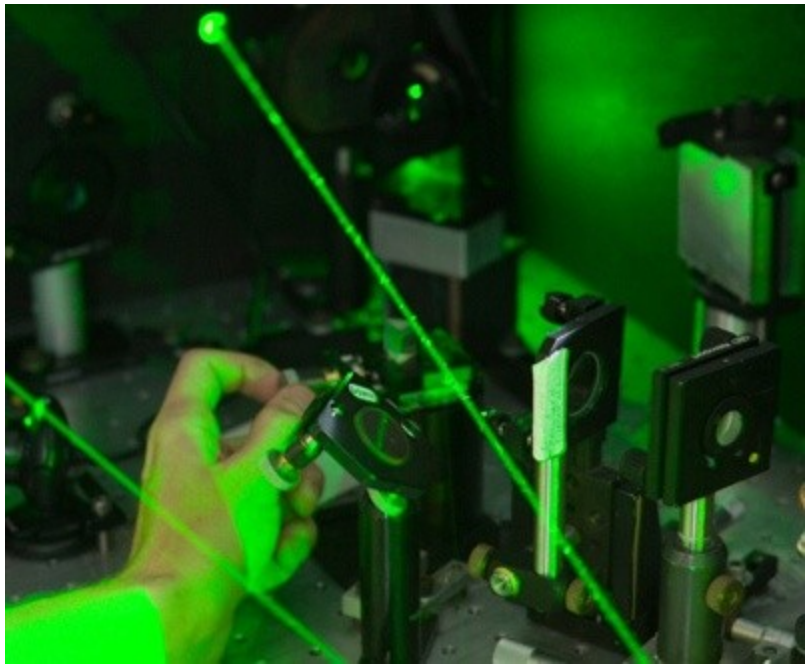

Spectroscopy of Quantum Dots

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Dec, 2010

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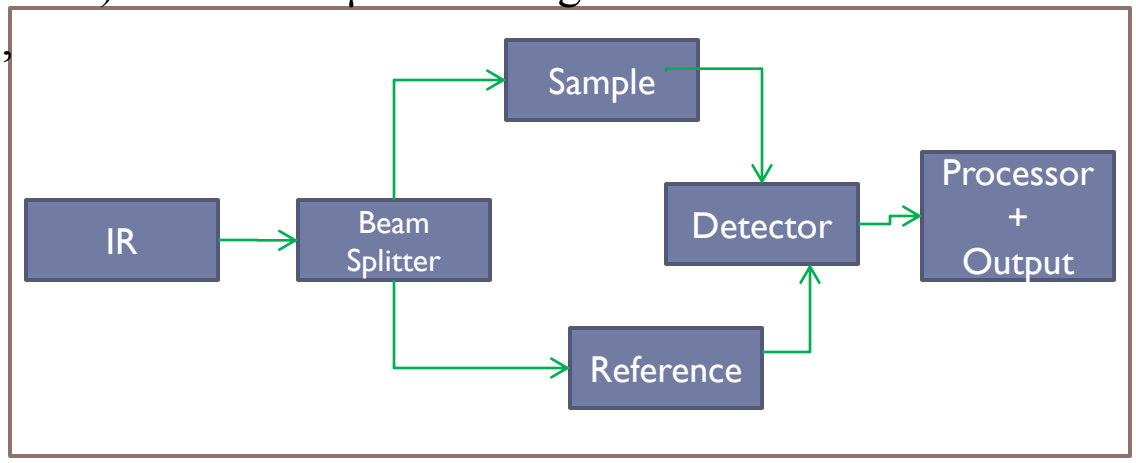
Frequency Resolution

- Spectroscopic analysis is carried out in either time (t) or frequency domain (f).
- Fourier transformation establishes the conversion of a function between time and frequency domain.
- Typical frequency resolution of spectra is performed in range of frequency (f) or different energy (E).
  - E (eV) = h × f, units eV or Joule

    where, h is Planck‘s constant and c = velociy of light in vacuum
  - Examples: Infrared (IR) spectroscopy, Photoluminescense spectroscopy, Ultraviolet (UV) spectroscopy, Raman spectroscopy e.t.c.

Infrared (IR) spectroscopy

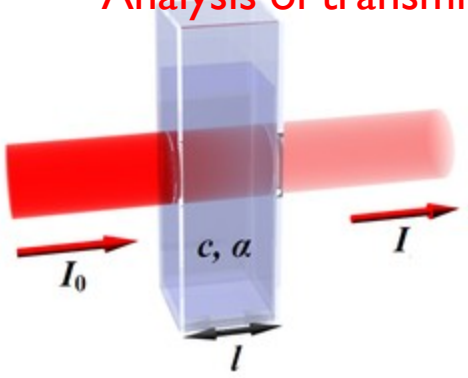
- Spectroscopy using Infrared radiation as source of radiation is an IR Spectroscopy.
- IR radiation varies from: NIR (Near infrared): 0.8 to 10 µm
  MIR (Middle infrared): 10-40 µm
  FIR (Far infrared): 40 to 1000µ wavelength
- Semiconductor lasers (MIR and NIR),
  Hot gas plasma (FIR),
  Blackbody radiation (NIR)
  are typical IR sources.



$$A_{gas} = -\ln\left(\frac{I}{I_o}\right) = -\ln(T) \quad \text{.....(1)}$$

Where,
T = Transmittance (at certain λ)
A_{gas} = Absorbance in gaseous phase
I_o = Intensity of incident light
I = Intensity of outgoing light

Analysis of transmittance or absorbance of a sample



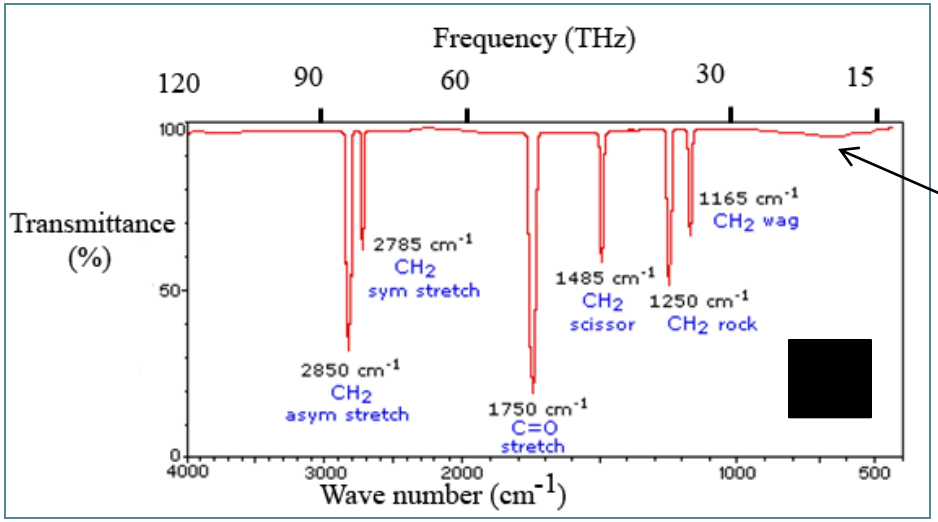
According to Beer-Lamberts law

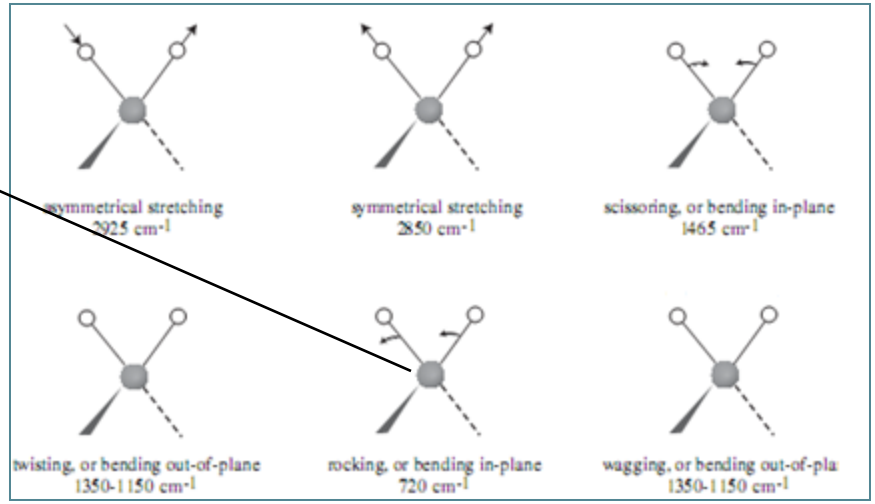
$$T = e^{-\alpha x}, \quad \text{.....(2)}$$

T = Transmittance (at certain λ)
α = attenuation coefficient
x or l = Path distance within sample

[1] http://en.wikipedia.org/wiki/Transmittance

IR spectroscopy of formaldehyde





Gas phase IR spectroscopy of Formaldehyde molecule $CH_2=O$

Mathematically predicted stretching and bending vibration mode For C-H_2 group.

[2]http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/InfraRed/infrared.htm#ir1

Only certain vibration modes are IR active, which induces change in the dipole moment of the molecule.

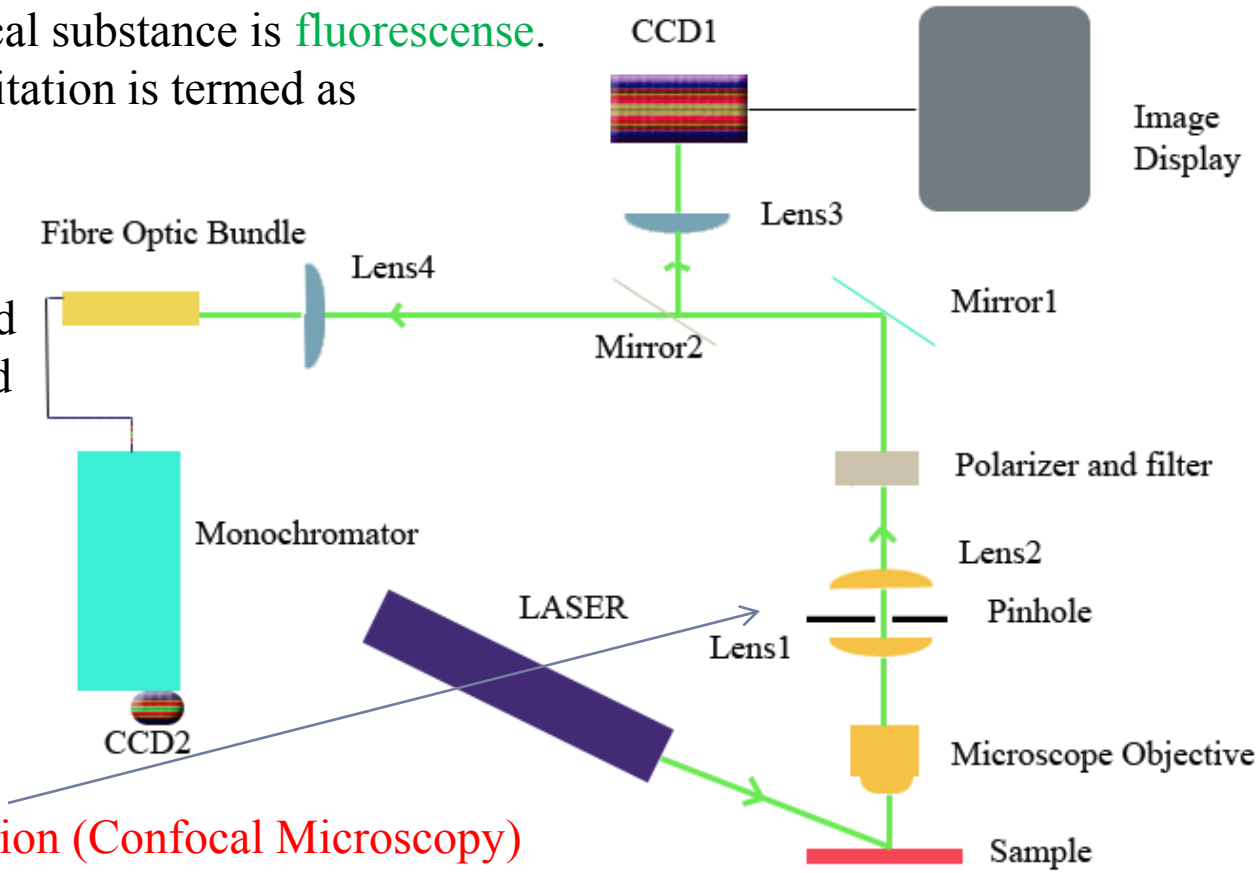
$$f = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad \text{.....(3)}$$

k = force constant, f is vibrating frequency and m is mass.
In accordance with Hook's law.

For molecule: $CH_2=O$
No. of atoms (n) =4
Degrees of Freedom (being nonlinear molecule)
= 3n-6 = 6
Hence, there exists 6 fundamental vibration modes.

Photolumniescense(PL) spectroscopy

- Photolumniescense involves excitation of a particle to higher energy state, and on returning to ground state system emits photon radiation.
- Similar process for chemical substance is fluorescense.
- Electric field induced excitation is termed as electroluminescense.
- In semiconductor, when electron are excited to conduction band, generated electron hole pair is termed as an exciton pair.
- LASER is typical source of excitation for PL.
- Photomultiplier or CCDs are the PL detectors.



Pinhole help us to access individual point of observation (Confocal Microscopy)

Sample and CCD (Charged Coupled Devices) sensors are placed in cryogenic environment.

Quantum Dots (QD) Spectroscopy- Introduction to QDs

- Quantum confinement effect for excitons.
- Discrete states (atomic behavior for excitons).
- Ultra narrow photoluminescence spectra is observed.
- Coloumbs blockade (discrete energy levels)

QD-Quantum confinement

Bohr radius of exciton is the physical representation of distance in the crystal when electron leaves the hole in the valence band and reach the conduction band.

$$E_{1s-1s} = E_{gap} + \frac{h^2(n_1^2 + n_2^2 + n_3^2)}{2m_e^* d^2} + \frac{h^2(n_1^2 + n_2^2 + n_3^2)}{2m_h^* d^2} - \frac{e^2}{8r\pi\varepsilon} \quad \text{.....(4)}$$

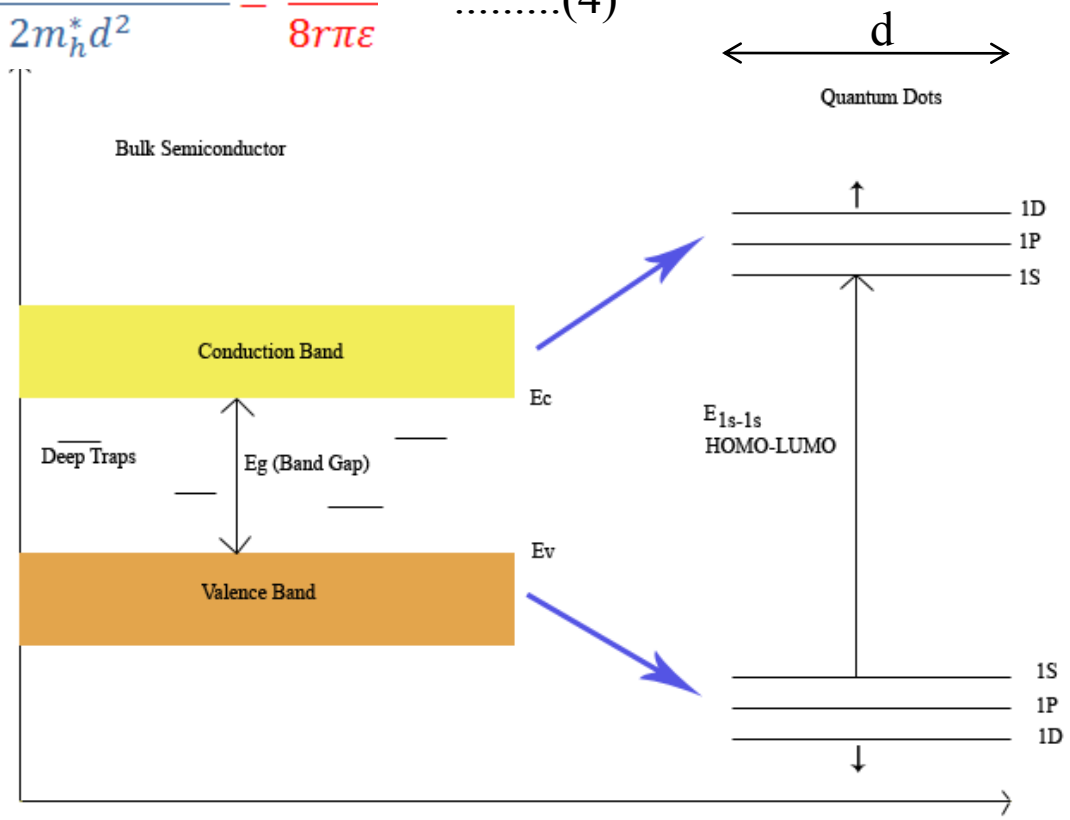
Where, h is Planck's constant, n is quantum number, m is corresponding reduced mass, ε is dielectric property and d is the size of the DOT, r is the separation distance between electrons and holes.

For radius < Bohr radius of exciton:

- Quantum confinement
- Kinetic energy dominates (Blue shift in energy)
- Coloumb contribution is diminished

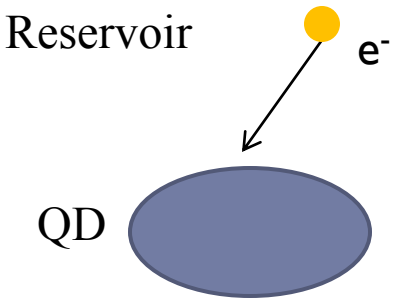
Bulk: Small band gap with distinct band edges (Ec and Ev).

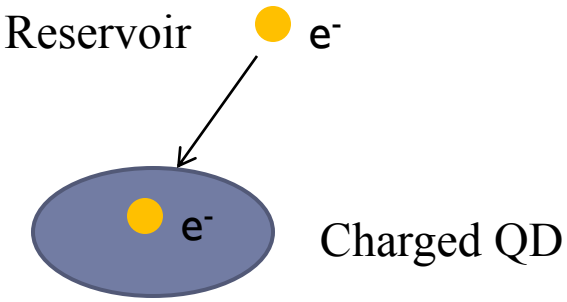
QD: Large band gap with distinct discrete exciton levels in CB and VB.



[3] Y. Masumoto, T. Takagahara, 'Semiconductor Quantum Dtos-Physics, Spectroscopy and Applications', Springer (2002)

Coloumbs Blockade in Charged QD





Very little work is to be done in transfering first electron to the QD.

To add additional electron into the charged QD we have to overcome the repulsive force between two electrons.

There, also exists corelation effect based on occupation of atomic orbital and electron spin in multielectronic QD.

Charging Energy (Ec) = $e^2/C >> K_B*T$ (25meV at 300K)

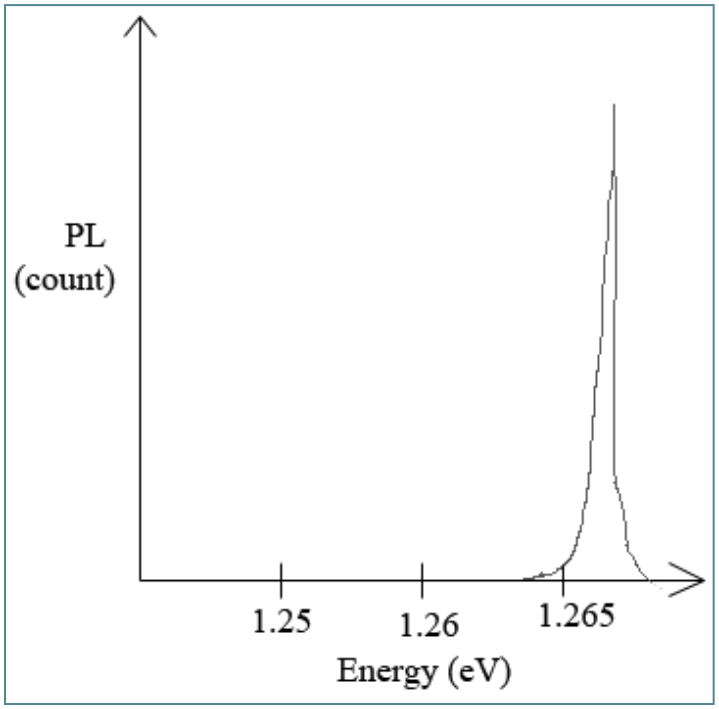
Where, e = $1.6 * 10^{-19}$ Coloumb,

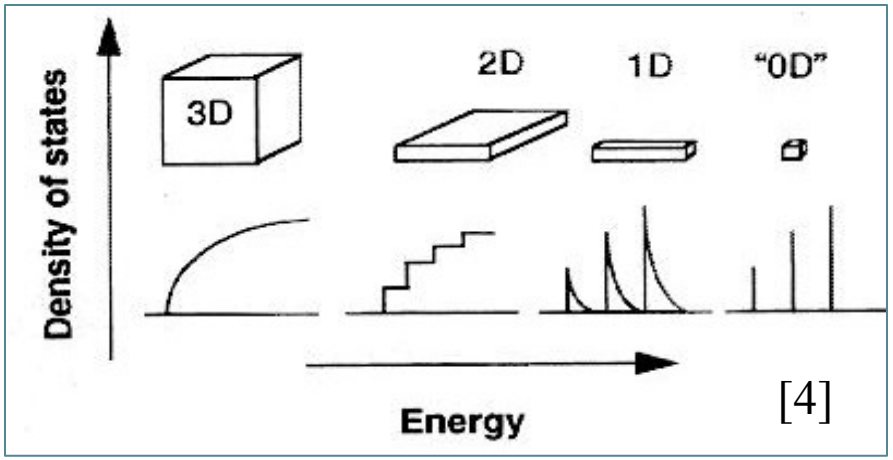
T = Absolute temperature,

K_B = Boltzman's Constant, and

C is the Capacitance between the dot and reservoir

Discrete Energy State in QD





$$DOS_{0D} = \sum_{E_n<E} \delta\,(E - E_n) \text{.....(5)}$$

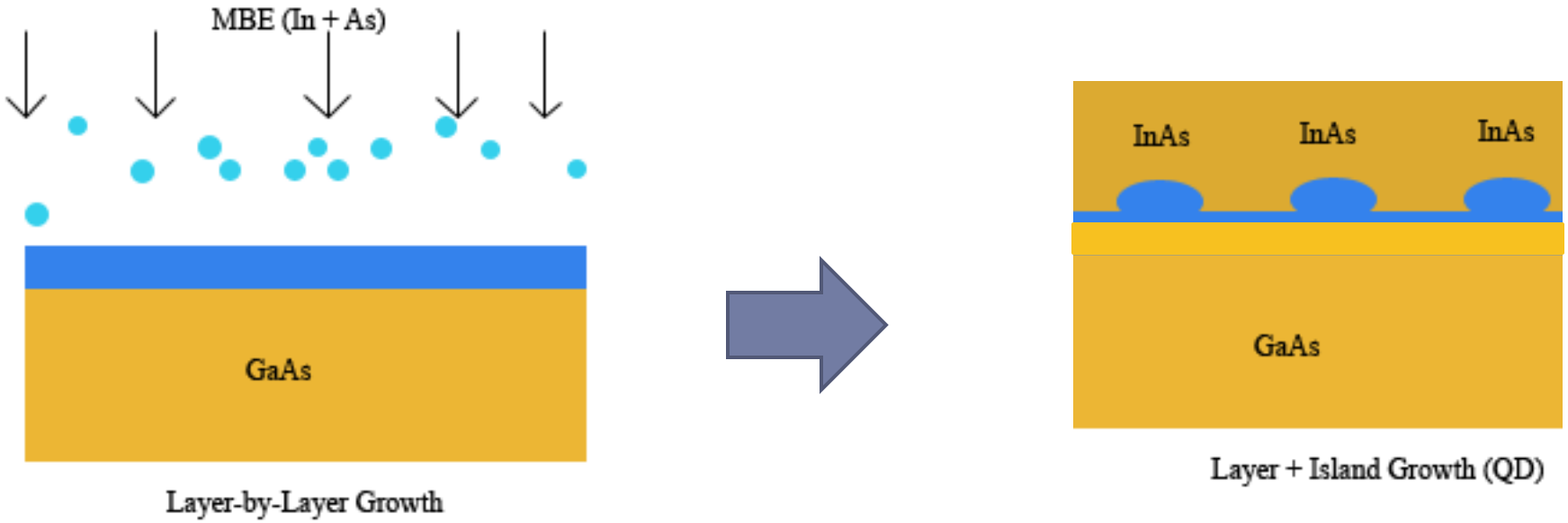
PL spectra of InAs QD in GaAs layer, pumped by laser diode (822nm, 1μW) at 4.3K with -0.76V gate potential.

Thus, Photolumnescense (PL) spectra of QD must exhibit a sharp line.

[4] R. J Warbuton, C. Schäflein, D. Haft, F. Bickel, A Lorke, Lett. Nat. Nano. (1999)

[5] S. Bandyopadhyay, H. Nalwa, 'Quantum Dots and Nanowire', ASP (2003)

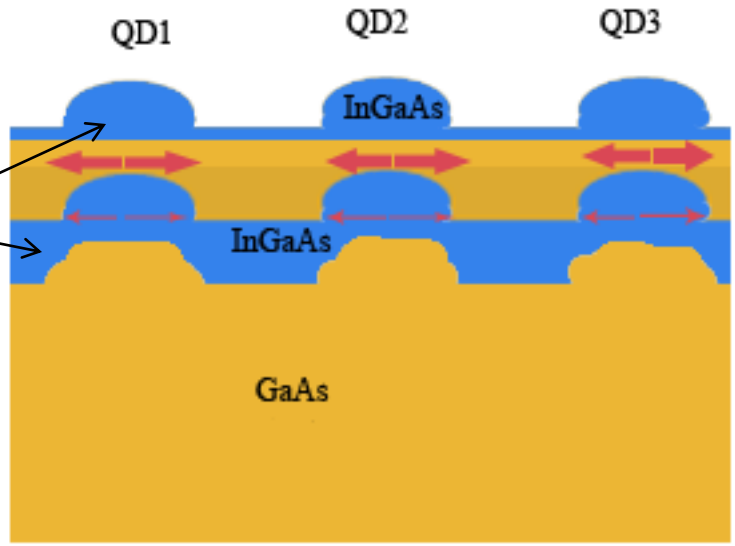
Nucleation and Growth of Island-QD formation (III-V Self assemble dots)



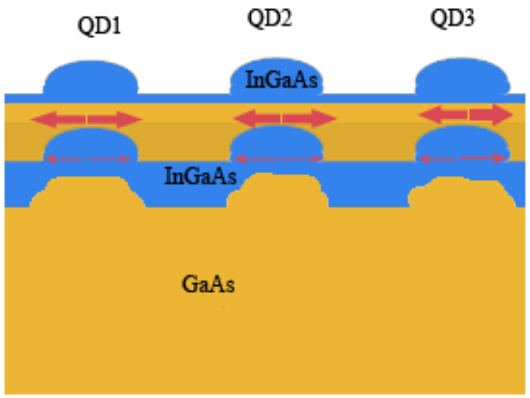
Molecular Beam Epitaxy (QD growth process)

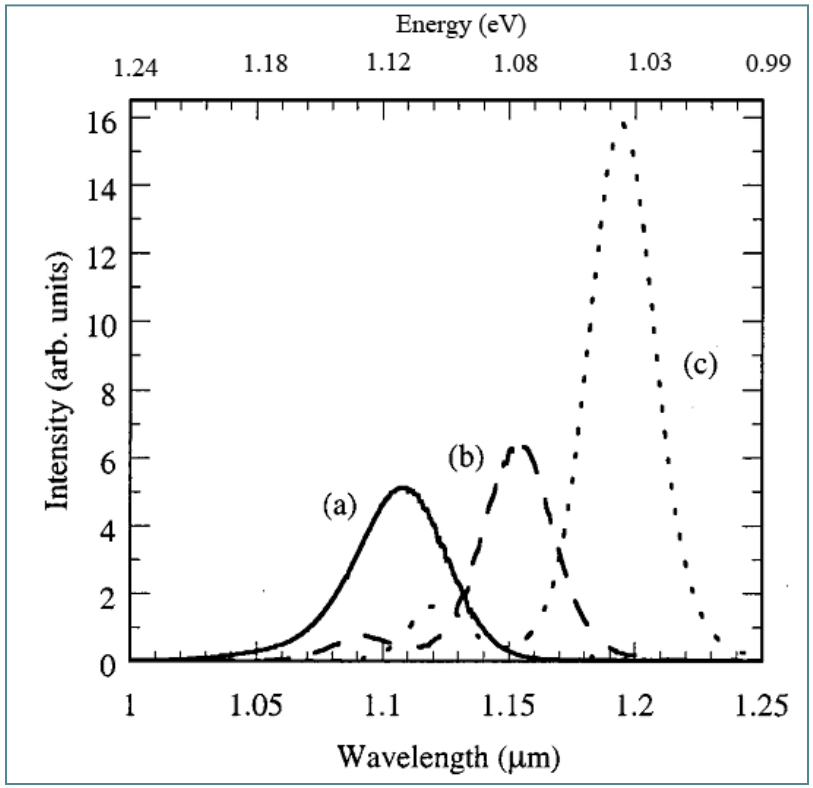
- A. Uncontrolled process
- Lattice mismatch between two heterostructure (GaAs and InAs) results in strain within the lattice.
- Lattice constant of GaAs = 5.65 A° and InAs = 6.0584A°, GaAs goes strained and InAs goes compressed.
- High diffusion length (no strain) result in Layer by Layer growth but low diffusion length (huge strain+ surface energy) results in Layer + Island Growth.
- Deposited QD size cannot be controlled.

- B. Controlled process
  - Applying a capping layer of InGaAs within the GaAs layer.
  - ➡ High Stress region
  - → Low stress region
  - Epitaxial growth of nucleated islands (wetting layer) occurs above the capping layer, above the region of high stress.
  - Is the controlled and widely applied Self assembled (SA) QD growth process.



Growth rate dependent spectroscopy of InAs/GaAs QDs





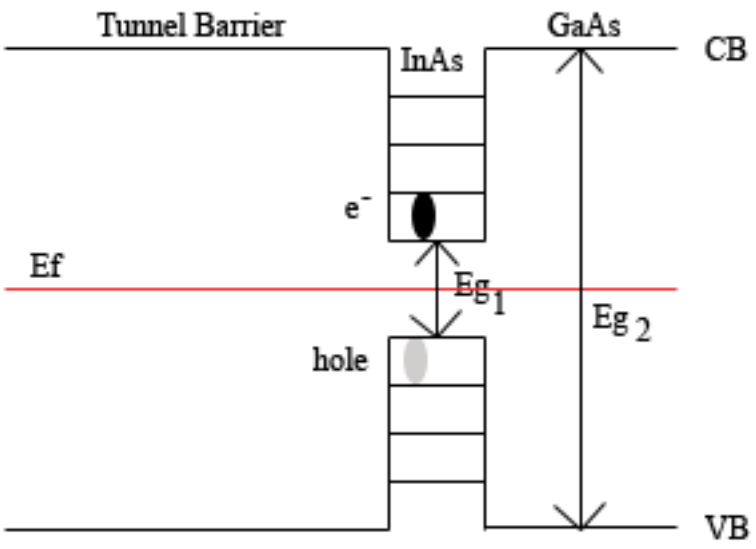
•Wetting layer (2.2ML at 10K) is varied from (a)0.55 (b)0.016 (c)0.0065 ML/s monolayer/sec) and Capping layer is deposited for 2.7ML at 490°C.

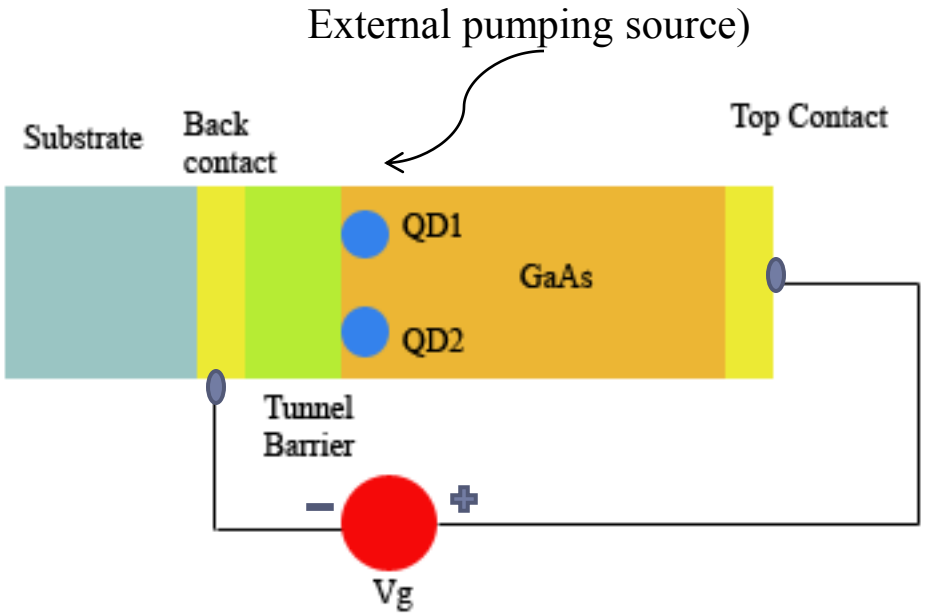
[6] P Joyce, T. Krzyzewski, G. R. Bell, T. S. Jone, Phy. Rev. Lett. B 62(10891)

Results:

- Reduced growth rate reduces the quantum dot density and increase in volume of dot. In accordance with equation (4), larger is the dot, there is shift in the emission peak towards red. (Emission of (a) is at higher energy than (c)).
- Increase in intensity is due to higher percentage of In for slowly deposited QD (c).
- Narrow intensity line of slow deposited QD(c) is result of uniformly deposited QD.

Electronic Property of QDs (InAs/GaAs)





QD Structure-band diagram (Eg_1=1.348eV, Eg_2=0.38eV), CB is conduction band and VB is valence Band, Ef is fermi energy level, for undoped semiconductor.

Optical property of charged QD. InAs QD fabricated in GaAs with 25nm tunneling barrier. Experiment was carried Using laser diode at1μW pumping power emitting at 822nm wavelength at 4.2K

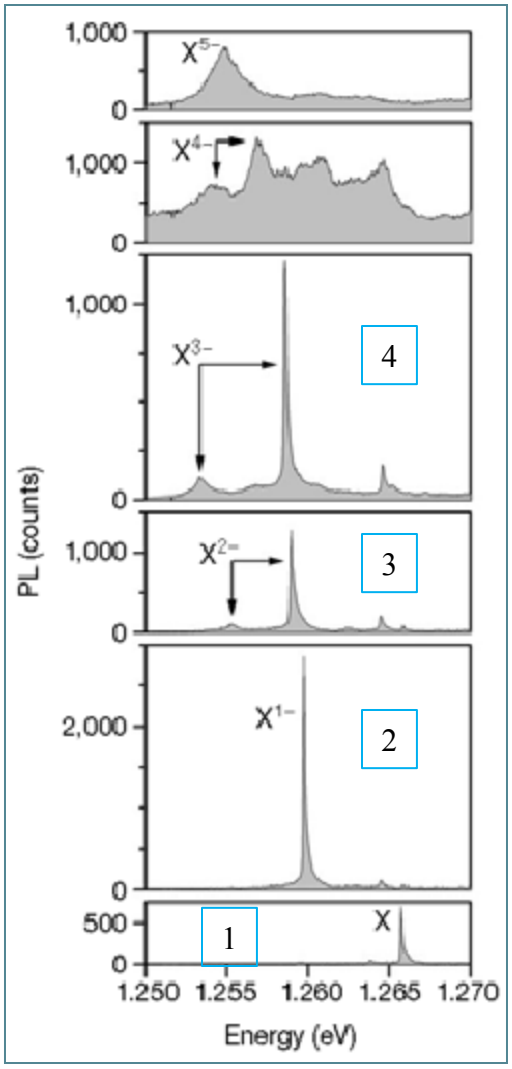
[4] R. J Warbuton, C. Schäflein, D. Haft, F. Bickel, A Lorke, Lett. Nat. Nano. (1999)

By changing the gate voltage, we can shift the fermi level of semiconductor, and control the number of exciton pair within the dot.

Charged and Neutral QD Spectra

1. X- Ground State electron-hole pair (exiton) recombination (Vg=-0.76V)
2. X^{1-}-Single electron in the dot
   Is the singlet state (Vg=-0.16V)-Binding energy of exciton
3. X^{2-} Two electrons in the quantum dots (Vg=-0.1V)
   Small satellite peak at higher energy appears addition to main peak.
   Indicates: Two possible final states (singlet or triple state).
   X^{3-} is similar to X^{2-} only intenstiy of satellite and main peak is higher.
4. X^{4-} - PL becomes very broad (0.4V)

- Red shift in the charging energy (1 to 2 e-). (addition of electron incresaes the dot capacitance)
- Charging energy while completely filling an orbital is large (Step 3).



Spectroscopy of charged QD

[4] R. J Warbuton, C. Schäflein, D. Haft, F. Bickel, A Lorke, Lett. Nat. Nano. (1999)

Applications

- QD lasers,
- Single photon source from QD
- Single spin storage
- Manipulation of single electron spin (quantum infomation) for storage and processing e.t.c.

Conclusion

- Frequency resolved spectroscopy is versatile method of spectroscopic analytic method.
- Vibration modes of organic molecule can be observed in frequency resolved IR spectra.
- Many fundamental property Quantum dots can be studied using this method.
- QD bridges between the bulk and the molecular system.