MBE Growth of Lattice-Matched ZnCdMgSe Quaternaries and ZnCdMgSe/ZnCdSe Quantum Wells on InP Substrates

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We report the growth and characterization of a new wide bandgap II-VI alloy, $Zn_xCd_yMg_{1-x-y}Se$, grown lattice-matched to InP. High quality quaternary layers with bandgaps ranging from 2.4 to 3.1 eV were grown by molecular beam epitaxy. The bandgaps and lattice constants were measured using photoluminescence and single crystal Θ-2Θ scans. Quantum well structures with quaternary barriers and ZnCdSe wells were also grown, entirely lattice matched to InP. Their photoluminescence properties suggest that these materials are suitable for the design of visible semiconductor lasers spanning the blue, green, and yellow regions of the visible range. The absence of strain in these heterostructures is expected to improve the reliability of the materials in device applications.

Key words: II-VI compounds, II-VI/III-V heteroepitaxy, blue emitters, molecular beam epitaxy, wide bandgap semiconductors, (Zn,Cd,Mg)Se

INTRODUCTION

Wide bandgap II-VI compounds have potential applications as blue (visible) light emitters. In fact, they are the only materials that have been successfully used to date to fabricate blue-green semiconductor lasers. However, despite a great deal of optimism generated by a number of recent significant successes, the performance of the devices is still not adequate, and many issues remain to be solved before practical devices are realized. In particular, rapid degradation of the material leading to very short lifetimes of the devices is of great concern.

Currently reported semiconductor lasers[1–3] are based on heterostructures of ZnSe-based alloys that are grown on GaAs substrates. Pseudomorphic structures are obtained by using ZnMgSSe and ZnSSe lattice-matched to the GaAs substrate as the barrier and waveguiding layers in the structures, respectively. A thin, strained $Zn_{0.8}Cd_{0.2}Se$ quantum well layer is used as the active region, and a ZnSe/ZnTe graded superlattice[4] has been the most successful approach for obtaining ohmic contacts to the top p-cladding layers. The presence of strain in the active layer and the formation of misfit dislocations in the contact layer region due to the relaxation of the very large lattice-mismatch between ZnTe and the rest of the structure are likely sources of degradation of these devices. Therefore, it is of interest to explore other wide bandgap II-VI materials that may be used to design entirely lattice-matched structures that also meet the band structure requirements of this complex device.

In this paper, we report the growth by molecular

(Received July 25, 1995; revised October 30, 1995)

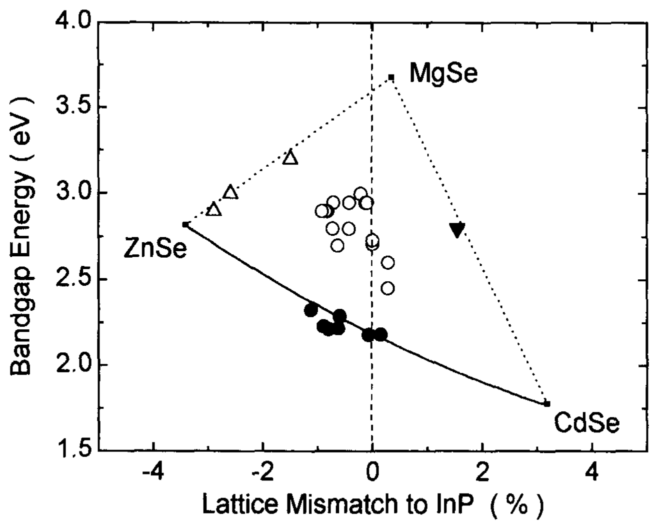

Fig. 1. Bandgap versus percent lattice-mismatch to InP for $Zn_xCd_yMg_{1-x-y}Se$ quaternary layers grown on InP substrates, as described in the text. The ZnMgSe points (open triangles) are taken from Ref. 8.

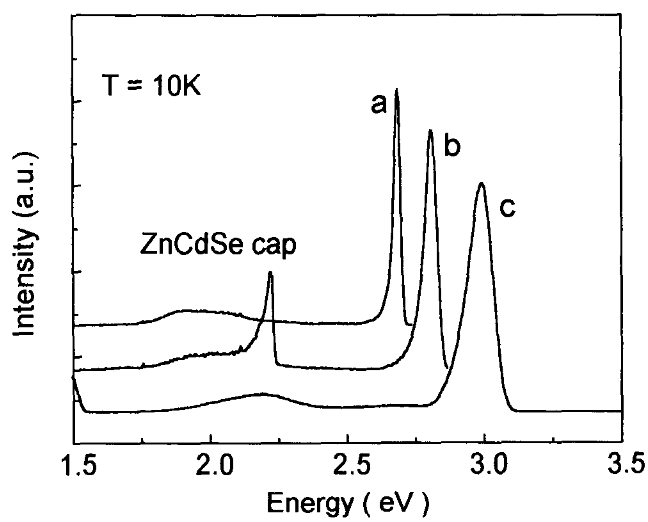

Fig. 2. Low temperature (10K) photoluminescence spectra for three quaternary $Zn_xCd_yMg_{1-x-y}Se$ layers grown on InP substrates. The calculated alloy compositions are: (a) $Zn_{0.47}Cd_{0.27}Mg_{0.26}Se$, (b) $Zn_{0.32}Cd_{0.30}Mg_{0.38}Se$, and (c) $Zn_{0.36}Cd_{0.20}Mg_{0.44}Se$. Sample b has a 100Å ZnCdSe cap layer whose emission is indicated.

beam epitaxy (MBE) and the properties of a new quaternary material system, $Zn_xCd_yMg_{1-x-y}Se$, that can be used in the design and fabrication of blue (visible) semiconductor lasers. We show that by growing these layers and structures on InP substrates, entirely lattice-matched heterostructures can be obtained. These lattice-matched quaternary layers encompass a wide range of bandgaps, from 2.18 eV, which is the bandgap of the lattice-matched ZnCdSe ternary, to above 3.5 eV for lattice-matched ZnMgSe, and thus enable the growth of device structures that emit in the blue, green, and yellow regions. The use of InP substrates also allows the growth of a symmetrically strained[5] ZnSe/ZnTe superlattice for ohmic contact formation, eliminating the formation of misfit dislocations in the contact layer. These features are expected to improve significantly the over-all material quality and the performance of the laser structure.

EXPERIMENTAL

The layers were grown by MBE in a Riber 2300P growth chamber. Elemental Zn, Cd, Mg, and Se sources were used. Growth was performed under Se-rich conditions with a beam equivalent pressure (BEP) ratio of the group-VI to group-II fluxes of ~4. Growth temperatures of 270°C and growth rates of about 1 μm per hour were used. InP(100) substrates having defect densities of $<5 \times 10^3$ cm^{-3} were obtained from Sumitomo Electric. Prior to use, the substrates were etched in H_2SO_4:H_2O_2:H_2O (4:1:1) for 1–2 min. As previously reported,[6] oxide desorption of the InP substrate was performed by heating the substrate with an As flux inpingent on the InP surface. The best results were obtained by heating the substrate quickly to ~500°C, then lowering the temperature to the initial growth temperature of 170°C. Once growth was initiated, and after 1 min of growth, the temperature was raised to the optimum growth temperature of 270°C. Using these conditions, featureless, defect-free surfaces and two-dimensional nucleation of the II-VI layer on the InP substrate, as indicated by the presence of a streaky reflection high energy electron diffraction (RHEED) pattern throughout the nucleation and growth, were routinely obtained.

The layers were characterized by low temperature photoluminescence (PL) at 10K using the 325 nm line of a He-Cd laser, at 0.25 mW power, as the excitation source. Lattice-mismatch was determined by single crystal x-ray diffraction measurements and crystalline quality was assessed in a few samples using double crystal x-ray rocking curves. Layers of ZnCdSe grown on InP using the conditions for InP substrate preparation, layer nucleation, and growth described above exhibit excellent PL quality (8 meV full width at half maximum [FWHM] and the near absence of defect-related deep level emission) and double crystal x-ray rocking curves (270 arc sec FWHM), the best properties reported for ZnCdSe layers grown on any substrate.[7]

RESULTS AND DISCUSSION

Figure 1 summarizes the bandgaps at 10K, measured by PL, plotted as a function of percent lattice-mismatch to InP ($\Delta a/a \times 100$), for most of the $Zn_xCd_yMg_{1-x-y}Se$ quaternary layers grown. A comparison between the PL emission wavelength and photoreflectance signals for several samples confirmed that the PL spectra are in fact dominated by near-bandedge emission. The points shown for the ZnMgSe ternary compositions are taken from the literature.[8] The remaining points are for 1 μm thick layers grown in our laboratory on InP substrates, as described above, for which both PL and x-ray data were obtained. As can be noted, there are only a few points for samples having a positive lattice-mismatch. Although a number of samples whose compositions are consistent with positive lattice-mismatch were grown, these layers often exhibited poorer crystalline quality. As a result, some of these realtively thin layers did not yield sufficient x-ray signal for measurement of the lattice-mismatch and could not be included in the plot. The zero-mismatch position is indicated in the figure by a dashed-line. The solid line represents the empirical fit to the ZnCdSe data reported in the literature.[9]

The PL spectra for three quaternary layers having different compositions are shown in Fig. 2. The calculated compositions for these layers are given in the figure caption. These calculations were made by constructing a cubic mathematical expression to describe the quaternary surface, based on the known ZnCdSe function[9] and assuming linear dependences for the ZnMgSe and MgCdSe ternary boundaries. Based on these calculations, the Mg content in our layers is as high as 44%. Efficient PL bandedge emission was observed from the samples. As can be seen, the linewidths of the PL peaks increase as the Mg composition, and thus the bandgap of the layers, increases. High quality layers having bandgaps as high as 3.1 eV were obtained. Attempts to further increase the bandgap by increasing the Mg content resulted in layers for which the RHEED pattern gradually degraded, becoming spotty as the growth progressed. Further optimization of the growth conditions may be necessary to achieve higher Mg compositions. Under our Se-rich growth conditions, control of the solid composition, and thus of the bandgap, was achieved by varying the group-II flux composition during growth. Details of the growth conditions will be reported elsewhere. The width (FWHM) of the double crystal x-ray rocking curve for a lattice-matched ($\Delta a/a < 0.05\%$) quaternary layer having a bandgap of 2.73 eV was 760 arc sec.

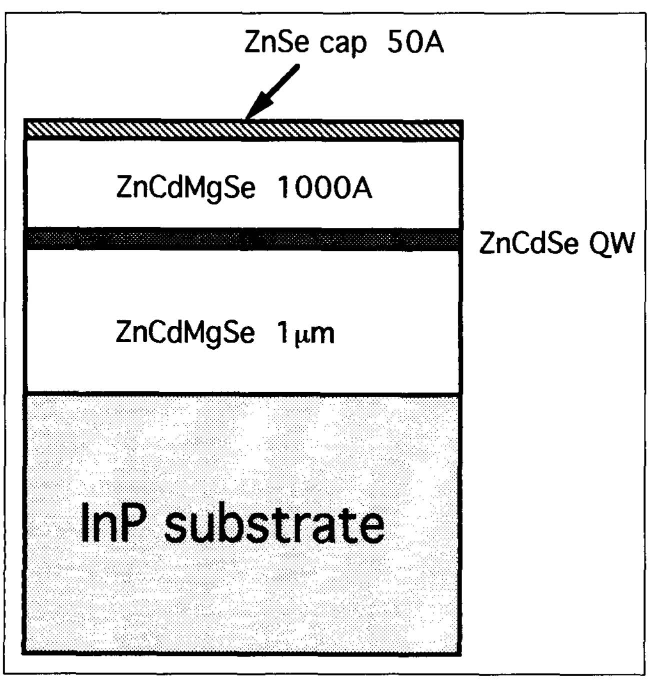

Fig. 3. Schematic of the quantum well layer structure grown.

Using these quaternary layers, a lattice-matched ZnCdMgSe/ZnCdSe quantum well (QW) structure was grown and investigated by low temperature PL. The structure, shown in Fig. 3, consisted of a 1 µm quaternary buffer layer, a nominally 28Å thick QW-layer, a top 1000Å quaternary barrier, and a 50Å ZnSe cap. The PL spectrum is given in Fig. 4. The emission from a thick ternary layer having the same composition as the QW layer was also measured at 2.27 eV and is indicated in the figure by the arrow. Strong, sharp PL emission is observed from the quantum well at 2.45 eV, corresponding to green emission. The emission from the quaternary barrier at 2.98 eV is also evident.

Several structures having different QW layer thickness were grown under similar conditions to those for

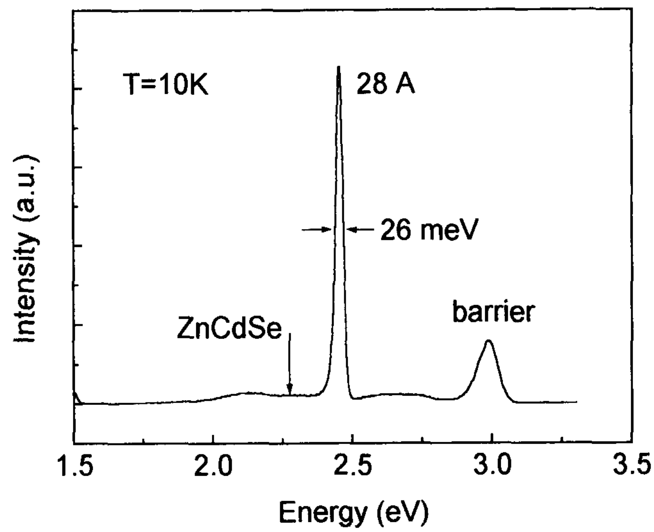

Fig. 4. Low temperature photoluminescence spectrum for a quantum well structure having a nominally 28Å thick quantum well layer.

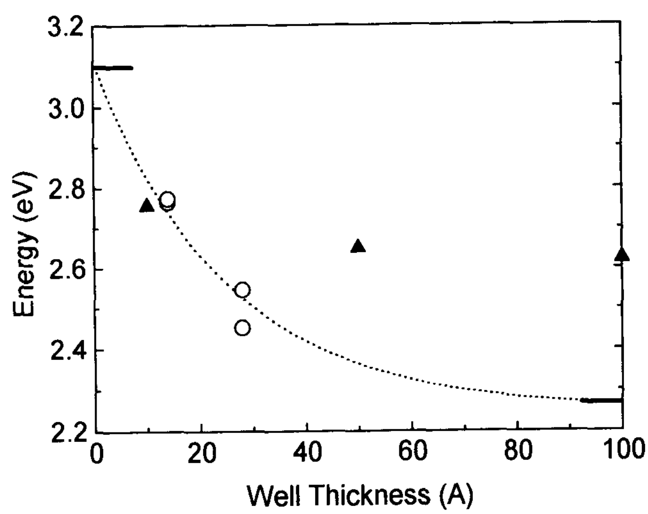

Fig. 5. Quantum well (QW) photoluminescence (PL) emission energy measured at 10K, as a function of QW layer thickness, for several ZnCdMgSe/ZnCdSe QW structures lattice-matched to InP. The bandgap for the quaternary barrier and the ternary QW material are indicated by bars in the left and right axes, respectively. The dashed line is drawn to illustrate the range of emission energy available, as a function of QW thickness. The solid triangles are taken from data in Ref. 10.

the structure in Fig. 4. A plot of the QW emission energy as a function of the QW thickness is given in Fig. 5. The quaternary barrier had an average bandgap of 3.08 eV, indicated by a bar in the left-hand axis of the plot. The bandgap for a thick ternary layer having the same composition as the well layers was measured by PL to be 2.27 eV, and is marked by a bar in the right-hand axis of the plot. Blue and green emissions are obtained from the 14 and 28Å QWs, respectively. Also plotted, for comparison, are the emission energies reported for strained-layer QWs made from the ZnSSe/ZnCdSe materials typically used in the blue-green lasers reported in the literature.[10] The comparison shown in Fig. 5 between our structures and the data of Ref. 10 suggests that there is a much larger degree of tunability of the QW emission wavelength in the new material system that we propose. By only varying the quantum well width, the emission wavelength of our samples can be varied, in principle, over an 800 meV range which covers nearly all the visible wavelength range, while this range is less than 200 meV for the materials in Ref. 10. This tunability could be potentially useful for practical device applications. In addition, a very large confinement energy, greater than 200 meV, is obtained with our materials materials, even for QWs emitting at 2.75 eV (i.e., in the blue). This feature is also desirable for improved device performance. Further investigations are under way to explore the tunability and other QW properties of our materials.

CONCLUSIONS

We have grown high quality ZnCdMgSe quaternary layers lattice matched to InP substrates, having bandgaps as high as 3.1 eV, that exhibit good PL properties and good crystalline quality. We have also grown and investigated lattice-matched quantum well structures having quaternary barrier layers and ternary ZnCdSe wells. Efficient blue and green luminescence was obtained from several quantum well structures, having 14 and 28Å thick quantum well layers, respectively. Our results suggest that tunability of the emission wavelength over most of the visible range can be easily achieved from these materials, by varying only the QW thickness. These entirely lattice-matched structures are likely to produce materials that are less susceptible to degradation than the strained-QW materials presently used, and thus are potentially useful for improved blue (visible) laser fabrication.

ACKNOWLEDGMENTS

The authors acknowledge the support of the New York State Science and Technology Foundation through its CUNY Center for Advanced Technology on Photonic Materials and Applications, the National Science Foundation (NSF) Center for the Analysis of Structures and Interfaces under cooperative agreement number RII-9353488 and the NSF grant number ECS-932045. We would also like to thank Dr. J.M. Arias (Rockwell International) for the double crystal x-ray measurements.

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