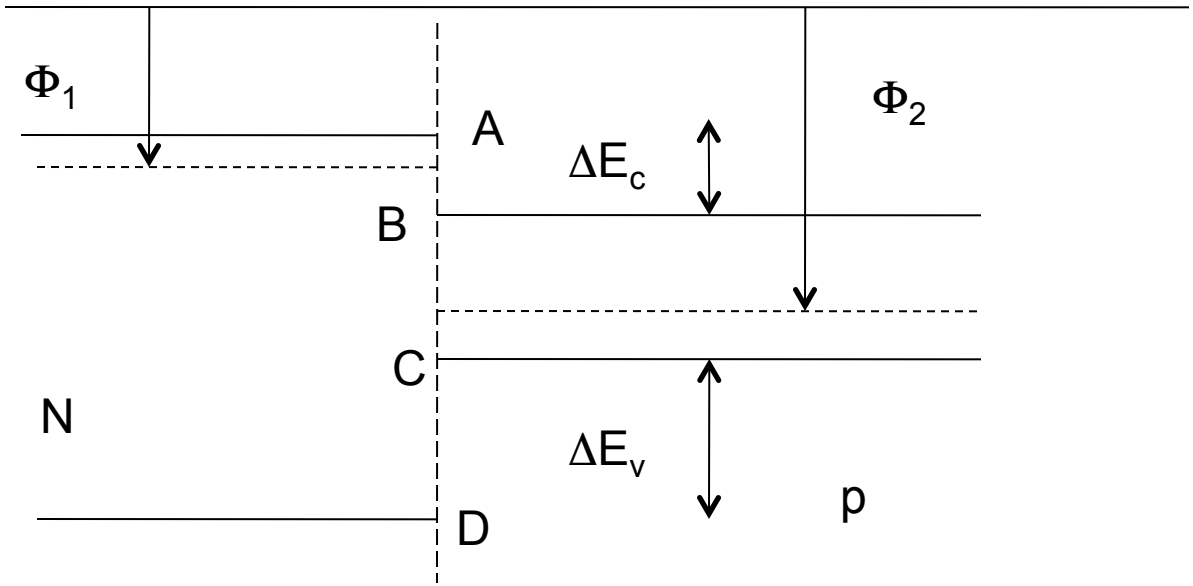
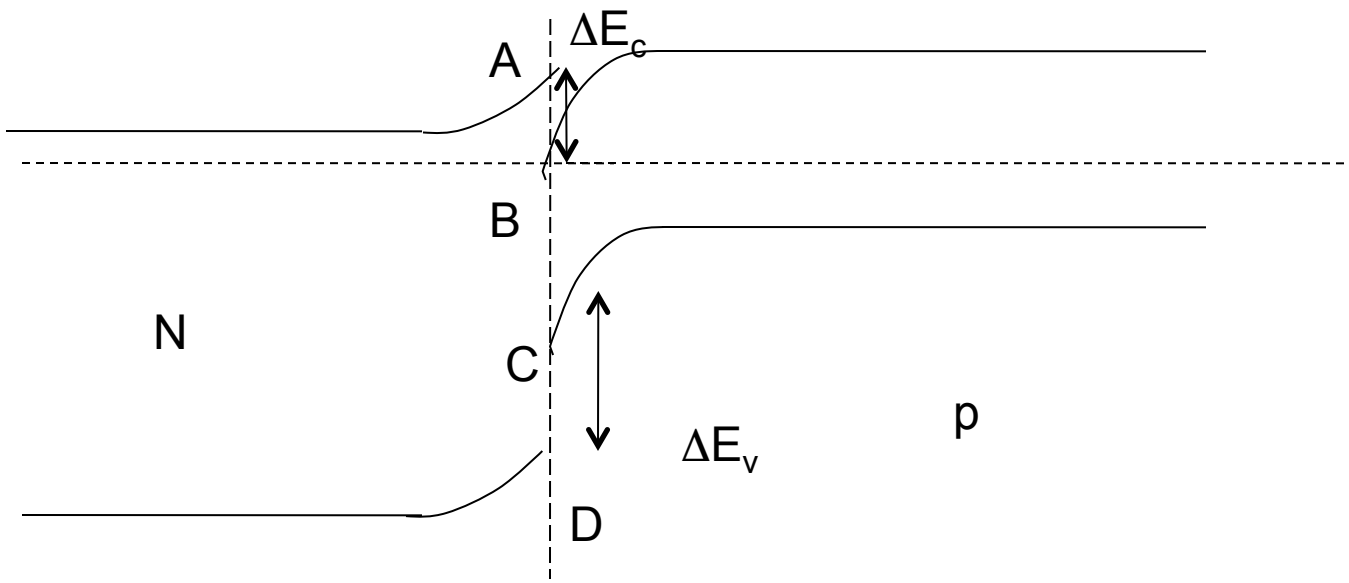
III-V Compounds

Heterojunctions



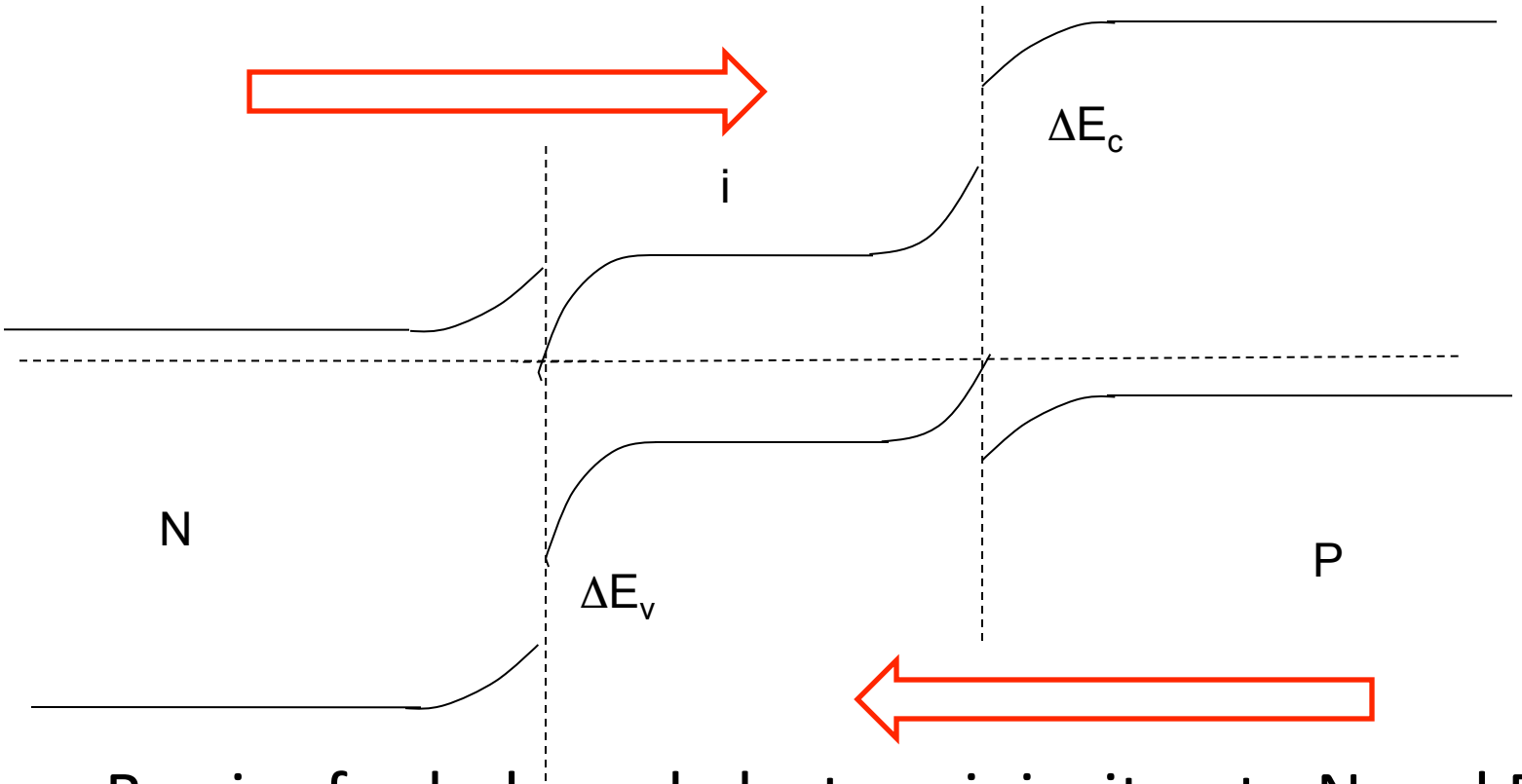
- Φ are the work functions(vacuum to Fermi level)
- Electrical Potential is continuous;
- ***D*** = ε***E*** normal is continuous; (without charge traps)
- Energy LevelsE-V(x)
- Energy spacing AB, BC, CD are fixed;

Heterojunction



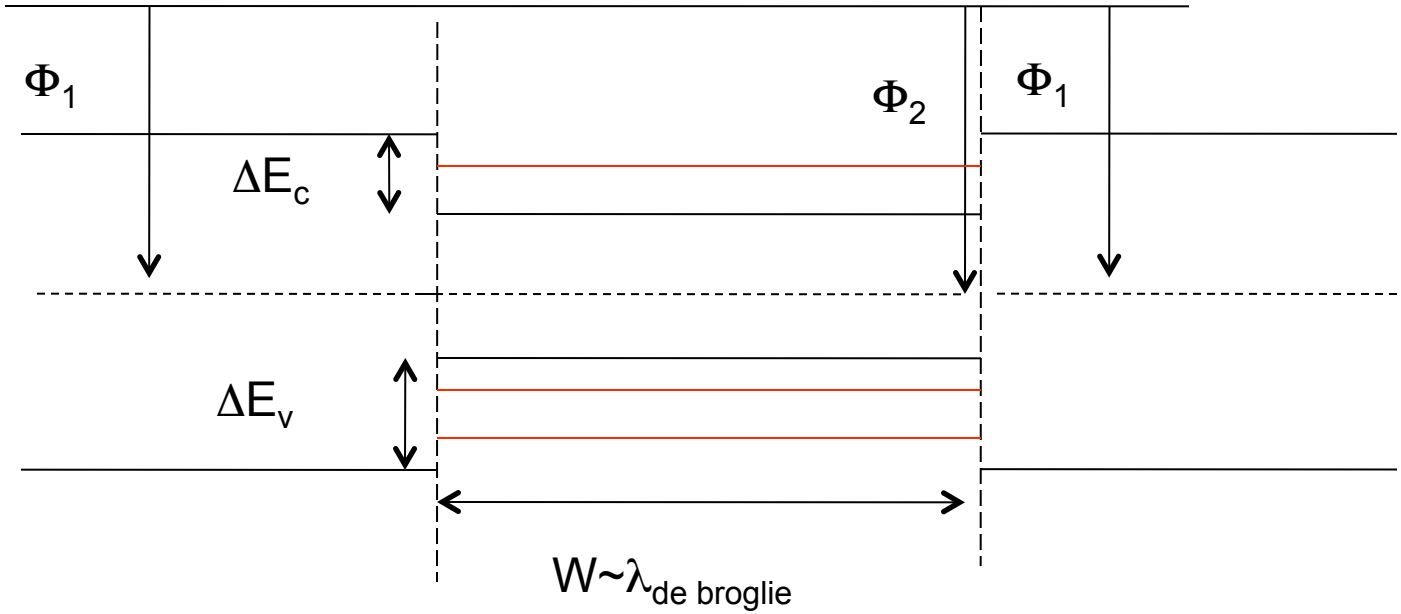
- Electron accumulation and barrier for hole injection on the p-side;
- Barrier on N-p is only the built-in potential
- E(-dV/dx) is not continuous ;
- Barrier depends on the gap and work function differences;
- In general, one has depletion, accumulation, inversion using heterojunctions

Double heterostructure diode.



- Barrier for hole and electron injeciton to N and P sides, respectively;
- Electron and Hole accumulation in the i-layer

Heterojunction (Quantum well)



- Very thin layer sandwiched between larger gap materials. (Neglect built-in potential)
- Quantum confinement (ΔE_c) in the conduction band and (ΔE_{vlh}) for light holes and (ΔE_{vhh}) for heavy holes.
- The quantum confinement can be 1D(this case); 2D (quantum wires); and 3D (quantum dots)
- Material properties start to depend on the geometry of the confinement – nanotecnology.

Materials

- Crystalline layer sequence with abrupt and defect less interfaces;
- Demands crystal growth;
  - Crystal growth with same crystal orientation: epitaxy;
  - Demands materials with same lattice constant;
- High Mobility, speed and strong light matter interaction (Direct band-gap) ;
- **Most important materials III-V compounds**

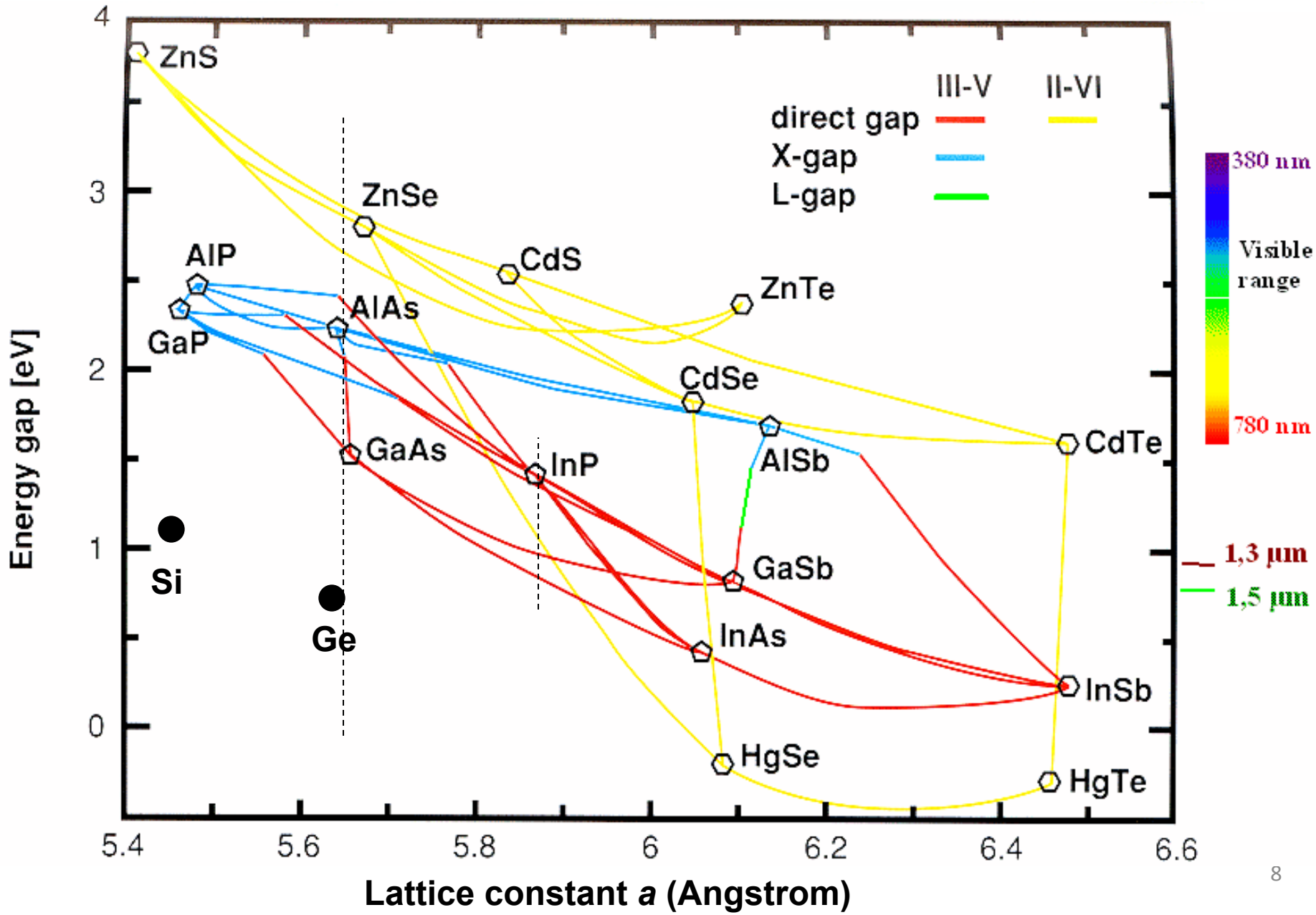
Periodic Table of the Elements

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 * La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 + Ac	104 Rf	105 Ha	106 106	107 107	108 108	109 109	110 110								

III - V

* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

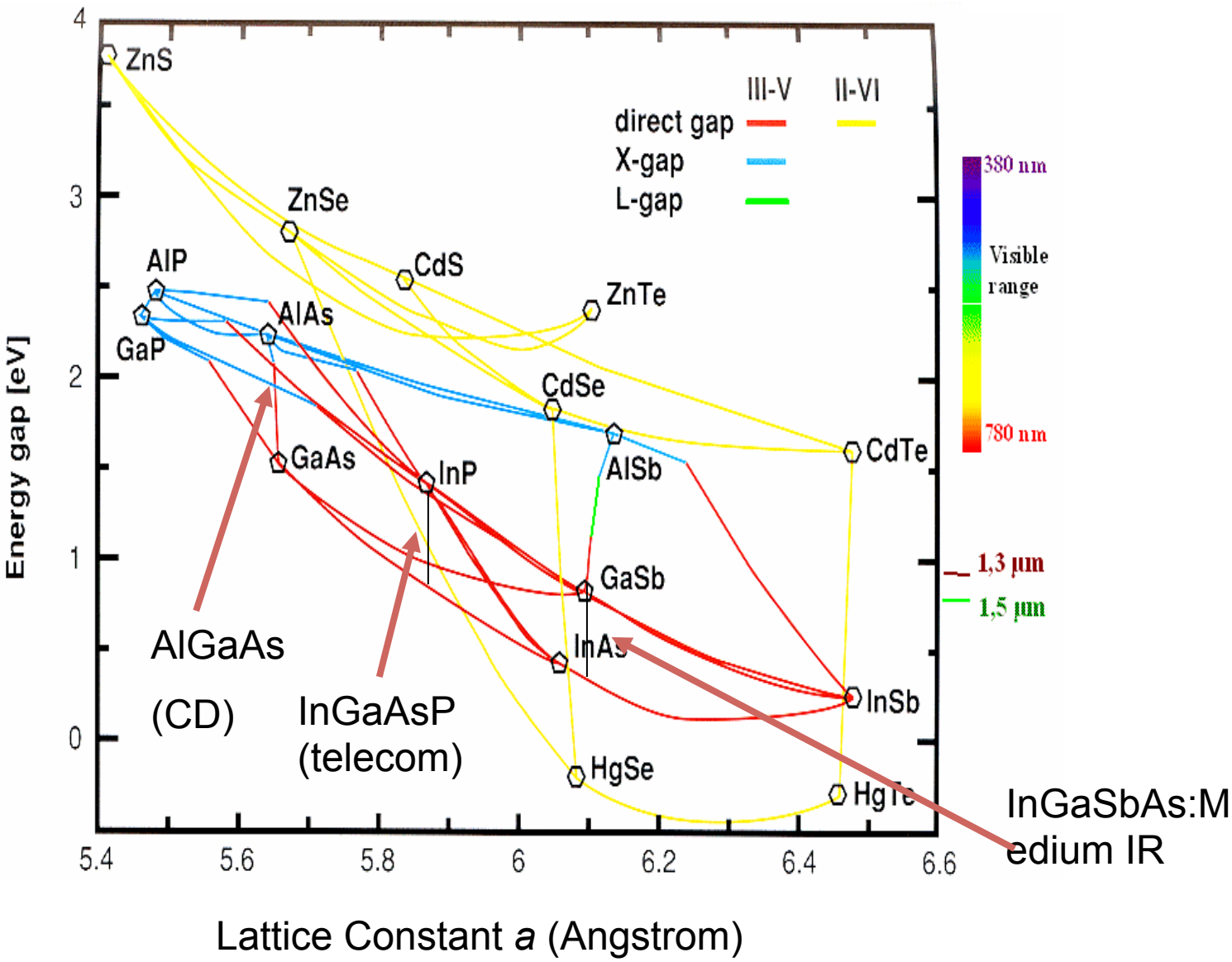
Energy Gap vs lattice constant(III-V)



Heterojunction Engineering

- Binary compounds:
  - A point in the E_G *vs. a* plot.
- Alloys:
  - Allows an almost continuous control of the material properties between its constituents;
  - Segregation and ordering limits alloy formation.
  - Examples:
    - Ternary: $Al_{1-x}Ga_xAs$; almost fixed a with varying E_G.
    - Quaternary: $In_{1-x}Ga_xAs_yP_{1-y}$ (can be used to control a and EG) can be made lattice matched to InP and emit at 1550 nm)
    - Quaternary $In_{1-x-y}Ga_xAl_yAs$ Add In to the ternary above; allows matching to InP.
    - Quaternary: $In_{1-x-y}Ga_xAl_yN$ (large lattice constant variation but bandgap reaching entire visible spectrum and UV)

Aplications



Nitrides
(High brightness LED´s

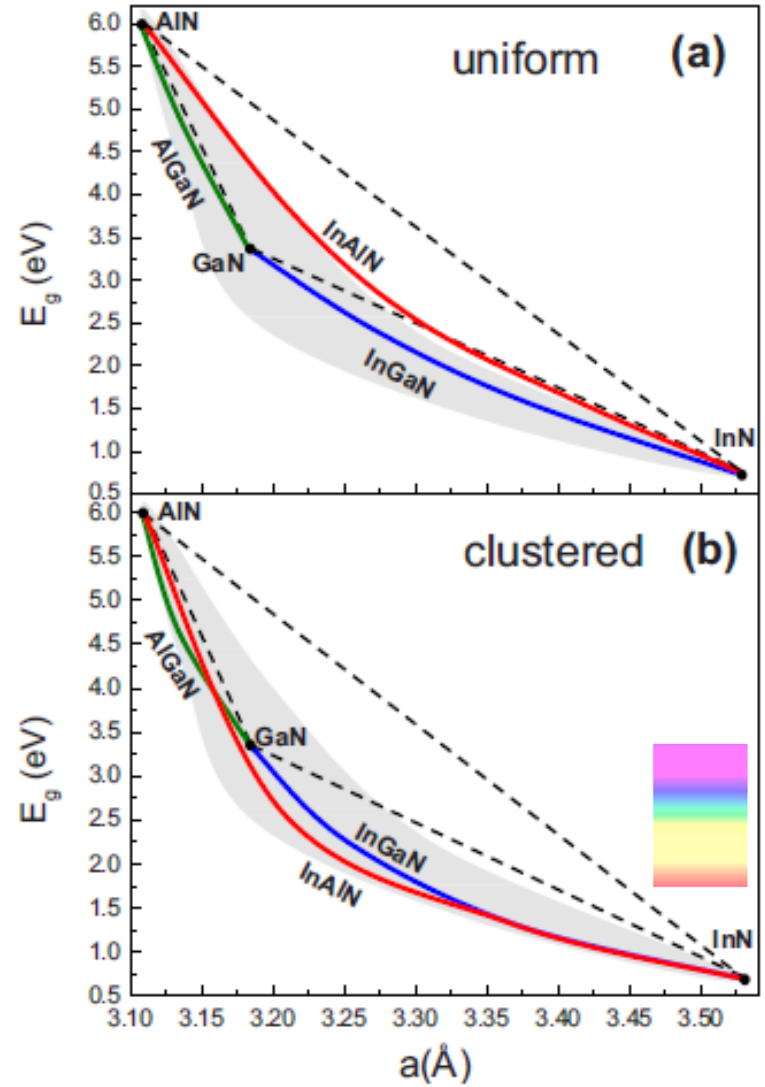


FIG. 1. (Color online) Energy gaps of $Ga_xAl_{1-x}N$, $In_xGa_{1-x}N$, and $In_xAl_{1-x}N$ as functions of lattice parameter, *a*, for a uniform (a) and clustered (b) distribution of cations. The triangle formed by dashed lines corresponds to a linear approximation of the relation between band gaps and lattice parameters. The shaded area covers the region where the experimental points are lying.

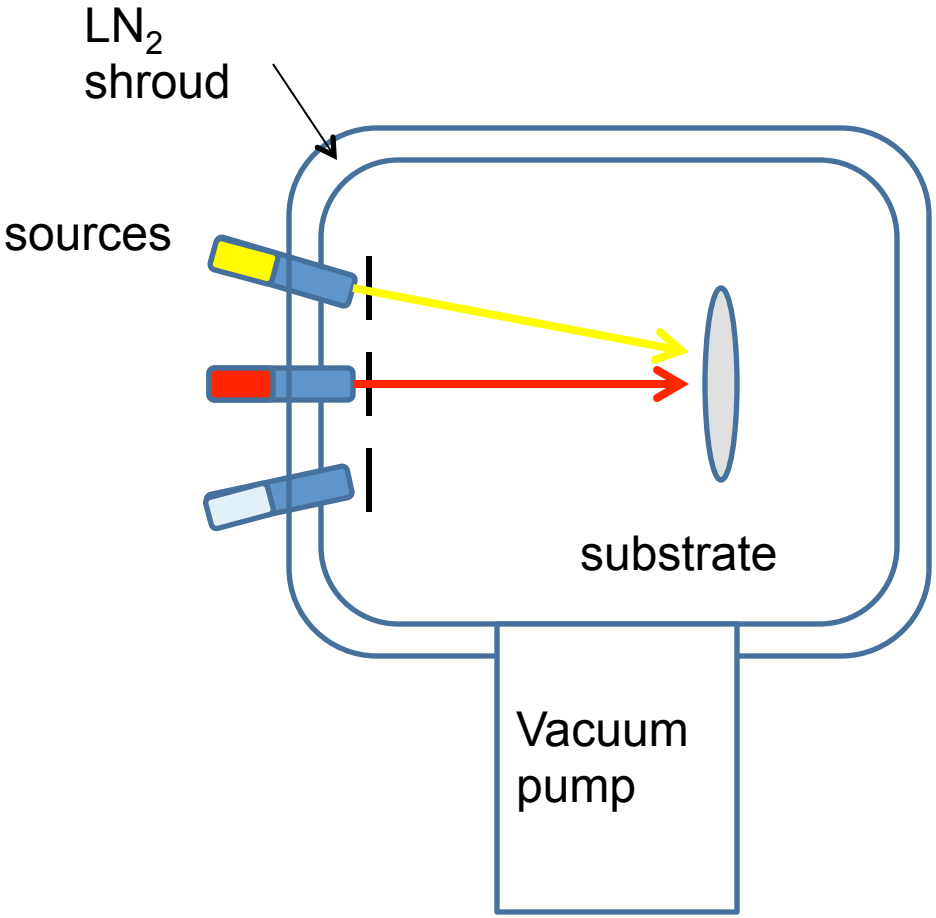
Limitations to band gap tuning in nitride semiconductor alloys

I. Gorczyca,1,a T. Suski,1 N. E. Christensen,2 and A. Svane2
II. APPLIED PHYSICS LETTERS **96, 101907 2010**

III- V Growth

- Epitaxy : crystal growth following same orientation as the substrate;
- In general requires same lattice constant for the substrate and over layer. Difference in lattice constant leads to strain that limits thickness .
- Most used substrates (telecom and optical storage): GaAs e InP
- Nitrides: Safire e SiC (Large mismatch; requires thick dislocation relieve buffer layers)
- Techniques:
  - LPE: Liquid Phase Epitaxy
  - MBE: Molecular Beam Epitaxy
  - GSMBE: Gas Source MBE
  - CBE: Chemical Beam Epitaxy
  - MOCVD (OMVPE) : Metalorganic Chemical Vapor deposition (Organomettalic Vapor Phase Epitaxy)

MBE; GSMBE; CBE



Sources (III, V, dopants):

MBE: all solid; heated cells

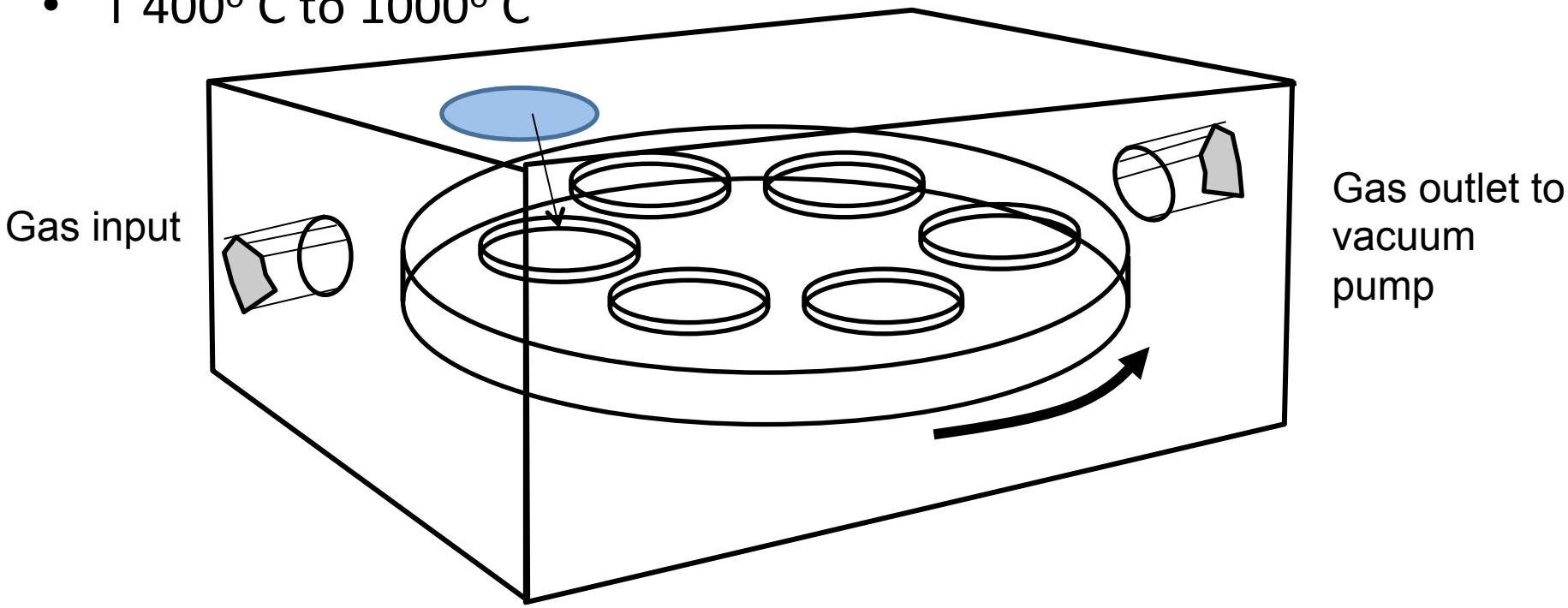
GSMBE: group V gas (arsine and phosphine through crackers); group III and dopants are solids

CBE: : group V gas (arsine and phosphine through crackers); group III organometalics and bublers; dopants are usually solid

UHV free mean path larger than chamber dimensioin: balistic flux of source;
Temperature: 400° C to 800° C (resistive heating)
Over pressure of group V (group V does not deposit on group V terminated crystal)

MOCVD

- Low vacuum system;
- Creates a stagnant layer;
- Group V source is phosphine and arsine
- Group III are organometalic (TMG, TEG, TMI, etc)
- Dopants: organometalic (DMZn, etc.) or gases (silane);
- Hydrogen carrier gas
- T 400° C to 1000° C



Compounds Material Properties *

- Linear interpolation between binary compounds ;
- Given the binary compounds AB, AC, BC and BD; one can obtain the quaternary alloy $A_xB_{1-x}CyD_{1-y}$:
- A given property P of the alloy can be obtained as a linear average (interpolation) of the binaries:
- $P(A_xB_{1-x}C_yD_{1-y}) = P(AC)xy + P(AD)x(1-y) + P(BC)(1-x)y + P(BD)(1-x)(1-y)$
- Bandgap energy is an exception (usually quadratic interpolation)

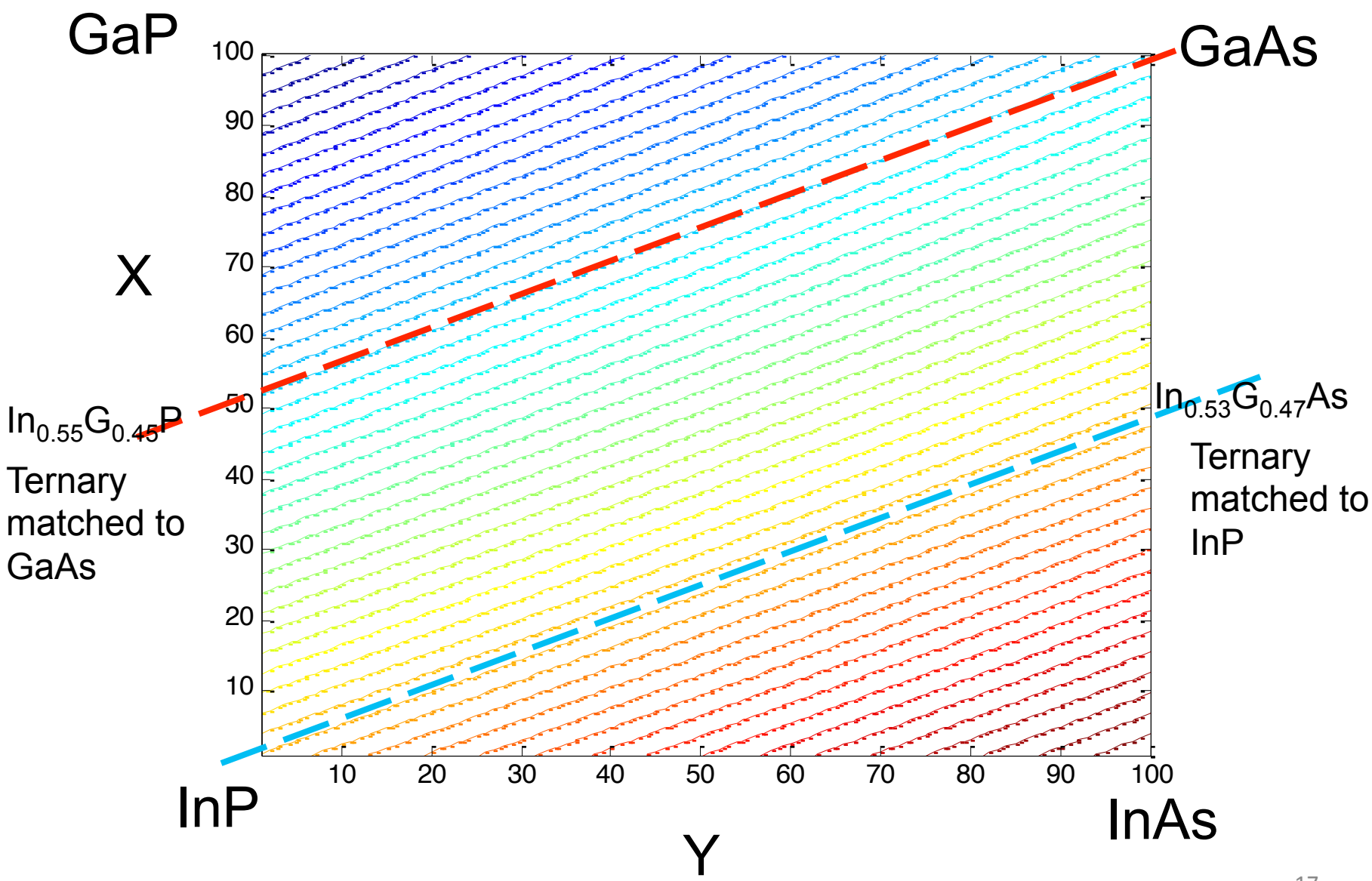
* J. Minch et al, IEEE JQE, 35 (5),p.771, 1999

$In_{1-x}Ga_xAs_yP_{1-y}$

- $P(In_{1-x}Ga_xAs_yP_{1-y})=P_{GaAs}xy+ P_{GaP}x(1-y)+ P_{InAs}(1-x)y+ P_{InP}(1-x)(1-y)$;
- Lattice constant

aInP = 5.8688;
aGaP = 5.4505;
aInAs = 6.0584;
aGaAs= 5.6533;

$In_{1-x}Ga_xAs_yP_{1-y}$ iso lattice constant plot



- If we look for a family of $In_{1-x}Ga_xAs_yP_{1-y}$ with a given binary property P we obtain a function x(y):
- $P(In_{1-x}Ga_xAs_yP_{1-y})=P(InP)$:
- $P(In_{1-x}Ga_xAs_yP_{1-y})=P_{GaAs)}xy+ P_{GaP}x(1-y)+ P_{InAs}(1-x)y+ P_{InP}(1-x)(1-y)=P_{InP;}$ then:

$$x(y) = \frac{y(P_{InP} - P_{InAs})}{(P_{GaAs} - P_{GaP} - P_{InAs} + P_{InP}) + (P_{GaP} - P_{InP})}$$

- If P is the lattice constant:

$$x(y) = \frac{0.1896y}{0.4183 - 0.0132y} \approx 0.45y$$

Blue dashed line on page 19

- For the matching with a GaAs property:
- $P(In_{1-x}Ga_xAs_yP_{1-x})=P(GaAs)$:
- $P(In_{1-x}Ga_xAs_yP_{1-x})=P_{GaAs}xy+P_{GaP}x(1-y)+P_{InAs}(1-x)y+P_{InP}(1-x)(1-y)=P_{GaAs}$; then:

$$1-x=\frac{(1-y)(P_{InP}-P_{InAs})}{(P_{GaAs}-P_{GaP}-P_{InAs}+P_{InP})(1-y)+(P_{GaP}-P_{InP})}$$

- If P is the lattice constant:

$$1-x=\frac{0.1896(1-y)}{0.4183-0.0132(1-y)}\Rightarrow x(y)=0.55+0.45y$$

$$x>0.55$$

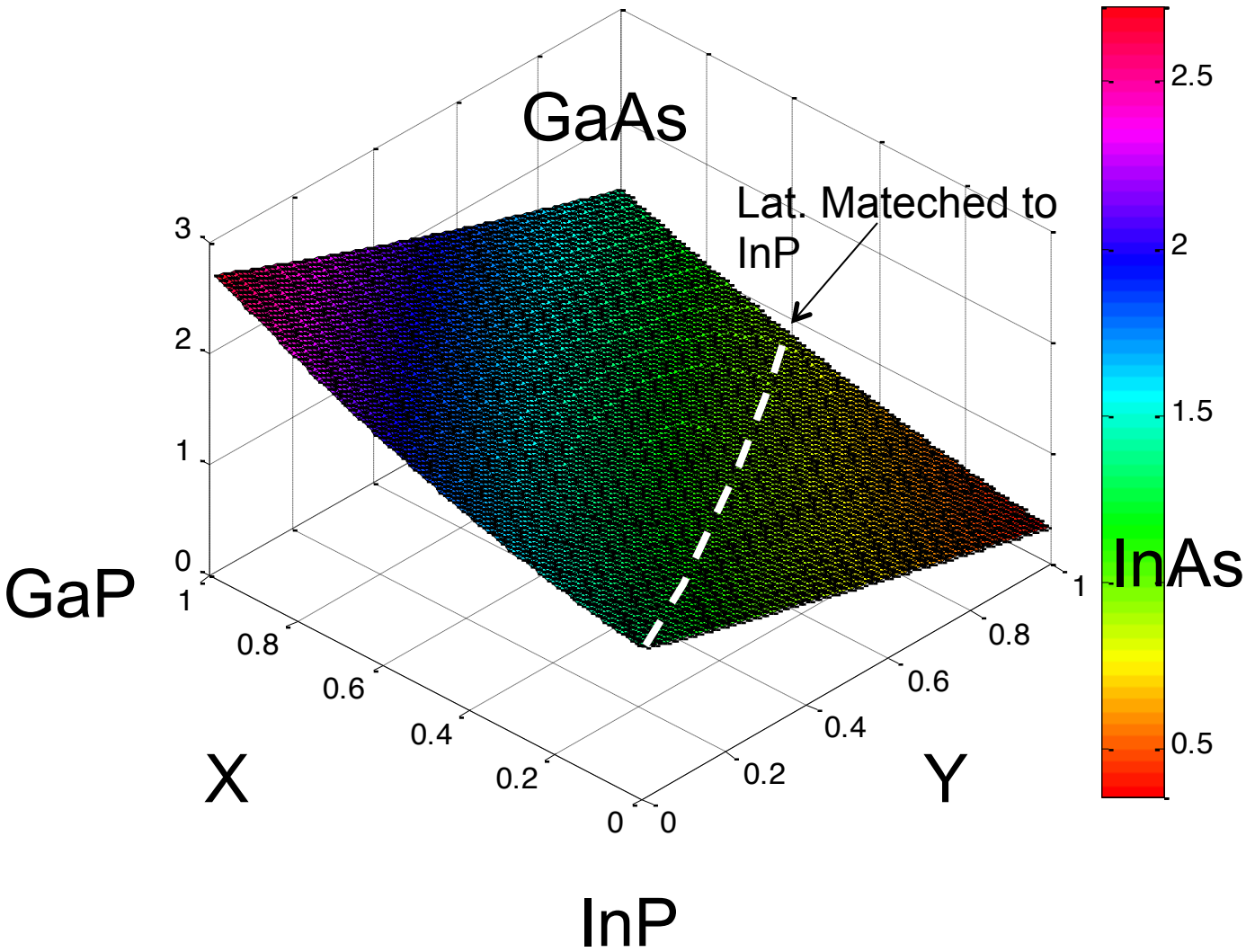
Red dashed line on page 19

- For the bandgap energy the interpolation is quadratic $In_{1-x}Ga_xAs_yP_{1-y}$ (Vegard´s law):

$$E_G(x,y)=1.35+0.642x-1.101y+0.758x^2+0.101y^2-0.159xy-0.28x^2y+0.109xy^2 \text{ (eV)};$$

This is obtained indirectly from $E_G[a(x,y)]$ for a given family of alloys. And $E_G(a)$ is quadratic (Vegard´s law)

E_G for $In_{1-x}Ga_xAs_yP_{1-y}$



$In_{1-x-y}Ga_xAl_yAs$

- $P(In_{1-x-y}Ga_xAl_yAs)=(1-x-y)P_{InAs}+ xP_{GaAs}+ yP_{AlAs}$
- Lattice Constant

$a_{AlAs}=5.66;$
$a_{InAs}=6.0584;$
$a_{GaAs}=5.6533;$

J. Minch et al, IEEE JQE, 35 (5),p.771, 1999

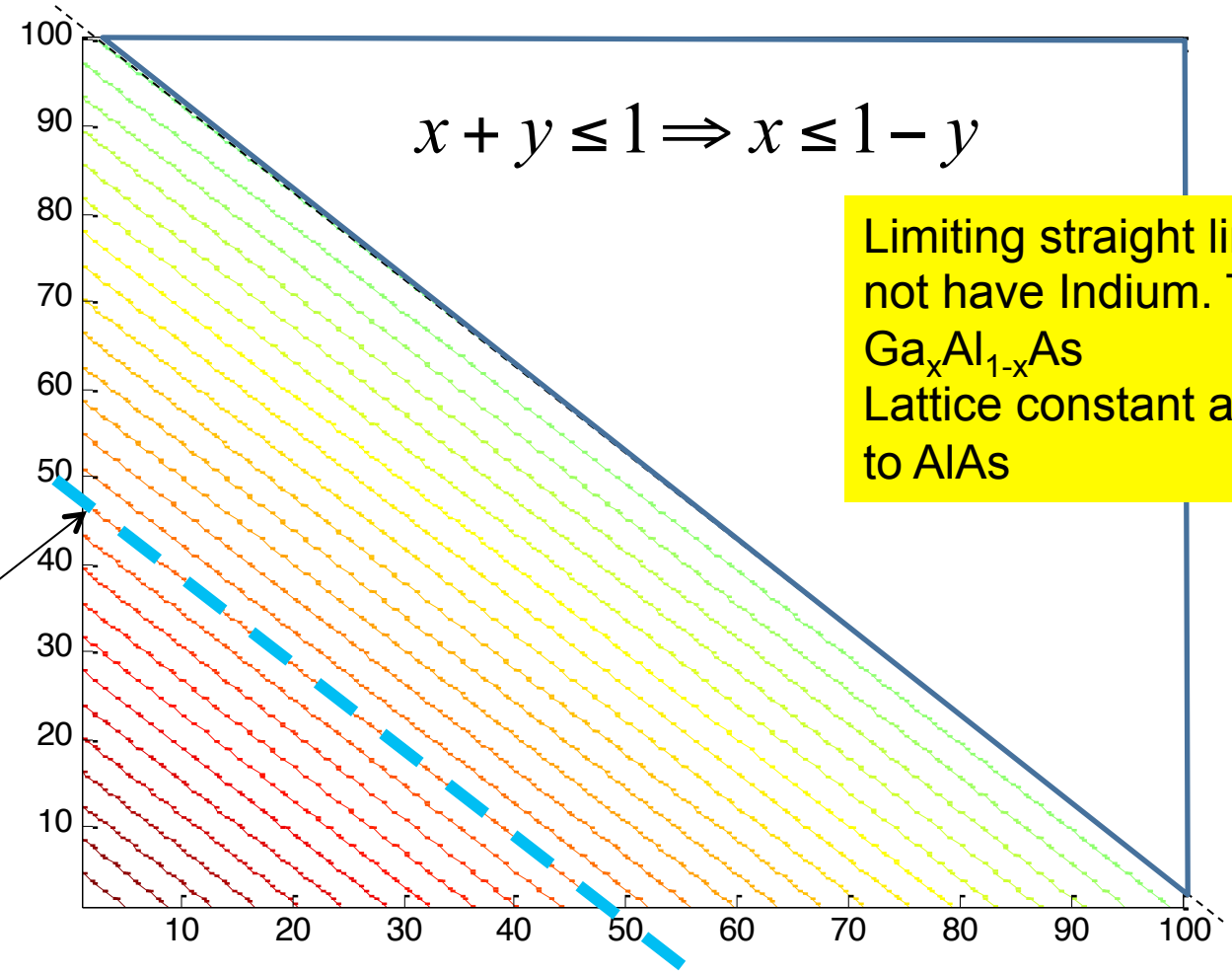
$In_{1-x-y}Ga_xAl_yAs$ iso lattice constant plot

GaAs

X

$In_{0.53}G_{0.47}As$

Ternary matched to InP



Limiting straight line x=1-y, does not have Indium. Therefore it is $Ga_xAl_{1-x}As$
Lattice constant almost matched to AlAs

InAs

Y

AlAs

- If we look for $In_{1-x-y}Ga_xAl_yAs$ alloys matched to InP, we obtain x(y:
- $a(In_{1-x-y}Ga_xAl_yAs)=a(InP)$, então:

$$(1-x-y)P_{InAs} + xP_{GaAs} + yP_{AlAs} = P_{InP} \Rightarrow$$

$$x = 0.468 - 0.985y$$

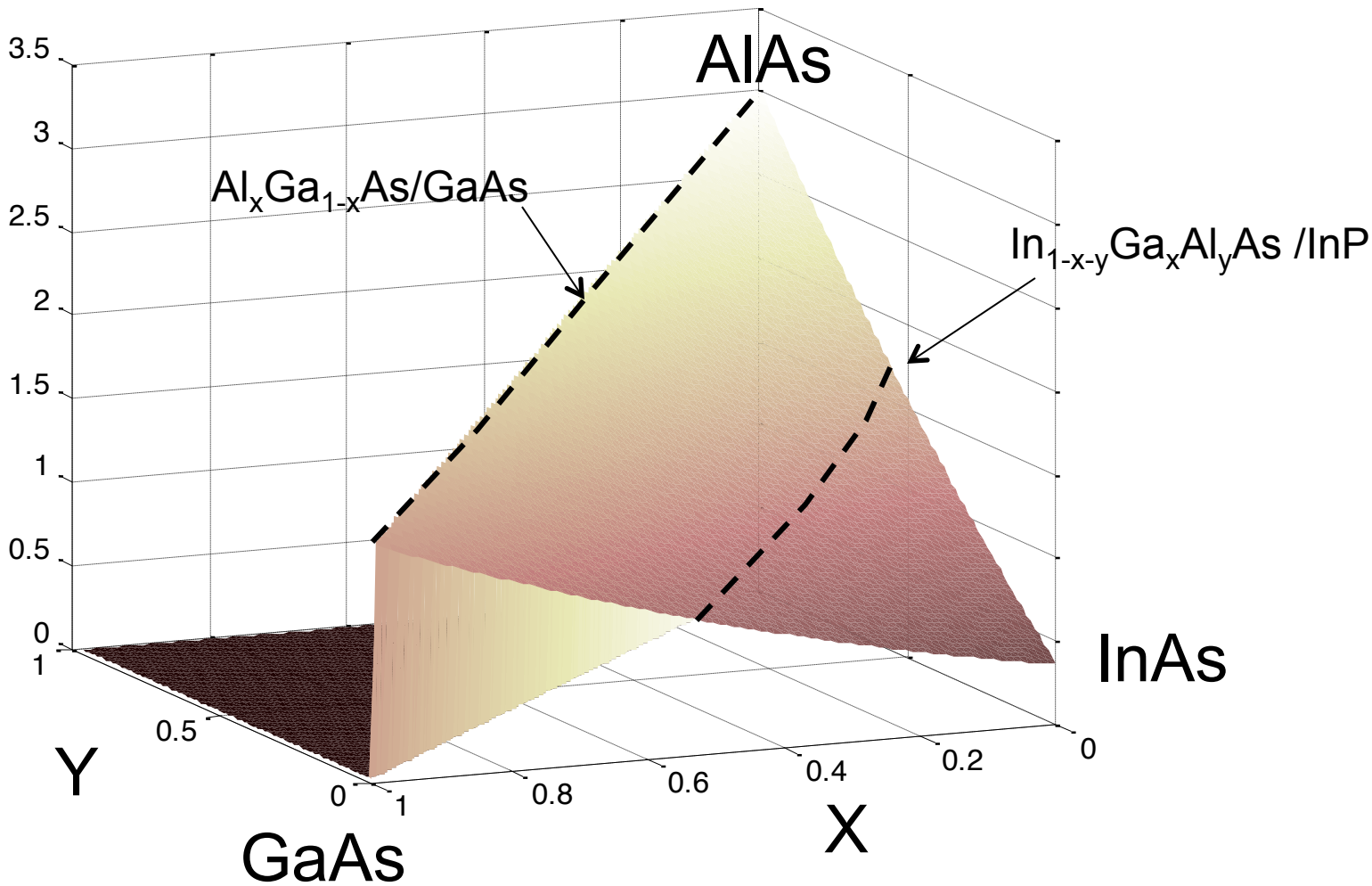
Blue line on p. 22

- E_G for ($In_{1-x-y}Ga_xAl_yAs$):
- Also quadratic:

$$E_G(x,y)=0.36+2.093y+0.629x+0.577y^2+0.436x^2+1.013xy-2xy(1-x-y)\ (eV);$$

$In_{1-x-y}Ga_xAl_yAs$

$$x + y \le 1 \Rightarrow x \le 1 - y$$



$Al_xGa_{1-x}As/GaAs$

Energy gap:

$x<0.45$ $1.424+1.247x$ eV (direto)

$x>0.45$ $1.9+0.125x+0.143x^2$ (indireto)

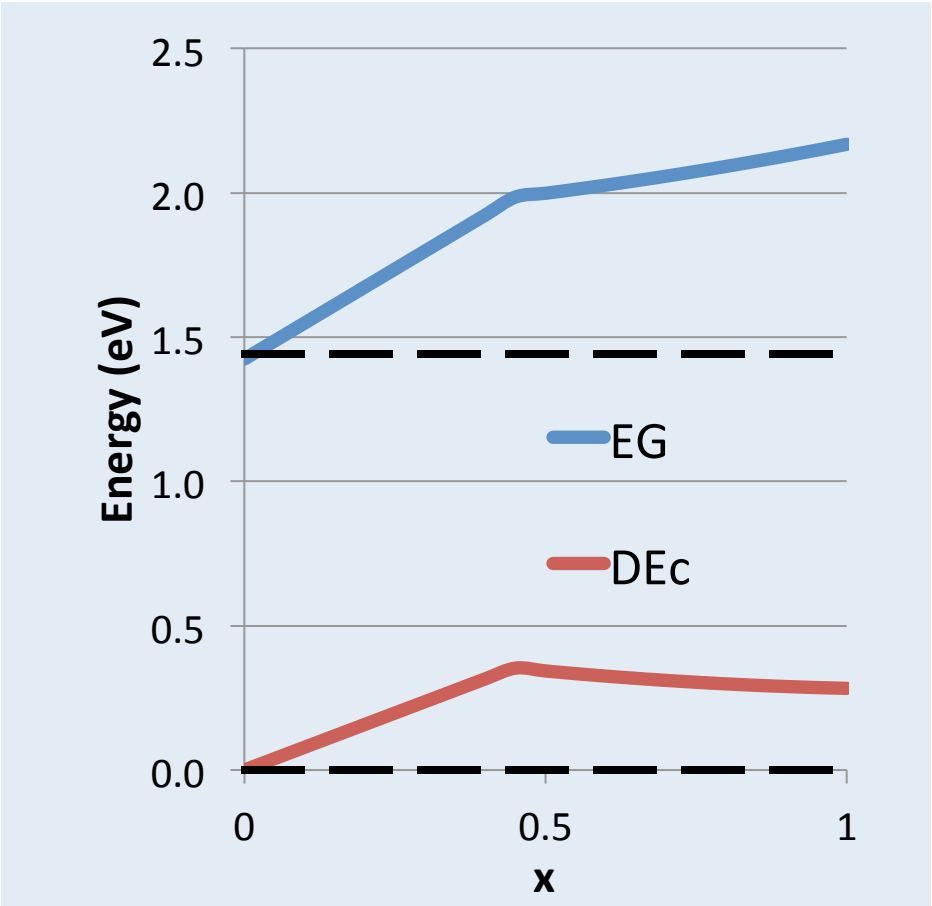
Effective electron mass m_e	$0.063+0.083x\ m_o$ ($x<0.45$)
Density-of-states electron mass m_{cd}	$0.85-0.14x\ m_o$ ($x>0.45$)
Conductivity effective mass m_{cc}	$0.26\ m_o$ ($x>0.45$)
Effective hole masses m_h	$0.51+0.25x\ m_o$
Effective hole masses m_{lp}	$0.082+0.068x\ m_o$

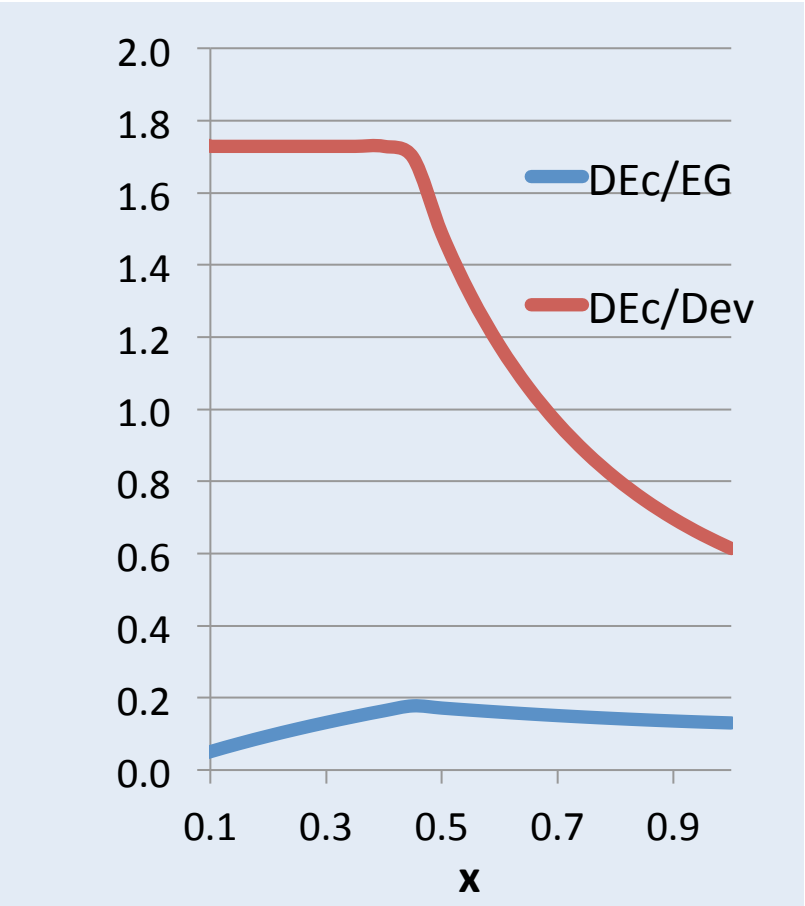
x<0.41 $\Delta E_c = 0.79x$ *(eV)*

x>0.41 $\Delta E_c = 0.475-0.335x+0.143x^2$ *(eV)*

http://www.ioffe.rssi.ru/SVA/NSM/Semicond/

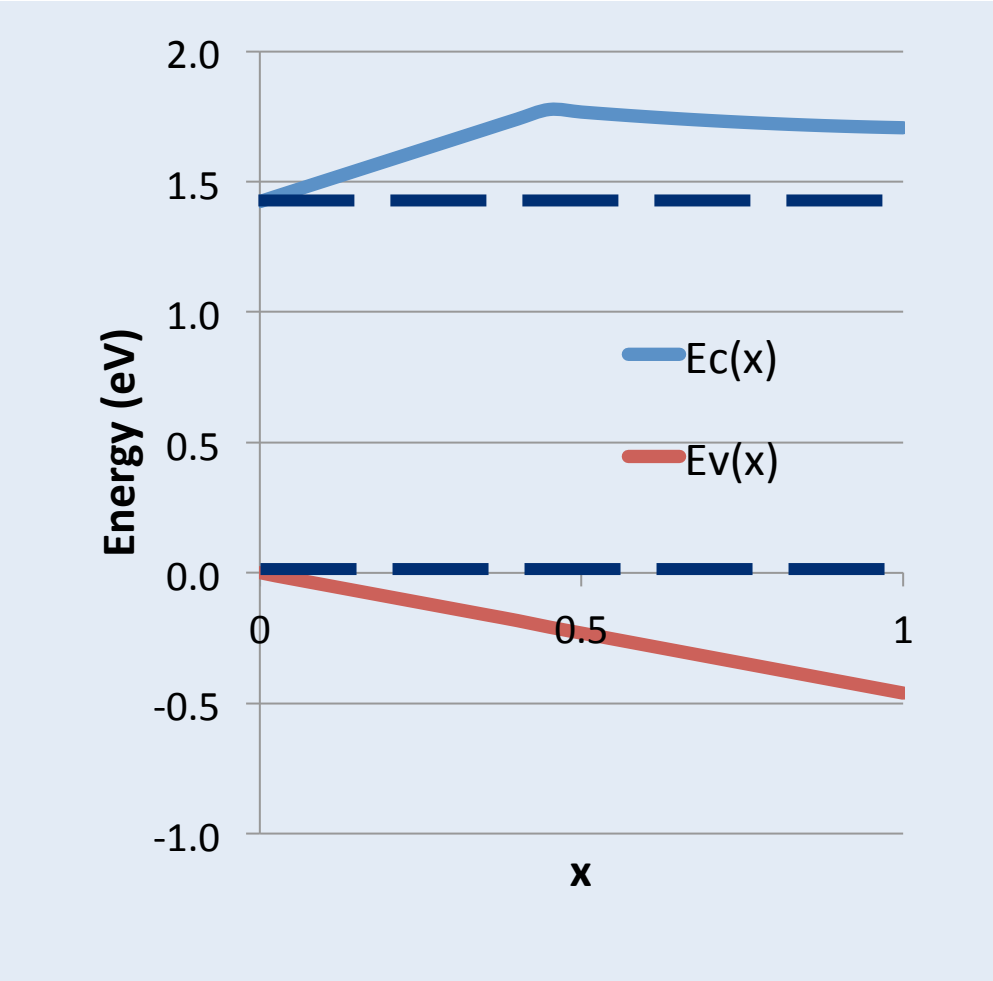
$Al_xGa_{1-x}As/GaAs$





http://www.ioffe.rssi.ru/SVA/NSM/Semicond/

$Al_xGa_{1-x}As/GaAs$



Conduction band discontinuity is always higher at the conduction band for x < 0.5

http://www.ioffe.rssi.ru/SVA/NSM/Semicond/

ΔEc e Δev InGaAsP and InGaAlAs

- As descontinuidades em função da composição podem ser obtidas pelos modelos (Harrison e Model-Solid) e também por fitting dos dados. Os dados para estes parâmetros se encontram na referência citada (Minch et al.). Para o caso de parâmetro de rede casado com InP temos os resultados (do artigo):
- InGaAsP/InP ($\Delta E_C/\Delta E_G$ ~ 0.4)
- InGaAlAs/InP $\Delta E_C/\Delta E_G$ ~ 0.3-1.5y

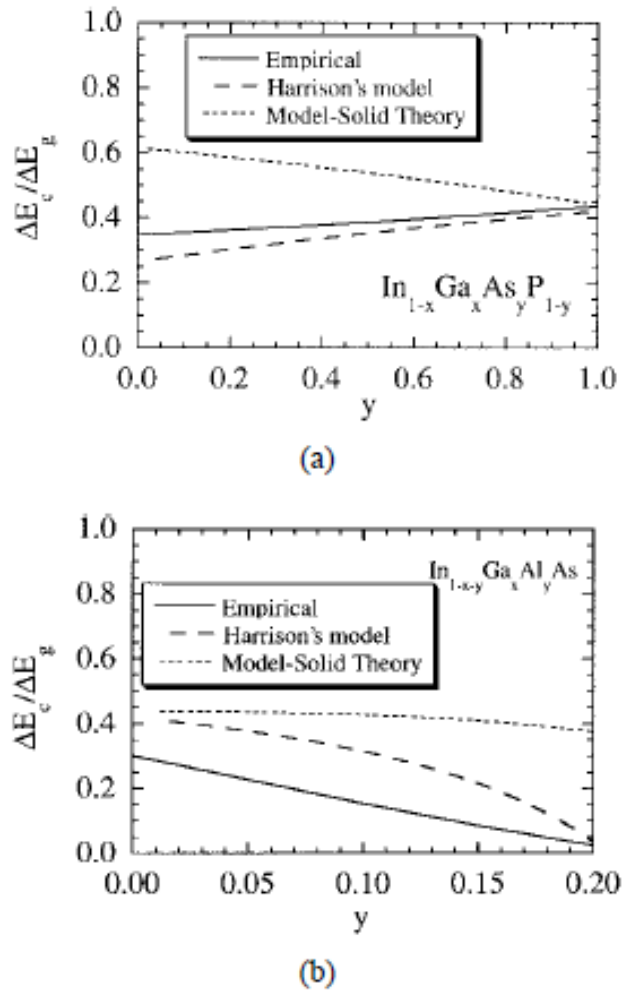
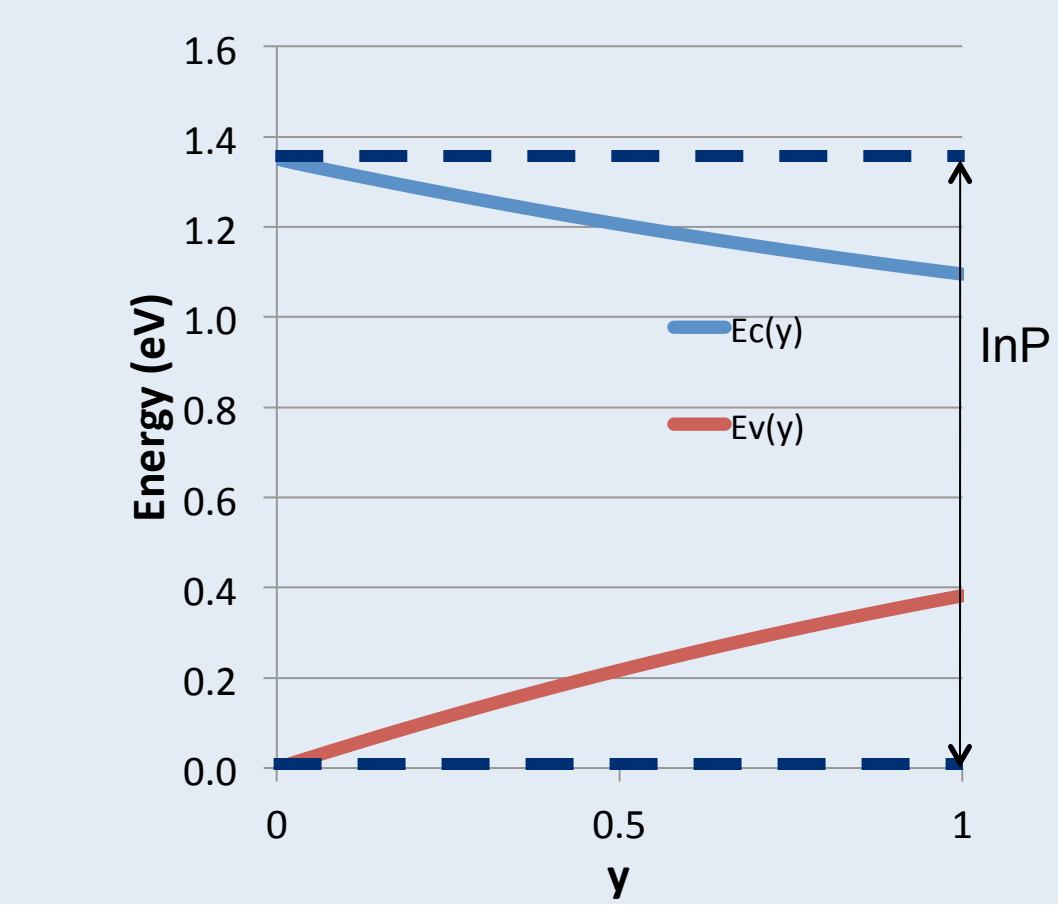


Fig. 3. The conduction band offset for (a) $In_{1-x}Ga_xAs_yP_{1-y}$ and (b) $In_{1-x-y}Ga_xAl_yAs$ lattice-matched to InP. The solid lines show empirical results [14], [15] obtained from experimental data. Dashed lines show calculations using the model-solid theory and Harrison's model.

J. Minch et al, IEEE JQE, 35 (5),p.771, 1999

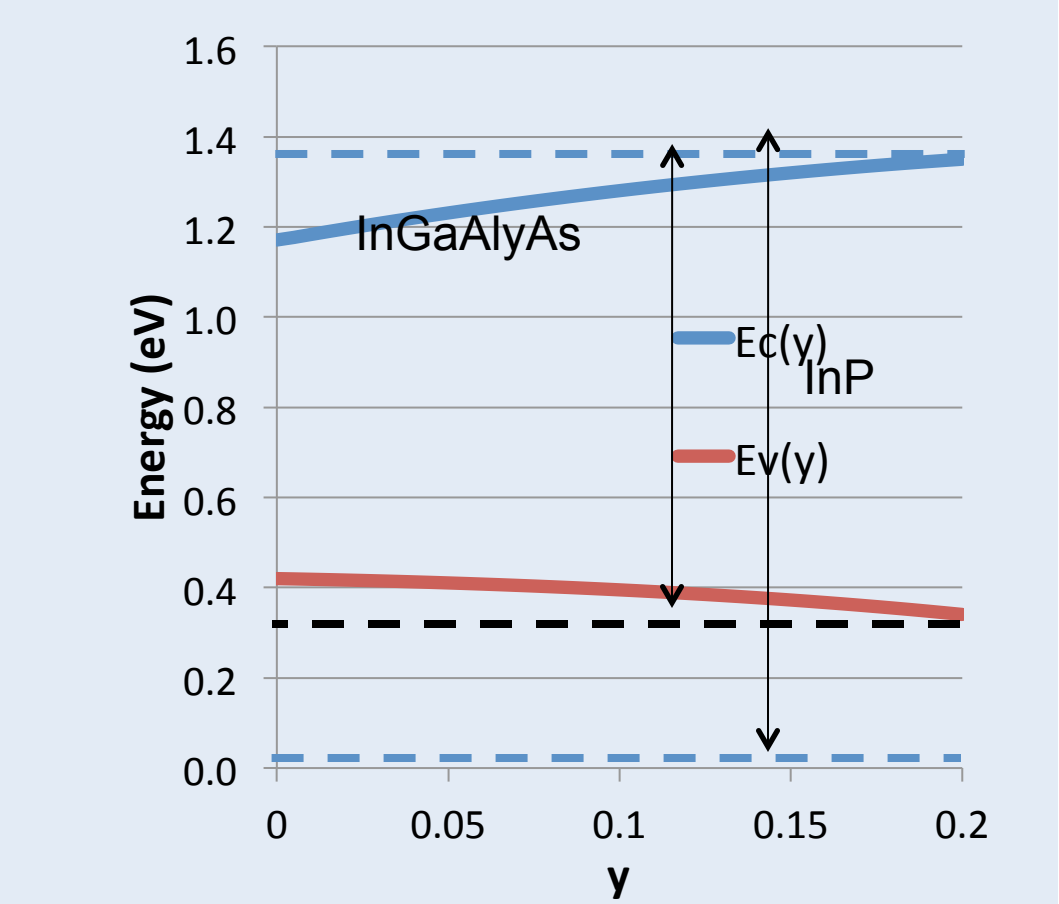
InGaAsP/InP

InGaAsP/InP heterojunction has always ΔEc smaller that ΔEv; worse electron confinement : electron leakage
and excessive hole confinement : hole pilling



$In_{1-x-y}Ga_xAl_yAs$ /InP

InGaAlAs / InGaAlAs has always larger ΔEc than ΔEv; (better electron confinement)



$$x = 0.468 - 0.985y$$

Strain

- When the growth layer has a different lattice constant from the substrate there appears a biaxial pressure or strain (compressive or tensile) :
- $\varepsilon=\varepsilon_{xx}=\varepsilon_{yy}=(a_0-a)/a$; a_0 is the substrate lattice constant and
- $\varepsilon > 0$ tensile
- $\varepsilon < 0$ compressive
- The orthogonal strain is $\varepsilon_{zz}=-2C_{12}\varepsilon/C_{11}$; C_{12} and C_{11} are elastic constants (distortion), the strain in z over the strain in x is the Poisson ratio:

$$\varepsilon_{zz} = -\frac{2\eta}{1-\eta}\varepsilon_{xx};$$

$$\frac{\eta}{1-\eta} = \frac{C_{12}}{C_{11}} \Rightarrow \eta = \frac{C_{12}/C_{11}}{1+C_{12}/C_{11}}$$

Strain

- The conduction and vallence bands energy are affected by the strain which depends on composition.
- One has:

$$\delta E_c(x,y) = a_c(x,y)(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) = 2a_c(x,y)(1 - \frac{C_{12}(x,y)}{C_{11}(x,y)})\varepsilon(x,y);$$

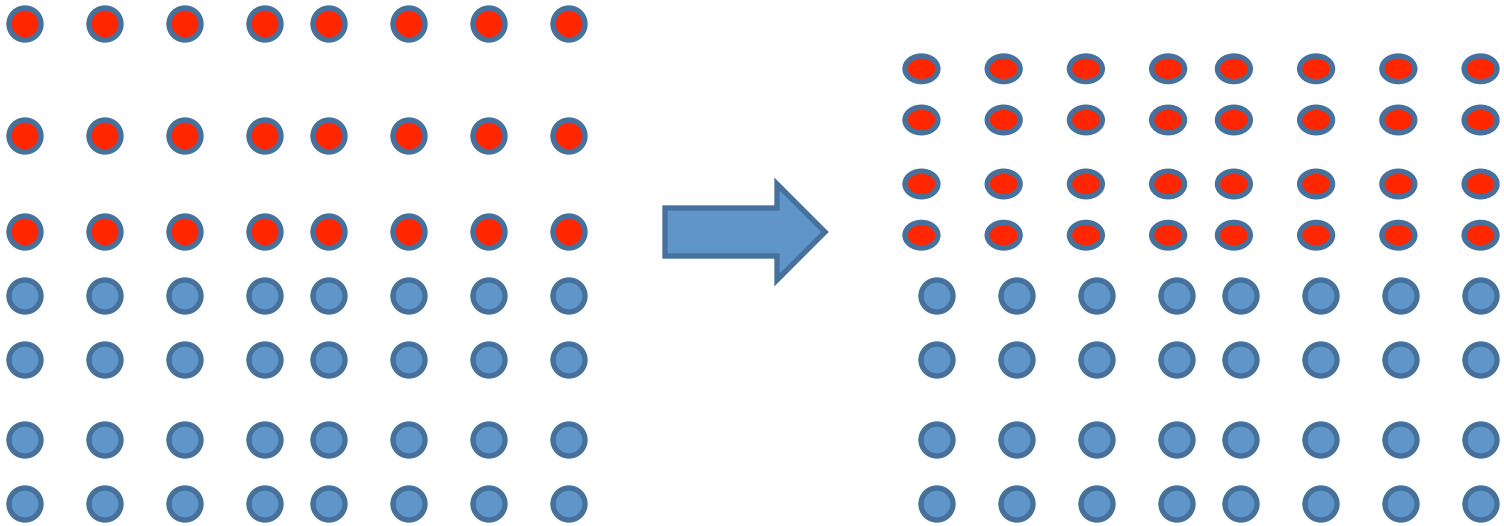
$$\delta E_{vhh}(x,y) = -P_\varepsilon - Q_\varepsilon;$$

$$\delta E_{vlh}(x,y) = -P_\varepsilon + Q_\varepsilon;$$

$$P_\varepsilon = -a_v(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}); Q_\varepsilon = -\frac{b}{2}(\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz})$$

Strain

- In order toor the strain to affect the bands there can´t be relaxation.
- There is a critical thickness where relaxation occurs leading to misfit dislocation.



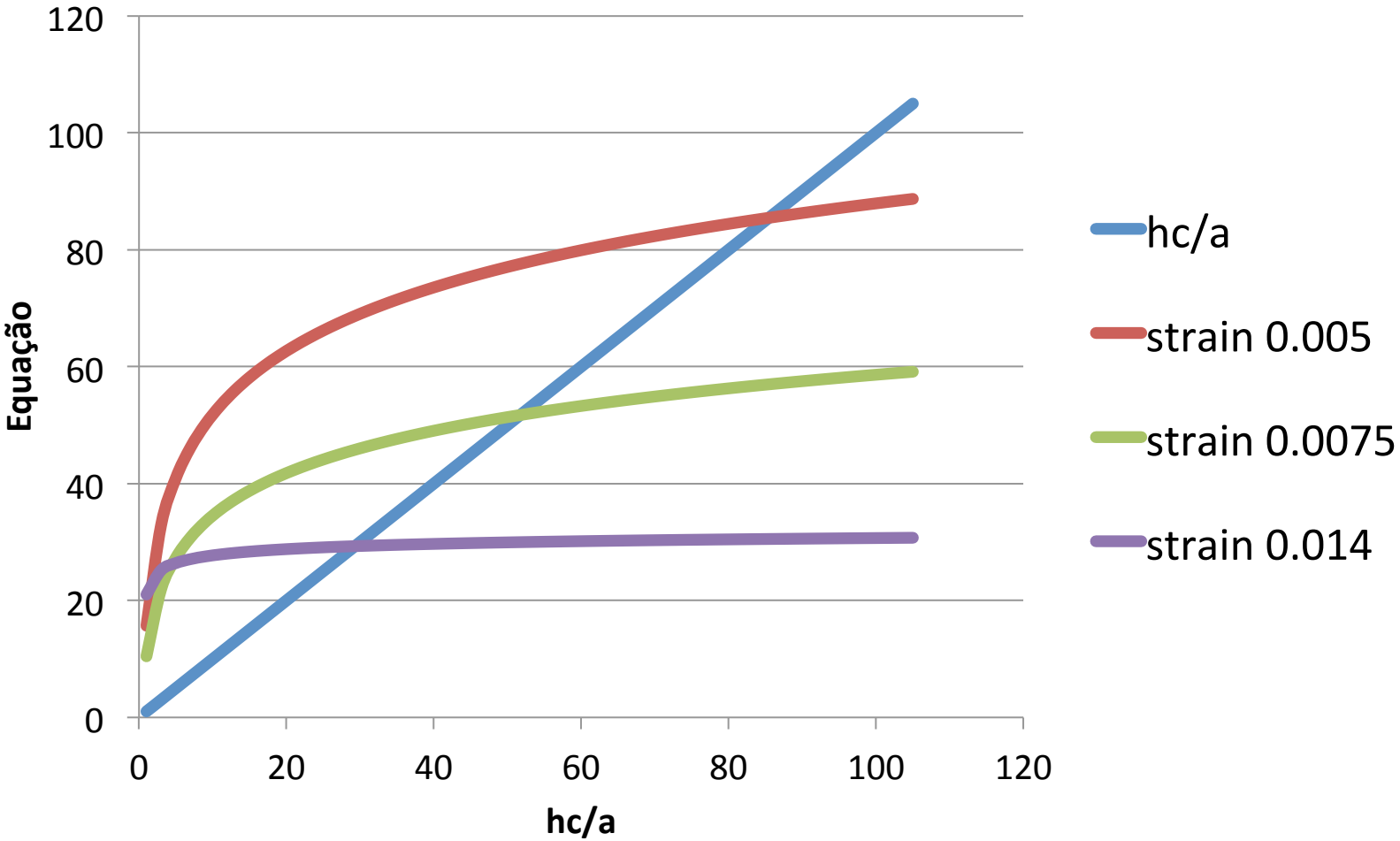
Crictical Thickness(Mathews and Blakslee)

- h_c is given by the transcendental equation:

$$\frac{h_C}{a} = \frac{1}{k\sqrt{2}\pi\varepsilon}\frac{(1-0.25\eta)}{(1+\eta)}\left[\ell n\left(\frac{h_C}{a}\right)+1\right]$$

- where *a* is the strained layer lattice parameter, ε is the strain, η is the Poisson ratio and k = 4 for an overlayer and k = 2 for a sandwich.

Example $In_xGa_{1-x}As$ on GaAs



- η = .32 e K=2;
- In0.2Ga0.8As/GaAs has a strain of 0.014 and lattice constant of 5.734. hc= 29x5.734 = 166.286 Angstroms for a quantum well.

Quantum Well

- Para podermos resolver o poço quântico temos que ter:
  - Potential barrier (ΔE_C) for electrons
  - Potential barrier for holes ΔE_V (heavy and light) a;
  - Effective masses;
- For the alloys this needs to be interpolated as a fucntion of the composition (x,y);
- In the presence of slight mismatch , one needs to include strain effects on these parameters.

Effective Mass

- Effective mass can be obtained from interpolation

	GaAs	InAs	InP	GaP	AlAs
m_c/m_0	0.067	0.023	0.077	0.25	0.15
m_{hh}/m_0	0.5	0.4	0.6	0.67	0.79
m_{lh}/m_0	0.082	0.026	0.089	0.14	0.15

Quantum Wells

- Considering the thicknes comparable to the deBroglie wavelength but much larger than the lattice parameter we can ude the effective mass approach:

$$\Psi_{k,n}(r) = \frac{e^{ik_{//}.\rho}}{2\pi} fn(z) U_{k_{//}}(\rho)$$

$$\left[-\frac{\hbar^2}{2m_{c(v)}} \frac{\partial^2}{\partial z^2} + V_{c(v)}(z) - E_n \right] f_n(z) = 0$$

- Neglecting (here for simplicity) the valence band mixing, we use the Kane model:

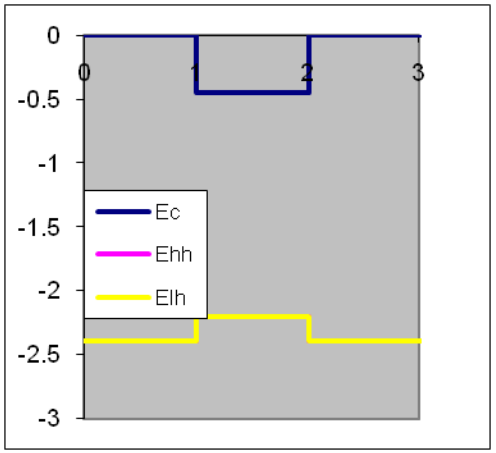
$$E_c(k,n) = E_G + \frac{\hbar^2 k^2}{2m_c} + E_{cn};$$

$$E_{vhh}(k,n) = -\frac{\hbar^2 k^2}{2m_{vhh}} - E_{vhhn};$$

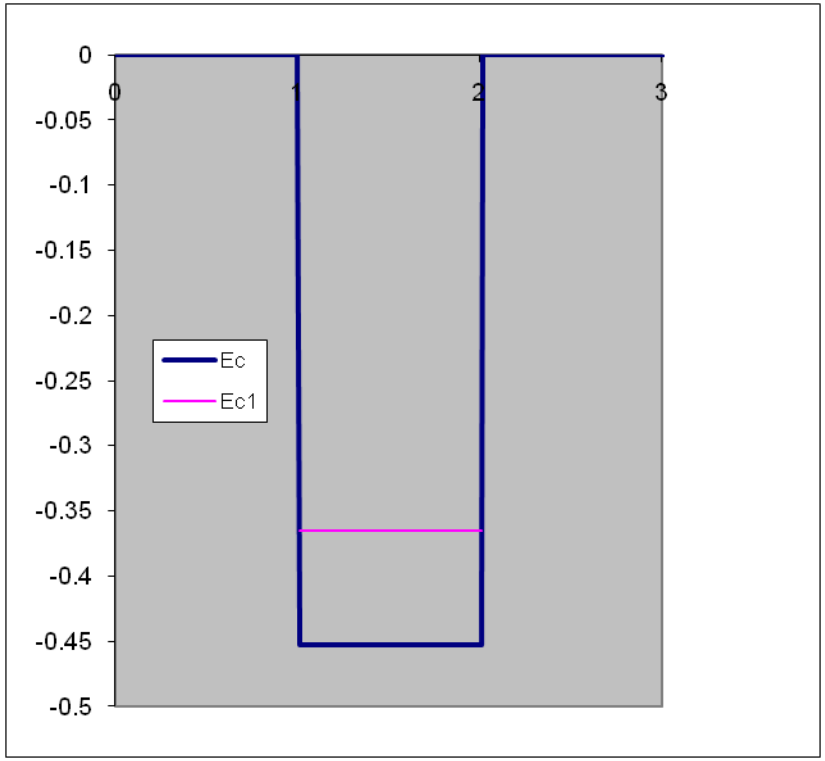
$$E_{vlh}(k,n) = -\frac{\hbar^2 k^2}{2m_{vlh}} - E_{vlhn};$$

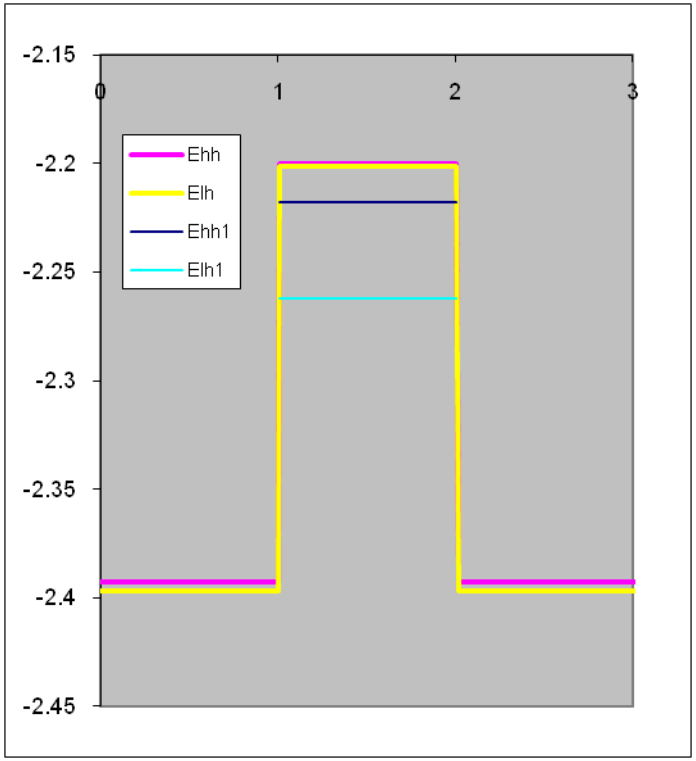
- The quantum confinemetn already lifts the degeneracy at the gama point between heavy and light holes. because $E_{vhhn} \neq E_{vlhn}$.

QW Examples

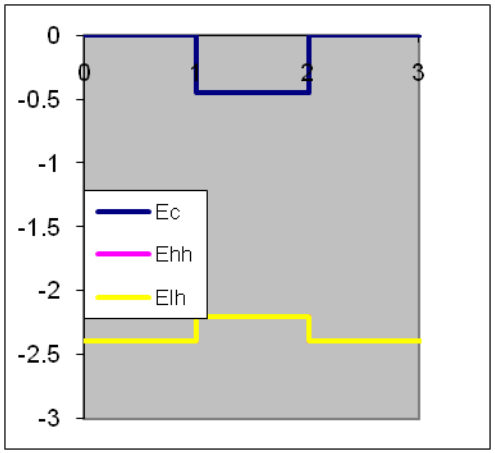


- $Al_{0.6}Ga_{0.4}As/Al_{0.2}Ga_{0.8}As$
- 5 nm
- No strain

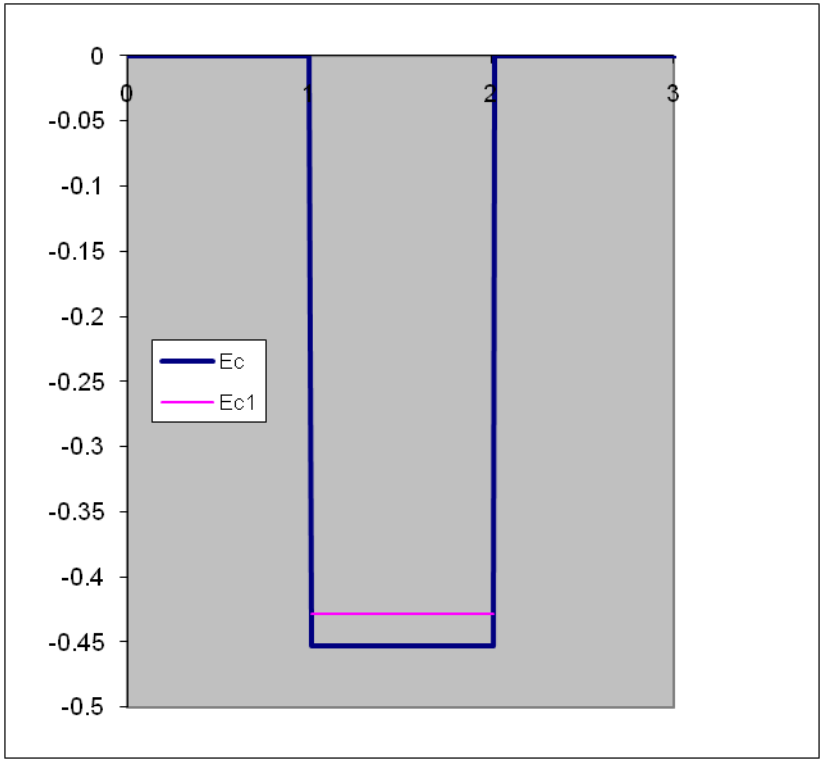


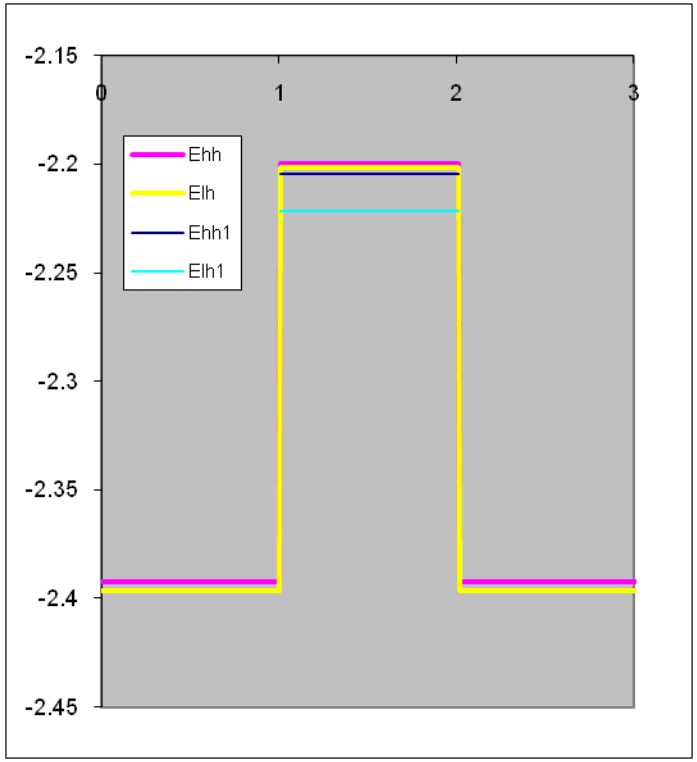


(higher barrier)

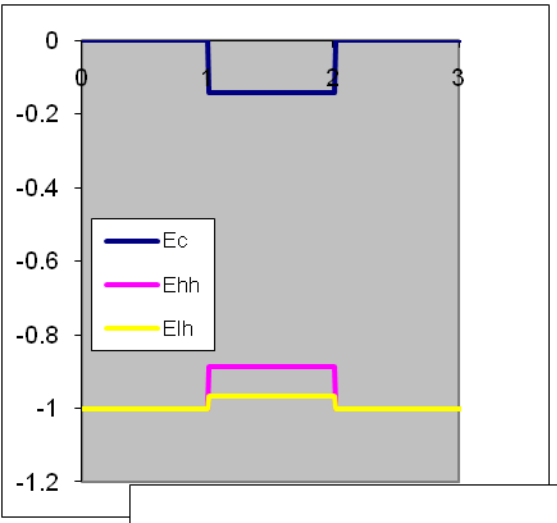


- $Al_{0.6}Ga_{0.4}As/Al_{0.2}Ga_{0.8}As$
- 5 nm
- No strain

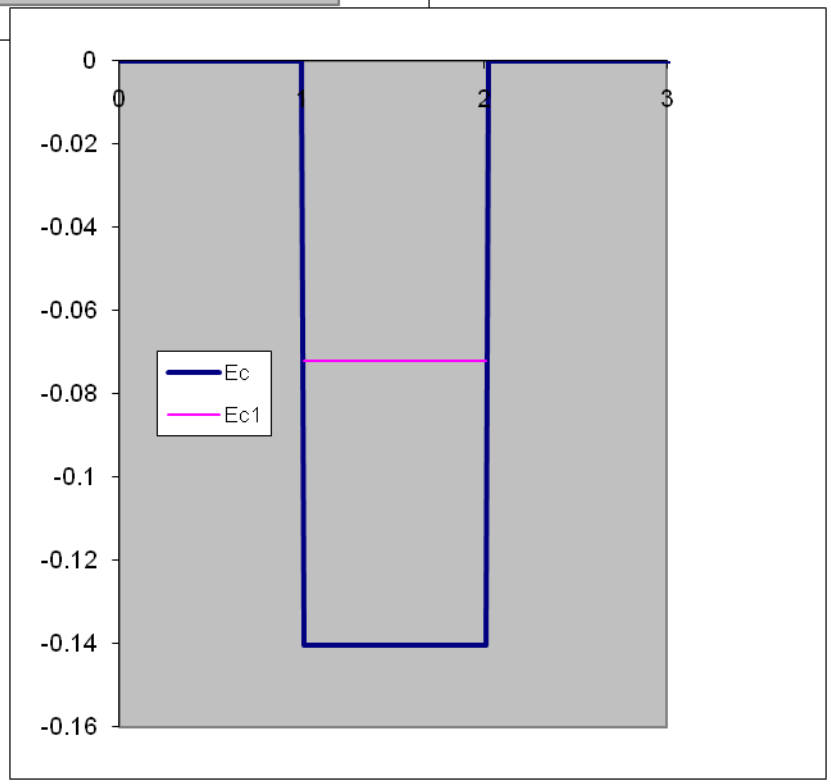


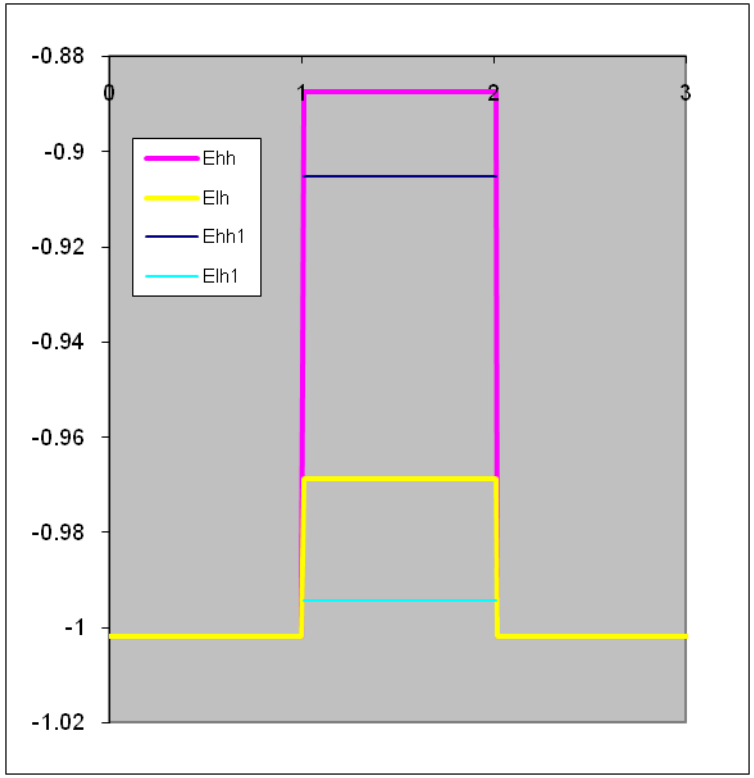


(Comp. Strain)

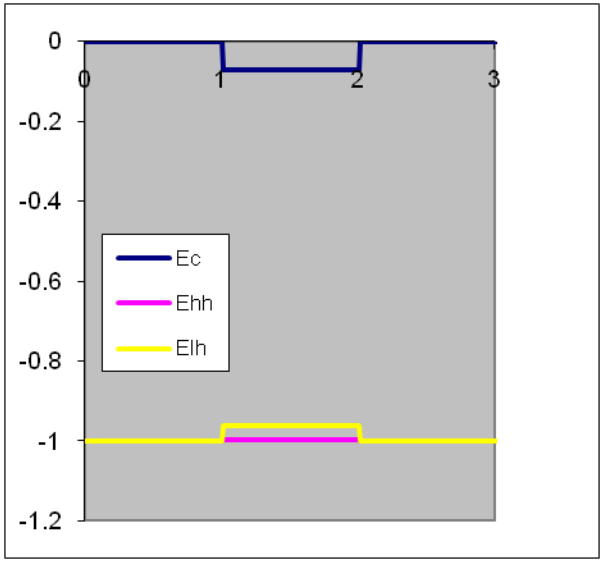


- $In_{0.43}Ga_{0.27}Al_{0.2}As/In_{0.7}Ga_{0.2}Al_{0.1}As$
- 5 nm
- Compressive Strain
- HH raises

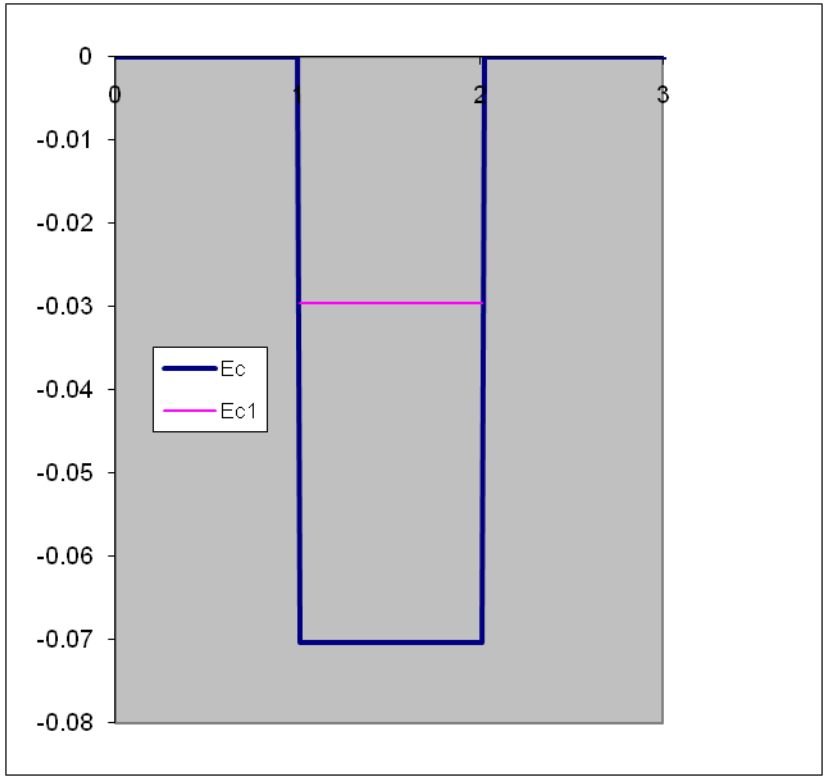


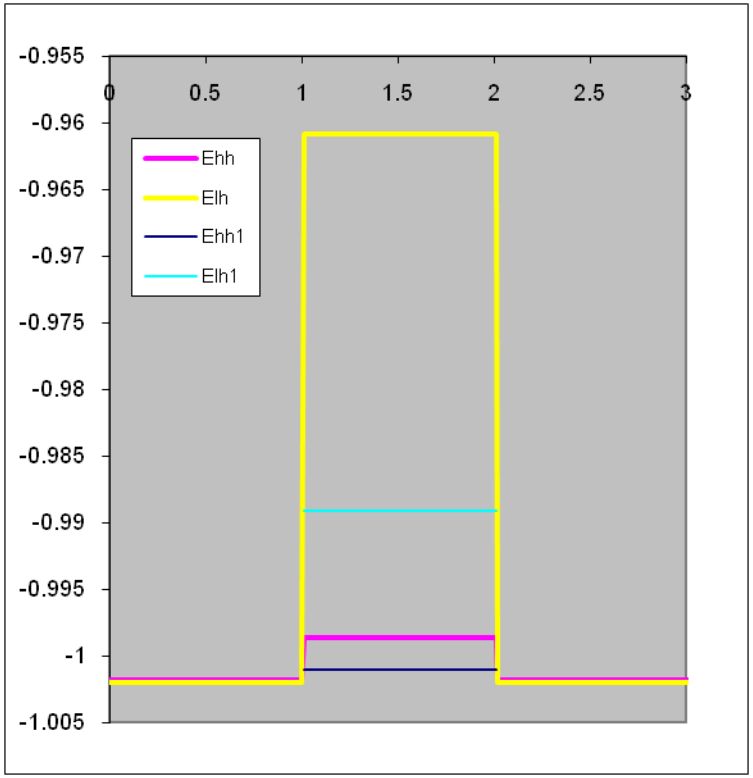


Tensile Strain



- $In_{0.43}Ga_{0.27}Al_{0.2}As/In_{0.45}Ga_{0.45}Al_{0.1}As$
- 5 nm
- Tensile strain
- LH raises





Summary

- Heterojunctions are fundamental for electronics and optoelectronics;
  - Control o carrier injection and distribution
  - Control of optoelectronic properties
  - Quantum confinement: use of geometry for the control of optoelectronic properties;
- III-V compounds allow a complete set of materials for bandgap-strain engineering;
  - Light sources with efficient carrier injection and light emission (direct bandgap)
  - Engineering of mobility;
  - Material properties obtained by interpolation
  - InGaAsP or InGaAlAs /InP TELECOM
  - Nitrides: illumination – blue ray
- III-V are obtained by crystal growth (MBE or MOCVD)
- Incompatibility to Silicon