University of Exeter / School of Physics

Charge-Capture & Coulomb-Attraction Dependent Defect-Reaction Kinetics in Silicon Solar-Cell Photon-Induced Efficiency-Degradation

Talk
by

Derek W Palmer
(University of Exeter)

2009.04.27

University of Exeter Web-Site
http://newton.ex.ac.uk/research/qsystems/people/palmer/

Semiconductors-Information Web-Site
http://www.semiconductors.co.uk

This Talk

Personnel Involved in the Research

Experimental Work and Data

Institut für Solarenergieforschung Hameln/Emmerthal (ISFH),
in Ohrberg 1, Emmerthal, Germany

Jan Schmidt and Karsten Bothe (Doctoral Student)

Theoretical Work and Data

University of Exeter

James Adey (PhD Student of Bob Jones)

Bob Jones

Derek Palmer

Some of the Relevant Publications

Glunz S W, Rein S, Lee J Y & Warta W, J Appl Phys 90 (2001) 2397

"Minority-Carrier-Lifetime Degradation in Boron-Doped Czochralski Silicon"

Schmidt J, Bothe K & Hezel R, Appl Phys Lett 80 (2002) 4395

"Oxygen-Related Minority-Carrier Trapping Centers in P-Type Czochralski Silicon"

Bothe K, Schmidt J & Hezel R, Proc. 3rd World Conf on Photo-Voltaic Energy Conversion, 2003

"Comprehensive Analysis of the Impact of Boron & Oxygen on the Metastable Defect in CZ Silicon"

Adey J, PhD Thesis, University of Exeter, 2004

"Boron-Related Point Defects in Silicon"

Adey J, Jones R, Palmer D W, Briddon P R & Oberg S, Phys Rev Lett 93 (2004) 055504

"Degradation of Boron-Doped Czochralski-Grown Silicon Solar Cells"

Schmidt J, Bothe K, Macdonald D, Adey J, Jones R & Palmer D W, J Mater Res 21 (2006) 5

"Electronically Stimulated Degradation of Silicon Solar Cells"

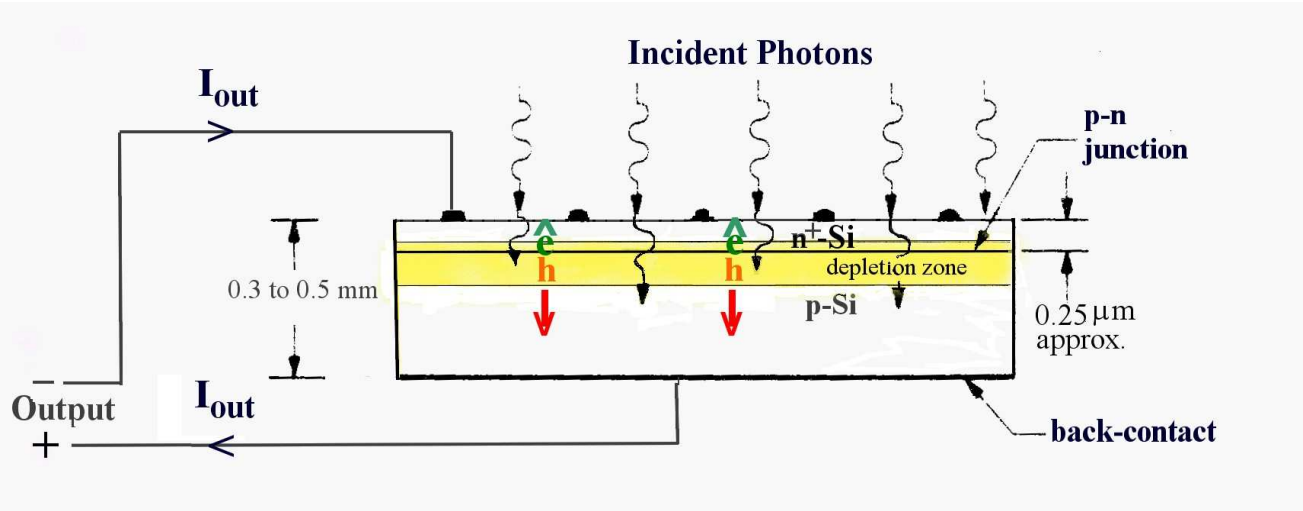
Palmer D W, Bothe K & Schmidt J, Phys Rev B 76 (2007) 035210

"Kinetics of the Electronically Stimulated Formation of a Boron-Oxygen Complex in Cryst. Si"

Dubois S, Enjalbert N & Garandet J P, Appl Phys Lett 93 (2008) 103510

"Slow Down of the Light-Induced-Degradation in Compensated Solar-Grade Multicrystalline Silicon"

Silicon Solar Cell



Incident Photons create $e^- - h^+$ pairs in the silicon by electron excitation across E_g

The $e^- - h^+$ pairs diffuse in the silicon and some reach the depletion region.

The strong electric field of the depletion region separates the e^- and the h^+ and moves them in opposite directions towards the respective surfaces as shown.

That e^- and h^+ motion produces the external current.

<u>BUT</u>: That external current is diminished by $e^- - h^+$ combination, which can occur by successive capture of e^- and h^+ at impurities and defects.

The Solar-Cell Efficiency

Solar-Cell Efficiency = Output Electrical Power / Input Illumination Power

It depends on

- **The photon spectrum compared to E_g**
- **The reflection coefficient of the top surface**
- **The absorption coefficient (photon-energy dependent) of the silicon**
- **The series resistance of the whole solar cell**
- **The distance that the e^- and h^+ diffuse before e^- - h^+ recombination,**
- **especially for the holes in the p-type silicon, because that is thick.**
- **L_D = Diffusion Length = $(D \tau_r)^{0.5}$**
- **where τ_r = the $e^- - h^+$ recombination lifetime**
- **τ_r can be strongly reduced by $e^- - h^+$ combination at impurities & defects**
- **and that produces a corresponding decrease in the solar cell efficiency.**

Silicon Solar Cells n+ / p-Si where the p-Si is Si (B, O)

- **Czochralski Silicon where the Oxygen comes from the SiO_2 crucible**
- **Doping by boron is easy and therefore economic manufacture**
- **Solar Cell Efficiency is typically close to 20%, and that is satisfactory.**
- **But the Efficiency is Decreased down to about 18% by the Solar Illumination**

- **Illumination-induced efficiency decrease does not occur**
- **if the p-Si (B) is oxygen-free**
- **if the p-Si is Si (Ga, O)**

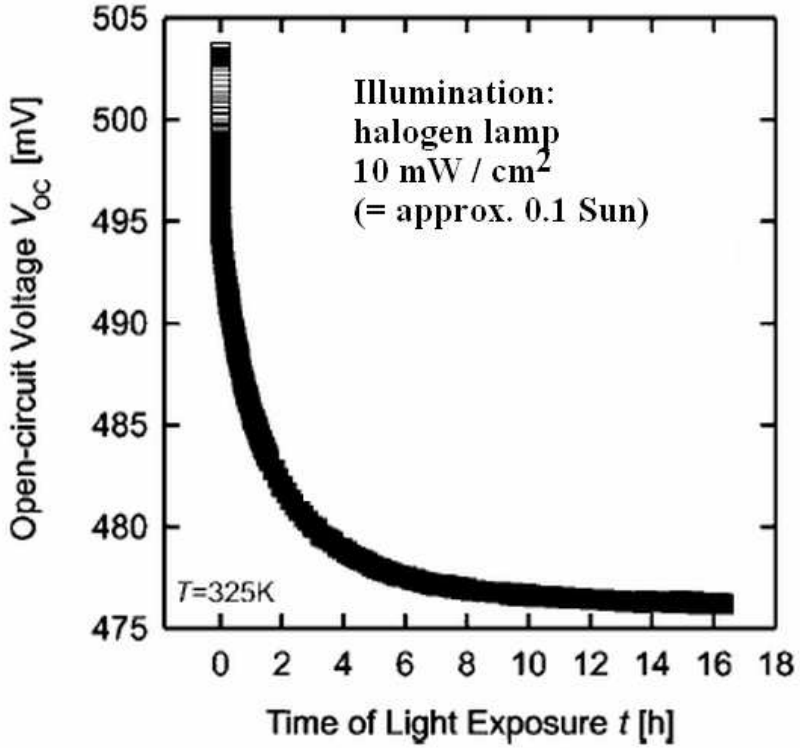
- **Oxygen in silicon mostly occupies interstitial sites in the silicon lattice**
- **much of the oxygen being as $(O_{2i})^{2+}$ in the p-Si (work by Bob Jones et al)**

- **The conclusion is that Illumination causes Diffusion of $(O_{2i})^{2+}$ to B_S^- atoms thus forming a $[\,(O_{2i})^{2+} - B_S^-\,]$ complex that is an efficient e^--h^+ combination centre.**

Experimental Data

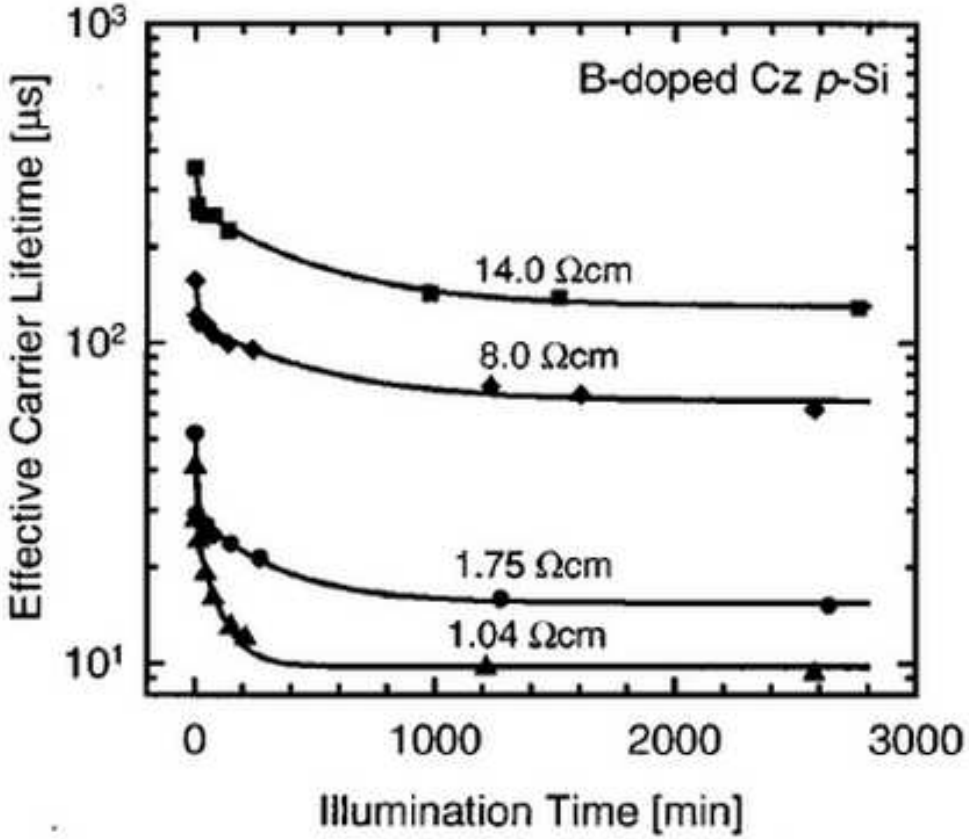
Silicon n^+-p Solar Cell

the p-region being 1.8 ohm-cm Czochralski Si(B,O)



Bothe K & Schmidt J, J Appl Phys 99 (2006) 013701

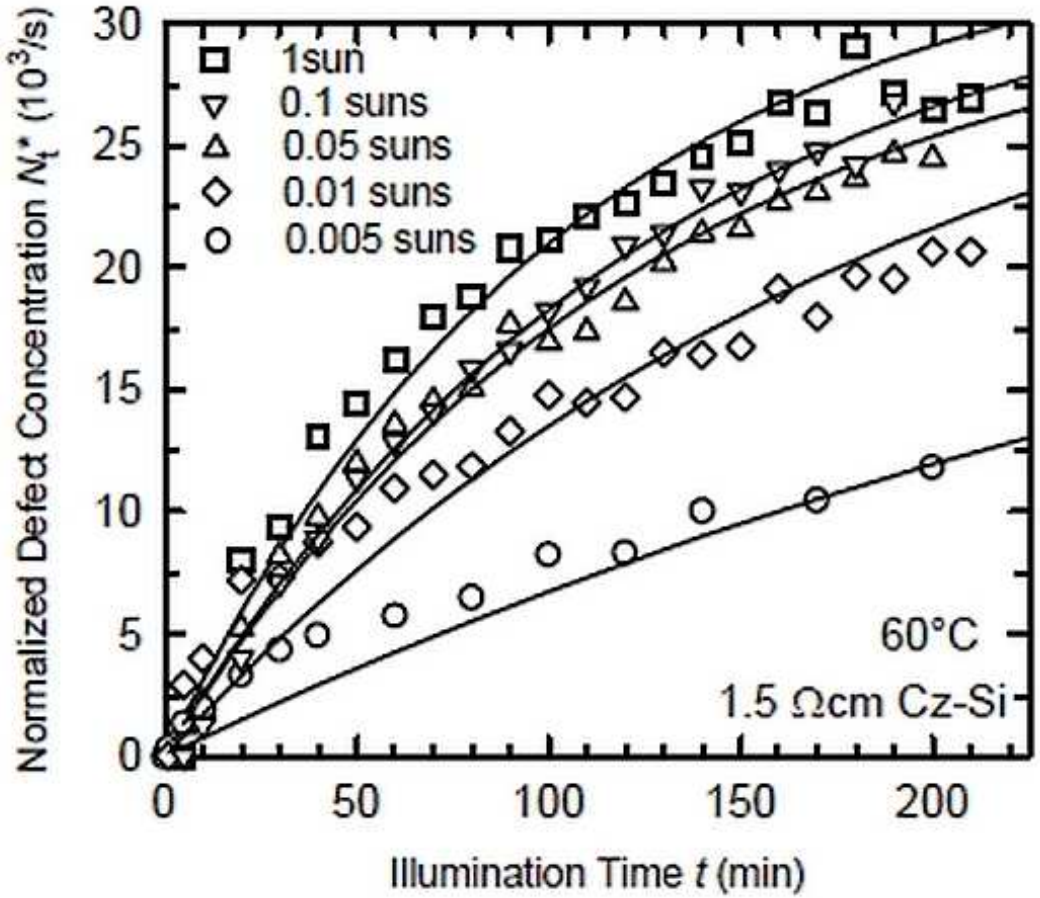
Experimental Data



(halogen lamp, intensity 100 mW/cm^2, 25 °C)

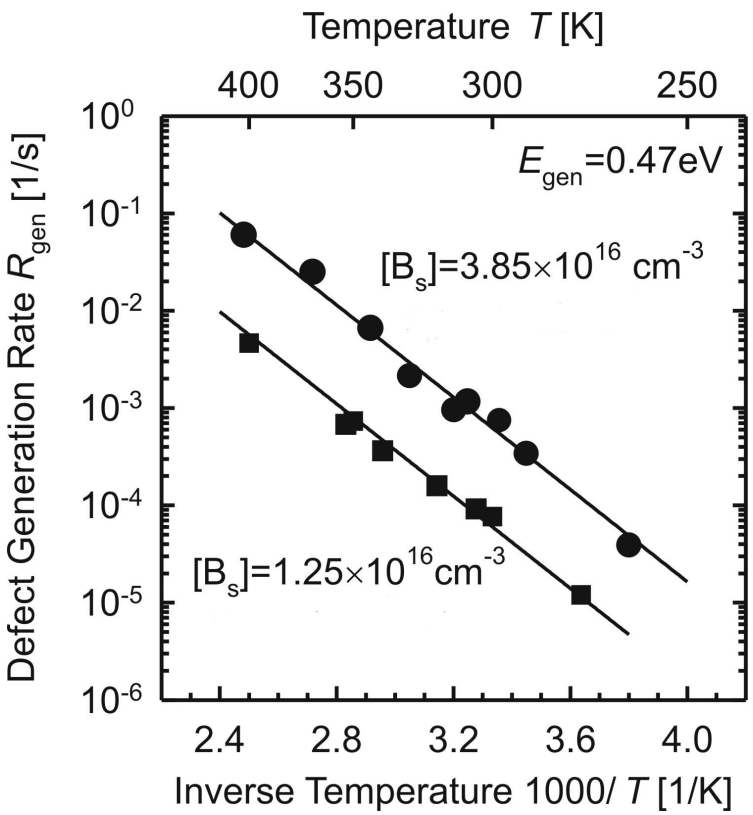
Schmidt J and Cuevas A, J Appl Phys 86 (1999) 3175

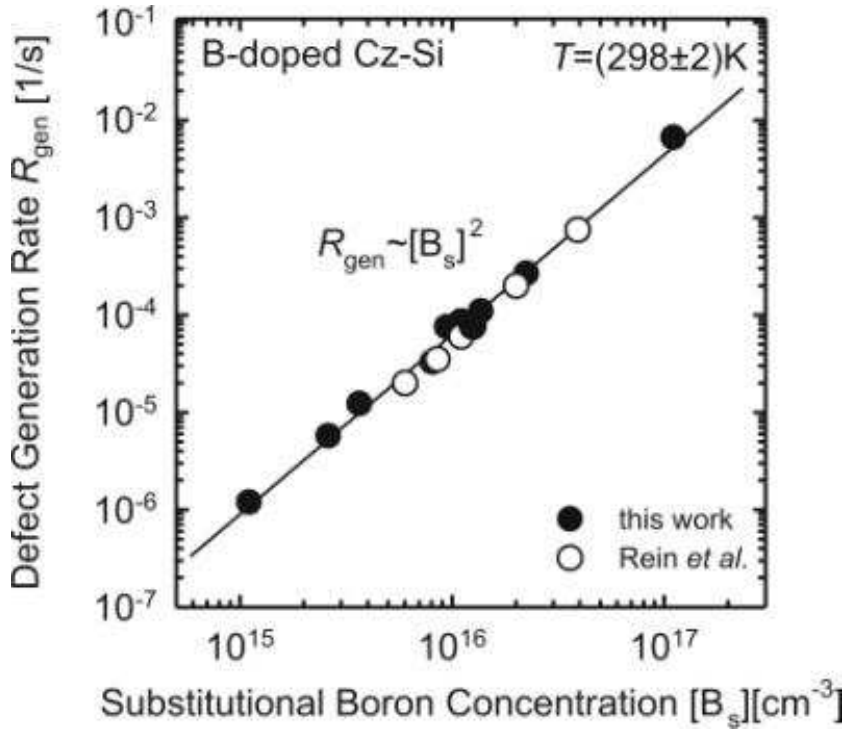
Deduced from the Experimental Carrier Lifetime Data



Schmidt J, Bothe K and Hezel R
3rd World Conf on Photo-Voltaic Energy Conversion, 2003, Osaka, Japan

Experimental Data





Palmer D W, Bothe K & Schmidt J, Phys Rev B 76 (2007) 035210

Jump-Rate Analysis

We consider the reaction $A + B \rightarrow C = AB$ **in the Si(B,O)**

where

A = a oxygen interstitial dimer O_{2i}^{2+}, which can become mobile in the Si

B = a substitutional boron atom B_s^-

C = the complex defect AB = $(B_s O_{2i})^+$

The boron concentration $[B_s^-]$ is a few x 10^{16} / cm^3, ie about 10^{-6} of [Si] .

Therefore, in random diffusion-jumping in the silicon, the O_{2i} needs to make about 10^6 jumps in the lattice to reach a B_s.

The "standard" jump rate j of $O_{2i} \approx 10^{12}\ s^{-1} \exp(- 0.47eV / k_B T) \approx 11300\ s^{-1}$ at 298K.

Therefore time needed at 298K for an O_{2i} to reach a $B_s \approx$ 90 seconds, <u>which is << the experimentally observed time of about an hour.</u>

Therefore the O_{2i} jump rate must be << 11300 jumps / sec. **<u>BUT WHY ?</u>**

The Information

From Experimental Data

- The efficiency-degrading defect in the Si (B,O) is an **oxygen-boron complex** that results from diffusion of oxygen atoms to immobile substitutional boron dopant atoms.
- At 300K, those complex defects are formed with a time constant of **about an hour.**
- The thermal activation energy for the process is **0.47 eV.**
- The thermal activation energy for diffusion of single interstitial atoms of oxygen in silicon is about 2.5 eV (Mikkelsen J C, 1986), and so they are not mobile at room temperature.
- The final concentration of the complex is proportional to $[\ 0_i\ ]^2$,
  and that strongly suggests that **the complex includes O_{2i}**
- The initial rate of formation of those complexes is proportional to the **square of the boron concentration** (well established in many studies by Bothe and Schmidt). **BUT WHY ?**

From Theoretical Data (Jones R, Adey J et al)

- **Oxygen in Si(B,O) can exist as stable interstitial oxygen dimers O_{2i} .**
- **That dimer O_{2i} can exist stably in two structural forms in silicon.**
- **The complex defect (B_sO_{2i}) can exist in stable structural forms in silicon.**

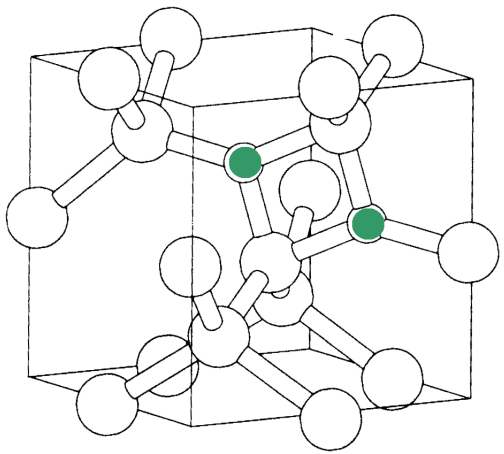
Structures & Electronically Activated Diffusion of O_{2i}

Calculated Lowest Energy Structures of the Oxygen Interstitial Dimer O_{2i} in Silicon

(Calculations by the "AIMPRO" program of Jones R et al)

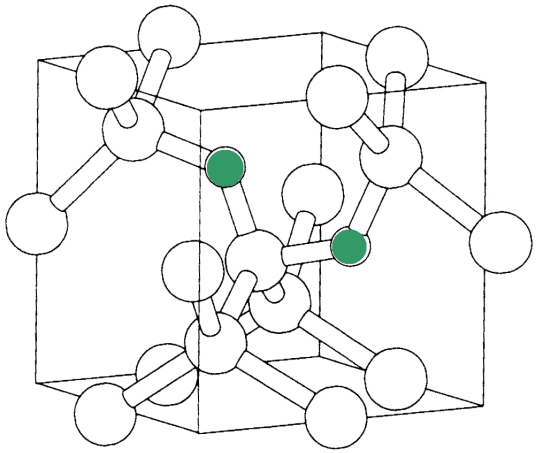
Silicon Atom

Oxygen Atom



$(O_{2i})^{2+}$

Structure Name O_{2i}^{sq}



$(O_{2i})^{+}$ or $(O_{2i})^{0}$

Structure Name O_{2i}^{st}

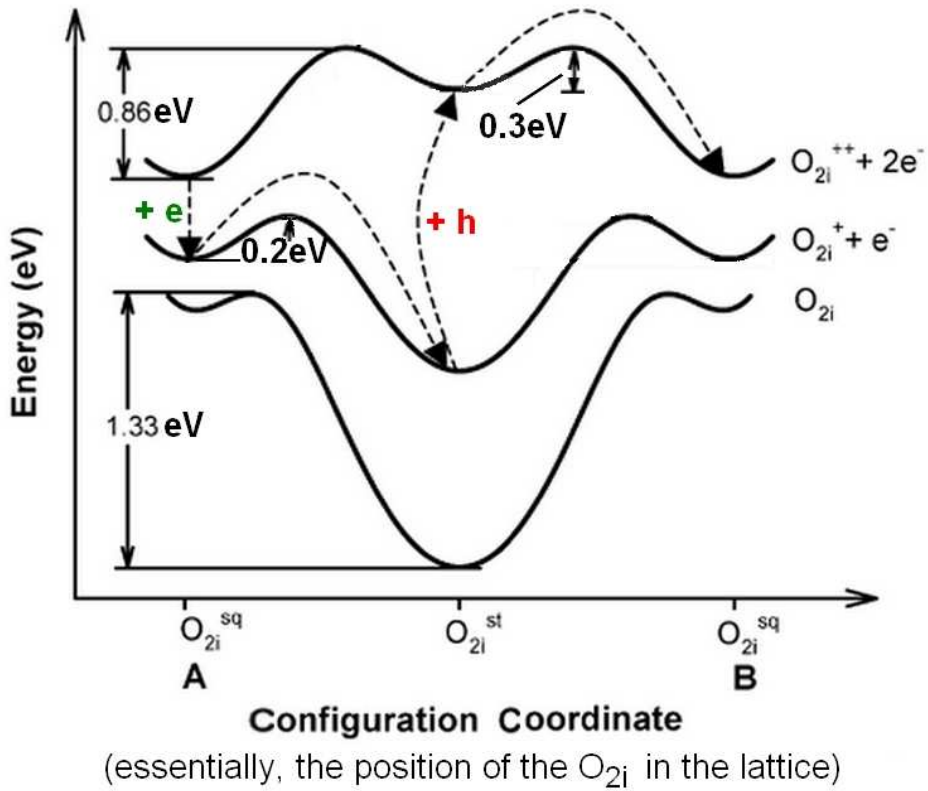
Adey J, PhD Thesis, University of Exeter, 2004

Adey J, Jones R, Palmer DW, Briddon PR & Oberg S, Phys Rev Lett 93 (2004) 055504

Electronically Activated Diffusion of O_{2i} : Details

The Illumination creates e^- and h^+, and that strongly increases the <u>e^- concentration</u> in the p-Si.

→



Adey J, Ph.D Thesis, University of Exeter, 2004

Adey J, Jones R, Palmer D W, Briddon P R and Öberg S, Phys Rev Lett 93 (2004) 055504

Diffusion by the <u>Bourgoin-Corbett Mechanism</u>

(Jacques Bourgoin, Jim Corbett)

Capture Rates of e^- and h^+ by O_{2i}

Capture Rate of e^- = ν_e = $v_e \sigma_e n$ ≈ $2.6 \times 10^8\ s^{-1}$ *

Capture Rate of h^+ = ν_h = $v_h \sigma_h p$ ≈ $3.4 \times 10^6\ s^{-1}$ *

* when one inserts the values of **v_e & n** and of **v_h & p**

and assumes likely values for σ_e and σ_h .

Therefore the diffusion rate of the O_{2i} is <u>controlled by the h^+ capture</u>.

Therefore, also, the formation rate of B_s- O_{2i}
is proportional to (ν_h x probability per sec that O_{2i} finds a B_s),

ie, proportional to [B_s] x [B_s],

ie, proportional to [B_s]^2

in accordance with the experimental observation.

Palmer D W, Bothe K & Schmidt J, Phys Rev B 76 (2007) 035210

Time Needed for an O_{2i} to reach a B_s by h^+-capture-activated diffusion

Diffusive Jump Rate of O_{2i} = j = $\nu_h \exp(-0.47\text{eV} / k_B T)$

$\approx 3.8 \times 10^{-2}\ s^{-1}$

But in random diffusion-jumping in the silicon,

the O_{2i} needs to make about 10^6 jumps in the lattice to reach a B_s.

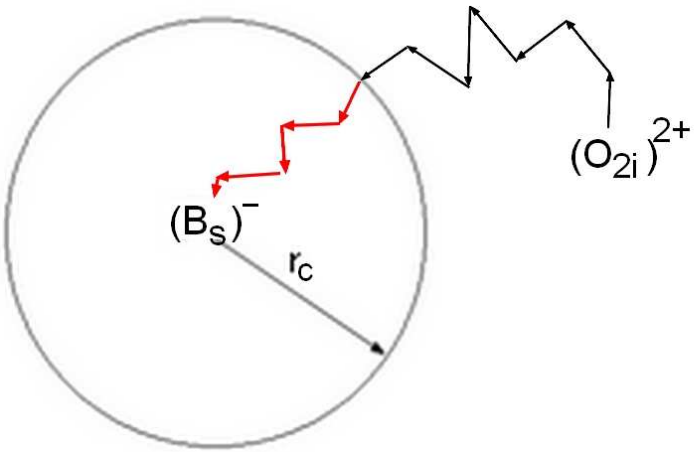
Therefore the time needed for that $\approx 10^6 / 3.8 \times 10^{-2}\ s^{-1}$

$\approx 2.6 \times 10^7$ s $\approx$ 7300 hours.

But that is >> the experimentally observed time of about one hour.

So what effect or process has not yet been considered ?.

Coulomb-Field-Enhanced Capture



r_c = the coulomb-capture radius, defined by the expression

$$\frac{q_1 q_2}{4 \pi \kappa \varepsilon_0 r_c} = k_B T$$

where κ = the dielectric constant of silicon = 11.9

That gives r_c = 9.4 nm at 298K

Then, for capturing an O_{2i} defect, each B_s atom site is equivalent to all the lattice sites on the spherical surface area $4 \pi r_c^2$

The result is that the rate of capture of O_{2i} by B_s is speeded by a factor of about 10^4,

Therefore the theoretically predicted time is now about one hour, ie, as experimentally

Palmer D W, Bothe K & Schmidt J, Phys Rev B 76 (2007) 035210

The Processes of Diffusion of O_{2i} to B_S
Summary

Experimental Data:

The formation rate of the B_s-0_{2i} is proportional to **[B]^2** .

At one-sun illumination, the time needed is **about one hour.**

Considered Theoretical Models

If **ordinary diffusion of O_{2i}**, then the time would be **only about 1.5 minutes**.

If h^+-capture-controlled diffusion of the O_{2i} simply to B_s atoms,
then the formation rate of the B_s-O_{2i} is **indeed proportional to [B]^2**
but the time needed would be **about 7300 hours**.

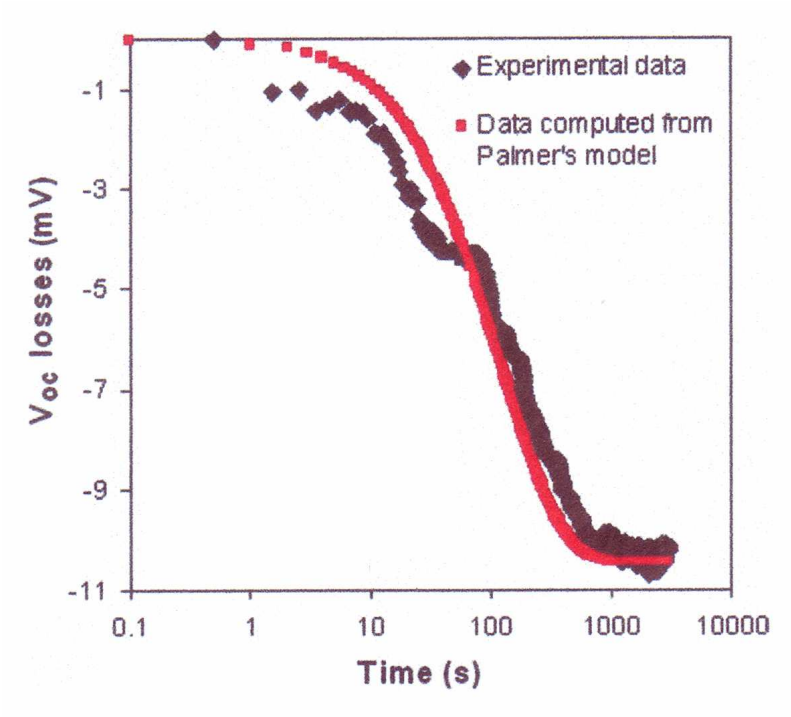
If h^+-capture-controlled diffusion of O_{2i} AND coulomb-field-enhancement
of the O_{2i} – B_s interaction, then the time would be **about one hour**
ie, in agreement with experiment.

Support for Coulomb-Attraction Model

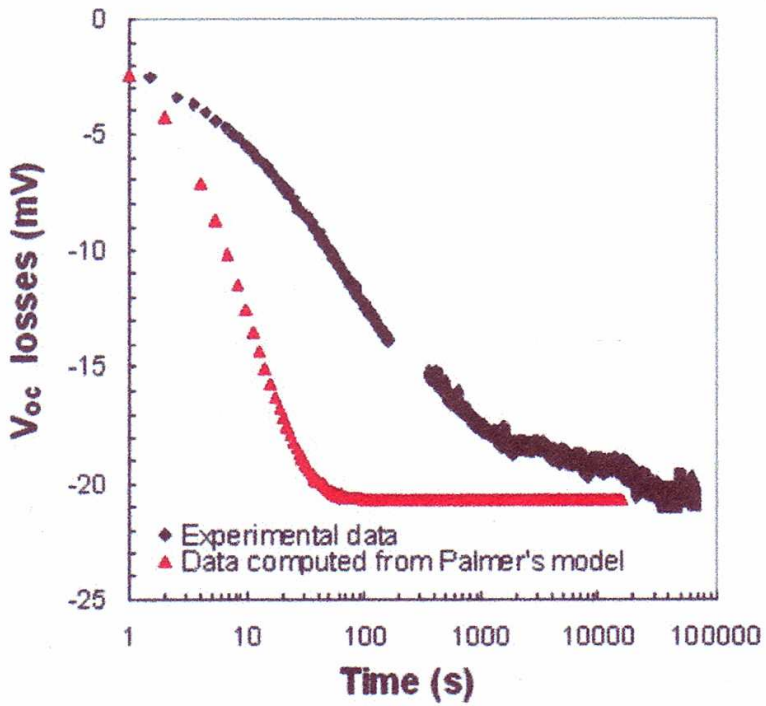
Dubois S, Enjalbert N & Garandet, Appl Phys Lett 93 (2008) 103510

Multicrystalline n+-p Si(B,O) Solar Cells

Illumination-Induced Decrease of V_{oc} (Illumination = One-Sun)



Standard p-type Si(B,O)



Special p-type Si(B.O)

(partially phosphorus^{+} compensated)

Overall Summary

1. **The illumination-induced decrease in the efficiency of n^+-p Si(B,O) solar cells is due to the formation of the B_s0_{2i} defect which is a strong e^- - h^+ recombination centre.**

2. **That formation occurs by electronically activated diffusion of the oxygen dimer O_{2i} by successive capture of e^- and h^+.**

3. **The rate of that diffusion of the O_{2i} is controlled by the capture of the h^+, ie by $[B_s]$**

4. **The trapping rate of diffusing O_{2i} at B_s is proportional to $[B_s]$.**

5. **Due to (3.) and (4.), the formation rate of B_s0_{2i} is proportional to $[B_s]^2$, as observed.**

6. **The trapping rate of O_{2i} at B_s is strongly enhanced by the coulomb attraction between the $O_{2i}{}^{2+}$ and $B_s{}^-$.**

7. **Quantitative consideration of the processes above leads to very good agreement with the experimentally observed rate of illumination-induced solar-cell efficiency loss.**

That's It, Folks.

Thank You For Your Attention.