Crystalline Organic Photovoltaic Cells

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(Intended for Peer Reviewers)

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3 year program goals

- Demonstration of 10% power conversion efficiency at 1 sun, AM1.5 (solar spectrally corrected) illumination.
- Demonstration of extrapolated lifetime of 5 years under 1 sun AM1.5 illumination, and 50^{o}C operation.
- Fabrication of cells with uniform performance over 10 cm^2

Team

Principal Investigator

- Stephen Forrest

Graduate (PhD) Students

- Brian Lassiter (Growth and Device Fab)
- Richard Lunt (Growth)
- Guodan Wei (Device Char and Modeling)

Group Administrator

- Beth Talbot

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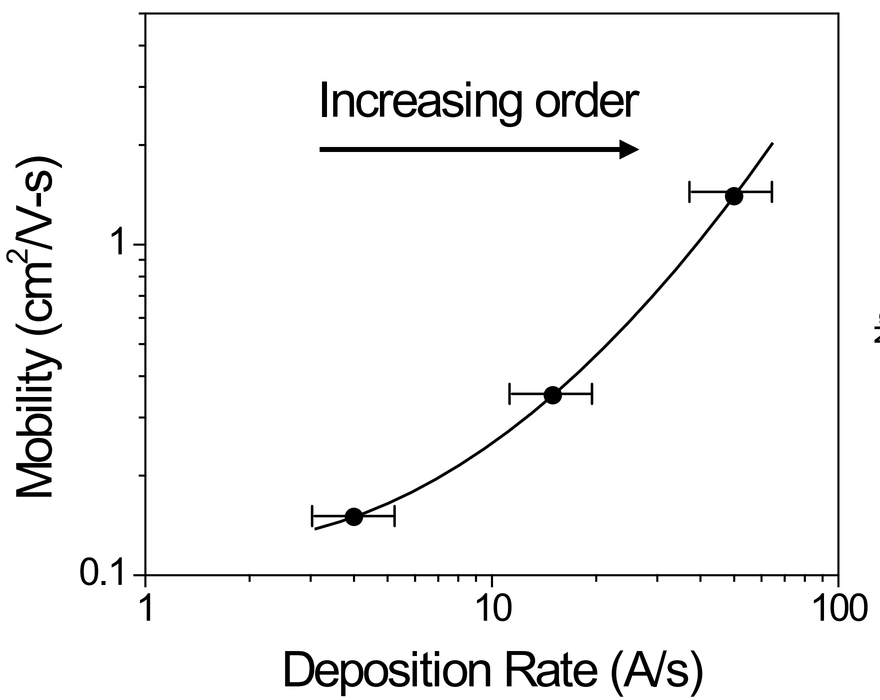
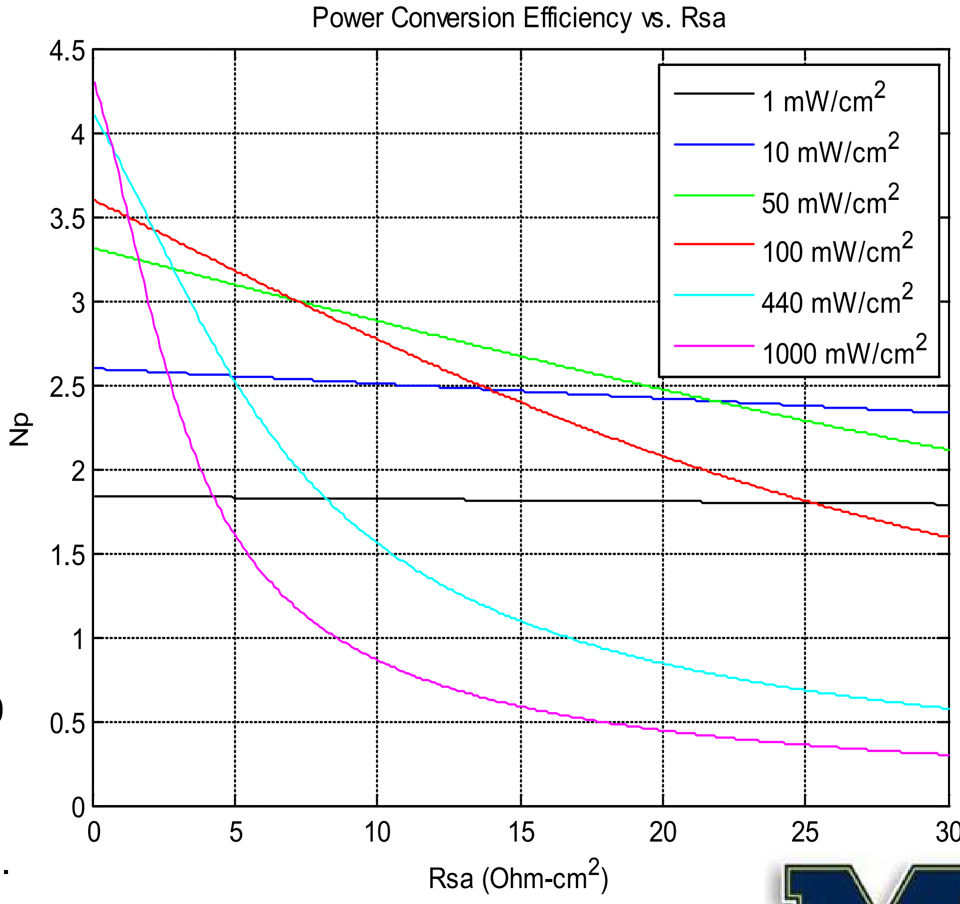
Mobility and Resistance Key to OPV performance

PTCDA Growth in Vacuum

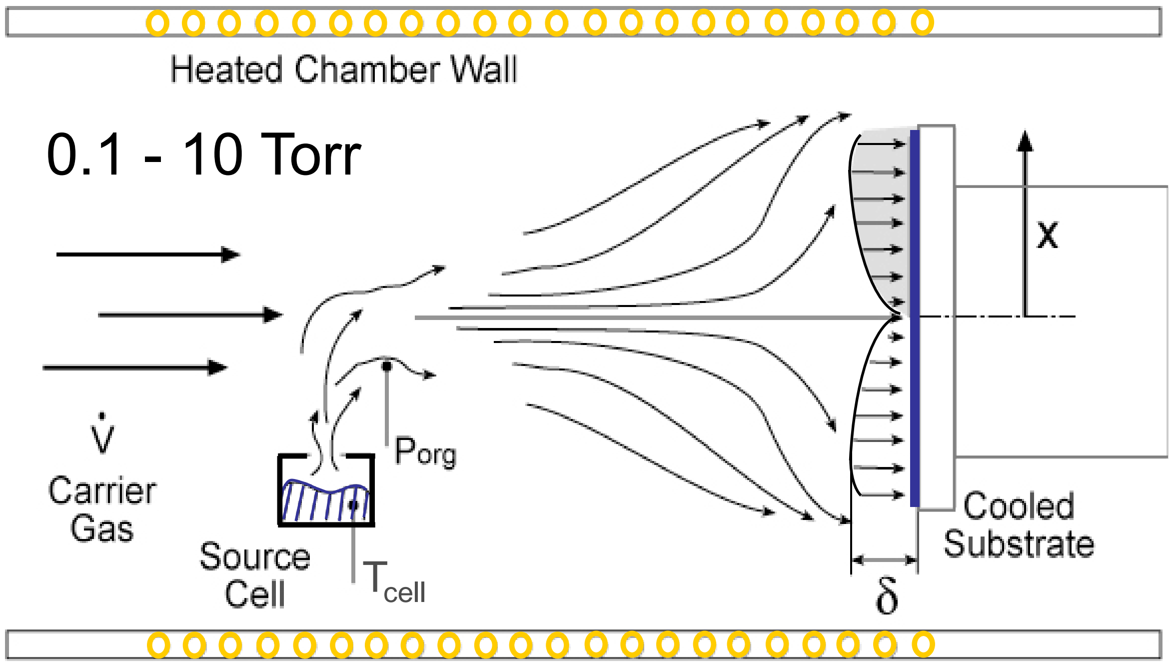


S. R. Forrest, et al., *J. Appl. Phys.*, **56**, 543, (1984).



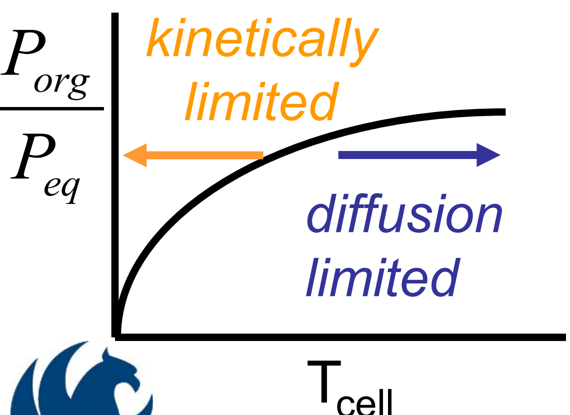
Program Approach: Achieve highly ordered films to increase PCE

Organic Vapor Phase Deposition: *Concept*

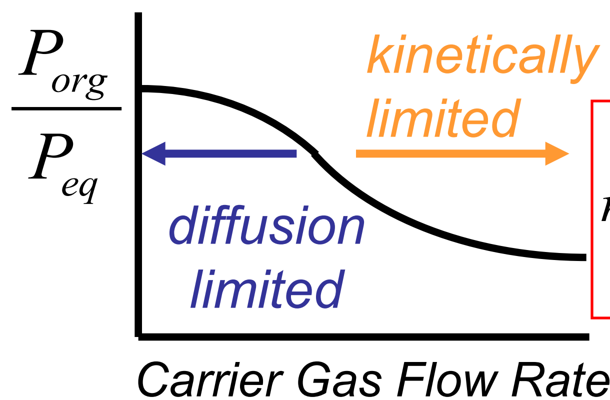


- **Controlled and accurate doping (gas saturated with organics ⇒equilibrium)**
- **Dust free chamber**
- **Efficient materials use**
- **Control of film crystal structure**

Constant Flow Rate



Constant Temperature



$$r_{out} = \frac{\dot{V}_{src}}{RT_{cell}} \cdot \frac{P_0 \exp(-\Delta H / RT_{cell})}{1 + \dot{V}_{src} / A_{evap} \cdot k}$$

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M. Shtein, et al., J. Appl. Phys., **89**, 1470 (2001).

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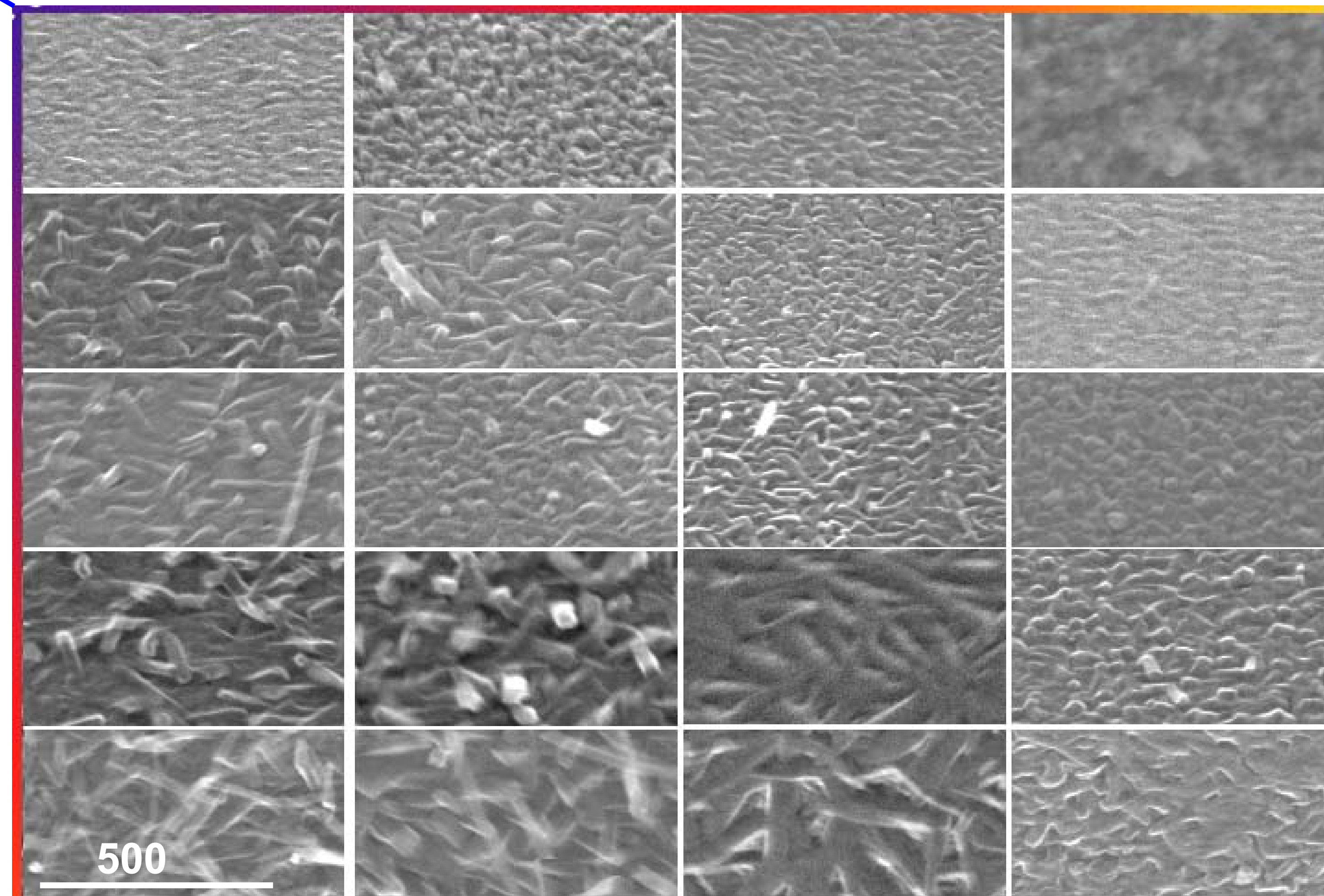
Morphology control by temperature

(flowrate = constant, pressure = constant)

T_{cell} (°C): 420, 432, 446, 460

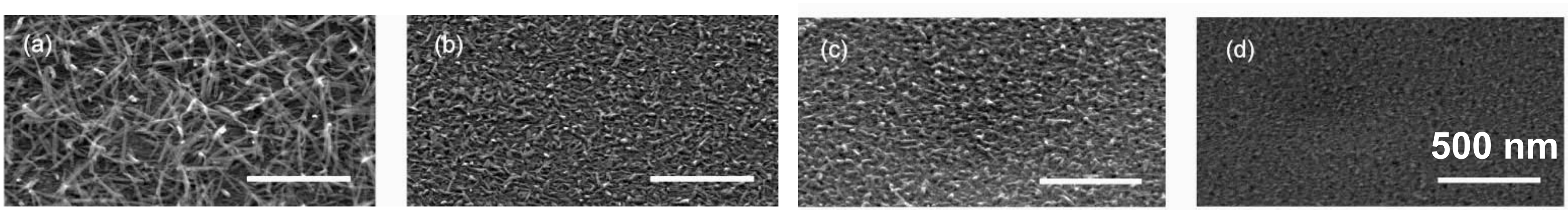
T_{sub} (°C): 2, 26, 50, 74, 98



Morphology control by flow rate

(fixed source and substrate temperatures)

N_2 flow rate: 100 sccm 125 sccm 150 sccm 200 sccm

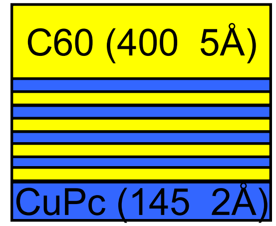


Increasing carrier gas flow rate

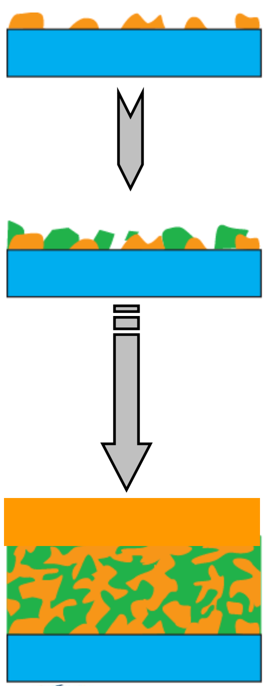
Crystals	Needle Long, large	Flat Uniaxial, small
Source temperature	Low	High
Substrate temperature	High	Low
Carrier gas flow rate	Low	High
Chamber pressure	Low	High

Growth of nanocrystalline bulk heterojunctions by OVPD

$[C_{60}(32\pm2Å)/$
$CuPc(32\pm Å)] \times n$



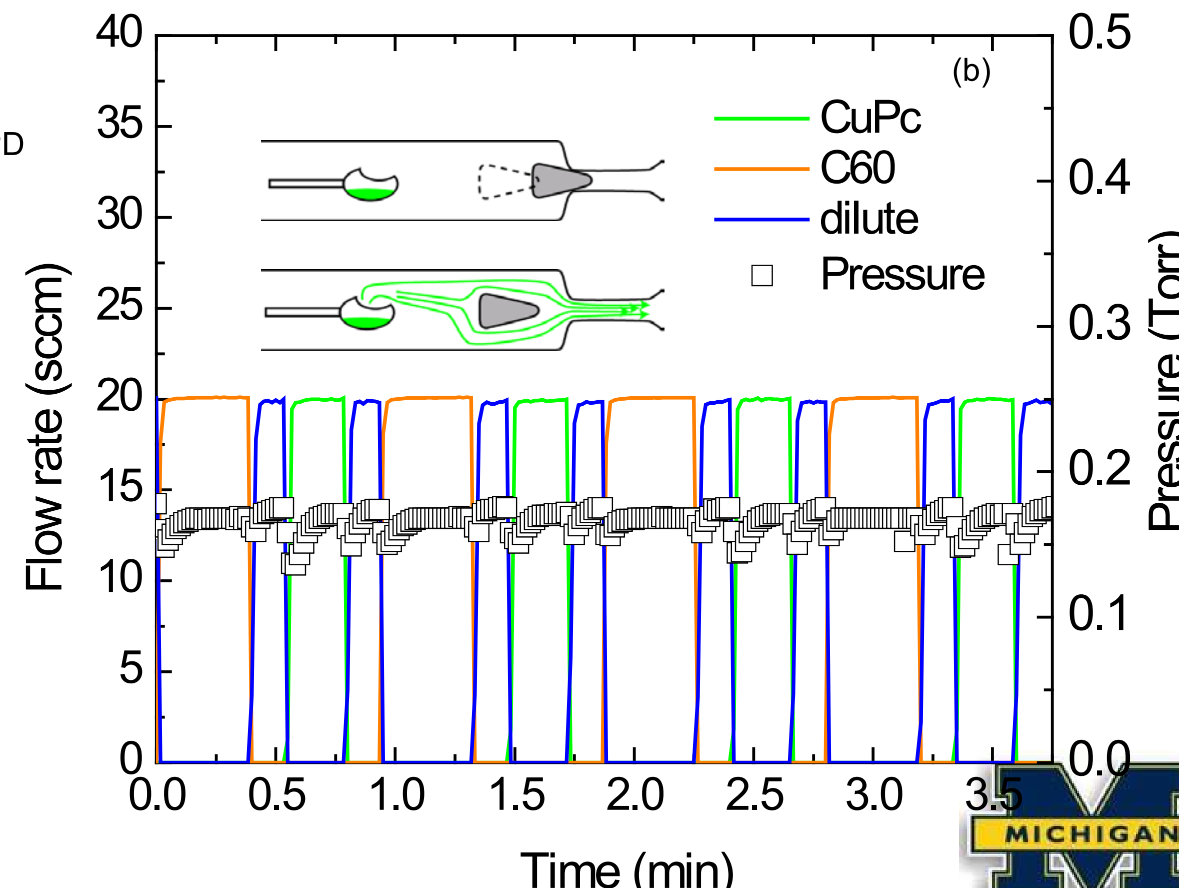
Multilayer OVPD growth leads to nanocrystals



Step 1:
Grow of the 1st non-continuous layer by OVPD

Step 2:
Grow of the 2nd non-continuous layer by OVPD

Final structure:
Interconnected nano-crystallites



Actual multilayer growth

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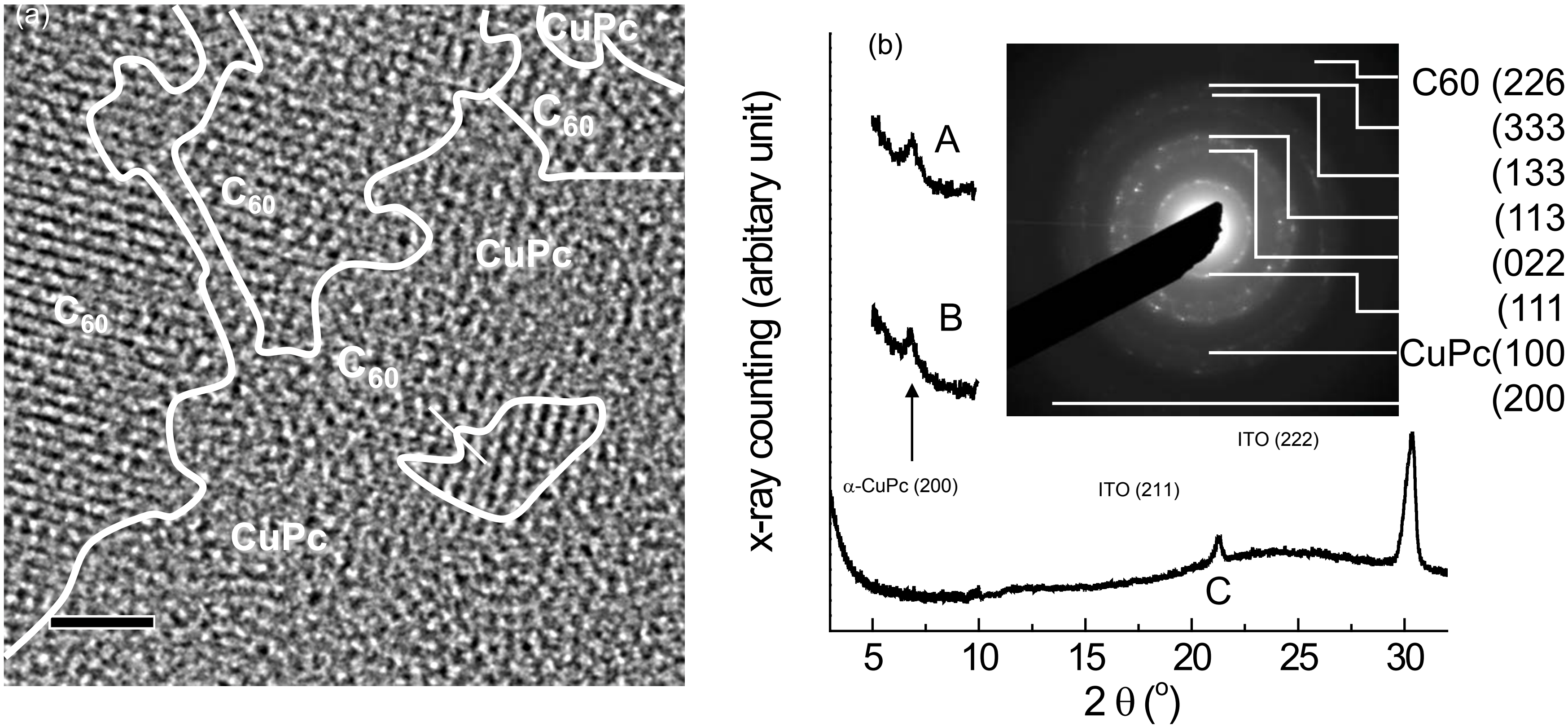
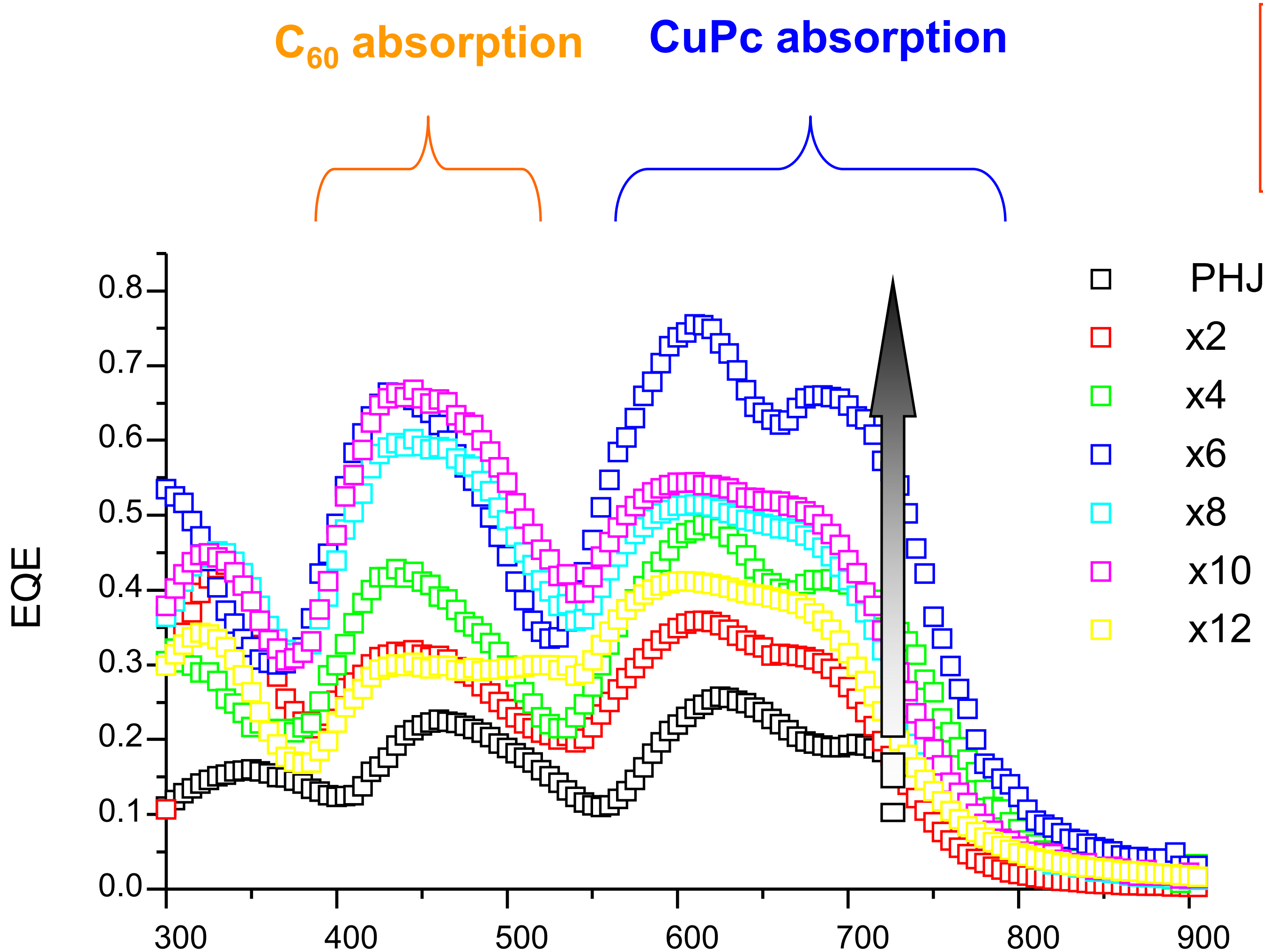
Analysis of OVPD-grown structure



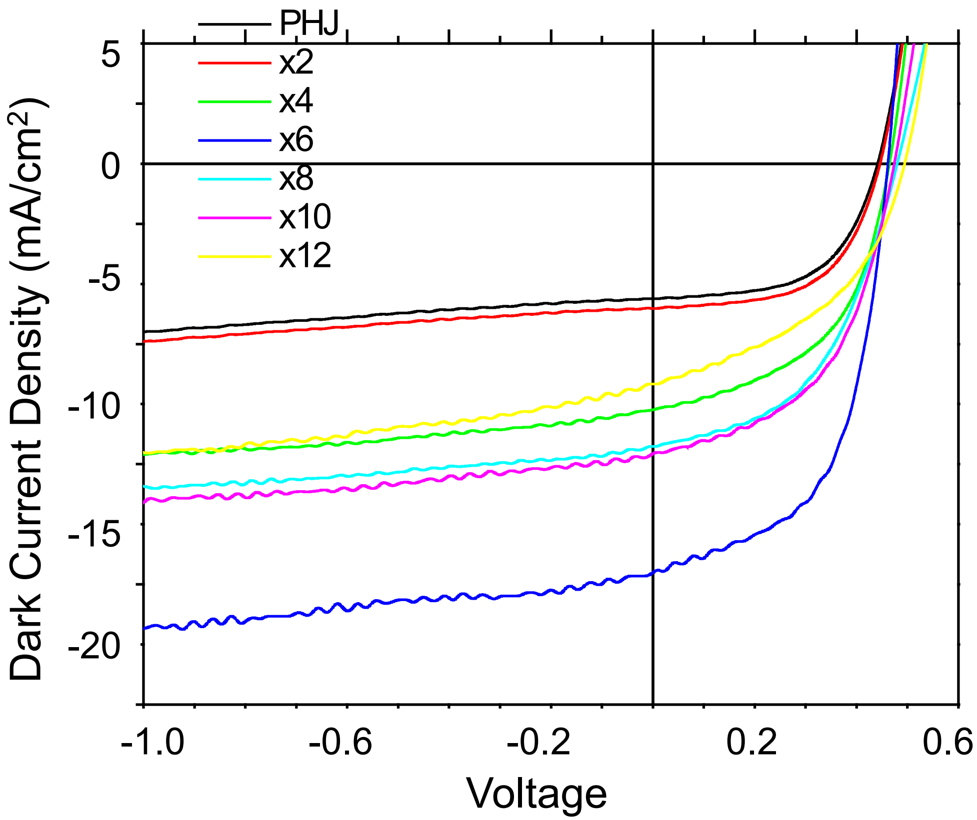
Nano Xstal Efficiency vs Number of Layers

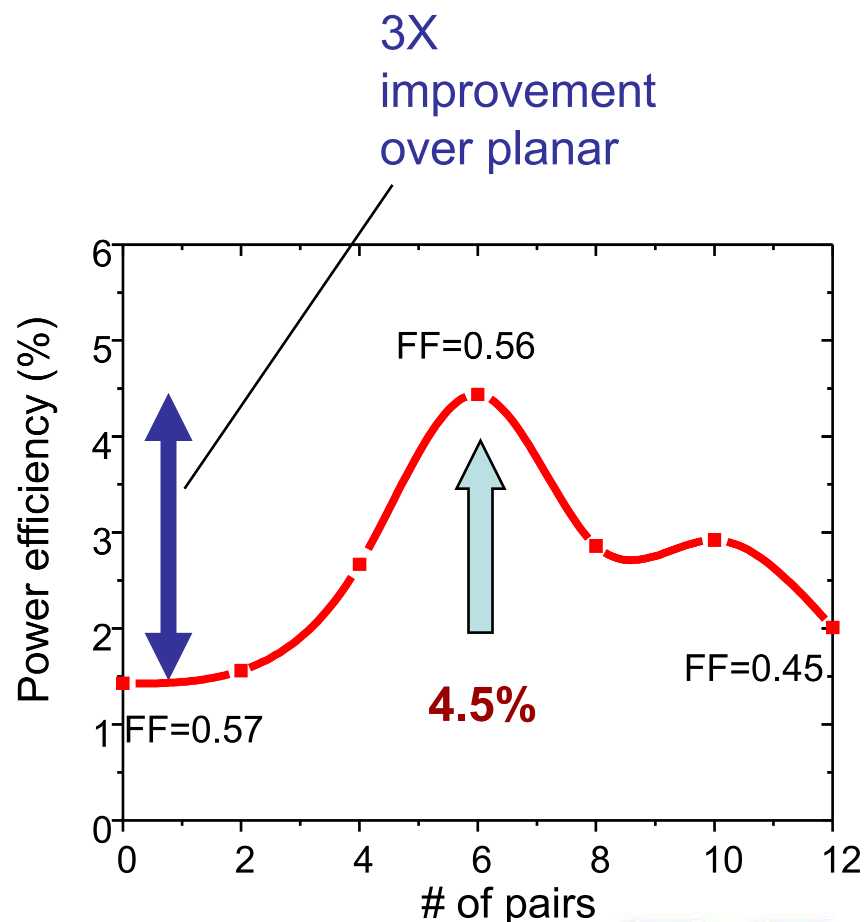
Performance measured at 110 5 mW/cm^2, AM 1.5G illumination (NREL calibrated Si Detector)



Quantum efficiency increases with nanocrystalline network thickness

Nanocrystalline solar cell performance





•Performance measured at 110 5 mW/cm², AM 1.5G illumination (NREL calibrated Si Detector). Solar corrected

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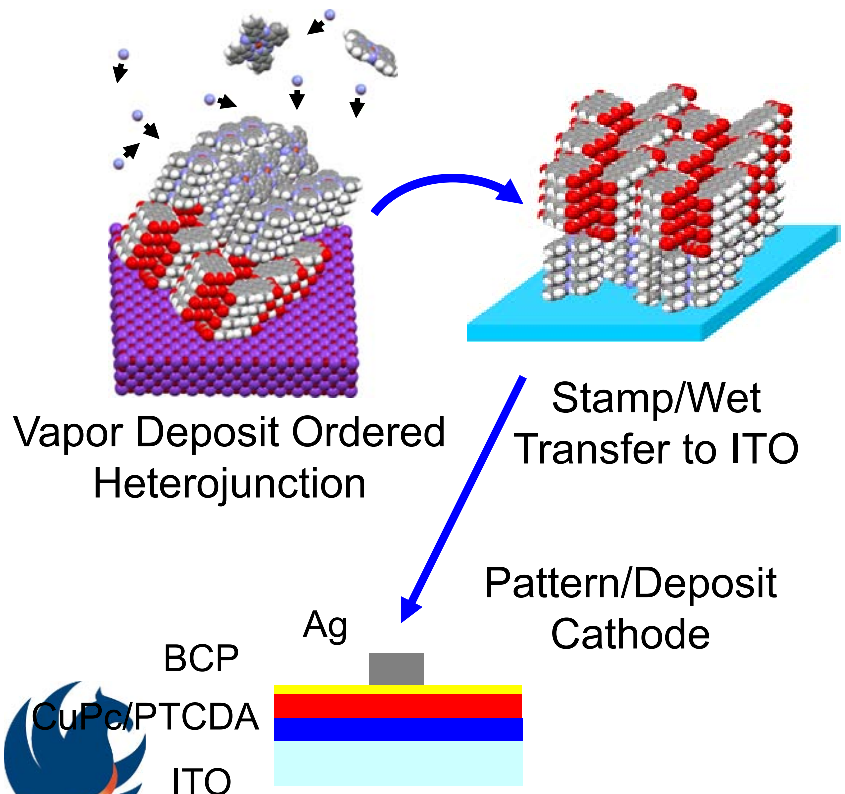
Crystalline Solar Cells

Two Avenues:

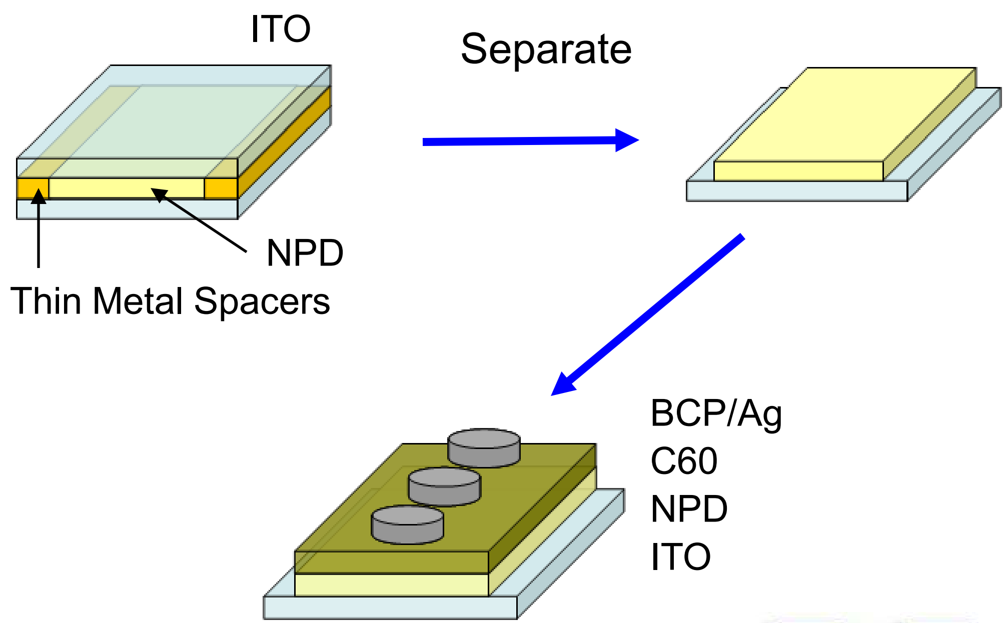
1) Previous Method: Epitaxial Growth in OVPD on Templ. Surface → stamp transfer
   i.e. CuPc/PTCDA solar cell (PTCDA = acceptor, CuPc = donor)
2) Melt Process 1 layer → try to template subsequent growth
   i.e. Melt NPD – NPD/C60 solar cell (C60 = acceptor, NPD = donor)

Method 1)



Method 2)

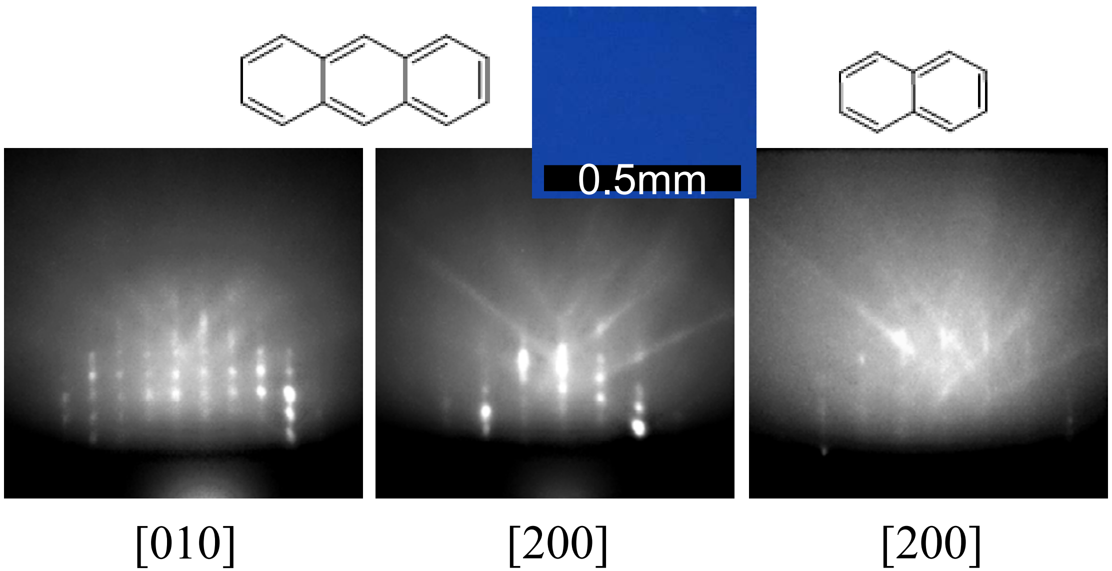
Cavity (fixed gap) put in molten NPD → slow cooled



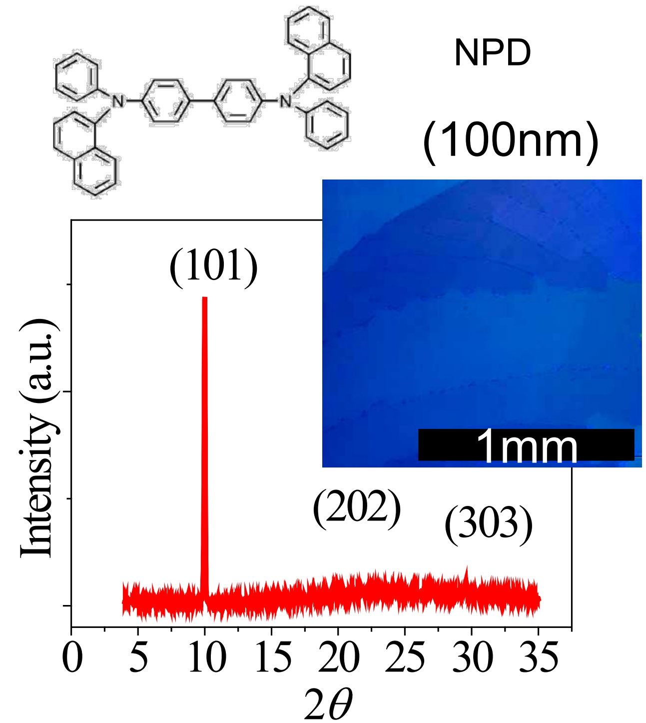
Vapor Deposit-Template Last Layers

Growth of Large Grain Crystalline Films (Method 2)

Organic Grown from the Melt → Polycrystal and Single Crystal Films



HP-RHEED patterns of Melt Grown Films – Kikuchi Pattern Observation – Single Crystal (2x2 cm^2)



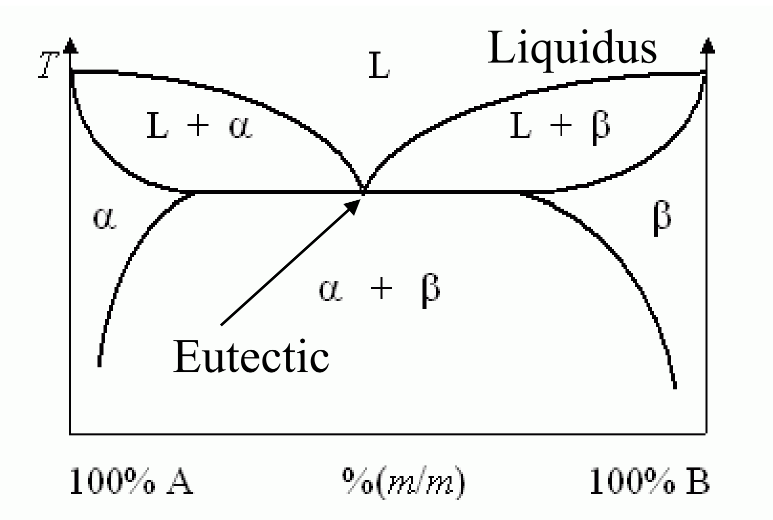
Polycrystalline Films (0.1x0.5 mm^2)

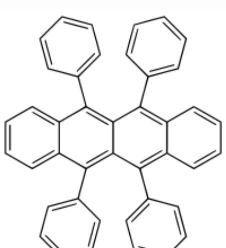
Control of Thickness between 70nm – 10μm

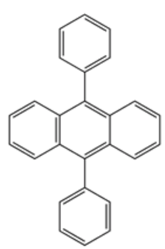
Lunt, et al.,Phys. Rev. Lett., **102**, 065504(2009).

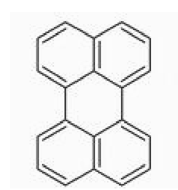
Expand Range Materials for Melting

- **Difficult to Access Liquid Phase due to Vaporization/Decomposition (i.e. Rubrene)**
- **Employ Concept of Organic Alloying to reduce melting point**





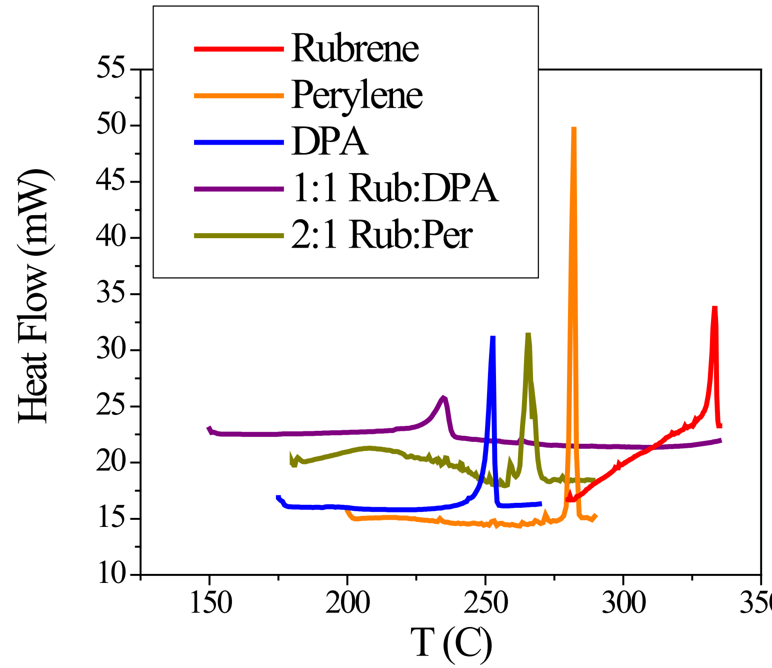




Rubrene Tm* = 333ºC

DPA Tm = 253ºC

Perylene Tm = 282ºC

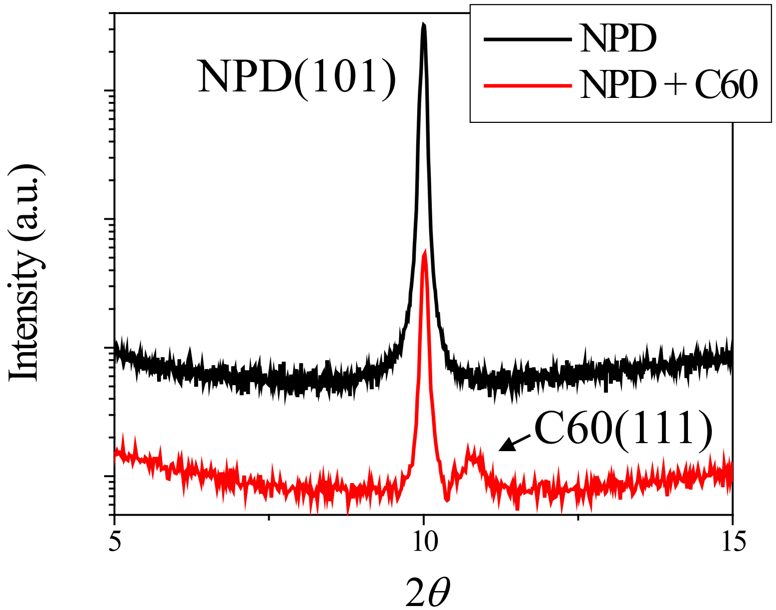


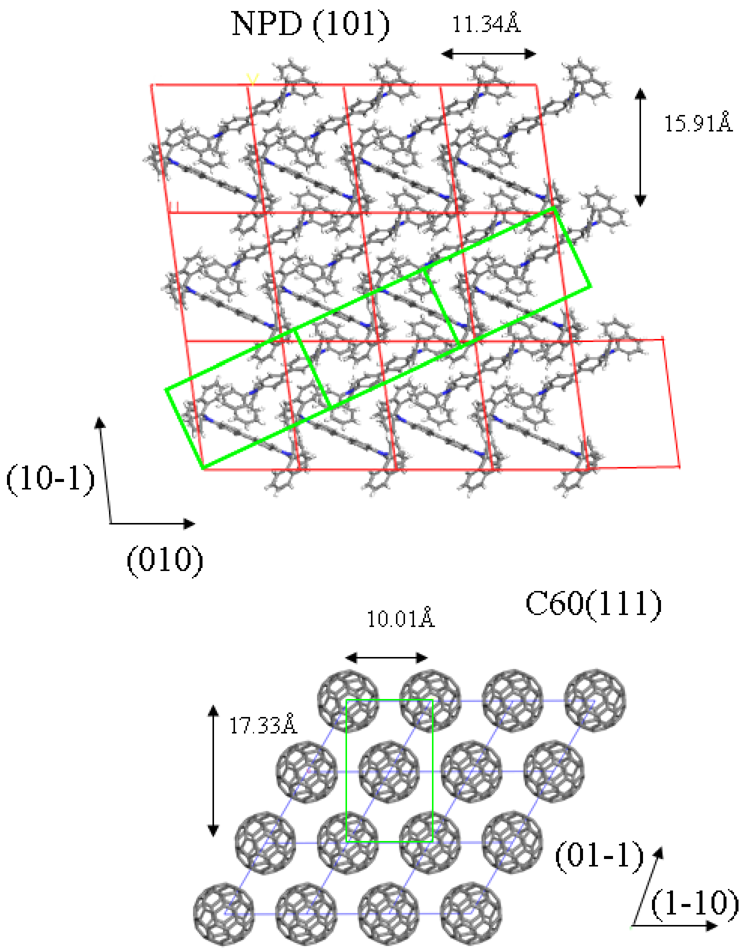
1:1 Rub:DPA – Tm = 235ºC

2:1 Rub: Pery – Tm = 265ºC

Template Growth

C_{60} (400Å) Vapor Deposited on Crystalline NPD(1000Å)





Some coincident superlattice alignments (i.e. [3,1]C60 - 35º to [2,4] NPD)

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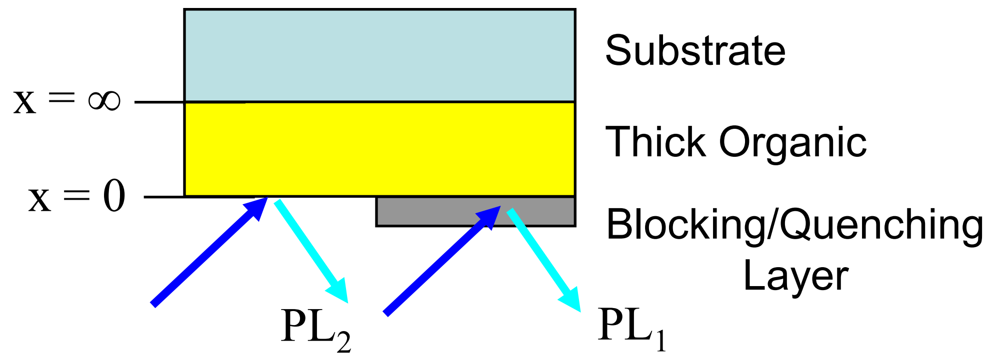
Diffusion Length Measurement

Want method for measuring diffusion length with a single substrate → explore EDL of polycrystalline/single crystalline materials

Use thick samples → no interference effects

Scan PL intensity vs. wavelength → connect to absorption coefficient

Self-normalized (no dipole alignment-collection effects)



Diffusion Equation

$$\frac{\partial n}{dt} = D\nabla^2 n - \frac{n}{\tau} + I_0 \alpha e^{-\alpha x}$$

$$\left.\frac{\partial n}{\partial x}\right|_{x=0} = 0 \;\; (BCP) \;\; or \;\; n\big|_{x=0} = 0 \;\; (C60)$$

$$n\big|_{x\to\infty} = 0$$

$$\eta_{Quench}(\alpha) = \frac{PL_2}{PL_1}(\alpha) = \frac{\int_0^d n_{Bare}(x,\alpha)dx}{\int_0^d n_{C60}(x,\alpha)dx}$$

$$\eta_{Quench}(\alpha) = \alpha L + 1$$

Expected quenching as a function of absorption and diffusion length

Exciton Diffusion Lengths Measured

Material	Exciton	Crystallinity (Orient.)	L_D (nm)
NPD	S	Amorphous	5.1 (±1.0) *
CBP	S	Amorphous	16.8 (±0.8) *
SubPc	S	Amorphous	8.0 (±0.3)
SubPc-Cl	S	Amorphous	10 (±0.5)
PTCDA	S	Cryst - 35nm (flat)	8.2 (±0.3)
PTCDA	S	Cryst - 55nm (flat)	10.4 (±1.0)
DIP	S	Cryst - >150nm (upright)	16.5 (±0.4)
DIP	S	Cryst - 30nm (flat)	21.8 (±0.6)
PtTPBP	T	Amorphous	5.7 (±0.5)
PtOEP	T - Mon.	Cryst - (upright)	18.0 (±0.6)
PtOEP	T - Aggre.	Cryst - (upright)	13.1 (±0.5)

* Corrected for Förster Energy Transfer

Crystallinity/Crystal size determined from x-ray diffraction

Crystal Orientation → anisotropy (even for polycrystalline films)

- Next slide explore Diffusion Length in PTCDA as function of Crystalline Order

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Lunt, et al.,J. Appl. Phys.,*(In Press)* (2009).

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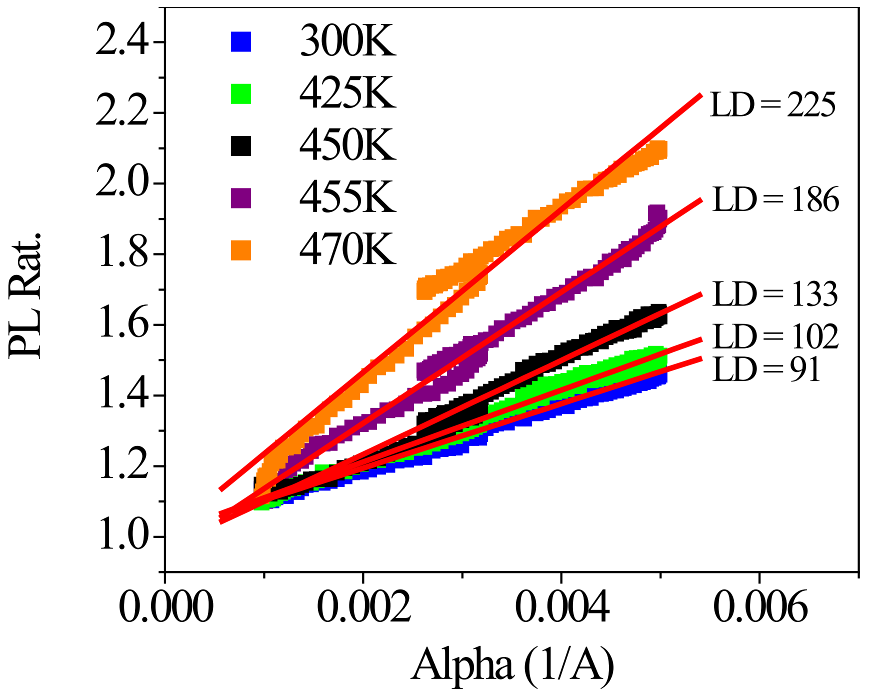
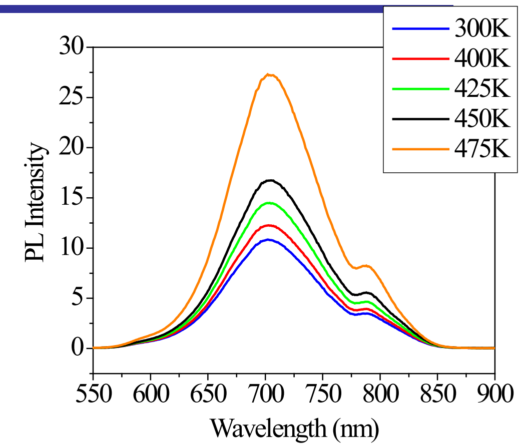
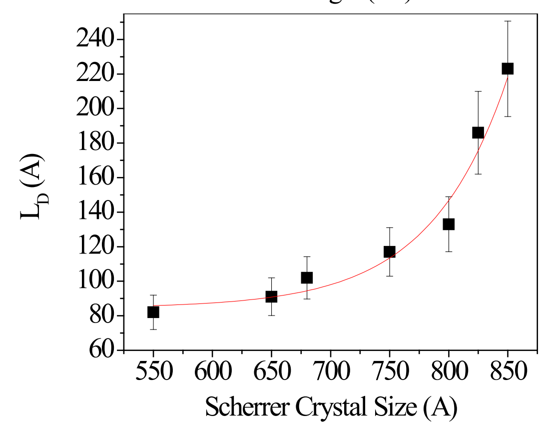
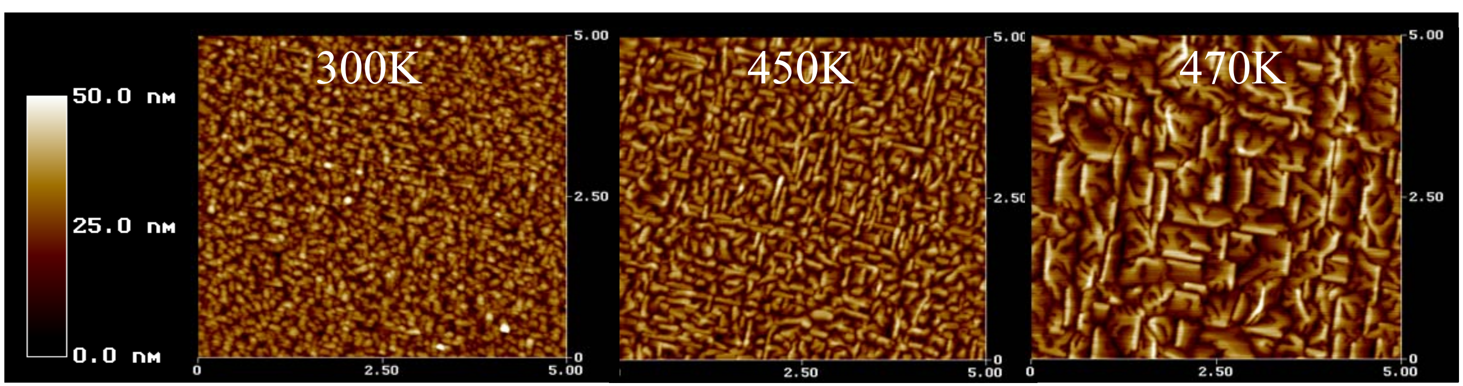
Crystal Size - Exciton Diffusion





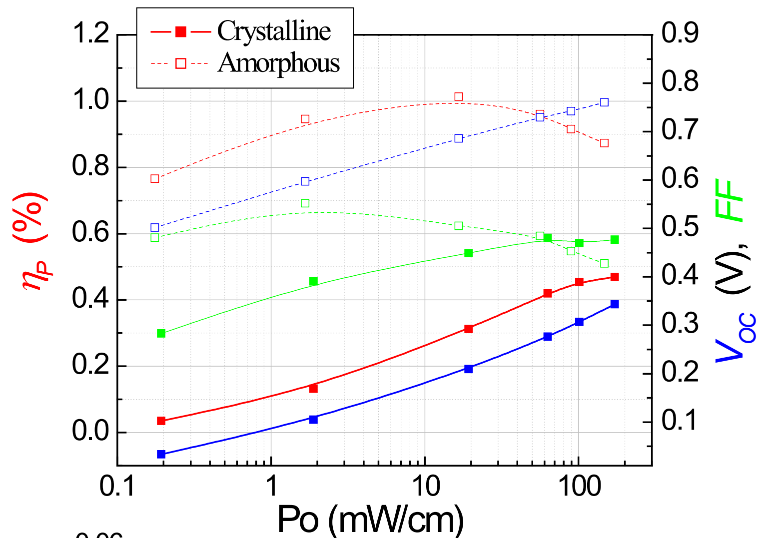


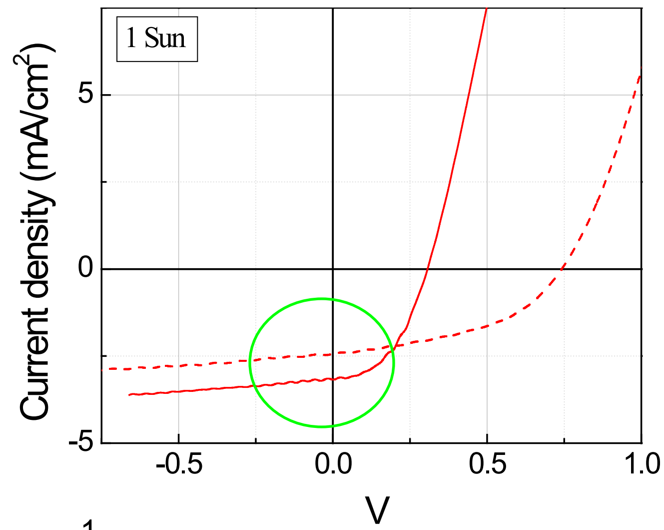


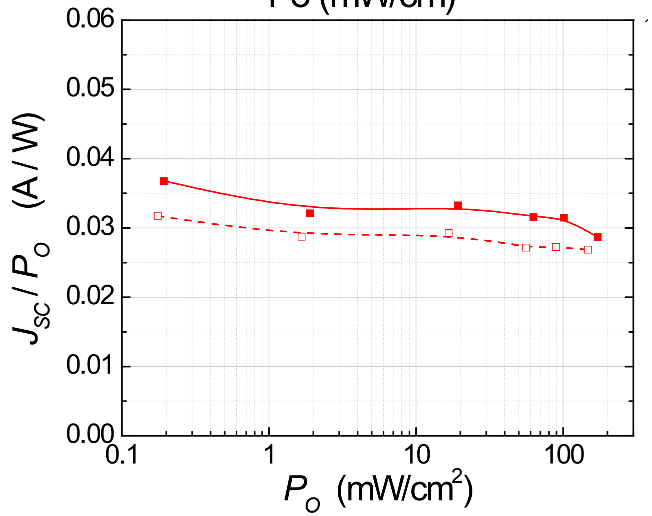
Preliminary Crystalline HJ Data

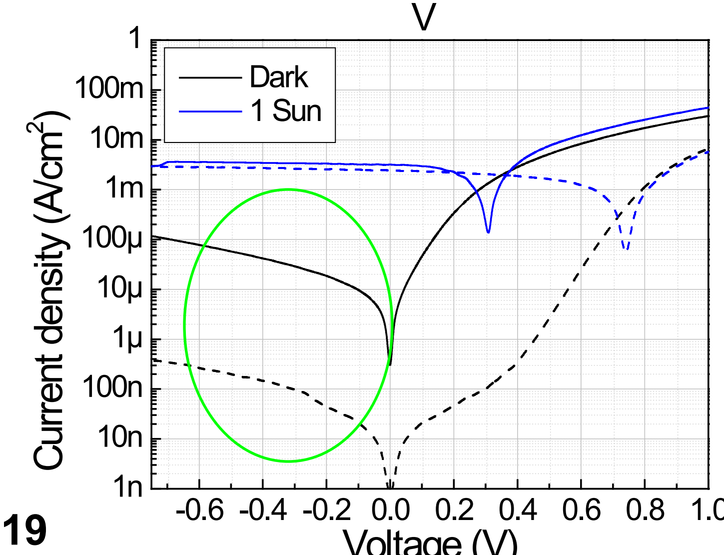
Amorphous: ITO/NPD(100Å)/C_{60}(400Å)/BCP(100Å)/Ag - - - - - - -

Crystalline: ITO/NPD(1000Å)/C_{60}(400Å)/BCP(100Å)/Ag ———









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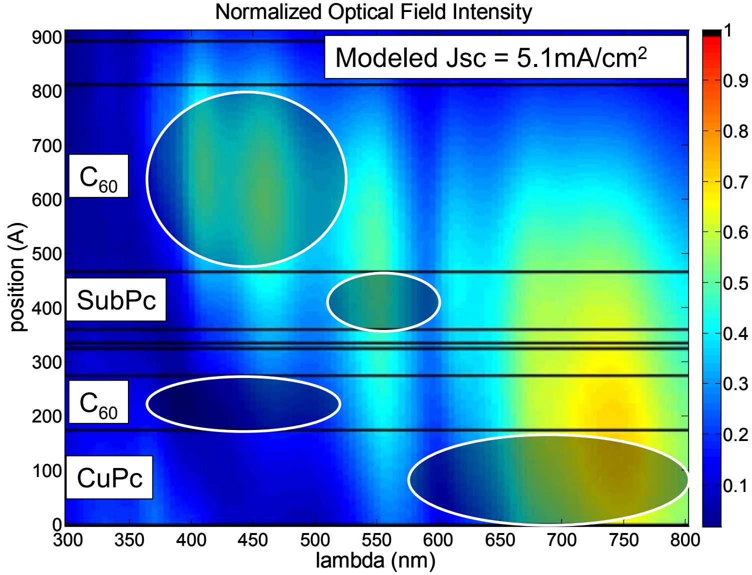
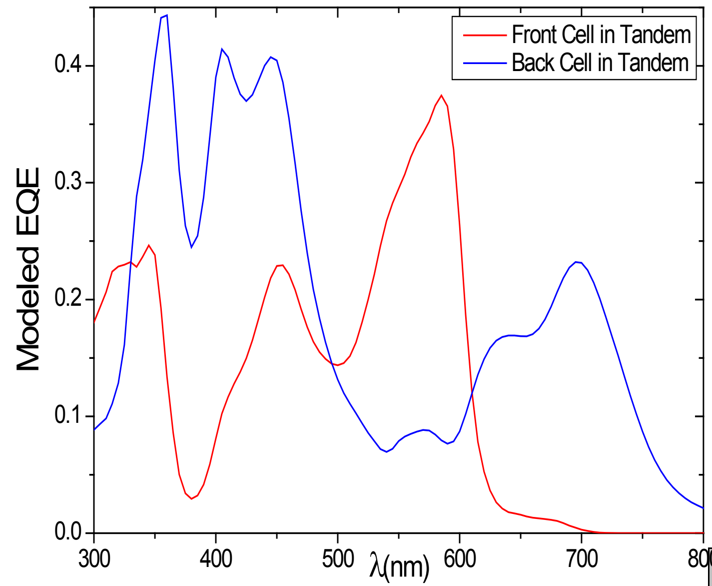
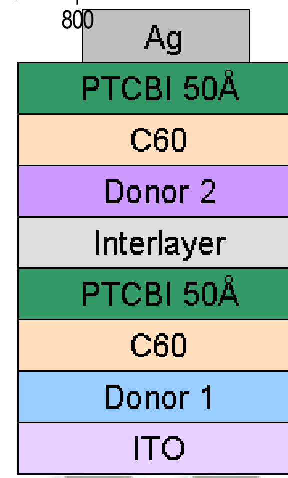
Preliminary Tandem Modeling

Modeling Tandem Jsc:



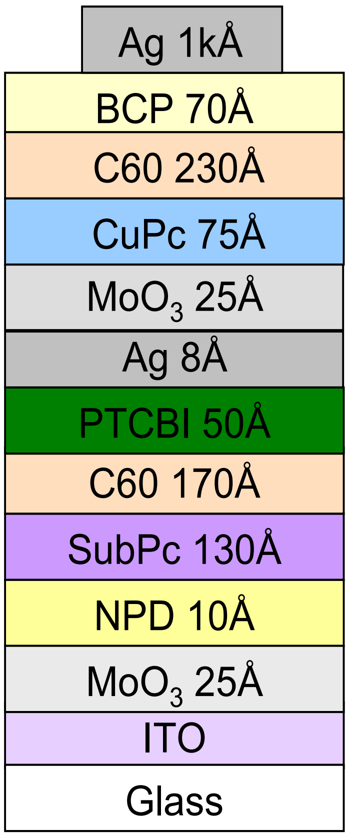


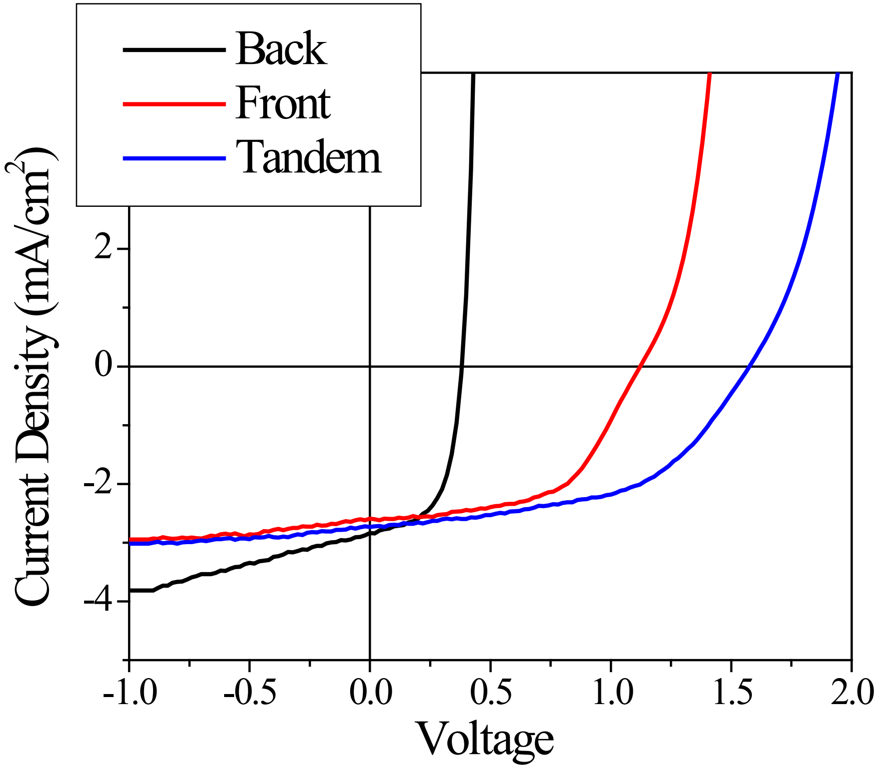


Planar/Mixed/Planar	Model J_{sc} (mA/cm^2)	V_{oc} (V)	η_p(%)
CuPc/SubPc	5.1	1.6	4.9
SnPc/SubPc	5.8	1.5	5.2
ClAlPc/SubPc	5.4	1.8	5.8

Assuming FF=0.6

Preliminary Tandem Structures





Device	η_p (%)	V_{oc} (V)	FF	J_{sc} (mA/cm^2)	Model J_{sc}
Front Only	1.7	1.12	0.55	2.7	3.7
Back Only	0.66	0.38	0.59	2.9	5.7
Tandem	2.3	1.57	0.52	2.8	3.2

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Program Tasks

BUDGET PERIOD 1:

- Demo. growth of a HJ with long range order
- Demo. growth of crystalline HJ organic PV cell.
- Begin measurement operational lifetime of crystalline cells
- Establish activation energies for crystalline and microcryst. cells.

BUDGET PERIOD 2:

- Demo. growth of an optimized, crystalline HJ PV cell
- Demo. crystal cells with areas >10 cm^2.
- Demon. crystalline tandem cell with both visible and near infrared coverage.
- (Efficiency targets: 10% @ 1 sun, AM1.5).
- Measure lifetime of crystal cells (objective >5 yrs).

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Critical Milestones

[End of Program Year 2]

- Extrapolated Lifetime >1 year
- Power conversion efficiency: >4%
- Establish that long range order has been achieved, and results in increased exciton diffusion efficiency and charge mobility.

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