

## Carrier Transport and Band Offsets in Two Dimensional Heterostructures

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### Abstract

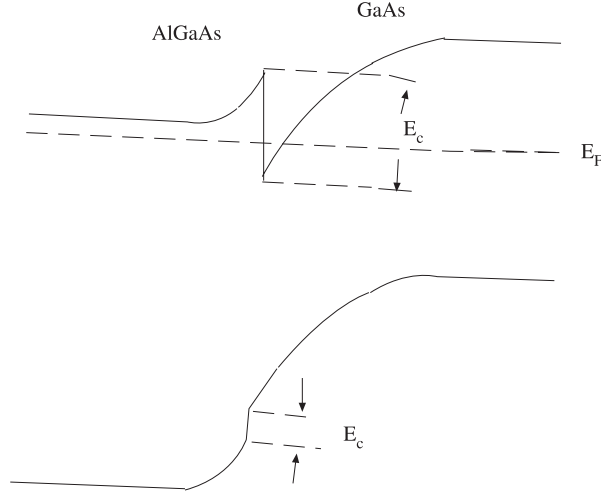
Advances in the low dimensional heterojunction device technology cannot be complete without adequate and reliable analytic model for determining interface properties such as band offsets needed to study the carrier transport and to evaluate the device performance at high temperatures and pressures. In this article, using the extended universal tight binding model of semiconductors, a new way of determining the band offsets in heterostructures is presented. In this model the band offsets are first determined by aligning the vacuum level, defined relative to valence band maximum which is screened by optical dielectric constant of semiconductors, at the interface at absolute zero temperature and standard pressure and then using the thermochemical principles for electrons and holes in intrinsic semiconductors the temperature and pressure effects are included. Excellent agreement is obtained between model predictions and experiment.

### Introduction

Progress made over the years in the science and technology of heterostructures opened new directions in making novel electronic and optical devices. There are issues that must be investigated in order to appreciate the high potential of heterostructures for making submicron devices. One of the most important parameters is the offset occurring in the valence and conduction band edges at interface, illustrated in Figure for two dimensional AlGaAs/GaAs heterostructures. As can be easily realized, such offsets determine the charge transport and other physical properties of the heterostructure bipolar transistors (HBTs) and of the two dimensional electron gas field effect transistors, so called the modulation doped FETs (MODFETs); a complete discussion can be found in ref. [1].

Qualitatively reliable and quantitatively precise determination of these offsets is desirable for the design of novel heterostructures as high speed, high power, and low noise

bipolar and unipolar transistors operating at elevated temperatures and pressures and received considerable attention among device scientists and engineers over the years; a complete discussion can be found in refs. [1] and [2].



**Figure 1.** Energy band diagram of two dimensional AlGaAs/GaAs heterostructure.

### Extended Tight Binding Model of Band Offsets

Most often band offsets are obtained using the universal tight binding theory [3] which treats the bonding and antibonding states in terms of the eigenvalues of the s- and p-states of anion and cation atoms separately. One aligns the external reference levels (vacuum level) of semiconductors A and B ( $E_{vac}(A)$  and  $E_{vac}(B)$ ), defined relative to the valence band maximum ( $E_v$ ) for establishing the charge neutrality across an A/B heterojunction. Considering only interactions between the first nearest neighbor atoms [3], the average valence band maximum, defined relative to vacuum level, of tetrahedral semiconductors is determined from the solution of the determinant of a  $(2 \times 2)$  matrix equation and is given by

$$E_v^o = \frac{E_p^a + E_p^c}{2} - \sqrt{\left(\frac{E_p^c - E_p^a}{2}\right)^2 + V_{xx}^2} \quad (1)$$

$E_s^a(E_s^c)$  and  $E_p^c(E_p^a)$  are the Hartree-Fock atomic term values for the s- and p- state eigenvalues of anion and cation atoms,  $V_{xx}=4E_{xx}$  is the interatomic matrix element between the atomic p-states and their nearest neighbors. Here  $\Delta/3$  is added to  $E_v^o$  to include the effect of spin orbit splitting on valence and energy. Alignment of  $E_{vac}(A)$  and  $E_{vac}(B)$  for the charge neutrality across an A/B semiconductor heterointerface gives the valence band offset

$$\Delta E_v(nat) = E_v^o(A) - E_v^o(B) \quad (2)$$

This is known as the *natural valence band offsets* since only free atomic term values of chemical elements are used in the calculations [3]. Equation (2) generally yields good agreement with experiment but has been questionable or heterojunctions involving compounds having the same anion (e.g. AlAs/GaAs) [2].

Harrison and Tersoff [4] have later on tried to make a connection between the tight binding theory [4] and charge neutrality level model [5] and improve the predictions of equation (2) by arguing that the alignment of  $sp^3$  average hybrid energies  $\bar{E}_h(A)$  and  $\bar{E}_h(B)$  of semiconductors A and B is analogous to the alignment of charge neutrality point (CNP) energies  $E_B$  [6] across an A/B heterointerface. Here the average hybrid energy is equal to  $\bar{E}_h=(E_h^a + E_h^c)/2$  where  $E_h^a$  and  $E_h^c$  are anion and cation hybrid energies:  $E_h = (\epsilon_s + 3\epsilon_p)/4$  defined in the bond orbital approximation [3] which treats the energies of bonding and antibonding states in terms of the hybrid  $sp^3$  states of anion and cation atoms and gives the valence band energy as

$$E_v = \frac{1}{2}(E_h^a + E_h^c) - \sqrt{V_{3h}^2 + V_{2h}^2} \quad (3)$$

where  $V_{3h} = (E_h^c - E_h^a)/2$  is the polar (ionic) contribution and  $V_{2h}=3.22\hbar^2/md^2$  is the homopolar (covalent) contribution to the bond energy. Since  $\bar{E}_h(A) - \bar{E}_h(B)$  is small and  $\epsilon_{infly}(A)-\epsilon_\infty(B)$  is large for most of tetrahedral semiconductors, Harrison and Tersoff neglect the screenign of  $\bar{E}_h(A)-\bar{E}_h(B)$  by  $\epsilon_\infty^{av}$  and obtained the valence band offsets using the following equation

$$\Delta E_v(pin) = (\bar{E}_h - E_v^o)_A - (\bar{E}_h - E_v^o)_B \quad (4)$$

Equation (4) improves the predictions of equation (2) for a number of lattice matched and mismatchde heterojunctions. However, Kraut [6] pointed out that the model of Harrison and Tersoff [4] does not obey the observed scaling relation for lattice matched Ge row heterojunctions.

In this article we propose that the fundamental difficulty with equation (4) arises from the fact that the tight binding theory treats the bonding and antibonding states in terms of the eigenvalues of the s- and p- states of anion and cation atoms, while the bond orbital approximation treats the energies of bonding and antibonding states in terms of the hybrid  $sp^3$  states of anion and cation atoms. The natural valence band energy  $E_y^o$  is derived from the eigenvalues of p- states and the hybrid energy  $\bar{E}_h$  is derived from the eigenvalues of s- and p- states. It is proposed here that the predictions of tight binding theory (described by equation (2)) can be improved if the valence band maximum  $E_y^o$  relative to  $E_{vac}$  is screened by the optical dielectric constant of semiconductors  $\epsilon_\infty$  and a more accurate band offset values can be obtained from the following equation

$$\Delta E_v(ETB) = \left(\frac{E_v^o - E_{vac}}{\epsilon_\infty}\right)_B \left(\frac{E_v^o - E_{vac}}{\epsilon_\infty}\right)_A \quad (5)$$

where  $\epsilon_\infty$  is the optical dielectric constant and  $E_v^o$  is given by equation (1).

## Discussion

It is well known that increase in temperature and pressure alters the conduction and valence band energies in semiconductors and semimetals [7,8,9]. It is therefore natural to expect that any increase in temperature, interface mismatch strain and pressure alter the band offsets that determine the carrier transport in heterojunction devices. Because of the lattice vibrations and volume change,  $\Delta E_c$  and  $\Delta E_v$  will be modified with temperature, strain and pressure which can be incorporated in the model by considering the formation of free electrons ( $e^-$ ) in the conduction bands and holes ( $e^+$ ) in the valence bands in an intrinsic semiconductor [7,8,9]. Increasing temperature above zero leads to the release of electrons from their original position at the valence band maximum and move into empty states in the conduction band minimums, leaving behind empty states (holes) in the valence band [7,8,9]. Gibbs equilibrium condition requires that the steady state charge neutrality is maintained if the rate of recombined electron-hole pairs is equal to the rate at which they are generated

$$e^- + e^+ = e^- . e^+ \quad (6)$$

$e^-$  and  $e^+$  are products with (+1) as their stoichiometric coefficient and  $e^- . e^+$  is reactant with (-1) as its stoichiometric coefficient of the reaction.

Since free electrons and holes are considered as electrically charged weakly interacting quasichemical particles [7] and their standard state properties are described by a chemical potential  $\mu_i^o$ , Gibbs free energy per particle  $\partial G^o / \partial N_i$ , at a given temperature and pressure. The pressure effects on valence and conduction band offsets at any temperature can then be written as

$$\Delta E_v(T, P) = \Delta E_v(T) + \delta E_{vs}(T, P) - \delta E_{vf}(T, P) \quad (7)$$

$$\Delta E_{ci}(T, P) = \Delta E_{gi}(T, P) - \Delta E_v(T, P) \quad (8)$$

**Table** Comparison of the proposed extended tight binding model (ETB) predictions with the corresponding values of self consistent tight binding model (SCTB) [3] and Charge Neutrality Point model (CNP)[5] and with experimental data for valence band offsets of some important heterojunctions [2].

System	ETB	SCTB	CNP	EXP.
AlAs/CdTe	0.34	0.12	0.35	0.39
HgTe/CdTe	0.34	0.03	0.51	0.36
AlSb/GaSb	0.29	0.09	0.38	0.40
GaAs/Ge	0.35	0.66	0.52	0.45
AlAs/Ge	0.70	0.78	0.87	0.78
ZnSe/Ge	1.38	2.01	1.52	1.40
ZnSe/GaAs	1.03	1.35	1.00	0.98
CdTe/InSb	0.84	0.15	0.84	0.87

$\delta E_{vf}(T,P)$  and  $\delta E_{vs}(T,P)$  are the pressure shifts in the average valence band edges and  $\Delta E_{gi}(T,P)$  is the difference between bandgaps of film and substrate

$$E_{gi}(T, P) = E_{gi}(T) - \frac{a_{gi}}{B} \left[ 1 - \frac{P}{2B} - \frac{1+B'}{6B^2} p^2 \right] P \quad (9)$$

$E_{gi}(T)$  is the temperature dependent bandgap

$$E_{gi}(T) = E_{gi} + \Delta C_{iP}^o T(1 - \ln T) + 3a_{gi} \alpha \parallel (T)T \quad (10)$$

where  $a_g = -B(\partial E_g / \partial P)$  is the bandgap deformation potential [8] and  $\Delta C_P^o$  is the specific heat capacity of reaction for the band transition in heterolayer and substrate obtained from fitting of  $E_{gi}$  to measured bandgaps. A precise value of  $\Delta C_P^o$  is obtained by comparing  $E_{gi}(T)$  with the measured  $E_g(T)$  fitted to the following expression [10]

$$E_g(T) = E_g - \frac{\alpha T^2}{\beta + T} \quad (11)$$

where constants  $\alpha$  and  $\beta$  are obtained by fitting this expression to measured bandgaps. As shown in Table, equation (5) greatly improves the predictions of the original universal tight binding theory of Harrison [3] and of the self consistent tight binding theory of Harrison and Tersoff [4] and of the charge neutrality point model of Tersoff [5] relative to experiment [2].

For a thin film grown on a thick substrate with (001) orientation, strain components parallel and perpendicular to the interface are equal in the substrate ( $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz} = \epsilon_{\parallel}$ ) but are different in the thin film ( $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{f\perp}$  and  $\epsilon_{zz} = \epsilon_{\parallel}$ ) [1,2].  $\epsilon_{f\perp}$  and  $\epsilon_{\parallel}$  are the strains in thin film perpendicular and parallel to the interface:  $\epsilon_{f\perp} = (a_{f\perp} - a_f)/a_f$  and  $\epsilon_{f\parallel} = -(C_{12}/C_{11})_f \epsilon_{f\perp}$ .  $a_{f\perp} = a_f[1 - D_f(a_{f\parallel} - a_f)]$  is the change in the lattice constant  $a_f$  under the strain perpendicular to the interface and  $D_f = 2C_{12}/C_{11}$  where  $C_{11}$  and  $C_{12}$  are the elastic constants. For a thin film grown on a thick substrate  $a_{f\parallel} = a_s$  [10]. Since  $\epsilon_{sm}=0$  for substrate, the effects of mismatch on  $\Delta E_c$  and  $\Delta E_v$  is obtained using  $P = -2B_f C_f \epsilon_{fm\perp}$  for heterolayer and  $P = -3B_s \epsilon_{sm}=0$  for substrate.

## Conclusion

Band offsets in low two dimensional heterostructures are calculated using the extended tight binding model in which the valence band energies are screened by the optical dielectric constant. It is shown that there is a good agreement with experiment for lattice matched heterojunctions. Good agreement between calculated and actual valence band offsets suggests that bulk band structures properties play significant role in determining the band offsets for lattice matched heterojunctions.

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**PREFACE**

Within the next the average volume of information and communications traffic is estimated to grow, worldwide, by a more than two orders of magnitude. Therefore, existing networks will be insufficient to meet the demand for the high speed trafficking of such large volumes of information. Novel materials for ultra-fast components imposed by giant future systems will be continually needed. One very important class of such high-speed devices is based on low dimensional semiconductors (LDS). Many of these devices have already found applications in the photonics industry in the form of High Electron Mobility Transistors, Quantum Well lasers, electro-absorption modulators, microwave emitters, quantum cascade lasers, infrared detectors, pixels and light logic gates, etc. Quasi-1 and 0 dimensional devices are also pushing their way from the laboratory bench onto the conveyor belt. Despite all these major advances in the LDS technology there is still an ever increasing push for faster integrated devices which has reached to the point where the speed is only limited by the time-constants of fundamental interactions in the semiconductor such as e-e, e-phonon scattering. The aim of this issue of Turkish Journal of Physics is to collate some of the important fundamental physical processes together with the device applications of low dimensional structures. The articles presented in this issue deal with both theory and experiment and range from linear and non-linear carrier dynamics to device applications of novel concepts, such as quantum dots, and novel materials, such as GaN. These articles are selected from the invited and contributed paper presented in V. International Research Workshop on Low Dimensional Semiconductors: Physics and Devices; Scattering Mechanisms and Device Performance held at Akdeniz University, Antalya, 8-11 September 1998.

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