

Growth and characterization of patterned ZnCdSe structures for application in integrated R-G-B II–VI light-emitting diodes

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We report the growth and characterization of patterned ZnCdSe structures on GaAs substrates as our initial attempt to use shadow mask selective area molecular-beam epitaxy (MBE) to integrate II–VI (Zn,Cd,Mg)Se-based red-green-blue (R-G-B) light-emitting diodes (LEDs). Patterned ZnCdSe thick layers and ZnCdSe/ZnSe quantum wells (QWs) were grown on GaAs substrates using a silicon shadow mask mounted on a mask fixture that allows the mask to be placed and removed within the MBE growth system. Excellent pattern definition and good optical properties were obtained. Integration of patterned ZnCdSe/ZnSe QWs having different thickness and Cd composition, therefore different emission wavelengths, on a single GaAs substrate was also achieved. These results will be applied to the (Zn,Cd,Mg)Se material system to integrate R-G-B LEDs on a single InP substrate. © 2000 American Vacuum Society. [S0734-211X(00)05703-6]

I. INTRODUCTION

Wide-band-gap II–VI compounds have potential applications in semiconductor lasers and light-emitting diodes (LEDs). Using ZnMgSSe and ZnSSe alloys lattice matched to GaAs as cladding and waveguiding layers and strained ZnCdSe as active layer, blue-green laser diodes with lifetimes of about 400 h under continuous wave operation have been achieved.¹ The newly developed (Zn,Cd,Mg)Se material system has the additional feature of enabling lattice matched or pseudomorphic laser and LED structures to be designed on InP substrates with emission throughout the entire visible spectrum, from blue to red, by using ZnCdMgSe layers as cladding and waveguiding layers and a ZnCdSe layer as the active layer. The red, green, and blue (R-G-B) emission can be achieved from almost identical structures where only the ZnCdSe quantum well (QW) thickness and/or composition are varied, so that, integrated full color display devices can be considered.²

Selective area epitaxy (SAE) is an appealing way to achieve device integration. It has been reported that by using susceptor and reactor designs in metalorganic chemical vapor deposition (MOCVD) that allow the relative motion between a GaAs substrate and a GaAs or Si mask, GaAsP and GaAs based multiple detectors with different cutoff wavelengths and multiple color LEDs can be integrated on a single GaAs substrate.³ Selective molecular-beam epitaxy (MBE) for integrated *nnp/pnp* heterojunction bipolar transistor⁴ and monolithic integration of multiple wavelength vertical-cavity surface emitting lasers⁵ have been reported

using either a moveable shadow mask or a deposited SiO₂ mask.

In this article, we report the shadow mask SAE growth and characterization of patterned ZnCdSe thick layers and buried ZnCdSe QWs using ZnSe barriers on GaAs substrates. These patterned ZnCdSe structures were grown using a silicon shadow mask mounted on a specially designed mask fixture that allows the mask to be placed and removed within the MBE growth system. Patterned ZnCdSe/ZnSe QWs with different thickness and Cd composition were integrated on a single GaAs substrate by performing multiple step SAE using this mask fixture. These results can be applied to the integration of II–VI (Zn,Cd,Mg)Se-based full color displays by combining ZnCdSe QWs of different thickness and/or composition on a single InP substrate using identical ZnCdMgSe barrier layers.

II. EXPERIMENT

The growth was performed in a Riber 2300P MBE system that includes two growth chambers, one for II–VI materials growth (II–VI chamber) and one for III–V materials growth (III–V chamber). In the II–VI chamber, conventional effusion cells for Zn, Cd, and Se are positioned at the center ports of the source flange (near normal incidence) to minimize the mask shadowing effect. Figure 1 shows the scanning electron microscopy (SEM) pictures of the silicon shadow mask used in this experiment. It consists of stripe and square window openings with sizes ranging from 15 to 60 μm at the narrow opening side which is placed toward the substrates. A view of this side is shown in Fig. 1(a). The mask was fabricated using conventional photolithography followed by wet chemical etching on (001) Si wafers. The

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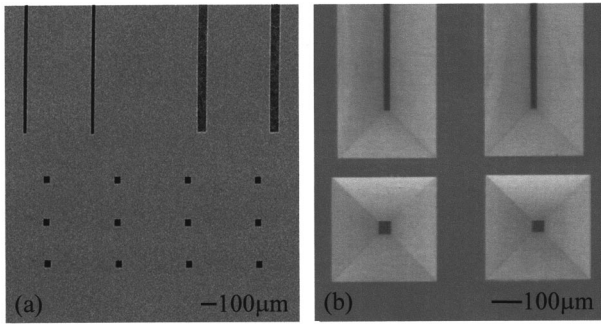


FIG. 1. SEM micrograph of the silicon shadow mask viewed (a) from the back (narrow opening) side and (b) from the top (wide opening) side.

stripes and squares are aligned along the [110] direction and the sidewalls are the (111) planes. Figure 1(b) shows a high magnification SEM micrograph of two typical stripe and square windows viewed from the wide opening side of the mask revealing the well-defined sidewalls. The mask was contained in a mask fixture that allows the mask to be placed and removed within the vacuum system. SAE growth of patterned epilayers can be carried out wherever desired within the structure and multiple step SAE can be performed. The details of the mask fixture design have been reported elsewhere.⁶

The patterned ZnCdSe structures were grown on GaAs(001) substrates using ZnSe as buffer layer and as the barrier layer for the ZnCdSe QWs. The GaAs substrates were etched *ex situ*, loaded into the III–V chamber and *in situ* cleaned by heating up to $\sim 600\text{--}620^\circ\text{C}$ for oxide desorption. GaAs buffer layers of $\sim 2000\text{ \AA}$ thick were grown to improve surface morphology and II–VI nucleation. Growth of the ZnSe buffer layers ($\sim 3000\text{ \AA}$ thick) was performed at 250°C in the II–VI chamber without any special growth optimization steps such as Zn-irradiation or migration enhanced epitaxy (MEE).⁷ The growth was interrupted to allow the silicon shadow mask to be placed on the ZnSe layers. Patterned ZnCdSe structures (with various Cd content from 20% to 50%) were then grown also at 250°C . For ZnCdSe/ZnSe QWs, $\sim 1000\text{ \AA}$ thick flat ZnSe cap layers were grown on the patterned ZnCdSe QW layers after the mask was removed.

The structural characterization was performed by SEM using a JEOL JSM-6301F scanning microscope and by atomic force microscopy (AFM) using a Digital Instruments MultiMode™ Scanning Probe Microscope. The thickness and edge width of the patterned ZnCdSe structures were measured by Alpha-Step 200 surface profiler. The optical properties were assessed by photoluminescence (PL) measurements at 77 K using the 325 nm line of a He–Cd laser with a photomultiplier tube detector. PL images were obtained at room temperature using a PL setup with an optical multichannel analyzer (OMA) which consists of a grating spectrograph equipped with a 256×1024 element charge coupled device (CCD) detector array. In this case, a frequency-tripled Nd:YAG laser was used for excitation.

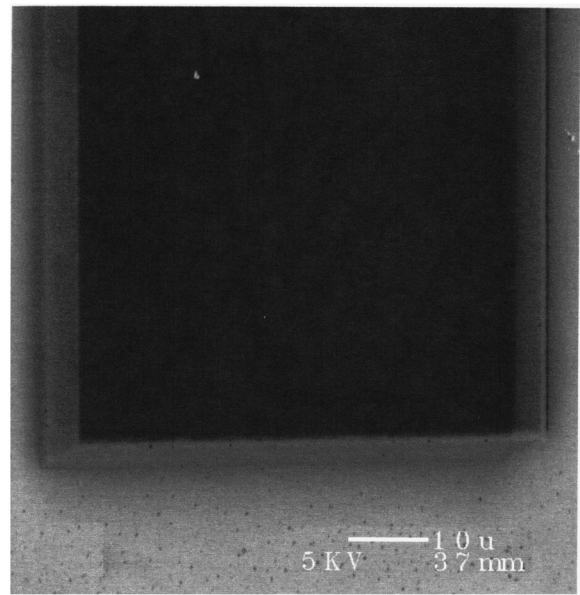


FIG. 2. High magnification SEM micrograph of the end of a $60\text{ }\mu\text{m}$ wide thick ZnCdSe stripe. It is viewed at a tilted 60° angle.

III. RESULTS AND DISCUSSION

Patterned ZnCdSe thick layers ($\sim 0.5\text{ }\mu\text{m}$) were initially grown to establish the feasibility of the shadow mask SAE process for this ternary material. The pattern definitions of the resulting ZnCdSe thick layers are excellent, replicating well the shape of the silicon shadow mask. Figure 2 shows a high magnification SEM picture of the end of a $60\text{ }\mu\text{m}$ wide ZnCdSe stripe (the black dots in the region of the flat ZnSe buffer layer are due to surface charging during SEM measurement and are not present when viewed with an optical microscope). Smooth, featureless surface and sidewalls are evident. The sidewalls taper over $\sim 5\text{ }\mu\text{m}$ according to the surface profiler measurement. The masked ZnSe region remains clean and featureless, which enables the deposition of subsequent patterned or planar layers without any surface preparation. 77 K PL measurements indicate that the patterned ZnCdSe epilayers have good optical properties. The PL spectrum obtained from a $40\text{ }\mu\text{m}$ wide stripe is shown in Fig. 3(a). The ZnCdSe band-edge emission is at 2.446 eV (corresponds to $\sim 35\%$ Cd concentration) and the full width at half maximum (FWHM) is 23 meV. The small peak near 2.8 eV originates from the nearby ZnSe region since the laser excitation spot used in the conventional PL setup is large, in the tens of microns range. Figure 3(b) shows the PL spectrum collected from the region with only the ZnSe buffer layer. One sharp ZnSe band-edge emission at 2.767 eV with FWHM of 21 meV was observed. These optical measurements indicate that no deleterious effects were caused by the use of the mask on the patterned ZnCdSe or the masked flat ZnSe regions.

For the buried patterned ZnCdSe/ZnSe QWs, although the QWs are very thin, the patterned structures can still be identified from the top surface by the naked eyes or with an optical microscope due to the interference of the light. This

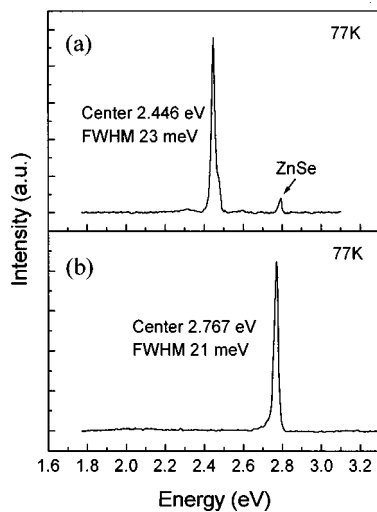


FIG. 3. 77 K PL spectra obtained from (a) patterned ZnCdSe thick layer and (b) flat ZnSe buffer layer which was covered by the mask during SAE growth of ZnCdSe.

feature makes the subsequent characterization much easier. AFM surface topography measurements were performed to investigate the pattern definition of these thin QW layers. Figure 4 shows an AFM image of a square shaped ZnCdSe QW layer (~ 140 Å) without a top ZnSe cap layer. It exhibits a well-defined shape with sharp sidewalls. The surface of the patterned QWs with and without a ZnSe cap layer show similar lateral and vertical dimensions suggesting that the patterned QW shape is preserved well after the flat ZnSe layer overgrowth. More detailed studies such as cross-sectional transmission electron microscopy (TEM) are needed to fully characterize the growth habits of ZnSe layers

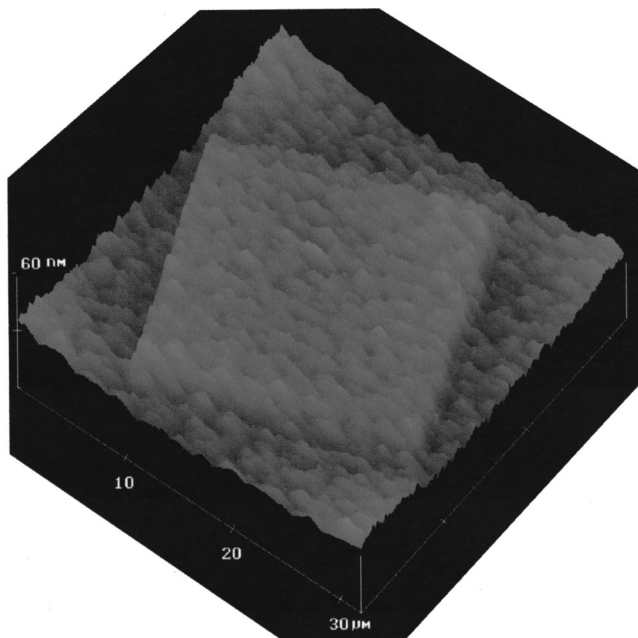


FIG. 4. AFM image of a patterned ZnCdSe QW without a ZnSe cap layer. The measurement was done using a SiN probe tip in contact mode.

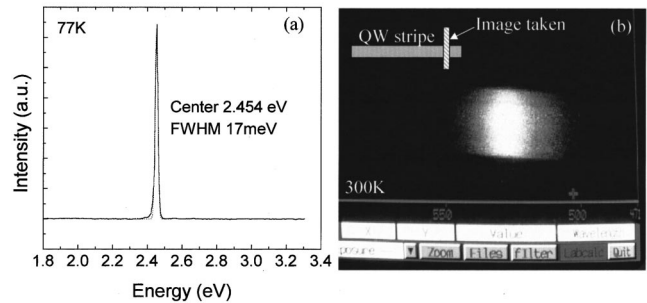


FIG. 5. (a) 77 K PL spectrum obtained from the patterned ZnCdSe/ZnSe QW and (b) the corresponding PL image taken at room temperature with an OMA detector. In (b), the horizontal axis is the wavelength in nm and the vertical axis is the position along the measurement bar.

on nonplanar structures. The surface roughness of these patterned QW layers was measured by AFM and compared to that of corresponding flat layers grown under the same conditions. Comparable surface roughness was observed indicating that the use of the silicon shadow mask did not perturb the growth as far as the surface morphology is concerned.

The patterned ZnCdSe/ZnSe QWs exhibit strong and narrow QW emission as evidenced from the 77 K PL measurements. Figure 5(a) shows a PL spectrum obtained from a 50 μm wide ZnCdSe/ZnSe QW stripe with emission at 2.454 eV and a FWHM of 17 meV. The QW thickness and composition are estimated to be ~ 60 Å thick with $\sim 35\%$ Cd composition. The patterned ZnCdSe/ZnSe QW PL linewidth is comparable to that obtained from flat QWs grown under similar conditions. A similar PL spectrum as that shown in Fig. 3(b) was observed from the nonpatterned (ZnSe only) region. All these results suggest that high quality patterned ZnCdSe/ZnSe QW structures have been grown and the use of the shadow mask and the additional growth interruption needed during the placement and removal of the shadow mask did not affect the optical quality of the QWs and the overgrown ZnSe layers.

The uniformity of the QW emission from these patterned structures was assessed using a PL setup employing an OMA. Figure 5(b) shows a PL image obtained at room temperature from a section of a 50 μm wide QW stripe. The inset in the figure illustrates where the image was recorded. The width of the bar along which the spectra are collected is only 1 μm , corresponding to the entrance slit of the OMA. The horizontal axis in this figure is the wavelength (shown) in nm while the vertical direction represents the position along the bar where the measurements were taken. The brightness corresponds to the intensity of the QW luminescence. The QW exhibits uniform emission centered at ~ 520 nm. The ZnSe layer outside the QW region in the same measurement bar has emission wavelength below 470 nm, therefore, its luminescence can not be seen in this image. The spatial resolution of this measurement along the vertical axis is less than 1 μm .

Finally, three sets of patterned ZnCdSe/ZnSe QWs each having different thickness and Cd composition were grown by rotating the mask and performing sequential SAE steps so

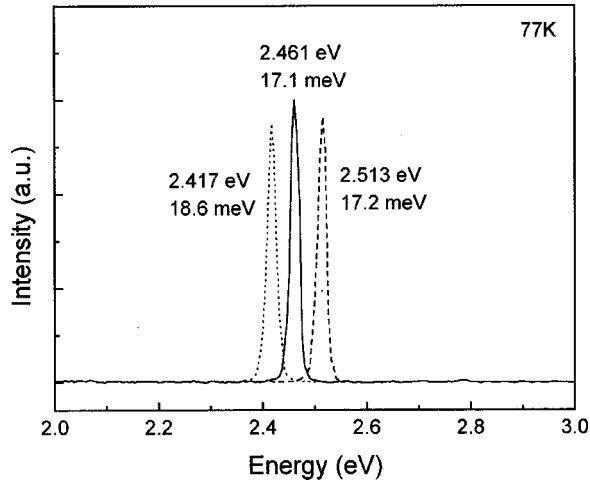


FIG. 6. 77 K PL spectra of three patterned ZnCdSe/ZnSe QWs of different thickness and Cd composition, therefore different emission wavelength, grown on a single GaAs substrate.

that different ZnCdSe QWs were deposited on the different areas of the same substrate. In this way, ZnCdSe/ZnSe QWs with different emission wavelengths were integrated on a single substrate. These different QWs were grown by varying the growth time and Zn flux while keeping Cd flux fixed. The thicknesses of the QWs are nominally controlled to be ~ 60 Å. Their exact composition and thickness are not known since no reference samples were grown. Figure 6 shows the 77 K PL spectra obtained from three QW stripes, each having different thickness and Cd composition. Three emission lines centered at 2.513, 2.461, and 2.417 eV were obtained. The FWHMs are 17, 17, and 19 meV, respectively, indicating that the three QWs grown sequentially by multiple step SAE are of comparable good quality. This result demonstrates that multiple step SAE is a feasible approach to combine QWs of different composition and/or thickness on the same substrate. It also indicates the potential of using this shadow mask SAE technique for the fabrication of integrated R-G-B LEDs when applied to the (Zn,Cd,Mg)Se-based material system.

IV. SUMMARY

Growth of patterned ZnCdSe thick layers and buried ZnCdSe/ZnSe QWs has been performed on GaAs substrates using shadow mask SAE. Excellent pattern definition and good optical properties were obtained from these patterned structures. Patterned ZnCdSe/ZnSe QWs with different thickness and Cd composition, therefore different emission wavelength, have been grown on a single GaAs substrate to demonstrate the potential of using shadow mask SAE for device structure integration. We are currently calibrating the growth conditions of lattice-matched ZnCdSe and ZnCd-MgSe layers on InP substrates. We will apply this shadow mask SAE technique to the (Zn,Cd,Mg)Se-based material system and integrate R-G-B ZnCdSe/ZnCdMgSe QWs on a single InP substrate to fabricate integrated R-G-B LEDs.

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