Center for Thin Film Devices

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Introduction

- Dark forward bias J_D-V characteristics have been applied in characterizing the mechanisms limiting a-Si:H cell performance and gap states in the i layers
- The direct correlation between results on film and solar cells has been investigated and extended to metastable gap states
- The creation and annealing kinetics of metastable defect states has been characterized with J_D-V characteristics on cells and photoconductivity measurements on corresponding i layer films
- New results relevant to mechanisms for creation of metastable defect states have been obtained

Forward Bias J_D-V Characteristics

J_D-V characteristics have been applied in:

- Separation and characterization of:
  - p and p/n contacts
  - potential barriers in i layers adjacent to the contacts
  - carrier recombination in p/i regions
  - carrier recombination in bulk
- Directly obtaining the densities and energy distribution of gap states in the i layers of cells
- Characterizing the creation and annealing of metastable defect states in a-Si:H
- Addressing reliable and quantitative correlation of cell properties with those on corresponding i layer films

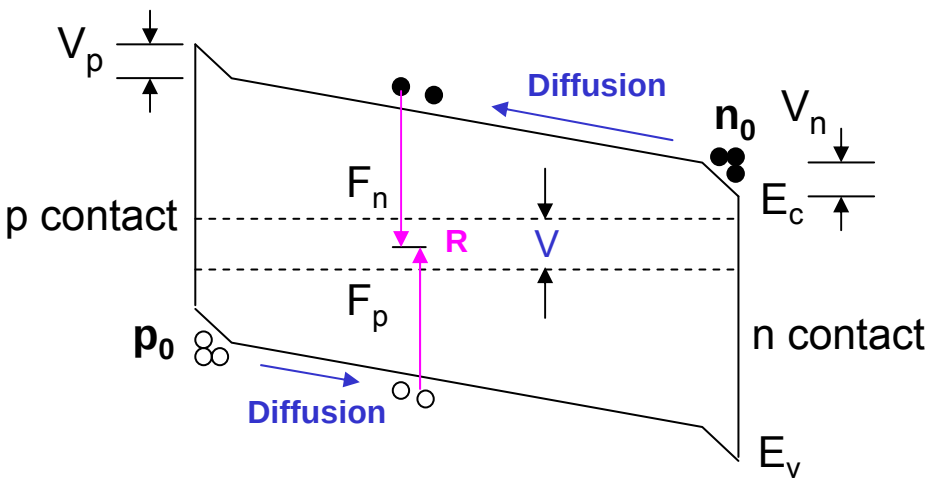
Correlation of Light Induced Changes in Films and Cells

- Kinetics of light induced changes in films and cells highly dependant on microstructure—need characterization on films and cells with corresponding i-layer.
- No unique correlations between densities of light induced defects measured with α (1.2), ESR and $\mu\tau$ as well as cell FF's
- Qualitative correlations have been obtained between $\mu\tau$ and FF
- In films addressed characterization of light induced defect states and kinetics of their creation with $\alpha(E)$ analysis based on multiple defect states, photoconductivity measurements with different generation rates
- Novel approach taken in the correlation of results on films with those on cells using J_D-V characteristics rather than FF

Creation and Annealing of Metastable Defects States

- Issue of fast and slow defect states is addressed—the defect states created faster anneal out faster; their relative ratio depends on illumination intensity
- The kinetics of creation and annealing of defect states under 1 sun illumination, relevant to operating conditions of solar cells, have been investigated
- Kinetics on thin films have been characterized with photoconductivities obtained with generation rates corresponding to 1 to 10^{-5} illuminations; solar cells with J_D-V characteristics
- The recently discovered 25°C annealing of metastable defect states created midgap by **1 sun illumination** has been investigated in both films and corresponding solar cells
- Contributions to the kinetics of quasi-Fermi level splitting and photogenerated carriers have been characterized

Energy band diagram of p-i-n cell under forward bias

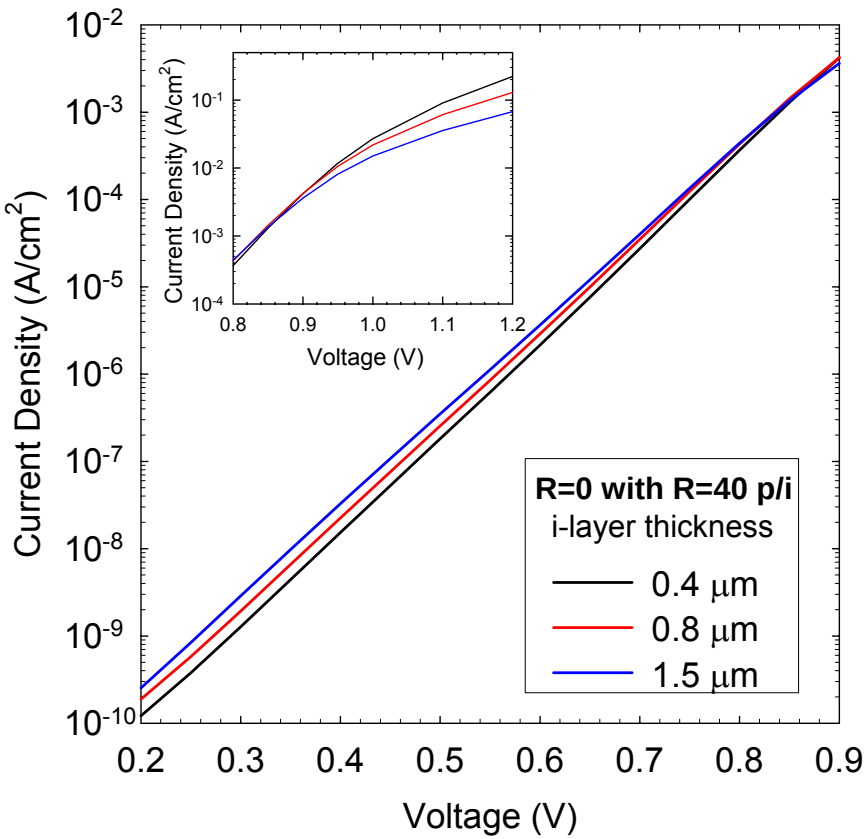


References:

J. Deng et al. Appl. Phys. Lett. ***82*** *(3023) 2003*
J. Deng et al. Mater. Res. Soc. Proc., ***808*** *(A8.8) 2004*
J. Deng et al. 31st IEEE PVSC, 2005 (in press)
J. Deng et al. J. Appl. Phys. 2005 (in press)

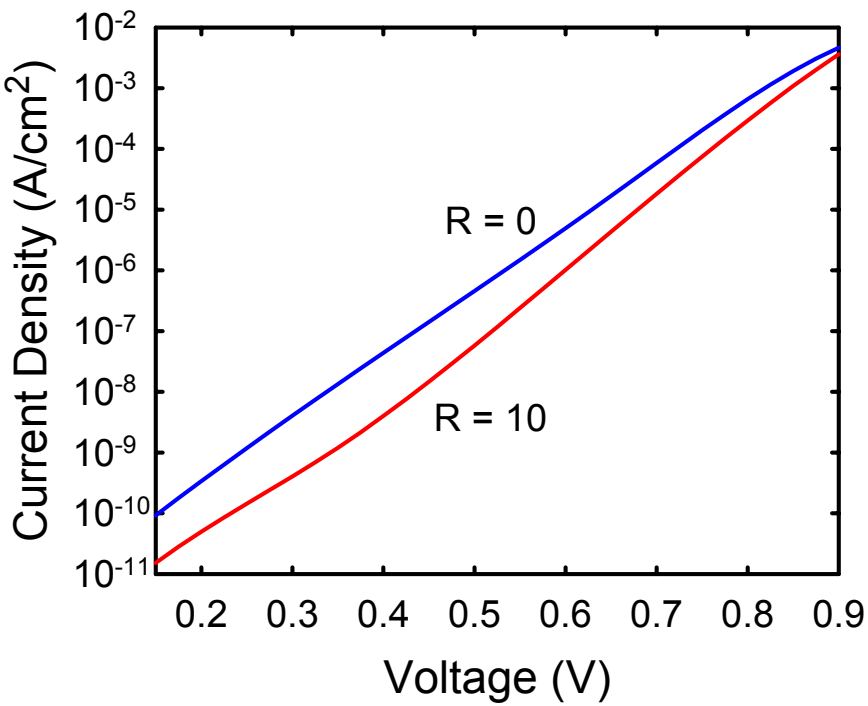
- V_n, V_p potential barriers – depend on p, n contacts and gap states in adjacent i-layer
- Bulk recombination determined by diffusion, SRH recombination through continuous distribution of states across gap

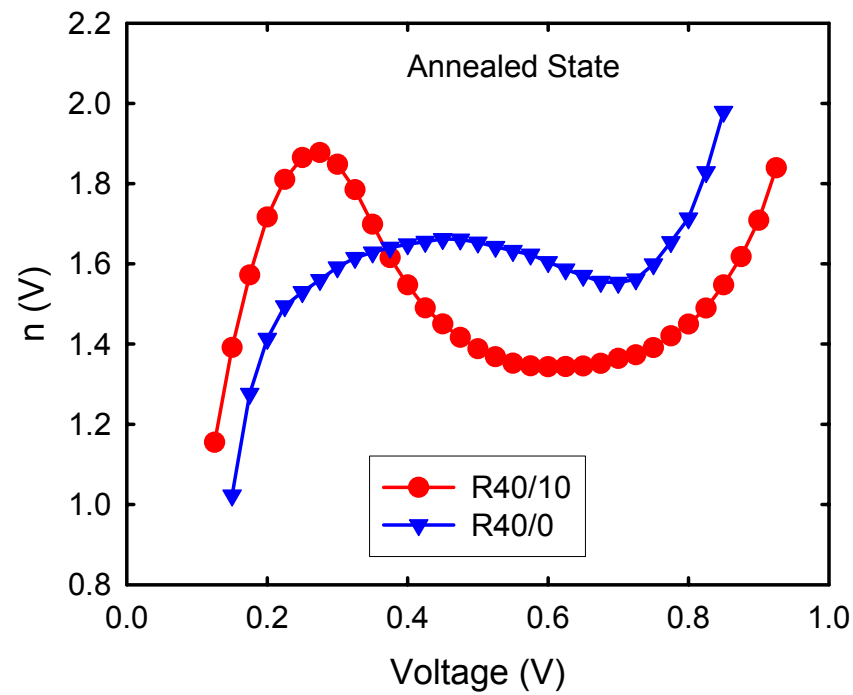
Thickness Dependence of Bulk Recombination



- In high quality cells – p/i recombination much less than in bulk
- Low densities of gap states uniform across i-layer, V_n, V_p ~ 0.1V
- J_D over extended voltage dominated by bulk recombination
- V_n, V_p limit currents approaching built-in potential V_{bi}
- $V > V_{bi}$, drift currents
- Expected results obtained for diffusion/SRH and drift recombination

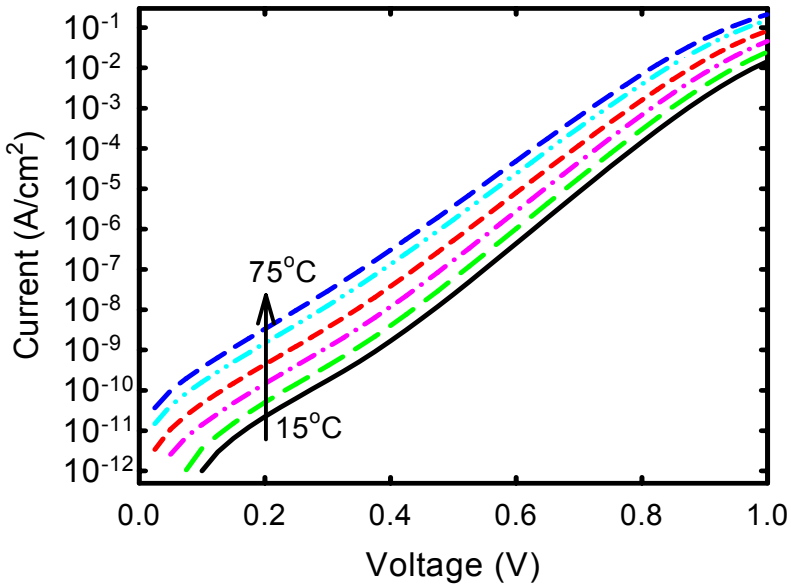
J_D-V characteristics for undiluted (R=0) and protocrystalline (R=10) 4000 Å p-i-n cells with p/i recombination minimized with 200 Å R=40 p/i interface regions

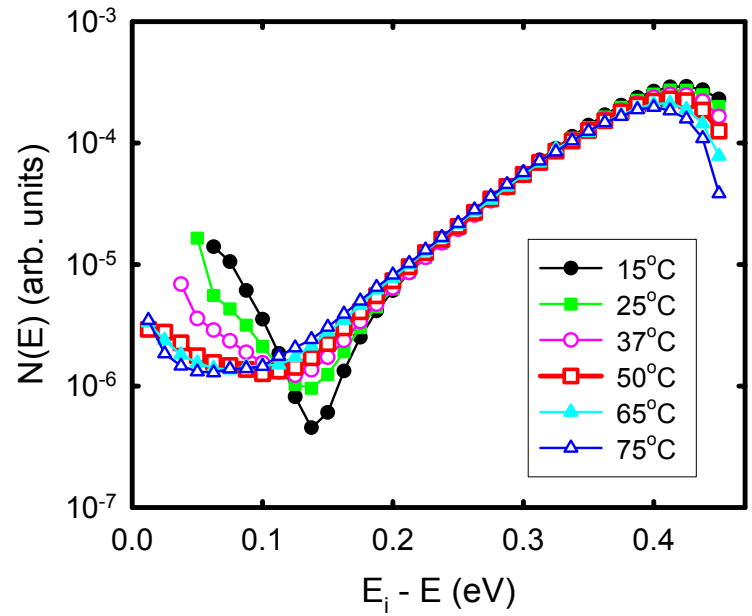




- Bulk recombination – voltage dependent "effective diode quality factor" n(V)
- Magnitude of J_D depends on band gap and density of states

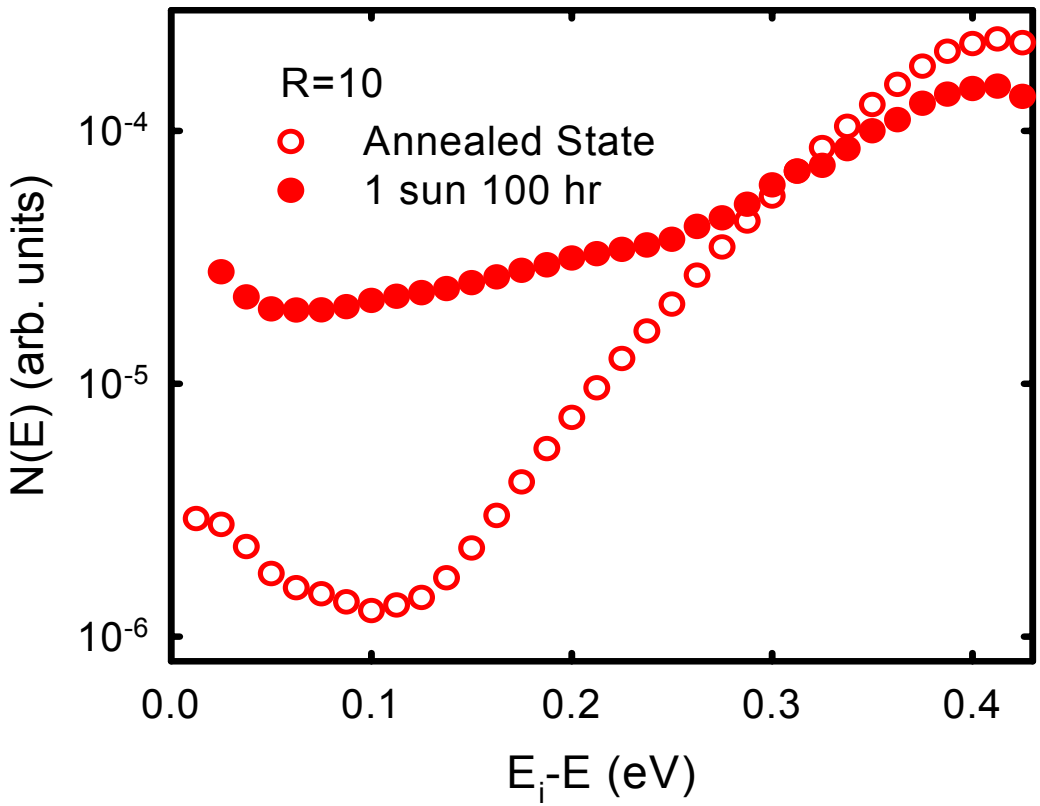
Distribution of Gap States from J_D-V Characteristics





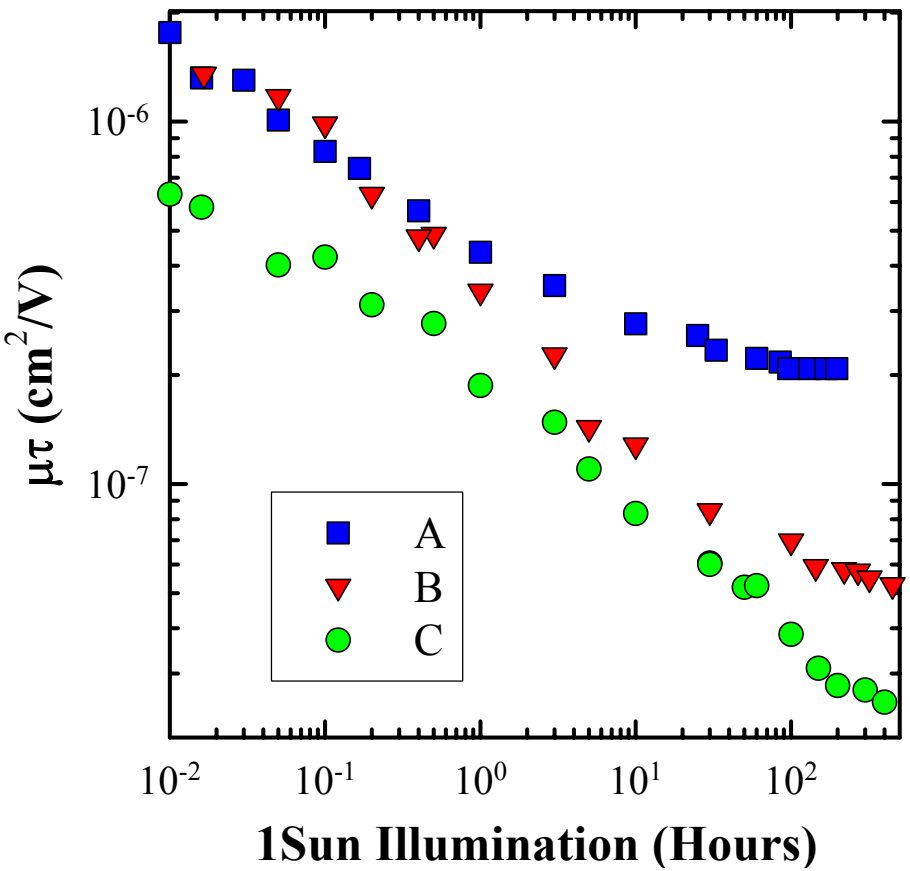
- From activation energy of J_D-V characteristics E_g ~ 1.77 eV
- Below 50°C contributions of shunts at very low biases; at ≥ 0.8V limitations of carrier injection by V_n, V_p
- As expected distribution of gap states derived from SRH analysis is temperature independent
- Consistent with AMPS simulations consisting of 3 Gaussian distributions below midgap

Light Induced Defect States



Relative change in the densities and energy distribution of gap states at and below midgap in the i-layers of protocrystalline cells (*J. Deng et al. MRS 2005 Spring, in press*)

Kinetics of $\mu\tau$ ($G=10^{19}$) Changes with 1 Sun Illumination at 25°C for Three a-Si:H Films

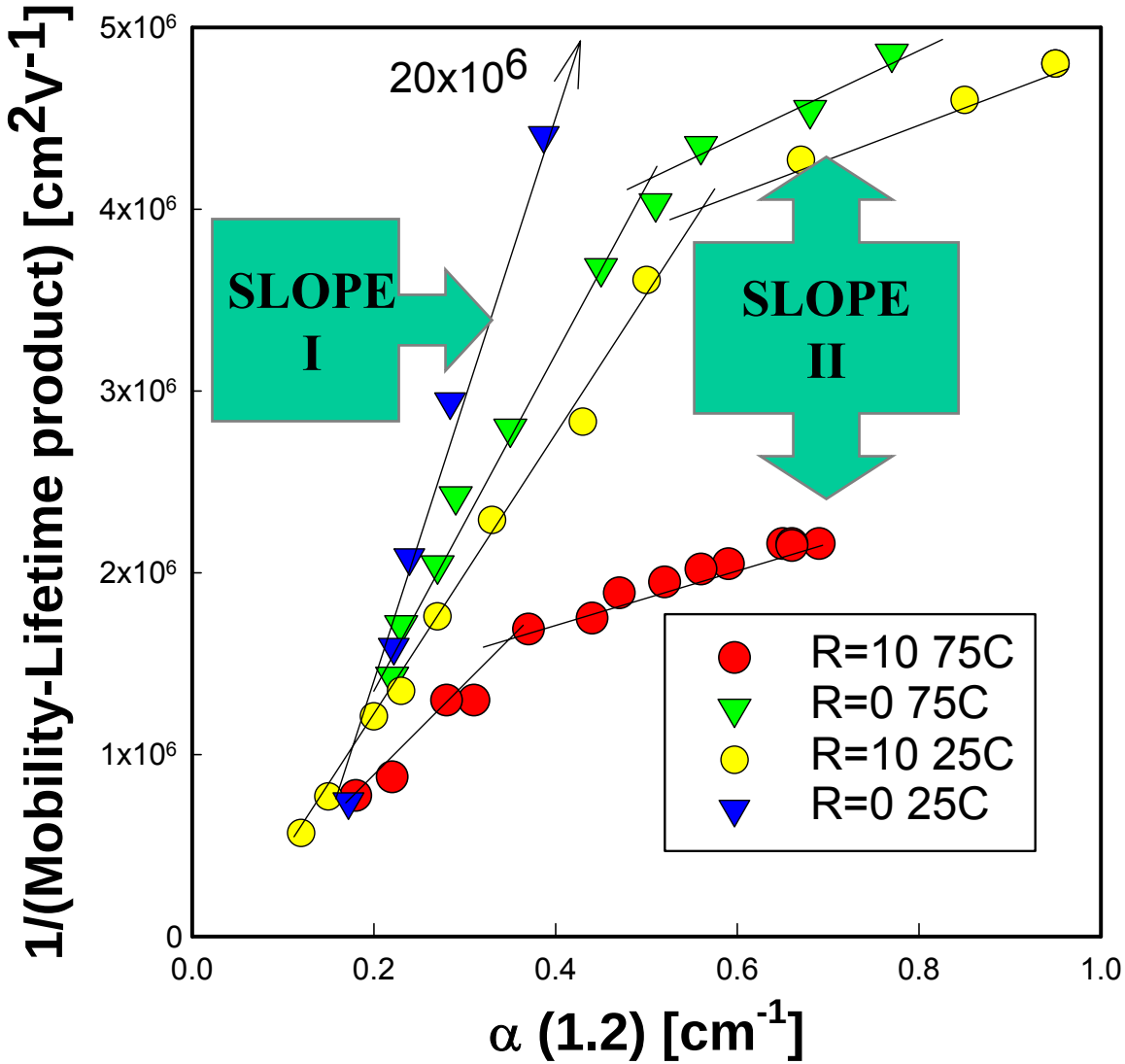


- A – R=10, B – R=0 [1.5 Å/s]

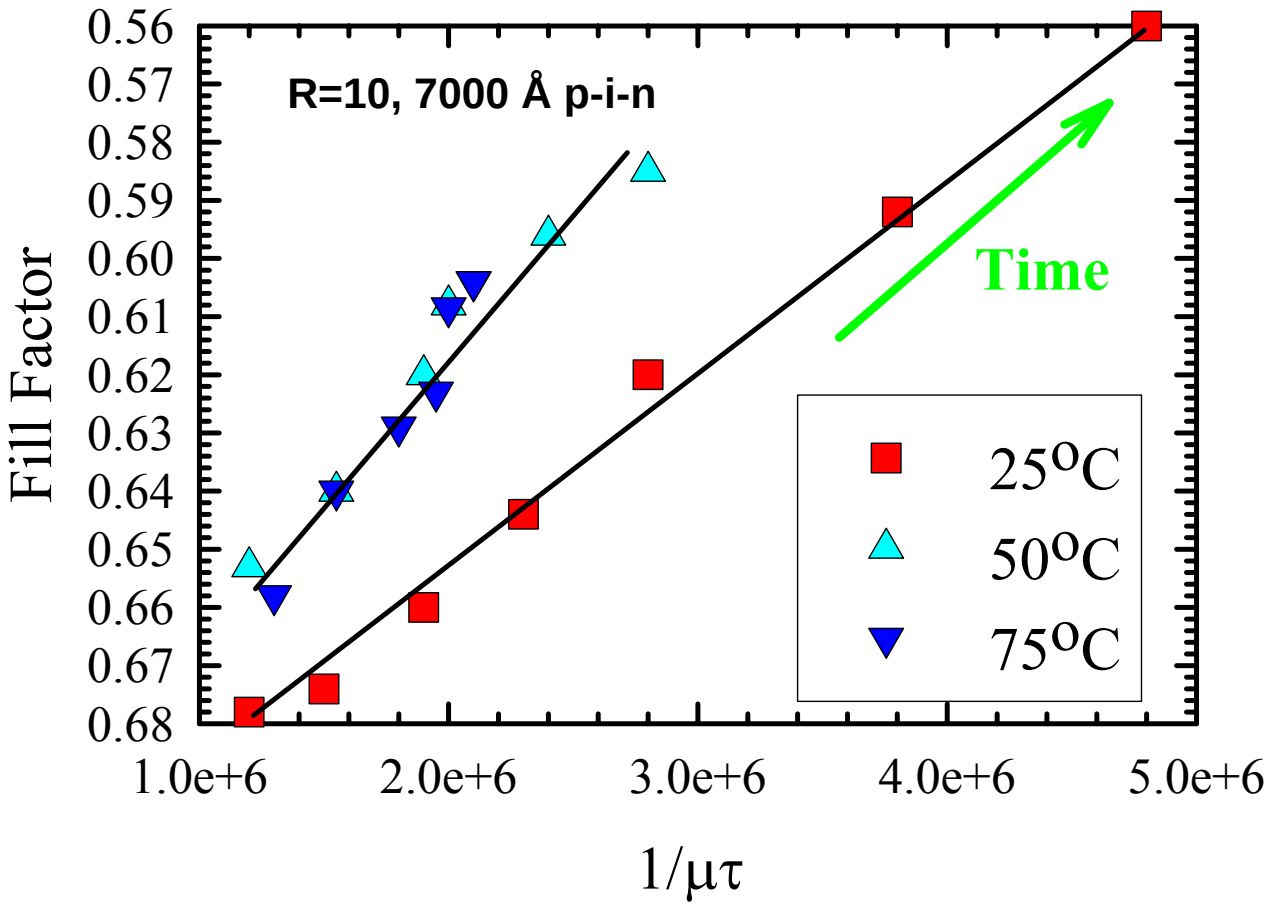
  C – R=0 [20 Å/s]
- Significant differences due to microstructure
- Distinctly different duration of $t^{-1/3}$ regime present before approach to a DSS
- Microstructure has very large effect on eventual densities of the states created and temperature dependence of kinetics (e.g. kinetics for over 100 hrs exactly same at 75°C)

Fast and Slow Processes

- Kinetics of changes for μτ ($G=10^{19}$ $cm^{-3}s^{-1}$) versus subgap α(1.2eV) commonly used to characterize densities of light induced defects
- Two distinct slopes obtained (R=10 at 25, 75°C, R=0 at 75°C) – different light induced defect states, creation kinetics
- Dependence on degradation temperature – striking similarity between R=10 25°C and R=0 75°C
- After 100 hours no correlation between α(1.2eV), ESR and cell FF's.

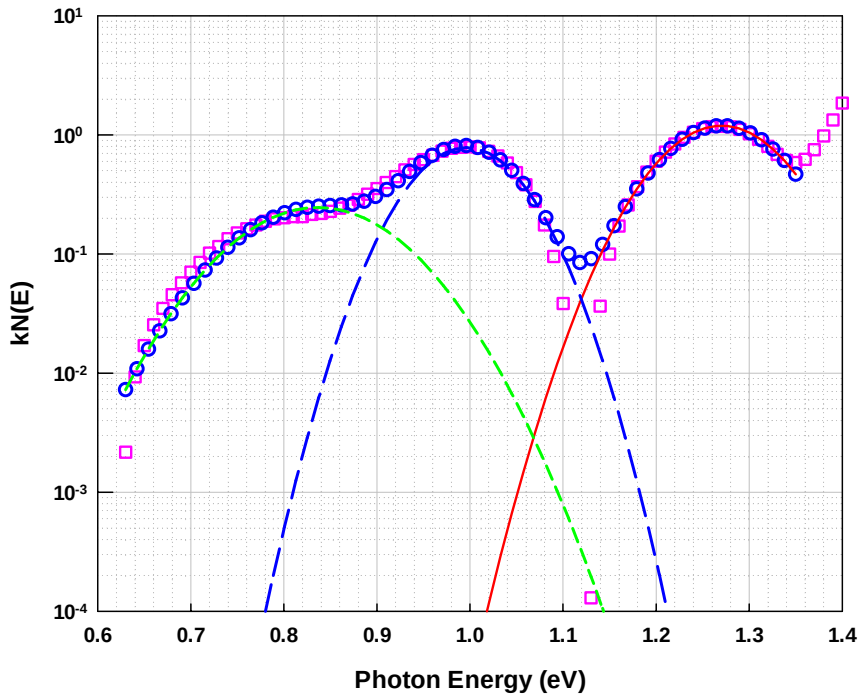


Cells and Film Correlation



Qualitative correlations obtained between 1/μτ and FF for both R=10 and R=0 cells in kinetics of long term degradation

Analysis on Subgap Absorption Obtained from Dual Beam Photoconductivity



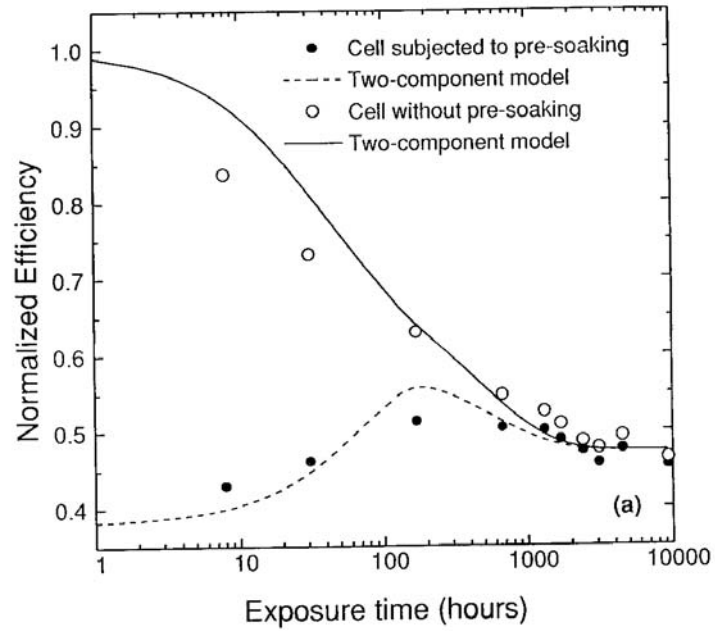
Electron occupied states kN(E) are obtained from:

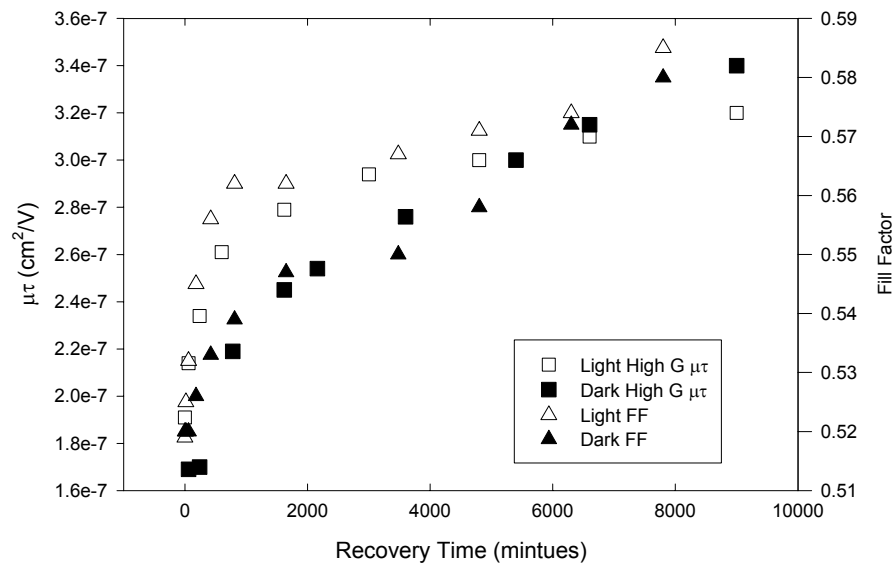
$$KN(E) = \frac{d(\alpha(h\nu)}{d(h\nu)} - \alpha(h\nu)$$

- kN(E) spectra for R=10 film after 25 hour of 1 sun illumination
- Presence of multiple defects at and around midgap clearly seen
- kN(E) can be fitted with three Gaussians as indicated in the figure

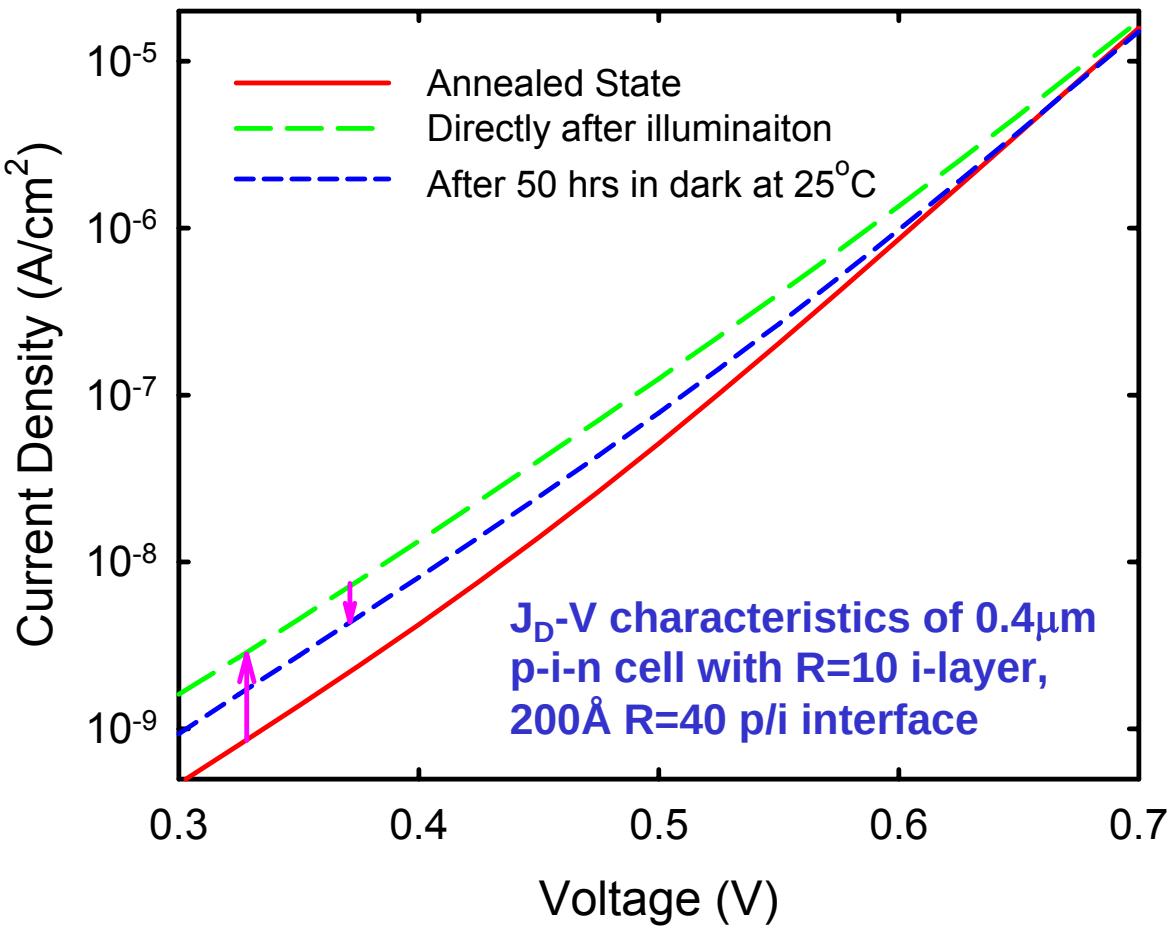
"Fast" and "Slow" Defect States

- Fast, slow light induced defect states proposed from two step annealing results on solar cells (*L. Yang and L. Chen, APL, **63**, 1993*).
- Similar results obtained on cells and films after 10 sun degradation 50°C (both for 1 sun, dark annealing) (*J. Pearce et al. 17th PVSC, 2001*)



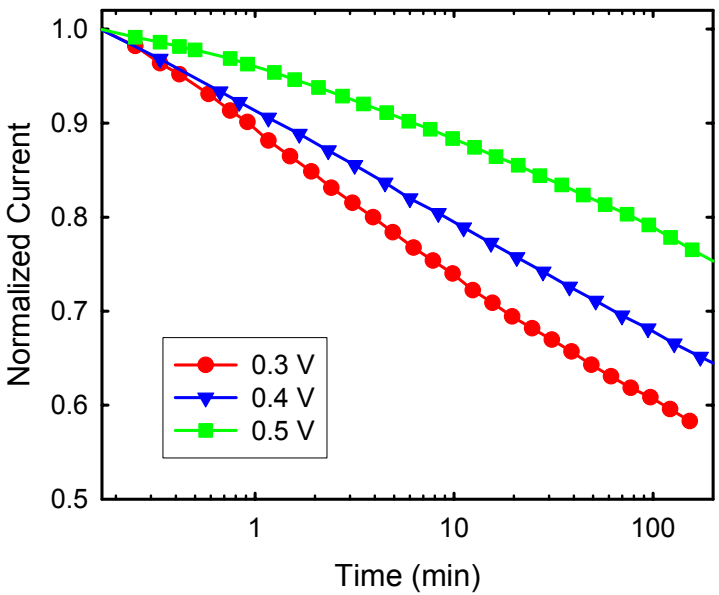


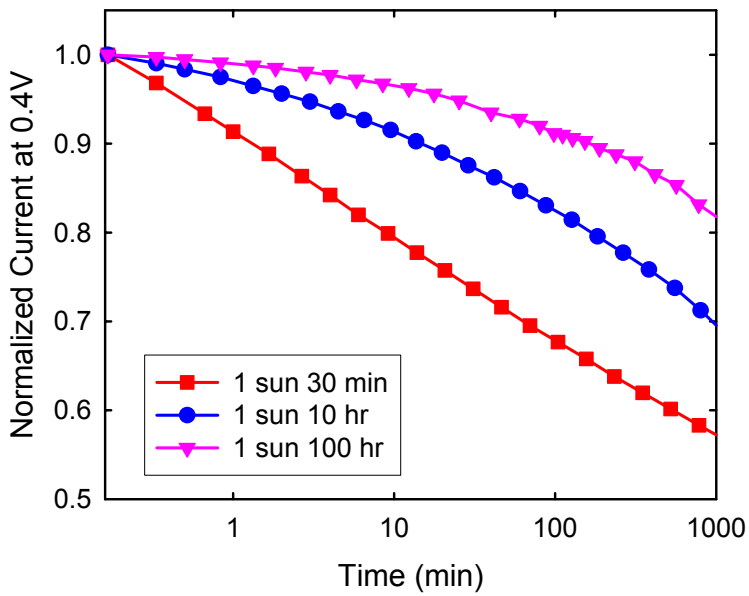
Room Temperature Relaxation of Bulk Recombination after 1 Sun Illumination



- 30 minutes 1 sun illumination at 25°C
- Bulk recombination: large increase after illumination; big decrease after 50 hours in the dark at 25°C
- Consistent with annealing of "fast" states observed with cells after high intensity illumination
- Differences in relaxation between R=10 and R=0

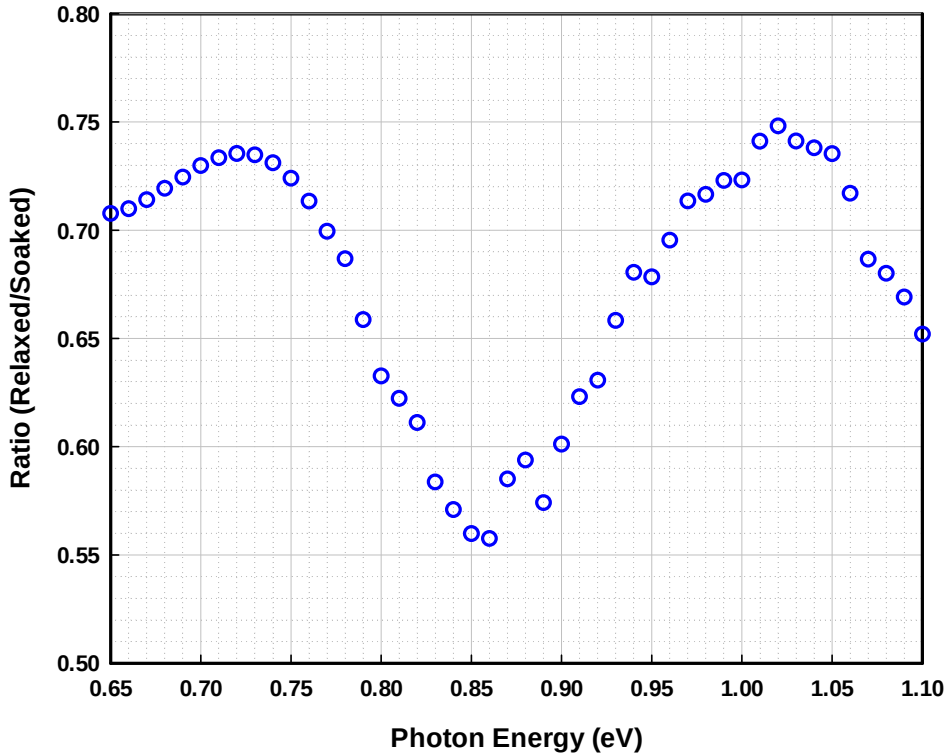
Relaxation in J_D after 1 Sun Illumination at 25°C





- Relaxation Kinetics in form A·log(t) – indicative of dispersive process
- Systematic decrease in A with voltage – carrier recombination under larger quasi-Fermi splitting
- After prolonged illumination – onset of delay to A·log(t) with A remaining constant suggestive of two processes

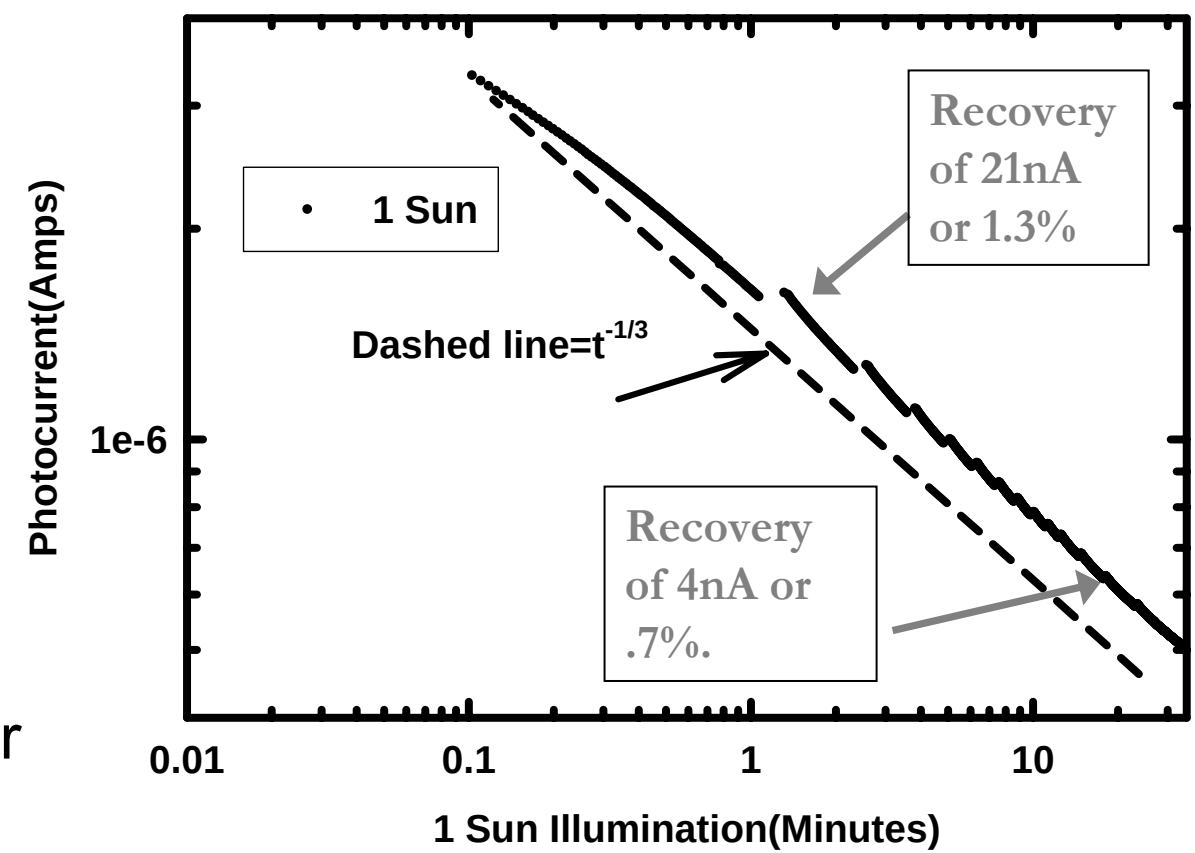
Relaxation of the kN(E) Spectra Corresponding to States around Midgap



Ration of kN(E) spectra of after 15 hours of relaxation in dark to that immediately after 30 minutes of 1 sun illumination

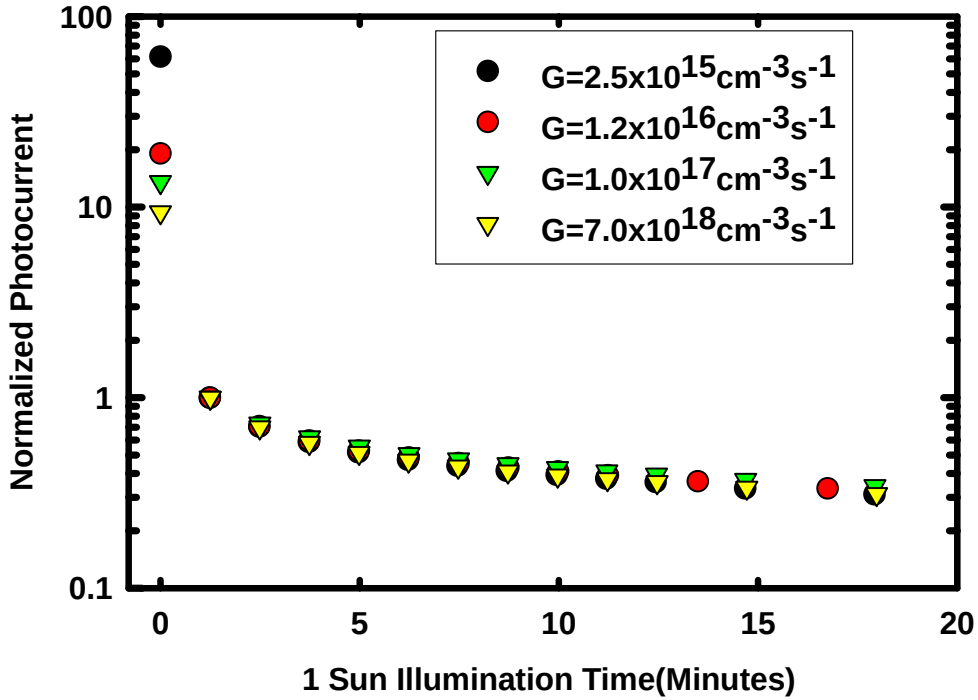
Evidence of Fast State Creation in Films during 1 sun Illumination

- Recovery in 1 sun photocurrents subsequent to a 10 sec interruption.
- $t^{-1/3}$ degradation rate over only 2 hours before transition to significantly slower rate approaching degraded steady state at 100 hours



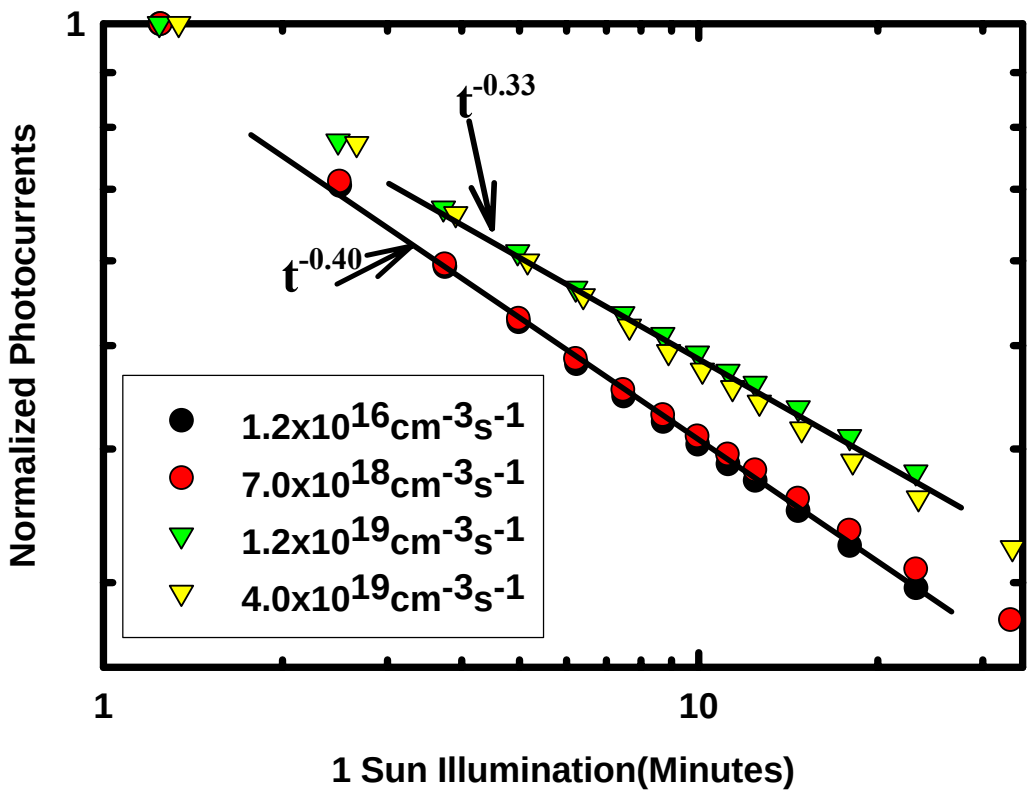
Very Rapid Changes

- Degradation, annealing kinetics characterized with probe photocurrents (G = 10^{15} – 10^{19} $cm^{-3}s^{-1}$) (*M. Albert et al. MRS 2005 Spring*)
- Very rapid changes in probe photocurrents after 1 minute of 1 sun degradation (*L. Jiao et al., APL, **69** (3713) 1996*)
- Attributed to surface/interface state – band bending reduced by very rapid creation of acceptors or elimination of donor states
- Evolution of bulk photocurrents after 1 minute highly reproducible and representative of defect state creation in the bulk



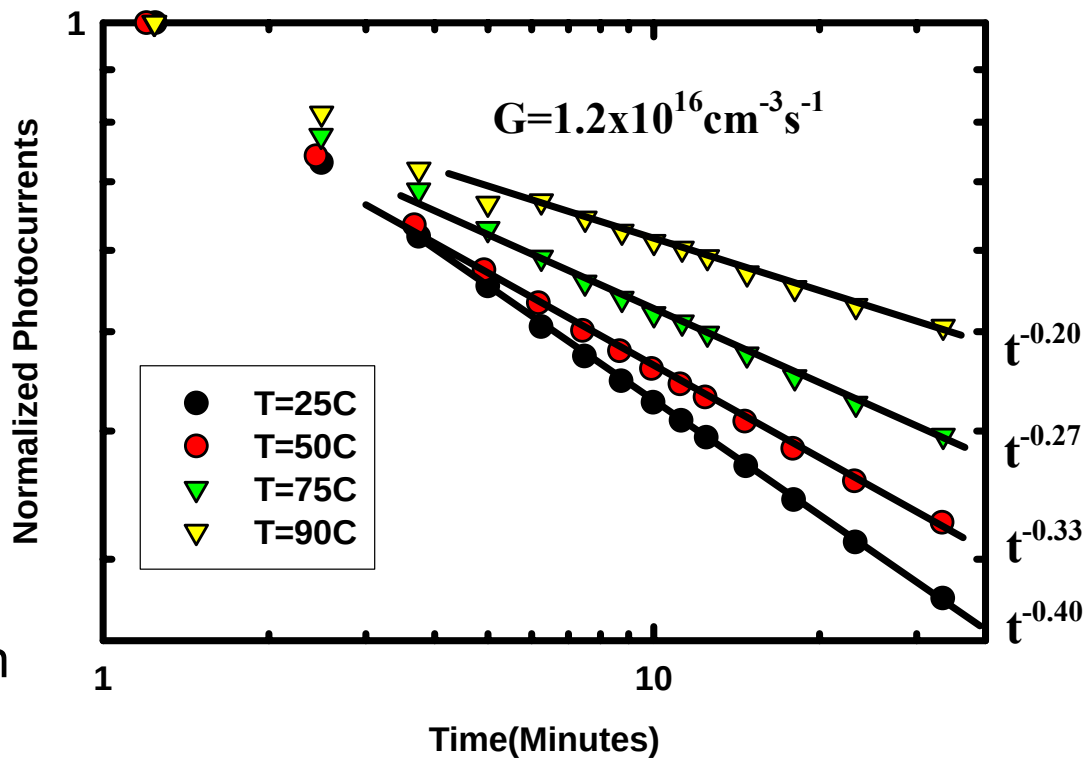
Two types of defect state kinetics

- Defect created not universally described by $t^{-1/3}$
- Two distinctly different kinetics for defect creation: near midgap $t^{-0.40}$; $t^{-0.33}$ when recombination includes defects away from midgap
- Low G kinetics inconsistent with the $t^{1/3}$ dependence associated with ESR states around midgap
- Transition in kinetics occurs at $G \sim 1 \times 10^{19} cm^{-3} s^{-1}$ (~10% 1sun illumination)



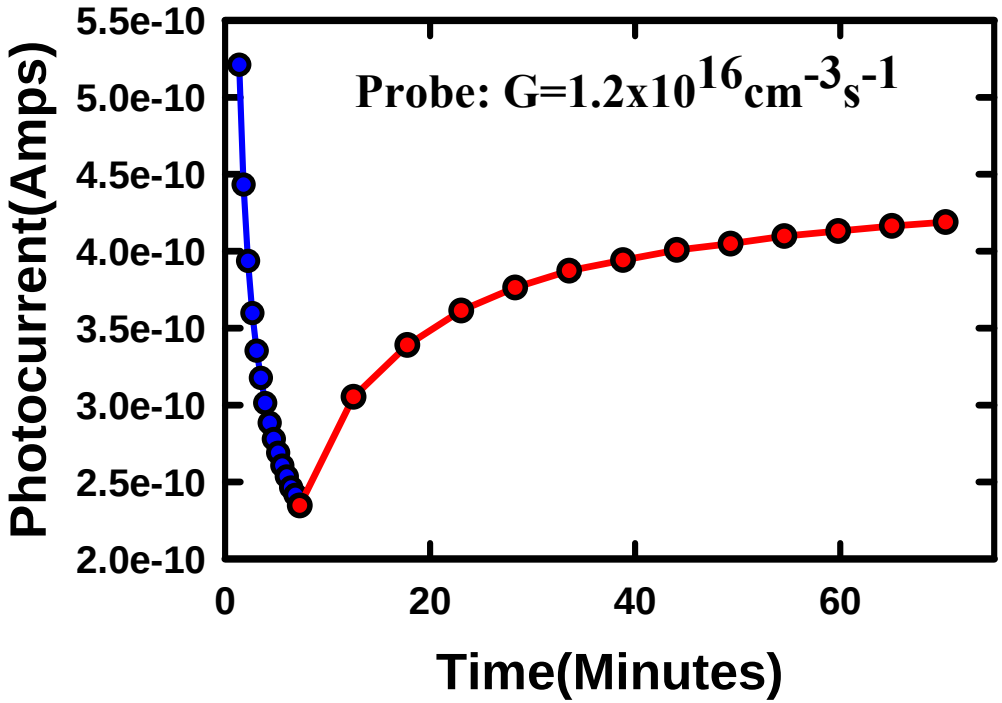
Large Temperature Sensitivity of Kinetics Associated with Gap States around Midgap

- Creation of defect states near midgap clearly affected by thermal processes even at T<<100°C
- Since 1 sun carrier recombination rates are ~independent of temperature, results suggest presence of another process involved in creation of defect states around midgap.



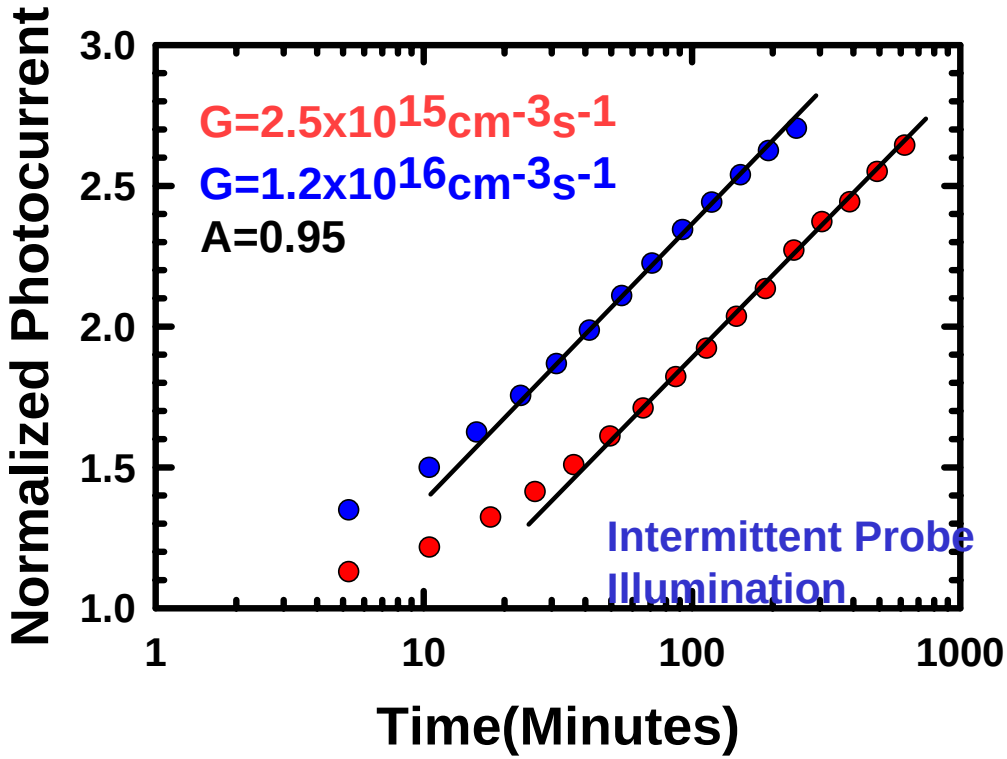
States Created Rapidly Anneal out Rapidly

- Thermal annealing characterized with intermittent low G probes
- Dramatic recovery in probe photocurrents after 5 minutes of illumination – 80% to 1 minute values after 1 hour
- Relaxation of photocurrents reflecting recombination through gap states around midgap consistent with solar cell results and bulk effect



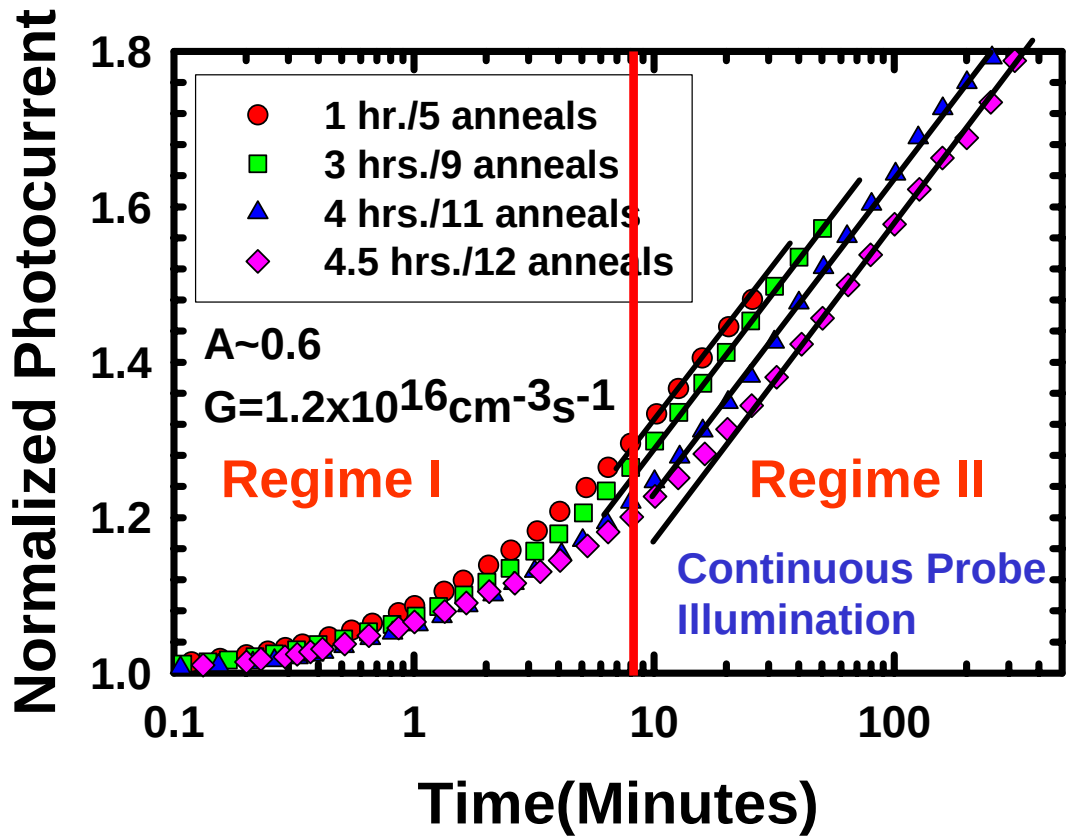
Thermal Annealing after 30 Minutes 1 Sun Illumination

- Two distinct features in kinetics: initial "delay" regime with subsequent A·log(t) regime.
- Indicative of two processes in creation/annealing of defect states
- Photogenerated carriers affect "delay" regime but not the second where A remains the same
- Unexpected efficiency of photogenerated carrier on annealing kinetics with G ~ 10^{-5} that of 1 sun illumination – clearly observed with continuous probe illumination



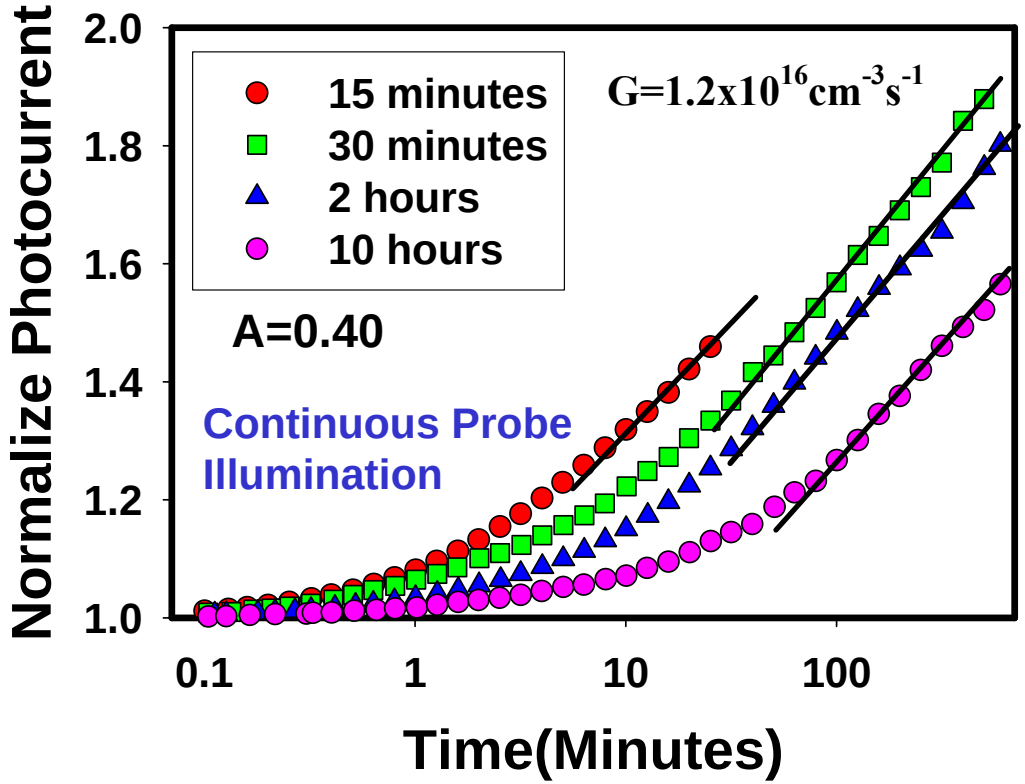
Irreversible Aging Process in Relaxation Kinetics

- An irreversible aging process is discovered
- Phenomenon observed on different samples. Carefully studied to insure not experimental artifact
- Systematic increase in delay regime after cumulative soak time or total number of anneals – no effect on A
- Effect present even after 200°C anneal (film deposition temp)
- Aging has to be taken into account in reliably characterizing and quantifying the first regime

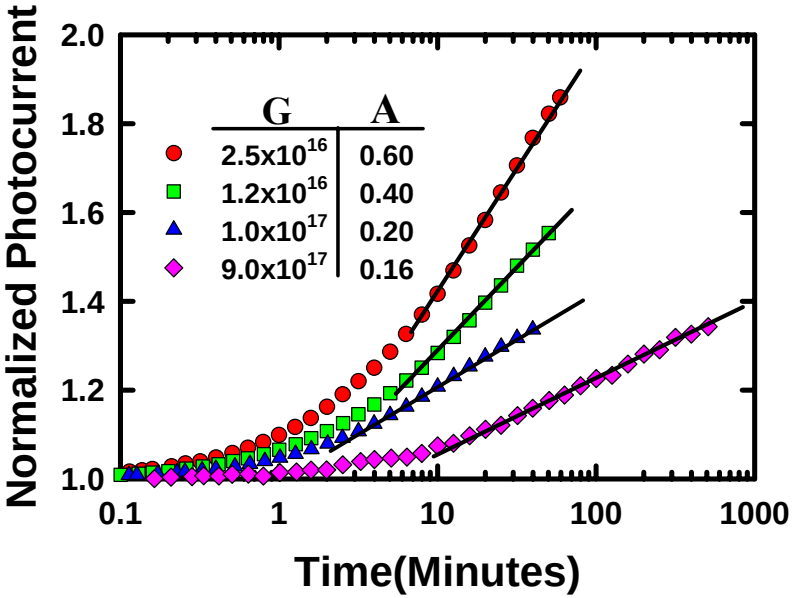


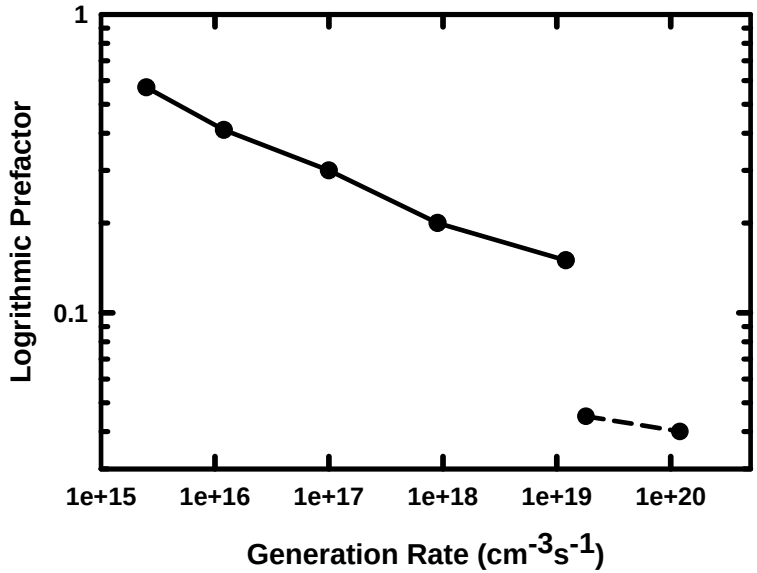
Dependence of Kinetics on Time of Degradation

- Length of Regime I systematically increases with increasing illumination time
- A of regime II independent of degradation time.
- Further indication of two processes involved in creation and annealing of defect states



Dependence of Kinetics on Continuous Illumination Intensity

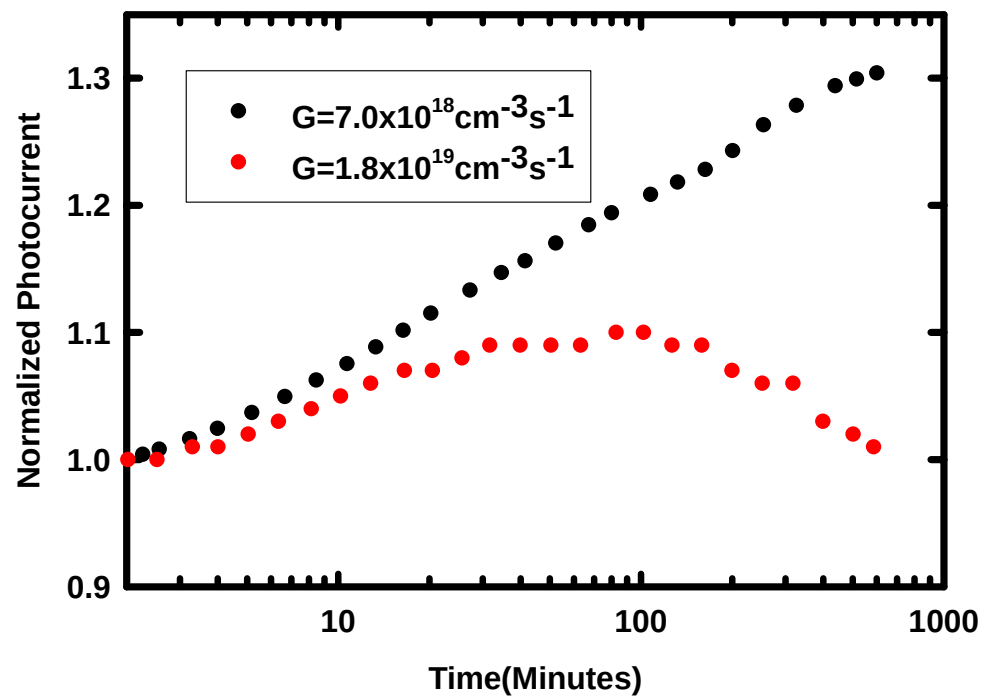




- Low levels of illumination(10^{-5} sun) not expected to perturb annealing process.
- Continuous changes in kinetics observed in the form of a systematic decrease in logarithmic prefactor A with increase in G.
- Clear discontinuity in dependence of A on G at ~10^{19}cm^{-3}s^{-1} (~0.1 sun)
- This G is the same at which transition in degradation kinetics from approximately $t^{-0.4}$ to $t^{-0.33}$ present

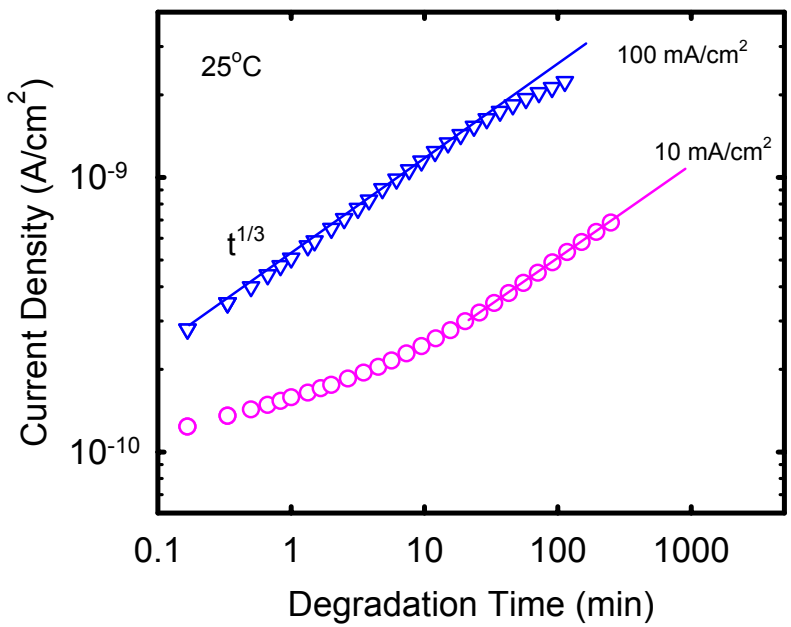
"Light Induced Annealing"

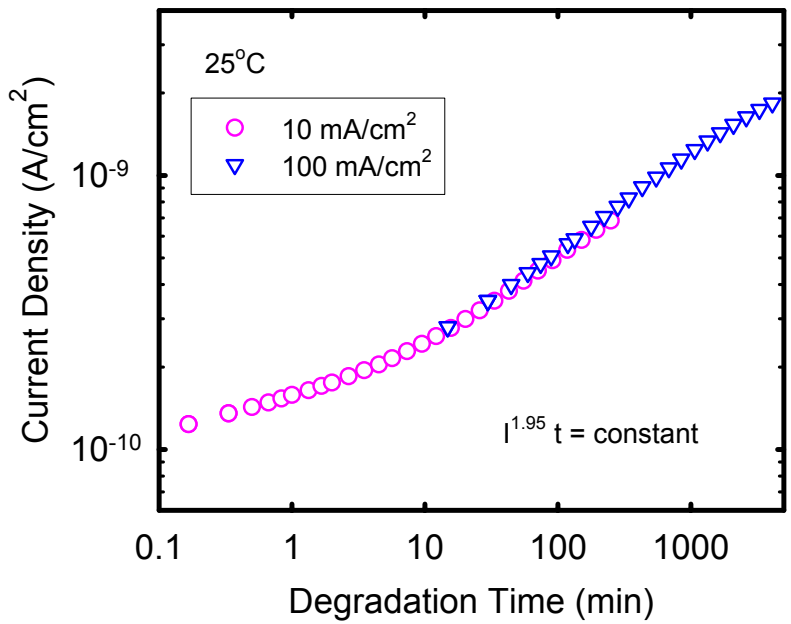
- So called "light induced annealing" has been proposed as contributing to degradation kinetics under 1 sun and higher illuminations
- Any beneficial contribution to the annealing out of defect states by photogenerated carriers is not observed – as reflected in the increased suppression of annealing with higher G
- For carrier recombination approaching 1 sun illumination not only is further suppression observed but also the expected degradation



Kinetics of Metastable Defect Creation by Far Forward Bias Currents I

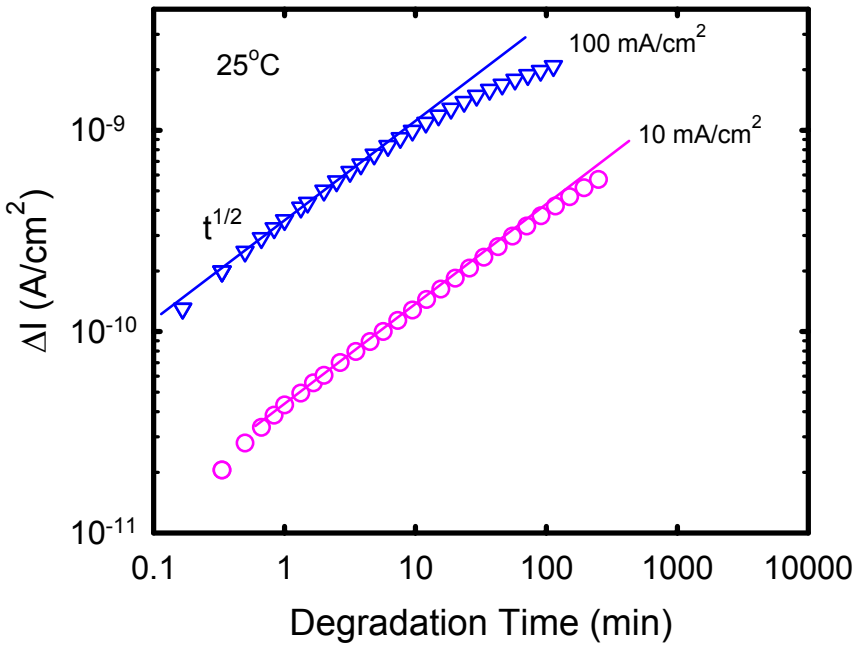
(I of 10, 100 mA/cm^2 correspond to 1, 10 sun illumination)

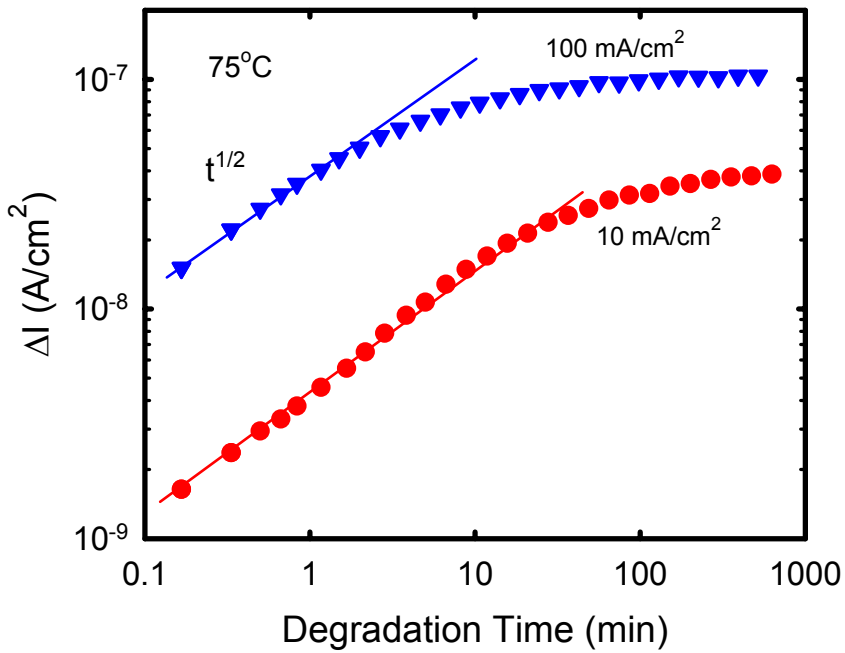




- **Evolution of defect states created around midgap measured by J_D at 0.4V directly (not with FF)**
- **$t^{1/3}$ for different degradation currents I**
- **Clear saturation observed within 1000 minutes at 75°C**
- **Intensity dependence follows approximately I^2t = constant**

Evolution of Purely Metastable Defects

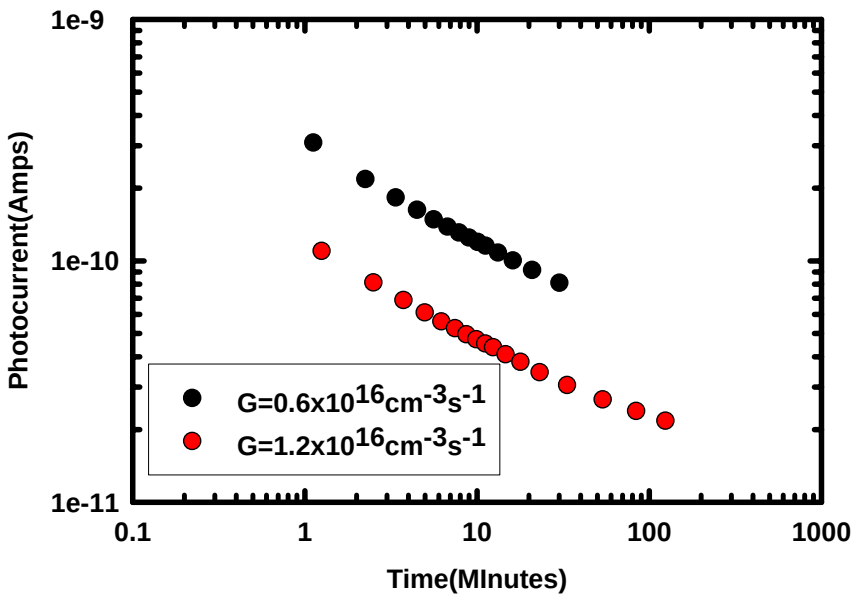


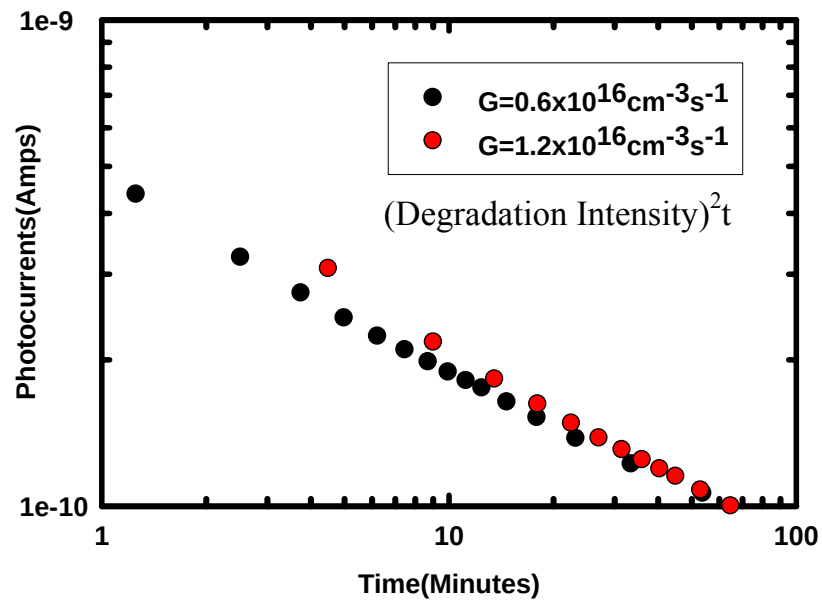


- **Relative changes in J_D, at 0.4V which correspond to creation of purely metastable defect states, follow $t^{1/2}$ relation instead of $t^{1/3}$**
- **I^2t = constant still holds**

New insights into defect creation mechanisms

Film Degradation Kinetics under 1 and 0.5 Sun Illumination at 25°C





G^2t=constant relation also present for probe photocurrents corresponding to recombination through gap states located around midgap

Summary

- New approaches have been applied to characterizing the creation and annealing of defect states in films and solar cells
- Direct correlations between results on films and cells with corresponding i layers have been obtained
- Cumulative evolution of metastable gap states in i layers with regions having $t^{1/3}$ dependence is observed
- Evolution of purely metastable defects, however, has a clear $t^{1/2}$ dependence
- A $t^{-1/3}$ dependence for changes in photoconductivities is found not to hold for recombination through gap states located around midgap
- The relation G^2t=constant for degraded states is found to hold for midgap recombination in films and solar cells
- Surprising large room temperature annealing out of defect states around midgap has been observed after 1 sun illumination in both films and cells
- Annealing kinetics point to the contribution of at least two different processes
- The systematic increase in suppression of annealing with higher photogenerated carrier concentration runs contrary to the proposed “light induced annealing” phenomenon proposed for 1 sun and higher illuminations