers) the epilayer is under tensile strain and the mismatch splitting would be $\Delta E_{ps} = 180 \text{ meV}$. For fully relaxed structure the splitting is due to thermoelastic strain. At 4.2K the value of thermoelastic strain is $\epsilon_{th} = 0.0029$ (15,17). The epilayer is also in tensile strain and the corresponding splitting is equal to 15 (meV). For all the epilayers investigated with reflectivity measurements (fig. 9) the values of splitting are closed to ΔE_{th} with a smaller value. Such a behavior reveals that epilayers are fully relaxed and that the thermoelastic strain is released by two dimensionnal stress of the substrate at the interface or to bending of the substrate (18, 19).

Table II : value of the energy splitting between the heavy E_{hh} and light E_{lh} hole bands and value of strain as a function of thickness

thickness (μm)	ΔE_{hh} (eV)	ΔE_{lh} (eV)	ΔE_s (meV)	ϵ (10^{-3})
0.45	2.8003	2.7885	11.8	60
0.50	2.8005	2.7899	10.6	54
1.55	2.8001	2.7914	8.7	44
2.2	2.8020	2.7950	7.0	35

Fig.9.- Derivative curve of reflectivity spectra at 4.2K of ZnSe epilayers grown on InP(001) for different thickness above the band-gap edge. The minima correspond to energy transition.

Table III and fig. 10 presents the different results of luminescence measurements. Near the band edge, I_2 peak, usually attributed to a donor-bound-exciton (20,21) the chemical nature of which is not clear, was observed. This peak is not very intense in those samples. ZnSe/GaAs studies show that this peak is higher for lower growth temperature (21).

Table III : list of assigned PL transitions at 4.2K in ZnSe layers grown on (100) InP versus layer thickness

thickness (μm)	I'_2	I_2	I_1	I_v	DAP
2.1	2.794	2.789		2.776	
1.55		2.789	2.785	2.777	2.684
0.50		2.789			2.684
0.45		2.789	2.784	2.771	2.685

I'_2 was also noticed in 2.1 μm thickness epilayers, which is either due to an excited state of I_2 or a strain effect on I_2 . I_1 peak was seen in 0.45 μm -thick and 1.55 μm -thick epilayer. It is usually interpreted as an acceptor bound exciton. The presence at the same time of donors and acceptors is confirmed in most samples by donor to acceptor transition peak (DAP), at the same position observed in ZnSe/GaAs layers, this DAP is followed by a group of phonon replica, separated by 31 MeV. A I_v (22) peak at 2.77 eV due to vacancy bound exciton was a recurrent feature in our epilayers. Such a peak is characteristic of high temperature grown samples (at 400°) in ZnSe/GaAs. It disappears at lower temperature. At a longer distance from the band edge, samples presents some "Cu green" band around 2.220 eV and shallow acceptors around 1.940 eV.

Luminescence experiments show an important compensation factor in the epilayers, which is revealed by DAP. The presence of vacancies is another defect deduced from the I_v peak. This work is presently in progress.

Fig.10.- Photoluminescence spectra of ZnSe epilayers at 4.2K for different thickness

Conclusion

Using OMVPE technique we performed a large serie of ZnSe, ZnTe thin film samples on various III-V substrates. In order to determine experimental conditions for obtaining such structures as ZnSe/ZnTe and ZnSe/ZnSe_{1-x}Te_x we have studied the microstructural quality of the layers obtained. By means of X-Ray analysis we have confirmed the good quality of the samples. Moreover for the structure ZnSe/ZnTe/InP X-Ray studies has not revealed gradient concentration at the interface and it is an indication for a steep interface. These systems are currently under examination using SIMS and ESCA.

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