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Optimization of the structural and optical properties of ZnS epilayers grown on (100)GaAs by MOVPE

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Abstract

The crystalline and optical quality of ZnS epilayers grown on (100)GaAs by MOVPE was investigated by channeling-RBS, 10 K photoluminescence and absorption spectroscopy for different growth conditions. The measurements point out that the crystalline and optical quality of the epilayers strongly depends on the VI/II precursor vapor phase stoichiometry as well as on GaAs surface treatments before the growth. Optimized MOVPE growth conditions have been determined.

1. Introduction

The achievement of efficient UV and blue light emitting diodes and lasers is one of the major challenges of todays optoelectronics technology. The use of wide bandgap II–VI semiconducting compounds based heterostructures is considered a viable technological route to the realization of such devices. Among II–VI materials, ZnS is a potential candidate for applications to devices emitting in the UV and deep-blue spectral region, its room temperature bandgap energy being 3.75 eV. Several attempts have been reported in the literature to the growth of high quality ZnS epilayers by metalorganic vapor phase epitaxy (MOVPE) [1–4].

We have previously reported on the use of (t-Bu)SH in combination with Me_2Zn:Et_3N for the growth of ZnS epilayers [5], as the use of the Me_2Zn:Et_3N adduct in substitution of Et_2Zn or Me_2Zn successfully suppresses the occurrence of prereactions with (t-Bu)SH, even at atmospheric pressure conditions. In this work, we report on further results about the optimization of the structural and optical properties of ZnS epilayers grown on (100)GaAs substrates by these precursors. To this purpose ZnS/GaAs samples grown under different VI/II precursors molar flow ratios (MFRs) and in situ H_2 annealing conditions of the GaAs substrates were studied by Rutherford backscattering spectrometry (RBS) in channeling conditions, low temperature photoluminescence (PL) and absorption spectroscopy. From the analysis of the present data we are able to determine the growth conditions which optimize the crystalline and optical quality of the ZnS epilayers.

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2. Experimental procedure

ZnS epilayers were grown on (100)GaAs in an Aixtron 200RD MOVPE reactor by using (t-Bu)SH and Me_2Zn:Et_3N as S and Zn precursors, respectively. Semi-insulating LEC-grown (100) $\pm$ 0.25° GaAs wafers were used as substrates. In order to study the influence of the substrate annealing temperature on the epilayer crystalline quality, a thermal treatment under H_2 flow was performed on the GaAs for about 30 min immediately before the growth. The temperature of the annealing process was varied in the range between 400°C and 600°C. The growth of the ZnS was performed at 304 mbar chamber pressure and 342°C. The relative transport rates between Me_2Zn:Et_3N and (t-Bu)SH were varied to achieve precursors MFRs ($F_{(t\text{-}Bu)SH}/F_{Me2Zn:Et3N}$) ranging between 1.0 and 5.2.

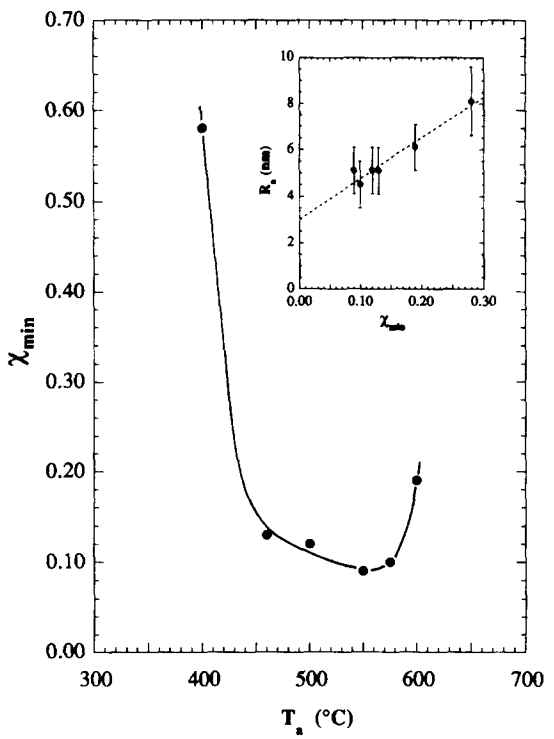

Fig. 1. Channeling minimum yield, χ_{min}, as a function of the GaAs substrate annealing temperature for samples grown under a precursors MFR of about 2.58. The average thickness of all the measured samples is 882 $\pm$ 32 nm. In the inset, the ZnS surface average roughness measured for the same samples is also reported as a function of χ_{min}.

More details about growth and surface preparation have been reported elsewhere [5].

The structural characterization of the ZnS epilayers was performed by ion channeling-RBS measurements at the Laboratori Nazionali di Legnaro (Italy). To this purpose, $^4He^+$ beams of 2 and 3.5 MeV energy were used as primary ion beams. A quantitative evaluation of the ZnS epilayer surface average roughness, R_a, was obtained routinely for all samples by using a surface profiler, having a vertical resolution of 0.5 nm and a lateral resolution of about 40 nm.

Absorption measurements were performed at 10 K in the near-band-edge region of the ZnS epilayers. To this purpose, a $\sim$ 100 μm diameter pin-hole was obtained by partly removing the GaAs substrate from the back of each sample, following the procedure described elsewhere [6]. The light of a 1 kW Xe lamp was thus focused onto the sample, the transmitted beam being dispersed by a 0.85 m double monochromator and finally detected by a cooled GaAs photomultiplier tube. The overall spectral resolution of the measurements was always better than 0.5 meV. PL measurements were performed at 10 K by using the ultraviolet line (1 W at 275.4 nm) of a large frame Ar^+ laser, using the same detection system as for the absorption measurements.

3. Results and discussion

RBS measurements were used throughout this work to assess the crystalline quality of ZnS epilayers. A certain appreciation of the surface crystalline quality of the ZnS is given by the ion channeling backscattering yield at the surface, normalized to the corresponding random yield, χ_{min}. In the case of high crystalline quality ZnS epilayers grown by H_2 transport vapor phase epitaxy, χ_{min} values around 5% were reported [7].

In Fig. 1 values of χ_{min} for a set of nominally identical ZnS epilayers grown under a precursors MFR = 2.58 are reported as a function of the GaAs substrate annealing temperature. All the RBS measurements were performed on ZnS/GaAs samples having an epilayer thickness of 882 $\pm$ 32 nm. The sharp decrease observed in the χ_{min} value with increasing annealing temperature indicates a strong

improvement in the crystalline quality of the ZnS epilayer. Indeed, a minimum value of about 9% is reached in a fairly broad temperature range centered at around 550°C. In this respect, preliminary SIMS measurements performed on ZnS/GaAs samples have shown that oxygen occurs at the heterostructure interface, indicating that residual oxides are still present on the GaAs surface after annealing at 460°C or below. Such oxides can well account for the worse crystalline quality of ZnS epilayers grown on substrates annealed below 500°C. The present data suggest that an annealing temperature of at least 550°C is necessary to desorb the oxide layer from the GaAs surface. However, the RBS results shown in Fig. 1 indicate that a further increase of the annealing temperature above about 580°C causes a rapid deterioration of the epilayer crystalline quality. Noteworthy, such a temperature value coincides fairly well with the onset temperature of non-congruent evaporation of GaAs.

Values of R_a of ZnS epilayers grown on substrates annealed at different temperatures are reported in the inset of Fig. 1 as a function of the χ_{min} values. It appears that a direct proportionality exists between these two quantities. As profilometry measurements have shown that the GaAs surface roughness does not change with the annealing temperature, the data shown in the inset of Fig. 1 strongly points out that the ZnS surface roughness is strictly related to the amount of surface defects occurring into the epilayers. Hence both the crystalline and surface morphological quality of the ZnS epilayers can be optimized by a careful selection of the GaAs annealing temperature. In the following an optimized annealing temperature of 550°C will be assumed for all samples.

In order to determine the best stoichiometric conditions for the growth of good crystalline and optical quality ZnS epilayers, several ZnS/GaAs samples were grown under different precursors MFRs. In Fig. 2 the χ_{min} values of these epilayers are reported as a function of the MFR. The epilayer χ_{min} monotonically decreases with increasing the VI/II precursors ratio in the vapor phase until a constant value at around 10% is reached for MFRs above ~ 2.0. In this respect, although no apparent improvement of the epilayer crystalline quality can be detected by RBS measurements, preliminary X-ray diffraction

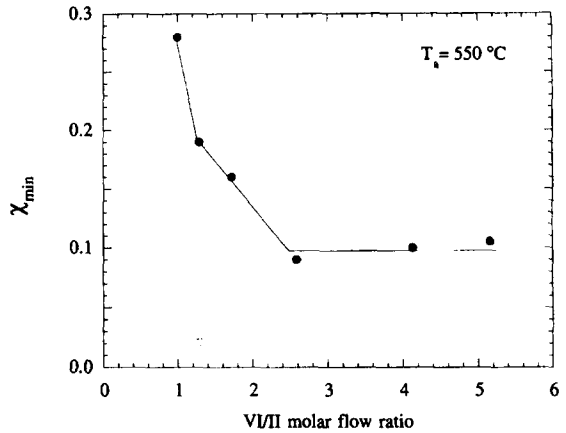

Fig. 2. Channeling minimum yield as a function of the precursors MFR. The samples were grown on GaAs substrates annealed at 550°C. The average thickness of all the samples is 882 ± 32 nm.

measurements performed on the same samples have shown that the ZnS crystalline quality still slightly improves by increasing the MFR above 2.0.

Systematic absorption and PL measurements performed on samples grown under different MFRs have shown that the best optical quality ZnS epilayers can be grown under MFRs larger than 4.0. In Fig. 3 curves (a) and (b) report typical PL and near-band-edge absorption spectra recorded at 10 K from a ZnS/GaAs sample grown under MFR = 4.47. In the PL spectrum the dominant feature is the peak at 3.7900 eV (I_2) which can be ascribed to a neutral donor bound exciton transition [8]. A weak peak (X) on the high energy side of the I_2 emission appears which can be identified with the ZnS light-hole (LH) free exciton transition, the heavy-hole (HH) contribution appearing as a faint shoulder on the high energy side of the X emission. These conclusions are supported by the analysis of the absorption spectrum where a sharp excitonic peak arises from both light-hole and heavy-hole excitonic resonance contributions, these resonances being energy splitted by a small residual strain in the layer. The line-shape fitting of absorption spectrum gives 3.797 and 3.802 eV for the energy positions of the LH and HH resonances, respectively. Furthermore, the onset of the continuum is clearly resolved at 3.840 eV along with a strong split-off resonance at around 3.868 eV, pointing out the very good optical quality of this

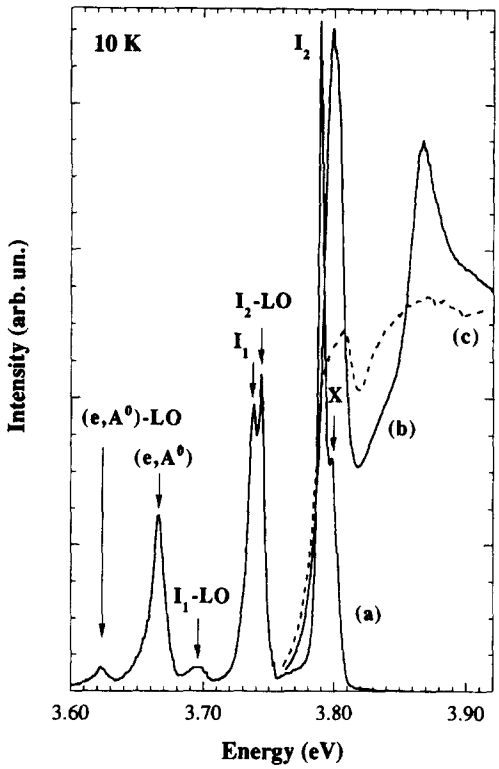

Fig. 3. PL (a) and absorption (b) spectra measured at 10 K for a 0.89 μm thick ZnS epilayer grown under MFR = 4.47 on a GaAs substrate annealed at 550°C. A typical absorption spectrum of a ZnS sample grown under MFR = 1.0 is also shown for comparison (c).

sample. In the PL spectrum two peaks appear at around 3.7435 eV (I_2-LO) and 3.7373 eV (I_1), the former being the LO phonon replica of the I_2 peak, whereas the latter can be ascribed to a neutral acceptor bound exciton emission, its LO phonon replica being observed at 3.6950 eV. Finally, a broad emission appears at 3.667 eV ((e, A^0) in the PL spectrum) ascribable to a free to bound acceptor transition [9], followed by its LO phonon replica at about 3.624 eV. For the sake of comparison, curve (c) in Fig. 3 reports the absorption spectrum recorded for a ZnS epilayer grown under MFR = 1.0, showing its poorer optical quality in comparison with the sample grown at MFR = 4.47 in agreement with the RBS results.

4. Conclusions

We have reported on the structural and optical characterization of ZnS/GaAs heterostructures grown by low pressure MOVPE. Despite the not excellent crystallographic quality of the present epilayers a very good optical quality can be achieved for samples growth under a precursor MFR $\geq$ 4.0 and for GaAs substrate annealing temperatures around 550°C.

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