Bandgap engineering

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Burstein–Moss effect

The **Burstein–Moss** effect is the phenomenon of which the apparent band gap of a semiconductor is increased as the absorption edge is pushed to higher energies as a result of all states close to the conduction band being populated. This is observed for a degenerate electron distribution such as that found in some Degenerate semiconductors and is known as a Burstein–Moss shift.

The effect occurs when the electron carrier concentration exceeds the conduction band edge density of states, which corresponds to degenerate doping in semiconductors. In nominally doped semiconductors, the Fermi level lies between the conduction and valence bands.

As the doping concentration is increased, electrons populate states within the conduction band which pushes the Fermi level higher in energy and in the case of degenerate level of doping, the Fermi level lies inside the conduction band.

In the case of a degenerate semiconductor, an electron from the top of the valence band can only be excited into conduction band above the Fermi level (which now lies in conduction band) since all the states below the Fermi level are occupied states.

Pauli's exclusion principle forbids excitation into these occupied states. Thus we observe an increase in the apparent band gap. Apparent band gap = Actual band gap + Moss-Burstein shift (as shown in the figure).

Marius Grundmann (2006). *The Physics of Semiconductors*. Springer Berlin Heidelberg New York: Springer

Franz–Keldysh effect

The Franz–Keldysh effect is a change in optical absorption by a semiconductor when an electric field is applied. The effect is named after the German physicist Walter Franz and Russian physicist Leonid Keldysh.

Karl W. Böer observed first the shift of the optical absorption edge with electric fields during the discovery of high-field domains and named this the Franz-effect. A few months later, when the English translation of the Keldysh paper became available, he corrected this to the Franz–Keldysh effect.

Origin of Franz–Keldysh effect

As originally conceived, the Franz–Keldysh effect is the result of wavefunctions "leaking" into the band gap. When an electric field is applied, the electron and hole wavefunctions become Airy functions rather than plane waves.

The Airy function includes a "tail" which extends into the classically forbidden band gap. According to Fermi's Golden Rule, the more overlap there is between the wavefunctions of a free electron and a hole, the stronger the optical absorption will be. The Airy tails slightly overlap even if the electron and hole are at slightly different potentials (slightly different physical locations along the field).

The absorption spectrum now includes a tail at energies below the band gap and some oscillations above it. This explanation does, however, omit the effects of excitons, which may dominate optical properties near the band gap.

Franz-Keldysh Effect for Bulk Material

- Bulk material
  Applied field $E \neq 0$
  Franz-Keldysh Effect:
  bands are tilted.
- Absorption below E_g because of exponential wave-function tails.
- Oscillations above E_g due to wave-function interference.

Franz-Keldysh Shift of Energy Gap in an Electric Field (no excitons)

W. Franz, Z. Naturforsch. 13a, 484 (1958).

L. V. Keldysh, Zh. Eksp. Teor. Fiz. 34, 1138 (1958) [Sov. Phys. — JETP 7, 788 (1958)].

Franz-Keldysh Shift of Exciton Energy Gap in Electric Field

J. D. Dow and D. Redfield, Phys. Rev. B 1, 3358 (1970).

Application of Franz–Keldysh effect

The Franz–Keldysh effect occurs in uniform, bulk semiconductors used for Electro-absorption modulators.

The Franz–Keldysh effect usually requires hundreds of volts, limiting its usefulness with conventional electronics – although this is not the case for commercially available Franz–Keldysh-effect electro-absorption modulators that use a waveguide geometry to guide the optical carrier.

Franz–Keldysh effect means an electron in a valence band can be allowed to be excited into a conduction band by absorbing a photon with its energy below the band gap.

Airy function Ai(x)

In the physical sciences, the Airy function Ai(x) is a special function named after the British astronomer George Biddell Airy(1801–92). The function Ai(x) and the related function Bi(x), which is also called the Airy function, but sometimes referred to as the Bairy function, are solutions to the differential equation

$$\frac{d^2y}{dx^2} - xy = 0,$$

known as the **Airy equation** or the **Stokes equation**. This is the simplest second-order linear differential equation with a turning point (a point where the character of the solutions changes from oscillatory to exponential).

The Airy function is the solution to Schrödinger's equation for a particle confined within a triangular potential well and for a particle in a one-dimensional constant force field. The triangular potential well solution is directly relevant for the understanding of many semiconductor devices.

Airy Function *Ai* (Z)

- Z>0: electron-hole energy+E_g < electric field potential
- Z<0: electron-hole energy+E_g > electric field potential, i.e. above bandgap → oscillation wavefunction

Exciton

- An **exciton** is a bound state of an electron-hole which are attracted to each other by the electrostatic Coulomb force.
- It is an electrically neutral quasiparticle that exists in insulators, semiconductors and in some liquids.
- The exciton is regarded as an elementary excitation of condensed matter that can transport energy without transporting net electric charge.

Origin of Exciton

An exciton can form when a photon is absorbed by a semiconductor.

This excites an electron from the valence band into the conduction band. In turn, this leaves behind a positively-charged electron hole (an abstraction for the location from which an electron was moved).

The electron in the conduction band is then effectively attracted to this localized hole by the repulsive Coulomb forces from large numbers of electrons surrounding the hole and excited electron.

This attraction provides a stabilizing energy balance. Consequently, the exciton has slightly less energy than the unbound electron and hole.

Frenkel excitons

In materials with a small dielectric constant, the Coulomb interaction between an electron and a hole may be strong and the excitons thus tend to be small, of the same order as the size of the unit cell. Molecular excitons may even be entirely located on the same molecule, as in fullerenes. This *Frenkel exciton*, named after Yakov Frenkel, has a typical binding energy on the order of 0.1 to 1 eV. Frenkel excitons are typically found in alkali halide crystals and in organic molecular crystals composed of aromatic molecules, such as anthracene and tetracene.

Wannier-Mott exciton

In semiconductors, the dielectric constant is generally large. Consequently, electric field screening tends to reduce the Coulomb interaction between electrons and holes. The result is a *Wannier exciton*, which has a radius larger than the lattice spacing. As a result, the effect of the lattice potential can be incorporated into the effective masses of the electron and hole.

Likewise, because of the lower masses and the screened Coulomb interaction, the binding energy is usually much less than that of a hydrogen atom, typically on the order of 0.01eV. This type of exciton was named for Gregory Wannier and Nevill Francis Mott. Wannier-Mott excitons are typically found in semiconductor crystals with small energy gaps and high dielectric constants, but have also been identified in liquids, such as liquid xenon.

In single-wall carbon nanotubes, excitons have both Wannier-Mott and Frenkel character. This is due to the nature of the Coulomb interaction between electrons and holes in one-dimension. The dielectric function of the nanotube itself is large enough to allow for the spatial extent of the wave function to extend over a few to several nanometers along the tube axis, while poor screening in the vacuum or dielectric environment outside of the nanotube allows for large (0.4 to 1.0eV) binding energies.

Often there is more than one band to choose from for the electron and the hole leading to different types of excitons in the same material.

Surface excitons

At surfaces it is possible for so called *image states* to occur, where the hole is inside the solid and the electron is in the vacuum. These electron-hole pairs can only move along the surface.

Atomic and molecular excitons

Alternatively, an exciton may be an excited state of an atom, ion, or molecule, the excitation wandering from one cell of the lattice to another.

When a molecule absorbs a quantum of energy that corresponds to a transition from one molecular orbital to another molecular orbital, the resulting electronic excited state is also properly described as an exciton. An electron is said to be found in the lowest unoccupied orbital and an electron hole in the highest occupied molecular orbital, and since they are found within the same molecular orbital manifold, the electron-hole state is said to be bound.

Molecular excitons typically have characteristic lifetimes on the order of nanoseconds, after which the ground electronic state is restored and the molecule undergoes photon or phonon emission. Molecular excitons have several interesting properties, one of which is energy whereby if a molecular exciton has proper energetic matching to a second molecule's spectral absorbance, then an exciton may transfer (*hop*) from one molecule to another. The process is strongly dependent on intermolecular distance between the species in solution, and so the process has found application in sensing.

Dynamics of Excitons

The probability of the hole disappearing (the electron occupying the hole) is limited by the difficulty of losing the excess energy and, as a result, excitons can have a relatively long lifetime. (Lifetimes up to several milliseconds have been observed in copper (I) oxide)

Another limiting factor in the recombination probability is the spatial overlap of the electron and hole wavefunctions (roughly the probability for the electron to run into the hole). This overlap is smaller for lighter electrons and holes.

The whole exciton can move through the solid. With this additional kinetic energy the exciton may present above the band-gap.

The exciton propagating through molecular crystal is one that is of greatest concern. Two mechanisms have been proposed in the literature where the first one is exciton energy dissipated due to interaction with phonon bath. The other one is energy carried away by radiation. Combinations of the two have also been studied.
Much like molecular systems that have well defined resonances, excitons can undergo internal conversions from higher- to lower-energy states by coupling to vibrational or electronic degrees of freedom.

Interaction of Excitons

Excitons are the main mechanism for light emission in semiconductors at low temperature (when the characteristic thermal energy kT is less than the exciton binding energy), replacing the free electron-hole recombination at higher temperatures.

The existence of exciton states may be inferred from the absorption of light associated with their excitation. Typically, excitons are observed just below the band gap.

When excitons interact with photons a so-called polariton (also exciton-polariton) is formed. These excitons are sometimes referred to as *dressed excitons*.

Provided the interaction is attractive, an exciton can bind with other excitons to form a biexciton, analogous to a dihydrogenmolecule. If a large density of excitons is created in a material, they can interact with one another to form an electron-hole liquid, a state observed in indirect bandgap semiconductors.

Additionally, excitons are integer-spin particles obeying Bose statistics in the low-density limit. In some systems, where the interactions are repulsive, a Bose–Einstein condensed state is predicted to be the ground state, and indeed such condensate has been already observed in recent experiments. The inference was obtained by cooling an exciton state below 5 K and further observing coherent light emission (with interference patterns) from it.

Exciton Absorption Spectra (schematics)

Without damping

With damping

- 2D and 3D exciton absorption spectra with zero/finite linewidth. The spectra is very sensitive to the temperature.

Excitonic effect at different temperature

(a)

(b)

Bulk GaAs

Absorption peak blueshifts because the bandgap becomes larger at lower temperature.

Quantum well (quasi 2D)

Band structure of Si at 300 K.

Temperature Dependences of Silicon Indirect and Direct Bandgap

- **Temperature dependence of the energy gap**

$$E_g = 1.17 - 4.73 \cdot 10^{-4} \cdot T^2/(T+636)\ (eV),$$

where T is temperature in degrees K.

- **Temperature dependence of the direct band gap EΓ2**

$$E\Gamma 2 = 4.34 - 3.91 \cdot 10^{-4} \cdot T^2/(T+125)\ (eV)$$

Absorption spectrum of high purity Si

Macfarlane, G. G., T. P. McLean, J. E. Quarrington, and V. Roberts, *J. Phys. Chem. Solids* 8, (1959) 388-392.

Absorption spectrum of high purity Si

Sze, S. M., *Physics of Semiconductor Devices*, John Wiley and Sons, N.Y., 1981

Jellison, Jr., G. E. and F. A. Modine, *Appl. Phys. Lett*- 41, 2 (1982) 180-182

Si absorption edge at different doping levels (T = 300 K)

•Wolfson, A. A. and V. K. Subashiev, *Fiz. Tekh. Poluprovodn.* 1, 3 (1967) 397-404 (in Russian)

Electrical and optical energy gap narrowing in Silicon with donor doping density

Van Overstraeten, R. J. and R. P. Mertens, *Solid State Electron.* 30, 11 (1987) 1077- 1087.

Dependence of the Silicon Energy Gap on Hydrostatic Pressure

$$Eg=Eg(0)-1.4\cdot 10^{-3} P \text{ (eV)}$$

Energy Gap Shift in Strained SnGe/Ge Semiconductor Heterostructures: Deformation Potential Theory*

Tetragonal distortion – 2 components

(1) hydrostatic compression

(2) uniaxial elongation

$$\Delta E_{hydro} = (\Xi_d + \frac{1}{3}\Xi_u - \gamma)\bar{1} \bullet \bar{e}$$

Conduction band

$$\Delta E_c^{(i)} = [\Xi_d \bar{1} + \Xi_u \{\hat{a}_i \hat{a}_i\}] : \bar{e}$$

Valence band

$$H^V = \frac{2}{3} D_u \left[\left(J_x^2 - \frac{1}{3}J^2\right) e_{xx} + c.p.\right] + \frac{2}{3} D_u' \left[\frac{1}{2}\left(J_y J_z + J_z J_y\right) e_{yz} + c.p.\right]$$

Hydrostatic Component inc. Eg

Symmetry of strain axis w.r.t Eg,min determines if splitting occurs

3. R. People, Phys. Rev. B **32**, 1405 (1985)

R. Ragan, Ph.D Thesis, California Institute of Technology, 2002

1. J. Bardeen and W. Shockley, Phys. Rev. **80**, 72(1950)
2. G.E. Kimball, J. Chem.Phys. **3**, 560 (1935)

Band structure of GaAs at 300 K

GaAs Energy Gap Temperature Dependences

Temperature dependence of the energy gap

$Eg=1.519-5.405\cdot 10^{-4}\cdot T^2/(T+204)$ (eV)

where T is temperatures in degrees K ($0 < T < 103$).

Temperature dependence of the energy difference between the top of the valence band and the bottom of the L-valley of the conduction band

$EL=1.815-6.05\cdot 10^{-4}\cdot T^2/(T+204)$ (eV)

Temperature dependence of the energy difference between the top of the valence band and the bottom of the X-valley of the conduction band

$EX=1.981-4.60\cdot 10^{-4}\cdot T^2/(T+204)$ (eV)

T-dependence of the relative populations of the Γ, L and X valleys in GaAs

Blakemore, J. S., *J. Appl. Phys.* 53, 10 (1982) R123-R181

GaAs absorption edge at 297 K at different p-type doping levels

Casey, H. C., D. D. Sell, and K. W. Wecht, *J. Appl. Phys.* 46, 1 (1975) 250.

Variation of PL with temperature and doping

- With increase in temperature:
  - Lattice spacing increases so bandgap reduces, peak shift to higher wavelength

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta}$$

  - Full width at half maximum increases due to increased lattice vibrations
  - Peak intensity usually reduces
- As doping increases
  - PL peak blueshifts due to band filling
  - FWHM can increase due to thicker band of states from which transition can be made
  - Intensity will also increase by enhancing the probability of radiative recombination

PL plots for InN crystal

(a) Temperature-dependent PL spectra measured from InN microcrystals. With decreasing temperatures, the *I*da emission emerged at the low-energy side of near-band-edge transition. (b) The PL peak energy vs temperature shows a well Varshni's fitting for the experimental data points. (c) Arrhenius plots of the integrated PL intensities for the InN microcrystals.

15 K variable excitation power densities PL spectra measured from InN microcrystals. The PL intensities were normalized to show a blueshift of peak energy with increasing excitation power density. The inset shows the plot of integrated PL intensity vs excitation power density at temperatures of 15 and 300 K.

Hsiao *et al.*, Appl. Phys. Lett. **91**, 181912 (2007)

Variation bandgap due to other factors

- Strain: Bandgap varies with strain as the lattice spacing changes (Franz-Keldysh effect)
- Electric field: Reduction in effective bandgap due to enhanced probability of tunneling
- Excitation intensity: Variation of the luminescence peak energy, same effect as increasing doping

Fig. 10. Exciton spectra of $Al_{0.244}Ga_{0.756}As$ recorded at various excitation densities (P). The relative gain used to record each spectrum is given on the left. The linewidth of the separate (D°, X) peak (FWHM) of each spectrum is given on the right.

GaN PL spectrum

Typical room temperature PL of GaN

- I_2 is the neutral donor bound recombination. A and B are free exciton lines associated with the A and B hole bands
- D^0A^0 is donor-acceptor (residual, background) pair recombination
- The "LO" refers to phonon replicas of the particular transitions, at multiples of LO phonon energies

PL variation with temperature

FIG. 1. Typical temperature dependence of the luminescence spectra of high quality undoped GaN. The spectra have been shifted vertically for clarity. The sample is grown by MOVPE.

$$E(T)(eV) = E(0) - 8.87\times 10^{-4} T^2/(T+874)$$

Bowing parameter --- δ(y)

- For conventional Ⅲ-Ⅴ ternary alloys :
  Vegard's law adding a quadratic correction $b_x(x-1)$.
  Such as : $In_xGa_{1-x}As$ with δ＝0.5 eV.

$$Eg\ (In_xGa_{1-x}As) = xEg\ (InAs) + (1-x)\ Eg\ (GaAs) + \delta x(x-1)$$

- But incorporating a small amount of nitrogen in Ⅲ-Ⅴ semiconductor results in a strong reduction of Eg.
  Such as : InPN (δ =16 eV), GaPN (δ =14 eV).
- However, GaAsN and InGaAsN need composition dependent bowing parameter δ(x).
  ex. : $GaAs_{1-x}N_x$ δ(x)=10~20 eV.

Bowing parameter --- δ(y)

$$Eg\ (In_{0.54}Ga_{0.46}P_{1-y}N_y) = yEg\ (In_{0.54}Ga_{0.46}N) + (1-y)\ Eg\ (In_{0.54}Ga_{0.46}P) + \delta y(y-1)$$

And $In_{0.54}Ga_{0.46}N$ band gap＝1.6338 eV [APL. 80, 4741 (2002)]

$In_{0.54}Ga_{0.46}P$ band gap＝1.8425 eV

Use PR fitting results:

$In_{0.54}Ga_{0.46}P_{1-y}N_y$	y	0	0.005	0.01	0.02	
bowing parameter	δ (y)	no	11.15	9.07	10.72	(eV)

The $In_{0.54}Ga_{0.46}P_{1-y}N_y$ and GaAs heterojunction. Approximate triangular potential wells and two-dimensional electron gas are formed at the junction. (a) For type Ⅰ alignment; (b) for type Ⅱ alignment.

Energy gaps vs. lattice constants

FIGURE 3.1. Plot of the lattice constant of various semiconductors against their minimum band gap E_g, expressed in eV and as a wavelength. Full lines show a direct band gap, with dashed lines for an indirect gap. [From Gowar (1993).]

Band alignment at hetero-interfaces

Anderson's rule for the band alignment (1)

FIGURE 3.4. Anderson's rule for the alignment of the bands at a heterojunction between materials A and B, based on aligning the vacuum levels.

None of the interface effects are considered.

Anderson's rule for the band alignment (2)

$$\Delta E_c = \chi^A - \chi^B$$

$$\Delta E_v = \chi^B + E_g^B - (\chi^A + E_g^A)$$

ΔE_c : conduction band offset

ΔE_v : valence band offset

$$\Delta E_c + \Delta E_v = E_g^B - E_g^A$$

Types of band alignment

FIGURE 3.5. Alignment of conduction and valence bands in two lattice-matched systems of semiconductors: $In_{0.53}Ga_{0.47}As$–$In_{0.52}Al_{0.48}As$–InP, which is widely used for high-speed electronic devices; and InAs–GaSb–AlSb, which shows types I, II, and III of matching. The convention is that $\Delta E_c, \Delta E_v > 0$ for type I. [Redrawn from Frensley (1994); data from Yu, McCaldin, and McGill (1992).]

Band bending in a doped hetero-junction (1)

FIGURE 3.10. Steps in the construction of the band diagram for a doped heterojunction between material A, n-type AlGaAs, and material B, p-GaAs.

Band bending in a doped hetero-junction (2)

(i) Start with flat bands in each material, with the bands in their natural alignment (given by Anderson's rule or something superior) and the Fermi levels set by the doping on each side. This gives the position of the bands relative to the Fermi level far from the junction on each side. To cancel out the effect of the discontinuities temporarily, draw lines on side A at $\bar{E}_c^A = E_c^A - \Delta E_c$ and $\bar{E}_v^A = E_v^A + \Delta E_v$. Note that $\bar{E}_c^A - \bar{E}_v^A = E_c^B - E_v^B = E_g^B$, so the 'effective' band gap is the same on both sides.

(ii) Align the Fermi levels. The difference in Fermi level far from the junction is set by any applied voltage. Assume that there is a positive bias v applied to side B, so $E_F^A - E_F^B = ev$.

(iii) Join $\bar{E}_c^A$ to E_c^B, and $\bar{E}_v^A$ to E_v^B, with parallel curves due to the electrostatic potential. The precise form of these curves must generally be found numerically. For a qualitative picture, sketch an S-shaped curve whose curvature is set by the sign of the charge density. Usually this gives a point of inflexion at the junction.

(iv) Now restore E_c^A on side A as a line at $\bar{E}_c^A + \Delta E_c$ and E_v^A at $\bar{E}_v^A - \Delta E_v$, including the discontinuities in E_c and E_v at the junction. This completes the sketch of the band diagram.

Heterojunction Band Offset

$$\Phi_{VBO}^{A-B} = \mu_B - \mu_A + e\Delta_{ISR}$$

bulk terms

interface term

Interface Sharpness

Interface sharpness directly impacts:

1. Shape (abruptness) of band offset
2. Interface width
3. Layer thickness and uniformity
4. Electronic structure, optical properties,
5. ...

How do we achieve high interface sharpness?

Considering that: in straight MBE growth at constant rates, interface sharpness is best at a intermediate temperature to minimize interdiffusion and surface roughness....

Band Offset

(a) Cross-section and band diagram of two semiconductors with different band gaps, (b)schematic *C-V* and 1/*C*^{2}-*V* plots. Real plots are smeared out and do not exhibit the sharp features shown here.

Band Offset and Schottky Barrier Height

Band structure modification by heterostructures – Concept of bandoffsets or bandgap discontinuity

Anderson model (electron affinity model):

$$\Delta E_C = e(\chi^A - \chi^B)$$

$$\Delta E_V = \Delta E_g - \Delta E_C$$

χ (chi) = electron affinity

There are several other models and experimental methods.

Band-structure Application – Band Offsets

- Heterojunctions are formed when two different types of semiconductor are joined together.
- Heterostructures are used extensively in the electronic (e.g. transistors) and optoelectronic (e.g. LED's) industry.

The Nobel Prize in Physics 2000

Zhores I. Alferov Herbert Kroemer

"for developing semiconductor heterostructures used in high-speed- and opto-electronics"

Classification of heterojunctions

Definitions:

$\chi \equiv$ Electron Affinity – energy needed to free a conduction electron into the vacuum level

$\gamma \equiv$ Ionization Potential – energy needed to free a valence electron into the vacuum level

Type I

Type I: Straddling (small Eg material is within large Eg band edges)

Type II

Type II: Staggered (small Eg material is outside of large Eg band edges – either above or below)

Type III

Type III: Broken Gap (One band edge of small Eg is within large Eg band edges – either above or below)

Band offset in Heterojunctions Type-I

Here we will assume the band offsets are equal. This is not usually the case.

E_{e-}

Band offset

Bandgap Engineering for LED

- Bandgap Engineering: *Quantum wells*
  - ✓ Note that the band offsets are not the same!

Figure 9.33. Conduction- and valence-band offsets for lattice-matched (a) $InP/In_{0.53}Ga_{0.47}As$, (b) $In_{0.52}Al_{0.48}As/In_{0.53}Ga_{0.47}As$ heterojunctions.

Calculating Band Offsets

- Knowledge of the band structures of the two individual materials is not sufficient to determine the band offset.
- Band energies are determined with respect to the average potential in the solid.
- It is also necessary to perform a *supercell* calculation to determine how the potentials are lined up with respect to each other.

The Average Potential

- The potential can be averaged across the *x*-*y* planes (junction normal to *z*).
- This is the *microscopic average* potential.
- The *macroscopic average* potential is calculated over the period over the microscopic potential.
- The band structures are measured relative to the macroscopic average.

$$\overline{\overline{V}}_{tot}(z) = \frac{1}{\lambda\lambda'} \int_{z-\lambda/2}^{z+\lambda/2} \int_{z'-\lambda'/2}^{z'+\lambda'/2} \overline{V}_{tot}(z'')dz''dz'$$

Band Line-up Using Potential

$$\Delta E_v = \left(\overline{\overline{V}}_{totL} + E_{vbmL}\right) - \left(\overline{\overline{V}}_{totR} + E_{vbmR}\right)$$

An Example: FeSi2 on Si

Offset is 0.4eV – useful for LED's and near-IR detectors

Band Offset Si/Oxides

Band Offsets

Calculated value

J Robertson, J Vac Sci Technol B **18** 1785 (2000)

Dielectric constant

SiO2; 4
Si3N4: ~ 7
Al2O3: ~ 9

Y2O3; ~10
Gd2O3: ~10

HfO2; ~23
La2O3: ~27

HfO2 was chosen for the 1st generation
La2O3 is more difficult material to treat

Calculation of Band Offset

B= - 0.9 eV
calculated
band-offset

30% off ….

The theoretical definition of band-offset is based on the assumption of a rigid translation of the respective averages of the **electrostatic potential across the interface**, with respect to the top of the VB (or HOMO) **calculated in the respective bulk**.

However, already in more complex semiconductor hetero-interfaces such a “transitivity” is not obeyed (see e.g.: Bratina et al., PRB 50 (1994) 11723).

Due to the restructuring of energy levels as a function of the **different** interface bonding configurations, such a rigid-shift hypothesis could be an over-simplification…

Band Offset in HfO2/Si(001) interface

Band Offset

Eg^{Si} :	0.77eV (cal.)
	1.12eV (exp.)
$Eg^{a\text{-}Hfo2}$:	3.39eV (cal.)
	5.7eV (exp.[a])

$$CBO = E_g^{a\text{-}Hfo2} - E_g^{Si} - VBO$$

$$VBO = VBM_{HfO2(0)} - VBM_{Si(0)} + \{\Delta core_{mix} - \Delta core_{sept}\}$$

2.97eV and 1.61eV inhibit the Schotty emission of electrons or holes.

The VBO(2.97eV) and CBO (1.61eV) inhibit the Schottky emission of electrons or holes.

Summary: What can we calculate with which method?

Property	DFT	GWA	QMC
Band gap	not always accurate[1]	very accurate	accurate
Effective mass	yes	yes	no
Transition levels	yes	very accurate	not done
Band offsets	not always accurate[1]	very accurate	not done
Defect energies	not always accurate[1]	no	accurate
Barriers	not always accurate[1]	no	accurate

[1] Improved accuracy for hybrid functionals

Dielectric constant values vs. Band Offset (Measured)

SiO_2	3.9
Al_xSi_yOz	
$(Ba,Sr)TiO_3$	200-300
$BeAl_2O4$	8.3-9.43
CeO_2	16.6-26
$CeHfO_4$	10-20
$CoTiO_3/Si_3N_4$	
$EuAlO_3$	22.5
HfO_2	26-30
Hf silicate	11
La_2O_3	20.8
$LaScO_3$	30
La_2SiO_5	
$MgAl_2O_4$	
$NdAlO_3$	22.5
$PrAlO_3$	25
Si_3N_4	7
$SmAlO_3$	19
$SrTiO_3$	150-250
Ta_2O_5	25-24
Ta_2O_5-TiO_2	
TiO_2	86-95
TiO_2/Si_3N_4	
Y_2O_3	8-11.6
$Y_xSi_yO_z$	
ZrO_2	22.2-28
Zr-Al-O	
Zr silicate	
$(Zr,Sn)TiO_4$	40-60

$\sqrt{\phi_B} * k$: Figure of Merit of High-k

C.A. Billmann et al.,, MRS Spring Symp., 1999,
R.D.Shannon, J. Appl. Phys., 73, 348, 1993
S. De Gebdt, IEDM Short Coyuse, 2004

T. Hattori, INFOS , 2003

Optimum band offset

- The confinement barriers are typically several hundred meV (>>kT)
- Due to Fermi-Dirac distribution of carriers in the active region, some carriers will have energy higher than that of the barriers
- In AlGaAs/GaAs and AlGaN/GaN the barriers are high
- In AlGaInP/GaInP the barriers are lower resulting in higher leakage currents (carrier loss)

Effect of Strain on SiGe Band Offset

SiGe on Si substrate

Si on relaxed SiGe

Band Offset: ab initio DFT + GW

[eV]	$\Delta\varepsilon_v$
SiO_2	-1,9
HfO_2	-0.7

VBO(LDA+G_0W_0) = 0,85 eV

VBO(XPS) = [0,95 ; 1,15] eV

Band offset model <=> dipole (DFT) + bulk energy levels (GW)

GW (=G0W0) calculation gives at least a semi quantitative agreement with exp.
See Shaltaf & al. PRL 2008

Band offset variability / chemical bonding

[eV]	WSi_2/HfO_2			W/HfO_2	TiN/HfO_2		
Interface	2*Si	1*Si	1*W		nitrided	oxidised	orientation [-1/2 5/2 -1]
VBO ($LDA+G_0W_0$)	3,6	3,8	3,9	3,6	3,4	3,5	4,0

VBO are directly comparable to IPE and UPS/XPS measurements

Chemical bonding at an interface is a combinatory problem

=> **Physical and ab initio characterizations are the key**

Band Gap of Si Nanostructures

Si CBM

Si VBM

FIG. 2. Energy gap vs confinement parameter $1/d$. Dots represent DFT with self-energy correction; dash lines: effective mass model for dots wires and slab confinement of both valence and conduction electrons assuming isotropic masses, full lines: finite barrier effective mass model.

Delley et al, APL 1995

Strain in mismatched materials improves certain properties:

Example: $In_{0.53}Ga_{0.47}As$ and $In_{0,52}Al_{0.48}As$ lattice matched to InP. In electronic applications large ΔE_C and small m* for electrons in $In_{0.53}Ga_{0.47}As$ is exploited. But if In in $In_{0.53}Ga_{0.47}As$ is increased to above 0.53, both ΔE_C and m* are improved at the cost of strain!

- Strain broadens the range of materials available for tuning the properties of interest such as band offsets and effective masses
- Stain has strong effects on valence band => strong tool for bandgap engineering
- Benefits of strain may allow to use desired layers on convenient but usually mismatched substrates

Si and Ge: Same type of lattice, but different lattice constants

Si: 5.43Å
Ge: 5.66Å

SiGe –Heterostructures ….

Strained SiGe on unstrained Si

Strained Si on unstrained SiGe

Tensile strained Si on relaxed $Si_{1-x}Ge$

- Biaxial stress in Si → conduction band offset!
- Energy level splitting
  → **High mobility for in-plane transport**

Effects of Biaxial tensile strain on Si Energy Bands

Strained Si grown on Relaxed $Si_{1-x}Ge_x$

biaxial tension

Conduction Band

Additional splitting:

- reduced intervalley scattering
- smaller in-plane effective transport mass

$$\mu = q\frac{\tau}{m_c^*}$$

Valence Band

HH/LH degeneracy lifted at Γ

- reduced interband scattering
- smaller in-plane transport mass due to band deformation

Mobility Enhancements in Strained Si for MOSFETs

Measured Room Temperature Characteristics

- electron and hole mobilities increase with tensile strain in Si
- peak mobility enhancement ratios: ~ 1.8X for 30% Ge substrate

Experimental Techniques for determining Band offsets

- Photoemission-determine valence band edge relative to vacuum or some standard for both materials forming the junction
- Optical emission can determine band offset directly in Type II offsets. Some Type I band offset can be converted to Type II by pressure.
- Other exotic techniques such as BEEM (Ballistic Electron Emission Microscopy)

How do we create Bandgap Engineered Structures? Epitaxy

- AlGaAs Materials system:

GaAs: direct bandgap materials
AlAs: indirect bandgap materials

$E\Gamma$: direct bandgap;
EX: indirect bandgap

$$E_{\Gamma}(\text{eV}) = 1.423 + 1.36x + 0.22x^2$$

$$E_{\text{X}}(\text{eV}) = 1.906 + 0.207x + 0.55x^2$$

For effective light emission the x < 0.4in GaxAl1-xAs

Refractive index of GaxAl1-xAs

- AlGaInP Materials system: main application is red diode lasere

RT *E*g, refractive index, and absorption coefficient of (Al*x*Ga1-*x*)0.52In0.48As (match GaAs)

$$E_{\Gamma}(\mathrm{eV}) = 1.89 + 0.64x$$

$$E_{\mathrm{X}}(\mathrm{eV}) = 2.25 + 0.09x$$

Band structure modification by alloying: Varying ‘a’ and ‘Eg’ change bandstructures

Semiconductor Alloys – $Be_xZn_{1-x}O$

Anion Replacement: $ZnO_{1-x}S_x$

ZnO (wurtzite)	3.43	
ZnO (zincblende)	3.30	3.33
ZnS (wurtzite)	3.91	3.94
ZnS (zincblende)	3.84	

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Fan, Shen, and Kuo, *New J. Phys* ***11***, *093008 (2009)*

Heterostructures with different layer sequences (bandgap engineering)

[Marius Grundmann, *The Physics of Semiconductors*, Springer, 2006]

a) Quantum well (**QW**)
b) Multiple quantum well (**MQW**)
c) Superlattice (**SL**)
d) Single-barrier tunneling structure
e) Double-barrier tunneling structure

Position of conduction and valence-band edges for a variety of semiconductors

[Marius Grundmann, *The Physics of Semiconductors*, Springer, 2006]

Doping and compositional superlattice

[P. Y. Yu and M. Cardona, Fundamentals of Semiconductors, Springer, 1996]

Doping superlattice
(nipi structure)

Compositional superlattice

Classification of multiple quantum well and superlattice

[P. Y. Yu and M. Cardona, Fundamentals of Semiconductors, Springer, 1996]

Type I

- The electrons and holes are both confined within the same layer e.g., GaAs/AlGaAs MQWs

Classification of multiple quantum well and superlattice

[P. Y. Yu and M. Cardona, Fundamentals of Semiconductors, Springer, 1996]

Type IIA (staggered)

- The electrons and holes are confined within different layers e.g., GaAs/AlAs, SiGe/Si

Classification of multiple quantum well and superlattice

[P. Y. Yu and M. Cardona, Fundamentals of Semiconductors, Springer, 1996]

Type IIB (misaligned)

- Only a very small energy gap between the electrons in one layer and the holes in the neighboring layer, it behaves like zero-gap or small-gap semiconductors, e.g., InAs/GaSb
- **Type III**
  a MQW formed by a semiconductor and a zero-gap semiconductor

Compound Semiconductors allow us to perform "Bandgap Engineering" by changing the energy bandgap as a function of position. This allows the electrons to see "engineered potentials" that "guide" electrons/holes in specific directions or even "trap" them in specific regions of devices designed by the electrical engineer.

Example: Consider the simplified band diagram of a GaN/ $Ga_{0.75}In_{0.25}N$/ GaN LED structure. Electrons and holes can be "localized" (trapped) in a very smal region – enhancing the chance they will interact (recombine). This is great for light emitters!