Defect Analysis of Phosphorus Doped Silicon Quantum Dots by Electron Spin Resonance

B. Kanten[1], K. Riskey[2], L. Wheeler[3], C. Taylor[2]

[1]Harvard University; Cambridge, Massachusetts

[2]Colorado School of Mines; Golden, Colorado

[3]University of Minnesota; Minneapolis, Minnesota

Silicon Quantum Dots in Solar Cells

- Perfectly crystalline silicon with a dopant provides free carriers in solar materials
- The crystalline structure of the lattice provides an ideal semiconductor
- Quantum dots have a better ability to collect electrical current than amorphous silicon
- Defects in silicon are defined as places where the crystalline lattice is not perfect such as a dangling bond
- ESR can be used to understand defects and discover the defect concentration of various silicon structures to determine their potential efficiency

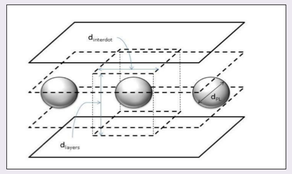

Figure 1 **Illustration of silicon quantum dots in a lattice configuration [1]**

Procedure

- Phosphorus doped silicon quantum dots used were obtained from Lance Wheeler
- The dots were synthesized using silane and phosphine gases by plasma enhanced chemical vapor deposition (PECVD)
- Samples were doped to increasing levels of phosphorus: 0.01%, 0.1%, 1%, 10%
- Samples were prepared both dry and in toluene solvent
- All samples characterized at three temperatures: 300K, 77K, 12K

Electron Spin Resonance Theory

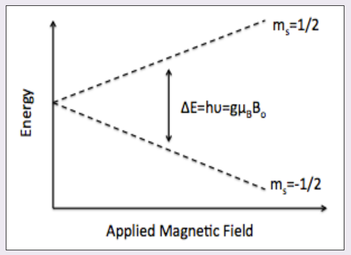

Figure 2 **The energy between the spin states of an electron increases with increasing magnetic field**

- ESR is used to characterize materials with unpaired electrons
- Unpaired electrons are excited in an external magnetic field and either align or anti- align with the field
- Electrons can move between spin states by absorbing or emitting a photon
- Microwave source supplies energy for spin transition
- Magnetic field increases causing the energy difference between the spin states to widen until it matches the energy of the microwave radiation; shown in Figure 2
- This results in resonance and absorption of energy which is detected by the spectrometer
- The spectrum given by ESR is the derivative of the absorbance spectrum

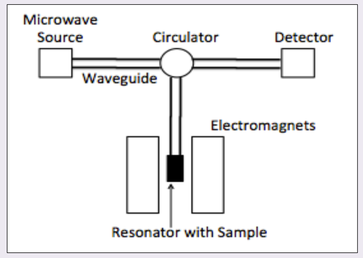

Figure 3 **Diagram of an ESR spectrometer**

Fluorine Hyperfine Interactions

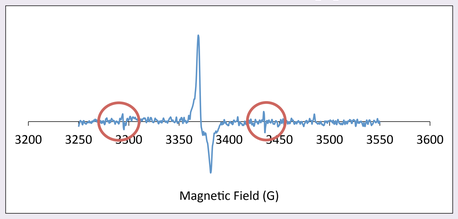

Figure 4 **Spectrum of 1% Phosphorus doped silicon quantum dot at 77K**

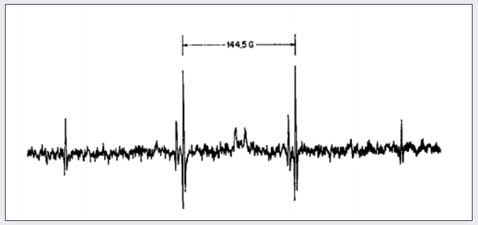

Figure 5 **Spectrum of fluorine hyperfine splitting caused by C2F6-CF4 at 110K, the two largest lines are those due to fluorine [3]**

- Hyperfine splitting lines in an ESR spectrum are caused by the interaction of the magnetic moment from the nucleus with that of the electrons
- The magnetic dipole of the nucleus induces a second magnetic field near the electron in addition to that produced by the ESR machine allowing for more resonant states
- Hyperfine interactions are unique to each atom and can be used to determine the number and identity of nuclei and the distance between the nucleus and the unpaired electrons

- **The presence of two hyperfine lines suggest an element with a spin ½ nucleus likely either fluorine or hydrogen**
- **The hyperfine lines at a width of ~140 Gauss in Figure 4 matches the width shown in Figure 5 and implies contamination of the sample with fluorine because it of its large magnetic moment as compared to hydrogen**
- **It was discovered that the dots were prepared in a glove box also used for the synthesis of silicon nano-crystals, a process that uses fluorinated precursors**

Intrinsic P_b Center

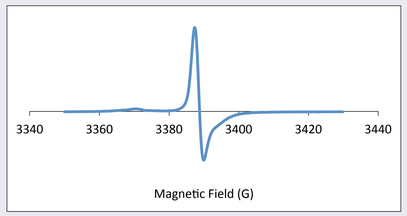

Figure 6 **Spectrum of intrinsic silicon quantum dots at 12K**

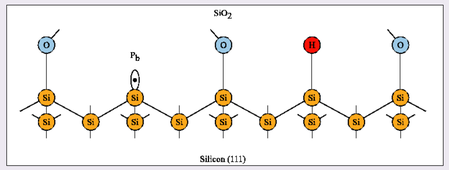

Figure 7 **Illustration of a P_b center defect at an Si/SiO2 interface [4]**

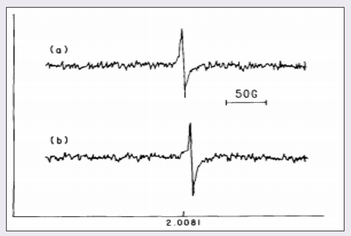

Figure 8 **ESR spectra of a P_b center in terms of g- value and including a scale for magnetic field (G) [5]**

- Silicon atoms have four valence electrons and require four more to satisfy their valence shell
- Within crystalline silicon all four valence electrons are bonded and the valence band is filled
- At the surface the silicon cannot bond with a neighboring atom due to lattice mismatching and sometimes leaves an sp_3 hybridized orbital free, this is called a dangling bond as shown in Figure 7
- This is the P_b center defect and it occurs at the boundary of crystalline silicon sometimes in the presence of SiO_2
- A P_b center is one of many types of centers in materials that can be shown with ESR
- A P_b center can be identified as a peak with a g- value of between 2.000 and 2.010 as shown in Figure 8
- A g- value is a constant defined by the equation in Figure 2

- **The g- value for the spectrum in Figure 6 was calculated to be 2.006 from the location of the center peak which falls within the range of g- values for P_b centers**
- **The width of the peak in Figure 6 is ~20 Gauss which is consistent with the spectra of known P_b centers in Figure 8**
- **The peak in Figure 6 seems to be caused by P_b centers on the surface of the dots**

Phosphorus

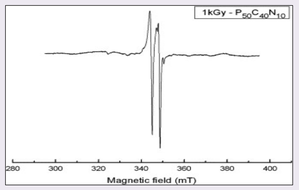

Figure 9 **Spectrum for P2O5-CaO-Na2O glass [2]**

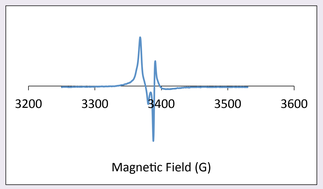

Figure 10 **Spectrum of 10% phosphorus doped silicon quantum dots with intrinsic feature subtracted at 77K**

Proof of phosphorus doping from ESR would come in two forms:

- A hyperfine interaction would appear from the phosphorus nucleus of spin ½ and the donated electrons. This would show one donated electron per dot.
- A resonance signal from many donor electrons in the conduction band. This would show two or more donated electrons per dot.

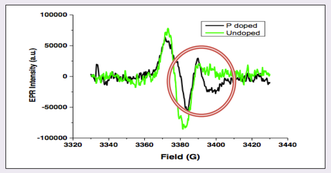

Figure 11 **Spectrum comparing phosphorus doped and intrinsic quantum dots [1]**

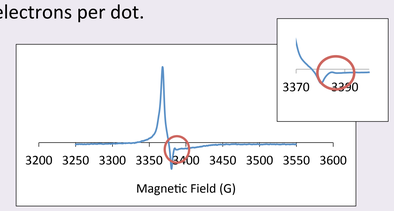

Figure 12 **Spectrum of 10% phosphorus doped silicon quantum dots at 12K**

- **A phosphorus oxide glass seems to have formed on the outside of the dots during the doping process shown by the distance between the peaks in Figures 9 and 10 being nearly equivalent: 5 mTesla and 40 Gauss**
- **Figure 11 shows that phosphorus doping causes a second resonance peak in the ESR spectrum just before 3400 G**
- **Figure 12 shows that the sample dots have the extra peak near 3400 G**
- **The dots seem to be successfully doped with phosphorus because we have ESR plausible evidence of electrons in the conduction band**

Future Work

Other doping techniques need to be understood, applied, and tested. The phosphorus glass on the outside of the dots suggests that the doping efficiency for this process is low and that little phosphorus penetrated into the bulk material within the dot. A higher doping efficiency will lead to lower materials and production costs, and higher efficiency solar cells.

Acknowledgements

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