Strained-layer interfaces between II–VI compound semiconductors

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(Received 3 February 1988; accepted 21 April 1988)

II–VI multilayer structures are eminently suitable for various optoelectronic devices covering from the infrared to the ultraviolet spectral range. We present a theoretical study of the band lineups at interfaces involving ZnS, ZnSe, ZnTe, CdTe, and HgTe based on the "model solid" theory. We also experimentally investigate the strains and band offsets in $ZnSe/ZnS_xSe_{1-x}$ strained-layer superlattices, using Raman and photoluminescence spectroscopy. The conduction-band offset at such interfaces is found to be small. Theoretical predictions for other interfaces include a large type-II offset in ZnSe/ZnTe, and a small average valence-band discontinuity in ZnTe/CdTe.

I. INTRODUCTION

Heterojunctions between II–VI compounds have many promising applications, such as infrared detectors and light-emitting devices in the visible region. Since most of these semiconductors have widely differing lattice constants (see Table I), strain will be present in the layers to allow pseudomorphic growth. These strains, together with alloy composition, choice of substrate, and layer thickness, provide additional degrees of freedom in tailoring the electronic band structure for the desired device properties. In this paper, we will discuss various interfaces involving ZnS, ZnSe, ZnTe, CdTe, and HgTe. The general theoretical study will be accompanied by experimental observations for $ZnSe/ZnS_xSe_{1-x}$ strained-layer superlattices (SLS), grown by molecular-beam epitaxy (MBE). Raman and photoluminescence spectroscopies allow us to study the effects of strain and carrier confinement, and obtain empirical values for the band offsets.

The potential applications of a particular materials combination depend critically on the values of the band discontinuities at the heterointerface. Experimental determination of these quantities is still a difficult problem, and measured values are often the subject of intense controversy. On the theoretical side, it has recently become possible to carry out first-principles, parameter-free calculations of the interfacial electronic structure.[2] This has resulted not only in explicit band-offset values for a wide variety of heterojunction systems, but also in the development of a model solid theory which allows quick and easy derivation of the discontinuities based on tabulated values.[3] Particularly in the case of strained-layer interfaces, where carrying out a first-principles calculation for every imaginable strain configuration would be unfeasible, the model solid theory can be a useful tool for exploring the band lineups for a wide variety of systems. Strain can be incorporated in a straightforward fashion, leading to reliable predictions in a number of experimentally established test cases. The model theory, and its connection to the full first-principles calculations, has been described in detail elsewhere.[2,3] Here we will only outline its application, and provide values for the II–VI compounds.

The rest of this paper is organized as follows: in Sec. II, we describe the formalism for evaluating the effect of strain on the band edges, and on the lineups at the interface. In Sec. III, we examine the $ZnSe/ZnS_xSe_{1-x}$ strained-layer interface, and report our experimental results. Finally, in Sec. IV, we discuss our results for II–VI interfaces in a general context.

II. EFFECTS OF STRAIN ON THE BAND EDGES AND THE BAND LINEUPS

When a sufficiently thin layer of a semiconductor is grown on top of another semiconductor with a different lattice constant, a pseudomorphic, epitaxial interface can be formed, provided the thin layer is appropriately strained. The strains

TABLE I. Lattice constant (in Å) and elastic constants[a] (in 10^6 kg/cm^2) for various II–VI compound semiconductors. Also listed are atomic configurations used for calculating reference levels in the model solid theory (Ref. 6).

	a	c_{11}	c_{12}	c_{44}	Atomic configurations
ZnS	5.40	1.067[a]	0.666[b]	0.456	$Zn{:}s^{1.02}p^{0.98}$;$S{:}s^{1.86}p^{4.14}$
ZnSe	5.65	0.826	0.498	0.400	$Zn{:}s^{1.02}p^{0.98}$;$Se{:}s^{1.86}p^{4.14}$
ZnTe	6.08	0.713	0.407	0.312	$Zn{:}s^{1.20}p^{0.80}$;$Te{:}s^{1.86}p^{4.14}$
CdTe	6.48	0.562	0.394	0.206	$Cd{:}s^{1.27}p^{0.73}$;$Te{:}s^{1.70}p^{4.30}$
HgTe	6.48	0.597	0.415	0.226	$Hg{:}s^{1.38}p^{0.62}$;$Te{:}s^{1.79}p^{4.21}$

[a] Ref. 1 except where indicated.
[b] R. B. Hall and J. D. Meakin, Thin Solid Films **63**, 203 (1979).

 0734-211X/88/041350-04$01.00

will insure that the lattice constant parallel to the interface remains the same throughout the structure, and can be determined from the elastic constants (listed in Table I) and the boundary conditions.[2,4] Here we assume that the strain values, as expressed in the strain tensor $\vec{\epsilon}$, are known for a particular layer. Since we will concentrate on (001)-grown structures here, this amounts to specifying $\epsilon_{xx} = \epsilon_{yy}$ and ϵ_{zz}.

All the II–VI materials under study here have direct band gaps; therefore, the relevant band edges are the (nondegenerate) conduction-band minimum at Γ, E_c, and the valence bands at Γ (degenerate in the absence of strain and spin-orbit splitting), which we will label by $E_{v,1}$, $E_{v,2}$ (the light and heavy hole bands, respectively), and $E_{v,3}$ (the split-off band). The average of these bands will be referred to as $E_{v,av}$. The biaxial components of the strain lead to the following shifts in the valence bands with respect to the average[5]:

$$\Delta E_{v,2} = \tfrac{1}{3}\Delta_0 - \tfrac{1}{2}\delta E_{001}, \tag{1a}$$

$$\Delta E_{v,1} = -\tfrac{1}{6}\Delta_0 + \tfrac{1}{4}\delta E_{001} + \tfrac{1}{2}\left[\Delta_0^2 + \Delta_0\delta E_{001} + \tfrac{9}{4}(\delta E_{001})^2\right]^{1/2},$$

$$\Delta E_{v,3} = -\tfrac{1}{6}\Delta_0 + \tfrac{1}{4}\delta E_{001} \tag{1b}$$

$$- \tfrac{1}{2}\left[\Delta_0^2 + \Delta_0\delta E_{001} + \tfrac{9}{4}(\delta E_{001})^2\right]^{1/2}. \tag{1c}$$

In these equations, Δ_0 is the spin-orbit splitting in the unstrained material (see Table II), and δE_{001} is given by:

$$\delta E_{001} = 2b(\epsilon_{zz} - \epsilon_{xx}), \tag{2}$$

where b is the shear deformation potential for a strain of tetragonal symmetry. Experimental values for this quantity are not available for all materials. Theoretical values for b have proven to be reliable,[2] and will be used here. They are listed in Table II.

In addition to these splittings, the hydrostatic components of the strain will cause shifts in E_c and in $E_{v,av}$. When dealing with bulk semiconductors, one usually considers only the *relative* shift of the conduction band with respect to the valence band; for the heterojunction problem, however, values for individual band edges are essential, since they will influence the discontinuities at the interface. The shifts are expressed as:

$$\Delta E_{v,av} = a_v(\Delta\Omega/\Omega), \tag{3}$$

where a_v is the hydrostatic deformation potential for the valence band, and $\Delta\Omega/\Omega = \mathrm{Tr}\,\vec{\epsilon} = (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})$ is the fractional volume change. Similarly,

$$\Delta E_c = a_c(\Delta\Omega/\Omega). \tag{4}$$

Values for a_v and a_c, derived within the model solid approach, are listed in Table II.

At this point, we have all the necessary information to describe the effect of strain on the band structure of an individual semiconductor. To determine the band offsets, we need to line up the bulk band structures at the interface, i.e., we need to know a reference level for each semiconductor on an absolute energy scale. Within the model solid theory, we have chosen the average of the valence bands as a reference. Values for $E_{v,av}$ in equilibrium are given in Table II. We stress that these "absolute" values for $E_{v,av}$ do not carry any meaning by themselves (and should certainly not be related to the ionization potential), but are only meaningful relative to similar quantities in other semiconductors. We also provide values for the conduction-band minima on the absolute energy scale. These have been derived by taking our calculated value for the valence band and adding to it the experimental band gap. When the semiconductor is strained, $E_{v,av}$ and E_c will be shifted due to hydrostatic strain components according to Eqs. (3) and (4).

We estimate the error bar on the band offsets obtained from the values in Table II to be on the order of 0.2 eV.[2] This is confirmed by the results of an explicit self-consistent interface calculation (following the methods of Ref. 2) for ZnS/ZnSe, which yielded lineups that were within 0.15 eV of the model-solid values.

Let us illustrate how to derive band offsets for a heterojunction A/B starting from the values in Table II. For lattice-matched interfaces, the discontinuity in the average valence bands is

$$\Delta E_{v,av} = E^B_{v,av} - E^A_{v,av}. \tag{5}$$

The sign convention is such that $\Delta E_{v,av}$ is positive when the valence band in B is higher in energy than the valence band in A. To obtain the position of the individual valence bands with respect to the average, the spin-orbit splitting Δ_0 (also listed in Table II) has to be introduced. The topmost valence band in A is then given by

$$E^A_v = E^A_{v,av} + \Delta^A_0/3. \tag{6}$$

For a strained-layer interface, hydrostatic and biaxial components of the strain will shift and split the valence bands. As an example we choose a ZnS/ZnSe interface. A thin layer of pure ZnS, deposited on a (001) ZnSe substrate, is subject to strains; $\epsilon_{xx} = \epsilon_{yy} = 0.046$, $\epsilon_{zz} = -0.058$. This results in a

TABLE II. Spin-orbit splitting Δ_0 and energy gap E_g of various II–VI compound semiconductors (Ref. 1). The values of $E_{v,av}$ (average of the three uppermost valence bands at Γ), $a_v = d(E_{v,av})/d(\ln\Omega)$, $a_c = d(E_c)/d(\ln\Omega)$, and $a = d(E_c - E_{v,av})/d(\ln\Omega)$ are all calculated within the model solid approach. Conduction-band values for HgTe refer to the Γ_6 band which lies below the top of the valence band in this material. Also listed are calculated values of the deformation potential b. All values are in eV.

	Δ_0	E_g	$E_{v,av}$	E_c	a_v	a_c	a	b
ZnS	0.07	3.84	−9.15	−5.29	2.31	−4.09	−6.40	−1.25
ZnSe	0.43	2.83	8.37	−5.40	1.65	−4.17	−5.82	1.20
ZnTe	0.91	2.39	−7.17	−4.48	0.79	−5.83	−6.62	−1.26
CdTe	0.93	1.59	−7.07	−5.17	0.55	−3.96	−4.52	−1.10
HgTe	1.05	(−0.30)	−6.88	(−6.83)	−0.13	−4.60	−4.48	−1.15

TABLE III. Experimental results for ZnS_xSe_{1-x} superlattices. Listed are the well (L_w) and barrier (L_b) layer thicknesses (in Å), the sulfur composition x, and the strain values in the ZnSe layers determined from Raman measurements ϵ_{xx}^R (%). Empirical valence-band offsets $\Delta E_v^{\rm exp}$ are determined by fitting to observed transition energies. For comparison, we also list $\Delta E_v^{\rm th}$ obtained from the model solid theory. ΔE_v is expressed in meV.

MBE No.	L_w/L_b	x	ϵ_{xx}^R	$\Delta E_v^{\rm exp}$	$\Delta E_v^{\rm th}$
111	30/128	0.26	−0.5	130	120
118	40/43	0.14	0.0	107	100
115	46/49	0.20	−0.2	90	84
43	55/60	0.19	−0.22	100	118

volume change $\Delta\Omega/\Omega = 0.035$. From Table II and Eq. (3):

$$E_{v,av}^{\rm ZnSe} = -8.37 \text{ eV},$$

and

$$E_{v,av}^{\rm ZnS} = -9.15 + 2.31\times 0.035 = -9.07 \text{ eV}.$$

This leads to $\Delta E_{v,av} = 0.70$ eV (higher in ZnSe). Adding in spin-orbit splitting in ZnSe raises the valence-band maximum by 0.14 eV. For ZnS, Eq. (2) gives $\delta E_{001} = 0.26$ eV. Equation (1) then yields: $\Delta E_{v,2} = -0.11$, $\Delta E_{v,1} = 0.26$, and $\Delta E_{v,3} = -0.16$. The uppermost valence band will therefore be $E_{v,2}$. We find: $\Delta E_v = 0.70 + 0.14 - 0.26 = 0.58$ eV. For the conduction bands, we have $E_c^{\rm ZnSe} = -5.40$ eV, and

$$E_c^{\rm ZnS} = E_c^{\rm ZnS,0} + a_c \times \Delta\Omega/\Omega$$
$$= -5.29 + (-4.09)\times 0.035 = -5.43 \text{ eV}.$$

This results in $\Delta E_c = 0.03$ eV. Finally, we note that band positions for alloys, such as ZnS_xSe_{1-x} can be obtained using linear interpolation between the pure materials, ZnS and ZnSe.

III. EXPERIMENTAL OBSERVATIONS

$ZnSe/ZnS_xSe_{1-x}$ superlattices were grown by MBE on [001] GaAs substrates at 350 °C. Each SLS was grown on a relaxed ZnSe buffer layer with thickness of about 1 μ. Thicknesses of the individual superlattice layers were kept well within their "critical thickness" to insure uniform strain and absence of misfit dislocations. Raman measurements were used to determine the sulfur composition of the barrier layers, and the biaxial strains. Layer thicknesses were determined by transmission electron microscopy. The low-temperature photoluminescence spectra allow identification of the free exciton peak, which clearly shows a shift towards higher energies. This blue shift is caused by a combination of the strain and confinement effects. More details of the experimental conditions can be found in Ref. 4.

Several superlattice structures were grown, ranging from ~1000 Å to ~5 μm *total* thickness. When the total thickness of the superlattice remains smaller than a certain critical thickness (on the order of 1000 Å) one expects it to assume the same lattice constant as the buffer layer. The superlattice grows pseudomorphically to the buffer layer, and the ZnSe layers are not strained. All the blue shift in the optical spectra can then be attributed to confinement effects only. On the other hand, if this total thickness becomes substantially larger than the critical thickness, the superlattice moves towards the "free standing" state and assumes a new equilibrium lattice constant. Both types of layers are now subject to strains, and transitions in the ZnSe layers are shifted due to strain as well. For an intermediate total thickness of the superlattice, relaxation to the equilibrium free-standing state may not be complete. For superlattices with a total thickness in the range of 0.1 to 1 μm, we found that the strains measured directly with the Raman probe (ϵ_{xx}^R) were much smaller than the ones that could be estimated based on the sulfur composition of the alloy layers and the ensuing lattice mismatch, *assuming* that the superlattice was free standing. This indicates that these superlattices had not reached their equilibrium, free-standing state yet. In the interpretation of the spectra, the Raman-measured strains are used. The relevant values for different MBE samples can be found in Table II. Notice that MBE sample No. 118 (total thickness ~1000 Å) was pseudomorphic to the buffer layer, as evidenced by the absence of strain in the ZnSe layers.

In addition to the strain effects on the energy bands, confinement of carriers in the wells will also shift transition energies to higher values. The confinement energies were calculated within the envelope-function approximation.[7] The band offsets were taken as adjustable parameters in the calculation of confinement energies, and then determined by fitting to the experimentally observed shifts. This leads to the values for ΔE_v listed in Table III. There, we also list the theoretical values obtained with the approach from Sec. II (and using the measured strain values). One observes that the agreement is very satisfactory. The corresponding conduction-band offsets ΔE_c (both from experiment and theory) are smaller than 10 meV in all cases.

IV. DISCUSSION

Experimental observations on $ZnSe/ZnS_xSe_{1-x}$ indicate a very small conduction-band offset. Since a larger barrier height for confinement of electrons is desirable in certain applications, one can try to look for systems with a larger ΔE_c. While it would be difficult to perform an exhaustive search experimentally, our theoretical approach allows us to readily examine all possibilities. We find that ΔE_v can be varied over quite a large range, especially if one increases the sulfur content of the alloy. For a particular alloy composition, variation of the strain has important effects on ΔE_v, mainly because of the sizable splitting caused by the biaxial strain. ΔE_c, on the other hand, will always remain very small. These observations illustrate the power of the model-solid theory, which allows a quick and reliable assessment for a wide variety of systems.

Let us finally examine some of the other systems that can be based on the materials listed in Table II. For ZnSe/ZnTe, it is immediately clear that we find a large valence-band offset and also a large conduction-band offset. Both the conduction and valence band of ZnTe are above the corresponding bands in ZnSe, leading to a type-II offset. This conclusion is independent of the specific strain configuration. Although the mismatch between ZnTe and ZnSe is larger than 7%, superlattices have reportedly been grown that show strong photoluminescence associated with the band edges.[8] These experiments are consistent with a type II offset.

Another system that has attracted attention is ZnTe/CdTe. The model-solid predictions lead to a small average valence-band discontinuity, $\Delta E_{v,av}$. From resonance Raman scattering experiments on ZnTe/CdTe superlattices, Menéndez *et al.*[9] concluded that the valence-band offset would be small. Duc *et al.*[10] used x-ray photoemission spectroscopy to determine ΔE_v. They found $\Delta E_v \sim -0.1$ eV, but this value was obtained using core-level to valence-band energies measured on unstrained materials, thereby neglecting important strain contributions.[11] If we take their value as indicative of some average lineup, however, it is in fair agreement with the $\Delta E_{v,av}$ that follows from the model solid approach.

ACKNOWLEDGMENTS

Thanks are due to R. Dalby, D. A. Dammack, and H. Cornelissen for supplying the MBE samples.

[1]Landolt–Börnstein, *Numerical Data and Functional Relationships in Science and Technology* (Springer, New York, 1982), Group III, Vol. 17 a–b.
[2]C. G. Van de Walle and R. M. Martin, Phys. Rev. B **34**, 5621 (1986); **35**, 8154 (1987).
[3]C. G. Van de Walle, in *Epitaxy of Semiconductor Layered Structures*, edited by R. T. Tung, L. R. Dawson, and R. L. Gunshor, Materials Research Society Symposia Proceedings, Vol. 102 (Materials Research Society, Pittsburgh, Pennsylvania, 1988) (to be published).
[4]K. Shahzad, D. J. Olego, and C. G. Van de Walle (to be published).
[5]F. H. Pollak and M. Cardona, Phys. Rev. **172**, 816 (1968).
[6]Atomic configurations were obtained from tight-binding calculations by D. J. Chadi (private communication).
[7]G. Bastard, Phys. Rev. B **24**, 5693 (1981).
[8]H. Fujiyasu, K. Mochizuli, Y. Yamazaki, M. Aoki, A. Sasaki, H. Kuwabara, Y. Nakanishi, and G. Shimaoka, Surf. Sci. **174**, 543 (1986).
[9]J. Menéndez, A. Pinczuk, J. P. Valladares, R. D. Feldman, and R. F. Austin, Appl. Phys. Lett. **50**, 1101 (1987).
[10]T. M. Duc, C. Hsu, and J. P. Faurie, Phys. Rev. Lett. **58**, 1127 (1987).
[11]J. Tersoff and C. G. Van de Walle, Phys. Rev. Lett. **59**, 946 (1987).