ELSEVIER

Journal of Crystal Growth 214/215 (2000) 1058–1063

JOURNAL OF CRYSTAL GROWTH

www.elsevier.nl/locate/jcrysgro

Full-color light-emitting diodes from ZnCdMgSe/ZnCdSe quantum well structures grown on InP substrates

M.C. Tamargo[a,*], W. Lin[a], S.P. Guo[a], Y. Guo[b], Y. Luo[a], Y.C. Chen[b]

[a]*Department of Chemistry, City College and Graduate School of the City University of New York, New York, NY 10031, USA*
[b]*Department of Physics, Hunter College and Graduate School of the City University of New York, New York, NY 10021, USA*

Abstract

We have grown p-type ZnCdMgSe quaternary layers and have fabricated light-emitting diodes (LEDs) from pseudomorphic quantum well (QW) structures of ZnCdSe/ZnCdMgSe grown on InP substrates that emit throughout the visible range. Nearly identical structures, differing only in the ZnCdSe QW layer thickness and/or composition can produce light ranging from blue to red. Good current–voltage characteristics are obtained from the diodes using p + ZnSeTe lattice matched to InP as the p-type contact layer. These structures have potential applications as integrated full-color display elements.

PACS: 42.55.Px; 72.80.Ey; 73.40.Lq; 78.60.Fi; 81.15.Hi

Keywords: Molecular beam epitaxy; Light-emitting diodes; II–VI semiconductors; Full-color displays; Electroluminescence

1. Introduction

Semiconductor lasers and light-emitting diodes (LED) that emit in the visible range have potential applications in full-color displays. In particular, high-definition and high-brightness display panels may benefit from semiconductor laser-based technology. Currently, full-color displays rely on different materials grown on different substrates as the three primary colors: red, green and blue (R–G–B). For example, room-temperature cw blue lasers made from GaN materials [1] have been reported, while green lasers are made from ZnSe-based materials on GaAs [2], and red lasers are available from GaP-based III–V materials [3]. In order to fabricate integrated systems, it is of interest to develop a single material grown on a single substrate that can be used for the full-color range. It would be difficult to combine the materials above into a single substrate for device integration. Thus, it is of interest to explore compatible materials that produce the three colors and that may be grown in high quality on a single substrate.

Wide bandgap (Zn, Cd, Mg)Se is a quaternary materials system that can be used in the design and fabrication of R–G–B full-color displays [4,5]. These layers can be grown lattice matched to InP substrates with a wide range of bandgaps, from 2.18 to ~3.2 eV. We have recently shown that by using ZnCdMgSe layers as cladding and waveguiding layers and a ZnCdSe layer as the active layer, we

* Corresponding author. Tel.: + 1-212-650-6147; fax: + 1-212-650-6848.

E-mail address: tamar@scisun.sci.ccny.cuny.edu (M.C. Tamargo).

PII: S0022-0248(00)00274-8

can design totally lattice matched or pseudomorphic laser structures with emission ranging throughout the entire visible range, from blue to red. R–G–B emission can be achieved from almost identical structures where only the quantum well (QW) thickness and/or composition are varied. Furthermore, we have shown that controlled and high-level n-type doping of the quaternary layers is possible with $ZnCl_2$ as the dopant source [6]. Levels above $10^{18}/cm^3$ were obtained in layers lattice matched to InP that have bandgaps as high as 2.8–2.9 eV, suitable for LED barrier layers. We also recently reported the controlled growth and doping of p + ZnSeTe layers lattice matched to InP [7]. These can be used as a p-type ohmic contact layer in the device structures.

In this paper, we will present new results in the p-type doping of the ZnCdMgSe quaternary materials. Moreover, we will utilize our earlier findings about heterostructure design and doping of the ZnCdMgSe layers and ZnSeTe grown on InP substrates to fabricate QW LEDs. We will present the growth and characterization of p–n junction LED structures that vary only in the thickness and/or composition of the QW layer and that exhibit electroluminescence (EL) emission throughout the visible range, a unique property, not currently available from any other single semiconductor materials system. Our results clearly demonstrate the potential for these materials in the fabrication of integrated full-color display elements and are the first step to fabricate R–G–B semiconductor lasers.

2. Experimental procedure

The layers were grown by molecular beam epitaxy (MBE) in a Riber 2300P MBE system consisting of two growth chambers connected by UHV, one for the growth of As-based III–V compounds and the other for wide bandgap II–VI materials. Solid source Zn, Cd, Mg, Se and Te as well as $ZnCl_2$ for doping are available for II–VI growth. A nitrogen RF plasma source (Oxford) is also included for p-type doping. Growth was performed on n + (0 0 1)InP substrates doped with sulfur. Prior to use, the substrates were degreased and etched as previously described [8]. Oxide desorption of the InP substrates was performed in the III–V chamber by heating to ~490°C with an As flux impinging on the InP surface. A lattice-matched InGaAs buffer layer (~0.1 μm) was grown and the substrate with the buffer layer was transferred to the II–VI chamber. Growth of the II–VI material was performed under Se-rich conditions with a VI/II beam equivalent pressure ratio of ~4. The growth was initiated at a low temperature of 170°C by growing a ~50 Å ZnCdSe interfacial layer. Then, the temperature was raised to the growth temperature of 270°C with a 4 min interruption, after which the desired structure was grown. This procedure has been shown in the past to produce high-quality quaternary layers [9].

Both single layers of nitrogen-doped ZnCdMgSe and p–n junction QW structures were grown. Single layers of various compositions were grown to achieve lattice-matched quaternaries of various bandgaps in the range of 2.3–2.7 eV. They were capped with a thin (50–100 Å) p-ZnCdSe cap layer to avoid oxidation due to the large Mg concentrations. For the device structures (see top of Fig. 2) a 1000 Å InGaAs buffer layer doped with Si to an n-type doping level of $10^{18}/cm^3$ was first grown on the InP substrate. This was followed by a ~50 Å ZnCdSe interfacial layer grown at low temperature (170°C). The n-type quaternary barrier layer has a nominal thickness of 0.5 μm and is doped with $ZnCl_2$ to a level of $5\times10^{17}/cm^3$. Its composition is such that it is lattice matched to the InP substrate and its bandgap is 2.9 eV. The quaternary is followed by a QW layer of ZnCdSe, and a p-type quaternary barrier layer of the same composition as the first. The thickness and the composition of the ZnCdSe QW were chosen according to the desired emission range. In the range from blue to yellow, the lattice-matched composition with a nominal bandgap of 2.2 eV was used. The emission range was tuned by changing the ZnCdSe QW thickness. In the red range, a lattice-mismatched (1.2%) ZnCdSe QW layer with a thickness of 100 Å was used. The p-type quaternary layer was grown only 1000 Å thick in order to minimize the device resistance. Finally, a top ZnSeTe p + layer was deposited. The thickness of this layer was varied between 1000 and 150 Å. The optimum value is 150–200 Å.

The devices [both for capacitance–voltage (C–V) measurements or LED testing] were fabricated by depositing either a Au or an In dot on the surface and attaching Au wires to the back n + InP substrate surface and the top metal contact. The size of the In dot varied while the Au dot was $\sim 0.3\ mm^2$. No post-growth annealing of the metal contact was performed. The single nitrogen-doped ZnCdMgSe layers were characterized by C–V measurements using a Keithley 590 CV Analyzer. Low-temperature photoluminescence (PL) at 77 K and (4 0 0) single-crystal X-ray diffraction were used to measure the layers bandgap and lattice constant, respectively. The I–V characteristics of the LEDs were measured with a Keithley 236 source unit. The surface EL emission of the diodes under pulsed operation at various current levels, was collected by a microscope objective and focused into an optical multi-channel analyzer to analyze the spectral characteristics of the device.

3. Results and discussion

Table 1 summarizes the materials properties for ZnCdMgSe layers and structures that we have reported in the past, and that are relevant to the design of LEDs. N-type doping concentrations of the ternary ZnCdSe and quaternary ZnCdMgSe lattice matched to InP have been demonstrated to be greater than 10^{18} carriers/cm^3 for layers with bandgaps up to 2.9 eV. We have also shown that low defect density quaternary layers and structures can be routinely achieved on InP substrates by growing a III–V buffer layer with a (2×4) As-termination, using a Zn irradiation of the III–V surface prior to II–VI layer growth, and initiating the growth at 170°C with a thin (~ 50 Å) ZnCdSe interfacial layer. Finally, the growth of lattice-matched p + ZnSeTe with hole concentrations in the 10^{19} carriers/cm^3 levels were also reported, making it possible to make p-type ohmic contacts to the lattice-matched device structures.

Table 1
Materials parameters relevant for LED fabrication of ZnCdMgSe structures lattice matched to InP

Bandgap emission range	2.0–3.0 eV
Defect densities	$< 5\times10^4/cm^2$
ZnCdMgSe n-type doping	$> 1\times10^{18}/cm^3$
ZnCdMgSe p-type doping	$\sim 1\times10^{16}/cm^3$
ZnSeTe p-type doping	$> 1\times10^{19}/cm^3$

In order to make diodes, the maximum p-type doping levels of the ZnCdMgSe layers was also explored. Fig. 1 shows the C–V plot for a quaternary layer of bandgap 2.5 eV that has a net acceptor concentration ($N_A - N_D$) of $\sim 7\times10^{15}/cm^3$. The layer is uniformly doped using a nitrogen plasma source as a source of nitrogen. The nitrogen plasma source was operated with an RF-discharge power of 400 W. It was necessary to use about one-half of the nitrogen flux used for maximum p-type doping of ZnSe in order to maintain a good crystalline quality as monitored by RHEED. Similar doping levels were obtained for all the samples regardless of the bandgap or doping conditions used.

Although only low p-type conductivity has been achieved, a p–n junction structure was designed and fabricated to investigate the electroluminescence from these materials. Three LED structures were grown with the different layer structure parameters given in Table 2. The principal parameter that varied in the structures was the QW thickness and/or composition. The QW thickness values given in Table 2 are nominal values based on measured growth rates of ZnCdSe thick layers and the growth times used for the QW growth. The lattice mismatch values ($\Delta a/a$) are obtained on thick (~ 1 μm) layers of ZnCdSe of the same composition

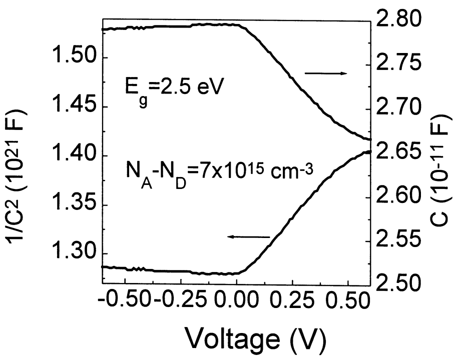

Fig. 1. Capacitance–voltage (C–V) plot for a ZnCdMgSe quaternary layer with bandgap of 2.5 eV doped with nitrogen. The $N_A - N_D$ level is $7\times10^{15}/cm^3$.

as the QW. The QW parameters used were selected in an attempt to obtain emission spanning a broad range of the visible spectrum. Table 2 also lists the EL properties of the three structures.

Fig. 2 shows the *I–V* characteristics of one of these diodes. Low turn-on voltages (<4 V), no reverse breakdown of the devices even at voltages below −10 V, and output currents of ~100 mA at 5 V were typically observed for these simple LED structures. Based on this *I–V* curve, the estimated device resistance is not substantially greater than that of commercial LEDs.

Table 2
Parameters for the three LED structures investigated

LED color	QW		EL (300 K)	
	$\Delta a/a$ (%)	Thickness (Å)	Energy (eV)	FWHM (meV)
Blue–green	< 0.2	20	2.385	78
Yellow	< 0.2	60	2.244	70
Red	1.2	100	1.967	90

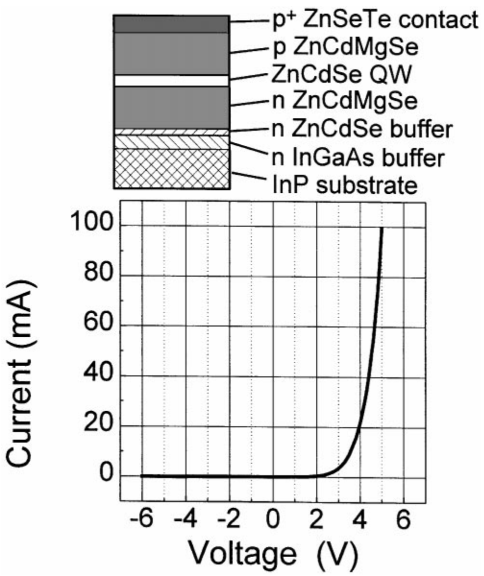

Fig. 2. Current–voltage (*I–V*) characteristics of a ZnCdMgSe-based LED structure. The top contact is a Au dot (~ 0.3 mm^2). The top shows a schematic of the LED layer structure grown. Similar *I–V* characteristics were obtained with samples having a 1000 Å or 200 Å thick ZnSeTe p-contact layer.

The EL spectrum was measured from the top surface near the edge of the contact, under pulsed operation of the device at 100 mA with 100 ns pulses and 0.1% duty cycle. Quantum efficiency measurements are not possible with this simple geometry since most of the emission is lost within the contact region. The as-measured EL spectra at room temperature are shown in Fig. 3. Three emission lines, one in the red (1.967 eV), one in the yellow (2.244 eV) and a third in the blue–green (2.385 eV) region of the visible range were observed from the three structures, demonstrating the feasibility of these devices for full-color display elements. A slightly thinner QW layer, with a higher subband energy level, would be needed to reach the blue emission. It should be pointed out that blue emission was achieved from similar structures in optically pumped lasers although the nominal QW thickness in those was greater, suggesting that blue emission can be achieved, but our thickness estimates are not accurate. The EL line shapes are symmetric and have full-widths at half-maximum (FWHM) of 70–90 meV which are comparable to reported data from ZnSe-based QW LEDs (46–85 meV) [10–12] and significantly narrower than the typical widths from blue GaN-based LEDs (~200 meV) [13,14]. The increase in EL intensity from the green to the red diode varies nearly proportionally with the QW thickness for each structure, suggesting that the quantum efficiencies for the three structures are comparable.

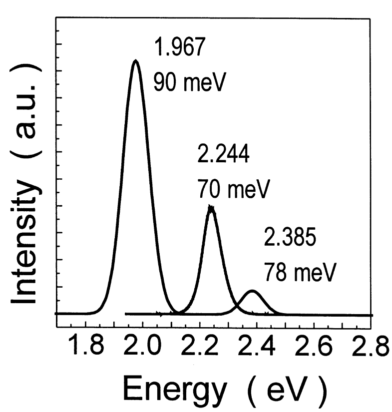

Fig. 3. Surface electroluminescence (EL) spectra for three LED structures that differ only in the QW thickness and/or composition used. Emission throughout the visible range is observed.

Initially the EL measurements were made on the as-grown wafers, some of which had 1000 Å thick ZnSeTe p+ contact layers. In those structures a broad red emission EL was observed regardless of the QW thickness. The solid line in Fig. 4 shows the EL spectrum of one of these diodes. A broad EL band is observed centered at 1.835 eV. After chemical thinning of the ZnSeTe layer the red emission was removed and the QW-related EL peak could be clearly observed. The EL spectrum of the same structure after etching of the ZnSeTe layer down to a thickness value of ~200 Å is shown by the dashed line in Fig. 4. This result indicates that most of the QW emission is absorbed by the *thick* ZnSeTe layer, which then exhibits a very strong and dominant re-emission. The room-temperature bandgap of lattice-matched ZnSeTe layers is expected to be at about 2.1 eV, thus absorption of the QW emission is likely for yellow, green or blue LEDs. ZnSeTe layers of this composition exhibit a broad PL emission form isoelectronic centers within the gap, at about 2.0 eV [15]. The observed emission from the LEDs is somewhat lower in energy, at 1.835 eV, and may indicate that it is due to recombination occurring at the type-II interface between the ZnCdMgSe barrier layer and the ZnSeTe cap. Although the band alignment between these two materials is not known, a type-II alignment is likely. Strong luminescence has been previously observed from II–VI type-II heterostructures [16]. The elimination of the red emission and observation of QW EL after etching shows that an optimum thickness for this layer must be used, thin enough to suppress the absorption of the QW emission but thick enough to insure good ohmic contact characteristics. Our experience suggests that 150–200 Å is appropriate.

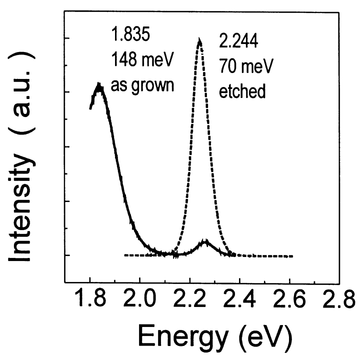

Fig. 4. Surface electroluminescence (EL) spectra for an LED structure with a thick (1000 Å) ZnSeTe p+ contact layer (solid line). The dashed line represents the EL for the same structure after etching the top ZnSeTe layer to 150 Å. The broad red emission in the as-grown structure originates from the ZnSeTe cap layer and not from the QW.

Two principal issues remain to be resolved before practical integrated full-color display elements can be seriously considered with these materials. The first is increasing the p-type doping level of the quaternary barrier layer. This is particularly important for the development of injection laser structures from these materials. Delta-doping methods may be useful to address this issue. The second is the development of a method to fabricate the three structures on a single substrate (device integration). An approach toward this goal, is the use of shadow mask selective area epitaxy [17] as a means to pattern QW region, so that the different thicknesses/composition QWs can be deposited on a single substrate.

4. Conclusion

We have grown p-ZnCdMgSe quaternary layers and have fabricated p–n junction light-emitting diode (LED) structures made from ZnCdSe/ZnCdMgSe QWs grown lattice matched to InP substrates. The highest p-type level achieved in ZnCdMgSe layers doped with nitrogen is $\sim 1 \times 10^{16}/cm^3$. In spite of the relatively high resistance of the p-ZnCdMgSe barrier layer, the *I–V* characteristics of the diodes are good, exhibiting low turn-on voltages. Electroluminescence spectra spanning nearly the entire visible spectrum were observed from three diode-structures in which only the QW thickness and/or composition were varied. These results clearly show the potential for these materials to fabricate integrated full-color display elements. It was also shown that the thickness of the top p+ ZnSeTe contact layer must be kept thin (150–200 Å) in order to avoid absorption of the QW emission and re-emission in the red from this layer.

Acknowledgements

This work was performed under the auspices of the New York State Center for Advanced Technology (CAT) on Ultrafast Photonic Materials and Applications. We would also like to acknowledge the support of the National Science Foundation through grant number ECS9707213 and the NASA Minority University Research and Education Division through grant number NAG5-6952.

References

[1] S. Nakamura, M. Senoh, S.-I. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto, H. Kiyoku, Appl. Phys. Lett. 70 (1997) 1417.
[2] S. Taniguchi, T. Hino, S. Itoh, K. Nakano, N. Nakayama, A. Ishibashi, M. Ikeda, Electron. Lett. 32 (1996) 552.
[3] K. Koga, T. Yamaguchi, Prog. Crystal Growth Charact. 23 (1991) 127.
[4] M.C. Tamargo, A. Cavus, L. Zeng, N. Dai, N. Bamba, A. Gray, F. Semendy, W. Krystek, F.H. Pollak, J. Electron. Mater. 25 (1996) 259.
[5] L. Zeng, B.X. Yang, A. Cavus, W. Lin, Y.Y. Luo, M.C. Tamargo, Y. Guo, Y.C. Chen, Appl. Phys. Lett. 72 (1998) 3136.
[6] W. Lin, A. Cavus, L. Zeng, M.C. Tamargo, J. Appl. Phys. 84 (1998) 1472.
[7] W. Lin, B.X. Yang, S.P. Guo, A. Elmoumni, F. Fernandez, M.C. Tamargo, Appl. Phys. Lett. 75 (1999) 2608.
[8] A. Cavus, L. Zeng, M.C. Tamargo, N. Bamba, F. Semendy, A. Gray, Appl. Phys. Lett. 68 (1996) 3446.
[9] L. Zeng, S.P. Guo, Y.Y. Luo, W. Lin, M.C. Tamargo, H. Xing, G.S. Cargill III, J. Vac. Sci. Technol. B 17 (1999) 1255.
[10] W. Xie, D.C. Grillo, R.L. Gunshor, M. Kobayashi, G.C. Hua, N. Otsuka, H. Jeon, J. Ding, A.V. Nurmikko, Appl. Phys. Lett. 60 (1992) 463.
[11] D.B. Eason, Z. Yu, C. Boney, J. Ren, L.E. Churchill, J.W. Cook Jr., J.F. Schetzina, N.A. El-Masry, J. Crystal Growth 138 (1994) 703.
[12] B.J. Wu, L.H. Kuo, J.M. DePuydt, G.M. Haugen, M.A. Haase, L. Salamanca-Riba, Appl. Phys. Lett. 68 (1996) 379.
[13] S. Nakamura, J. Crystal Growth 145 (1994) 911.
[14] M. Bremser, H. Protzmann, B. Wachtendorf, O. Schoen, M. Schwambera, B. Schineller, M. Heuken, E. Woelk, D. Schmitz, H. Juergensen, Proceedings of the Second International Symposium on Blue Lasers and Light Emitting Diodes, Chiba, Japan, 1998, p. 449.
[15] M.J.S.P. Brasil, R.E. Nahory, F.S. Turco-Sandroff, H.L. Gilchrist, R.J. Martin, Appl. Phys. Lett. 59 (1991) 1206.
[16] S.O. Ferreira, H. Sitter, W. Faschinger, R. Krunp, G. Grunthaler, J. Crystal Growth 146 (1995) 418.
[17] Y. Luo, A. Cavus, M.C. Tamargo, J. Wan, F.H. Pollak, J. Vac. Sci. Technol. B 16 (1998) 1312.