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Growth and properties of wide bandgap $(\text{MgSe})_n(\text{Zn}_x\text{Cd}_{1-x}\text{Se})_m$ short-period superlattices

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Abstract

We report the molecular beam epitaxy (MBE) growth and properties of $(\text{MgSe})_n(\text{Zn}_x\text{Cd}_{1-x}\text{Se})_m$ short-period superlattices (SPSLs) for potential application in II–VI devices grown on InP substrates. SPSL structures up to 1 μm thick with effective bandgaps ranging from 2.6 eV to above 3.42 eV are grown and characterized, extending the typical range possible for the $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ random alloy beyond 3.2 eV. Additionally, $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ single and multiple quantum well structures using the SPSL barriers are also grown and investigated. The structures are characterized utilizing reflection high-energy electron diffraction, X-ray reflectance, X-ray diffraction and photoluminescence. We observed layer-by-layer growth and smoother interfaces in the QWs grown with SPSL when compared to the $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ random alloy. The results indicate that this materials platform is a good candidate to replace the random alloy in wide bandgap device applications.

Keywords

A3. Superlattices; A3. Molecular beam epitaxy; B1. Nanomaterials; B2. Semiconducting II–VI materials

1. Introduction

Short-period superlattices (SPSL), also known as digital alloys or pseudo alloys, are heterostructures of alternating binary or ternary alloys with periods of a few monolayers (ML) each. The properties of these SPSLs resemble those of random alloys of similar compositions [1]. SPSL materials have been shown to be an attractive replacement for ternary [2] and quaternary [3,4] alloys in device applications due to the ability to suppress the propagation of defects [5,6] and the highly advantageous ability to change alloy effective composition without source temperature changes during molecular beam epitaxy (MBE) growth. Recently, the wide-bandgap $\text{Zn}_x\text{Cd}_{1-x}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ material system lattice matched to InP has been shown to be an excellent candidate for several novel device applications. Green-light photo pumped lasers show promising results [7]. Also, intersubband infrared devices based on this material system are the most advanced outside

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the well-established III–V materials. Specifically, room temperature electroluminescence from quantum cascade structures has been demonstrated at 4.7 μm [8,9] and 6.8 μm [10]. Additionally, quantum well infrared photodetectors (QWIPs) with performance comparable to those made with III–V materials [11] have been reported. Indeed, II–VI based quantum cascade detectors (QCDs [12]) and broadband QCDs [13] perform as well as any reported QCDs in III–V materials. However, devices from these materials are limited at shorter wavelengths by the quality of a $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ component as we go to the wider bandgaps (2.9–3.2 eV), and bandgaps higher than 3.2 eV are not usually achieved in sufficiently good quality. At higher bandgaps (>2.9 eV) $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ growth becomes difficult due to rock-salt phase transformations of the metastable MgSe component [14]. We propose to replace the $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ barrier with short-period superlattices (SPSL) of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ and MgSe to develop novel wide bandgap engineered materials. Previously Shimbo et al. [15] demonstrated this system for visible light applications focusing on bandgaps below ~ 2.85 eV with excellent results. The flexibility of these alloys for this bandgap range was demonstrated and this work seeks to extend their results to higher bandgaps (3.0–3.42) where the SPSL becomes important for short wavelength intersubband devices. More recently Chen et al. explored using metastable MgSe barriers with the use of a ZnCdSe spacer to provide the phase stability [16]. Their work demonstrates the possibility of wavelengths as short as 1.55 μm in this material system, but the use of a thick ZnCdSe spacer limits the types of devices that can be executed. Another key technological advantage of the proposed SPSLs is that in MBE growth abrupt changes in the bandgap of these materials can be realized by modifying the shutter sequence rather than modification of the beam flux necessary for $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ barriers.

Here we report a systematic investigation of the growth, structural quality and optical properties of $(\text{MgSe})_n(\text{Zn}_x\text{Cd}_{1-x}\text{Se})_m$ SPSLs with various period thickness. The long-term aim is to replace the $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ in II–VI-based infrared, visible and terahertz devices lattice matched to InP. A comparison with $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ alloys of similar magnesium compositions is made. $(\text{MgSe})_n(\text{Zn}_x\text{Cd}_{1-x}\text{Se})_m$ SPSL with bandgaps ranging from 2.52 to 3.42 eV are demonstrated and characterized. Grown structures are compared to simple Kronig-Penney model calculations [17]. Quantum well structures utilizing SPSLs barriers are grown. Transfer matrix method (TMM) calculations are used to model these structures and predict the QW emission wavelengths.

2. Experimental

The short-period superlattices of $(\text{MgSe})_n(\text{Zn}_x\text{Cd}_{1-x}\text{Se})_m$ layers near lattice matched to InP(1 0 0) were grown in a dual chamber Riber 2300 molecular beam epitaxy (MBE) chamber. For all samples a lattice matched $\text{In}_{0.47}\text{Ga}_{0.53}\text{As}$ buffer of ~ 128 nm was grown on the epi-ready InP(1 0 0) semi-insulating substrate to smooth the growth surface. The $\text{In}_{0.47}\text{Ga}_{0.53}\text{As}$ was terminated with a 2×4 reconstruction to facilitate the heterovalent interface formation. The sample was then transferred via an ultra-high vacuum transfer system to a chamber dedicated to II–VI materials growth. A low temperature buffer layer was grown comprised of 30 s of zinc flux exposure followed by a $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ thin layer, both at a nominal temperature of 180 $^\circ\text{C}$. A detailed analysis of this growth procedure has been previously reported [18]. The substrate temperature was then raised to 280 $^\circ\text{C}$ and

alternating layers of MgSe and $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ were grown forming the SPSL. For bandgaps below 3.3 eV (samples 1–5) a $\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se}$ lattice matched composition was used for the $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ component; for the other samples the ratio of Zn to Cd was adjusted so the SPSL was strain balanced. The ternary alloys compositions used were $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{Se}$ for sample 6 and $\text{Zn}_{0.86}\text{Cd}_{0.14}\text{Se}$ for sample 7. The total thickness of the digital alloys varied from 350 to 1000 nm and the MgSe/ $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ ratio was controlled by varying the number of monolayers. The structural details of each sample are summarized in Table 1.

3. Results and discussion

During the growth of the samples, *in-situ* reflection high energy electron diffraction (RHEED) exhibited sharp and streaky patterns with a 2×1 reconstruction typical of high quality II–VI material for all samples (Fig. 1(a–d)). No significant change was observed throughout the growth of the samples and similar patterns to those observed for sample 2 (Fig. 1a and b) were observed for samples with bandgaps up to 3.25 eV (Samples 1–5 in Table 1). Samples with bandgaps higher than 3.25 eV showed a modulation in the $[1\ 1\ 0]$ streaky pattern (red circle in Fig. 1c), which is attributed to a reduction in the surface step length. We suggest this may be due to reduced surface mobility of MgSe as compared with ZnCdSe layers, and may be mitigated by an increase in substrate temperature when growing the higher bandgap $(\text{MgSe})_n(\text{Zn}_x\text{Cd}_{1-x}\text{Se})_m$ SPSLs. Before the growth of each sample RHEED intensity oscillations (Fig. 1e) were measured to determine the exact times needed to grow the thicknesses of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ and MgSe required. We observe very good surface recovery in the oscillations with each shutter sequence. The thicknesses of each period obtained by the RHEED intensity oscillations were then confirmed by analysis of X-ray diffraction satellite peaks for each SPSL structure (Fig. 2 and Table 1). This thickness was multiplied by the total number of periods to estimate the total thickness of the SPSL layer. X-ray diffraction (XRD) scans were performed to determine overall quality, thickness, roughness, and relaxation of the SPSLs. As described above the thickness of the SPSL was determined using high resolution 2θ - ω scans utilizing an analyzer crystal (HR-XRD), these results were also verified with X-ray reflectance (XRR) and were found to deviate less than 1%, and less than 3% from the measured thickness from RHEED oscillations. A representative XRD scan is shown in Fig. 2. The overall quality of the film remained very high in samples with bandgaps below 3.3 eV (samples 1–5) consistent with observations seen in RHEED. The roughness of the $(\text{MgSe})_n(\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se})_m$ SPSL was compared to $\text{Zn}_x\text{Cd}_{1-x}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ SPSL currently in use in intersubband devices utilizing XRR. A typical XRR scan for one of the QW structures is shown in Fig. 4a. We observed a considerable improvement relative to equivalent bandgap alloy material. We attribute this improvement to the reduction in alloy broadening. Strain data is summarized in Table 1 and was extracted by comparing the peak positions of the zero order superlattice peak in symmetric $(0\ 0\ 4)$ and asymmetric $(2\ 2\ 4)$ scans. We observe in-plane relaxation (R) of 6.7%, 9.7%, 25%. In-plane relaxation is defined here as:

$$R = \left(\frac{a_0 - a_{\parallel SL}}{a_0 - a_{SL}} \right) \cdot 100 \quad (1)$$

where a_0 is the lattice constant of InP, $a_{\parallel SL}$ is the measured in-plane lattice constant from (0 0 4) scans of the superlattice and a_{SL} is the superlattice lattice constant taken from the average of in-plane and out of plane measurements. The R value for samples ~400 nm thick (samples 1,2,5) is quite low, despite lattice mismatch ranging from 0.3% to 0.72%.

Relaxation of 26% was observed for the 1000 nm (sample 4) with a mismatch of 0.4%. This shows there is a significant increase in the critical thickness when compared to the $Zn_xCd_{1-x}Mg_{1-x-y}Se$ random alloy of similar lattice mismatch, as also observed by others in $(Si)_n(SiGe)_m$ SPSLs [6] This observation is of importance in magnesium containing II–VI alloys where strain induced transformation to rock salt limits the realization of good quality material and devices [14]. As the magnesium fraction increases, the strain tolerance of the

SPSL decreases. Strain values ($\varepsilon_{zz} = \left(\frac{a_0 - a_{\parallel SL}}{a_0} \right)$) below 0.01 were required to grow good crystalline quality material when the magnesium fraction exceeded 75%. This was achieved by strain balancing the composition of the $Zn_xCd_{1-x}Se$ component, as done in samples 6 and 7. This requirement may not be necessary if the wide bandgap SPSL component is kept thin when designing devices. The significance of these results is that even if strain is very low for the $Zn_xCd_yMg_{1-x-y}Se$ random alloy the crystalline quality of attempted samples beyond 3.1 eV is very poor, while high effective bandgaps can be achieved with high quality in the SPSLs.

Photoluminescence (PL) measurements were performed to determine the optical quality and bandgap dependence of the $(MgSe)_n(Zn_{0.49}Cd_{0.51}Se)_m$ SPSLs that were grown. The data are summarized in Table 2, where SPSL effective compositions were estimated by combining the measured SL period, the estimated MgSe thickness obtained from RHEED oscillations and the SPSL lattice constant obtained from the zero order SL peak in XRD. Good optical quality material is achieved for all the samples with the room temperature PL peak energy ranging from 2.07 to 3.42 eV (Fig. 3a). We also observe linewidths, plotted as the full widths at half maximum (FWHM) divided by the peak energy (or Γ/E), similar to the values reported for $Zn_xCd_yMg_{1-x-y}Se$ random alloy samples of similar bandgaps up to 3.1 eV grown under optimized conditions (inset of Fig. 3a). At peak energy values greater than 3.1 eV we note a significant reduction in the Γ/E observed for the SPSL samples. This improved behavior indicates that whereas the FWHM for the random $Zn_xCd_yMg_{1-x-y}Se$ alloy increases sharply at higher bandgaps, likely due to the formation of extrinsic defects, the FWHM of the SPSLs remain more narrow. Furthermore, the PL intensity for of the SPSLs samples was observed to be high for all compositions studied. We suggest that the improvement of the optical properties, in particular at high bandgaps, is due to reduced dislocations and reduced formation of rock salt domains in the SPSL where the $Zn_xCd_{1-x}Se$ component may be acting as a recovery layer. Calculated effective bandgaps utilizing Kronig-Penney calculations, using $m_{eb} = 0.23$, $m_{ew} = 0.13$, $m_{hhw} = 0.42$, $m_{hbb} = 0.67$ and a conduction band offset of 1.12 eV, taking strain into account, are in good agreement to the experimental values, with deviations of less than 60 meV (Table 2). Additionally, the effective bandgap of the $(MgSe)_n(Zn_xCd_{1-x}Se)_m$ SPSL shows a nearly linear behavior with the MgSe with x' , where $x' = n/(n + m)$ (Fig. 3b) and a good agreement with the estimated bandgaps ($E_g(\text{peak}) = 2.07 + 1.49x'$) of a random alloy assuming a linear combination of the bandgaps of the two end points: $Zn_{0.49}Cd_{0.51}Se$ (RT $E_g \sim 2.07$ eV) and MgSe (RT $E_g \sim 3.56$

eV). This allows us to determine the ratio of $(\text{MgSe})_{x'}$ to $(\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se})_{1-x'}$ needed to achieve a given bandgap.

Single (SQW1 and SQW2) and multiple quantum well (MQW) samples utilizing $(\text{MgSe})_n(\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se})_m$ SPSL as the barrier and $\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se}$ as the well layer material were grown to establish their potential for use in devices and to develop a model that could be used to simulate device designs. XRR measurements of a MQW sample (Fig. 3a) suggest interfaces superior to those of similar MQW samples grown previously using quaternary random alloy barriers. A period of 1.93 for the barrier SPSL and a period of 31 nm for the MQW superlattice structure were extracted from the XRR measurement. In 77 K PL measurements (Fig. 4b) we observe peak energies of 2.433 eV, 2.426 eV and 2.303 eV with a FWHM of 43 meV, 53 meV and 46 meV for MQW, SQW1 and SQW2, respectively. The MQW and SQW1 samples have similar quantum well and barrier designs with the only difference being that in the MQW the quantum well was repeated 30 times. We note that the FWHM is similar for the SQW1 and the MQW sample, suggesting that there is good reproducibility of thicknesses throughout the MQW structure. The line-width for the SPSL MQW structure is similar to that achieved with $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ barriers under optimal conditions (43 meV). We also observe that changing the barrier height (by changing the SPSL period as was done in SQW2) is possible without any change in source temperatures, a technological advantage of this approach. Transfer matrix method (TMM [17]) calculations were performed utilizing the same parameters used in the Kronig-Penney calculations above, yielding bandgaps of 2.439 eV for the designed 22 Å wells (MQW and SQW1) and 2.319 eV for 26 Å wells (SQW2), which are within 20 meV of the measured values. The good agreement obtained suggests that the parameters extracted from the data and used in the TMM calculations can be utilized in device design.

4. Conclusions

We demonstrated that $(\text{MgSe})_n(\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se})_m$ SPSLs are good candidates to replace the $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ random alloy in InP based II–VI devices and applications over the entire lattice matched composition range. We have shown that good quality material with bandgaps as high as 3.42 eV can be achieved with these SPSLs, whereas the quality with the random alloys greatly degrades above 3.2 eV. Overall, there is a significant improvement quality of the wider bandgap materials utilizing SPSLs, as measured by HR-XRD, XRR and PL. The QWs grown using the SPSL as barriers show good optical properties and thus, establish the potential for the use of these materials in the design and growth of novel high performance devices, such as infrared detectors, and others.

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Fig. 1.

(a–d) RHEED images of SPSLs in sample 2(a and b) and sample 6(c and d) with peak energies of 2.79 eV and 3.35 eV, respectively. Circled in red in image (c) is the slight modulation observed in higher bandgap SPSLs, indicative of degradation. (e) RHEED intensity oscillations for sample 2 used to determine the growth time for each component of the SPSL.

Fig. 2.
Representative XRD pattern for short-period superlattices, showing sharp superlattice fringes.

Fig. 3.

Photoluminescence spectra (a) at room temperature for SPSL samples showing the change in FWHM and bandgap with a change in MgSe and ZnCdSe ratio. (Inset) E/E vs peak energy of SPSL samples shown in blue dots, and $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ shown in red dots. The red line is the best fit to the data of the $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ samples (small red dots). We note a deviation of the SPSL data (large blue dots) to this line at high peak energies. (b) The dependence of the MgSe fraction to the photoluminescence peak energy for SPSLs shown as red dots, and best fit to peak energy dependence as described in the text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4.

(a) XRR spectra of MQW sample using a SPSL as the barrier, a period of 1.93 nm for the SPSL and 318 nm for the MQW can be extracted. Very good interfaces denoted by sharpness of interference fringes can be observed. (b) Photoluminescence spectra of a MQW and two SQW samples showing a peak energy of 2.433 eV with a FWHM of 43 meV for the MQW, 2.426 eV with a FWHM of 53 meV for SQW1 and 2.303 with a FWHM of 46 meV for SQW2.

Parameters of the various $(\text{MgSe})_n(\text{Zn}_x\text{Cd}_{1-x}\text{Se})_m$ short-period superlattices grown and investigated.

Table 1

Sample	n (ML)	m (ML)	XRD Period (Å)	SL t (nm)	$a_{ }$ (Å)	$a_{\perp}$ (Å)	R (%)	e_{zz}
1	2.5	4	19.3	370	5.9072	5.8709	6.7	0.006
2	4	4	22.5	340	5.9501	5.8733	9.7	0.014
3	5	3	21.0	1000	5.9141	5.8983	78	0.007
4	5	2	18.6	1000	5.9111	5.8761	26	0.007
5	6	1.5	22.0	435	5.9417	5.8798	25	0.012
6	6	1	20.5	885	5.8695	5.8695	100	0
7	9	1	–	500	5.8695	5.8695	100	0

Table 2
Compositions and the associated calculated and experimental bandgaps of SPSL grown.

Sample #	Mg%	Zn%	Cd%	KP Calc. Eg (eV)	Measured E _{peak} (eV)	FWHM PL (meV)
1	0.38	0.49	0.51	2.60	2.565	82
2	0.53	0.41	0.59	2.73	2.788	134
3	0.64	0.43	0.57	2.88	2.940	140
4	0.69	0.54	0.46	3.08	3.102	143
5	0.8	0.48	0.52	3.27	3.248	211
6	0.87	0.71	0.29	3.33	3.334	213
7	0.90	0.86	0.14	3.39	3.419	197