Engineering Nanostructured Cadmium Sulfide Charge Transfer Thin Films

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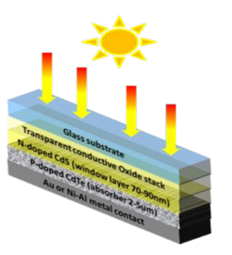
Introduction and Motivation

Cadmium Sulfide: A Versatile Semiconductor



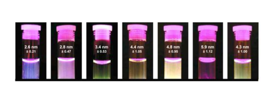
Cadmium sulfide (CdS)

n-type Semiconductor
Band gap: E_g = 2.4-2.5 eV
(absorbs UV to ~500nm)

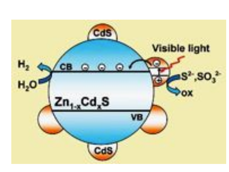
Crystallographic polymorphs:

- Hexagonal (a = 0.413 nm, c = 0.671 nm)
- Cubic (a = 0.583 nm)

Applications:



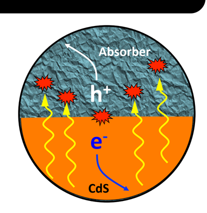
- Fluorescent Probes
- Photoresistors
- Pigments (Van Gogh, Monet, Matisse)
- Photocatalyst
- **Photovoltaics**
  - $Cu(In,Ga)Se_2$ (CIGS, >20%
  - InP
  - CdTe (>17%)

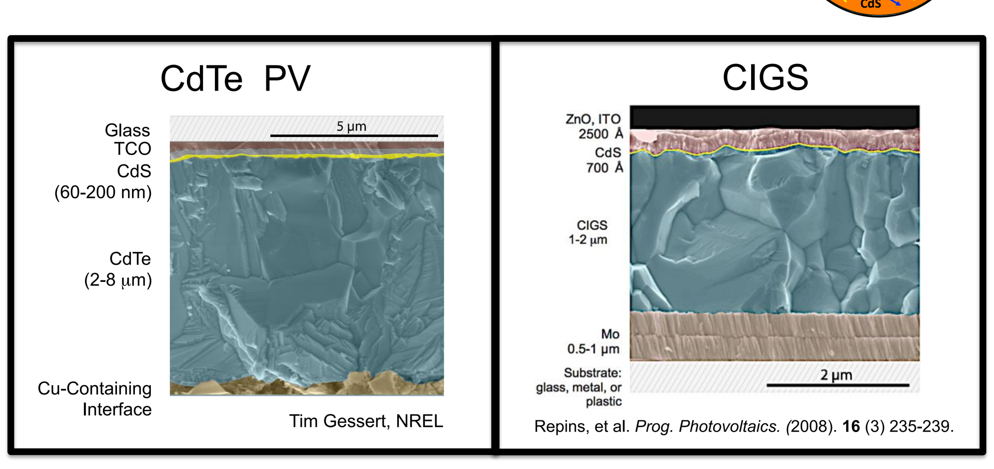


Cadmium Sulfide in Photovoltaics (PV)

CdS serves as a "window layer" in many thin film PV systems.

- n-type CdS creates a charge separation interface with p-type absorbers
- serves as an electron transport layer





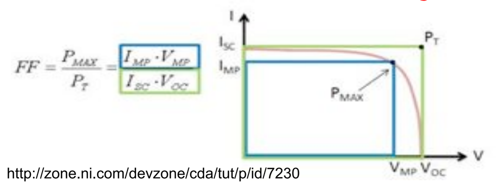
Tim Gessert, NREL

Repins, et al. *Prog. Photovoltaics.* (2008). **16** (3) 235-239.

How does the CdS layer affect device efficiency?

Efficiency is the product of open circuit voltage (V_{OC}), short circuit current (J_{SC}), and fill factor (FF).

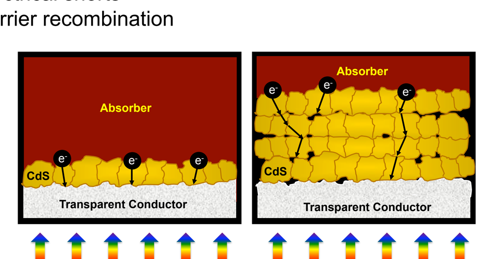
$$\eta = V_{OC} \times FF \times J_{SC}$$

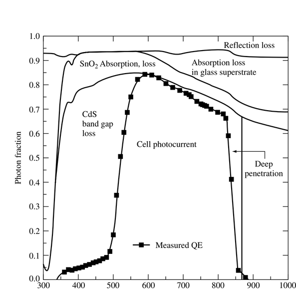


http://zone.ni.com/devzone/cda/tut/p/id/7230

Idea CdS layers will minimize factors that decrease V_{OC}, FF, and J_{SC}:

- Parasitic absorbance
- Series resistance
- Electrical shorts
- Carrier recombination





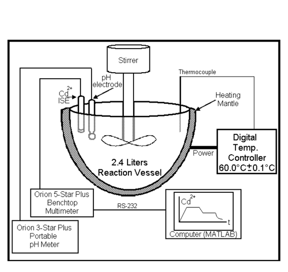
McCandless and Sites. *Handbook of Photovoltaic Science and Engineering* J (2003).

Objective: Create thin, dense CdS window layers, optimized for charge transport in thin film photovoltaics

Growing CdS Thin Films

How is CdS grown?

Sputtering
Evaporation
Vapor phase (e.g. CSS)
Chemical Bath Deposition (CBD)

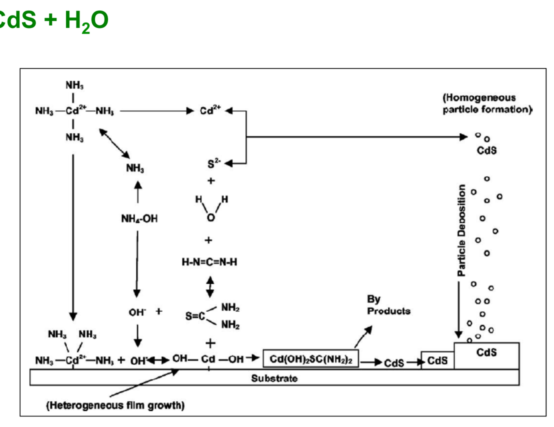


What's behind the CBD process?

$Cd^{2+}(aq) + S^{2-}(aq) \rightarrow CdS(s)$ X

$Cd(OH)_2 + CH_3C(S)NH_2 \rightarrow CH_3C(O)NH_2 + CdS + H_2O$

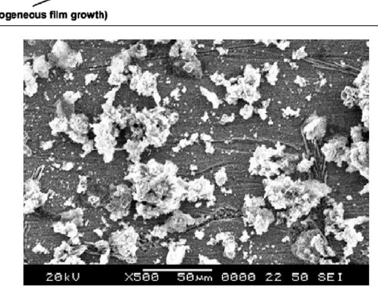
Uniform CdS thin film growth requires rigorous control over **reagent concentrations**, **temperature, and pH** to control dynamic reactions with *organic sulfur precursors, hydrated cadmium ions, and cationic chelators (e.g. ammonia).*



1. Ordonez, R. UTEP, 2010. (Master's Thesis)
2. Mugdur, P H, et al. *J. Electrochem Soc.*. 2007, 154, (9),. D482-D488.

Failure to control growth conditions can lead to non-uniform, low density films.

Films often need to be thicker (up to ~200 nm) thick to avoid pinholes.



Sanap, V.B. *et al.* Chalcogenide Lett. 2009, **6** (8), 415-419.

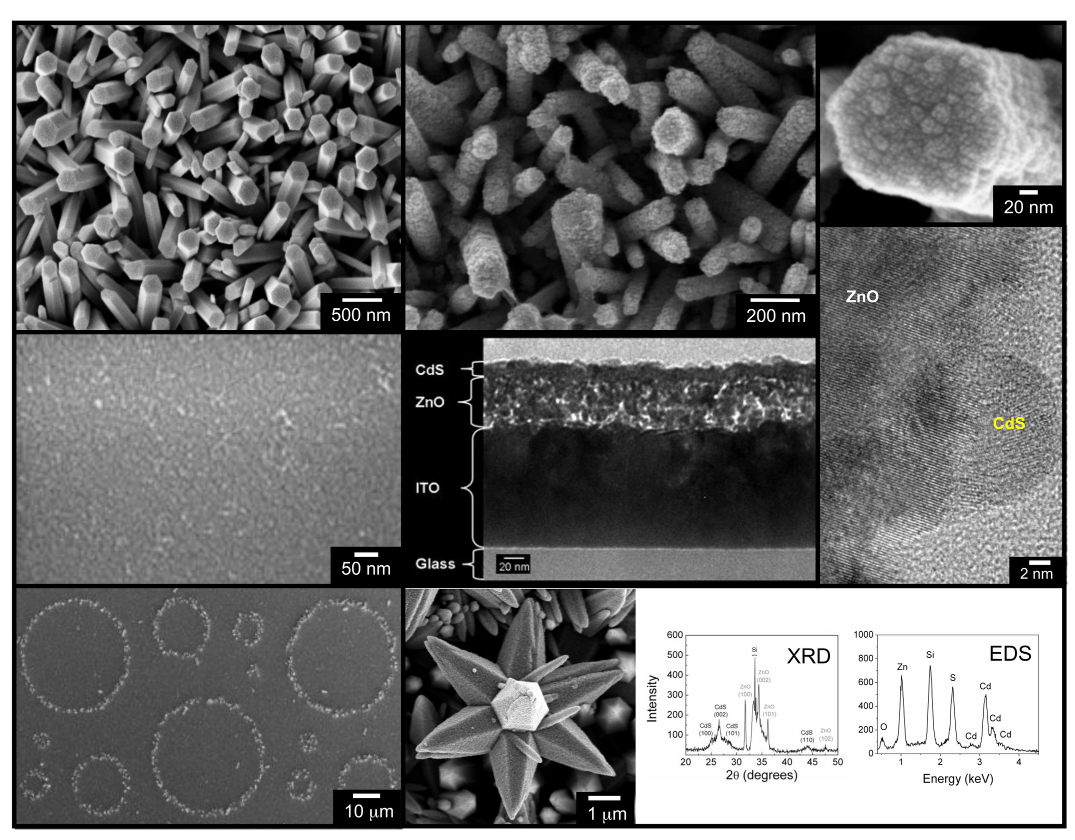
Nanocrystal Layer Deposition of CdS

NCLD: A room temperature, aqueous synthesis

NCLD is an aqueous surface-mediated growth process that produces selective, uniform, and conformally dense nanocrystalline CdS films on hydroxyl-rich surfaces (e.g. ZnO).

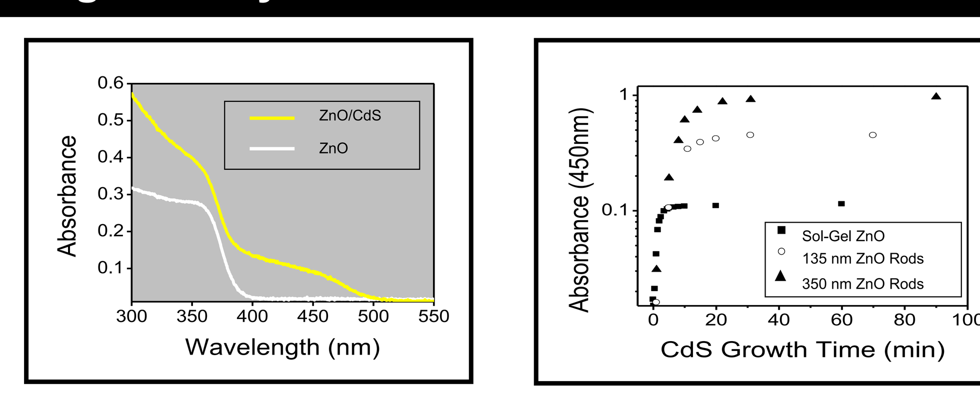
$$Cd^{2+} + CH_3C(S)NH_2 \xrightarrow{ZnO} CH_3C(O)NH_2 + CdS + H_2O$$

NCLD produces a dense CdS coating only a single nanocrystal thick on both 2-D and 3-D ZnO architectures.



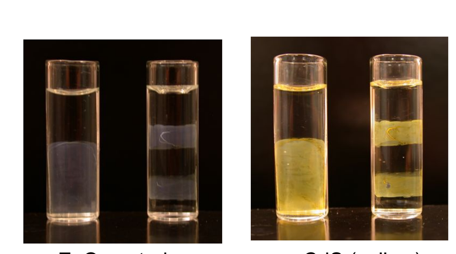
Spoerke, et al. J. Phys. Chem. C. 113, 16329 (2009)

CdS growth by NCLD is self-initiated and self-limiting



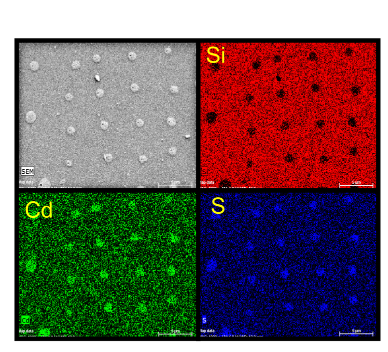
Monitoring CdS growth with absorbance shows that film formation is *self-limiting!*

CdS growth on ZnO is selective on both macro- and microscales

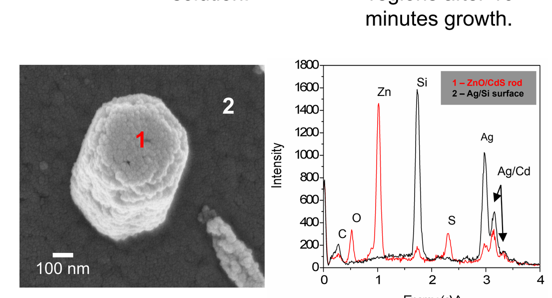


ZnO coated on glass slides at t_0 in CdS reaction solution.

CdS (yellow) selectively grown on ZnO-covered regions after 10 minutes growth.

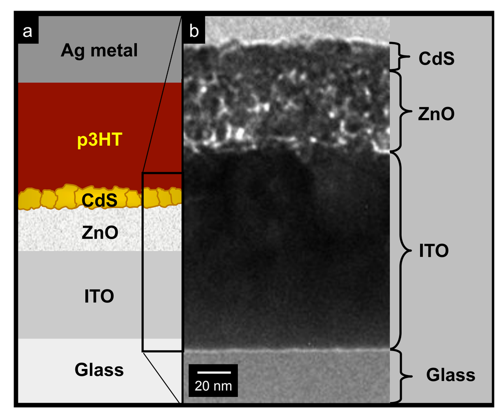


Stamped "micro-dots" of ZnO on Si produce selective CdS growth

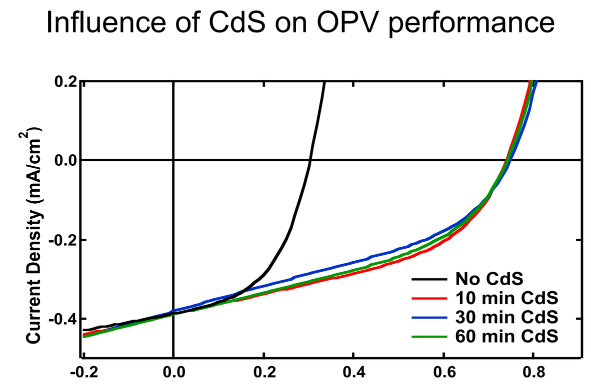


ZnO nanorods on Ag selectively template CdS

Evaluating PV Feasibility with Organic PV



Influence of CdS on OPV performance



CdS layer producess dramatic enhancement of V_{OC} and efficiency in OPV system.

CdS produced by NCLD is clearly suitable for PV applications.

CdS Growth (min)	Jsc (mA/cm²)	Voc (mV)	FF (%)	η (%)	Rs (Ω cm)
0	0.39	303	49.2	0.058	33.1
10	0.39	733	43.8	0.123	53.3
30	0.37	755	40.2	0.113	45.0
60	0.38	752	44.1	0.126	53.8

Spoerke, et al. Appl. Phys. Lett. DOI: 10.1063/1.3232231 (2009)

Tailoring CdS Properties

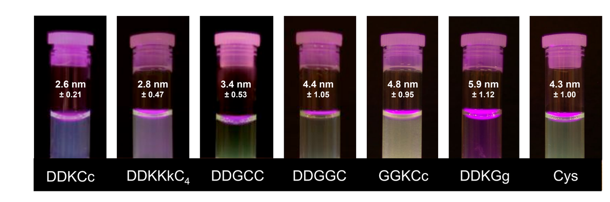
Tuning Band Structure with Growth Modifiers

20 nm thick nanocrystalline CdS produced by NCLD would be expected to reduce parasitic absorption.

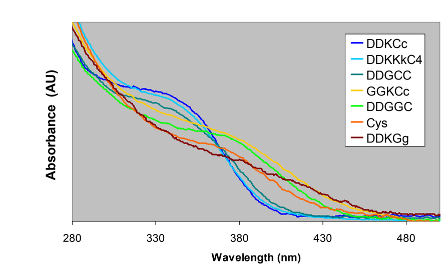
Can we further reduce CdS absorbance by increasing the CdS band gap?

CdS nanoparticle size can be tuned using peptides rich in amino acids such as cysteine (C), and aspartic acid (D) that bind aqueous Cd^{2+} cations.

Quantum confinement in small nanocrystals increases CdS band gap, resulting in a significant blue shift in absorbance (and photoluminescence).



Spoerke, et al. Adv. Funct. Mater. (2007) **17** (13). 2031-2037.

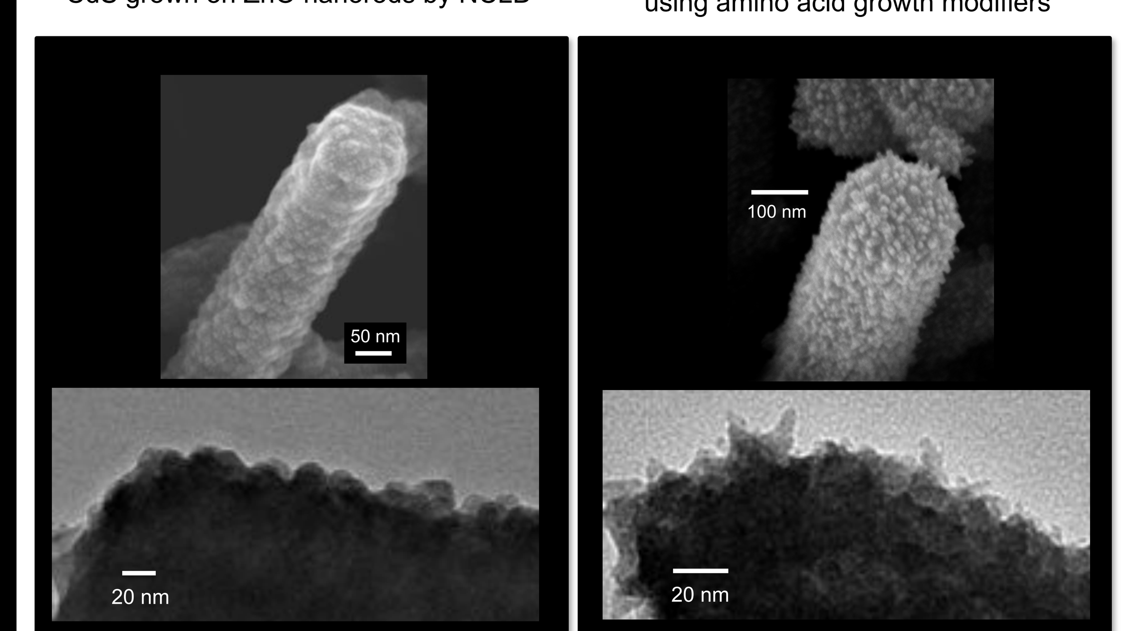


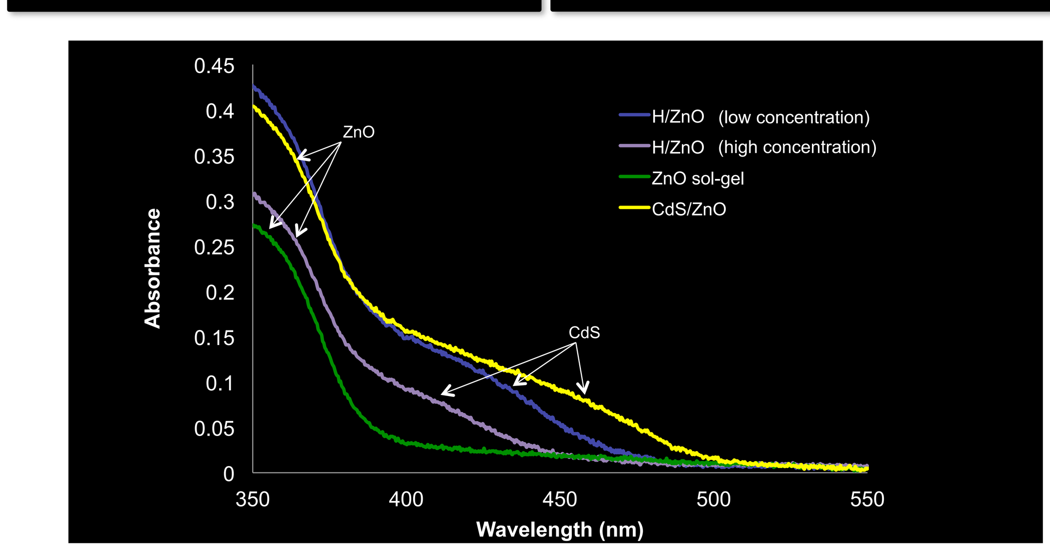
Growth Modifiers in NCLD

Controlled introduction of amino acids (e.g. cysteine, histidine, aspartate, glutamate) to the NCLD growth reaction dramatically changes CdS nanocrystal morphology.

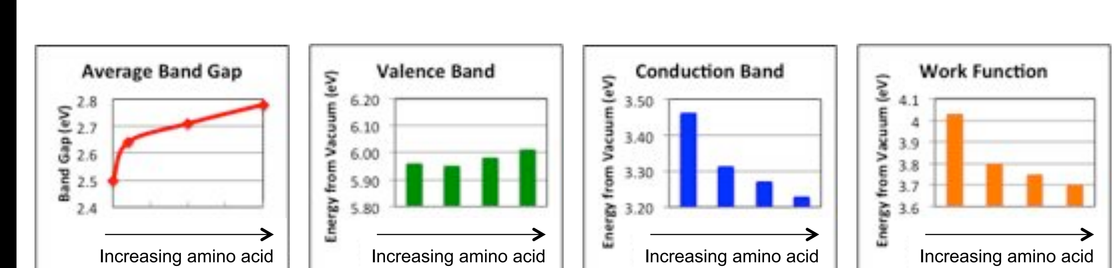
CdS grown on ZnO nanorods by NCLD

CdS grown on ZnO nanorods by NCLD using amino acid growth modifiers





Blue-shifted absorbance shows that by controlling the amount of amino acid growth modifier (e.g. cysteine, aspartic acid, histidine), the band gap of the CdS film can be tunably increased.



XPS and UPS measurements reveal that the increased band gap is due to the conduction band moving closer to vacuum. In addition, the shift in the work function suggests that n-doping in CdS is not sacrificed with conduction band movement.

Summary, Conclusions, and Future Work

- CdS is a critical element of thin film PV that can dramatically affect device efficiency.
- NCLD is a room temperature, aqueous synthesis that produces thin, conformal, nanocrystalline CdS coating.
- NCLD CdS is suitable for application in PV systems, even showing dramatic improvement of V_{OC} and device efficiency in OPV cells.
- Using functional amino acid growth modifiers, CdS morphology and optoelectronic properties of NCLD films can be tuned.
- Efforts are underway to incorporate these films into inorganic thin film PV (e.g. CdTe) systems.

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