Appendix D

Semiconductor Heterojunction Band Lineups in the Model-Solid Theory [1]

Semiconductor heterojunctions and superlattices have been under intensive investigation both theoretically and experimentally for the past three decades. The potential device applications using heterojunctions are tremendous. In this appendix, we discuss a simplified model to determine the energy band lineups of semiconductor heterojunctions based on the model-solid theory [1–4]. The goal is to develop a reliable model to predict band offsets for a wide variety of heterojunctions without the need for difficult calculations such as in the local-density-functional theory or ab initio pseudopotential method. The relation of the model-solid theory to the fully self-consistent first-principles calculations can be found in Refs. 2 and 3.

The major idea is to set up an absolute reference energy level. All calculated energies can then be put on an absolute energy scale, allowing us to derive band lineups. In the model-solid theory, an average energy over the three uppermost valence bands (the heavy-hole, the light-hole, and the spin–orbit split-off bands) $E_{v,\mathrm{av}}$ is obtained from theory and is referred to as the absolute energy level. The values of $E_{v,\mathrm{av}}$ for different semiconductors are usually tabulated [1] (Table K.2 in Appendix K) so that no calculations for these values are necessary. These results should be compared with those of the first-principle calculations whenever possible to justify the model. An estimate of the maximum possible error is about 0.1 eV. Band offsets should be checked with experimental data such as those in Refs. 5–19. The model-solid theory provides a simple guideline for estimating the band offsets for materials, especially ternary compounds with varying compositions for which experimental data may not be always available.

D.1 UNSTRAINED SEMICONDUCTORS

If materials A and B have the same lattice constants, we may have an ideal heterojunction and there is no strain in the semiconductors. For this case, the heavy-hole and light-hole band edges (E_{HH} and E_{LH}) are degenerate at the zone center, and their energy position is denoted as E_v:

$$E_v = E_{v,\mathrm{av}} + \frac{\Delta}{3} \tag{D.1}$$

where Δ is the spin–orbit splitting energy, and the spin–orbit split-off band-edge energy E_{SO} is

$$E_{SO} = E_v - \Delta = E_{v,av} - \frac{2\Delta}{3} \tag{D.2}$$

The conduction band edge is obtained by adding the band-gap energy E_g to E_v:

$$E_c = E_v + E_g \tag{D.3}$$

Note that in the model-solid theory, the spin–orbit splitting energy Δ and the band-gap energy E_g are taken from experimental results. The only input provided by the model-solid theory is the tabulated $E_{v,av}$ value. This $E_{v,av}$ value is essentially the same as the p-state energy E_p in Fig. 4.3a.

With the above results, the band lineups between materials A and B are shown in Fig. D.1. We have

$$\Delta E_g = E_g^A - E_g^B$$

and the band-edge discontinuities are

$$\Delta E_c = E_c^A - E_c^B \qquad \Delta E_v = E_v^B - E_v^A \tag{D.4}$$

$$\Delta E_c + \Delta E_v = \Delta E_g \tag{D.5}$$

The partition ratios of the band-edge discontinuities, $Q_c = \Delta E_c / \Delta E_g$ and $Q_v = \Delta E_v / \Delta E_g$, are obtained from this theory and can also be compared with experimental data.

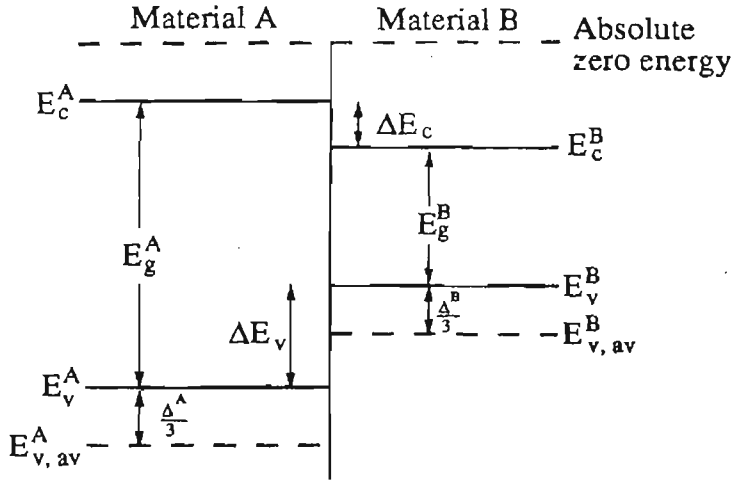

Figure D.1. Band lineups in the model-solid theory. $E_{v,av}$ in each material region is obtained from the model-solid theory and is tabulated in Appendix K. The bandgap energy E_g and the spin–orbit splitting Δ of each material are taken from experimental results.

D.2 STRAINED SEMICONDUCTORS

If a material A with a lattice constant a is grown on a substrate with a lattice constant a_0 along the z direction, we have

$$\varepsilon_{xx} = \varepsilon_{yy} = \frac{a_0 - a}{a} \tag{D.6a}$$

and

$$\varepsilon_{zz} = -2\frac{C_{12}}{C_{11}}\varepsilon_{xx} \tag{D.6b}$$

The band-edge shifts are

$$\Delta E_{v,\mathrm{av}} = a_v(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) \equiv -P_\varepsilon \tag{D.7a}$$

$$\Delta E_c = a_c(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) \equiv P_c \tag{D.7b}$$

The position of the average energy of the valence bands $E_{v,\mathrm{av}}$ under strain is shifted from its unstrained position $E^0_{v,\mathrm{av}}$ in (D.1) by $-P_\varepsilon$:

$$E_{v,\mathrm{av}} = E^0_{v,\mathrm{av}} - P_\varepsilon \tag{D.8}$$

We thus have the center of the valence-band-edge energy

$$E_v = E_{v,\mathrm{av}} + \frac{\Delta}{3} = E^0_v - P_\varepsilon \tag{D.9}$$

The heavy-hole, light-hole, and spin–orbit split-off band edges are

$$E_{\mathrm{HH}} = E^0_v - P_\varepsilon - Q_\varepsilon \tag{D.10}$$

$$E_{\mathrm{LH}} = E^0_v - P_\varepsilon - \frac{\Delta}{2} + \frac{Q_\varepsilon}{2} + \frac{1}{2}\left[\Delta^2 + 2\Delta Q_\varepsilon + 9Q_\varepsilon^2\right]^{1/2} \tag{D.11}$$

$$E_{\mathrm{SO}} = E^0_v - P_\varepsilon - \frac{\Delta}{2} + \frac{Q_\varepsilon}{2} - \frac{1}{2}\left[\Delta^2 + 2\Delta Q_\varepsilon + 9Q_\varepsilon^2\right]^{1/2} \tag{D.12}$$

The conduction band edge is shifted by P_c given by (D.7b):

$$E_c = E^0_v + E_g(x) + P_c \tag{D.13}$$

Note that in the limit of a large spin–orbit split-off energy $\Delta \gg |Q_\varepsilon|$, we can ignore the coupling of the spin–orbit split-off band and

$$E_{\mathrm{LH}} \simeq E^0_v - P_\varepsilon + Q_\varepsilon \tag{D.14a}$$

$$E_{\mathrm{SO}} \simeq E^0_v - P_\varepsilon - \Delta \tag{D.14b}$$

For a ternary alloy such as $A_xB_{1-x}C$ with a lattice constant $a(x)$,

$$a(x) = xa(AC) + (1 - x)a(BC) \tag{D.15}$$

which is a linear interpolation of the lattice constants $a(AC)$ and $a(BC)$ of the binary compound semiconductors, we use the following formula to calculate an energy level E ($= E^0_{v,\text{av}}$ for example):

$$E(A_xB_{1-x}C) = xE(AC) + (1 - x)E(BC) + 3x(1 - x)[-a_v(AC) + a_v(BC)]\frac{\Delta a}{a_0} \tag{D.16}$$

where the last term accounts for a *strain* contribution to the ternary alloy, and $\Delta a = a(AC) - a(BC)$ is the different between the lattice constants of two compounds AC and BC. Once $E^0_{v,\text{av}}$ is determined the band-edge energies for the strained ternary compound can be calculated following (D.6)–(D.13).

Many theoretical parameters for the electronic and optical properties such as those listed in Table K.2 in Appendix K can be found in the data books compiled by various groups (such as Refs. 20–23), review papers (such as Refs. 24–27), and research papers (Refs. 28–37).

Example GaAs/AlAs Heterojunction GaAs and AlAs have almost the same lattice constants. Therefore, the heterojunction has a negligible strain. We see from Table K.2 in Appendix K that

$$E_{v,\text{av}}(\text{GaAs}) = -6.92 \text{ eV}, \Delta(\text{GaAs}) = 0.34 \text{ eV}, E_g(\text{GaAs}) = 1.52 \text{ eV}$$

$$E_{v,\text{av}}(\text{AlAs}) = -7.49 \text{ eV}, \Delta(\text{AlAs}) = 0.28 \text{ eV}, E_g^{\text{dir}}(\text{AlAs}) = 3.13 \text{ eV}$$

Therefore,

$$E_v(\text{GaAs}) = -6.92 + \frac{0.34}{3} = -6.81 \text{ eV}$$

$$E_v(\text{AlAs}) = -7.49 + \frac{0.28}{3} = -7.40 \text{ eV}$$

$$\Delta E_v = -6.81 + 7.40 = 0.59 \text{ eV}$$

Also, the band-gap discontinuity is $\Delta E_g = 1.61$ eV, and the valence-band discontinuity ratio is $\Delta E_v/\Delta E_g = 0.37$. ■

Example $In_{0.53}Ga_{0.47}As/InP$ *Heterojunction*

$$a(\text{GaAs}) = 5.6533\ \text{Å},\ a(\text{InAs}) = 6.0584\ \text{Å},\ a(\text{InP}) = 5.8688\ \text{Å}$$

$$E_{v,\text{av}}(\text{In}_{1-x}\text{Ga}_x\text{As}) = xE_{v,\text{av}}(\text{GaAs}) + (1-x)E_{v,\text{av}}(\text{InAs}) + 3x(1-x)[-a_v(\text{GaAs}) + a_v(\text{InAs})]\frac{\Delta a}{a}$$

$$\Delta a = 5.6533 - 6.0584 = -0.4051\ \text{Å}$$

$$a(\text{In}_{1-x}\text{Ga}_x\text{As}) = xa(\text{GaAs}) + (1-x)a(\text{InAs})$$

$$\Delta(\text{In}_{1-x}\text{Ga}_x\text{As}) \simeq x\Delta(\text{GaAs}) + (1-x)\Delta(\text{InAs})$$

For $x = 0.47$, $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ is lattice matched to InP. Therefore, we do not have the strain terms ($P_\varepsilon = 0, Q_\varepsilon = 0$). We obtain

$$E_{v,\text{av}}(\text{In}_{0.53}\text{Ga}_{0.47}\text{As}) = -6.779\ \text{eV},\ \Delta = 0.361\ \text{eV}$$

Using $E_{v,\text{av}}(\text{InP}) = -7.04$ eV and $E_v(\text{InP}) = -7.003$ eV, we find $\Delta E_v = 0.344$ eV. From room temperature data for the band gap, $E_g(\text{In}_{0.53}\text{Ga}_{0.47}\text{As}) = 0.73$ eV, $E_g(\text{InP}) = 1.35$ eV, and $\Delta E_g = 0.62$ eV, we obtain the ratio $\Delta E_v/\Delta E_g = 0.55 = 55\%$. ∎

D.3 SOME EXPERIMENTAL REPORTS ON BAND-EDGE DISCONTINUITIES

There has been a considerable amount of experimental data on band offsets, mostly on unstrained systems. For strained semiconductors, the band offsets are complicated by the deformation potentials, which also shift the conduction and valence-band edges. Therefore, fewer data are available for strained heterojunctions.

1. $\text{GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$ system

$$E_g(\text{GaAs}) = 1.424\ \text{eV} \quad (300\ \text{K})$$

$$E_g(\text{Al}_x\text{Ga}_{1-x}\text{As}) = 1.424 + 1.247x\ \text{eV} \quad (300\ \text{K})$$

$$\Delta E_g(x) = 1.247x\ \text{eV}$$

$$\Delta E_c = 0.67\Delta E_g \qquad \Delta E_v = 0.33\,\Delta E_g$$

$$(\Delta E_c = 0.69\,\Delta E_g,\ \Delta E_v \cong 0.31\,\Delta E_g,\ \text{Ref. 11})$$

2. $In_{0.53}Ga_{0.47}As/InP$ ($\sim$ 0 K) [18]

$$E_g(InP) = 1.423 \text{ eV}$$
$$E_g(In_{0.53}Ga_{0.47}As) = 0.811 \text{ eV}$$
$$\Delta E_g = 0.612 \text{ eV}$$
$$\Delta E_c = 0.252 \text{ eV} = 0.41\,\Delta E_g,$$
$$\Delta E_v = 0.360 \text{ eV} = 0.59\,\Delta E_g$$

3. $In_{0.52}Al_{0.48}As/InP$ ($\sim$ 0 K) [18]

$$E_g(InP) = 1.423 \text{ eV}$$
$$E_g(In_{0.52}Al_{0.48}As) = 1.511 \text{ eV}$$
$$\Delta E_g = 0.088 \text{ eV}$$
$$\Delta E_c = 0.252 \text{ eV} = 2.86\,\Delta E_g,$$
$$\Delta E_v = -0.164 \text{ eV} \quad \text{(Type II)}$$

The above results for $In_{0.53}Ga_{0.47}As/InP/In_{0.52}Al_{0.48}As$ band offsets and their transitivity relations are illustrated [18] in Fig. D.2. The transitivity relations give $\Delta E_c = 0.504$ eV $= 0.72\,\Delta E_g$, and $\Delta E_v = 0.196$ eV $= 0.28\,\Delta E_g$ for an $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ heterojunction.

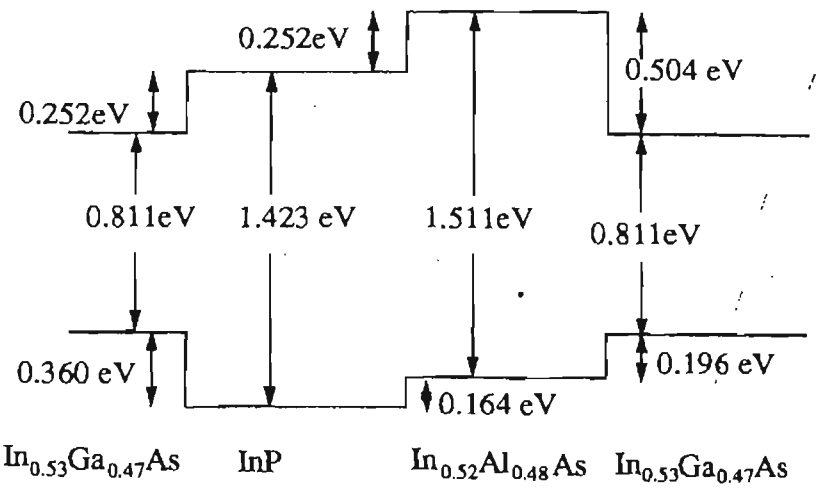

Figure D.2. Band offsets and transitivity of $In_{0.53}GA_{0.47}As/InP$ ($\Delta E_c = 0.41\,\Delta E_g, \Delta E_v = 0.59\,\Delta E_g$) and $In_{0.52}Al_{0.48}As/InP$ ($\Delta E_c = 0.252$ eV $= 2.86\,\Delta E_g > \Delta E_g = 0.088$ eV) at low temperatures (0 K) [18].

4. $In_{1-x}Ga_xAs_yP_{1-y}$/InP lattice-matched system [22]
   For $In_{1-x}GA_xAs_yP_{1-y}$ quaternary semiconductor lattice matched to InP substrate,

$$x = \frac{0.1896y}{0.4176 - 0.0125y}$$

$$E_g = (In_{1-x}Ga_xAs_yP_{1-y}) = 1.35 - 0.775y + 0.149y^2 \text{ eV}$$

$$\Delta E_g(y) = 0.775y - 0.149y^2 \text{ eV}$$

$$\Delta E_v(y) = 0.502y - 0.152y^2 \text{ eV}$$

$$\Delta E_c(y) = \Delta E_g(y) - \Delta E_v(y) = 0.273y + 0.003y^2 \text{ eV}$$

   where $\Delta E_v(y)$ was determined experimentally. ■

Some reports on strained $In_xGa_{1-x}As$/InP, $In_xGa_{1-x}As/In_{0.52}Al_{0.48}As$, InGaAs/InGaAsP, and $In_xGa_{1-x}As$/GaAs can be found in Refs. 7–9, 14, 15, and 19.

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