ELSEVIER

Materials Science and Engineering B43 (1997) 97–101

MATERIALS SCIENCE & ENGINEERING B

Deep blue emitting ZnS/ZnSe multiple quantum well lasers grown by MOVPE on (001) GaAs

M. Mazzer[a,*], L. Calcagnile[b], G. Leo[a], G. Salviati[c], C. Zanotti-Fregonara[c], N. Lovergine[b], P. Prete[b], G. Imbriani[b], R. Cingolani[b], A.M. Mancini[b], F. Romanato[d], A.V. Drigo[d]

[a]*Istituto per lo studio di nuovi Materiali per l'Elettronica (IME), CNR Via Arnesano, 73100 Lecce, Italy*

[b]*Istituto Nazionale per la Fisica della Materia (INFM) and Dipartimento di Scienza dei Materiali, Università di Lecce, Via Arnesano, 73100 Lecce, Italy*

[c]*MASPEC-CNR, Via Chiavari 18, 43100 Parma, Italy*

[d]*Istituto Nazionale per la Fisica della Materia (INFM) and Dipartimento di Fisica 'G. Galilei', Università di Padova, Via Marzolo 8, 35131 Padova, Italy*

Abstract

The optimisation of ZnSe/ZnS multi-quantum-wells grown by metal–organic vapour phase epitaxy (MOVPE) for lasers was carried out with the help of structural and electro-optical characterisation techniques. Good-quality quantum wells were obtained using a lower growth temperature (315°C) with respect to the ZnS buffer layer (342°C). Although even the best samples contain a high density of microtwins crossing the active layer, the luminescence efficiency is quite good and the threshold for the stimulated emission at 10 K is as low as 170 kW cm^{-2}. © 1997 Elsevier Science S.A.

Keywords: Lasers; Multi-quantum wells; Molecular beam epitaxy

1. Introduction

ZnSe/ZnS multi-quantum-well (MQW) structures are quite attractive for many technological applications involving blue-green and deep blue lasers. Laser emission has been demonstrated at room temperature in ZnSe/ZnS superlattices grown by molecular beam epitaxy (MBE) [1]. Although the threshold carrier density is already comparable with what is found in similar III–V lasers, the problem of the short lifetime of II–VI lasers is still far from being solved. Laser degradation due to the generation and the propagation of failure defects originating from the pre-existing extended defects have been discussed by Guha et al. [2]. In particular, microtwins are observed in many II–VI layers grown on (001) GaAs [3]. Despite their importance for the device lifetime, the non-radiative recombination strength of twin boundaries can be quite modest, as discussed by Durose and Russel [4], causing a very small effect on the spontaneous luminescence efficiency.

In this paper, the structural and optical quality of ZnSe/ZnS MQWs grown by metal–organic chemical vapour deposition (MOCVD) are presented and discussed. The assessment of the structural quality of the samples was done by transmission electron microscopy and Rutherford backscattering spectrometry (RBS), while cathodoluminescence (CL) and photoluminescence (PL) were used to study the optical properties of the MQWs. The samples were grown with different combinations of growth temperatures and growth interruption times in order to maximise the uniformity of the MQWs and to minimise the density of extended defects.

2. Experimental

The ZnSe/ZnS MQW heterostructures were grown on (100) ± 0.25° oriented LEC-grown semi-insulating GaAs substrates by low-pressure metal–organic vapour phase epitaxy (MOVPE) in an Aixtron model AIX 200RD horizontal reactor. To this purpose, high-purity

* Corresponding author. Tel.: + 39 832 320233.

PII S0921-5107(96)01840-5

tertiarybuthyl-mercaptan [(t-Bu)SH], ditertiarybuthyl-selenide [$(t\text{-Bu})_2Se$] and dimethyl-zinc:triethyl-ammine ($Me_2Zn{:}Et_3N$) alkyls from Epichem were used as S, Se and Zn precursors, respectively [5,6]. The reactor total pressure was kept fixed at 304 mbar for all growth runs. Two different growth temperatures were used for the present samples (i.e., 315 or 342°C). Both ZnSe and ZnS compounds in the heterostructures where grown by using a VI/II alkyl molar flow ratio (MFR) of around 5.0 [7]. The MOVPE growth parameters of ZnS and ZnSe were chosen to obtain similar values of their growth rates, which remain almost unchanged when the temperature is varied between 342 and 315°C. More details on the GaAs substrate preparation and the growth of ZnS and ZnSe epilayers were reported elsewhere [5,7]. All ZnSe/ZnS MQWs were deposited on a 0.5 μm thick ZnS buffer layer, the latter being grown on a thin (2 nm) ZnSe epilayer directly deposited on the GaAs substrates. MQWs of 30 periods, having 1.3 nm thick ZnSe wells and 6.0 nm thick ZnS barriers were thus grown, followed by a 0.2 μm thick ZnS cap layer. Finally, growth interruption times (GITs), varying between 10 and 30 s, were adopted at the MQW interfaces to improve their sharpness and the MQWs optical quality.

For the TEM analysis, a JEOL 2000 FX machine was used. Bright-field and dark-field observations were done at 200 kV on $< 110 >$ oriented cross-sections prepared by mechanochemical thinning followed by low temperature Ar ion-milling on a Gatan 600 Duo-mill system.

Rutherford backscattering measurements were performed on the ZnS/ZnSe MQW by using 2 MeV $^4He^+$ beam, delivered from the AN2000 accelerator of Laboratori Nazionali di Legnaro (Italy). Computer simulations of the RBS spectra recorded in random geometry allow us to estimate the thickness of both the ZnS barrier and the ZnSe well with an error lower than 10%.

CL measurements were performed on a Cambridge Stereoscan 350 scanning electron microscope (SEM) fitted with an Oxford Instruments Mono-CL system at the CNR-MASPEC laboratory in Parma (Italy). Analysis were carried out both at room temperature and at liquid-nitrogen temperature, the electron beam energy being varied between 15 and 20 keV.

High-intensity emission measurements were carried out by using the third harmonic (355 nm) line of a Nd:YaG laser delivering 5 ns pulses at a repetition rate of 10 Hz. Investigations of stimulated emission were carried out in edge configuration, detecting the radiation emitted from a cleaved edge of the sample. Samples for stimulated emission measurements were reduced in form of cavities with average cavity length of 0.5 mm. The incident radiation was focused on the sample by using a cylindrical lens and its intensity was determined by using calibrated pinholes and by measuring the incident power. The radiation emitted from the sample was dispersed by a 0.45 m double monocroma-

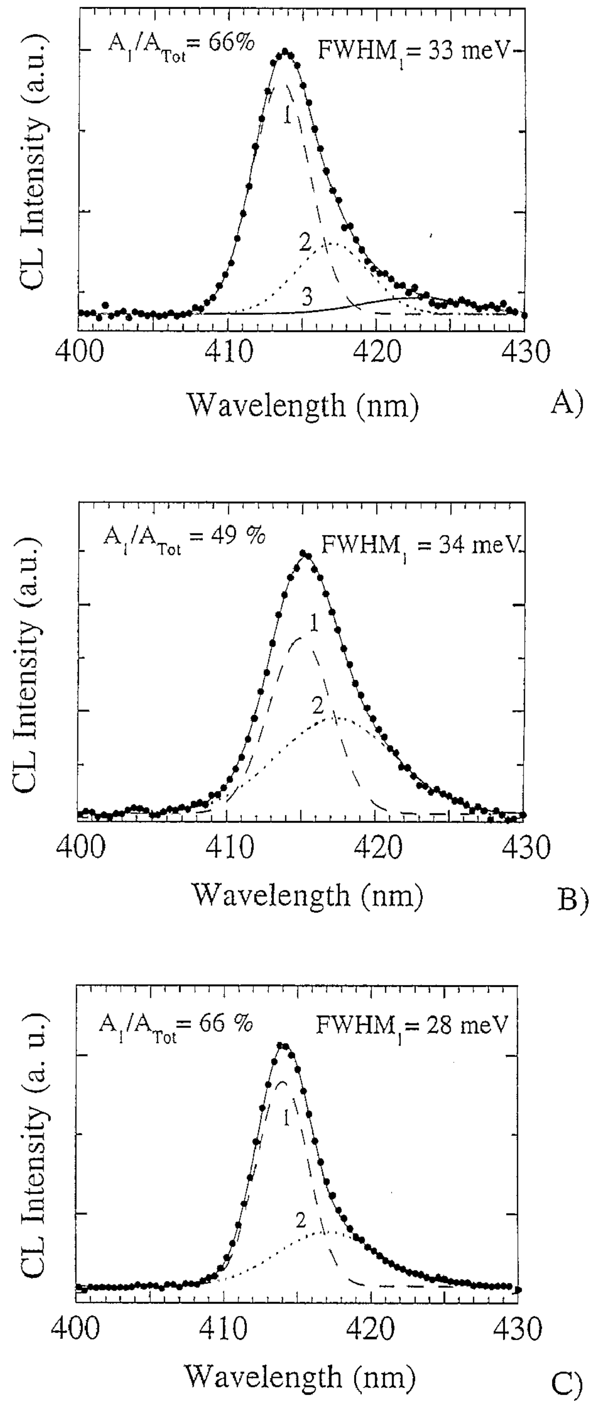
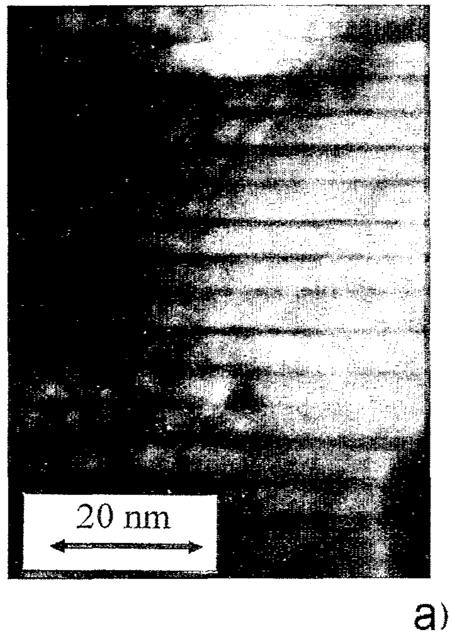


Fig. 1. CL spectra recorded at 10 K with a beam voltage of 10 kV and a beam current of 1 nA. The Gaussian peaks resulting from the deconvolution of each spectrum are labelled with increasing numbers. The full width at half maximum (FWHM) of the principal peak is reported on the graphs, together with the ratio between the area of the principal peak and the total area: (a) sample 1, (b) sample 2 and (c) sample 3.



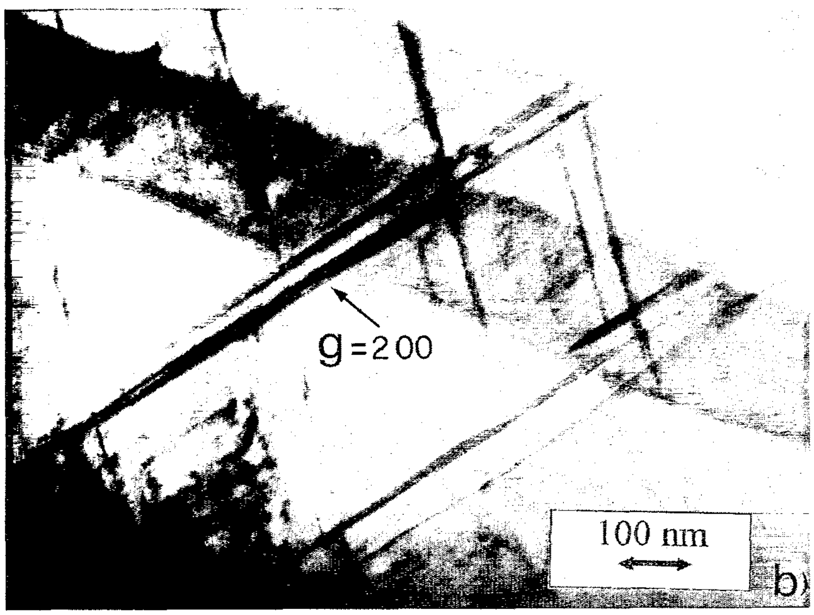


Fig. 2. TEM micrographs of sample 3 showing (a) a detail of the MQW structure, (b) twin boundaries propagating from the ZnS buffer layer (bottom), crossing the MQW and reaching the ZnS cap layer (top).

tor and detected by a GaAs photomultiplier in collection with a lock-in amplifier.

3. Results and discussion

In the following, the experimental results of the three most representative samples are presented and discussed. Samples 1 and 2 were grown at fixed temperatures of 342 and 315°C, respectively, while for sample 3, two different growth temperatures were used for the buffer layer and for the MQW (342 and 315°C, respectively).

Fig. 1 shows three CL spectra obtained at low magnification, the scanning area of the electron beam being 100×100 μm^2, in order to assess the quality of the samples over a significantly large area. The three spectra where collected at 10 K using the same beam voltage (10 kV) and beam current (1 nA). All the spectra are dominated by the free-exciton emission in the MQW even if the peak is asymmetric on its low energy side, due to exciton localisation at defects or impurities.

Sample 1 is clearly affected by two different problems. In fact, in addition to the presence of defects which are responsible for the shoulder just below the energy of the free-exciton emission, significant fluctuations of the thickness of the wells also occur. This is actually observed in monochromatic-CL and confirmed by TEM. To reduce the effect of thickness fluctuation, it is necessary to lower the growth temperature in order to reduce or suppress the formation of three-dimensional islands of ZnSe, which is expected to occur because of the high mismatch between ZnSe and ZnS. This is contrary to the requirement for a good-quality buffer layer. In fact, sample 2, where both the buffer layer and the MQW were grown at 315°C, appears to be good in terms of uniformity of the thickness of the wells, but the amount of defects crossing the MQW is much higher than in the case of sample 1. Sample 3 is a compromise between the two requirements, the buffer layer and the MQW being grown at 342 and 315°C, respectively, with a GIT at the MQW interfaces of 10 s. It is the best of a series of three samples which were grown with 20 s and 30 s interruption time, the differences in quality being relatively small compared with the improvement associated with the change in growth temperature. The density of defects in sample 3 is roughly the same as in sample 1 but the uniformity of the wells is now quite good, as shown in the TEM image in Fig. 2(a). The period of the MQW as measured from the TEM image is 6.0 nm. This value is in good agreement with the thickness of wells, t_w, and barriers, t_b, as measured by RBS over a much larger area of the sample (0.2 mm^2). To obtain the well and barrier thickness by RBS, the experimental spectrum

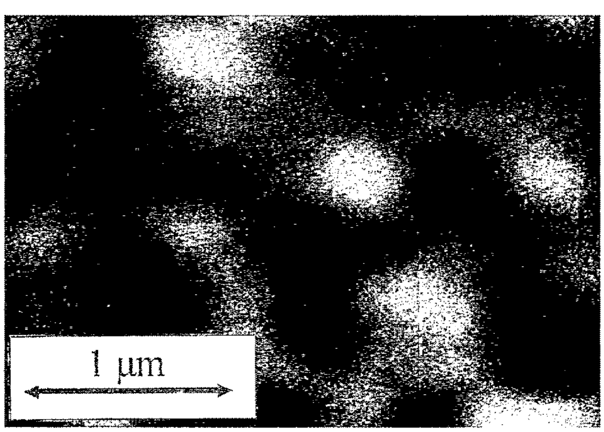


Fig. 3. Panchromatic CL image of sample 3 at 10 K showing non-radiative recombination at the microtwins.

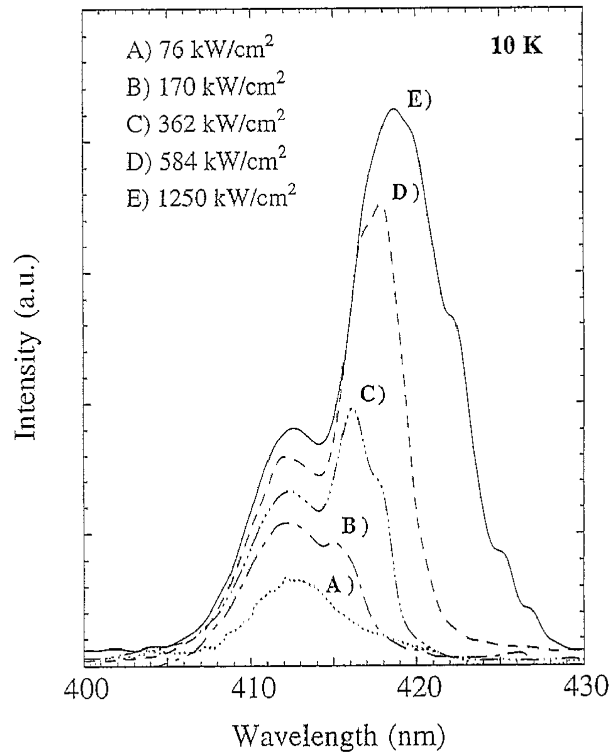


Fig. 4. Spontaneous and stimulated emission spectra of sample 3 at 10 K.

was simulated by treating the MQW as a single ternary ZnSSe layer having the same average Se content and the same thickness of the MQW. Then, given the number of periods in the MQW, the composition corresponding to the best simulation of the experimental spectrum was used to compute t_w and t_b, which turned out to be 5.4 ± 0.6 nm and 1.3 ± 0.2 nm, respectively.

The TEM micrograph in Fig. 2(b) shows the nature and the distribution of the defects in sample 3. Threading dislocations are confined within the ZnS buffer layer, while stacking disorder, mostly microtwins, propagates through the whole of the epitaxial structure. In particular, the MQW is crossed by a high density of twin boundaries which originate mostly at the interface between the buffer layer and the GaAs substrate. The effect of microtwins on the optical properties of the structure was studied by CL. Fig. 3 shows a panchromatic-CL image of sample 3 recorded at 10 K. It is important to note that not only is the CL-contrast due to the microtwins quite weak but the resolution is essentially controlled by the lateral dimension of the e–h pair generation volume. This means that the diffusion of the pairs generated by the electron beam is essentially negligible compared with the recombination time and that the recombination strength of the microtwins is quite low. As a consequence, the radiative recombination in the MQW is dominant in spite of the high density of defects.

Finally, Fig. 4 shows the stimulated emission in sample 3 at 10 K. The lasing threshold is found at a level of 170 kW cm^{-2} which is more then one order of magnitude lower than the threshold observed in sample 1. The stimulated peak emerges about 30 meV below the peak of the spontaneous emission and it tends to shift toward the red with increasing pumping power. Lasering is observed up to a temperature of about 200 K.

4. Conclusions

MOVPE-grown ZnSe/ZnS MQW structures have been optimised by eliminating the fluctuations in the thickness of the wells and by controlling the density of microtwins crossing the active region of the structure. The best results were obtained by growing the MQW at a lower temperature with respect to the ZnS buffer layer. High-efficiency luminescence due to free excitons was observed despite a high density of microtwins. This is due to the relatively low non-radiative recombination velocity associated with coherent twin boundaries. Stimulated emission was observed up to a temperature of 200 K, the threshold pumping power at 10K being 170 kW cm^{-2}.

References

[1] H. Wang, K.S. Wong, I.K. Sou and G.K.L. Wong, *Appl. Phys. Lett.*, *66* (1995) 3140.
[2] S. Guha, J.M. DePuydt, M.A. Haase, J. Qiu and H. Cheng, *Appl. Phys. Lett.*, *63* (1993) 3107.
[3] P.D. Brown, Y.Y. Loginov, W.Y. Stobbs and C.J. Humphreys, *Philos. Mag. A*, *72* (1995) 39.
[4] K. Durose and G.J. Russel, *Int. Phys. Conf. Ser.*, *87* (1987) 327.
[5] P. Prete, N. Lovergine, S. Oktik, M. Longo, R. Cingolani, A.M. Mancini and L. Vasanelli, *Proc. Int. Symp. Blue Laser and Light Emitting Diodes, Chiba, Japan, Mar. 5–7, 1996.*
[6] N. Lovergine, M. Longo, D. Manno, A.M. Mancini and L. Vasanelli, *J. Cryst. Growth*, *156* (1995) 45.
[7] G. Leo, N. Lovergine, P. Prete, M. Longo, R. Cingolani, A.M. Mancini, F. Romanato and A.V. Drigo, *J. Cryst. Growth*, *159* (1996) 144.