Innovative Characterization of Amorphous and Thin-Film Silicon for Improved Module Performance

J. David Cohen

Department of Physics and Materials Science Institute
University of Oregon, Eugene, OR 97403

Relevance/Objective

Support the development of two thin-film technologies

1. Thin Film Silicon-Based Devices

- Characterize the electronic properties of nanocrystalline silicon to help optimize for bottom cell component in multijuction cells.
- Aid in developing better high deposition rate materials, particularly the amorphous silicon-germanium alloys
- Understand mechanisms of light-induced degradation

2. Copper Indium Di-Selenide Based Devices

- Identify factors limiting performance of commercial devices relative to high performance laboratory cells

A. Technical Focus of Recent Activities

1. Evaluate the effects of oxygen contamination on the electronic properties of high quality NREL hot-wire CVD amorphous silicon-germanium alloys
2. Examine the electronic properties of United Solar nanocrystalline silicon, their relationship with cell performance, and their light-induced degradation.
3. Examine correlations between the electronic properties of high performance NREL CIGS materials and associated cell performance.*

* Not to be included in this presentation due to lack of time

B. Participants in Recent Activities

University of Oregon Personnel:

Name	Primary Activity in Current Period
J. David Cohen	Program Manager
Shouvik Datta Research Associate	Studies of NREL HWCVD amorphous silicon-germanium alloys
Peter Hugger Research Assistant	Evaluation of USOC nanocrystalline silicon materials
Pete Erslev Research Assistant (part-time)	Electronic properties of $Cu(In,Ga)Se_2$ materials in NREL laboratory cells

Thin-Film Partnership Collaborators:

Organization	Primary Personnel Involved
NREL	Yueqin Xu, A.H. Mahan, Howard Branz, Miguel Contreras, Rommel Noufi
United Solar Ovonic	Baojie Yan, Jeffrey Yang, Subhendu Guha

C. Experimental Methods Employed

I. Transient Photocapacitance Spectroscopy

A type of sub-band-gap optical absorption spectroscopy

Discloses: Band-tail distributions, deep defect distributions and properties, minority carrier transport

II. Admittance/Drive-level capacitance profiling

Discloses: Majority carrier density, majority carrier mobility, deep defect densities and their capture cross sections

Comparison of Sub-band-gap Optical Spectroscopies

Method	Detected Quantity	Disadvantages
Direct	Transmitted/Reflected Light	Not Sensitive enough for thin films
Photothermal Deflection (PDS)	Absorbed Energy	Dominated by surface defects for low bulk defect samples
Constant Photo-current Method (CPM)	Carriers Photoexcited into Majority Band	Carrier mobility influences spectra; Dominant current path may not reflect internal bulk properties
Photoemission	Electrons ejected into vacuum	Very surface sensitive
Photocapacitance Spectroscopy	Photoexcited released charge from depletion region	Requires reasonably good barrier junction, moderate conductivities

This last method is thus naturally suited for examining sub-band-gap optically induced defect transitions within photovoltaic devices.

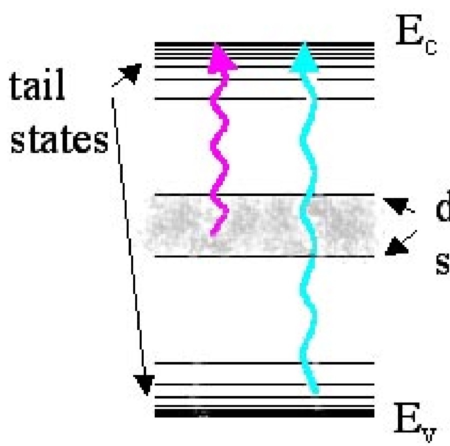
Photocapacitance Spectra for Disordered Semiconductors

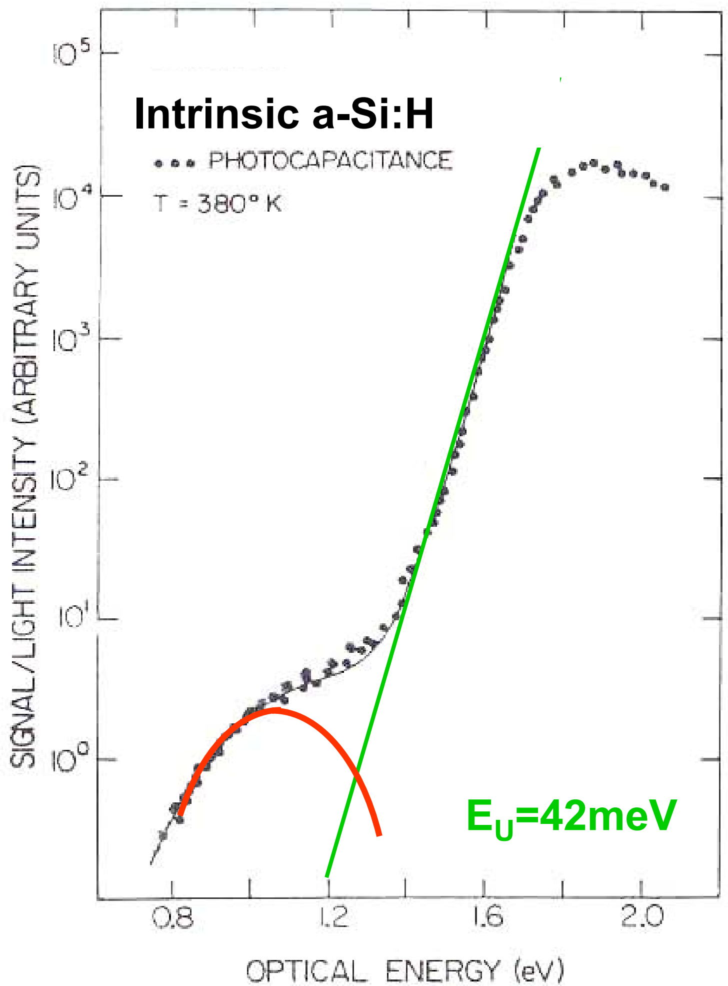
Gelatos, Mahavadi, Cohen, and Harbison, Appl. Phys. Lett (1988)

Two Primary Features:

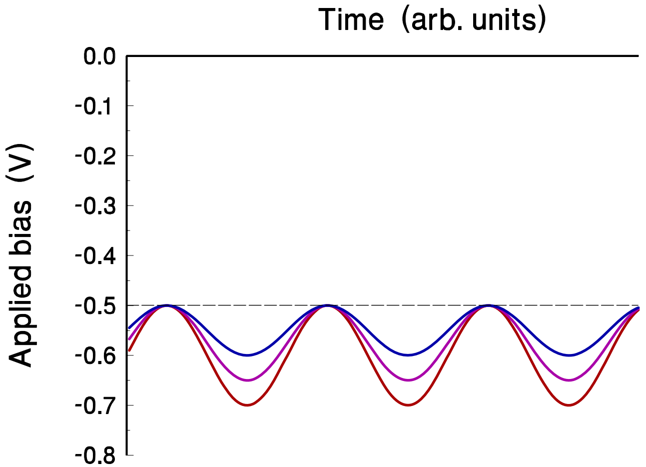
(1) **Exponential "Urbach" Tail.** $g(E) \propto \exp(E/E_U)$ where E_U indicates degree of disorder

(2) **Dominant Deep defect band.** Usually well fit to a Gaussian distribution of transitions

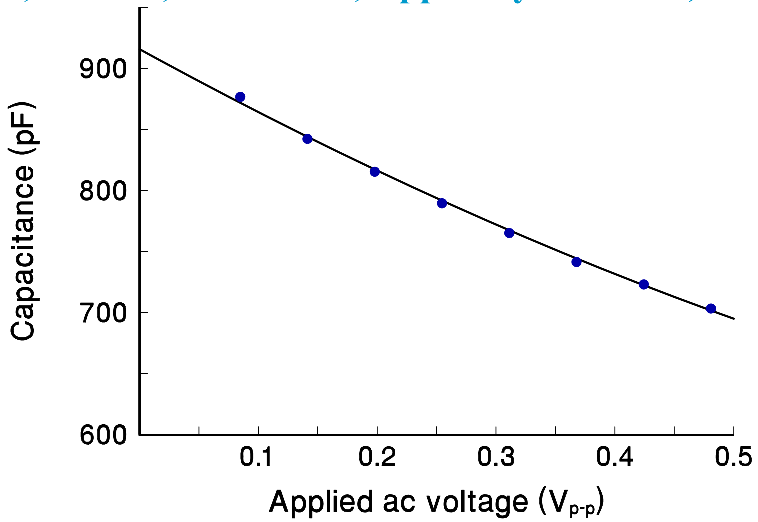




Drive level capacitance profiling (DLCP)



Michelson, Gelatos, and Cohen, Appl. Phys. Lett. 47, 412 (1985).



- **Junction capacitance is determined as a function of the frequency and the amplitude of the applied oscillatory voltage.**

$$C = C_0 + C_1\delta V + C_2\delta V^2 + \ldots$$

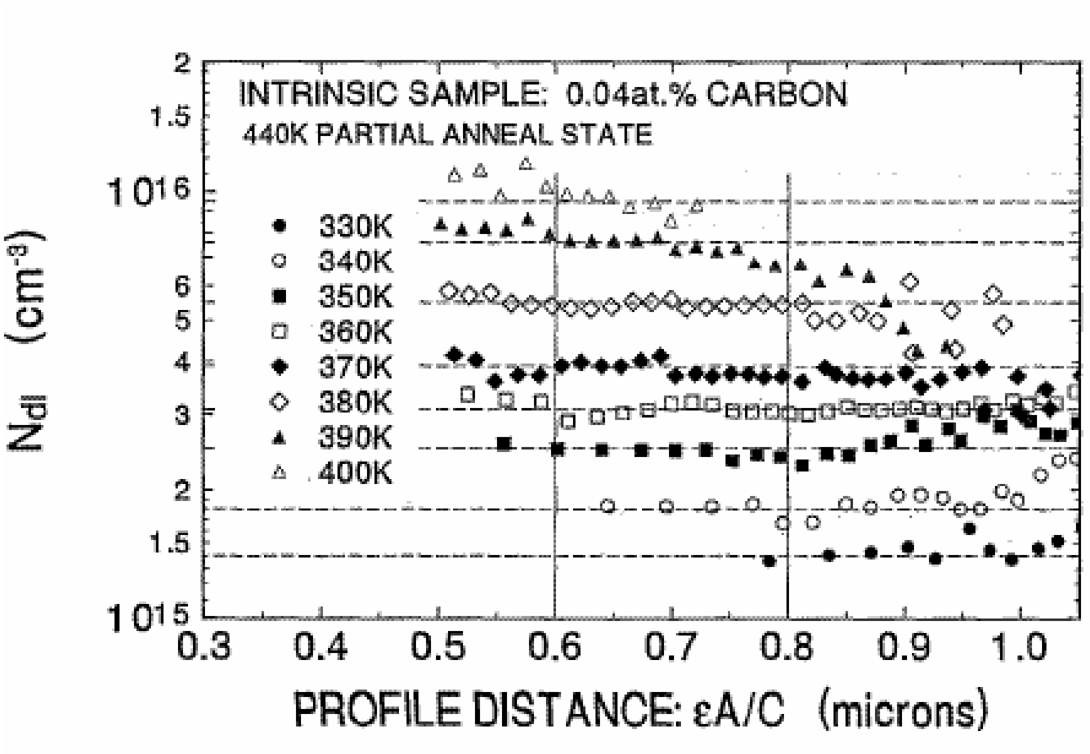
- **One obtains a direct integral over defect states down to an emission cutoff energy, E_e:**

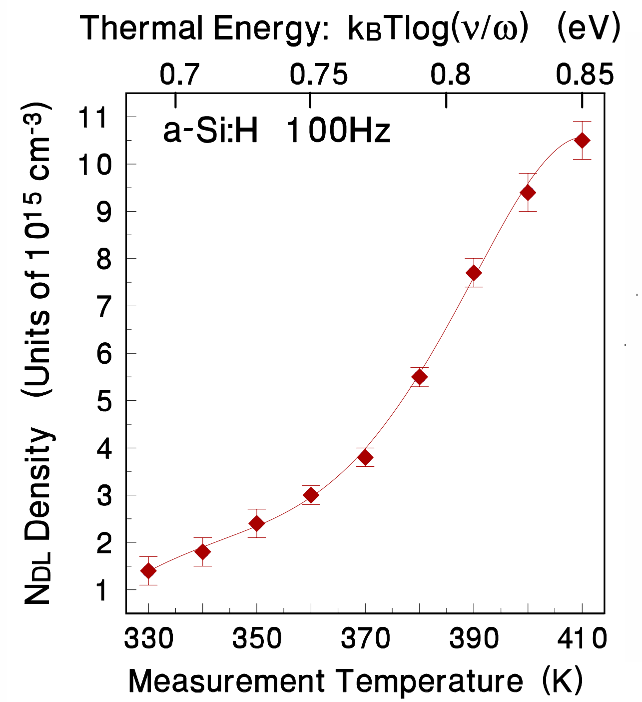
$$N_{DL} = -\frac{C_0^{\,3}}{2q\varepsilon A^2 C_1} = n + \int_{E_C - E_e}^{E_F} g(E,x)\,dx$$

- **Procedure is then repeated at different dc bias to produce spatial profile.**

$$E_e = k_B T \log(\nu/\omega)$$

Drive-level Profiles for Amorphous Silicon Sample





We infer a broad deep defect about 0.8eV below E_C of density ~ 1.5 x 10^{16} cm^{-3}

$$N_{DL} = -\frac{C_0^{\ 3}}{2q\varepsilon A^2 C_1} = n + \int_{E_C - E_e}^{E_F} g(E,x)dx \approx \int_{E_C - E_e}^{E_F} g(E,x)dx$$

where $E_e = k_B T \ln(\nu/\omega)$

Expenditures: October 2005 to January 2007

Project Task(s)	Total Value
High growth rate a-Si,Ge:H alloys	**40%** (~$90K)
Nanocrystalline Si films and devices	**40%** (~$90K)
CIGS electronic properties vs. devices	**20%** (~$40K)
Grand Total over 16 months	~$220K

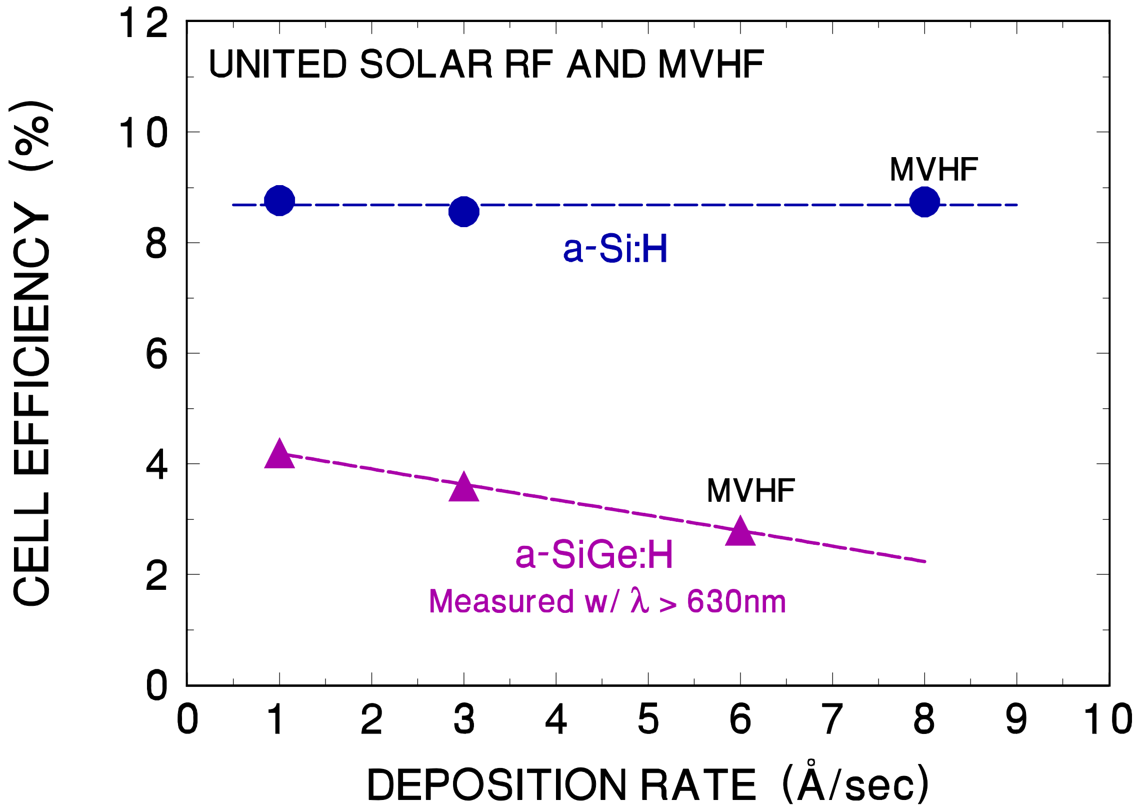
(1) HWCVD Amorphous Silicon-Germanium Alloys

With Yueqin Xu, Harv Mahan, and Howard Branz NREL

- *Background*: Need for higher deposition rate a-Si,Ge:H material
- Improved Hot-Wire CVD Deposited a-Si,Ge:H seems promising
- Loss of Optimum Properties Due to Oxygen Contamination?
- Results on 2006 Sample Series with Controlled Oxygen Leak

Critical Need: a-SiGe:H Cells at Higher Growth Rates

- United Solar devices – All in Light Degraded State
- Specular Stainless Steel -- No back reflector



Electronic Properties of High Growth Rate Materials

Cell performance deteriorates as growth rate is increased, and this appears to be uncorrelated with deep defect densities

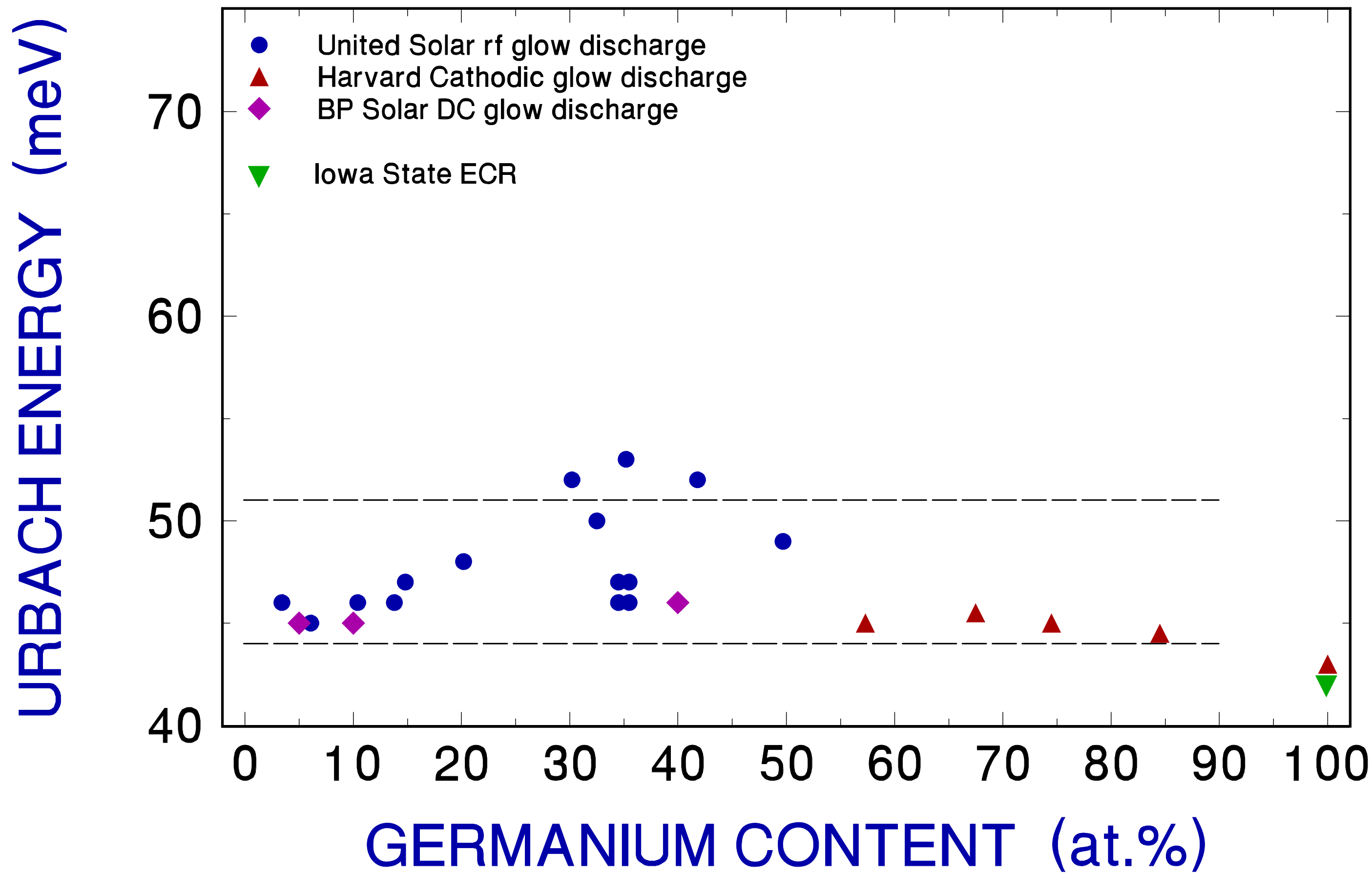
Higher Urbach energies (bandtail widths) appear to be strongly correlated with higher growth rates and poorer cell performance

Higher frequencies for PECVD growth yield higher performance (and narrower bandtails). Not as successful for a-Si,Ge:H.

Possible solution explored at NREL: Hot-wire CVD of a-Si,Ge:H

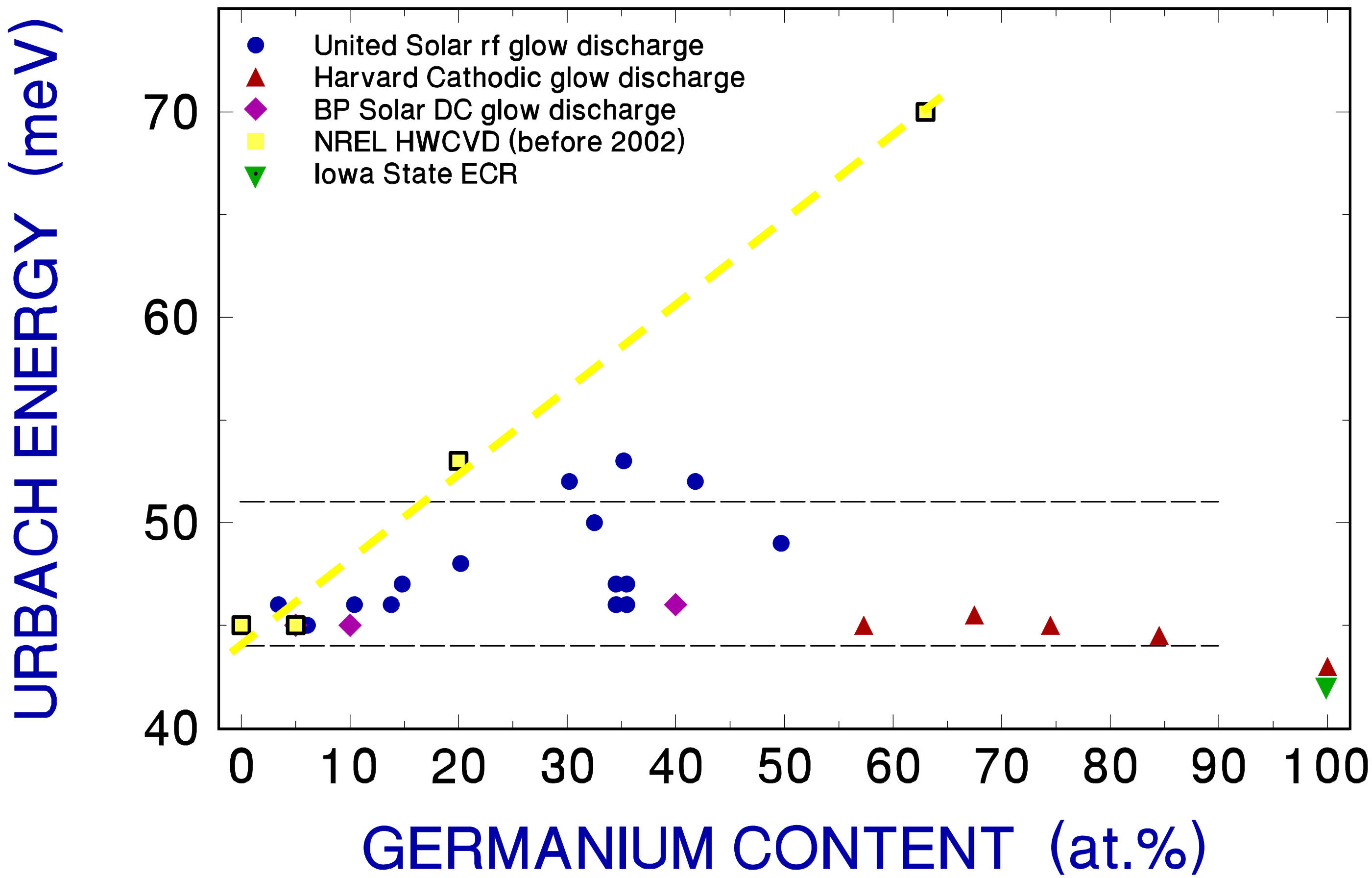
Accomplishments: Background

Urbach Energies for the Best PECVD a-SiGe:H



Accomplishments: Background

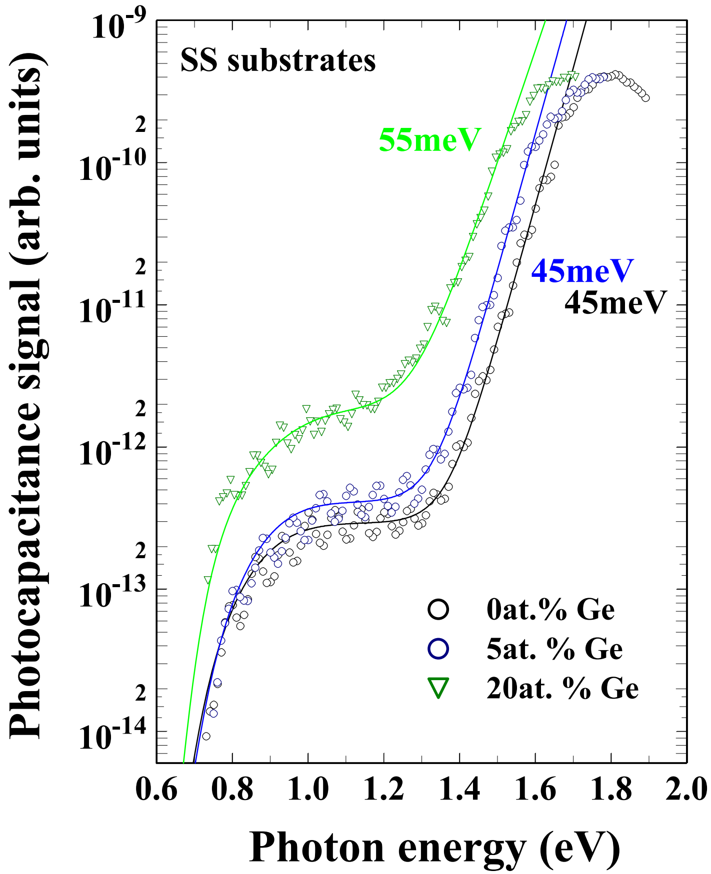
The Best PECVD vs. HWCVD a-Si,Ge:H



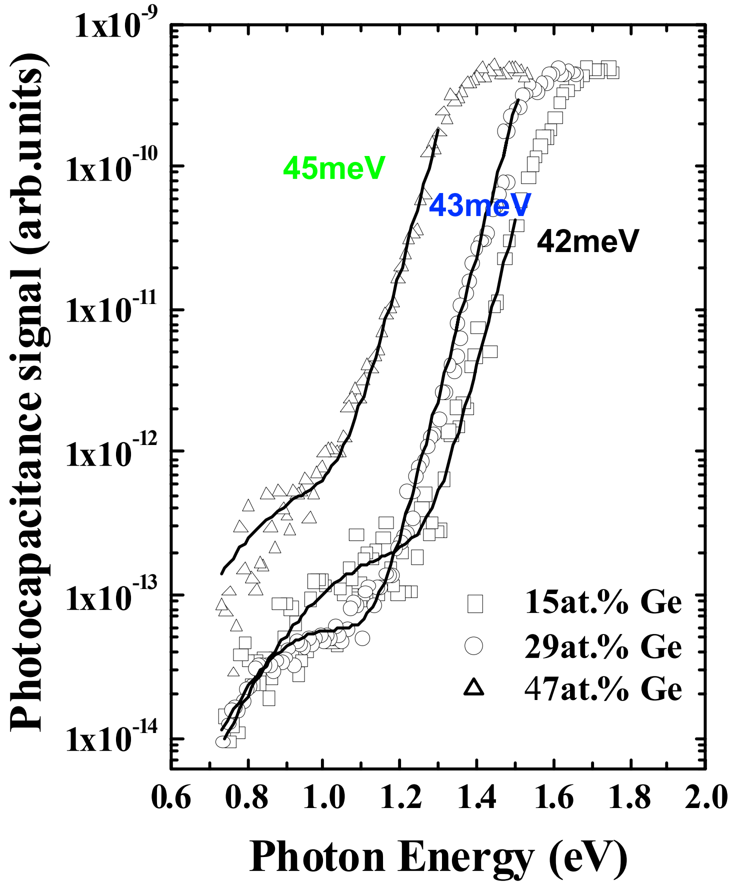
Accomplishments: Background

Spectra for NREL HWCVD a-Si,Ge:H

2000°C Tungsten Filament

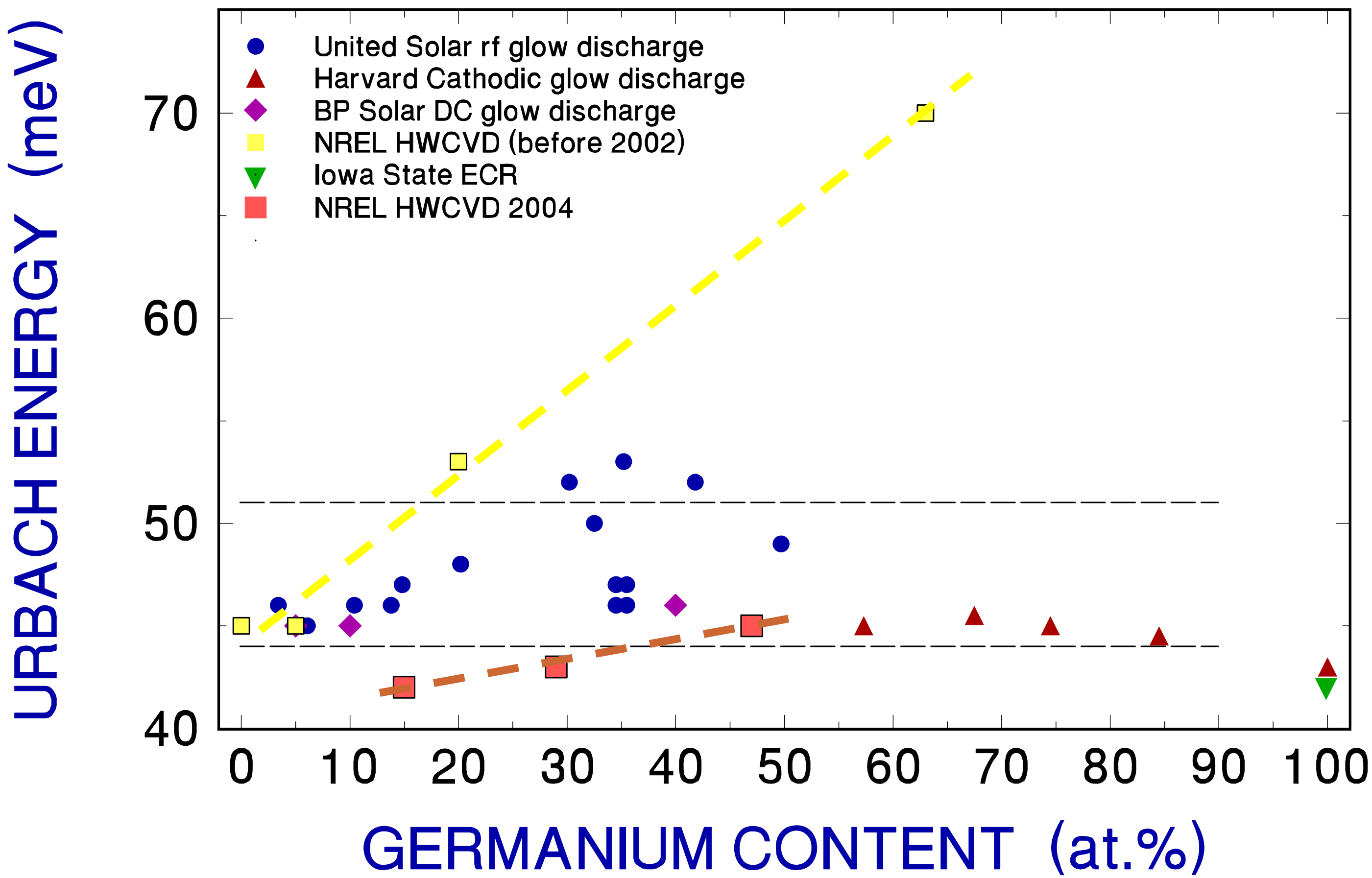


1800°C Tantalum Filament



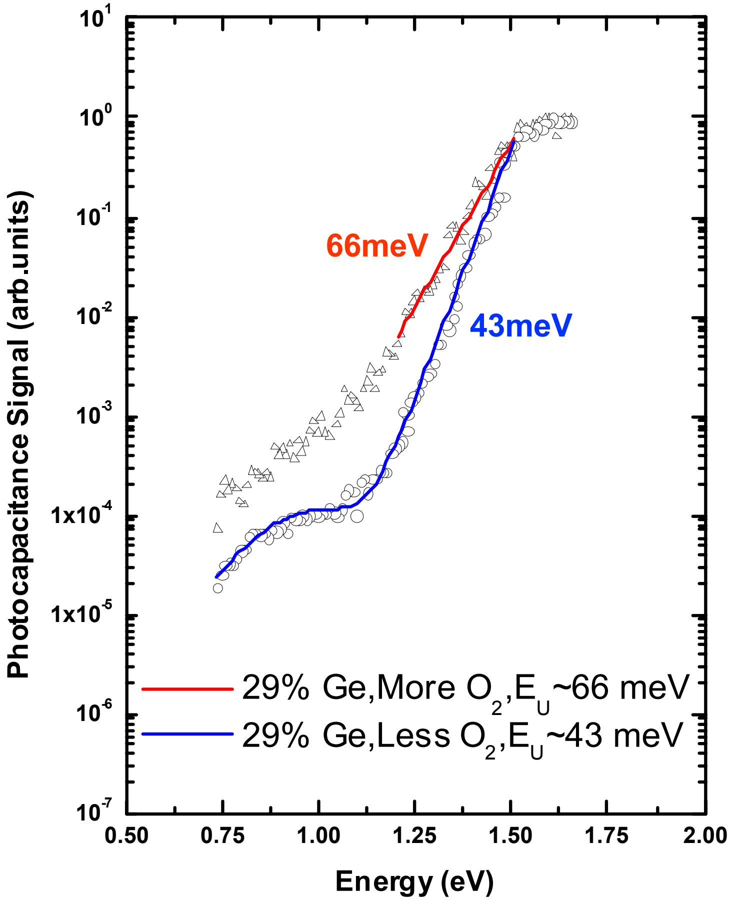
Accomplishments: Background

The Best PECVD vs. HWCVD a-Si,Ge:H

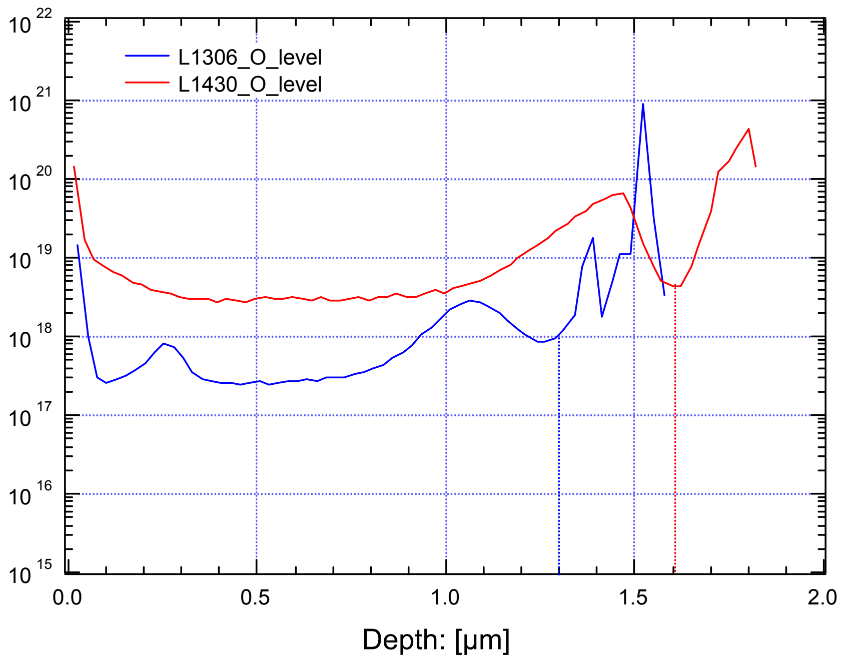


2005 Samples Exhibited Poorer Properties

Photocapacitance Spectra: 29at.% Ge

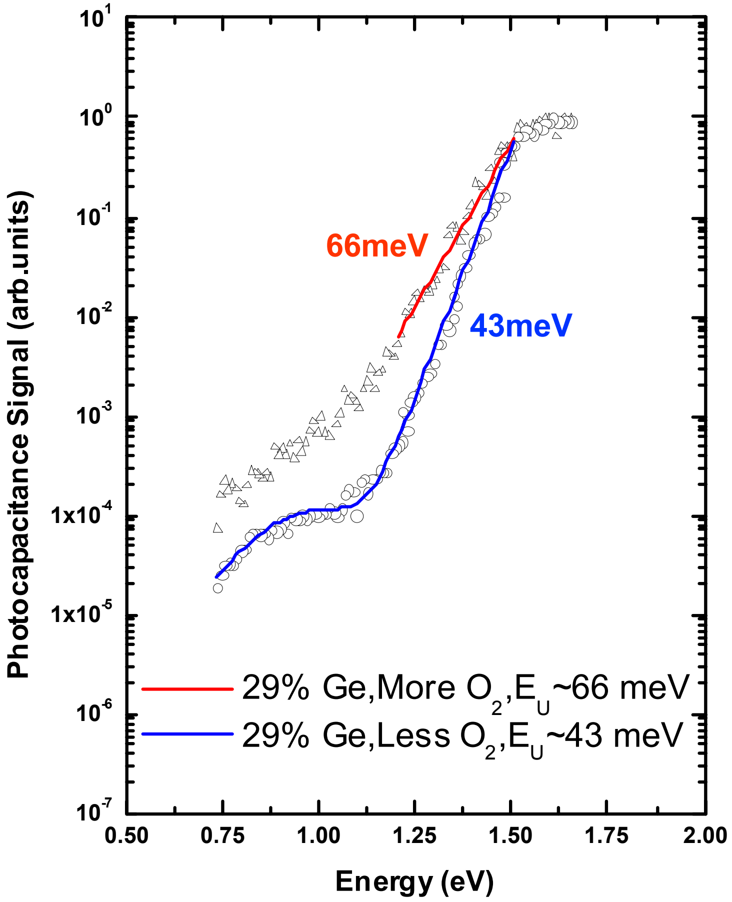


Oxygen SIMS Profiles



Oxygen Contamination Problem Resolved

Photocapacitance Spectra: 29at.% Ge



- **Fall 2005: Leak source identified and eliminated**
- **Controlled leak valve added**
- **New sample series deposited by Yueqin Xu in early 2006 with varying air leak contamination levels**

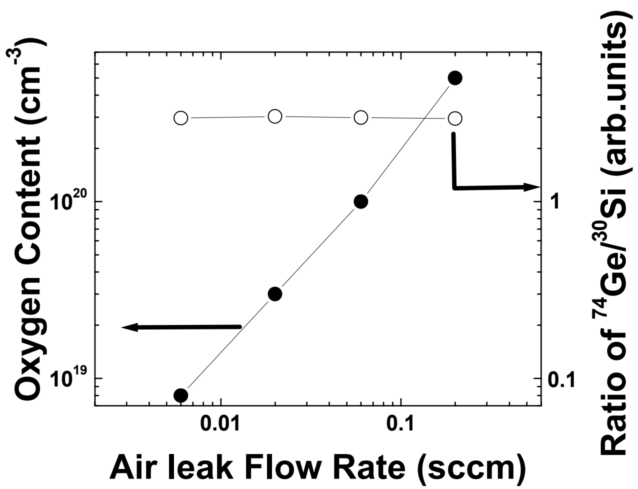
HWCVD a-Si,Ge:H Sample Series with Controlled Air Leak

Sample	Air leak Flow rate (sccm)	Oxygen Content (cm^{-3})	Thickness (μm)	Initial Substrate Temp (°C)	Final Substrate Temp (°C)	Gas Ratio $GeH_4/(GeH_4+SiH_4)$
A	0.00	~8×10^{18}	1.80	204	289	0.19
B	0.02	~3×10^{19}	1.60	204	289	0.19
C	0.06	~1×10^{20}	1.75	204	284	0.19
D	0.20	~5×10^{20}	2.20	204	275	0.19

SIMS Analysis:

Germanium content 29-32at.% for all samples

Systematic oxygen level variation



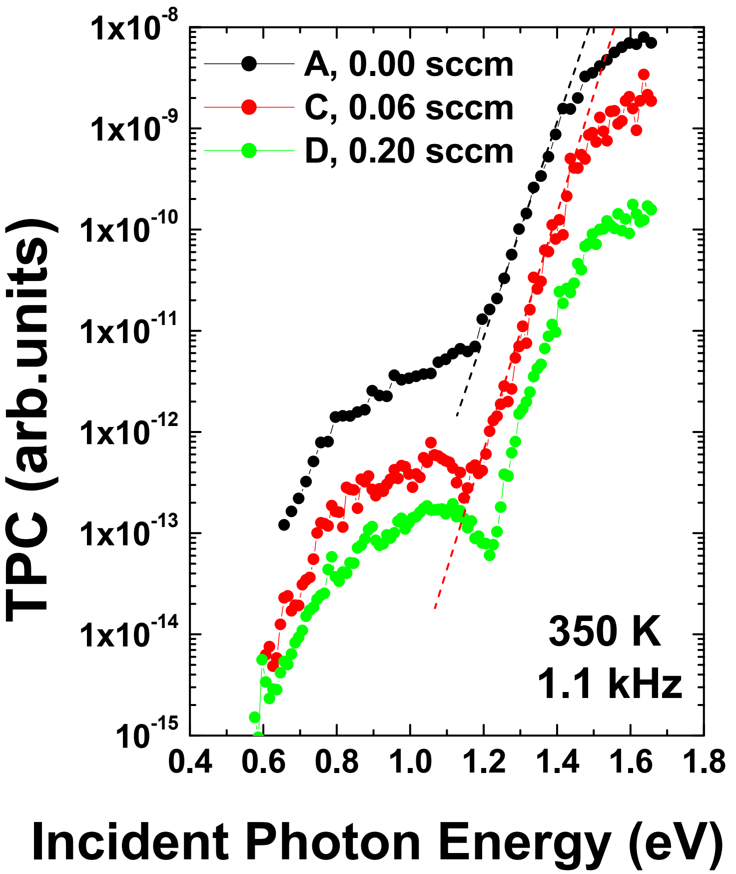
Photocapacitance Spectra for Oxygen Series

Sample A exhibits E_U = 43.5meV

Sample B exhibits E_U = 38 meV (?)

Does this mean low levels of oxygen actually improves the electronic properties of HWCVD a-SiGe:H materials?

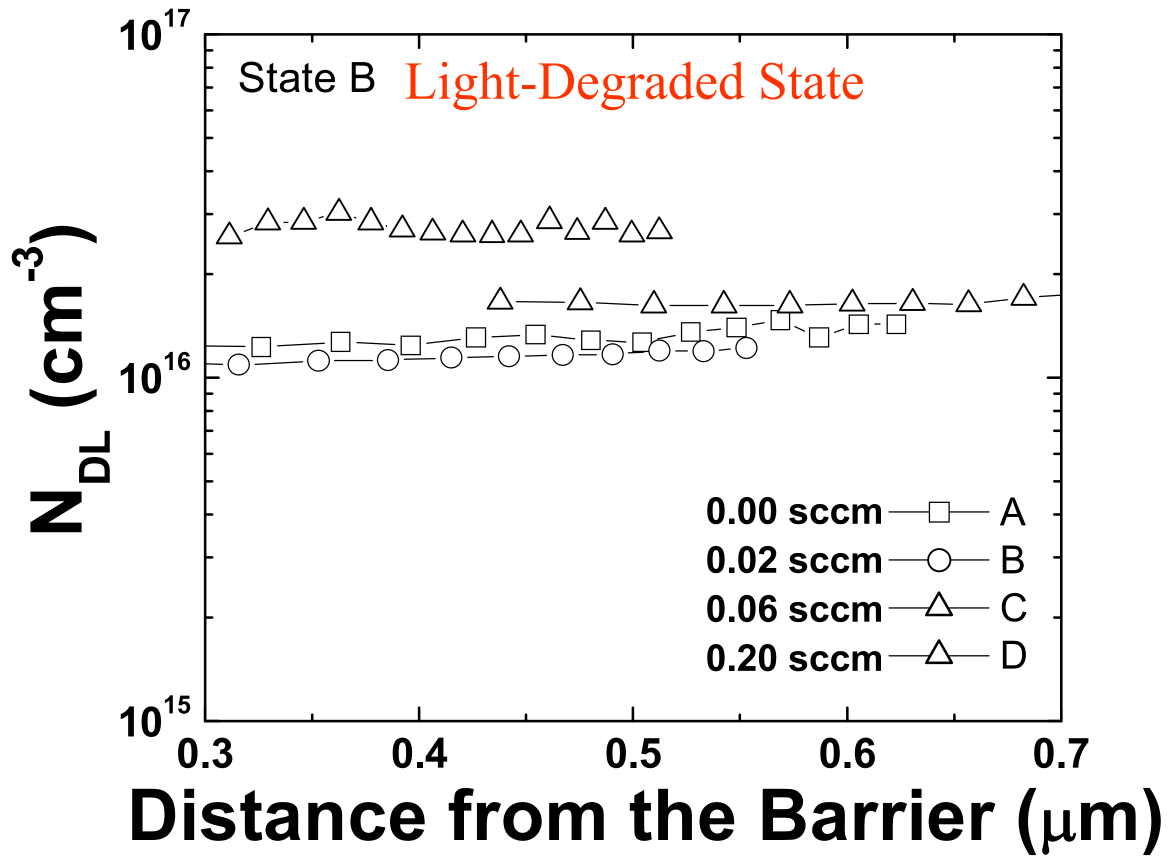
(NO, but it doesn't hurt that much either)



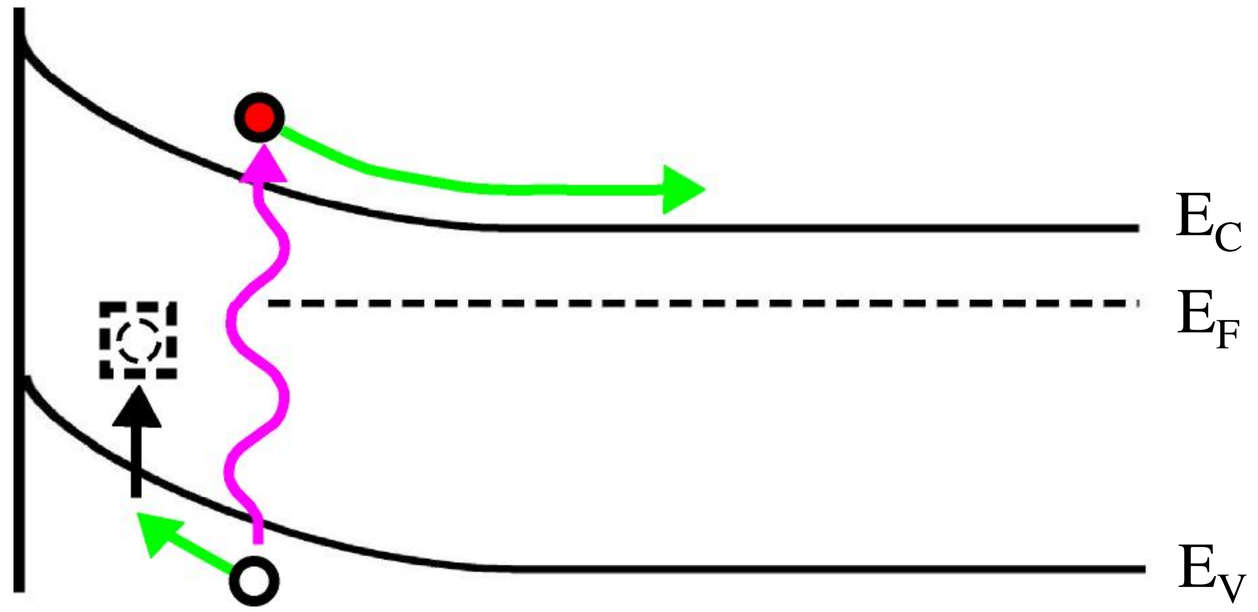
Defect Densities from DLCP Measurements

Mid-gap defect densities are low and vary roughly by a factor of two over range of oxygen

Larger density in higher leak samples may be due to effects of oxygen weak donor level



Sensitivity to Minority Carrier Collection



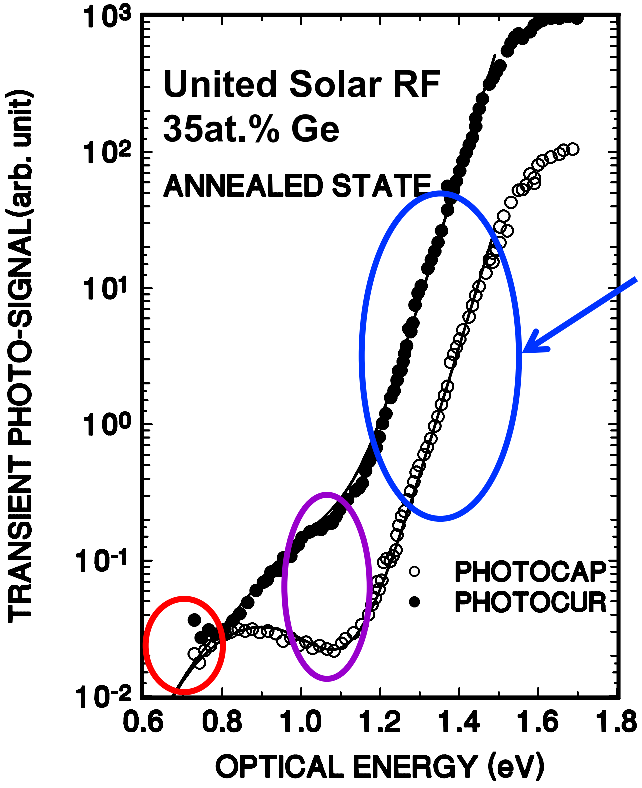
- For optical energies near the gap, electrons and holes generated ***equally***
- If both escape depletion region there is no net change in charge density

⇒ Small photocapacitance signal, but larger junction photocurrent signal

Photocapacitance signal ∝ n - p while Photocurrent signal ∝ n + p

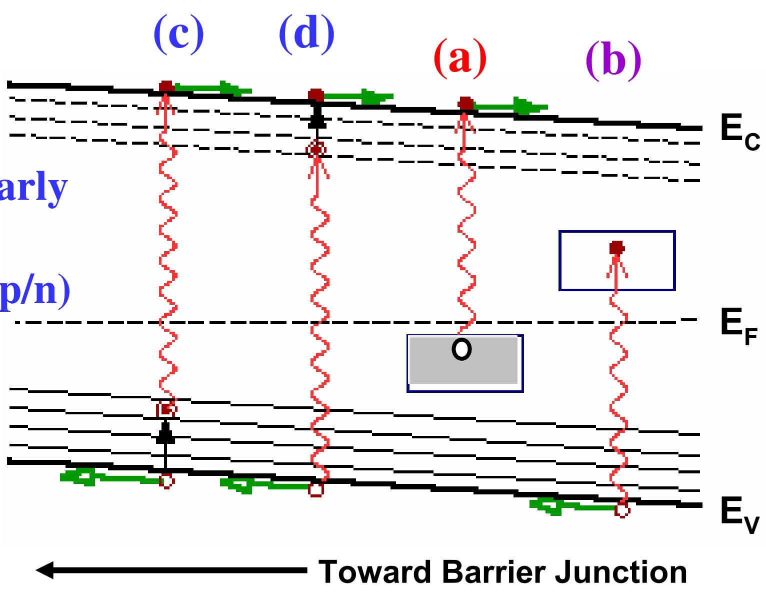
Measuring Fraction of Collected Holes in a-Si,Ge:H

Compare transient photocapacitance and photocurrent spectra



Ratio is nearly a constant:

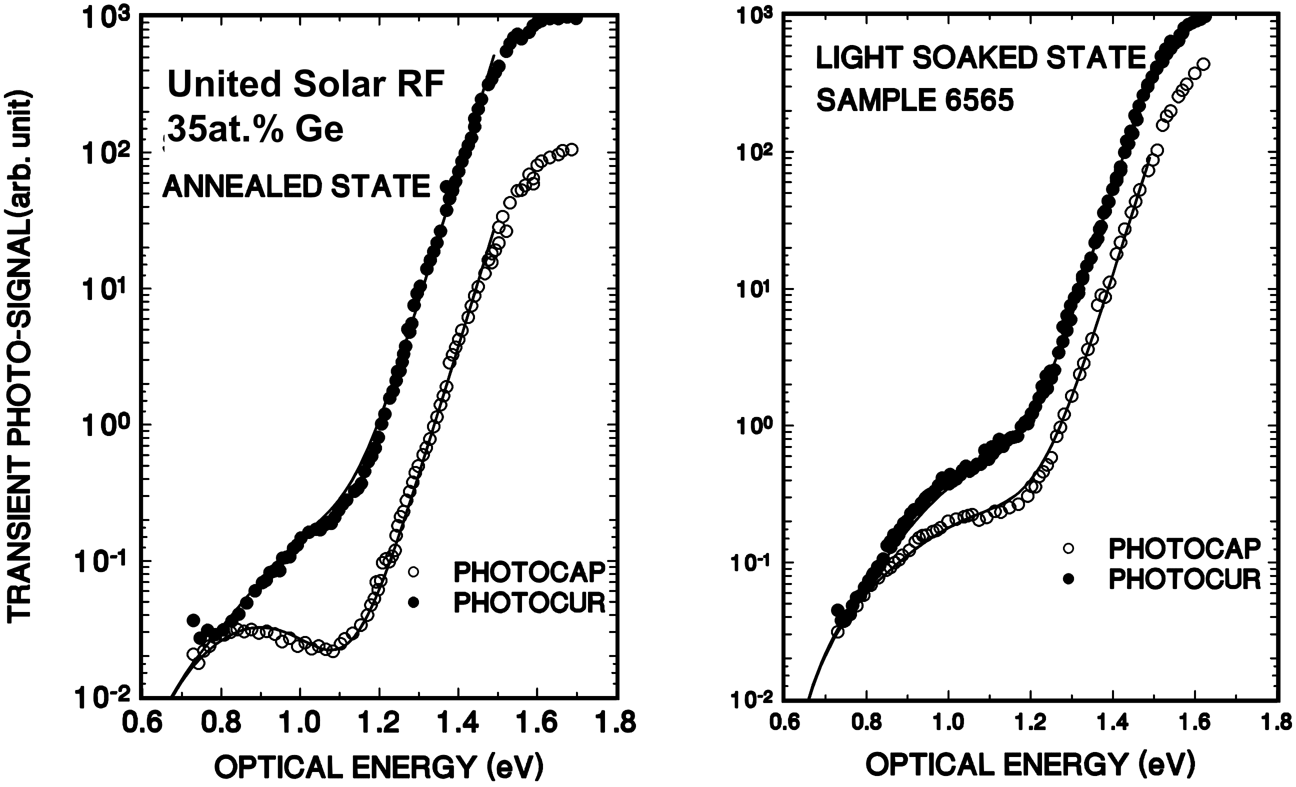
$(1+p/n)/(1-p/n)$



Ratio of signals in bandtail region
$\Rightarrow$ the hole collection fraction is $\approx$ 95%
under our experimental conditions

Measuring Fraction of Collected Holes

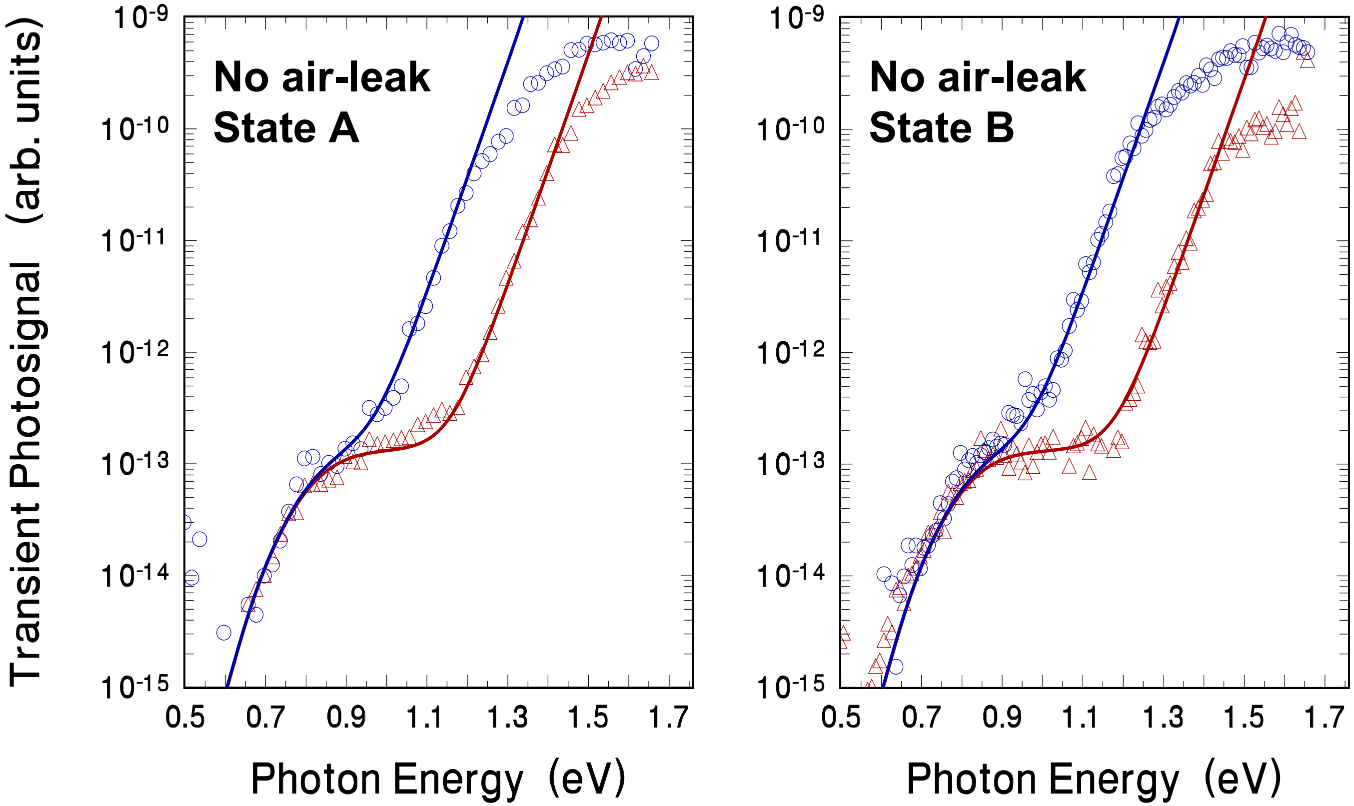
United Solar RF PECVD 35at.% Ge Sample



Hole Collection: 95% **66%**

Measuring Fraction of Collected Holes

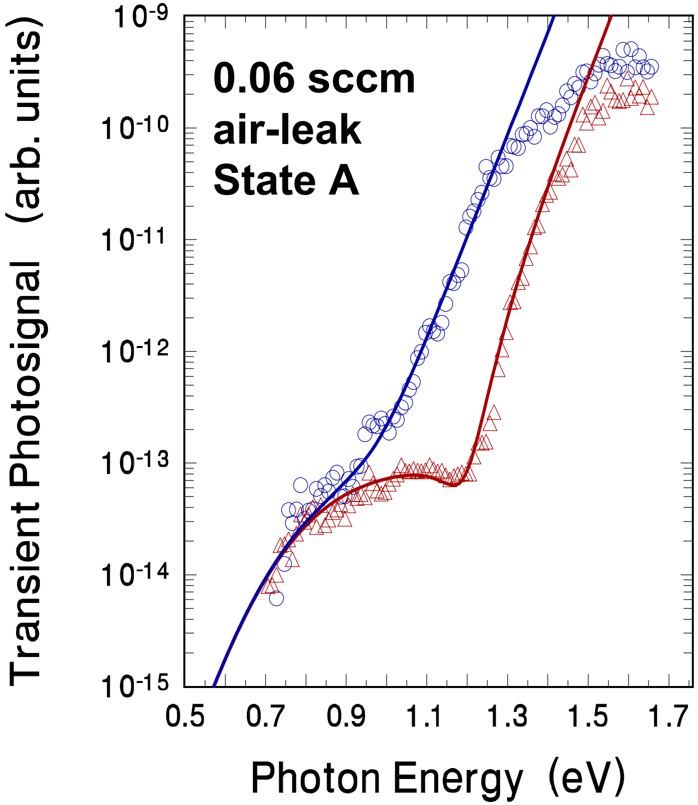
NREL Hot-Wire CVD 29at.% Ge, No air-leak

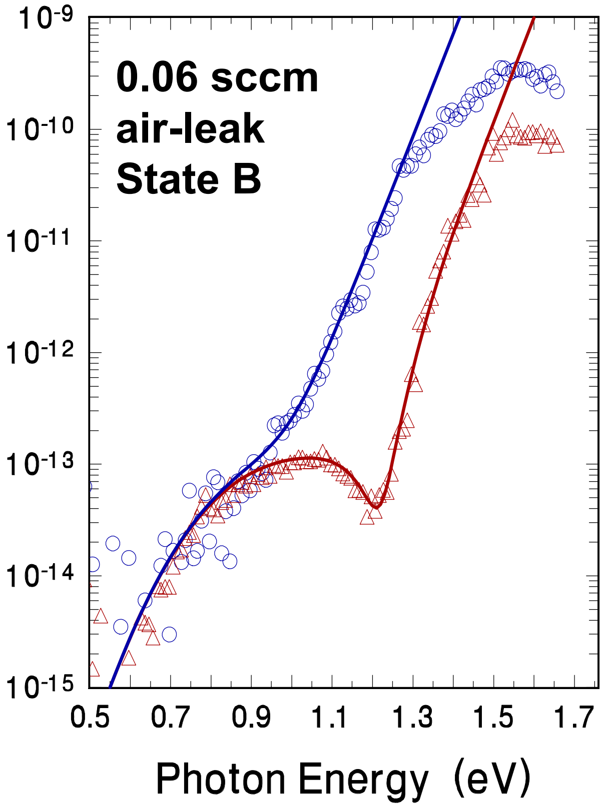


Hole Collection: 98% **99%**

Measuring Fraction of Collected Holes

NREL Hot-Wire CVD 29at.% Ge, 0.06sccm air-leak





Hole Collection: 95% **97%**

Effect of Extra Oxygen: New Defect Transition

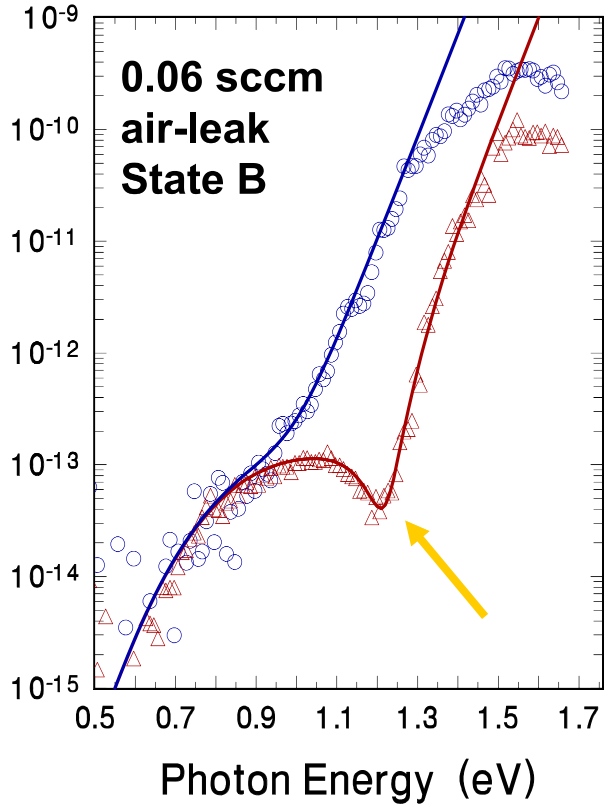
NREL Hot-Wire CVD 29at.% Ge, 0.06sccm air-leak

Dip in TPC Spectrum is due to a 1.4eV transition from VB into empty defect level

Introducing this defect transition (in addition to usual mid-gap deep defect) allows excellent fits to both TPC and TPI (thin lines shown)

Urbach is actually 47meV, not the < 40meV value that seemed to fit TPC by itself

Moderate oxygen levels do *not* appear to greatly impair hole collection, or the susceptibility to light-induced degradation



HWCVD a-Si,Ge:H Summary

Bad News: Oxygen wasn't the problem, so we really don't know why the samples produced during 2005 were so poor!

Good News: HWCVD a-Si,Ge:H Samples again exhibit excellent electronic properties! (in some respects, even better than the best PECVD samples)

Interesting: Oxygen introduces new defect transition into gap: The oxygen donor level predicted as long as 24 years ago?

(2) Nanocrystalline Silicon Materials Properties

with Baojie Yan, Jeffrey Yang, and Subhendu Guha UNITED SOLAR OVONIC

TPC Spectra reveal mixed phase nature of nanocrystalline Si

Temperature variation shows degree of minority carrier collection

New Sample Series Studied

High efficiency working n-i-p devices examined directly

Hole Collection Determined via TPC vs. Device Performance

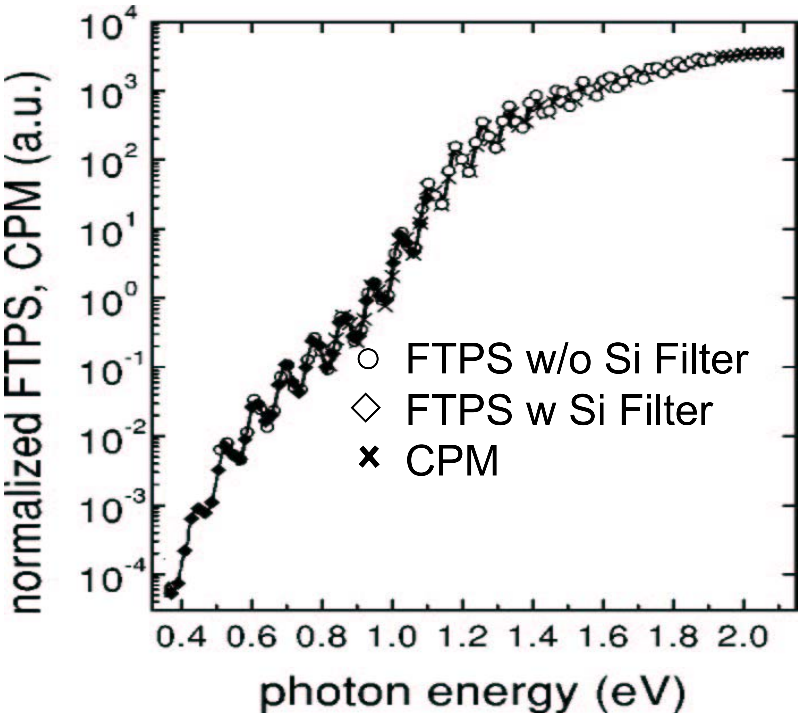
Is there a correlation?

Nature of light-induced degradation

Possible model is proposed

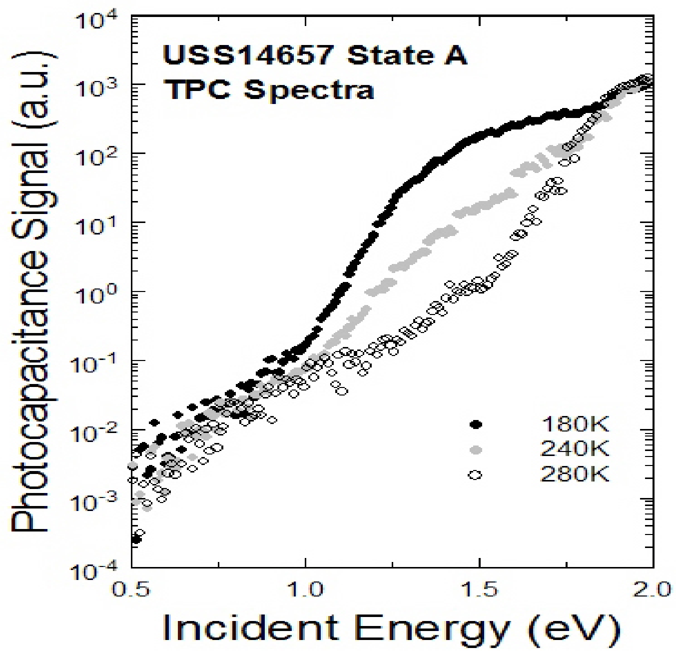
Comparing CPM and Photocapacitance Spectrum for nc-Si:H

Fourier-Transform Photo Current Spectroscopy(FTIR) and CPM Spectra



M. Vaněček, A. Poruba, Z. Remeš, N. Beck, and M. Nesládek, J. Non-Cryst. Solids **227-230**, 967 (1998).

United Solar nanocrystalline Si spectrum from TPC spectroscopy



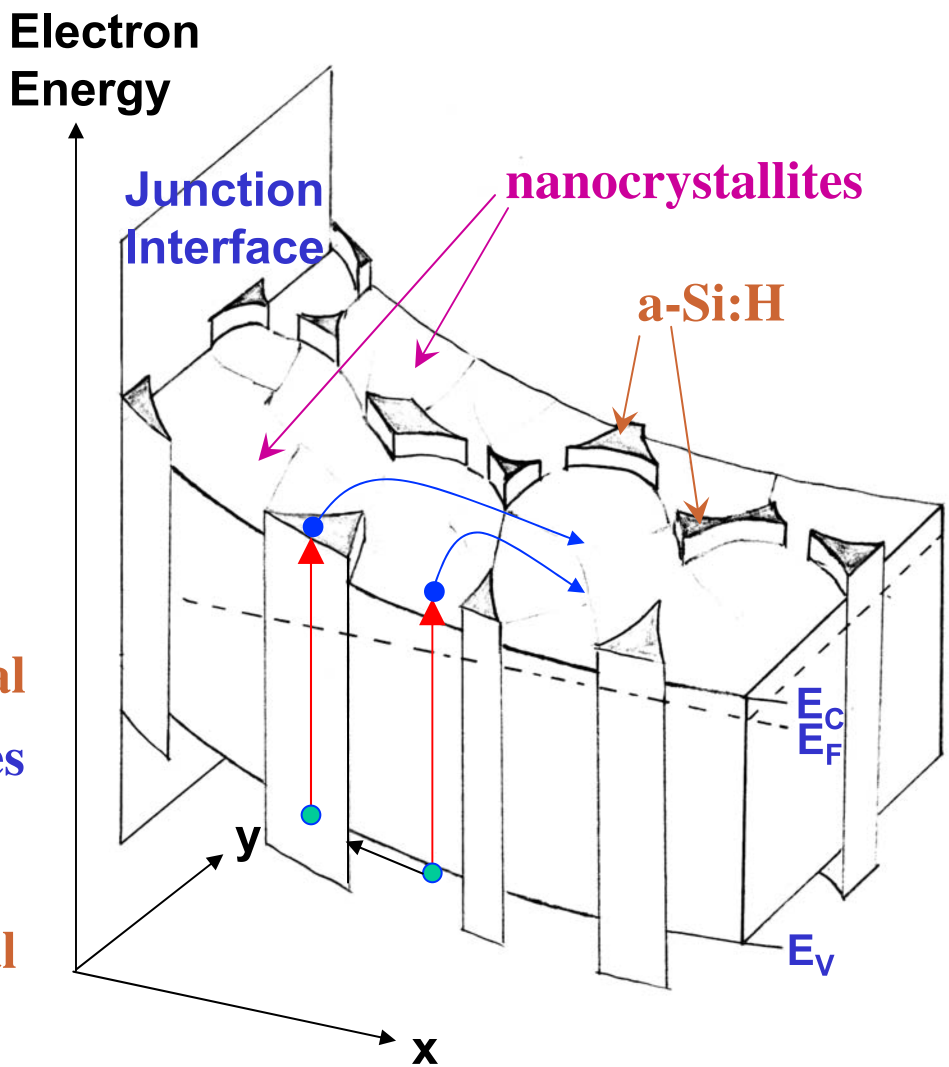
Very temperature dependent !

Hole Collection Inhibited in a-Si:H Component

At photon energies greater than 1.1eV, free electrons and holes excited in nano-crystallites.

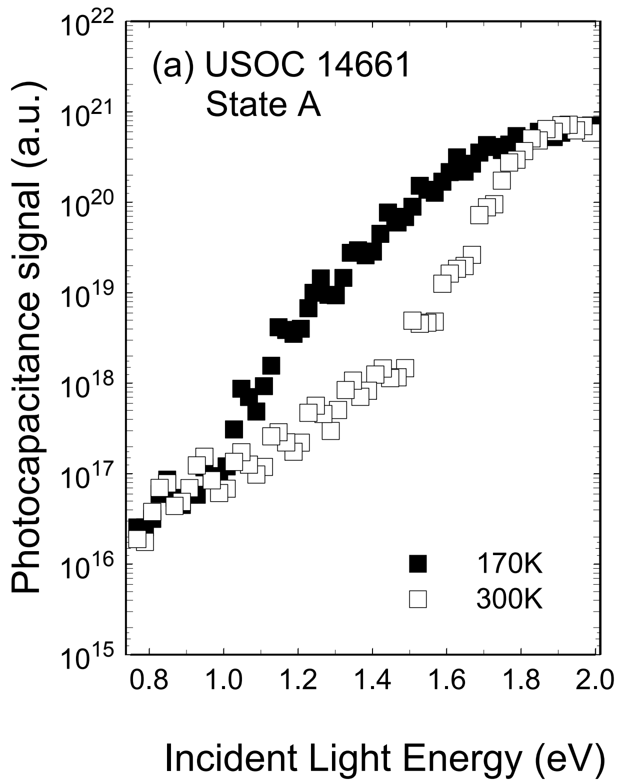
At moderately high temper-atures both carriers escape
⇒ little change in charge
⇒ small photocapacitance signal

In a-Si:H component many holes remain trapped
⇒ mostly electrons escape
⇒ large photocapacitance signal



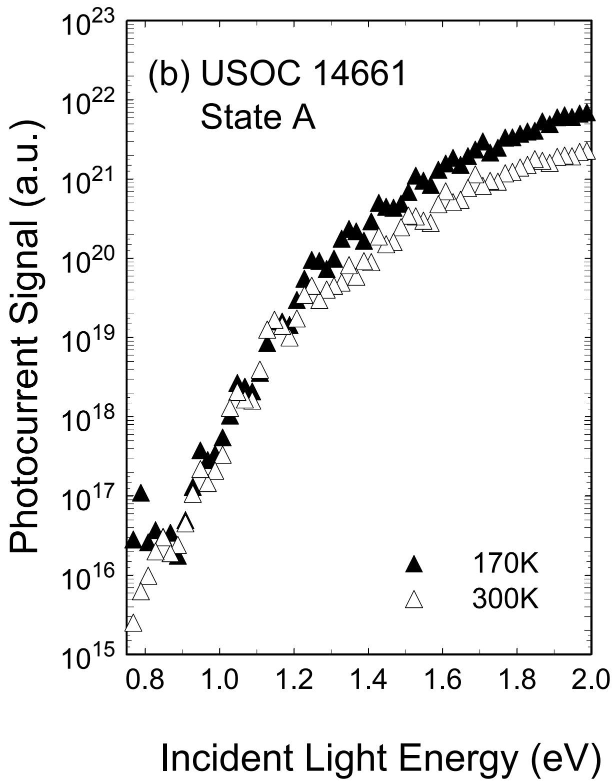
Minority Carrier Collection Increases with T

Transient Photocapacitance



Increased minority carrer collection suppresses signal in nanocrystallites

Transient Junction Photocurrent



Photocurrent signal dominated by nanocrystallite component at all T

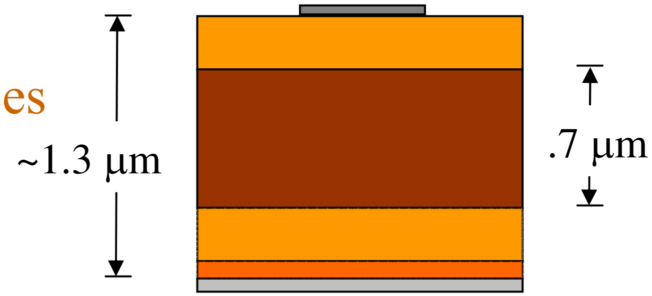
Types of Nanocrystalline Si Devices Studied

Deposited at : United Solar Ovonic Corp.

SANDWICH

SS/n+/a-Si:H/nc-Si:H/a-Si:H

Most sample devices examined prior to Fall, 2005.



Advantages:

- Purely intrinsic layers
- Blocks diffusion of O_2

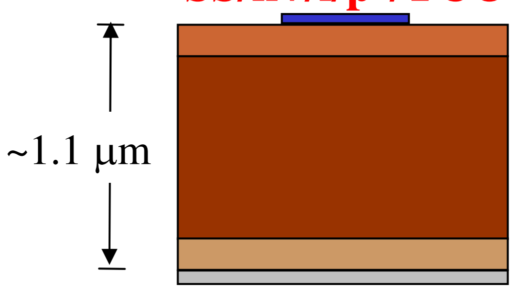
Disadvantages:

- Contains a-Si:H layers
- Differs from working device

n-i-p

SS/n+/i/p$^+$/TCO

Sample devices studied since late 2005



Advantages:

- Purely nc-Si:H
- Working device allows compar-ison with cell peformance

Disadvantages:

- Contains thin p^+ and n^+ layers

Early 2006 United Solar nc-Si:H Device Series

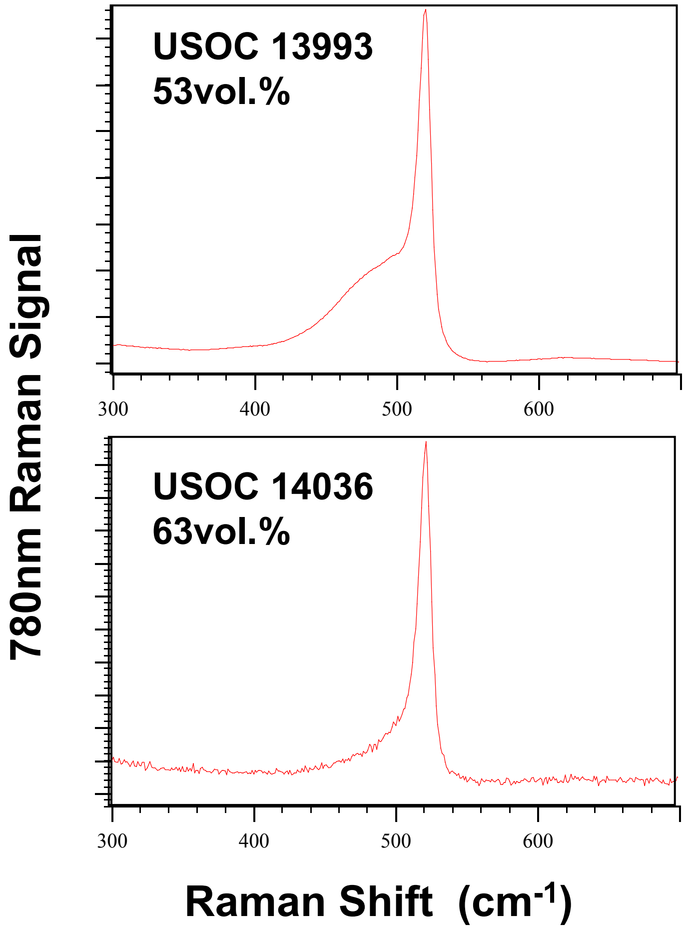
All are n-i-p devices with either Specular Stainless (SS) substrates, or with textured Ag/ZnO back reflectors. All i-layers were more than 1 micron thick.

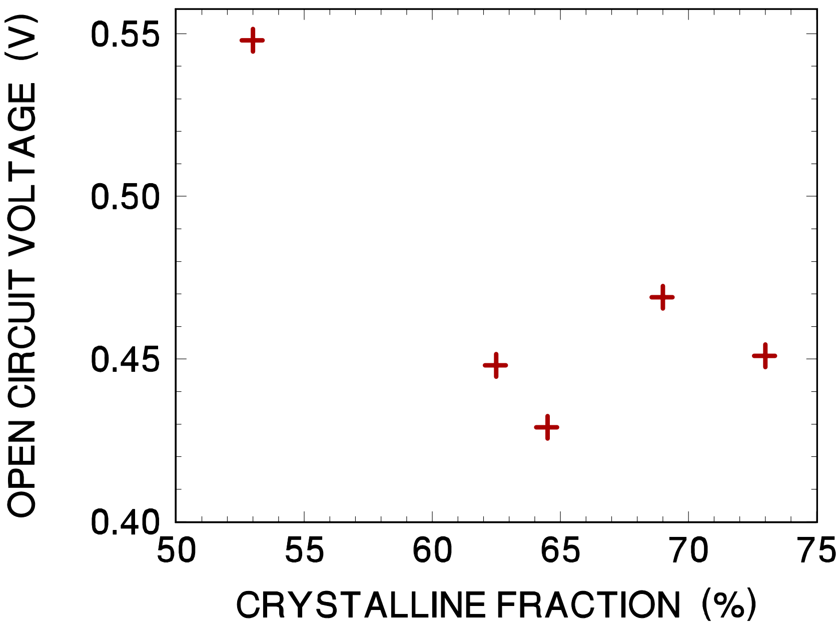
Samples were deposited either using a constant level of hydrogen dilution, or with a linear ramp variation in hydrogen dilution to control crystallite size

Sample No	Substrate	Jsc	Voc	FF	Eff (%)	H2 Dilution
14027	Ag/ZnO	26.5	0.469	0.581	7.22	Ramping
14036	SS	17.38	0.448	0.568	4.42	Ramping
14037	Ag/ZnO	25.99	0.429	0.512	5.71	Constant
14038	SS	17.36	0.451	0.531	4.16	Constant
13993	Ag/ZnO	24.39	0.548	0.641	8.57	Ramping

Final sample in list is close to the current best nc-Si:H United Solar device

Crystalline Fractions Revealed by Raman Spectroscopy



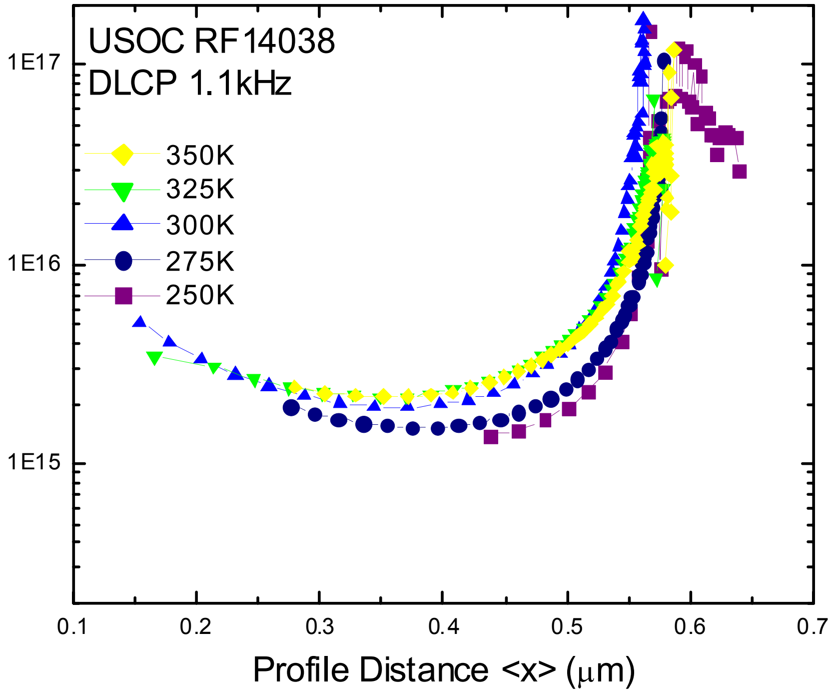


Low crystalline fractions yield highest V_{OC}'s

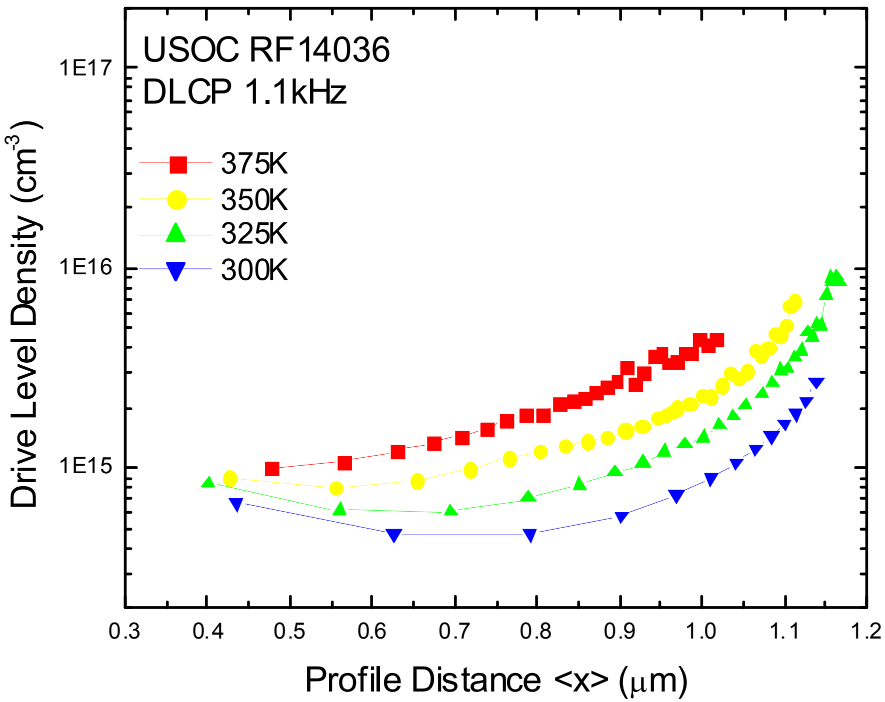
No clear correlations for fractions above 60vol.%

DLC Profiles for Constant *vs.* Ramped H-dilution

Constant H-dilution



Linearly Ramped H-dilution

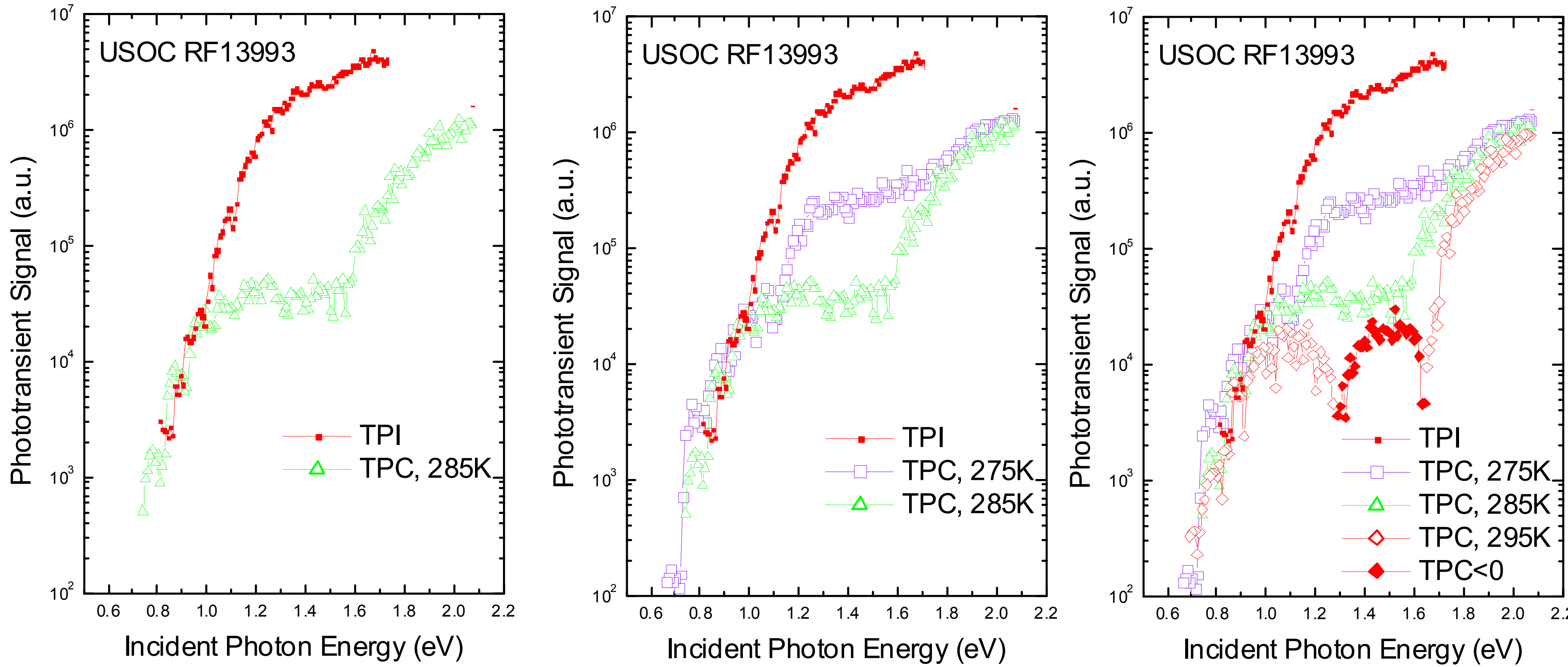


Consequences of employing varying H-dilution to limit crystallite size:

Large defect density near n-i junction can be decreased

Lower defect density maintained through most of bulk film region

Spectra for 8.57% Textured n-i-p Device



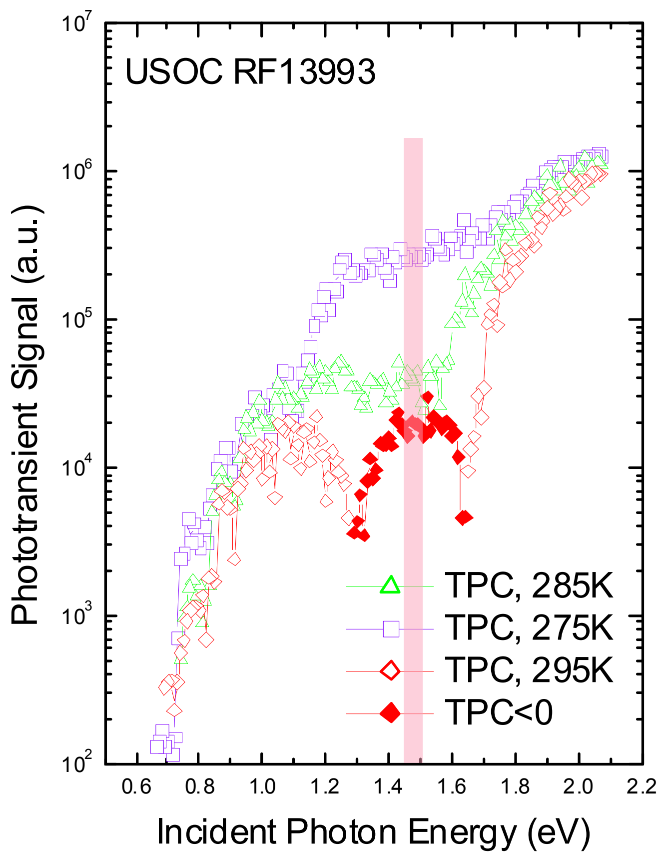
Here an a-Si:H component is clearly in evidence

Reducing the temperature increases nanocrystallite signal

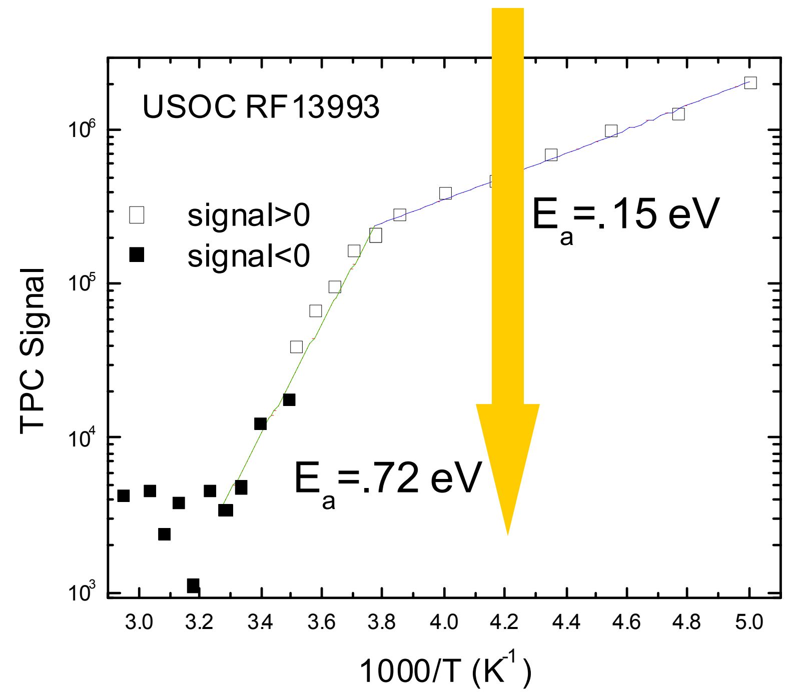
Increasing the temperature actually yields a negative TPC signal near 1.5eV !

Temperature Dependence of Hole Collection in nc-Si:H

TPC spectra from 8.57%
n-i-p sample device



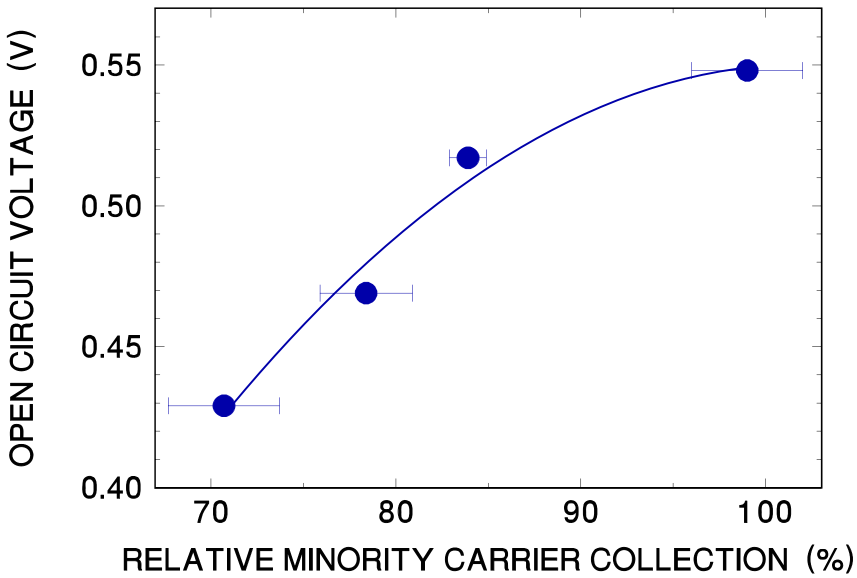
Increasing hole collection

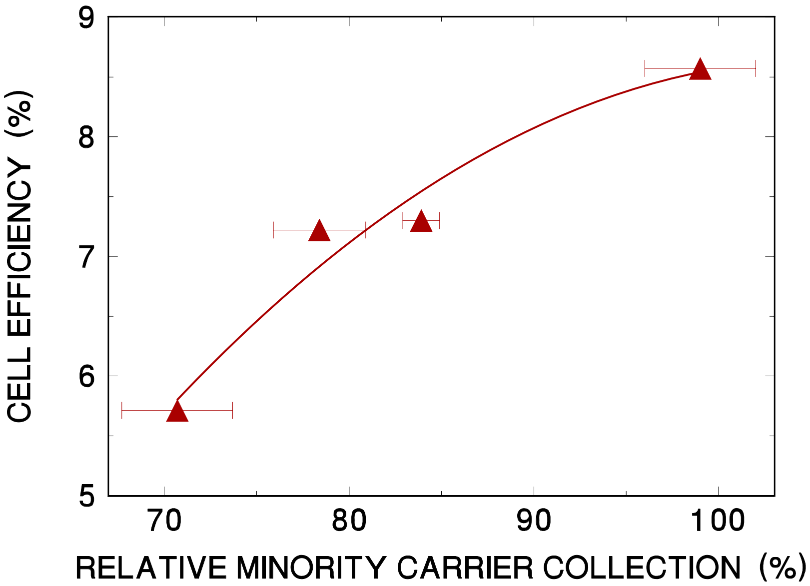


Two activated hole trap processes seem to be evident in this sample

Correlation with Cell Performance

Comparison of the three Ag/ZnO Devices plus one from previous sample series



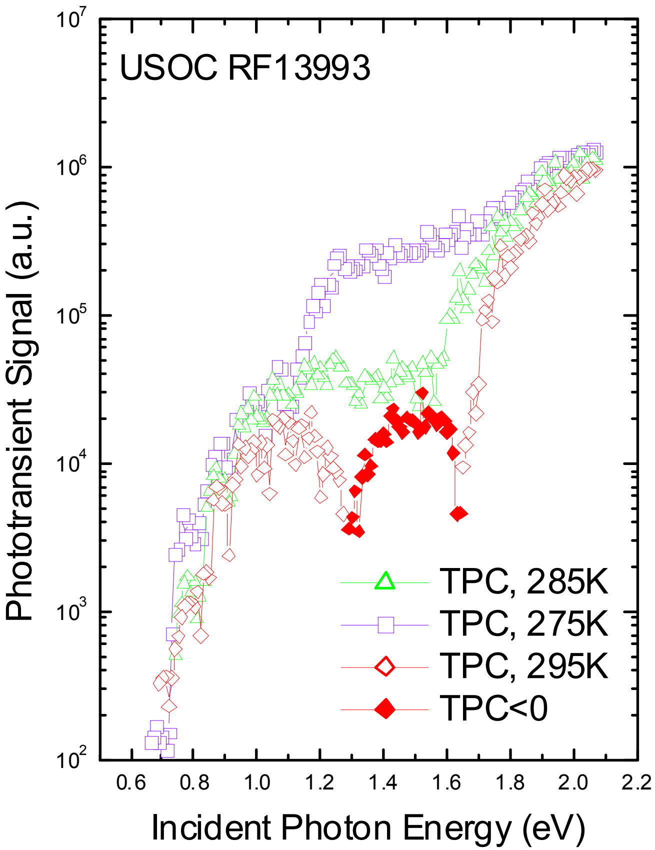


Minority carrier collection determined from TPI/TPC ratio at 300K near 1.5eV

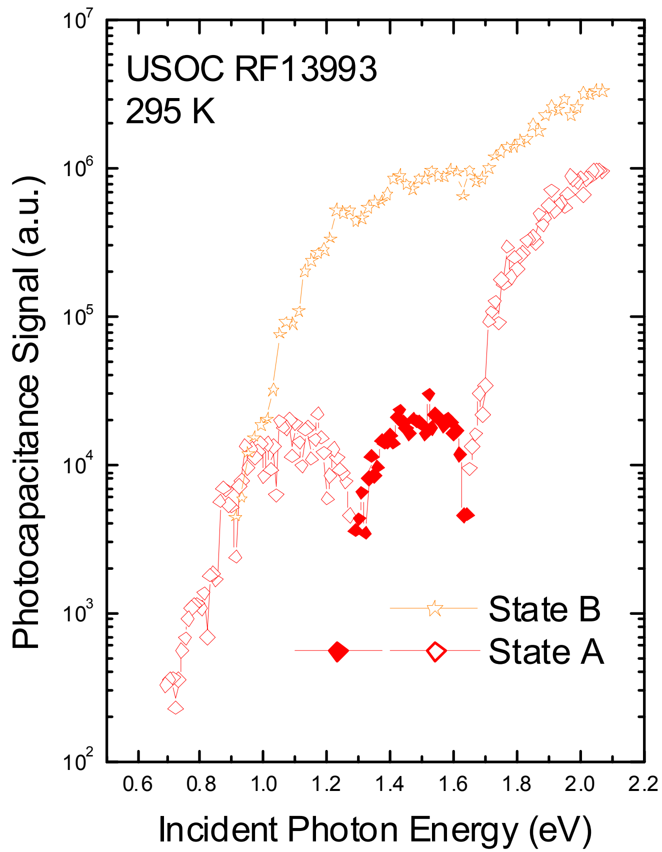
Correlation looks promising, but data from more sample devices need to be added

Effect of Light Soaking on TPC Spectra

Effect of varying temperature



Annealed vs. light-soaked state

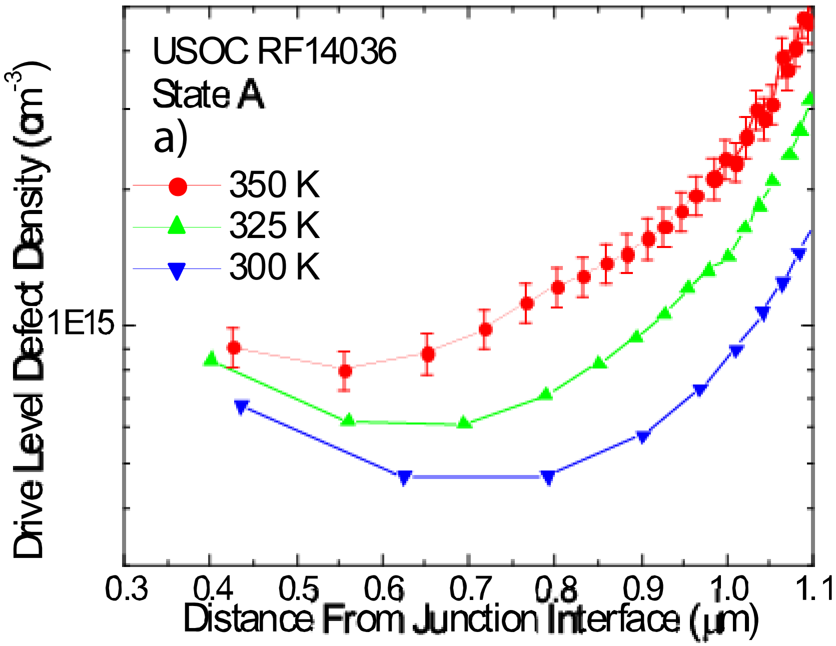


50 hours of light- soaking of 610nm filtered ELH light at 500mW/cm^2

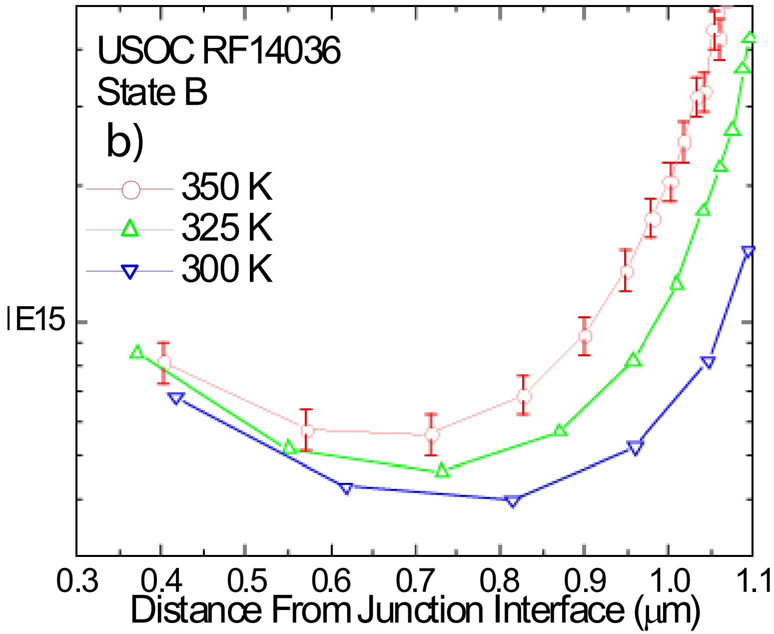
Light-soaking significantly reduces hole collection

Effect of Light Soaking on Capacitance Profiles

Annealed State



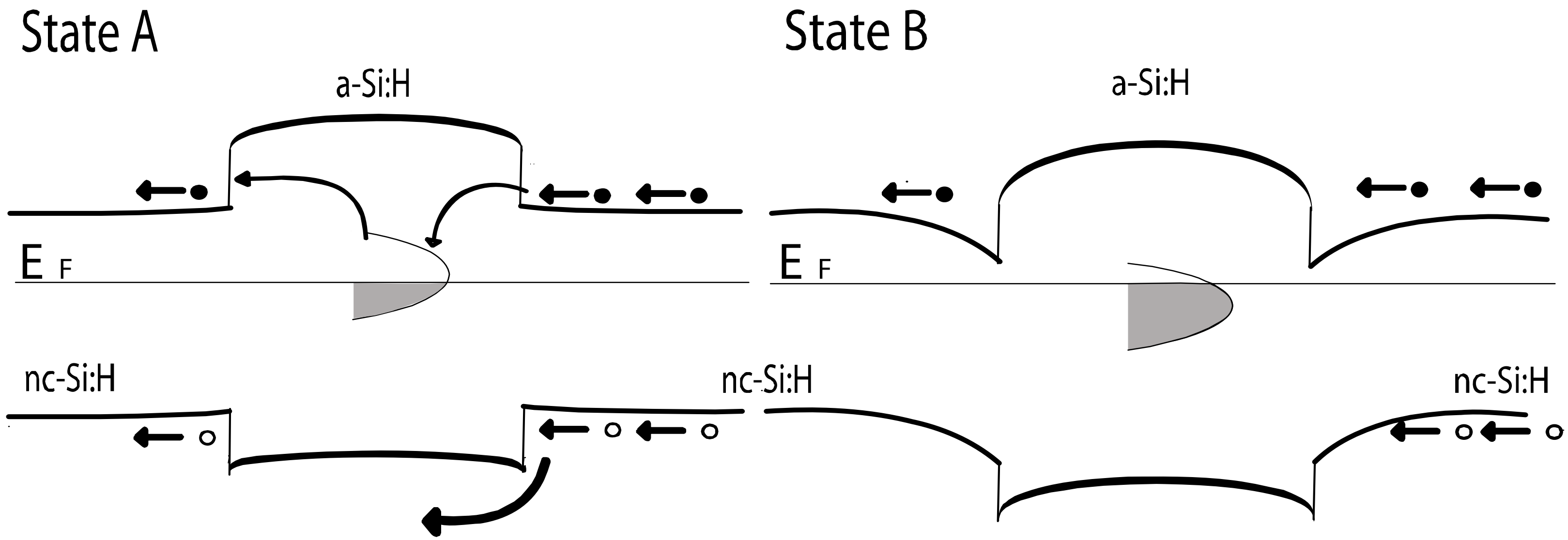
Light-soaked State



Does light soaking actually reduce the density of deep defects?

No, we believe it increases the an activation barrier that inhibits its response

Proposed Model to Explain Changes with Light-Soaking



In light-soaked State B, defects shift down in energy with respect to the bulk conduction band.

As illustrated, positive charge collects at the a-Si:H/crystallite interfaces, while compensated by negative charge in the a-Si:H region, and the crystallites nearby.

Holes have larger potential barriers at the phase boundary. Also, the activation energy for exchanging electrons between deep defects and conduction band increases.

Key Findings and Conclusions

- **Our measurements continue to show superior electronic properties for lower filament temperature NREL HWCVD a-Si,Ge:H alloys.**
- **The minority hole collection appears nearly as good as the best PECVD alloys with possibly less deterioration after light soaking.**
- **Previous problems with air contamination were solved; moreover, a distinct oxygen related defect state has been identified.**

- **We have successfully carried out TPC and TPI sub-band-gap spectroscopy on nc-Si:H n-i-p devices employing both SS and textured Ag/ZnO substrates.**
- **A correlation appears to exist between the minority carrier collection fraction deduced by the TPC measurements and the device performance.**
- **Light-induced degradation exists and reduces minority carrier collection. A possible mechanism to explain our observations has been formulated.**

Broad Future Plans

NREL HWCVD a-Si,Ge:H

Work with NREL as they seek to incorporate and optimize performance of their HWCVD a-Si,Ge:H materials within photovoltaic devices.

Evaluate the electronic properites of NREL HWCVD a-Si,Ge:H under higher deposition rates (greater than the ~2Å/s materials studied to date)

Examine alloys with other Ge fractions, and determine whether the effects of oxygen contamination appear similar.

United Solar nanocrystalline Si

Examine properties of nc-Si:H closer to a-Si:H transition region to help understand how far one can go toward maximizing V_{OC} without reducing J_{SC}

Explore the effects of hydrogen profiling over a greater range of parameter space

Test the implications of proposed light-induced degradation model; for example, by varying photon energies, or examining such effects under applied bias.

THANK YOU!

Accomplishments

Studies of NREL Fabricated CIGS Devices using Admittance Spectroscopy and DLCP

Eight NREL Devices from Three Depositions

Sample devices provided by Miguel Contreras

Three depositions: Each such sample contained 6 devices

8 devices with varying levels of performance were chosen for study

Device areas were 0.406 cm^2 in all cases

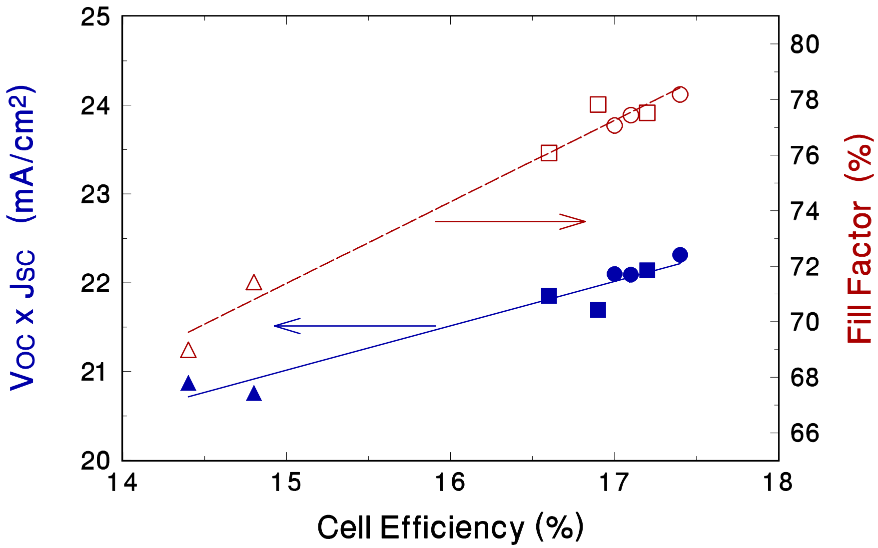
Device #	V_{OC} (volts)	J_{SC} (mA/cm^2)	Fill Factor (%)	Efficiency (%)
C1919-11 Cell 3	0.630	32.95	71.43	14.833
C1919-11 Cell 4	0.642	32.51	68.99	14.393
C1813-21 Cell 3	0.657	33.26	76.08	16.613
C1813-21 Cell 4	0.664	32.67	77.82	16.888
C1813-21 Cell 6	0.667	33.19	77.52	17.168
C1924-1 Cell 4	0.724	30.82	78.19	17.449
C1924-1 Cell 5	0.717	30.81	77.44	17.118
C1924-1 Cell 6	0.714	30.95	77.07	17.039

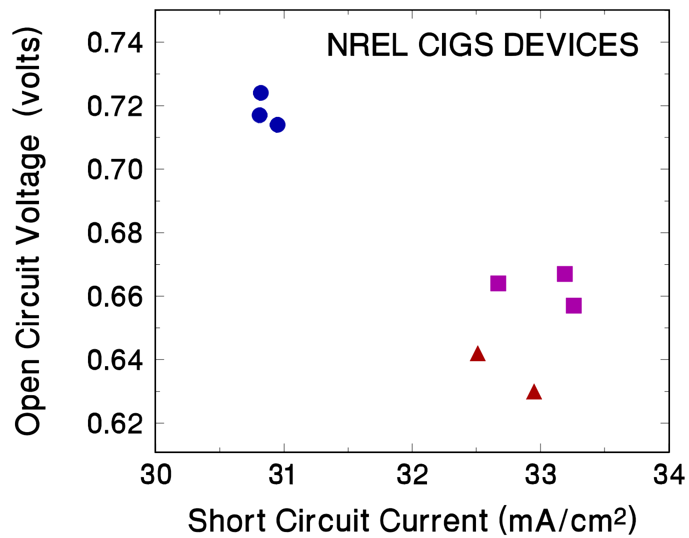
Eight NREL Devices from Three Depositions

Relationship of $V_{OC} \times J_{SC}$ products and Fill Factors to Device Efficiencies

▲: C1919 devices, ■: C1813 devices, and ●: C1924 devices

Fill factor variations account for most of the differences in efficiencies

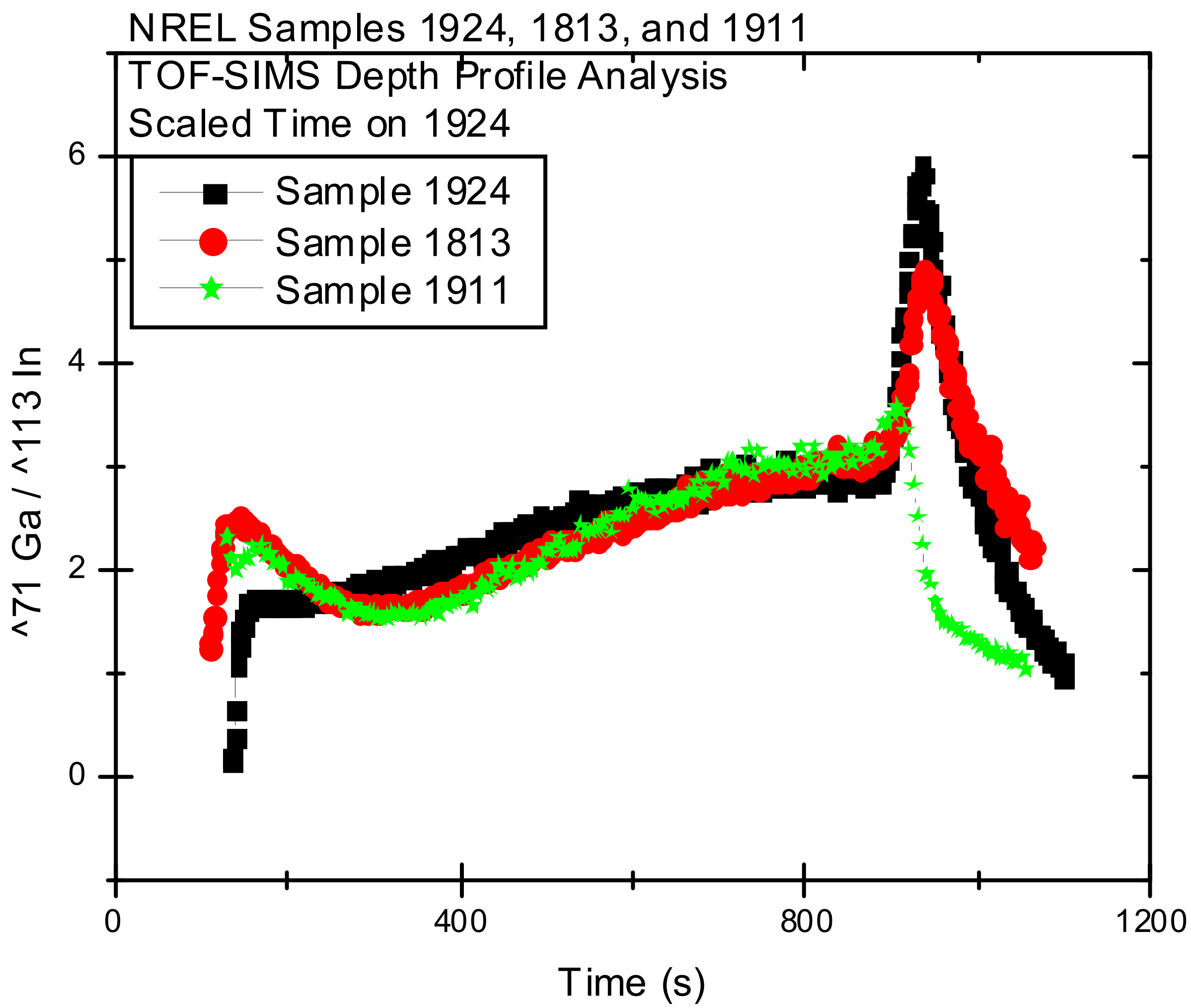




- **The C1924 devices differ somewhat from the C1919 and C1813 devices, exhibiting higher V_{OC}'s and lower J_{SC}'s.**
- **The C1924 devices have a slightly higher Ga fraction.**

SIMS Analysis: Ga to In Ratios

Depositions for samples 1813 and 1911 have nearly identical composition profiles, while deposition for sample 1924 is significantly different.

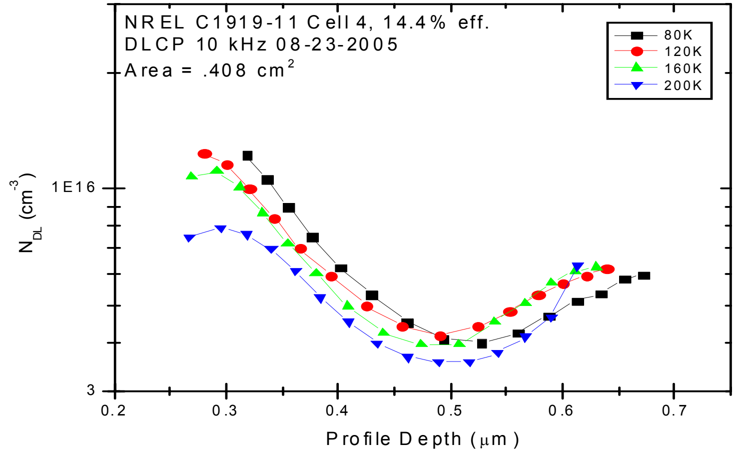


Comparison of DLC Profiles

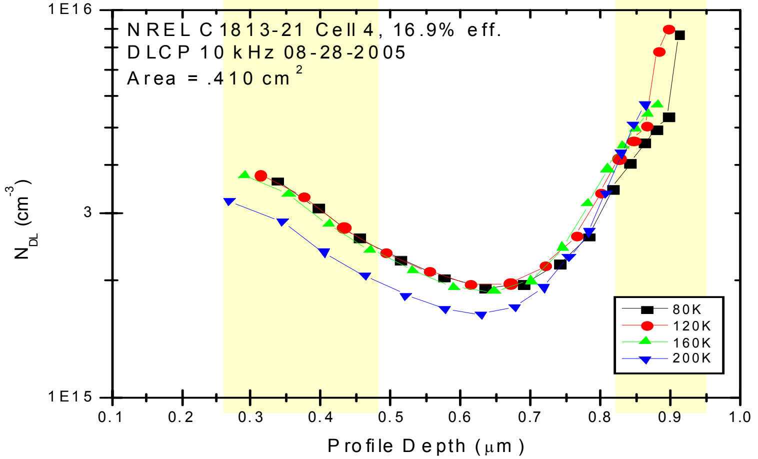
Depletion Region DLCP Density

Zero-Field Region DLCP Density

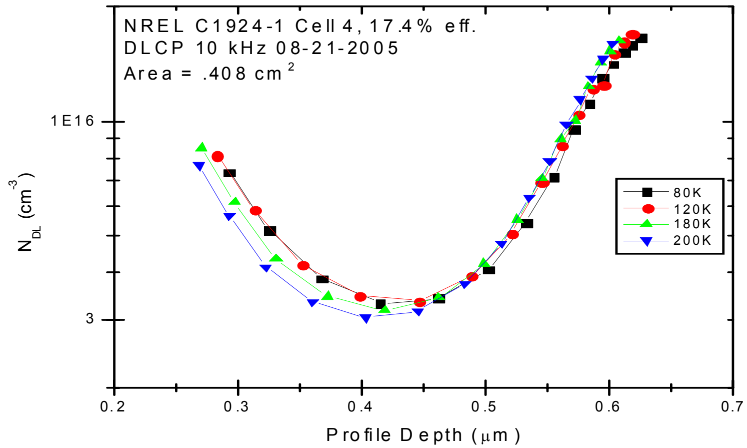
2) NREL C1919 Cell 4: 14.4%



3) NREL C1813 Cell 4: 16.9%

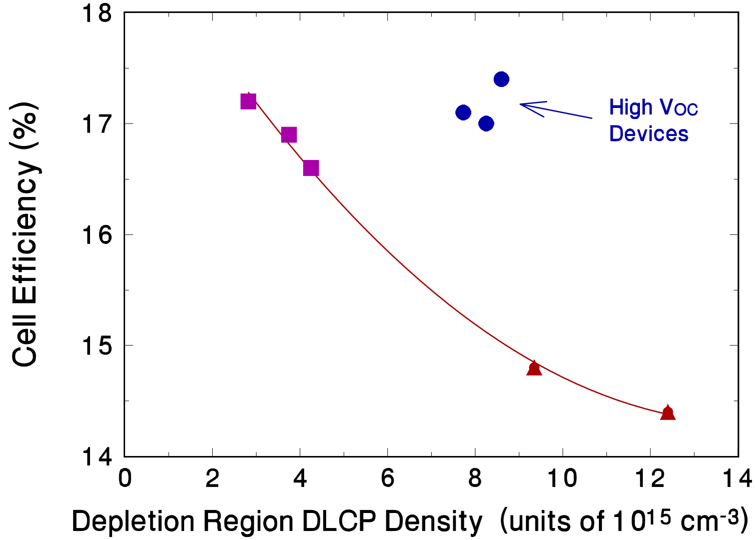


4) NREL C1924 Cell 4: 17.4%

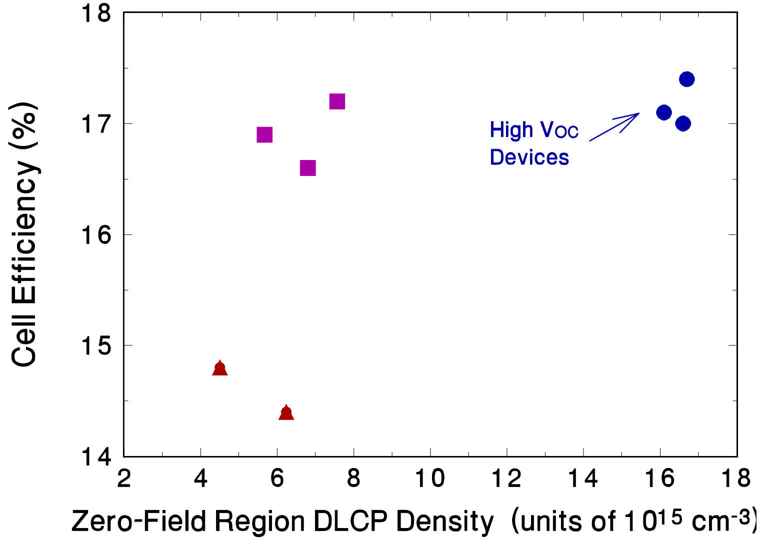


Correlation of Device Efficiencies with DLCP Densities in Different Absorber Regions

DLCP Densities in Region Close to Barrier



DLCP Densities in Zero-Field Region



Correlation of efficiencies to DLCP density close to barrier is quite good, except for the 3 high V_{OC} devices from sample C1924-1

For those 3 devices we believe the higher value of V_{OC} is due to a slightly higher Ga fraction, and because the carrier density is higher outside the depletion region.