Impedance Measurement as a Diagnostic Tool for Device Degradation

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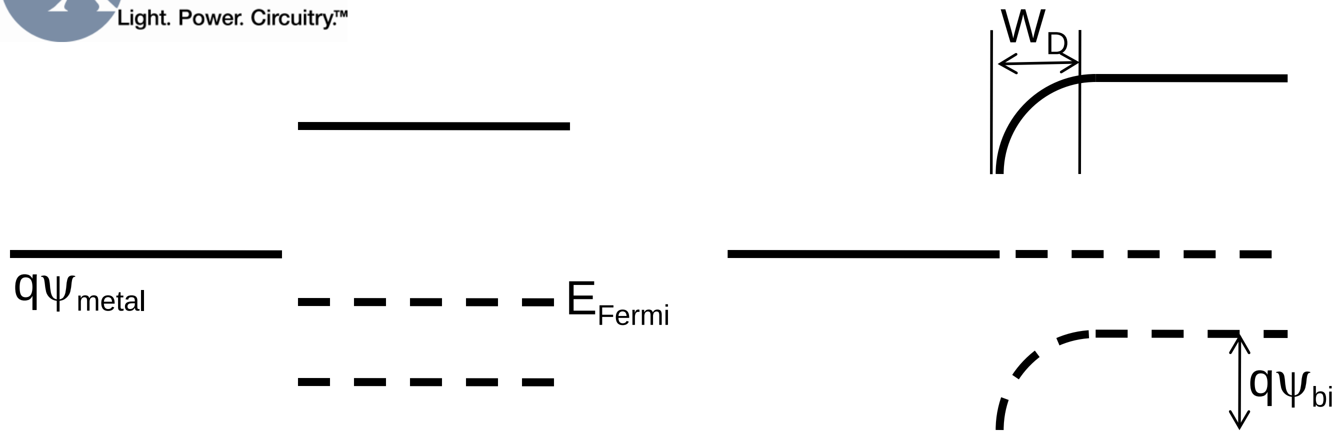
What We Can Learn From Impedance Measurements

Measurement	Analysis	What is Learned
Impedance under dark vs. bias voltage	Nyquist plot: Im(Z) vs. Re(Z)	• Number of capacitances in the device becomes apparent. • Extract fitted values of C, R.
	C vs. bias voltage (C-V)	• Origin of capacitance (e.g. geometric vs. chemical) is revealed by bias dependence.
	Mott-Schottky plot: $1/C^2$ vs. bias voltage	• Build-in potential. • Concentration of intrinsic dark carriers.
Impedance vs. light	C vs. Voc	• Chemical capacitance, derived from the photo-carriers, is probed. • Carrier lifetime.

Not included in this study but possible: impedance vs. temperature.

Mott-Schottky Analysis*



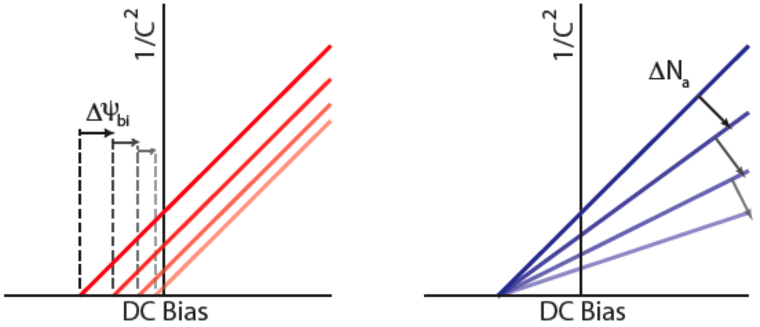
$$\boxed{\frac{1}{C_D^2} = \frac{2\left(\Psi_{bi} - V - \frac{q}{kT}\right)}{q\varepsilon N_A}}$$

W_D: depletion width
ψ_{bi}: built-in potential of the barrier
C_D: depletion layer capacitance per unit area
N_A: charge carrier density in the barrier

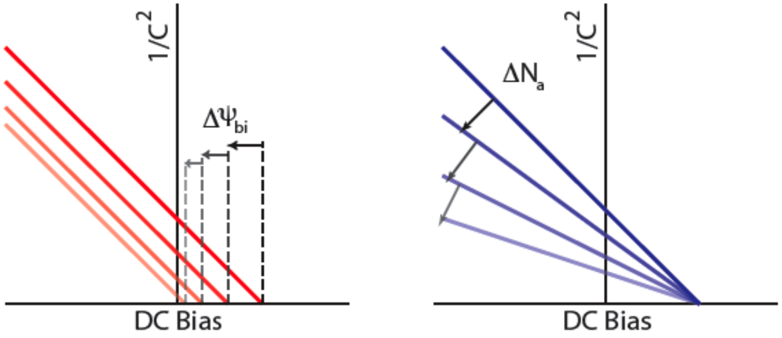
$$N_A = \frac{2}{q\varepsilon}\left[-\frac{1}{d\left(\frac{1}{C_D^2}\right)/dV}\right]$$

*S. M. Sze, *Physics of Semiconductor Devices*, 2nd Ed. John Wiley & Sons, New York, 1981.

Depletion region at hole extracting electrode

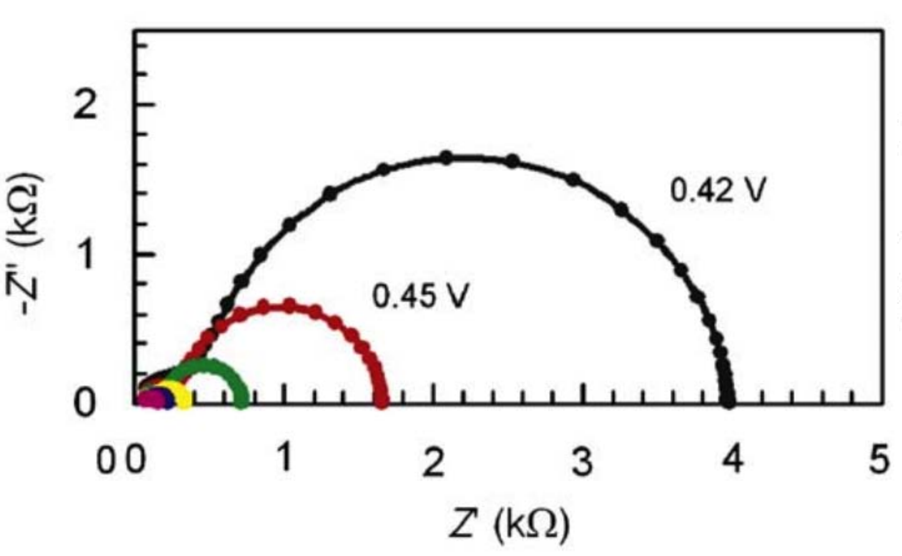


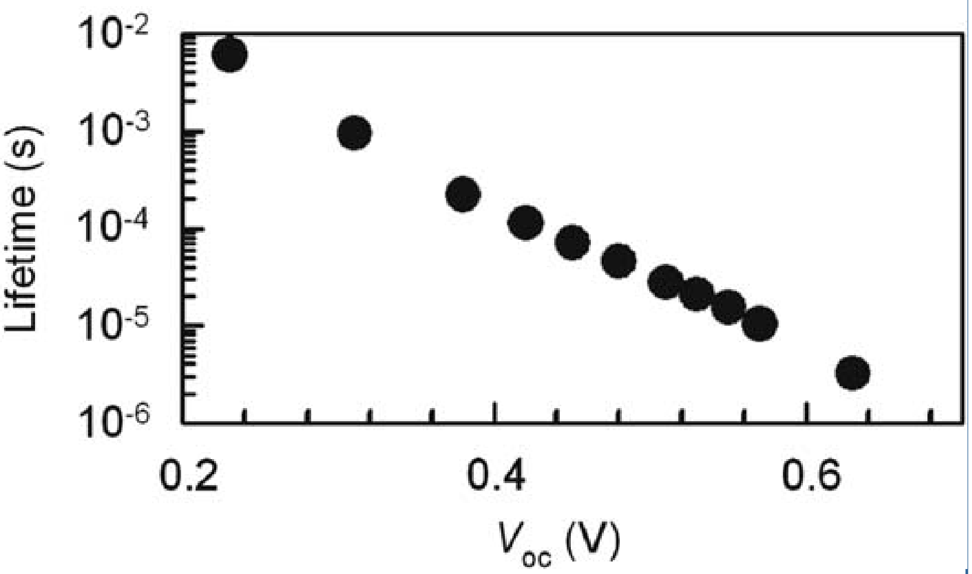
Depletion region at electron extracting electrode



Carrier Lifetime Calculation

- Photo-carrier lifetimes can be measured by impedance spectroscopy of devices under illumination*.
- Photo-generated carriers result in a photo-capacitance that is analyzed as a RC circuit, where C is the photo-capacitance, R is recombination resistance.
- In this analysis, the RC time-constant is the photo-carrier lifetime.

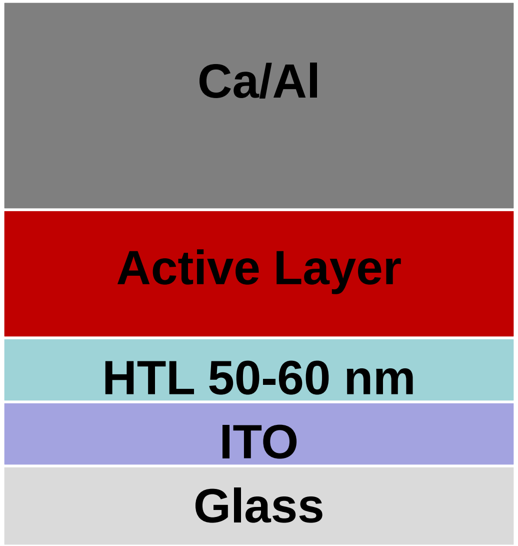




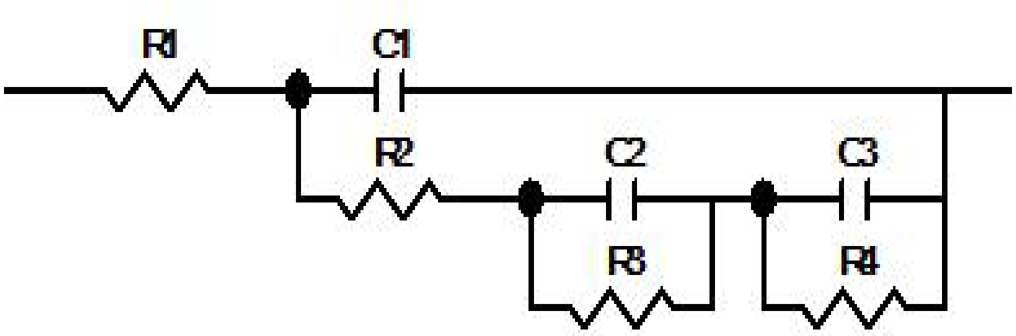
*G. Garcia-Belmonte, P. P. Boix, J. Bisquert, M. Sessolo, H. J. Bolink, “Simultaneous determination of carrier lifetime and electron density-of-states in P3HT:PCBM organic solar cells under illumination by impedance spectroscopy”, Solar Energy Materials and Solar Cells (2009).

Experimental Methods

- **Measurement Instruments**
  - Impedance Analyzer: Agilent 4294A.
  - Solar Simulator: NREL's user facility XT-10.
- **Devices** (encapsulated with getter and cap glass)
  - 5323-2, Plexcore® PV1000
  - 5323-6, Plexcore® PV2000
  - 5409-2, Plexcore® PV2000 (294 nm, active layer + HTL)
  - 5409-6, Plexcore® PV2000 (193 nm, active layer + HTL)
  - 5409-8, Plexcore® PV2000 (129 nm, active layer + HTL)
- **Accelerated Tests**
  - 1 Sun Xe
    - 5409-2, measurement points: 2, 24, 96 hours,
  - 2.5 Sun Xe 60°C / 60% RH Weathometer
    - 5409-6, measurement points: 2, 24 hours.
  - ~0.8 Sun Sulfur
    - 5409-8, measurement points: 2, 47, 191 hours.



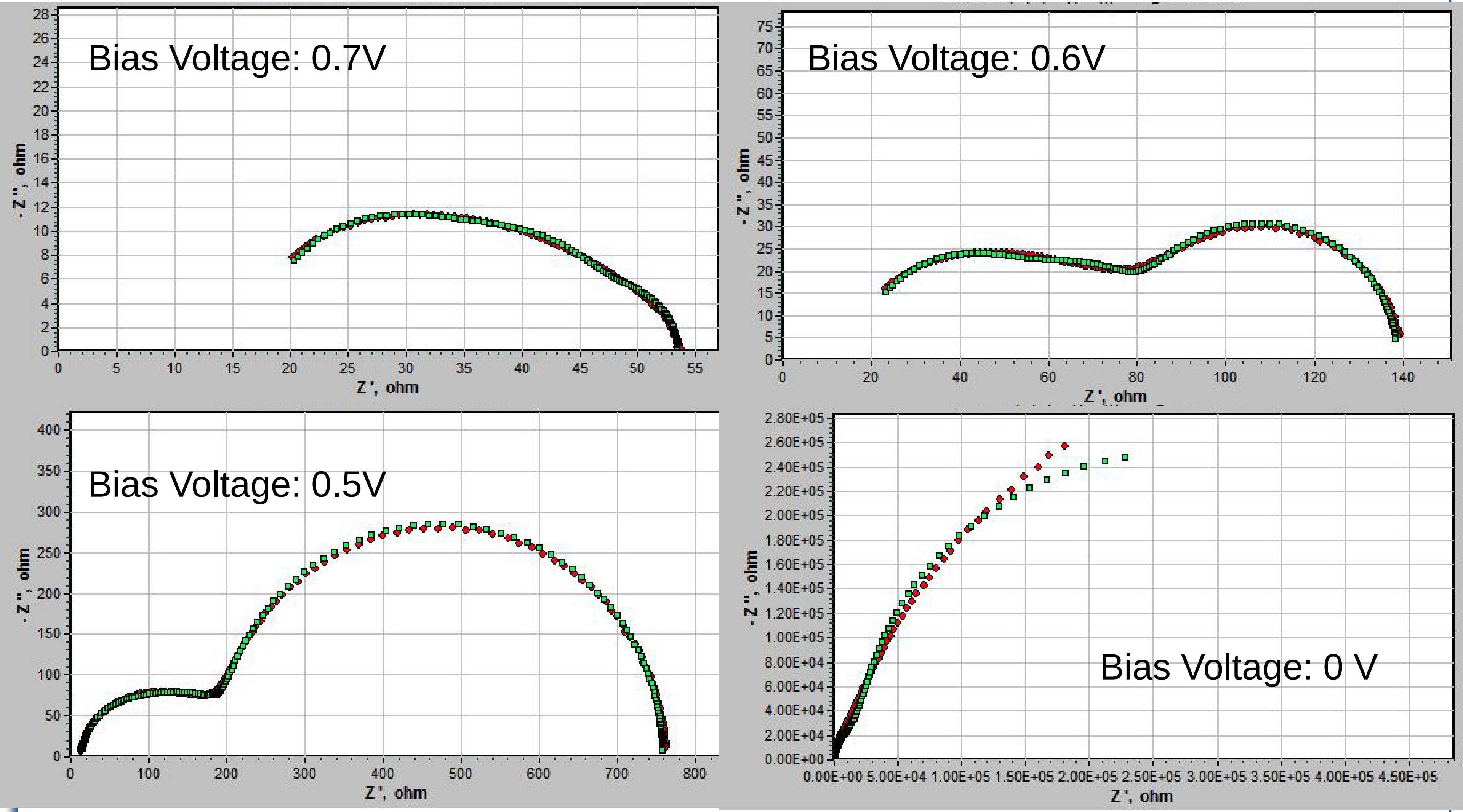
Establish Equivalent Circuit*



- C1: geometric capacitance of the active layer
- C2: depletion capacitance at HTL / active layer interface
- C3: depletion capacitance at active layer / metal interface

* A similar equivalent circuit has been reported: M. Knipper, J. Parisi, K. Coakley, C. Waldauf, "Impedance spectroscopy on polymer-fullerene solar cells", Z. Naturforsch, 62a, 490-494 (2007).

Nyquist Plots and Fitting



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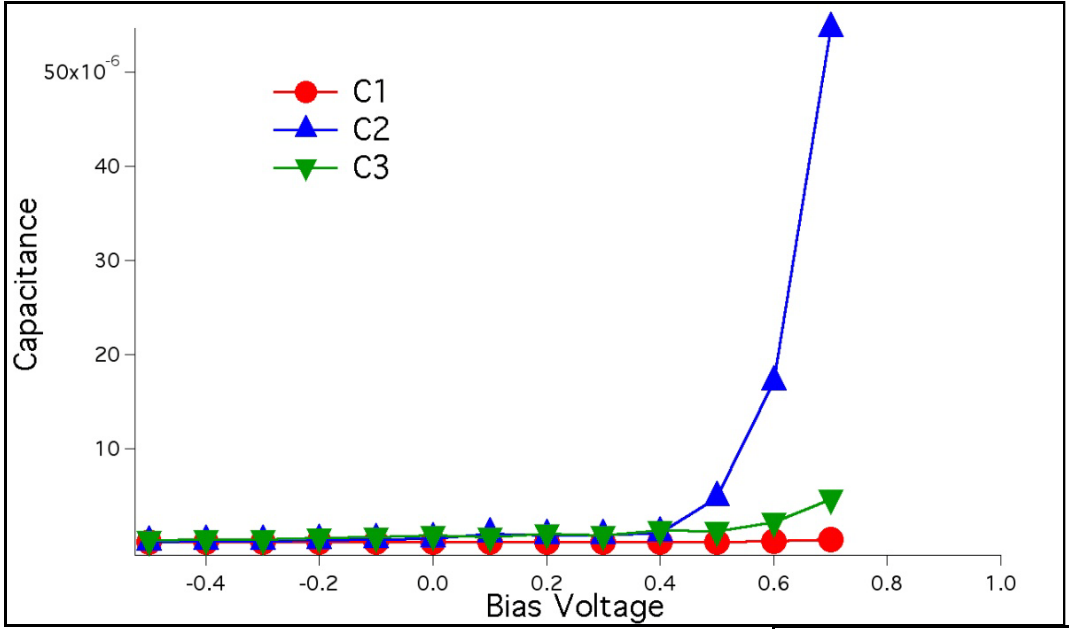
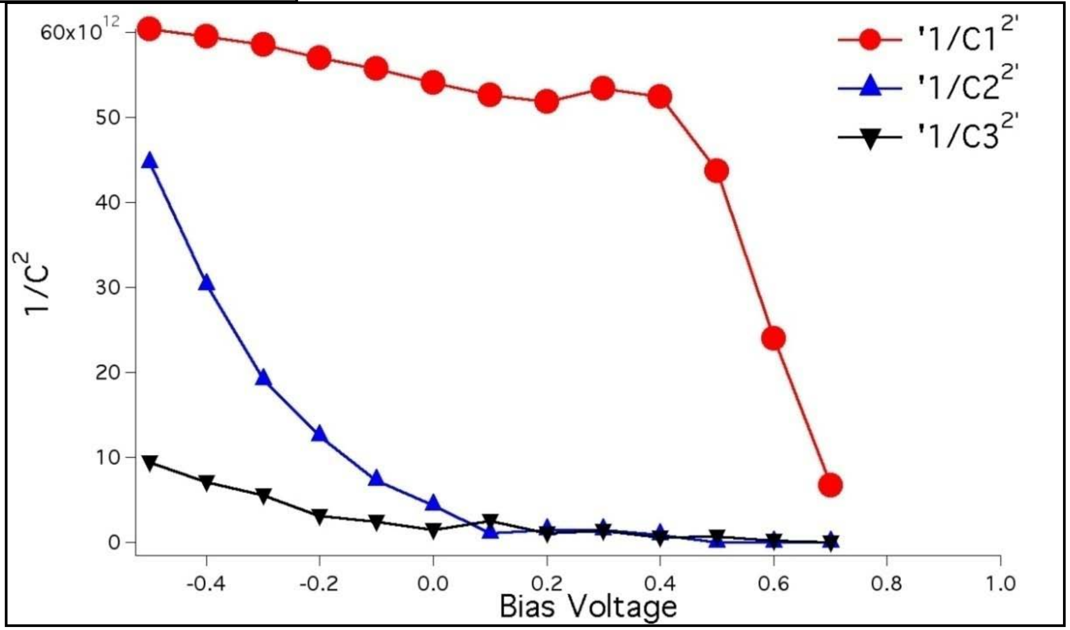
- ● Measured
- ■ Calculated

C-V and Mott-Schottky Plots





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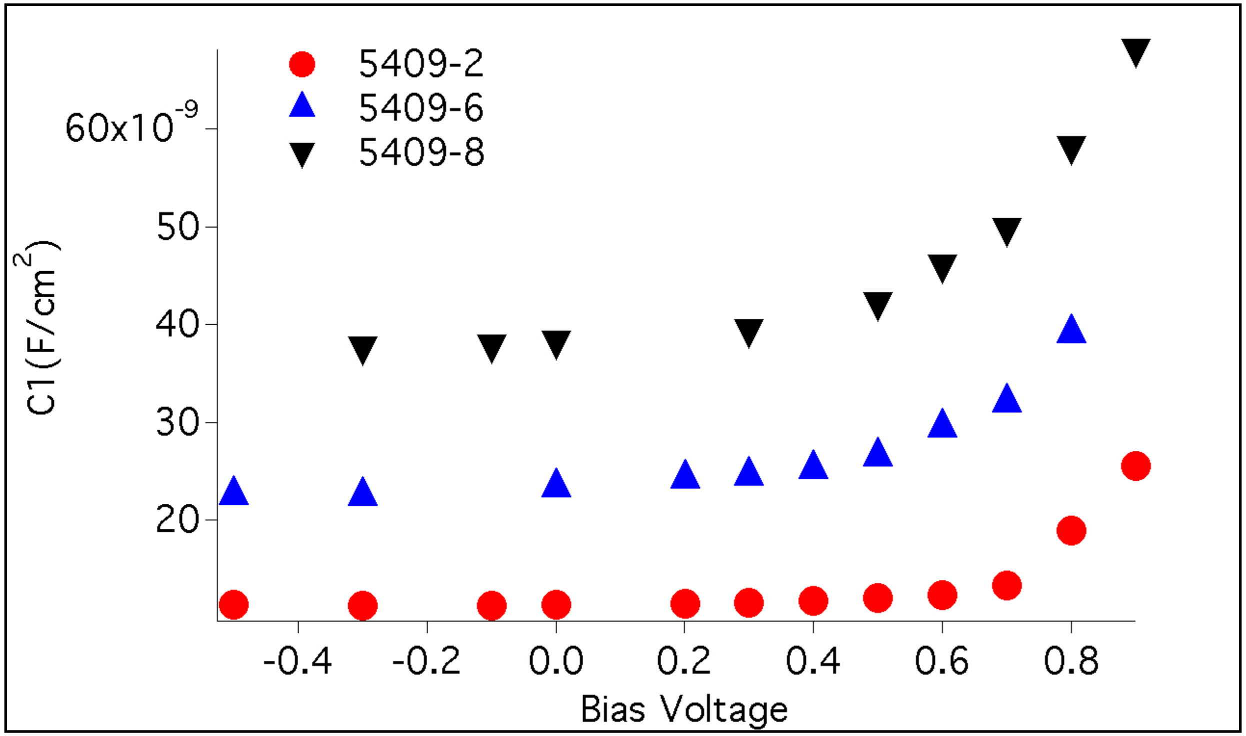
Thickness Dependence_C1



Geometric capacitance did not change much with bias voltage.

Geometric Capacitor C1	5409-2 (239 nm)	5409-6 (138 nm)	5409-8 (74 nm)
Calculated	1.17E-8	2.03E-8	3.77E-8
Fitting data	1.13E-8	2.3E-8	3.8E-8

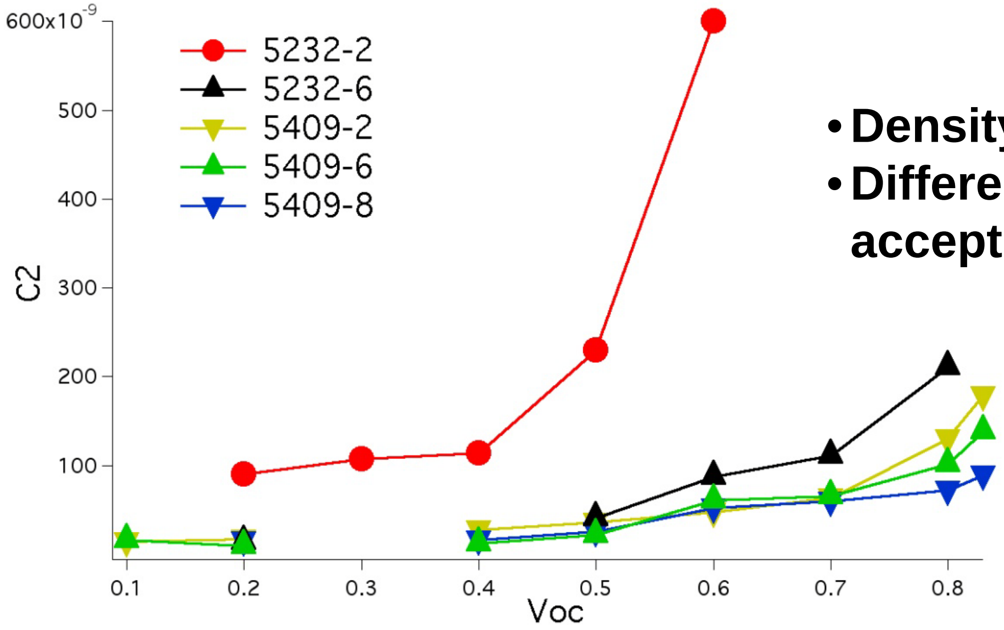
- HTL is considered part of the electrode.
- Calculated values assume relative dielectric constant of 3.5.

Thickness Dependence_C2, C3

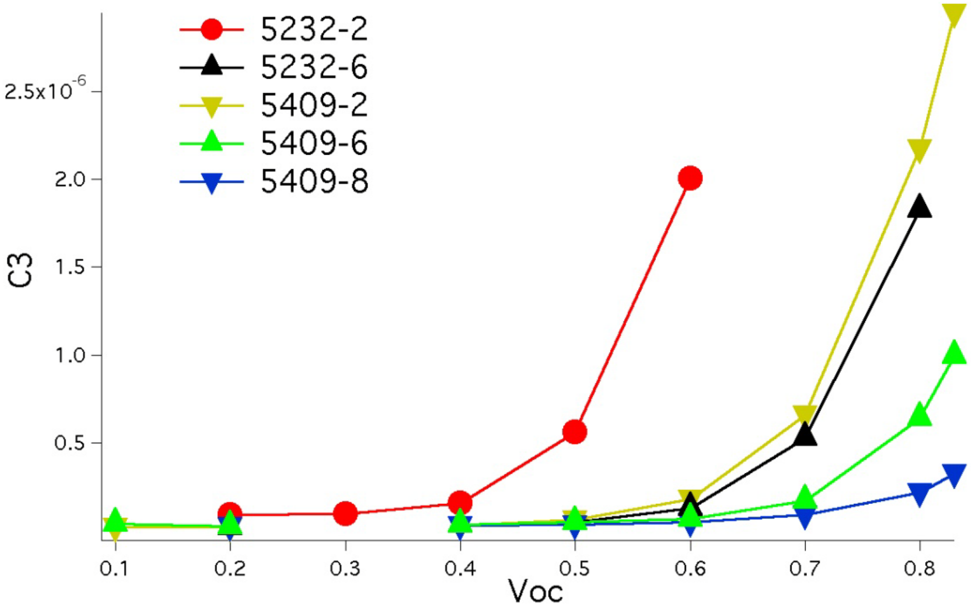
	C2_N_A (cm^{-3})	C2_V_{bi} (V)	C3_N_A (cm^{-3})	C3_V_{bi} (V)
5409-2	1.34E+15	0.462	8.68E+15	0.606
5409-6	1.45E+15	0.595	1.78E+16	0.697
5409-8	2.71E+15	0.604	1.51E+16	0.776

Dark carrier density appears to increase as the active layer becomes thinner.

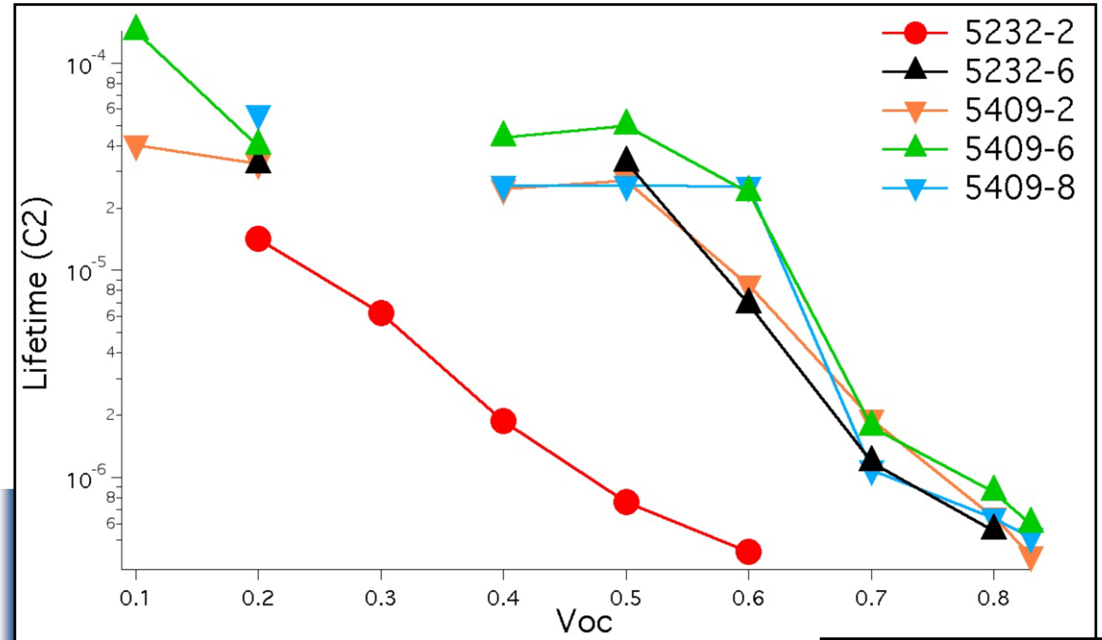
Thickness and Light Dependence_C2, C3



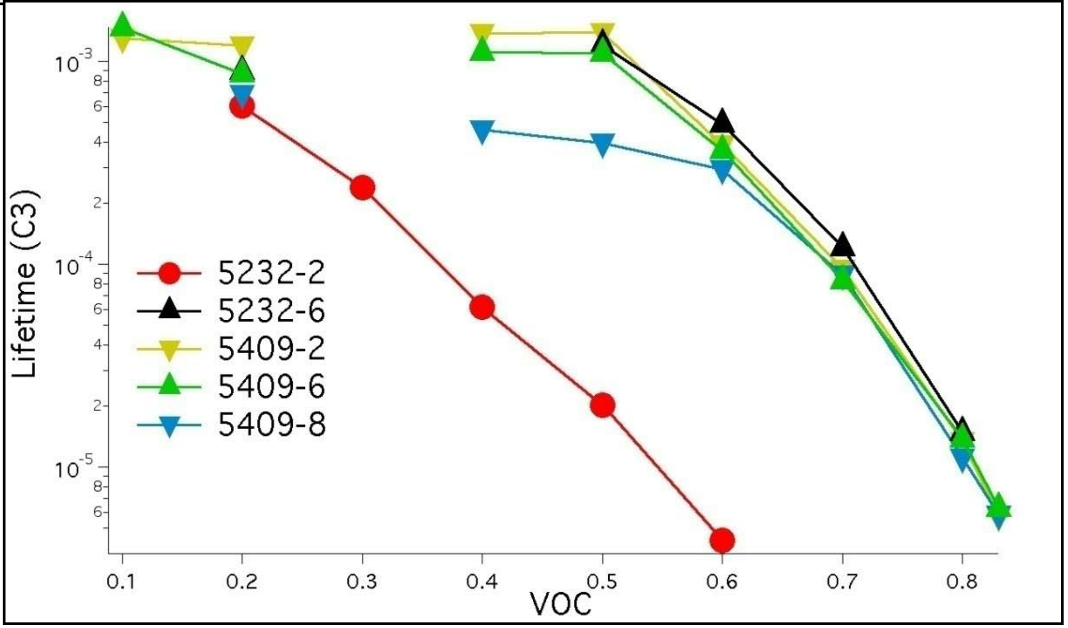
- Density of states: 5409-2 > 5409-6 > 5409-8
- Different morphologies of the donor-acceptor blend?



Carrier Lifetime_C2, C3



Reasonable carrier lifetimes are extracted from the light-induced capacitance.



Apply to Device Degradation

Cause of Degradation	Impact on the Device	Measurement
Delamination / dark spots	Active area effectively lowered. Jsc ↓.	
Electrode oxidation	Rs ↑. Change in depletion capacitance or Vbi possible. An extra capacitor could potentially form if oxidation is severe.	Nyquist dark, Mott-Schottky
Active layer chemical decomposition or morphology changes	Recombination ↑. Carrier lifetime ↓. Voc, Jsc, and FF ↓.	Nyquist light
Active layer doping. Source of dopants can be either extrinsic (i.e. oxygen ingress) or intrinsic (diffusion from electrodes)	Rs ↓. Depletion capacitance ↑. Voc, Jsc and FF could go ↑ or ↓.	Nyquist dark, Mott-Schottky
Shunting of device due to electromigration of metal	Rp ↓. Voc, Jsc, and FF ↓.	Nyquist dark

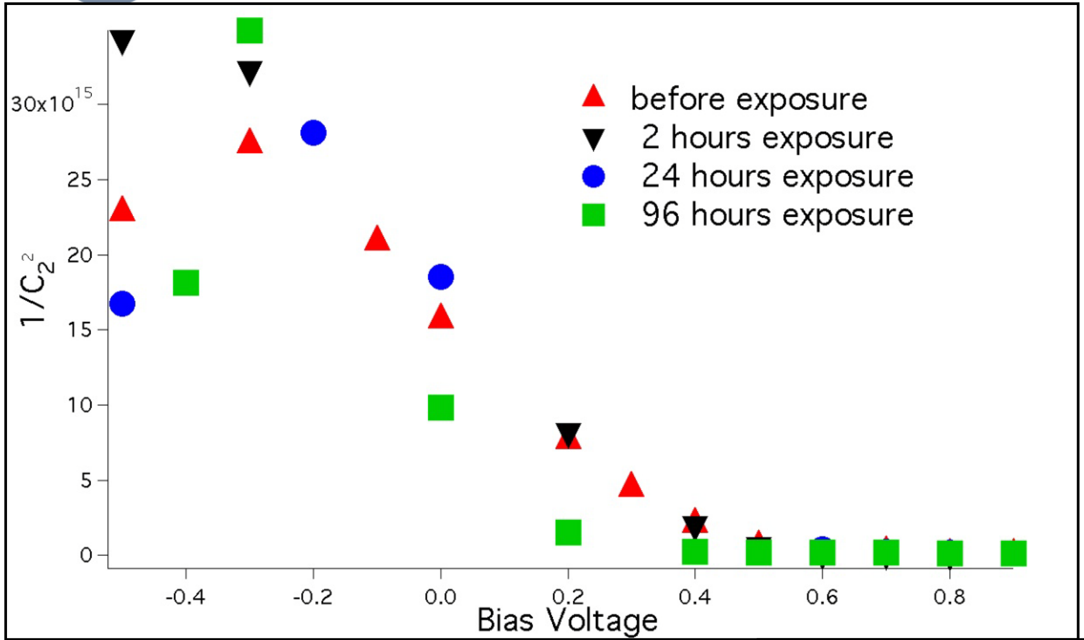
J-V Characteristics

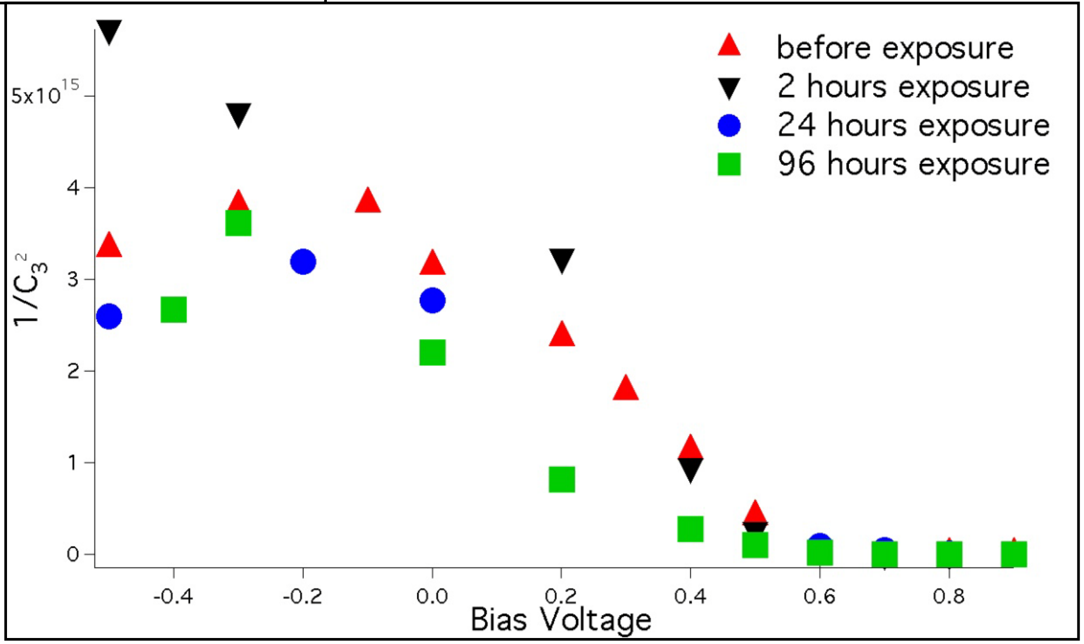
5409-2	Voc (V)	Jsc (mA/cm^2)	FF	PCE	R@Voc (Ω)	R@Jsc (Ω)	Rs (Ω) Spice	Rp (Ω) Spice
Before exposure	0.8076	10.01	64.9%	5.25%	124	9.85E3	40	12.5E3
2 hours	0.8102	11.20	61.6%	5.59%	135	8.06E3	56	11.2E3
24 hours	0.7066	9.891	55.7%	3.89%	182	5.85E3	116	8.35E3
96 hours	0.6345	8.640	51.8%	2.84%	238	3.91E3	116	6.15E3

5409-6	Voc (V)	Jsc (mA/cm^2)	FF	PCE	R@Voc (Ω)	R@Jsc (Ω)	Rs (Ω) Spice	Rp (Ω) Spice
Before exposure	0.8188	5.401	59.4%	2.63%	231	9.07E3	55	12E3
2 hours	0.7084	5.943	56.4%	2.37%	240	7.09E3	79	11.8E3
24 hours	0.5950	5.598	54.9%	1.83%	238	7.31E3	64	11.2E3

5409-8	Voc (V)	Jsc (mA/cm^2)	FF	PCE	R@Voc (Ω)	R@Jsc (Ω)	Rs (Ω) Spice	Rp (Ω) Spice
Before exposure	0.8499	5.176	58.0%	2.55%	230	6.84E3	64	9E3
2 hours	0.8557	5.158	58.1%	2.56%	228	7.56E3	72	9.65E3
47 hours	0.8315	5.635	50.2%	2.35%	313	5.40E3	152	6.25E3
191 hours	0.7748	5.391	55.2%	2.31%	291	6.32e3	140	7.45E3

Mott-Schottky Plots_5409-2





Mott-Schottky Analysis

5409-2	C2_N_A (Carrier Density)	C2_V_{bi} (Built-in Voltage)	C3_N_A	C3_V_{bi}
before stress	1.34E+15	0.462	8.68E+15	0.606
2 hours	3.45E+15	0.463	2.69E+16	0.629
24 hours	4.20E+15	0.6	3.52E+16	0.636
96 hours	2.08E+15	0.193	2.84E+16	0.422

5409-6	C2_N_A	C2_V_{bi}	C3_N_A	C3_V_{bi}
before stress	1.45E+15	0.595	1.78E+16	0.697
2 hours	6.88E+15	0.721	1.17E+17	0.683
24 hours	7.16E+15	0.506	1.07E+17	0.572

5409-8	C2_N_A	C2_V_{bi}	C3_N_A	C3_V_{bi}
before stress	2.71E+15	0.604	1.51E+16	0.776
2 hours	1.09E+16	0.682	5.27E+16	0.713
24 hours	1.17E+16	0.657	9.95E+17	0.885
191hours	2.69E+16	0.806	4.39E+17	0.798

Carrier density increased after initial stress, suggesting doping.

Carrier Lifetime_5409-2

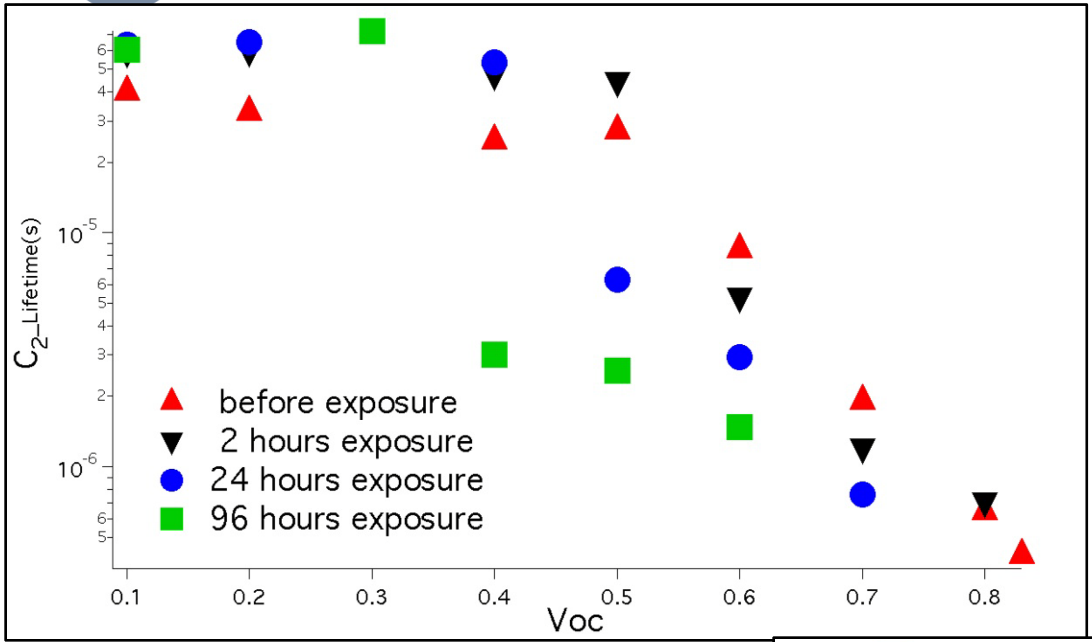
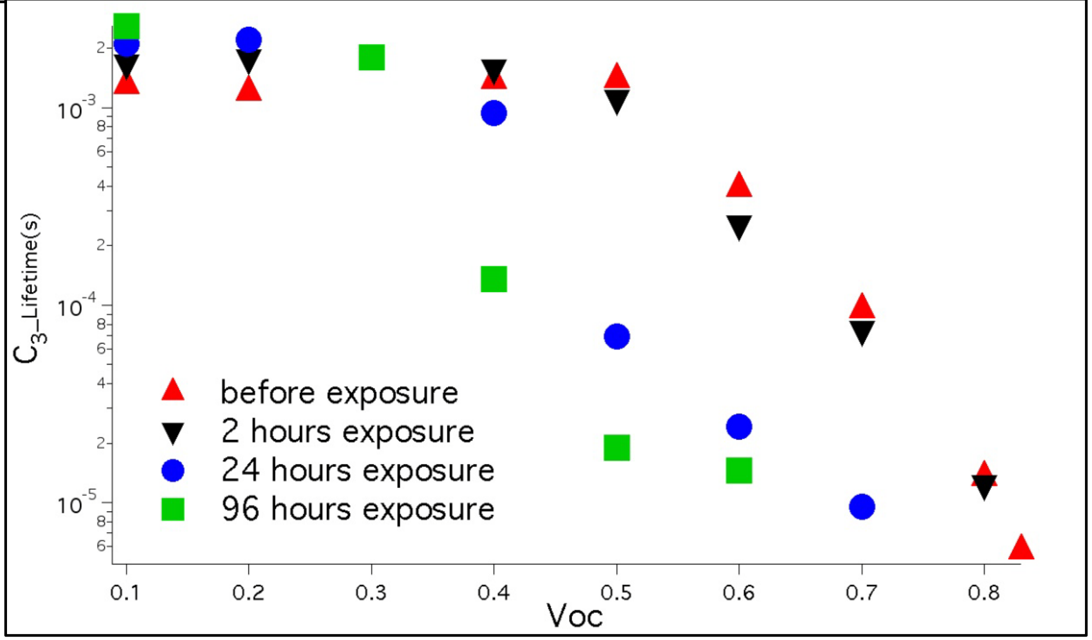
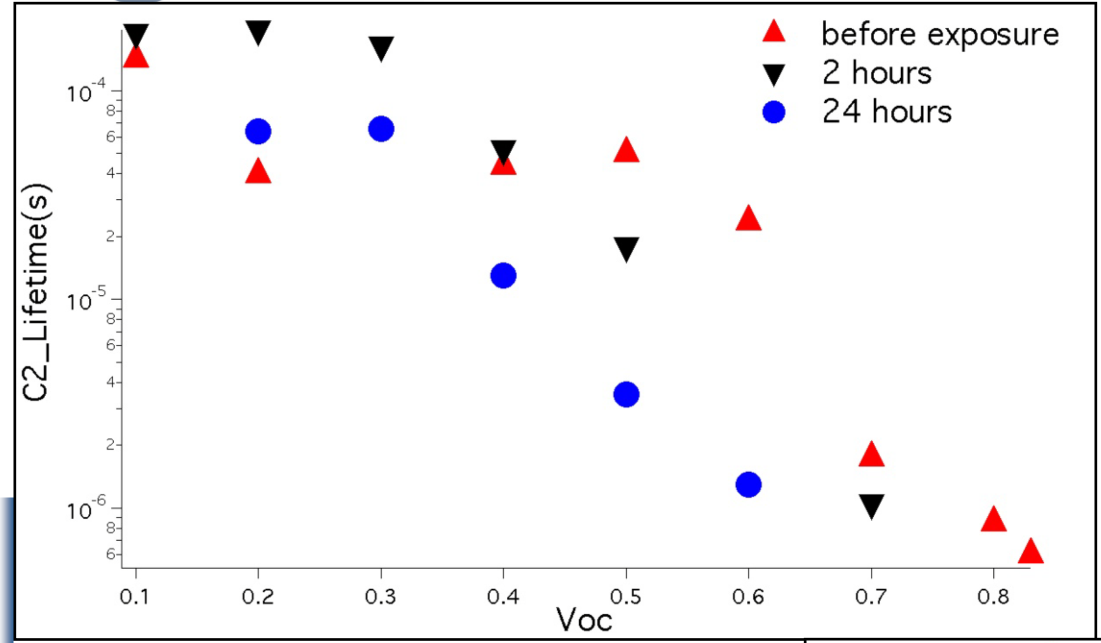


Photo-carrier lifetime decreased by order of magnitude upon Xe stress.



Carrier Lifetime_5409-6



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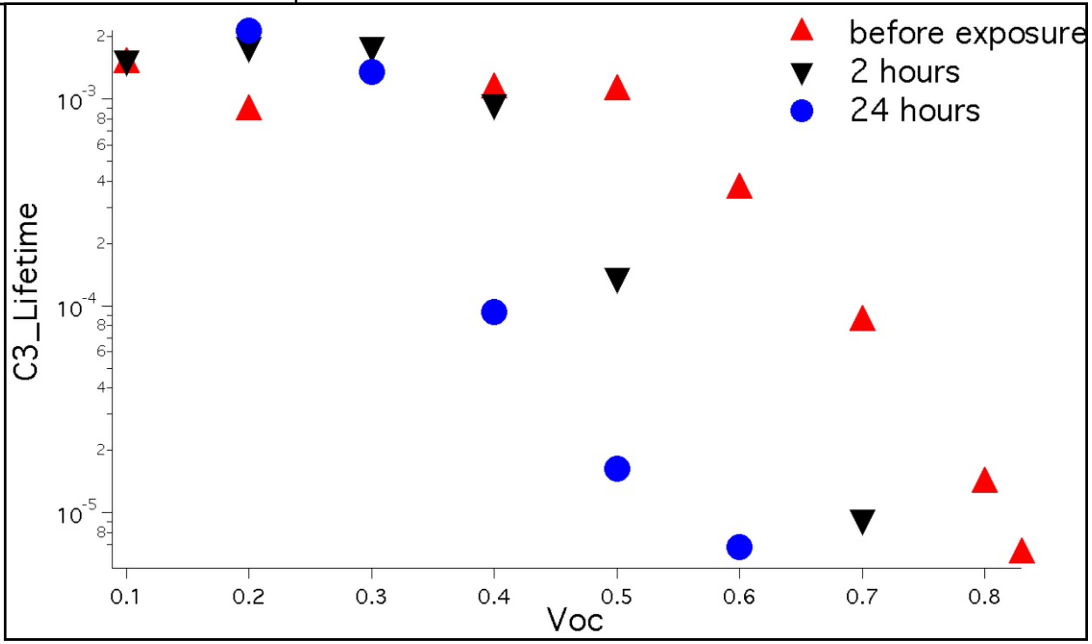


Carrier Lifetime_5409-8

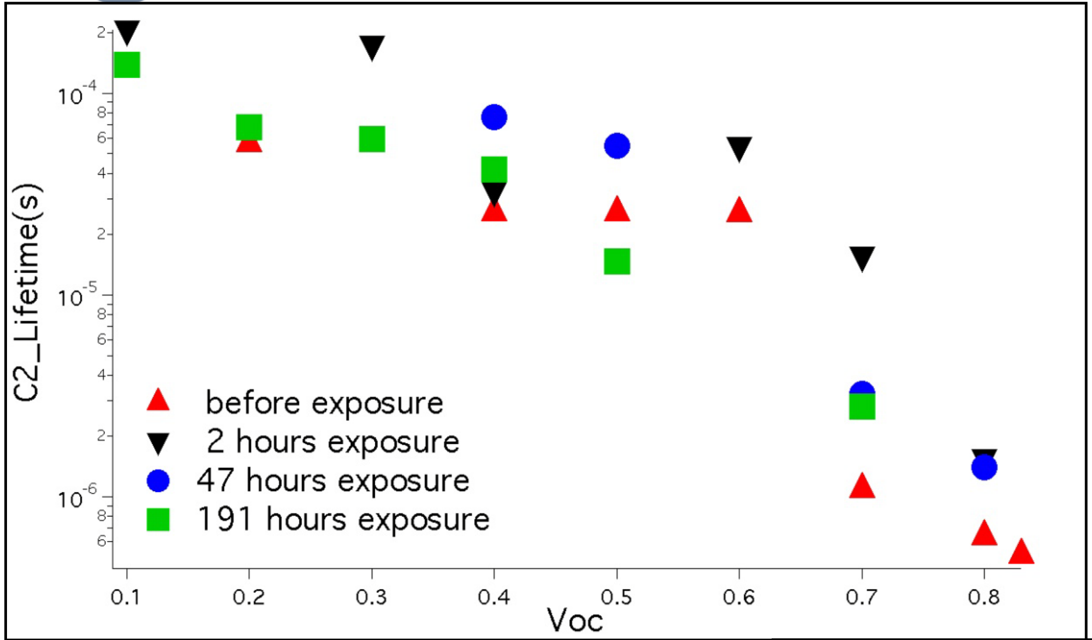
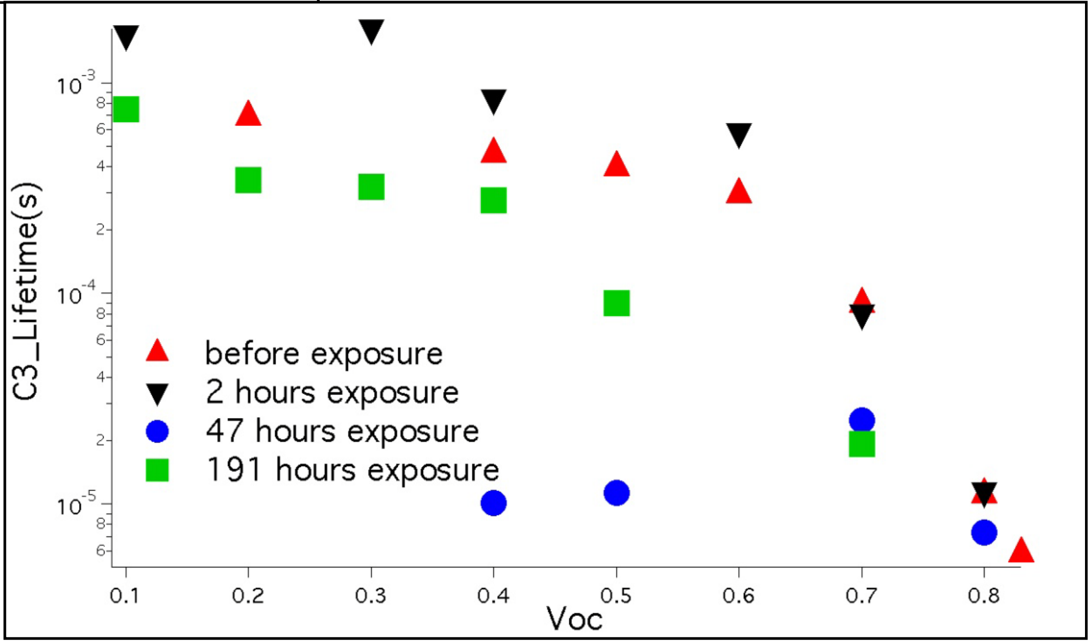


Photo-carrier lifetime was affected much less under sulfur plasma compared to Xe.



Summary

- A three-capacitor model was found to fit our devices over a wide range of bias voltage and active layer thicknesses.
  - C1: geometric of active layer; C2: interfaces with HTL; C3: interface with metal.
  - C-V analysis showed geometric capacitance C1 did not change much with bias voltage.
  - Mott-Schottky analysis yielded build-in voltage and intrinsic dark carrier concentrations for C2 and C3.
- As a function of decreasing active layer thickness:
  - C1: fitted data agreed well with calculated assuming a relative dielectric constant of 3.5.
  - C2 and C3: dark carrier densities appeared to increase; density of state decreased; reasonable carrier lifetime was extracted.
- As devices were stressed under Xe:
  - Photo-carrier lifetime decreased, suggesting photo-chemical degradation of the active layer components;
  - Carrier density increased, consistent with doping from photo-chemical degradation .
- Sulfur plasma caused less damaging than Xe:
  - UV component is likely a large contributor to the degradation.

Impedance measurement and analysis are useful tools to derive equivalent circuit model, study carrier concentration, build-in voltage, carrier lifetime. These parameters in turn can be used to probe degradation mechanisms.