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ScienceDirect
Thin Solid Films 516 (2008) 1608–1612
www.elsevier.com/locate/tsf

Band offset calculations of $ZnS_xSe_{1-x}/ZnS_ySe_{1-y}$ heterostructures

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Available online 1 August 2007

Abstract

In order to design devices based on II–VI materials, it is necessary to know the potential across the interface between two materials. Following our recent calculations which prove that the band gap energy of ZnS_xSe_{1-x} alloy has a nonlinear behaviour versus the sulphur composition x, it appears that an accurate knowledge of band offsets for $ZnS_xSe_{1-x}/ZnS_ySe_{1-y}$ structures will be useful to model devices based on this heterostructure. On the basis of a model-solid theory, we report in this work the band offset calculations for zinc blende pseudomorphically strained $ZnS_xSe_{1-x}/ZnS_ySe_{1-y}$ interface. From the results obtained, we have calculated the band gap energies of ZnS_xSe_{1-x} layers pseudomorphically strained on ZnS_ySe_{1-y} substrate as a function of compositions x and y in the whole range $0 \le x,y \le 1$. Also, the band gaps of bulk ZnS_xSe_{1-x} deposed on ZnS_ySe_{1-y} for several values of y have been calculated versus the sulphur content x. Analytical formulas fitting these bands have been obtained. In view of the lack of theoretical calculations, our results seem likely to be useful especially in the design of ZnS_xSe_{1-x} structures for optoelectronic devices applications.

Keywords: Band offset; Strain effect; Strained gap; Optical properties; II-VI heterostructures

1. Introduction

For a long time there has been a regained interest in the study of II–VI compounds. These materials are interesting with regard to their electronic and optical properties due to the large scale provided by their fundamental gap going up to 3.67 eV for ZnS [1]. Especially, ZnS and ZnSe are considered promising materials to the realization of blue light emitters and UV photodetectors [2–4]. For this reason, different research activities have been carried out in the epitaxy of small structure systems containing zinc–selenide (ZnSe) and zinc–sulphide zinc–selenide alloys (ZnS_xSe_{1-x}) and their applications in optoelectronic and microelectronic devices [5–7]. Some of these devices are obtained from the mentioned materials by layered structures such as heterostructures and superlattices. Their optical and electronic properties are mainly driven by the potential across the interface between the two compounds. This potential is known as the band offset. However, critical issues must be resolved before the calculation of the band offsets. Indeed, the computation of the band offsets requires the knowledge of some electronic band parameters such as the band gap energy and the electron and the hole effective masses. Our results reported in a recent paper [8] proves that the band gap energy has a nonlinear behaviour versus the sulphur composition x. Indeed, we have shown that the incorporation of the sulphur gives a decreasing tendency band gap for small composition and an increasing one for the remained range of x. Such strong deviation from the linear behaviour encourages us to calculate the band edge alignment for $ZnS_xSe_{1-x}/ZnS_ySe_{1-y}$ interface.

In this work, using the model solid theory, we have computed the valence and conduction band offsets for $ZnS_xSe_{1-x}/ZnS_ySe_{1-y}$ (001)-oriented interface along the range of sulphur compositions x and y varying between 0 and 1. Then we have calculated the band gap energy of ZnS_xSe_{1-x} layers pseudomorphically strained on ZnS_ySe_{1-y} substrate versus the compositions x and y in the whole range $0 \le x,y \le 1$. The band gaps of bulk ZnS_xSe_{1-x} deposed on ZnS_ySe_{1-y} for y equal to 0, 0.5 and 1 have been calculated versus the sulphur composition x.

2. Band offset calculations

2.1. Theoretical background

In the purpose to calculate the band alignment across (001)-oriented $ZnS_xSe_{1-x}/ZnS_ySe_{1-y}$ pseudomorphically strained

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doi:10.1016/j.tsf.2007.07.172

interfaces, we have adopted the procedure outlined by Van de Walle et al. [9,10]. The model solid theory developed in this reference has two main aspects. The first is the generation of an accurate band structure by performing density-functional calculation on individual bulk semiconductors. The second consists in the establishment of a reference level that can be used for a line up procedure. This reference denoted E_{v,a_v} is defined as the average over the three uppermost valence bands at Γ point of the Brillouin zone. This allows the evaluation of the energy levels on an absolute energy scale and also the derivation of band lineups.

The procedure of the computation of the valence band offset related to the heavy and light holes as well as the conduction band offset will be described hereafter.

For heavy holes, the valence band offset $\Delta E_{v,hh}$ at ZnS_xSe_{1-x}/ZnS_ySe_{1-y} heterointerface is expressed as:

$$\begin{aligned}\Delta E_{v,hh} &= E_{v,hh}^{str}(ZnS_xSe_{1-x}) - E_v^{uns}(ZnS_ySe_{1-y}) \\ &= \Delta E_v^{uns} + \delta E_{v,hh}\end{aligned} \quad (1)$$

where ΔE_v^{uns} is the natural valence band discontinuity and $\delta E_{v,hh}$ is the shift of the valence band energy due to the strain.

Similarly, for light holes, the valence band offset $\Delta E_{v,lh}$ reads:

$$\Delta E_{v,lh} = \Delta E_v^{uns} + \delta E_{v,lh} \quad (2)$$

where $\delta E_{v,lh}$ is the strain-dependent shift of the light-hole valence band.

The conduction band offset ΔE_c can be written as:

$$\begin{aligned}\Delta E_c &= E_c^{str}(ZnS_xSe_{1-x}) - E_c^{uns}(ZnS_ySe_{1-y}) \\ &= \Delta E_v^{uns} + \Delta E_g^{uns} + \delta E_c\end{aligned} \quad (3)$$

where ΔE_v^{uns} is the unstrained valence band discontinuity, ΔE_g^{uns} represents the band gap difference between the unstrained materials which constitute the heterojunction and δE_c is the shift of the conduction band provoked by the strain. To calculate ΔE_g^{uns}, we use the nonlinear expression of the band gap energy variation reported in a former work [8] and given by:

$$E_g^{\Gamma}(x) = 2.80 - 2.26x + 7.55x^2 - 4.43x^3 \qquad \text{eV}.$$

For the investigated heterointerface ZnS_xSe_{1-x}/ZnS_ySe_{1-y}, there is a strain due to the lattice parameters mismatch. The effect of this strain on energy levels can be decomposed into hydrostatic and shear contributions. The hydrostatic strain shifts the average valence band energy as well as the conduction band according to:

$$\delta E_{v,a_v}^{hy} = a_v(2\varepsilon_{//} + \varepsilon_{\perp}) \quad (4)$$

$$\delta E_c^{hy} = a_c(2\varepsilon_{//} + \varepsilon_{\perp}) \quad (5)$$

where $\varepsilon_{//}$ and $\varepsilon_{\perp}$ are the strain components tensor respectively in-plane and perpendicular to the plane interface. a_v and a_c are the hydrostatic deformation potentials for the valence and conduction bands. $\varepsilon_{//}$ is expressed in terms of the substrate and the over layer lattice constants $a_{//}$ and a such that:

$$\varepsilon_{//} = \frac{a_{//}}{a} - 1. \quad (6)$$

The perpendicular strain component is related to $\varepsilon_{//}$ by:

$$\varepsilon_{\perp} = -2\frac{c_{12}}{c_{11}}\varepsilon_{//} \quad (7)$$

where c_{11} and c_{12} are the elastic constants of the epitaxial layer material.

The shear contribution joined to the spin-orbit interaction leads to an additional splitting of the valence band. For a (001) interface, the energy shifts from the band relative to their unstrained positions are given by [9–11]:

$$\begin{aligned}\delta E_{hh}^{sh} &= -\frac{1}{2}\delta E_{001} \\ \delta E_{lh}^{sh} &= -\frac{1}{2}\Delta_0 + \frac{1}{4}\delta E_{001} + \frac{1}{2}\sqrt{\left(\Delta_0^2 + \Delta_0\delta E_{001} + \frac{9}{4}\delta E_{001}^2\right)}\end{aligned} \quad (8)$$

with: $\delta E_{001} = 2b(\varepsilon_{\perp} - \varepsilon_{//})b$ represents the uniaxial deformation potential for the valence band and Δ_0 is the spin-orbit splitting. The subscripts hh and lh refer to the heavy hole and the light hole bands respectively.

For zinc-blende ZnS_xSe_{1-x} material, the conduction band is of Γ character over the whole range of composition x. As a consequence, the uniaxial strain component has no effect on the energetic position of this band.

Table 1
Parameters used for the band offset calculations

	E_g^{Γ} (eV)	E_{v,a_v} (eV)	a_c (eV)	a_v (eV)	a (nm)	c_{11} (GPa)	c_{12} (GPa)	Δ_0 (eV)	b (eV)
ZnSe	2.80 [a]	−8.37 [b]	−4.17 [b]	1.65 [b]	0.5668 [c]	0.826 [d]	0.498 [d]	0.43 [e]	−1.20 [f]
ZnS	3.67 [a]	−9.15 [b]	−4.09 [b]	2.31 [b]	0.5409 [c]	1.067 [g]	0.666 [g]	0.07 [e]	−0.80 [f]

All symbols have the meanings given in the text.
[a] Ref. [1].
[b] Ref. [10].
[c] Ref. [16].
[d] Ref. [17].
[e] Ref. [19].
[f] Ref. [20].
[g] Ref. [18].