Multiple Exciton Generation in Quantum Dots

James Rogers
Materials 265
Professor Ram Seshadri
Exciton Generation

Single Exciton Generation in Bulk Semiconductors

Multiple Exciton Generation in Bulk Semiconductors

\[ E_g < E_{hv} < 2E_g \]

\[ E_{hv} > 2E_g \]
Singe exciton efficiency limits

- Record Laboratory efficiency for crystalline silicon under solar irradiation: 24.7%
- Thermodynamic limit for one photon-one exciton generation under solar irradiation: 33%
- Amount of incident energy lost as heat: 47%
Multiple exciton efficiency limits

- Theoretical efficiency if carriers are extracted prior to cooling: 67%

- For $E_{hv} > 2 \cdot E_g$ we consider three possibilities
  - 1 $e^-h^+$ pair per photon
  - 2 $e^-h^+$ pairs per photon
  - $M$ $e^-h^+$ pairs per photon

- Theoretical efficiency achieved through MEG: 43%
How does MEG occur?

• Impact ionization
  – Consider the familiar auger recombination process:
    - Auger electron
    - Scattered high energy e^-
    - Secondary e^-
  – Consider the inverse of this process:
    - High energy carrier
MEG is an unlikely process

• Competing processes
  – Inelastic carrier-carrier scattering \((10^{13} \text{ sec}^{-1})\)
    • Dependent on carrier concentration
  – Phonon scattering \((10^{12} \text{ sec}^{-1})\)
    • Independent of carrier concentration
  – Auger recombination
  – Exciton-exciton annihilation \((10-100 \text{ ps})\)
    • Exciton concentration dependent

*Impact ionization rates in bulk semiconductors surpass phonon scattering rates only when the electron kinetic energy exceeds \(~5\text{ ev}\).*
Effects of quantum confinement

Discretization of electronic structure

Change in bandgap energy

Importance of Surface States
Effect of particle size on band structure

Theoretical transitions for four PbSe QD sizes with experimental transitions superimposed.

Observable size effects on particle absorbance
MEG in semiconductor nanocrystals

- Tunable bandgap
- Phonon bottleneck
- Surface traps
Femtosecond (fs) transient absorption spectroscopy

Step 1:
- Expose particle to short pulse (~200 fs) with $E_{hv} > E_g$
- Measure absorbance

Step 2:
- Expose particle to short pulse (~1 ps) with $E_{hv} << E_g$
- Measure absorbance

Experimental observation of pulse and probe absorbance
Exciton generation vs. $E_g$

Exciton population decay dynamics obtained by probing intraband transitions

Quantum yield (QY) for exciton formation from a single photon vs. $E_{hv}$
Competing effects: Cooling rate vs. particle diameter

- Electron cooling rate increases as size decreases

- Exciton lifetime decreases as size decreases
State of current research
– Multiple exciton generation has been measured
– Carrier cooling rate has been slowed

Toward potential applications
– Must electronically couple NCs to their environment
– High collection efficiencies must be achieved
Schottky solar cells from NC films

- Simple device architecture (ITO/NC/Metal)
- High external quantum yields (EQE > 65%)
- Record short circuit currents ($J_{SC} > 21$ mA·cm$^{-2}$)
- Efficiency under solar illumination: 2.1%
Conclusion

• Semiconductor NCs are an inexpensive alternative to silicon devices which have the potential to achieve EQEs greater than 100%
• Particle size and composition precisely determine both MEG rate and cooling rate
• Practical application of this technology will require better electronic coupling and more efficient charge capture
References


