Band structure of ZnSe-ZnTe superlattices

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We report the first study of the band structure of ZnSe-ZnTe superlattices. Our calculations are based on second order $\mathbf{k}\cdot\mathbf{p}$ theory and include the effects of strain and spin-orbit splitting on the superlattice band structure. Since the valence-band offset for this system is not well known, we have investigated the dependence of the superlattice band gap on the valence-band offset. Based on the assumption that the photoluminescence from the superlattice is due to an isoelectronic Te_1-bound exciton in ZnSe, we have fitted the experimental photoluminescence data with $\mathbf{k}\cdot\mathbf{p}$ theory to obtain the best value of the valence-band offset. The value we find is 0.975 ± 0.098 eV. Alternatively, assuming that the photoluminescence is due to band-to-band transitions we obtain a valence-band offset of 1.196 ± 0.134 eV. We have also calculated the superlattice band gap as a function of the constituent-material-layer thicknesses for the first valence-band offset quoted. We expect these results to be important in gaining an understanding of the value of the band offset, and the nature of the photoluminescence from this system.

I. INTRODUCTION

ZnSe and ZnTe are II-VI compound semiconductors which have direct band gaps in the visible region of the spectrum. Thus the ZnSe-ZnTe superlattice is an interesting system as it offers considerable promise as a means of producing tunable light emitters by variation of the constituent-material-layer thicknesses. It is thought that these superlattices would be particularly promising in producing blue-light-emitting diodes (LED's) and short-wavelength semiconductor lasers.[1–4] The successful growth of these superlattices by molecular-beam epitaxy (MBE) and preliminary characterization studies have already been reported.[5] Photoluminescence from these superlattices has been studied by Kobayashi *et al.*[2] and Kuwabara *et al.*[6] However, the nature of the photoluminescence from this system is not well understood.

In this paper we have performed band-structure calculations for this superlattice using second-order $\mathbf{k}\cdot\mathbf{p}$ theory including strain and spin-orbit effects. We have investigated the band offset of the ZnSe-ZnTe system by comparing our results with the photoluminescence data.[2] In Sec. II we describe details of the $\mathbf{k}\cdot\mathbf{p}$ band-structure calculations. In Sec. III we examine the effect of strain and valence-band offset on the superlattice band structure. By attributing the photoluminescence of the ZnSe-ZnTe superlattice to a Te_1 bound exciton in ZnSe, and performing a fit to the experimental data, we arrive at a value for the valence-band offset.

The large lattice mismatch of $\approx 7.2\%$ that exists between these two materials causes strain to play an important role in determining the characteristics of the ZnTe-ZnSe superlattice. Our calculations indicate that the strain effects produced by this large lattice mismatch can change the positions of the band edges of the superlattice by as much as 100–200 meV relative to their unstrained positions. In our calculations we have assumed that the magnitude of the strain in each layer is given by minimizing the elastic free energy of the structure. This is the so called free-standing configuration. It is appropriate for most ZnSe-ZnTe superlattices owing to the magnitude of the lattice mismatch; critical thickness models suggest that strain distributions deviating substantially from the free-standing case can be maintained for only a few monolayers.[7] Experimental studies show that superlattices grown well beyond the critical thickness can adopt a relatively defect-free structure in which the in-plane lattice constant jumps to that of the free-standing superlattice.[7] This justifies our analysis of ZnSe-ZnTe superlattices with layer thicknesses on the order of 10–20 Å based on the free-standing assumption.

II. THEORY

In this paper we have studied the band structure of ZnSe-ZnTe superlattices using second-order $\mathbf{k}\cdot\mathbf{p}$ theory with strain and spin-orbit terms included. The method employed is similar to the previous work of Wu and McGill[8] on HgTe-CdTe superlattices. The bulk band structure of ZnTe and ZnSe is calculated using Kane's eight-band model.[9] The eight bands that make up the basis set are the four Γ_8 bands (light-hole and heavy-hole bands), two Γ_7 bands (spin-orbit split-off bands) and two Γ_6 (conduction bands). We have taken the parameters for our calculations from Lawaetz[10] with the corrections for the 77-K gaps. The values we used were $E_0^{\mathrm{ZnSe}}=2.810$, $E_0^{\mathrm{ZnTe}}=2.364$, $\Delta_0^{\mathrm{ZnSe}}=0.43$, $\Delta_0^{\mathrm{ZnTe}}=0.92$, $E_p^{\mathrm{ZnSe}}=24.2$, and $E_p^{\mathrm{ZnTe}}=19.1$. All of these energies are in eV. Here E_0 and Δ_0 are the fundamental band-gap and the spin-orbit splitting, respectively. E_p is related to the P-matrix element of II-VI semiconductors by the relation $E_p=2mP^2/\hbar^2$, where m is the free-electron mass. The effects of the higher bands are included through perturbation theory by the use of Luttinger valence-band parameters. These parameters were also taken from Lawaetz[10] to be $\gamma_1^{\mathrm{ZnSe}}=3.77$, $\gamma_1^{\mathrm{ZnTe}}=3.74$, $\gamma_2^{\mathrm{ZnSe}}=1.24$,

$\gamma_2^{ZnTe}=1.07$, $\gamma_3^{ZnSe}=1.67$, $\gamma_3^{ZnTe}=1.64$, $\kappa^{ZnSe}=0.64$, $\kappa^{ZnTe}=0.42$, $q^{ZnSe}=0.02$, and $q^{ZnTe}=0.05$. To preserve the isotropy of the bulk bands, we replaced the values of γ_2 and γ_3 of each material by the average of γ_2 and γ_3 listed above and set $q=0$. In our calculations we have taken the lattice constants of the unstrained bulks to be $a^{ZnSe}=5.669$ Å and $a^{ZnTe}=6.104$ Å.[11] The calculation of the complex band structure of the bulk materials as well as the superlattice band structure was performed according to the method outlined by Smith and Mailhiot.[12]

Strain effects are easily included in the bulk Hamiltonians by the observation that the elements of the strain tensor ϵ_{ij} transform like $k_i k_j$ in the Kane Hamiltonian. Here i,j label the directions of the axes and k denotes the electronic wave vector. For superlattices grown on [100] orientations, the strain terms due to lattice mismatch appear only as the diagonal components of the strain tensor. We have used a model with four deformation potentials to describe the effects of strain on the bulk band structure. Following the convention of Bir and Pikus,[13] we have defined the three independent parameters a, b, and d to describe the effects of strain on the valence bands. Here a describes the hydrostatic shift in energy originating in the p-like bands due to strain. Uniaxial strains are described by b and d. A parameter c describes the hydrostatic shifts in the s-like energy bands. The values we used were[14,15] $a^{ZnSe}=1.35$, $a^{ZnTe}=1.35$, $b^{ZnSe}=-1.20$, $b^{ZnTe}=-1.78$, $d^{ZnSe}=-3.81$, $d^{ZnTe}=-4.58$, $c^{ZnSe}=-2.82$, and $c^{ZnTe}=-2.70$. These deformation potentials are expressed in eV. The elastic constants were taken to be[16] $C_{11}^{ZnSe}=8.10$, $C_{11}^{ZnTe}=7.13$, $C_{12}^{ZnSe}=4.88$, $C_{12}^{ZnTe}=4.07$, $C_{44}^{ZnSe}=4.41$, and $C_{44}^{ZnTe}=3.12$. These elastic constants are expressed in 10^{10} N m^{-2}.

III. RESULTS

The values of the valence-band offset reported for this system span over a wide range.[17–21] Harrison and Tersoff[17] predict a valence-band offset of 0.29 eV. Katnani and Margaritondo[18] report a measured valence-band offset of 0.43 eV. In Fig. 1 we have shown the relative alignments of the energy bands for the Harrison[19] value of the valence-band offset of 1.080 eV. This value of the band offset was chosen purely for illustrative purposes to discuss the effects of strain on the bulk band structures of ZnSe and ZnTe. Since strain moves the band edges, the effective valence-band offset in the superlattice is different from the unstrained offset and depends on the particular strain distribution in the structure. Thus it is more meaningful to describe the valence-band offset as the difference of the valence-band edges of the two materials before strain is introduced. The quantity so defined has the advantage of being independent of strain and layer thicknesses, and will be commonly denoted as the band offset in this paper. The band offset defined above is an input parameter to our calculations, and is shown as the difference between the dashed lines of Fig. 1. With an assumed valence-band offset, we can then compute the relative shifts and splitting of the bulk band edges due to strain. The band structures of ZnSe and ZnTe in Fig. 1

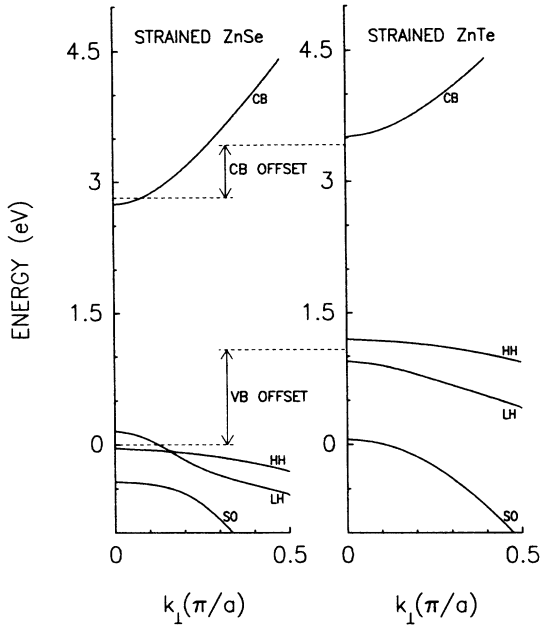

FIG. 1. Band structure of bulk ZnSe and ZnTe including strain appropriate to a 15 Å×15 Å free-standing superlattice. Zero of energy is taken to be the valence-band edge of ZnSe before strain is introduced. Harrison's (Ref. 19) valence-band offset $E_V^{ZnTe}-E_V^{ZnSe}=1.080$ eV is used. Dashed lines indicate the positions of the band edges of the unstrained bulks. The band structure shown is along the growth direction [100].

were calculated on this basis, assuming that the magnitude of the strain in each layer was equal to that of a free-standing 15 Å×15 Å superlattice. As described earlier, by a free-standing superlattice we mean a configuration in which the in-plane lattice constant is chosen to minimize the elastic free energy of the structure.

The band structures shown correspond to the strained bulks in the [100] direction with $k_\parallel=0$. ZnSe layers in the superlattice are under tensile strain, which has the effect of reducing the band gap of this material. Thus the valence bands of ZnSe move up, and the conduction bands move down with respect to their unstrained positions. In addition, the degeneracy of the heavy-hole and light-hole band is removed by the uniaxial strain. The dashed lines indicate the original positions of the band edges. In the superlattice of Fig. 1, the ZnSe light-hole bands are shifted up in energy by 157 meV, while the heavy-hole bands shift down in energy by 37 meV. The conduction bands of ZnSe are also lowered by 78 meV for this case. On the other hand the ZnTe layers of the superlattice are under compressive strain. This causes the conduction bands to move up, and the valence bands to move down with respect to their unstrained positions, increasing the band gap of this material. The heavy-hole and the light-hole bands are also split about their average position due to uniaxial terms. In Fig. 1, the ZnTe heavy hole moves up by 118 meV, the light hole moves down by 135 meV, and the conduction band moves up by 85 meV. We also see that the spin-orbit split-off bands play a more

important role in ZnSe than in ZnTe because they are closer to the light-hole band in ZnSe. We have shown the band structure only up to a quarter of the distance to the Brillouin zone edge along the growth direction of the superlattice.

In Fig. 2 we have shown the dependence of the band gap on the valence-band offset for a strained free-standing superlattice. Due to the large range of valence-band offsets reported for this system, we have presented results for a wide range of values. As the valence-band offset gets larger, the band gap of the superlattice decreases. This is due to the fact that the superlattice valence band is largely determined by the ZnTe heavy-hole bands while the superlattice conduction band is determined by ZnSe conduction bands. For the type-II alignment of the bands that exists in this superlattice, an increase in the valence-band offset brings the heavy-hole band of ZnTe and the conduction band of ZnSe closer to each other, reducing the superlattice band gap. We have shown three representative superlattices corresponding to layer thicknesses of 10 Å×10 Å, 15 Å×15 Å, and 20 Å×20 Å. The larger band gap is observed for the superlattice with the smallest period. This is due to the enhancement of the two-dimensional confinement of the wave functions of the superlattice as the layer thicknesses get smaller.

The studies by Kuwabara *et al.*[6] suggest that the photoluminescence is related to radiative recombination between band edge and localized centers, i.e., free to bound transitions. The work by Yao *et al.*[22] on Te isoelectronic traps in ZnSe suggests that the bound exciton transitions occur 160–170 meV below the band gap of ZnSe. Assuming that the effects of two-dimensional confinement on the bound exciton are negligible since it is tightly bound, we added this binding energy to the photoluminescence data to obtain the band gaps, and fit our calculated band gaps to the observed photoluminescence peaks from nine different superlattices. The value of the valence-band offset we find is 0.975±0.098 eV. However, since the nature of the photoluminescence from these superlattices is not well understood, the significance of this number is not certain. The results of a similar analysis assuming that the photoluminescence is due to band to band transitions gives us 1.196±0.134 eV. If strain effects are completely neglected, the trend is to get band offsets that are even higher than 1.196 eV by 100–200 meV.

Figure 3 shows a contour plot of the superlattice band gap as a function of the ZnSe and ZnTe layer thicknesses, based on a valence-band offset of 0.975 eV. To obtain the actual photoluminescence energies from Fig. 3, one has to subtract the binding energy of the exciton of 160 meV. In this figure the trend is to reduce the band gaps as either the ZnSe or the ZnTe layer thickness is increased. Since ZnSe acts as the barrier for the heavy-hole band the effect it has on the valence band is small. Thus, changes of the band gap in a direction parallel to the ZnSe axis come mainly from the motion of the conduction band. On the other hand, ZnTe acts as the barrier for the conduction band. Thus, changes of the band gap in a direction parallel to the ZnTe axis are derived mainly from the heavy-hole band.

IV. CONCLUSION

We have performed detailed band-structure calculations for the ZnSe-ZnTe superlattice. Currently the pho-

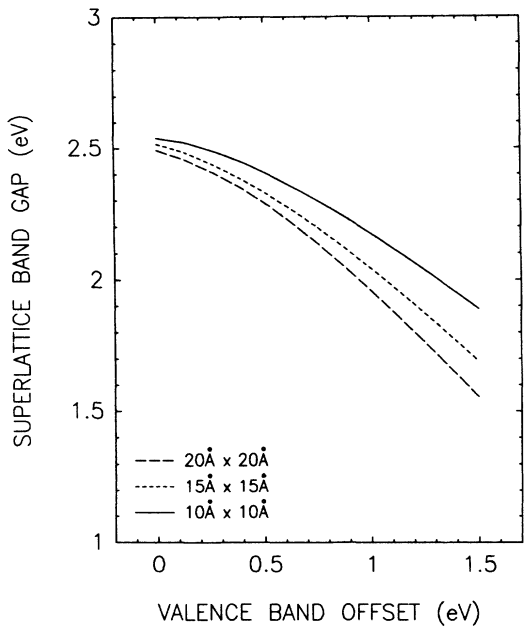

FIG. 2. Variation of the band gap of a few representative superlattices with the valence-band offset $E_V^{ZnTe} - E_V^{ZnSe}$. Notice that the band gap decreases as the valence-band offset is increased. The calculation includes effects due to strain. Structures were assumed to be coherently strained with an in-plane lattice constant determined by minimizing the elastic free energy of the superlattice (i.e., the free-standing limit).

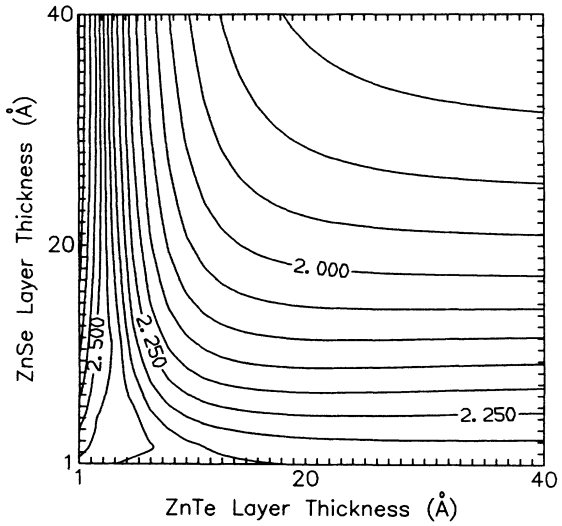

FIG. 3. Contour plot of the ZnSe-ZnTe superlattice band gap at 77 K as a function of the layer thicknesses of ZnSe and ZnTe within a single superlattice period. The valence-band offset is assumed to be 0.975 eV. The lattice constants correspond to that of a free-standing superlattice. The contour interval is 50 meV. A binding energy of 160 meV has to be subtracted from these band gaps to get the photoluminescence peaks.

toluminescence from this system seems to be due to a free to bound transition.[6] Assuming that a Te_1 isoelectronic trap is responsible for the photoluminescence, we obtain a valence-band offset of 0.975 ± 0.098 eV. Neglecting this binding energy gives us a band offset of 1.196 ± 0.134 eV. However, one cannot be definitive on the value of the valence-band offset until thorough investigations are done on the luminescence from this superlattice.

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