Organic Optoelectronic Devices: Materials, Models, and Design Rules

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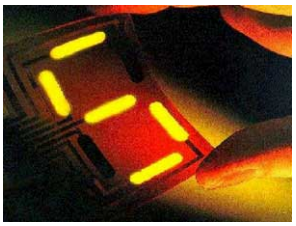
Acknowledgements: A. D. Rakić, A. Lu, The University of Queensland, Brisbane, Australia

Why Organic Light Emitting Diodes (OLEDs)?

- Simple and low cost production
- Large area
- Flexible substrates
- OLEDs - high brightness, large viewing angle



Flexible LEDs
(TNO-Holland)

Comparison between OLED and LCD display, Eastman Kodak

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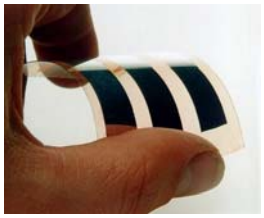
Why organic solar cells?



Flexible photovoltaic diodes (Johannes Kepler University, Linz-Austria)

- Low cost
- Large area
- Improved coverage of solar spectrum

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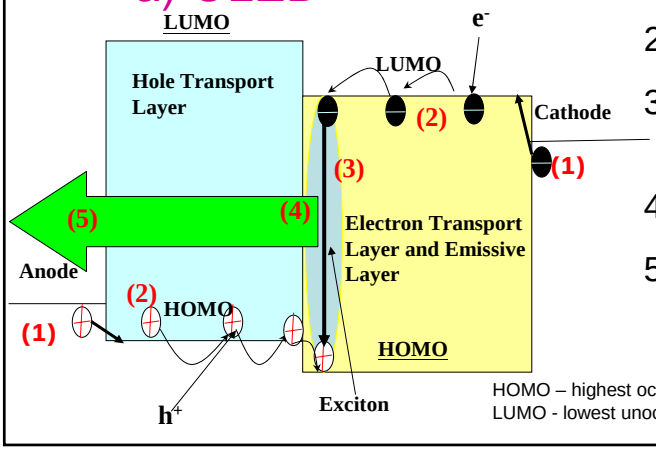
Operating principle

a) OLED



1) Charge injection
2) Charge transport
3) Charge recombination
4) Radiative decay
5) Extraction of photons

HOMO – highest occupied molecular orbital
LUMO - lowest unoccupied molecular orbital

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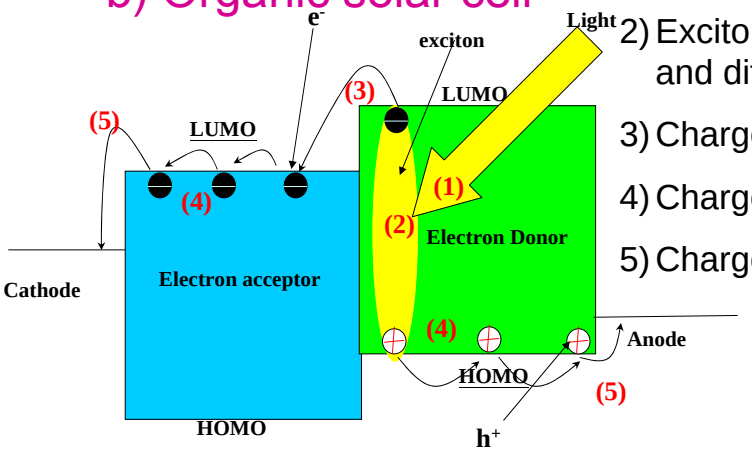
Operating principle

b) Organic solar cell



1) Light absorption
2) Exciton creation and diffusion
3) Charge separation
4) Charge transport
5) Charge collection

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OLEDs – fabrication methods

- Thermal evaporation
  - Properties affected by deposition rate, vacuum level, material purity, etc.

- Solution processing (spin-coating, dip-coating, ink-jet printing etc.)
  - Properties also dependent on process conditions

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OLEDs – device architectures

- Single layer devices
  - Transport: JOURNAL OF APPLIED PHYSICS 98 (6): Art. No. 063709 SEP 15 2005
  - Charge traps: JOURNAL OF APPLIED PHYSICS 99 (6): Art. No. 064509 MAR 15 2006
- Double layer devices
- Devices with doped layers
- Stacked multilayer structures

Review: PHYSICA STATUS SOLIDI A-APPLIED RESEARCH 202 (1): 9-36 JAN 2005

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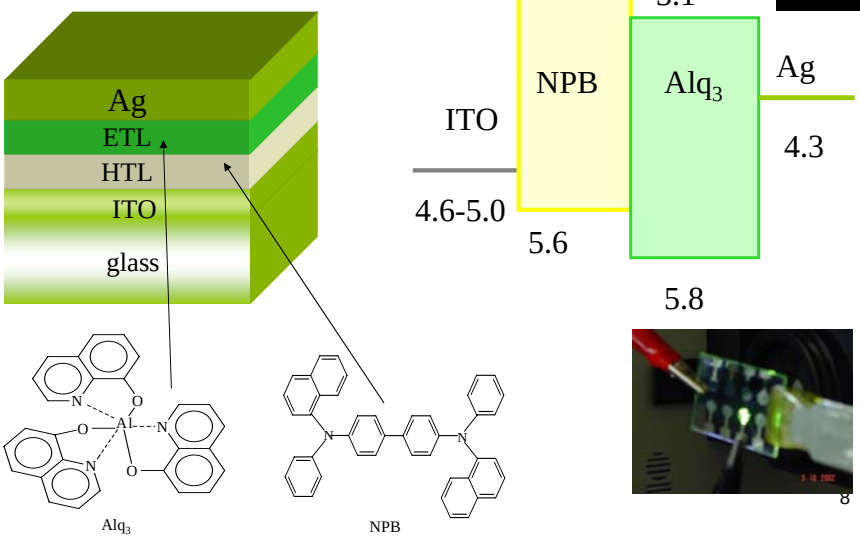
Common OLED device architecture



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OLEDs – design considerations

- Optimizing internal efficiency – material considerations
- Optimizing light extraction efficiency
  - Microcavities
    - APPLIED PHYSICS LETTERS 88 (7): Art. No. 073517 FEB 13 2006, CHEMICAL PHYSICS LETTERS 386 (1-3): 128-131 MAR 1 2004
  - Photonic crystals
    - JOURNAL OF APPLIED PHYSICS 96 (12): 7629-7636 DEC 15 2004
  - Nanopatterning
    - JOURNAL OF CRYSTAL GROWTH 288 (1): 119-122 FEB 2 2006, APPLIED PHYSICS LETTERS 82 (21): 3779-3781 MAY 26 2003
  - Capping layers
    - APPLIED PHYSICS LETTERS 89 (4): Art. No. 043505 JUL 24 2006 , APPLIED PHYSICS LETTERS 88 (15): Art. No. 153517 APR 10 2006, APPLIED PHYSICS LETTERS 88 (11): Art. No. 113515 MAR 13 2006
  - Microlens arrays
    - JOURNAL OF APPLIED PHYSICS 91 (5): 3324-3327 MAR 1 2002, OPTICS EXPRESS 14 (14): 6564-6571 JUL 10 2006
  - Aerogel layers, nanoporous substrates
    - JOURNAL OF APPLIED PHYSICS 96 (3): 1649-1654 AUG 1 2004, ADVANCED MATERIALS 13 (15): 1149+ AUG 3 2001

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Modeling Problems

- Parameters needed for device simulation not known
- Vacuum level shifts, interface dipoles
- More complex device architectures
- Treatment of doped organic layers

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Determination of unknown parameters

- HOMO and LUMO levels – cyclic voltammetry, Ultraviolet Photoelectron Spectroscopy (UPS)
- Mobility – Time-of-flight, Carrier Extraction by Linearly Increasing Voltage (CELIV), Field-effect transistor (FET) measurements
- Fermi level – UPS, Seebeck coefficient measurements

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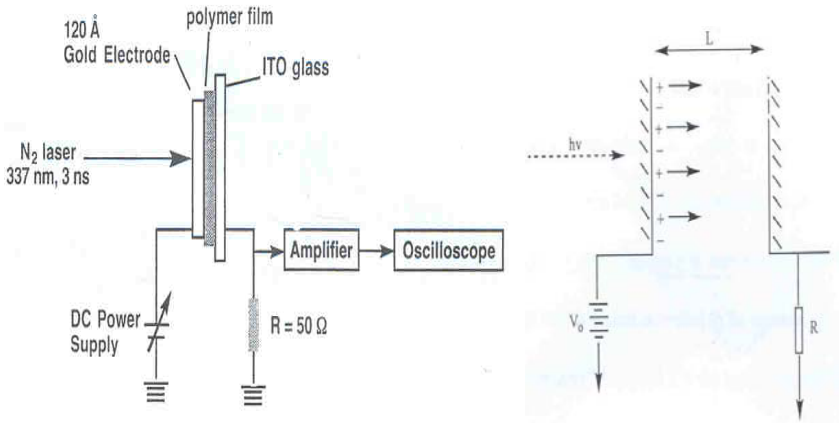
TOF measurement



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Definition of Mobility of Free Charges

$$Mobility \quad (cm^2V^{-1}s^{-1}) = \frac{Drift \quad velocity}{Electric \quad field \quad strength}$$

$$\mu = \frac{V_d}{E} = \frac{L/t_T}{V/L}$$

$$\mu = \frac{L^2}{V \times t_T}$$

μ = mobility of the free charges
V_d = drift velocity of the charges
E = electric field strength
L = distance between electrodes / thickness of film
t_T = transit time
V = voltage applied

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Limitation of time-of-flight (TOF) measurement

- Low mobility materials
- Thicker films (difficult for polymers)
  - Possible solution – lateral architecture JAPANESE JOURNAL OF APPLIED PHYSICS PART 1-REGULAR PAPERS SHORT NOTES & REVIEW PAPERS 43 (4B): 2326-2329 APR 2004
- Dielectric relaxation time > transit time

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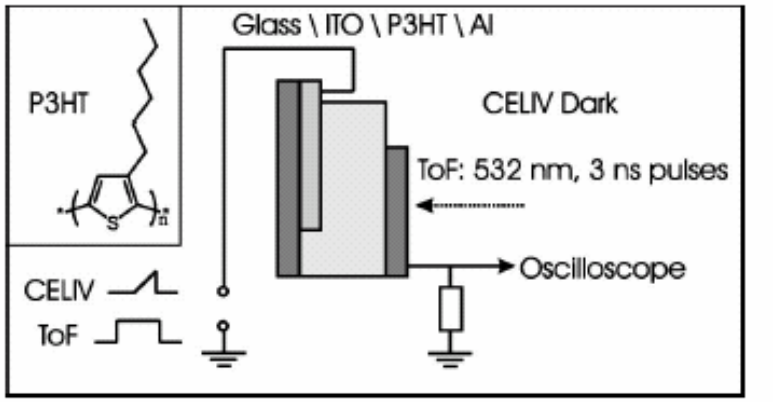
Setup for the TOF / Photo-CELIV measurement



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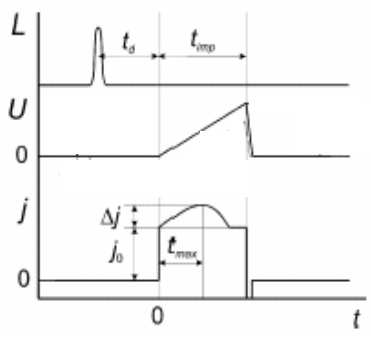
Definition of Mobility of Free Charges



$$\mu\,(cm^2V^{-1}s^{-1}) = \frac{2d^2}{3At_{\max}^2\left(1+0.36\frac{\Delta j}{j(0)}\right)} \quad if \quad \Delta j \le j(0)$$

μ = mobility of the free charges
d = sample thickness
A = voltage increase rate
t_{max} = time to reach maximum extraction current
Δj = extraction current
j(0) = displacement current

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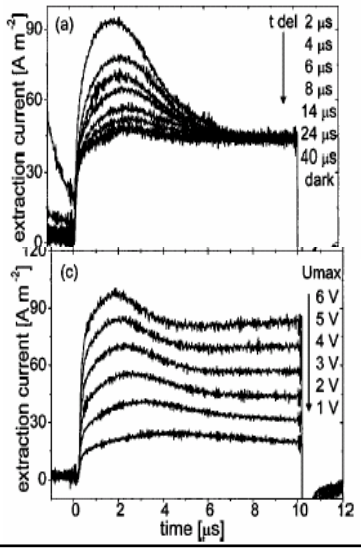
Measured Photo-CELIV curves at various delay times (t_{del}) & various applied voltage (U_{max})



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Advantages of CELIV measurement

- Convenient experimental setup
- Wide applicability to various materials
- Possibility to evaluate mobility of relatively well conducting materials

Disadvantage of CELIV measurement

- Only majority carriers can be studied

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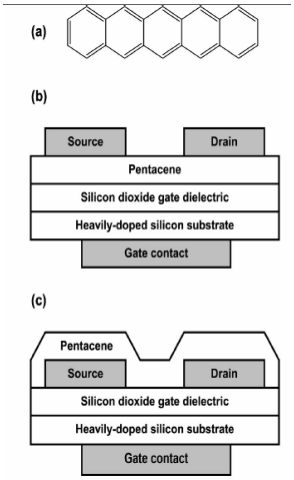
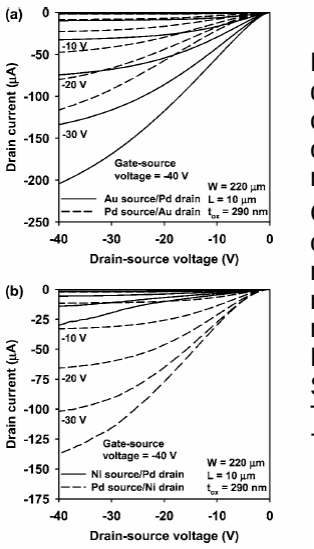
FET mobility





Results dependent on device architecture (top contact vs. bottom contact), contact material and film quality

Consequence: difficult to compare with other methods, no clear relationship with TOF mobility JOURNAL OF PHOTOPOLYMER SCIENCE AND TECHNOLOGY 18 (1): 75-78 2005

JOURNAL OF APPLIED PHYSICS (2): Art. No. 024509 JUL 15 2006

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Vacuum level alignment

- Inorganic/organic junctions
  - Interface dipoles may result in shifts up to 1 eV at organic/metal interfaces JOURNAL OF LUMINESCENCE 87-9: 61-65 MAY 2000; up to 2.1 eV dipole observed APPLIED PHYSICS LETTERS 88 (5): Art. No. 053502 JAN 30 2006
  - Fermi level pinning APL 88, 053502 (2006)
- Organic/organic junctions
  - Vacuum level shift and interface dipoles at interfaces:APPLIED SURFACE SCIENCE 252 (1): 143-147 SEP 30 2005
  - Substrate dependence of the electronic structure of the junction APPLIED PHYSICS LETTERS 88 (23): Art. No. 232103 JUN 5 2006
  - Doping due to mixing at the interface: APPLIED PHYSICS LETTERS 83 (19): 3930-3932 NOV 10 2003

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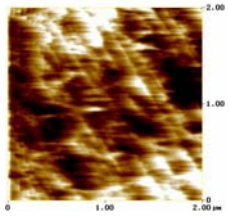
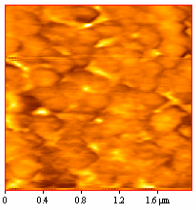
ITO problems

- Lots of variation in properties for ITO obtained from different manufacturers, even different batches from the same manufacturer.
- Very sensitive to deposition conditions and post-deposition treatments





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Problems for optical modeling

- N and k values often unknown
- Accurate thickness determination – step profiler vs. ellipsometry
  - Step profiler problems
    - Creating abrupt step for spin-coated films
    - Underestimation of thickness for some material
  - Ellipsometry problems
    - Transparent substrates
      - Analytical correction
      - Roughening the back of the substrate, different thickness
    - Change of growth modes on different substrates

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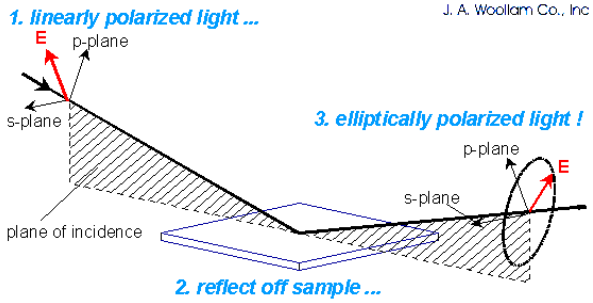
Ellipsometry Basics



- Characterize thin films, surfaces, and material microstructure
- usually determines thickness and optical constant : refractive index (n) and extinction coefficient (k)
- Use polarized light to shine on the sample the determine the relative phase change

$$\rho = \tan(\psi)e^{i\Delta} = \frac{\tilde{R}_p}{\tilde{R}_s}$$

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Modeling the optical functions

- Lorentz model can be used for organic semiconductors, while Lorentz-Drude model is used for PEDOT:PSS, ITO, and metal contacts.
- The Lorentz model can be expressed by the following equation:

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{F_j}{\omega_j^2 - \omega^2 + i\Gamma_j\omega}$$

where $\varepsilon(\omega)$ is the complex dielectric constant as a function of the frequency ω, ε_∞ is the dielectric constant when the frequency of light ω approaches infinity, j is the number of Lorentzian oscillators, and ω_j, F_j, Γ_j are the peak frequency, strength, and damping factor of the jth oscillator, respectively. The Lorentz Drude model is modified from the Lorentz model with ω_0 = 0. The refractive index n and extinction coefficients k can be calculated from $\varepsilon(\omega)$.

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Effective medium approximation (EMA)

- When the sample surface is rough, Bruggeman effective medium approximation (EMA) method needs to be used in the fitting process.
- The EMA model assumes the roughness surface is in spherical inclusion geometry. The mixture of the roughness and voids will be equivalent to a new effective medium layer.

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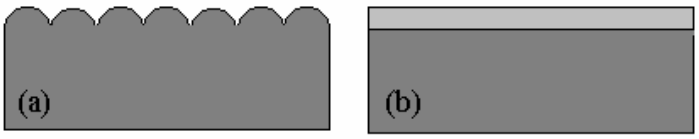
Effective medium approximation (EMA)



(a) A rough surface. (b) An upper layer is called an effective medium layer which is composed of the roughness and voids and the lower layer is the original material.

More complicated model needed to include substrate roughness.
ITO may have non-uniform composition with depth, resulting in optical functions difference.

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Bruggeman EMA model

- In Bruggeman EMA model, the equation showing the relationship between the effective medium, voids and the original material is:

$$f_1 \frac{N_1^2 - N_e^2}{N_1^2 + 2N_e^2} + f_2 \frac{N_2^2 - N_e^2}{N_2^2 + 2N_e^2} = 0$$

where N_1, N_2 and N_e are the index of refraction for the inclusions of types 1, 2 and effective medium, respectively. f_1 and f_2 are the volume fractions of inclusions 1 and 2, repectively.

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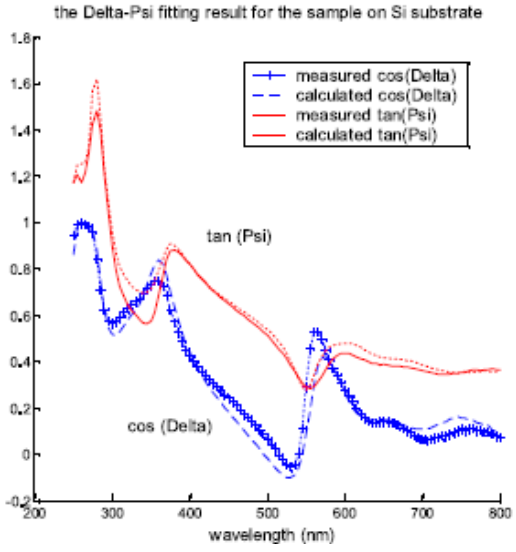
Goodness of fit without EMA method



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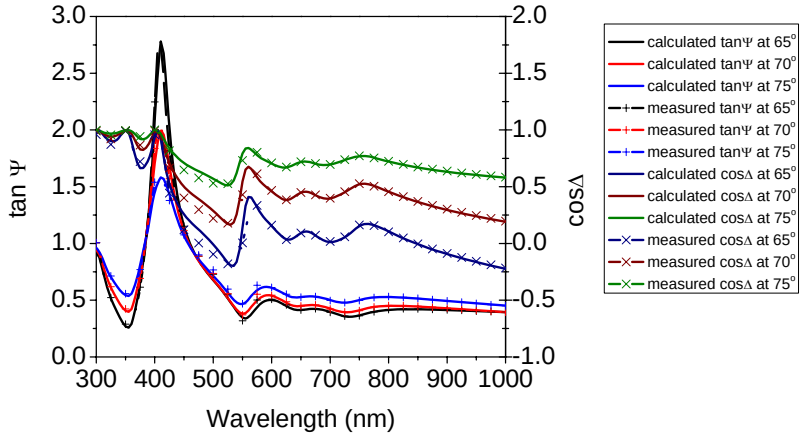
Goodness of fitting with EMA method



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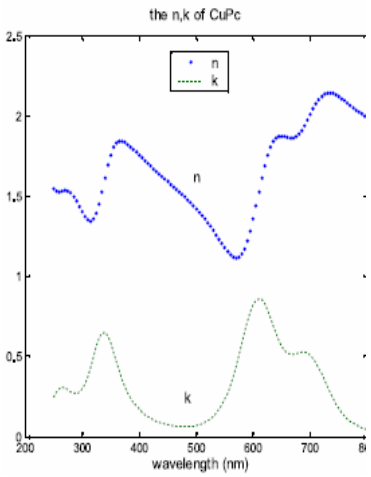
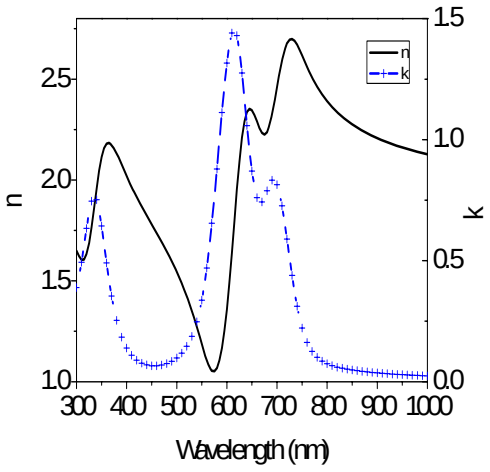
n and k of CuPc





EMA method was used

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Evaluate the fitting

- Compare experimental data with calculated data.
- How low is the MSE (mean squared error)? Can it be reduced further by increasing model complexity?
- Are fit parameters physical?
- There should be no zero or negative thickness values
- K can not be negative.

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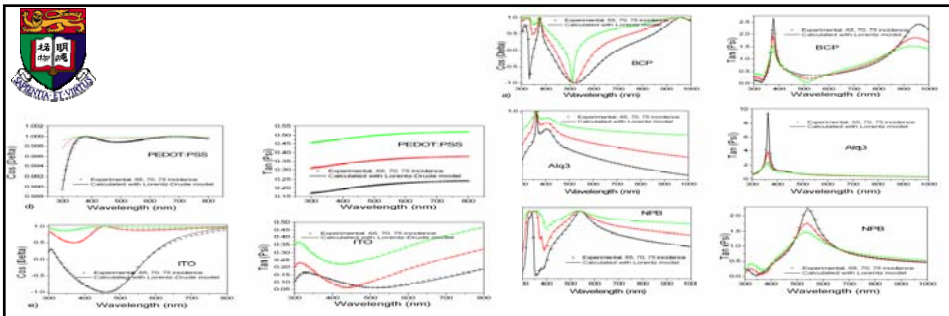

Figure 1. *The fitting results of the spectroscopic ellipsometry data for (a)BCP, (b)Alq$_3$, (c)NPB, (d)PEDOT:PSS and (e)ITO samples: (left) the calculated and experimental data of the cosΔ, (right) the calculated and experimental data of the tanψ*

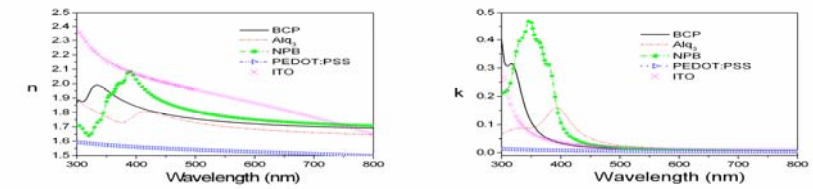

Figure 2. *The refractive index n and extinction coefficients k of BCP, Alq$_3$, NPB,PEDOT:PSS and ITO obtained by fitting the SE data.*

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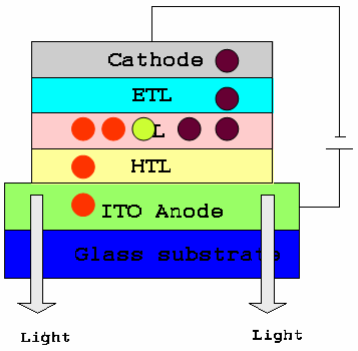
OLED Electrical Model

- Injection via
  - Tunneling
  - Thermionic injection
- Transport via
  - Carrier hopping
  - (due to material disorder)
- Recombination via
  - Carrier recombine to form exciton
  - Exciton decay leading to radiative emission



Bottom-emitting device

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Electrical Models – Silvaco Simulator

- Standard carrier transport model
  - One dimension Time-independent drift and diffusion model
  - Continuity equation
  - Poisson's equation
  - Schottky barrier with dipole lowering effect
- Carrier transport and recombination
  - Mobility – field dependent (Poole-Frenkel)
  - Carrier recombination – optical only (Langevin)
  - Exciton diffusion and emission

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Electrical Models – Equations

Continuity equation

- n=electron p=hole
- μ_n, μ_p = e-, hole mobility
- *Dn*, *Dp* = diffusion constants
- R = recombination rate

$$\frac{d}{dx}(-\mu_n n\frac{d\psi}{dx} + D_n\frac{dn}{dx}) = R$$

$$\frac{d}{dx}(\mu_p p\frac{d\psi}{dx} + D_p\frac{dp}{dx}) = R$$

Poisson's equation

- $\varepsilon_r\varepsilon_o$ = permittivity of material
- N_D, N_A = donor, acceptor concentrations

$$\frac{d^2\psi}{dx^2} = -\frac{e}{\varepsilon_r\varepsilon_o}[p(x) - n(x) + N_D - N_A]$$

Schottky barrier with dipole lowering effect

- ϕ = barrier height for e-, hole
- E_g = bandgap energy
- χ_c = affinity of organic material

$$\phi_{bn} = (\phi_m - \chi_c)$$

$$\phi_{bp} = (E_g - \phi_{bn}) = E_g - (\phi_m - \chi_c)$$

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Electrical Models – Equations

Field dependent Poole-Frenkel Mobility

- $\mu_{n,po}$ = zero field mobilities
- E_0 = characteristic field
- *E* = electric field

$$\mu_n(E) = \mu_{n0}\exp\left[\sqrt{\frac{E}{E_0}}\right]$$

$$\mu_p(E) = \mu_{p0}\exp\left[\sqrt{\frac{E}{E_o}}\right]$$

Optical Langevin recombination

- μ_R = effective recombination mobility (i.e. the larger or e- or hole mobility)

$$R_{opt} = \gamma(pn - n_i^2)$$

$$\gamma = \frac{4\pi e\mu_R}{\varepsilon_r\varepsilon_0}$$

Exciton diffusion and emission

- *F* = fraction of singlets formed
- *S(x)* = singlet exciton density along x
- τ = exciton lifetime
- D_s = singlet diffusion constant

$$\frac{dS}{dt} = F.R.n.p$$

$$-\frac{S}{\tau} + \nabla(D_s\nabla S)$$

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Silvaco – Method of Implementation

- Define Structure
  - Set Mesh
  - Define regions
  - Electrode
  - Amount of doping
- Specify Materials
  - Parameters
  - Contacts
  - Interface
- Select Numerical Method
- Solve and Extract Solution

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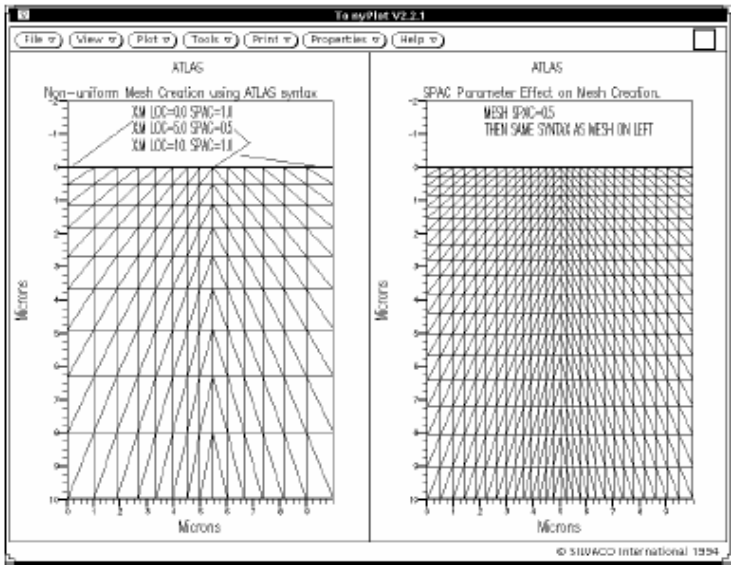
Silvaco Simulator – Mesh Grid



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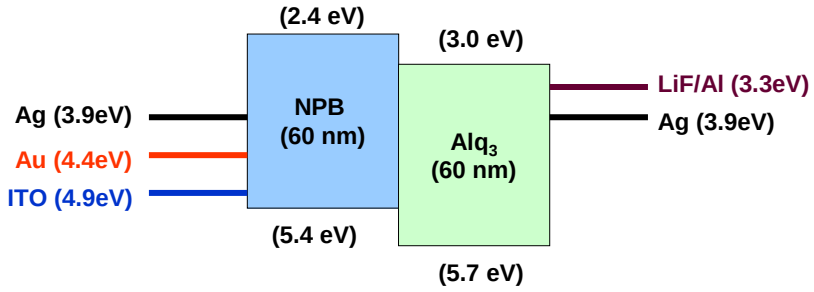
Electrical Models – Parameters Used



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Parameters	NPB	Alq
Relative Permittivity	3.0	3.0
μ_{no} (cm^2/ Vs)	6.1E-6	1.9E-6
μ_{po} (cm^2/ Vs)	6.1E-4	1.9E-8
E_0 (V/cm)	4.44E5	7.1E4
N_c(cm^{-3})	1E21	1E21
N_v(cm^{-3})	1E21	1E21
N_A(cm^{-3})	1E9	--
N_D(cm^{-3})	--	1E9
E_g (eV)	3.0	2.7
χ_c (eV)	2.4	3.0

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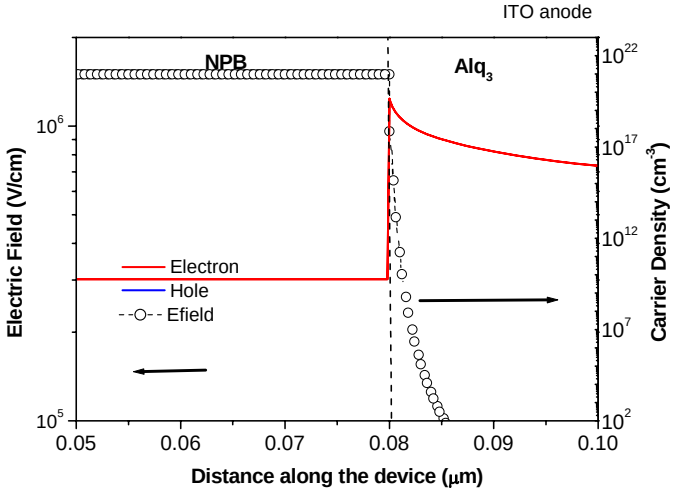
Results – Typical Device with LiF/Al Cathode and ITO anode



Quartz(1mm)/ITO(125nm)/NPB(60nm)/Alq3(60nm)/LiF(0.5nm)/Al(70nm)

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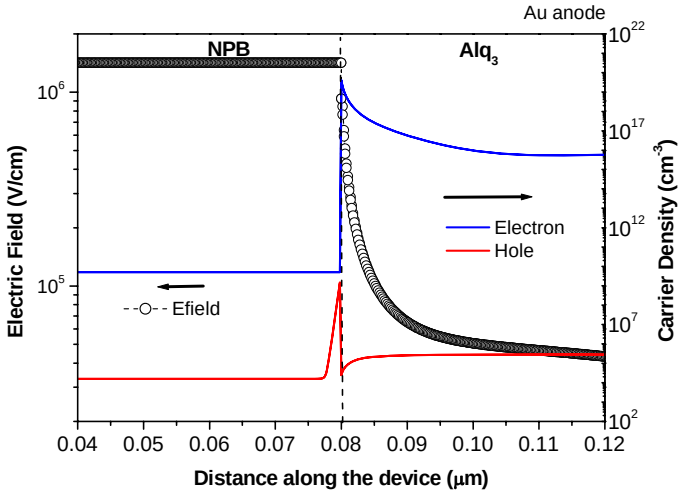
Results – LiF/Al Cathode and Au Anode



Quartz(1mm)/Au(20nm)/NPB(60nm)/Alq3(60nm)/LiF(0.5nm)/Al(70nm)

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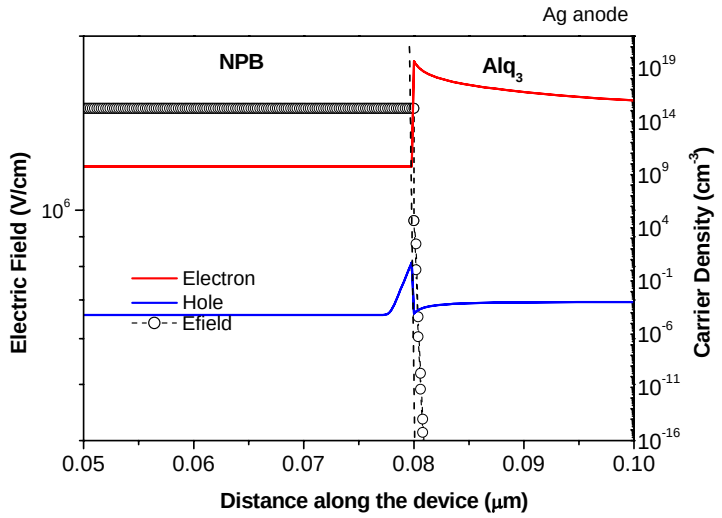
Results – LiF/Al Cathode and Ag Anode



Quartz(1mm)/Ag(20nm)/NPB(60nm)/Alq3(60nm)/LiF(0.5nm)/Al(70nm)

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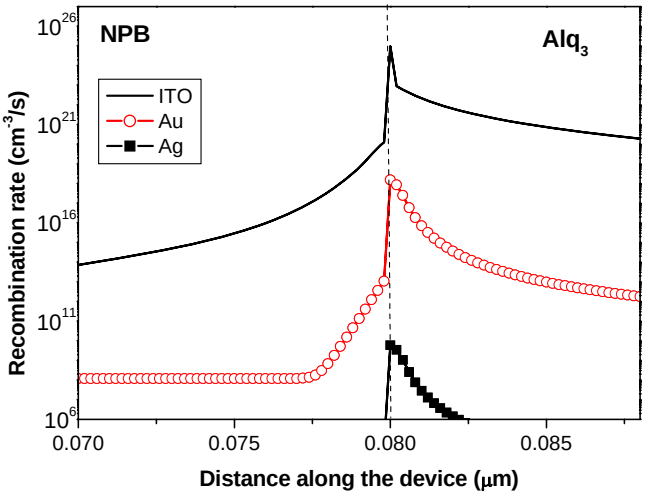
Recombination Rate



Quartz(1mm)/Anode/NPB(60nm)/Alq3(60nm)/LiF(0.5nm)/Al(70nm)

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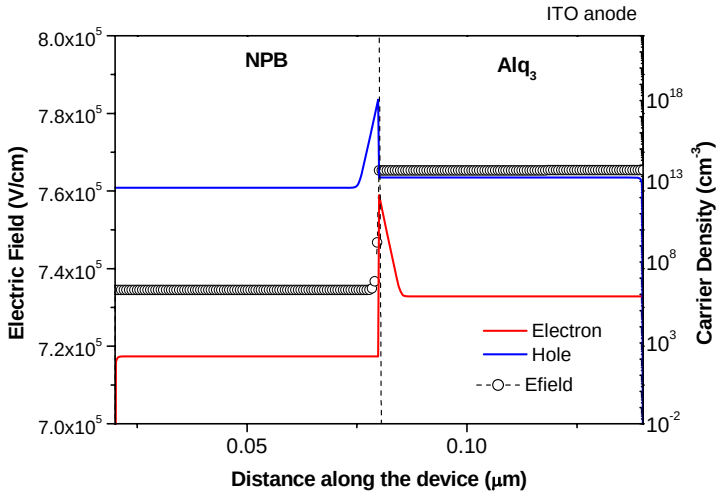
Results – ITO anode and Ag Cathode



Quartz(1mm)/ITO(125nm)/NPB(60nm)/Alq3(60nm)/Ag(70nm)

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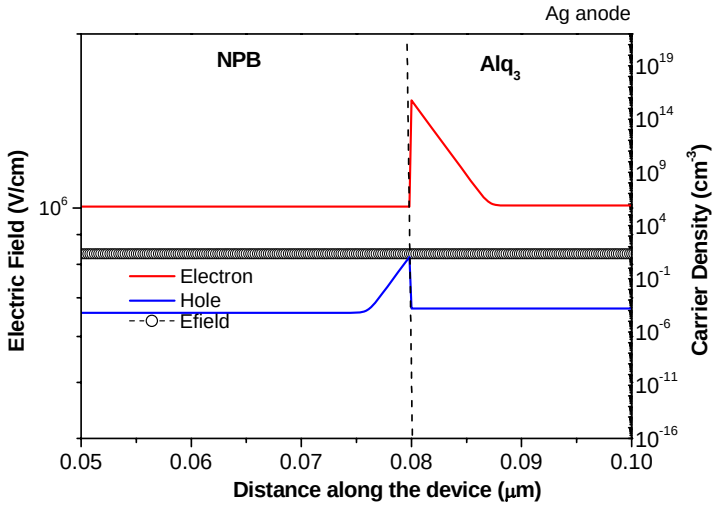
Results – Ag anode and Ag Cathode



Quartz(1mm)/Ag(20nm)/NPB(60nm)/Alq3(60nm)/Ag(70nm)

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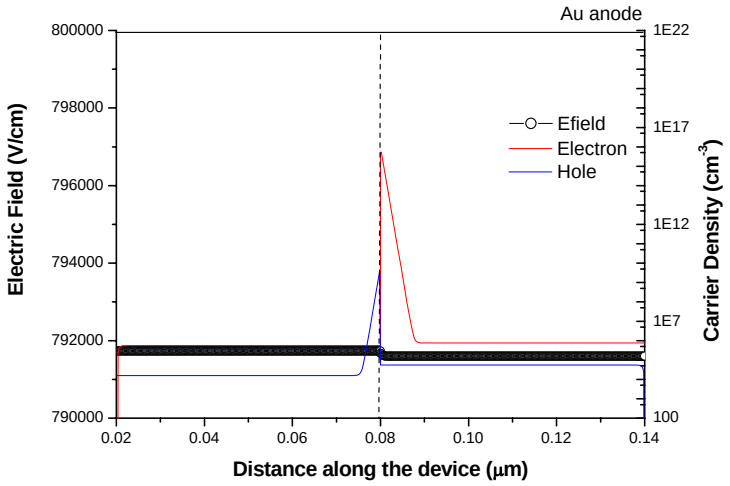
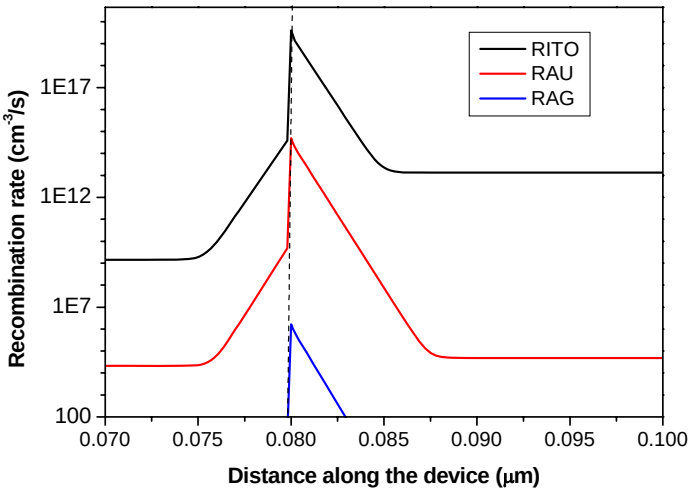
Results – Au anode with Ag Cathode



Quartz(1mm)/Ag(20nm)/NPB(60nm)/Alq3(60nm)/Ag(70nm)

47

Recombination Rate



Quartz(1mm)/Anode/NPB(60nm)/Alq3(60nm)/Ag(70nm)

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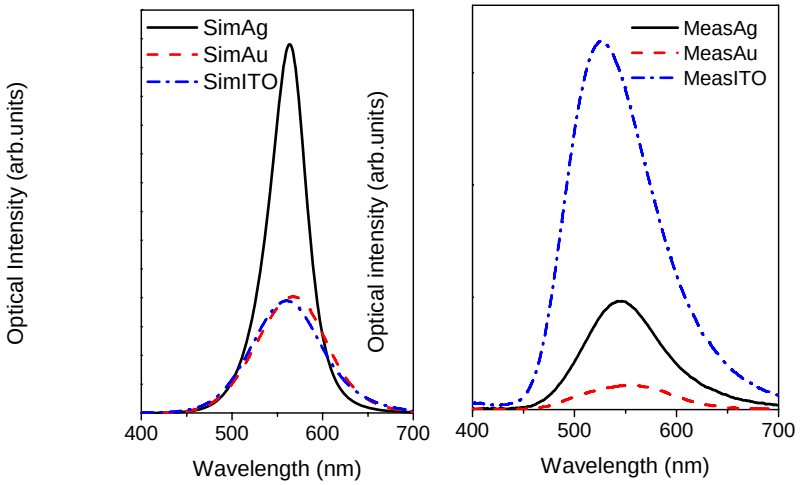
Optical model predictions



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Optical Simulation

- Modified spontaneous emission is a consequence of coupling between excitons and internal EM field.
- The typical OLED can be treated as organic layers sandwiched between two mirrors (which are the cathode and anode)
- The presence of Microcavity modifies the field distribution and thus the spontaneous emission
- Thus optical model is required to calculate the modified spontaneous emission
- We present two analytic models that are used widely

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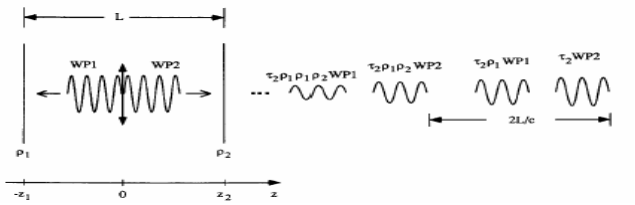
Optical Model 1 – Wave Packet Summation
(Dodabalapur's model)

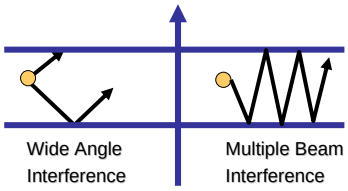
- Developed by Deppe et al. in 1994
- Later extended to multi-layers by Dodabalapur et al.
- Basically apply summation of the partially reflected and transmitted wave packets, then apply FT to obtain spectrum
- Simple, popular
- Does not handle high viewing angles well
- Deppe et al. solved this problem using both the
  - Quantum electro-dynamics
  - Classical electro-magnetic
  - Yielding same results
- Showing equivalence between power radiated by dipole antenna and probability of photon emission
- Assumes T=(1-R) in the emitting side mirror



Deppe et al, "Spontaneous Emission from Planar Microstructures", J. Mod. Opt., vol. 41, 325-344, 1994

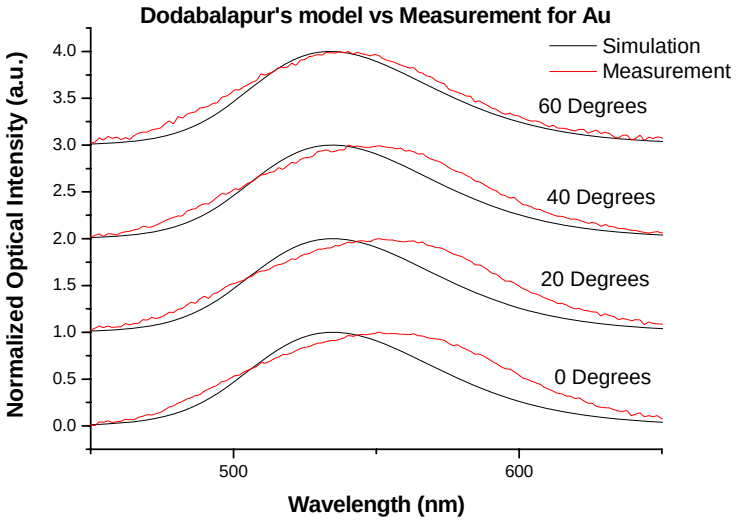
Optical Model 2 – Dipole Radiation in Microcavities
(Neyts' model)

- First developed by Lukosz [J. Opt. Soc. Am., 1977],
  - calculated dipole emission close to a plane interface
- Neyts et al. extended the method for multi-layers [J. Opt. Soc Am. 1998]
- More complex, but handles viewing angle dependence better
- Used extensively in recent works
- Had been shown to match measured results relatively well *for weak microcavities*



- Takes both the wide angle and multiple beam interference into account

Results for Model 1 – Dodabalapur's Model



Quartz(1mm)/Au(20nm)/NPB(60nm)/Alq3(60nm)/LiF(0.5nm)/Al(70nm)

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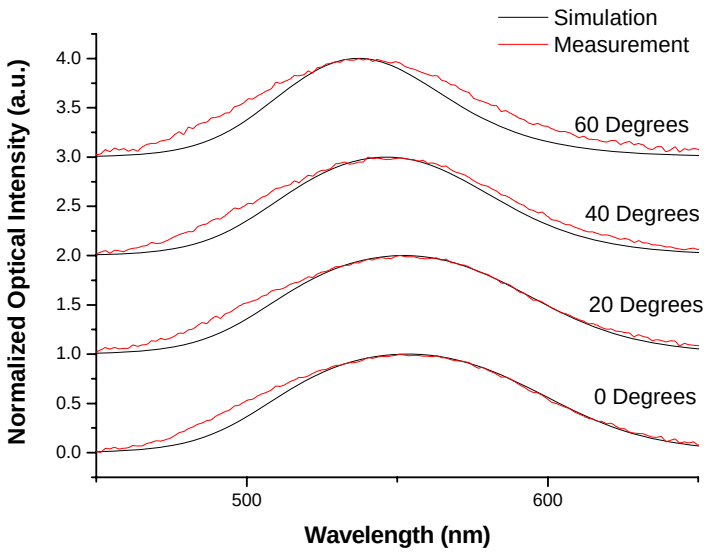
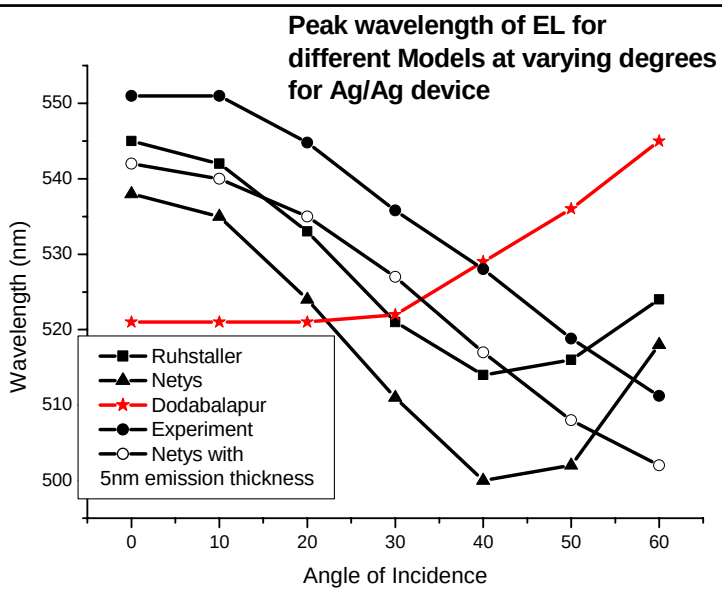
Results for Model 2 – Neyts' Model



Quartz(1mm)/Au(20nm)/NPB(60nm)/Alq3(60nm)/LiF(0.5nm)/Al(70nm)

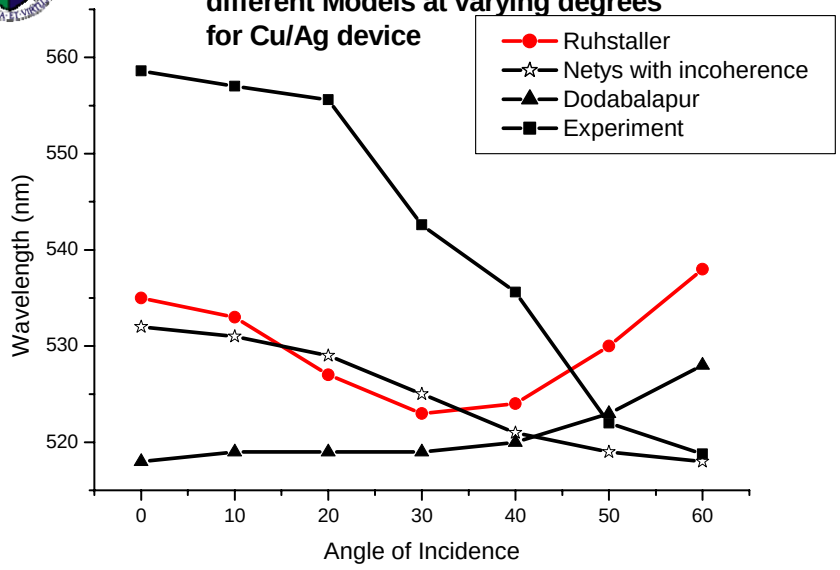
54



Quartz(1mm)/Ag(20nm)/NPB(210nm)/Alq(50nm)/Ag(70nm)

Ruhstaller - ETFOS Emissive Thin Film Optics Simulator, Center for Computational Physics, Switzerland, www.ccp.zhwin.ch, (2004)

55



Quartz(1mm)/Cu(25nm)/NPB(210nm)/Alq(50nm)/Ag(70nm)

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Comparison Between the Two Optical Models

- Though both models are quite accurate, Neyts' model depicts the characteristics of the microcavity better
  - Spectral peak perfectly matched
  - Shift of spectral peak with respect to viewing angle matched
- Dodabalapur's model has very limited spectral shift with respect to viewing angle change
  - Wouldn't describe microcavity OLEDs with metallic mirrors very well
  - This confirms that Neyts' model has superior angular characteristics

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Summary-OLEDs

- Accurate electrical modeling is crucial for device design
- The energy level alignment is very important
- Optical modeling can predict ways to improve extraction efficiency, but the use of metal mirrors without interface modification may be problematic

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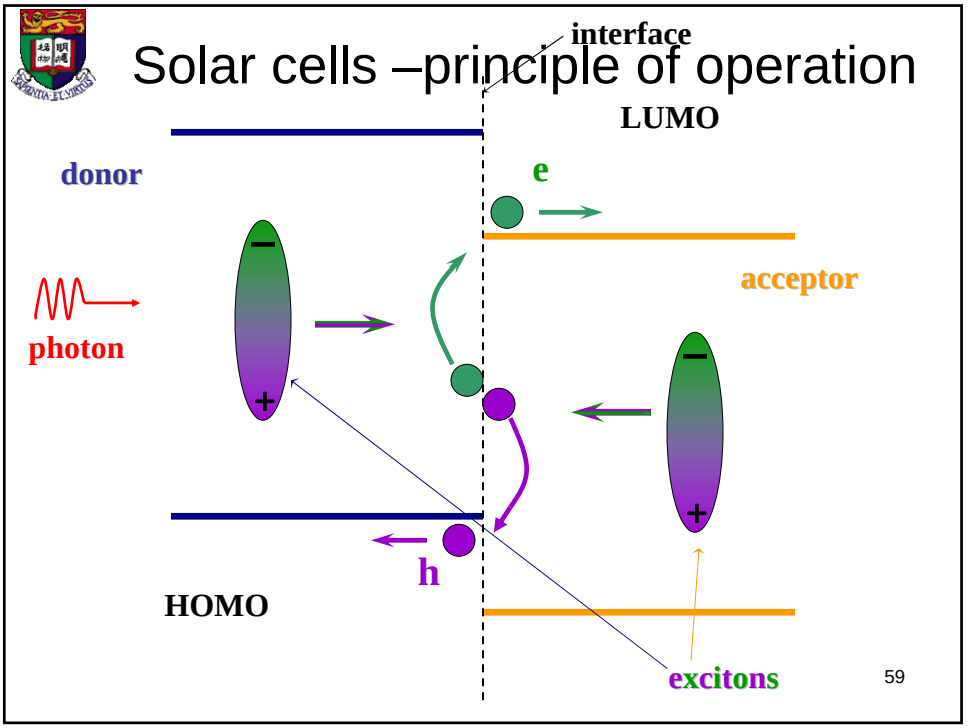
Solar cells –principle of operation



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Solar cells – device architectures

- Schottky barrier (single-layer) cells
- Bilayer and multilayer devices
- Bulk heterojunction devices
- Dye-sensitized solar cells
- Hybrid organic-inorganic solar cells

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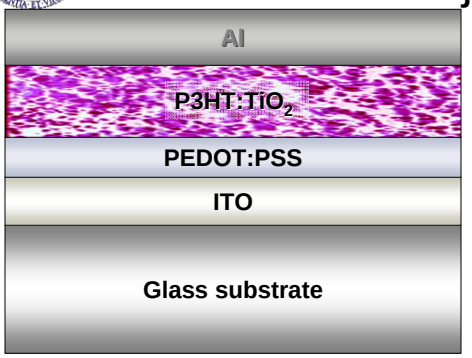
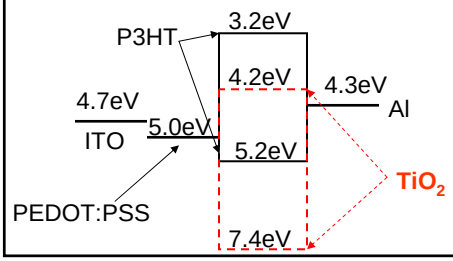
Solar cells – example of a hybrid bulk heterojunction cell





Chem. Phys. Lett. 384 (4-6) pp. 372-375 (2004).

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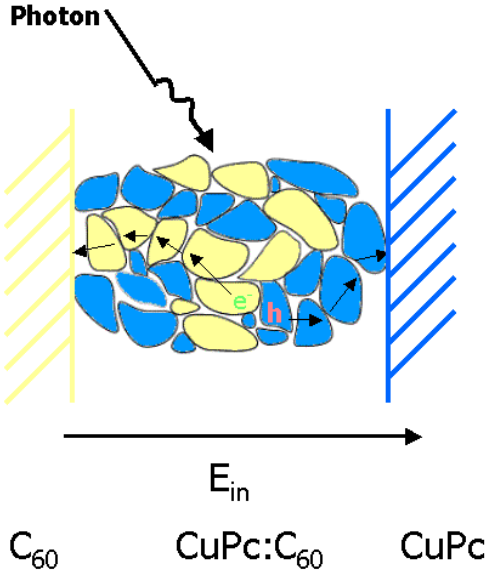
Bulk heterojunctions

- **Random arrangement of p- and n-type molecules in the mixed layer generates large interface for exciton dissociation**
- **Resistance of mixed layer cell is much smaller when compared to p-n junction solar cell.**
- **Large current density can be obtained.**



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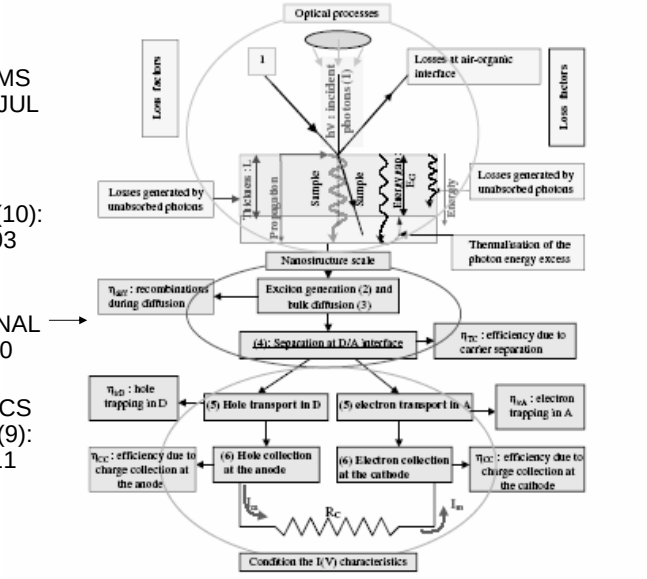
Solar cell modeling

THIN SOLID FILMS 511: 214-218 JUL 26 2006

JOURNAL OF APPLIED PHYSICS 99 (10): Art. No. 104503 MAY 15 2006

POLYMER INTERNATIONAL 55 (6): 583-600 JUN 2006

APPLIED PHYSICS LETTERS 88 (9): Art. No. 093511 FEB 27 2006



Organic Solar Cell Electrical Simulation using Silvaco

Involves two steps

1. Optical ray racing
   - Solar spectrum is constructed
   - Refractive index used to calculate optical intensity at each grid point
2. Light absorption model
   - Photon absorption model and carrier mobility model coupled to give new carrier concentration at each grid point
   - Extinction coefficient required

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Models used

- Similar to OLED simulation
- Standard carrier transport model
  - One dimension Time-independent drift and diffusion model
  - Continuity equation
  - Poisson's equation
- Carrier transport
  - Mobility – field dependent (Poole-Frenkel)
- Light Absorption
  - Photo generation model
  - Shockley-Read-Hall generation/recombination model

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Models used - equations

- Standard carrier transport model same as OLEDs
- Poole-Frenkel Mobility same as OLEDs
- Shockley-Read-Hall generation/recombination model
  - E_{trap} = difference between trap energy and Fermi energy
  - T_L = lattice temperature
  - τ_n , τ_p = carrier lifetimes

$$R_{SRH} = \frac{pn - n_{ie}^2}{\tau_p[n + n_{ie}e^{(E_{trap}/kT_L)}] + \tau_n[p + n_{ie}e^{(-E_{trap}/kT_L)}]}$$

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Models used - equations

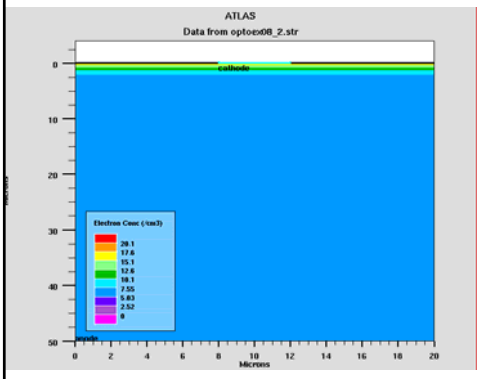
- Photo generation model
  - P* = effect of transmission, reflection and absorption over ray path
  - η_o = carrier pairs generated per photon
  - y = relative distance for ray in question
  - h = Planck's constant
  - λ = wavelength
  - C = speed of light
  - α = absorption coefficient

$$G = \eta_o \frac{P^* \lambda}{hc} \alpha e^{-\alpha y}$$

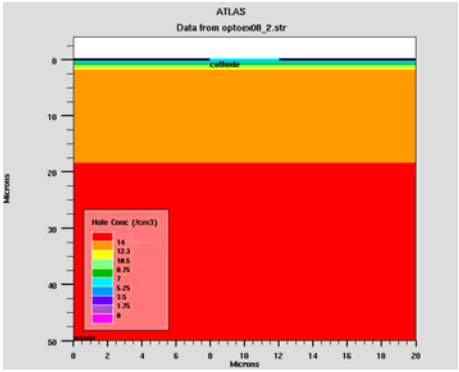
Parameters Calculated

- Junction characteristic
  - Open Circuit Voltage
    Define >1 contact as current controlled then set zero current
  - Short Circuit Current
    Define contact as voltage dependent and apply zero bias
- Light absorption rate distribution in device
- Spectral characteristic
  - Available photo current vs. wavelength
  - Source photo current vs. wavelength
  - Cathode current vs. wavelength

Electron distribution



Hole distribution



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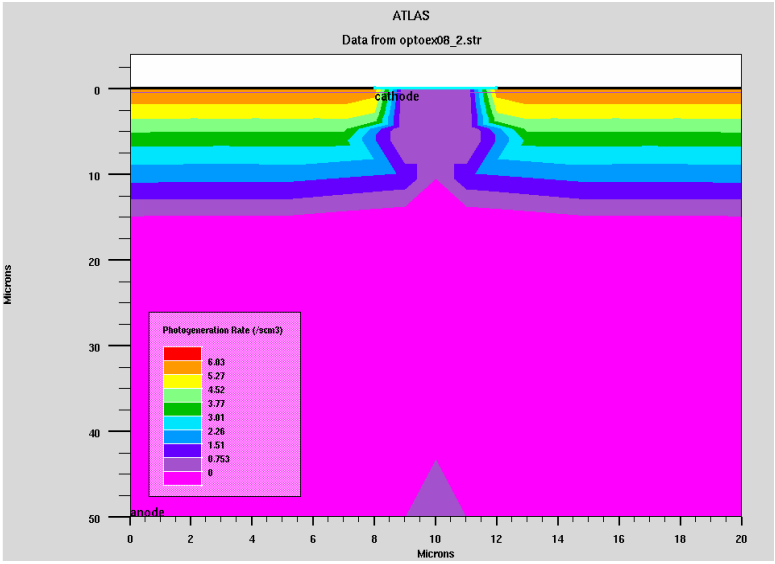
Photogeneration Rate (i.e. Light absorption)



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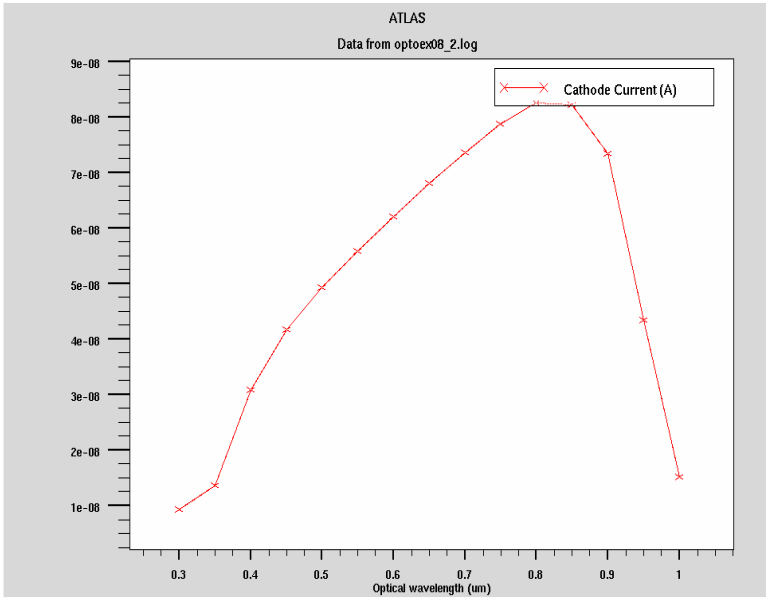
Cathode current vs. wavelength



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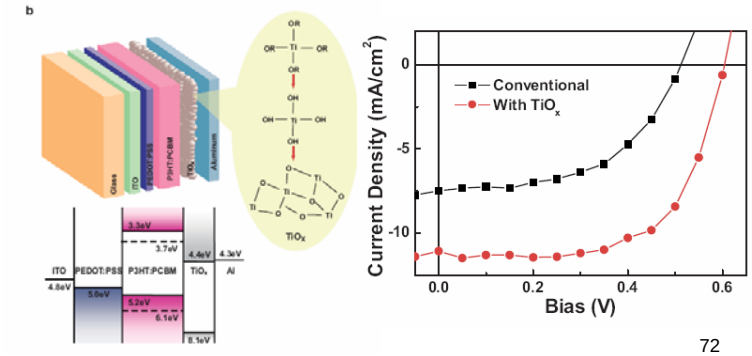
Solar cells-summary

- Less well established compared to OLED modeling
- Great potential – optimizing the cell by insertion of spacer layer to ensure maximum absorption by an active layer
- Example: ADVANCED MATERIALS 18 (5): 572+ MAR 3 2006



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