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Quaternary Alloy for Renewable Energy

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***Abstract*— the conduction/valence band offset is a very important parameter in any heterojunction device. In the present work we report some theoretical methods which are used for determinate the band offsets of the quaternary $Ga_{1-x}In_xAs_ySb_{1-y}$ alloys, lattice matched on GaSb substrate, these theoretical models are in good agreement with experiment data available in literature.**

***Keywords*— Band offsets, GaInAsSb, GaSb, alloy, modeling.**

I. INTRODUCTION

Much effort went into making Ge photovoltaic cells for TPV generators in the late1960's and early 1970's because Ge has a low energy band gap of 0.67 eV, but these cells never achieved high quantum efficiencies due to inherent problems ultimately related to the fact that Ge is an indirect band gap material. This problem can be circumvented bay switching to GaSb with is a direct band gap material and has a band gap of 0.72 eV with is only slightly higher than Ge [1].An advantage of the quaternary III-V semiconductors systems is that devices can be fabricated by molecular beam epitaxy on a suitable binary substrate, such as GaSb or InAs and the band gap and lattice constant can be adjusted more or less independently, to math requirement [2].Recently the quaternary $Ga_{1-x}In_xAs_ySb_{1-y}$ alloys are a more promising materials for optoelectronic such as photodiode, thermophotovoltaic and solar cells because they can be grown lattice matched to GaSb substrates for band gaps as low as 0.5 eV [3].

II. LATTICE PARAMETER

The composition of the quaternary alloy was determined by quantitative electron microprobe analysis. It corresponds to x=0.23 and y=0.2 lattice mismatch is given as formula:

$$\Delta a/a=(a_{layer}- a_{substrate})/a_{substrate} \quad (1)$$

In these conditions discussed above, lattice mismatch measured by double x-ray diffraction is $\Delta a/a=3\times10^{-4}$. For this epitaxial structure, which is convenient for photodetection, we have prepared mesa blind diodes (Fig. 1) of 200 µm diameter [4].

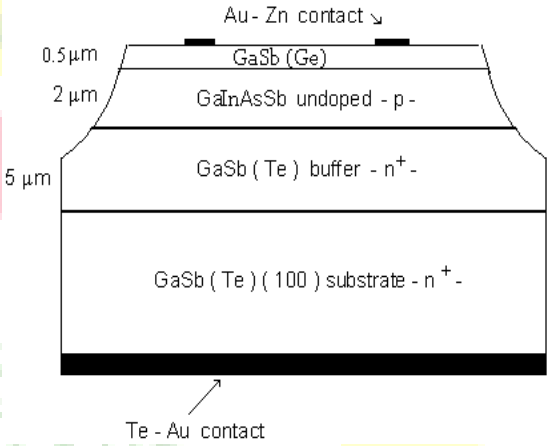

Fig. 1 Structure of GaInAsSb/GaSb blind diode (mesa area =$\pi\times10^{-4}$ cm^2)

III. INTERPOLATION SCHEME

The electronic energy band parameters of III-V compound alloys and their dependence on alloy composition are very important device parameters, and so they have received considerable attention in the past. Investigation of many device parameters have, however, been hampered by a lack of definite knowledge of various material parameters. This necessitates the use of some kind of interpolation scheme.

Although the interpolation scheme is still open to experimental verification, it can provide more useful and reliable material parameters over the entire range of alloy composition [5].

The quaternary material $A_X B_{(1-x)} C_y D_{(1-y)}$ is thought to be constructed from four binaries: AC, AD, BC, and BD. If one uses the linear interpolation scheme, the quaternary parameter Q can be derived from the Bs by:

$$Q(x,y)= x\ y\ B_{AC} + x\ (1-y)\ B_{AD} + (1-x)\ y\ B_{BC} + (1-x)\ (1-y)\ B_{BD} \quad (2)$$

Using (Eq. 2), lattice mismatching condition of the $Ga_{1-x}In_xAs_ySb_{1-y}$ on GaSb substrate, have the form [6].

$$y=(0.383\ x)\ /\ (0.442-0.021\ x) \qquad (0\leq x\leq 1.0) \qquad (3)$$

The (Eq. 2) can be whiting by using the approximation of Padé (m=2, n=0), as the formula:

$$y=0.866\ x+0.042\ x^2 \qquad (0\leq x\leq 1.0) \qquad (4)$$

When the relative error is lower than 2%.

IV. ENERGY BAND PARAMETERS

A. *band energy*

The bandgap energies of III–V quaternaries usually deviate from the simple linear relation of (Eq. 2). and have an approximately quadratic dependence on the alloy composition x. Table I Summarizes the lowest direct gap energy E_0 and the lowest indirect gap energies E_g^X and E_g^L for some III–V binaries of interest here. The corresponding nonlinear parameters C_{A-B} are listed in Table II.

TABLE I

BANDGAP ENERGIES, E_0, E_g^X AND E_g^L, FOR SOME BINARIES III-V AT 300 K [7]

Binary	Energies		
	E_0 (eV)	E_g^X (eV)	E_g^L (eV)
GaSb	0.72	1.05	0.76
GaAs	1.43	1.91	1.72
InSb	0.17	1.63	1.93
InAs	0.36	1.37	1.07

TABLE III

BOWING PARAMETERS FOR SOME III-V TERNARIES [7]

Ternary	Bowing parameters C_{A-B}		
	E_0 (eV)	E_g^X (eV)	E_g^L (eV)
GaAsSb	-1.43	-1.2	-1.2
GaInAs	-0.477	-1.4	-0.3
GaInSb	-0.415	-0.33	-0.4
InAsSb	-0.67	-0.6	-0.6

The band gap energies as function of the x-composition parameter for $Ga_{1-x}In_xAs_ySb_{1-y}$ lattice matched to GaSb is shown in (Fig.2). The absorption at the fundamental optical gaps in the $Ga_{1-x}In_xAs_ySb_{1-y}$/GaSb and $Ga_{1-x}In_xAs_ySb_{1-y}$/InAs quaternaries is expected to be direct within a whole range of the composition ($0 \leq x \leq 1.0$)[8]. It is also clear from the figures that the conduction band minimum at the Γ point is much lower than those at the L and X points, especially for smaller values of x. However, for the composition $x \geq 0.95$ the lower transition energy become at L point.

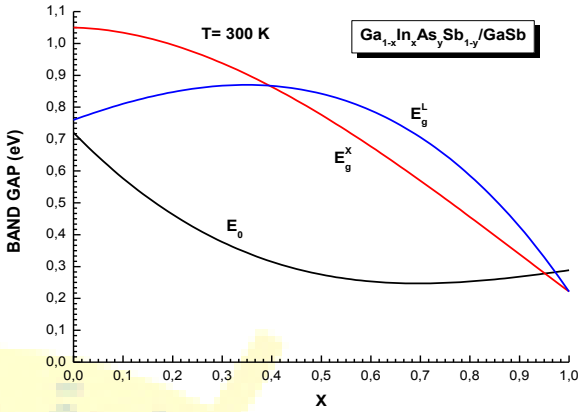

Fig. 2 band gap energies as a function of the x composition

V. MODELLING OF THE BAND OFFSETS

A. *band offsets*

The heterojunction band offset is an important parameter for the design of heterostructure based electronic and optoelectronic devices. The band offset is one of the parameters, which governs carrier confinement in the heterostructures.

The total band discontinuity distributed over the conduction and valance bands as ΔE_C and ΔE_V, depends on the semiconductors and the amount of mismatch strain at the interface. The ratio of ΔE_C : ΔE_V is not constant for different heterointerfaces. Several electrical and optical measurements of band offsets are well established [9]-[10]. In this paper we report some models theory largely used in the calculation of the band offsets, were the results are compared whit experiment data obtain in the literature.

B. *Model of Anderson*

Consider the energy-band profile of two isolated pieces of semiconductor shown in (Fig. 3). The two semiconductors are assumed to have different band gaps E_g, different dielectric constants (ε), different work functions (Φ) and different electron affinities (χ) In (Fig. 3) the band-edge profiles (E_{V1} , E_{V2} , E_{C1} , E_{C2}) are shown to be "horizontal". The difference in energy of the conduction-band edges in the two materials is represented by ΔE_C, and that in the valence-band edges by ΔE_V . The energy-band profile of such a junction at equilibrium is shown in (Fig. 4). the difference of electrostatic potential between two points in any single semiconductors can represented by the vertical displacement of the band-edges between these two point [11]. The band offsets are expressed

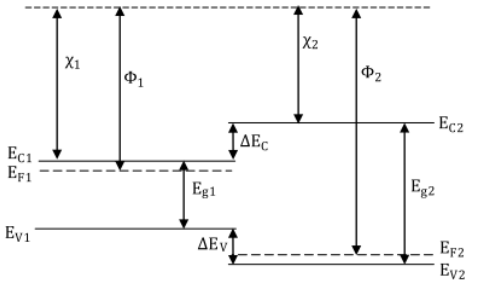

Fig. 3 Energy band diagram of n-p heterojunction

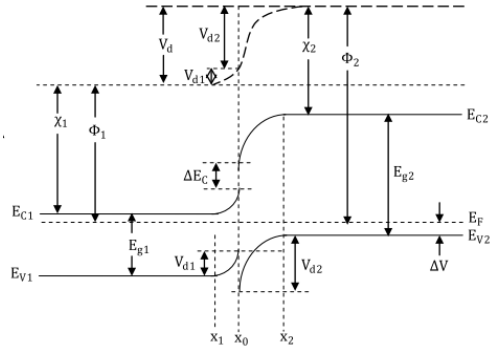

Fig.4 Energy band diagram of n-p heterojunction at equilibrium

by the following (Eq. 5).

$$\begin{cases} \Delta E_C = \chi_2 - \chi_1 = \Delta\chi \\ \Delta E_V = \Delta E_g - \Delta\chi \end{cases} \quad (5)$$

Where: $\Delta E_g = E_{g1} + E_{g2}$

C. *Model of electron affinities*

Electron affinity $\chi_Q(x,y) = a_{A_x B_{1-x} C_y D_{1-y}}$ of the quaternary alloy is estimated starting from an interpolation between the binary component [8]-[12]. The band offsets variation is sketched in(Fig. 5), and expressed by:

$$\begin{cases} \chi_{GaInAsSb} = 4.06 + 0.538\,x + 0.260\,x^2 + 0.012\,x^3 \\ \Delta E_C = 0.538\,x + 0.26\,x^2 + 0.012\,x^3 \\ \Delta E_V = -1.050\,x + 1.815\,x^2 - 0.327\,x^3 \end{cases} \quad (6)$$

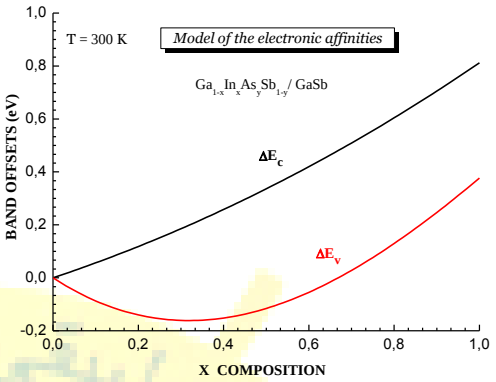

Fig. 5 Band offsets as a function of x-composition for $Ga_{1-x}In_xAs_ySb_{1-y}$/GaSb

D. *Model of electron affinities corrected rule*

This model is proposed to correct the precedent classic model, the idea with which this model was proposed, based in the fact that the term of curve (Bowing) tends to make decrease the gap [13]. The gap energy for the quaternary $Ga_{1-x}In_xAs_ySb_{1-y}$ alloy, lattice matched to GaSb can be expressed as the following form:

$$E_g = 0.72(1-x) + 0.286\,x - 0.912\,x\,(1-x) \quad (7)$$

and the electronic affinities corrected in this model are written:

$$\chi_{Corrected} = \chi_{linear\ Approximation} + C\,x\,(1-x) = \Delta E_C \quad (8)$$

The band offsets is plotted in the(Fig. 6), and expressed by :

$$\begin{cases} \chi_{GaInAsSb} = 4.06 + 2.192\,x - 1.772\,x^2 + 0.398\,x^3 + 0.044\,x^4 \\ \Delta E_C = 1.921\,x - 1.545\,x^2 + 0.4\,x^3 + 0.04\,x^4 \\ \Delta E_V = 0.518\,x - 0.124\,x^2 - 0.006\,x^3 \end{cases} \quad (9)$$

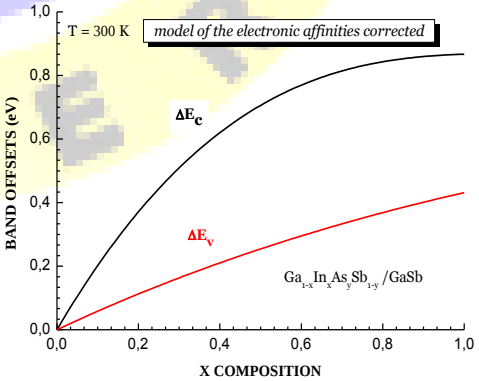

Fig. 6 Band offsets as a function of x-composition for $Ga_{1-x}In_xAs_ySb_{1-y}$/GaSb

E. Model of Jaros

It is shown that a realistic estimate of semiconductor heterojunction valence-band offsets can be made from a simple analytic model which depends only on the empirical values of the optical dielectric constant and the lattice constant materials [14].The optical dielectric constant of a semiconductor is approximated to the well-known formula:

$$\varepsilon = 1 + (\hbar\omega/E_g)^2 \qquad (10)$$

$\omega = (4\pi ne^2/m)^{1/2}$ is the plasma frequency.

n is the electron density which in a diamond or zinc-blende lattice is $32/a^3$.
a is the lattice constant and E_g is an average gap.

The band discontinuity at a heterojunction formed by two lattices matched model semiconductor A and B is:

$$\Delta E_V = [E_g\,(A) - E_g\,(B)\,]/2 \qquad (11)$$

Valence band offset is calculated by using (Eq. 11) and is shown in (Fig. 7).

$$\Delta E_V = 62\,x\,(x - 14.2) + 64\,x \qquad (12)$$

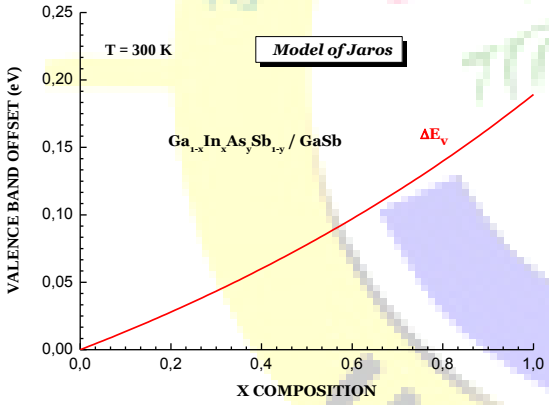

Fig. 7 Band offsets as a function of x-composition for $Ga_{1-x}In_xAs_ySb_{1-y}$/GaSb

F. Model of Van de Walle

Even when no shear strains are present the valence band is usually split due to spin-orbit effects. The valence band and conduction band are given as [15].

$$\begin{cases} E_v = E_{v,av} + \dfrac{\Delta_0}{3} \\ E_c = E_v + E_g \end{cases} \qquad (13)$$

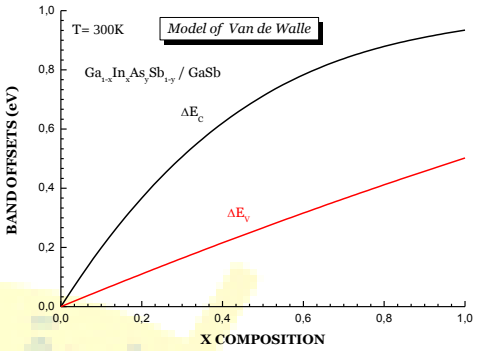

Fig. 8 Band offsets as a function of x-composition for $Ga_{1-x}In_xAs_ySb_{1-y}$/GaSb

$E_{v,av}$ is the average valence bands, the discontinuity in the average valence bands for heterojunction A/B is simply:

$$\Delta E_{v,av} = \Delta E^{B}_{v,av} - \Delta E^{A}_{v,av} \qquad (14)$$

In this paper, we have estimated the variation of the band offsets for the quaternary $Ga_{1-x}In_xAs_ySb_{1-y}$ alloy lattice matched to $GaSb$ by a transition of these parameters. The band offsets is explained by following expressions:

$$\begin{cases} \Delta E_v = \Delta E_{v,av} + \left(\dfrac{\Delta_0(B)}{3} - \dfrac{\Delta_0(A)}{3}\right) \\ \Delta E_c = \Delta E_v + \Delta E_g \end{cases} \qquad (15)$$

The calculations results is given in (Eq. 16), and plotted in (Fig. 8).

$$\begin{cases} \Delta E_C = 2.151\,x - 1.668\,x^2 + 0.403\,x^3 \\ \Delta E_V = 0.562\,x - 0.057\,x^2 \end{cases} \qquad (16)$$

VI. RESULTS AND DISCUSSION

The results obtained starting from the modeling of this quaternary system, are provided and compared with the experimental results available in the literature (Fig.9-10). In (Fig. 9) we can deduce that the model of electronic affinities corrected and that of Van de Walle are in very good agreement with the experiment results available in the literature particularly in the lowest range of x-composition. It is clear that the two models represent a weak difference when the composition $x \geq 0.45$. For a model of Jaros, the variation of the valence band offsets is perfectly linear with the x-composition. However In (Fig. 10) the two models; electron affinities corrected and Van de Walle gives a good results

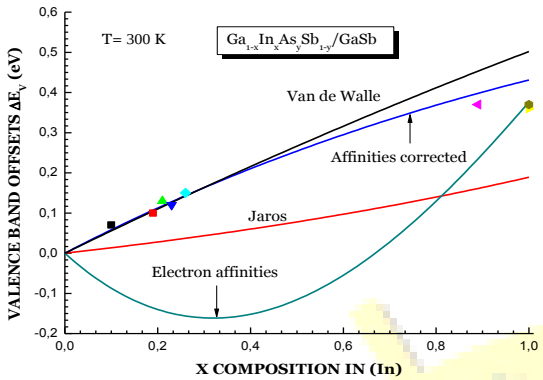

Fig. 9 Variation of valence band offsets as a function of x-composition

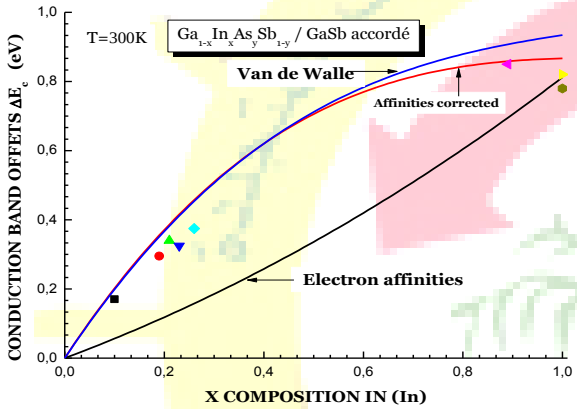

Fig. 9 Variation of conduction band offsets as a function of x-composition

with the experiment data for the conduction band offsets variation. By follows the model of electron affinities is completely isolated.

VII. CONCLUSION

In this paper, we have made a transition of some theoretical models, when they used at a first time for the binary alloys, our work show the possibility to calculate the band offsets variation by using these models for the ternary and quaternary alloys such as $Ga_{1-x}In_xAs_ySb_{1-y}$ and $Ga_{1-x}Al_xAs_ySb_{1-y}$ lattice matched to $GaSb$ or $InAs$.

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