Lattice Strain and Band Offsets Determination in ZnSe/ZnS Short-Period Superlattices Grown by MOVPE on (100)GaAs

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Abstract

We report a detailed calculation of the effects of residual lattice and thermal strains on the electronic states of nearly pseudomorphic ZnSe/ZnS short-period superlattices (SLs). Comparison is made with experimental electronic transitions derived from 10K absorption spectroscopy measurements performed on 30 periods ZnSe/ZnS SLs, having well and barrier thickness $L_w=1.4$ nm and $L_b=5.7$ nm, respectively. ZnSe/ZnS SLs were grown by metalorganic vapour phase epitaxy (MOVPE) on a 500 nm thick ZnS buffer layer and capped with a 210 nm thick ZnS epilayer. The whole structures were deposited on (100)GaAs. The intrinsic conduction to valence band offset ratio is finally found to be 8:92 for the above SL structure. The impact of the weak electron confinement on the SLs optical and electronic properties, with special attention to laser applications, is also discussed.

Introduction

ZnSe/ZnS SLs have demonstrated both spontaneous and photo-pumped stimulated emissions in the near-UV region of the visible light [1]. A precise determination of the band offsets between ZnS and ZnSe and of the SL electronic properties is possible by comparing what expected on the base of a Kronig-Penney model calculations and the results of 10K absorption measurements. However, this requires to carefully consider the actual strain occurring in the heterostructure for which the comparison with experimental data is made. In fact, even for a fully pseudomorphic ZnSe/ZnS SL, the -4.6% lattice mismatch between ZnSe and ZnS introduces a strain value that can be effectively altered by the occurrence of additional thermal deformations originated by the different thermal expansion coefficients of the SL materials, the buffer and the substrate. The overall strain thus distributes inside both ZnS barriers and ZnSe wells altering the effective band offsets and need to be taken into account for correct calculations.

Experimental

Short period ZnSe/ZnS MQW heterostructures were grown on (100)-oriented LEC-grown semi-insulating GaAs substrates by low pressure metal-organic vapour phase epitaxy (MOVPE) in an Aixtron AIX 200RD horizontal chamber reactor. The details of the MOVPE growth of the ZnSe and ZnS epilayers are reported elsewhere [2]. On a (100) GaAs substrate a 500 nm thick ZnS buffer layer was grown at 342°C, followed by 30 periods ZnSe/ZnS MQW grown at 315°C, the well width (L_w) being equal to 5ML (1.4 nm), while the barrier width (L_b) being of about 21 ML, (5.7 nm). A growth interruption time of 20 sec was used at each heterointerface, to obtain sharp interfaces. Finally, a 210 nm thick ZnS cladding layer was grown on top of the structure at the same growth temperature used for the SLs.

Optical absorption measurements were performed at 10K on the mechano-chemically thinned MQW samples prepared following the procedure described elsewhere [3]. The mechanically chopped light of a tungsten halogen lamp was focused onto the sample mounted on the cold finger

of a closed-circle He cryostat. The transmitted beam was dispersed and detected by a double monochromator (0.85 m) equipped with a photon counting detector.

Results and discussion

The excellent optical quality of the MQW samples is confirmed by the sharp excitonic peaks of the absorption spectrum shown in Fig. 1. Also, a clear step-like density of states with superimposed excitonic resonances appears. As the SL total thickness (213 nm) is bigger than the critical thickness expected for the plastic relaxation at the buffer interface, the SLs will not be completely pseudomorphic to the ZnS buffer. Thus, in order to correctly evaluate the excitonic transitions and the band offsets, the exact strain of the structure was determined. First, as cathodoluminescence images (not reported here) do not showed misfit dislocations at the ZnS cap layer/SL interface for the above sample, the cap layer was assumed to have exactly the same lattice parameter than that of the whole SL. The strain state of the ZnS cap layer has been thus measured by ion-channeling Rutherford backscattering spectrometry at room temperature (RT) and turned out to be +0.19%. From this measured strain value the in plane lattice parameter ($a_{\text{ZnS}}^{\text{II}}$) of the ZnS cap layer can be determined, according to the lattice strain definition:

$$\varepsilon_{\text{res/ZnS}} = \frac{a_{\text{ZnS}}^{\text{II}} - a_{\text{ZnS}}}{a_{\text{ZnS}}} \quad (1)$$

and we use the value of $a_{\text{ZnS}}^{\text{II}} = a_{\text{MQW}}^{\text{II}}$ to calculate the residual strain of the MQW structure at 300K:

$$\varepsilon_{\text{MQW}}(300\text{K}) = \frac{a_{\text{ZnS}}^{\text{II}} - a_{\text{MQW}}}{a_{\text{MQW}}} = -0.612\% \quad (2)$$

with the free-standing lattice constant of the ZnSe/ZnS SL expressed by [4]:

$$a_{\text{MQW}} = \frac{a_{\text{ZnS}} G_{\text{ZnS}} d_{\text{ZnS}} + a_{\text{ZnSe}} G_{\text{ZnSe}} d_{\text{ZnSe}}}{G_{\text{ZnSe}} d_{\text{ZnSe}} + G_{\text{ZnS}} d_{\text{ZnS}}} \quad (3)$$

where d is the thickness of each layer, a is the material lattice constant and G is the shear modulus given by:

$$G = 2 \cdot \left[C_{11} + C_{12} - \frac{2(C_{12})^2}{C_{11}} \right] \quad (4)$$

with C_{11} and C_{12} elastic stiffness constants. By using Eqs. 2-4 and the materials parameters listed in Tab. 1, the misfit $f_{\text{MQW/ZnS}}$ between the MQW and the ZnS buffer layer at 300K can also be calculated:

$$f_{\text{MQW/ZnS}} = \frac{a_{\text{ZnSbuffer}} - a_{\text{MQW}}}{a_{\text{MQW}}} = -0.80\% \quad (5)$$

It should be noted that, by cooling down the whole structure from RT to 10K for the absorption measurements, a thermal strain contribution $\Delta f_{\text{MQW/ZnS/GaAs}}^{\text{ther}}$ adds to the residual SLs strain derived in Eq. 2 from RBS measurements. It can be demonstrated that this additional thermal strain is given by the relationship:

$$\Delta f_{\text{MQW/ZnS/GaAs}}^{\text{ther}} = [1 + \varepsilon_{\text{ZnS/GaAs}}^{\text{res}}] \times \Delta f_{\text{MQW/ZnS}}^{\text{ther}}(T_m) + \frac{a_{\text{ZnS}}(T_m)}{a_{\text{MQW}}(T_m)} \Delta f_{\text{ZnS/GaAs}}^{\text{ther}} \quad (6)$$

where $\Delta f_{\text{MQW/ZnS}}^{\text{ther}}$ indicates the thermal mismatch between the MQW and the ZnS buffer calculated between 300K and $T_m=10\text{K}$, $\Delta f_{\text{ZnS/GaAs}}^{\text{ther}}$ is the analogous thermal mismatch between ZnS and GaAs and $\varepsilon_{\text{res,ZnS/GaAs}}$ represents the RT residual lattice strain of the ZnS buffer layer. In our sample $\varepsilon_{\text{res,ZnS/GaAs}}=0$ because the 500 nm thick ZnS buffer is almost totally relaxed [6]. Under these conditions the value of $\Delta f_{\text{ther,MQW/ZnS/GaAs}}$ turns out to be $+5.55 \times 10^{-4}$ and needs to be added to the lattice residual strain given by Eq. 2 to get the total MQW strain at 10K, that equals -5.57×10^{-3} . From the above strain value the in-plane lattice parameter of the SLs at 10K can be calculated

according to Eq. 2, which finally allows us to estimate the effective strains of wells and barriers. Thus, the value of strain in the ZnSe wells is equal to -4.32×10^{-2} and it amounts to $+2.29 \times 10^{-3}$ in the ZnS barriers, indicating that the wells suffer a compressive strain and the barriers a tensile strain. These strain values have been included in the Kronig-Penney calculations of the energy transitions for the SL structure. The absorption transitions were calculated as a function of the conduction band discontinuity. In this calculation it was included both the mass nonparabolicity and the band shift induced by the compressive strain in the well and the weak tensile strain in the barriers. The exciton binding energy was assumed to be in the 30-40 meV range [7]. The presence of the elastic strain causes a hydrostatic and uniaxial deformation inside the structure inducing shifts of the conduction band (CB), hh and lh band edges [8]. The total deformation potential α has been shared between the CB and the VB in the same proportion of the band offset.

Table 1: List of materials parameters used in the calculations.

Materials	ZnSe	ZnS
$a_{300K}(\text{\AA})$	5.6687 ^(a)	5.4060 ^(a)
$a_{10K}(\text{\AA})$	5.6610 ^(b)	5.4041 ^(a)
$C_{11}(\text{N/m}^2)$	8.26×10^{10} ^(c)	10.67×10^{10} ^(c)
$C_{12}(\text{N/m}^2)$	4.98×10^{10} ^(c)	6.66×10^{10} ^(c)
$E_g(\text{eV})$	2.821 ^(a)	3.840 ^(b)
m_e	0.16 ^(a)	0.27 ^(d)
m_{HH}	0.6 ^(d)	0.49 ^(d)
m_{LH}	0.16 ^(e)	0.4 ^(e)
α	-4.25 ^(f)	-4.53 ^(g)
$b(\text{eV})$	-1.2 ^(a)	-1.25 ^(a)
$\Delta_{SO}(\text{eV})$	0.43 ^(a)	0.07 ^(d)

^(a) Ref. 9

^(b) From thermal expansion coefficients

^(c) Ref. 5 ^(d) Ref. 10 ^(e) Ref. 11

^(f) Ref. 12 ^(g) Ref. 13

Fig.1 Absorption spectrum of the ZnSe/ZnS SLs. Inset: Interband transitions to evaluate the CB offset.

The inset of Fig. 1 shows the calculated interband transitions as a function of the CB discontinuity. The continuous lines represent the calculated transitions energies, while the dashed horizontal lines indicates the energy intervals of the corresponding transitions in the absorption spectrum of Fig.1. The spectral broadening of the absorption curve is indicated by the energy separation of the dashed lines. The vertical gray band represents the CB values that fit (within the experimental errors) the experimental data. From these results a CB offset of 83 ± 2 meV can be derived, which corresponds to a 8.4 % of the total band offset in the CB. Fig. 2 shows the calculated MQW band structure resulting from the above calculations. V_{CB} , $V_{VB(HH)}$ and $V_{VB(LH)}$ represent the CB and VB offsets, respectively. Electron (e), heavy-hole (hh) and light-hole (lh) energy levels in the CB and VB, respectively are indicated. The arrows in the inset of Fig. 1 indicate the electronic transitions corresponding to the thus calculated excitonic peak positions superposed to the experimental absorption spectrum. We can thus ascribe the two peaks at 3.048 eV and 3.260 eV in the absorption spectrum as the $n=1$ electron-to-hh and electron-to-lh transitions, respectively.

Finally, the calculated interband transition energies as a function of the well width are shown in Fig. 3. These results represents the envelope-function calculations in the effective-mass approximation for well width values ranging between 5ML and 21 ML, and assuming a fully pseudomorphic SLs. In this case the value of total strain in the ZnSe wells is equal to -4.40×10^{-2} and it amounts to $+1.48 \times 10^{-3}$ in the ZnS barriers.

Fig 2: Schematic of the valence and conduction band alignments for the measured ZnSe/ZnS SLs (10K). The electronic transitions are also shown by arrows.

Fig. 3: 10 K Interband transition energies as a function of the ZnSe well width for a fully pseudomorphic ZnSe/ZnS SL.

Conclusions

A detailed calculation of the effects of lattice and thermal strains inside nearly pseudomorphic short-period ZnSe/ZnS SLs on the heterostructure electronic states was reported. Comparison was then made with experimental electronic transitions derived from 10K absorption spectroscopy measurements performed on a partially relaxed 30 periods ZnSe/ZnS SL. The intrinsic conduction-to-valence band offset ratio was finally found to be 8:92 for this type of SL structure.

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