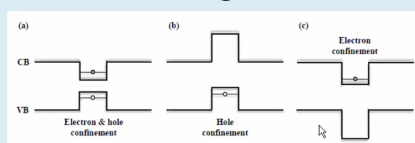


Outline

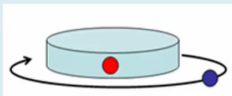
- Type-II Band Alignment (e.g. Quantum Dots)
 - General Expectation for PL behavior
- II-VI Type-II Stacked QDs grown by MBE-MEE
 - Growth, Model Structure, and Optical Properties
- Examples of Fundamental Studies
 - g -factors, spin lifetime, and optical anisotropy
 - Excitonic Aharonov-Bohm Effect (EABE) in Zn(Mg)Te/ZnSe QDs
 - Quantum Decoherence
- Type-II QDs for Intermediate Band Solar Cells
- Summary

3

Band Alignment

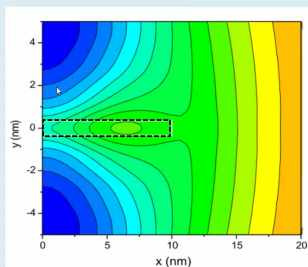


- **Type I:** Smaller band-gap material is a potential well for both types of carriers
- **Type II:** Each material is a potential well for one carrier, but a barrier for the other
 - Charge carriers are spatially separated in real space, *but* direct in k -space for direct bandgap materials
 - A [strong] blue shift of photoluminescence with increasing excitation
 - [Relatively] long radiative recombination lifetime
 - Small electron-hole (exciton) binding energies



4

“Ideal” Type-II Cylindrical Quantum Dots



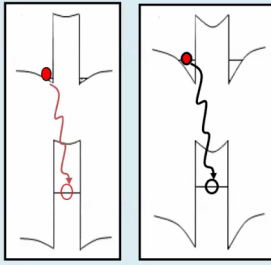
► Blue = Highest Electron Density

- One type of carriers is confined within the QD whereas the other is attracted via the Coulomb interaction, creating **spatially indirect (type-II) exciton**
- In other words: **Electric Dipole is formed**
- In ideal type-II QDs the ‘barrier’ carrier would locate **above-below the QD**

5

Photoluminescence

Weak Excitation Strong Excitation

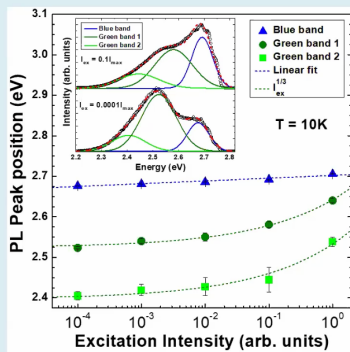


$h\nu_{weak} < h\nu_{strong}$

- **cw PL**
 - Emission energy, $h\nu$, shifts to higher values with increasing excitation
 - Often follows cubic root law, $h\nu \propto I_{ex}^{1/3}$
- **Time-resolved PL**
 - Long-lived due to weak overlap of the carriers' wave functions
 - Dependent on I_{ex} , for overlap of the wave functions depends on the concentration of photo-generated carriers

7

Type-II Quantum Dots: CL PL



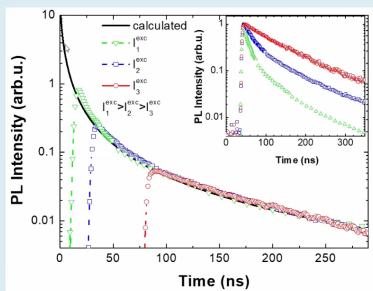
- **cw PL**
 - Emission energy shifts to higher values with increasing excitation

Roy et al., Eur. Phys. J. B, **86**, 31 (2013)

Shuvayev et al., PRB **79**, 115307 (2009)

8

Type-II Quantum Dots: TRPL

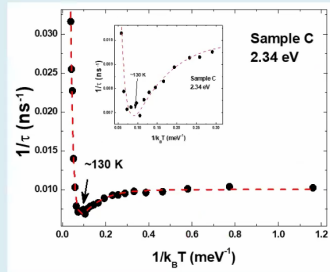


- **Time-resolved PL**
 - Long-lived due to weak overlap of the carriers' wave functions
 - Dependent on I_{ex} , for overlap of the wave functions depends on the concentration of photo-generated carriers

Shuvayev et al., PRB **79**, 115307 (2009)

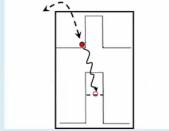
9

Excitonic Lifetimes and Binding Energies from Temperature Dependent TRPL



$$\frac{1}{\tau} = \frac{1}{\tau_{r0}} [1 - C \exp(-\varepsilon_b / k_B T)] + \frac{1}{\tau_{nr0}} \exp(-\varepsilon_a / k_B T)$$

Ionization/Re-capture



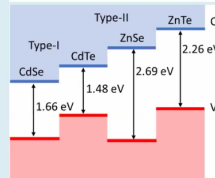
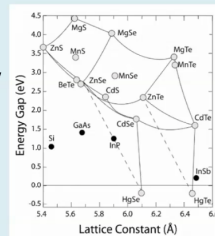
Sample	Photon Energy (eV)	Exciton Binding Energy (meV)	τ_{r0} (ns)	Nonradiative Activation Energy (meV)	τ_{nr0} (ns)
A	2.48	6.20	64.7	90.7	0.10
B	2.48	7.34	91.9	103.0	0.15
	2.36	7.44	93.1	111.1	0.18
C	2.34	11.30	99.9	83.1	1.37

Ji et al., J. Electr. Mat. **42**, 3297 (2013)

10

Type-II II-VI Wide Bandgap Semiconductors

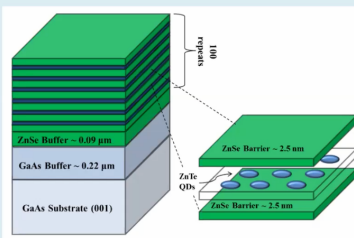
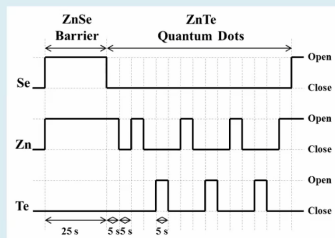
- ZnSe has 0.27% lattice mismatch with GaAs, ZnTe has almost 7%
 - Still very difficult to grown ZnTe QDs by Stranski-Krastanow method
- ZnCdSe can be lattice matched to InP, and has a band gap of ~ 2.1 eV
- Zn(Cd)Te-ZnCdSe VBO is ~1.0 eV, so an IB at ~0.7 eV can be engineered from the hole confinement within Zn(Cd)Te QDs
- Up to 300 layers of sub-monolayer QDs can be grown via MBE-MEE without a wetting layer
- Direct doping is achieved over many layers



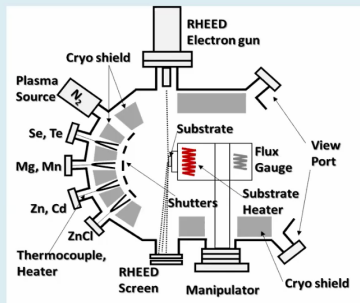
Deligiannakis et al, J. Crystal Growth, **512**, 203-207 (2019);
 Dhomkar et al, Sol. Energy Mater. Sol. Cells **117**, 604 (2013); J. Vac. Sci. Technol. B **31**, 03C119 (2013); Appl. Phys. Lett. **103**, 181905 (2013);
 Kuskovskiy et al., PRB **73**, 195306 (2006);

11

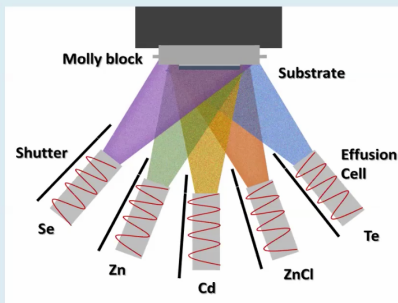
Example of Growth of Type-II QDs by Migration Enhanced Epitaxy



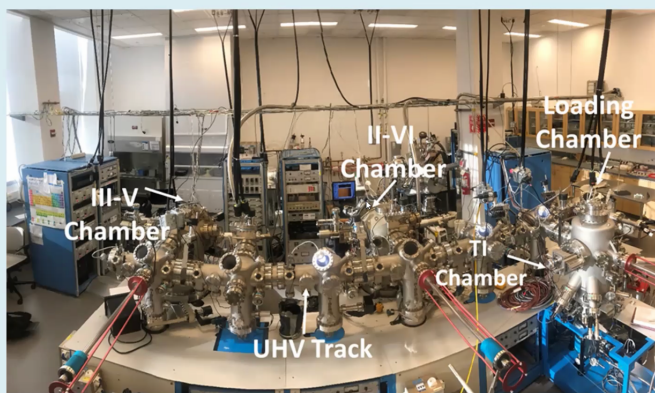
12



(a) Schematic of II-VI MBE system

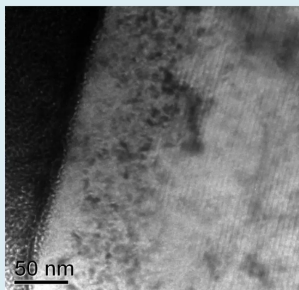


(b) Schematic diagram of MBE process.



Picture of the Riber 2300PMBE system in Tamargo's lab

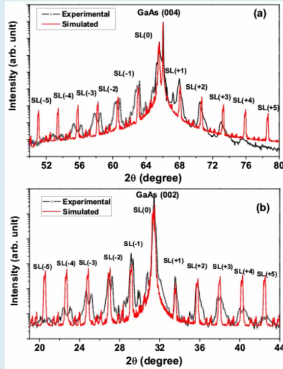
Example of Structural Studies: ZnMgTe/ZnSe



TEM, showing periodic structure – presence of Mg made contrast clear

Manna et al, JAP **111**, 033516 (2012)

Example of Structural Studies: ZnMgTe/ZnSe



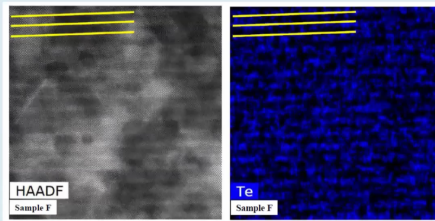
- XRD Showed superlattice peaks up to 5th order
 - Addition of Mg in the QD layers contributed to the much higher scattering intensity of the superlattice
- XRD simulations showed
 - that only a minimal amount of Te (< 1%) is inside the spacer
 - that there are ~ 32% of Mg inside the ZnMgTe QDs

Manna et al, JAP **111**, 033516 (2012)

15

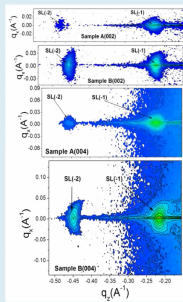
Example ZnTe/ZnSe Samples

TEM Chemical Analysis



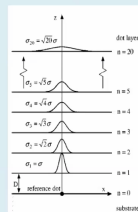
16

Samples Structure: Vertical correlated QDs (ZnCdTe/ZnCdSe)



- A Gaussian distribution of horizontal deviations from the underlying reference dot is assumed
- Standard deviation, ' σ ', captures the average vertical dot alignment and can be derived from half width half maxima (HWHM) along q_z

$$q_z^{HWHM} = \frac{\sigma^2}{D} q_x^2 + \frac{\mu}{D}$$



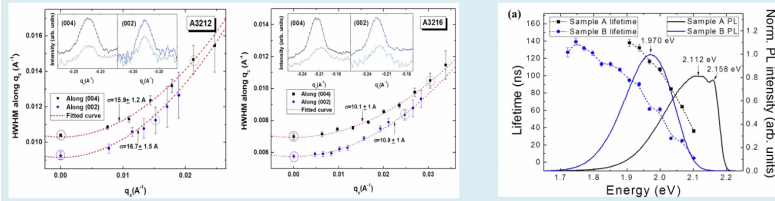
Dhondkar S. et al., *Appl. Phys. Lett.* **103**, 181905 (2013)

based on models and ideas of

Darhuber, A. A. et al., *Phys. Rev. B* **55**, 15652-15663 (1997); Kegel, I et al., *Phys. Rev. B* **60**, 2516 (1999)

18

Samples Structure: Vertical correlated QDs (ZnCdTe/ZnCdSe)



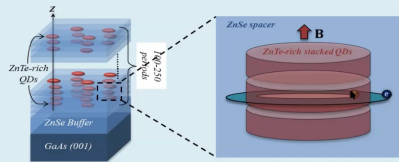
- Larger QDs exhibits ~ 85-93% of vertical correlation
- Smaller QDs show ~ 75-85% of vertical correlation

Dhomkar S. et al., *Appl. Phys. Lett.* **103**, 181905 (2013)

19

Samples: Model

- **Quantum Dots Form Stacks**
 - The electron moves around a whole stack, “averaging” out QDs size variations, so its orbit is larger than structural radius of QD
 - Electron and hole are ‘tightly’ bound, so the excitonic size is smaller than the QD radius, and move as a whole*

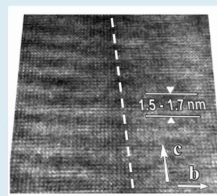


*Ji, et al., *J. Appl. Phys.*, **116**, 164308 (2014)

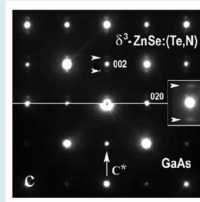
24

Samples Structure: Vertical correlated QDs

TEM Chemical Analysis

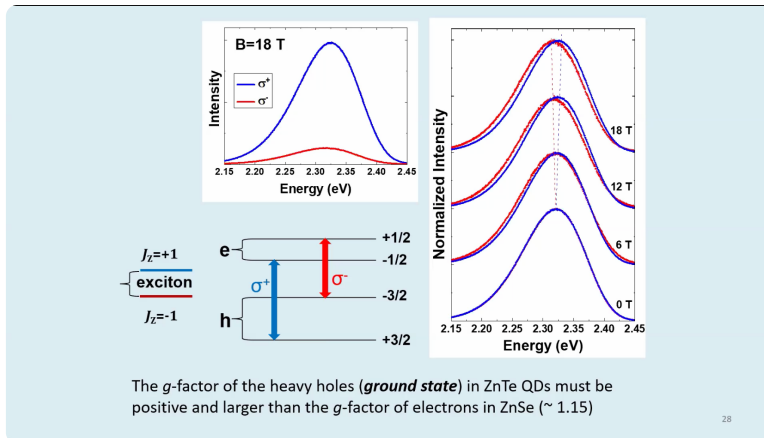


E-beam Diffraction



Kuskovskiy et al., *PRB* **73**, 195306 (2006)

25



[Heavy] Hole g -factor

- Find that [heavy] hole g -factor

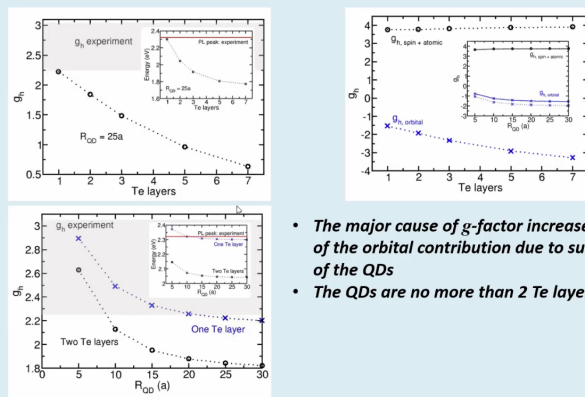
$$g_X = g_{hh} - g_e \approx 1.65 \pm 0.3$$

$$g_e \approx 1.1 \pm 0.1 \Rightarrow g_{hh} \approx 2.75 \pm 0.4$$

- This value is much larger than the g -factor of bulk ZnTe heavy holes, 0.85

*[Phys. Rev. B **45**, 3922(R) (1992)]; [Z. Phys. B **50**, 193 (1983)]

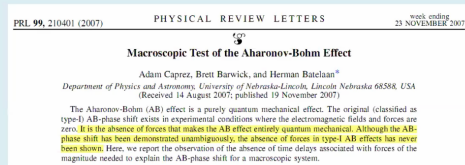
Calculations



* Tight Binding calculations by Garnett Bryant (NIST); See Ji et al., JAP, **124**, 144306 (2018)

Aharonov-Bohm Effect

- **Classical electrodynamics:** the vector potential, $\mathbf{A}$, is considered a mathematically convenient for calculations, but having no direct physical meaning
- **Quantum mechanics:** the potential(s) play a more significant role, for the Hamiltonian is expressed in terms of Φ and $\mathbf{A}$, not $\mathbf{E}$ and $\mathbf{B}$:
 - Nevertheless, it was taken for granted that there could be no electromagnetic influences in regions where $\mathbf{E}$ and $\mathbf{B}$ are zero
- **In 1959 Aharonov and Bohm showed that the vector potential can affect the quantum behavior of a charged particle even in regions where electromagnetic field is zero**



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Excitonic-AB Effect in Magneto-PL

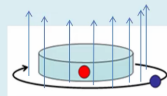
- **The Excitonic ["Optical"] AB Effect refers to observation of the effects of the AB phase in the optical emission of polarized excitons ["dipoles"]**
 - **Quantum Rings and Type-II Quantum Dots**
- As the flux increases, $|L|$ changes from 0 to 1, 2, ...
- Two important outcomes:
 - **Energy Oscillation(s)** ("known")
 - **PL Intensity Oscillation(s)** - due to selection rules
 - Multiple Oscillation in strong confinement or weak coupling
 - A single 'peak' in strong coupling regime

$$E_{\text{exc}} = E_{\text{exc}0} + \frac{\hbar^2}{2MR_0^2} \left(L + \frac{\Delta\Phi}{\Phi_0} \right)^2$$

$$\Delta\Phi = 2\pi(R_e - R_h)R_0B$$

$$L = l_e + l_h \quad R_0 = (R_e + R_h)/2$$

$$M = \frac{(m_e R_e^2 + m_h R_h^2)}{R_0^2}$$

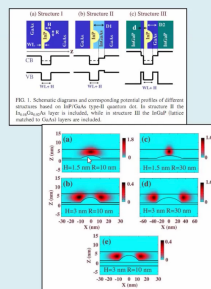


e.g., Kalameitsev, et al., JETP Lett. **68**, 669 (1998); Govorov, et al., PRB **66**, 081309 (2002); Janssens, et al., PRB **67**, 235325 (2003)

42

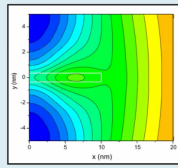
Single Type-II QD: Strain

- The AB effect was observed in InP/GaAs QDs (Ribeiro, et al., PRL, **92**, 126402 (2004))
- However, no oscillations were observed by de Godoy, et al., in the same system (PRB **73**, 033309 (2006))
- Madureira, et al., APL **90**, 212105 (2007) showed that the ability to observe it depends on the growth conditions and specifics of the system



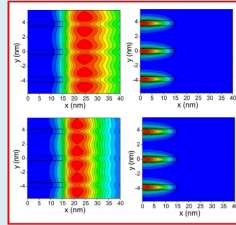
44

Stacked QDs or Single Dot?



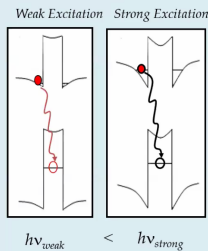
- **Blue** = Highest Electron Density
- **No AB Effect**

Magnetic Field ↑



- **Red** = Highest Electron Density (0 Tesla (upper) and 6 Tesla (lower))
- Well defined cylindrical symmetry along the magnetic field
- There is AB effect

Photoluminescence



- **cw PL**
 - Emission energy, $h\nu$, shifts to higher values with increasing excitation
 - Often follows cubic root law, $h\nu \propto I_{ex}^{1/3}$
- **Time-resolved PL**
 - Long-lived due to weak overlap of the carriers' wave functions
 - Dependent on I_{ex} , for overlap of the wave functions depends on the concentration of photo-generated carriers

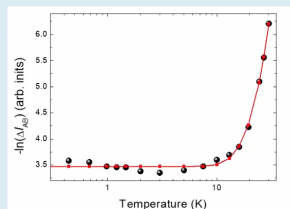
Exciton Decoherence Model

Following Bori, et al., PRB **71**, 115328 (2005)

- Exciton dephasing is fitted with two activation energies ('Independent Boson Model')
 - One such energy corresponds to LO phonon
- Two exponentials give activation energies of order of 2 and 7 meV
- Single exponent fits as well with ~ 6 meV.
 - $\hbar\Omega_{LO} = 25$ and 31 meV for ZnTe and ZnSe, respectively

$$\Delta I_{AB} \propto \exp[-\gamma(T)t_0]$$

$$\gamma = \gamma_0 + \alpha T + b_1 \frac{1}{e^{E_1/k_B T} - 1} + b_2 \frac{1}{e^{E_2/k_B T} - 1}$$



Hybrid Model of Decoherence

- ✓ Only electrons are scattered (as being in the barriers)
- ✓ Scattering is similar to that of transport electrons
 - $\gamma \sim T$ for e-e interaction
 - $\gamma \sim T^3$ for e-ph (acoustic) interaction*
- ✓ Matrix element of scattering is smaller than in transport because of electron-hole coupling, resulting in persistence of quantum coherence to unusually high temperatures**

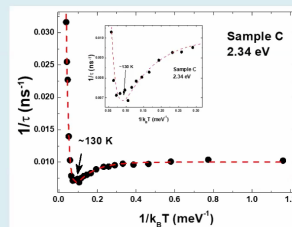
*M. Y. Reizer, Phys. Rev. B **40**, 5411 (1989)

** P. C. Kwok, Phys. Rev. **149**, 666 (1966) has predicted similar effect for donor bound electrons

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Hybrid Model of Decoherence

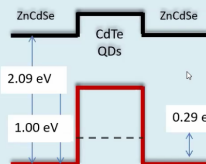
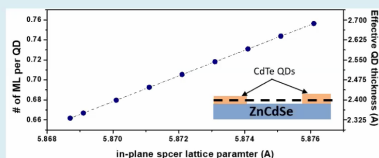
- Results of Fitting:
 - $t_0\beta \sim 9.2 \times 10^{-5} \text{ K}^{-3}$
 - $t_0\alpha \sim 0.04 \text{ K}^{-1}$
- To extract the actual value we assume that 'travel' time, t_0 , equals radiative lifetime, which is **~100 ns**
- Thus: $\beta \sim 10^{-6} \text{ ns}^{-1} \text{ K}^{-3}$
- This is much smaller than estimated for ZnSe, using $\beta = \lambda_{e-ph} \frac{k_B}{\hbar \Theta_D^{**}}$
- $\beta_{\text{ZnSe}} \sim 10^{-3} \div 10^{-4} \text{ ns}^{-1} \text{ K}^{-3}$



M. Y. Reizer, Phys. Rev. B **40, 5411 (1989)

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Results of HRXRD CdTe/ZnCdSe/InP QDs



- **Spacer:**
 - Cd composition is ~ 51%
 - Bandgap is ~2.1 eV due to strain
- **Quantum Dots:**
 - Sub-monolayer coverage:
 - average QD layer thickness ~ 0.27 nm
 - QD are partially relaxed
 - The bandgap is ~1.38 eV
 - VBO = 1.00 eV; CBO = 0.30 eV
 - Energy for IB = 0.29 eV

- **Still need to make dots thicker ...**
 - Further shorten off-time in the whole cycle
 - Increase number of cycles