The Relationship of Silicon Dihydride Sites to the Metastable Defects in a-Si:H

Abstract

We use proton nuclear magnetic resonance to probe stable silicon dihydride existing in high defect density hydrogenated amorphous silicon. The silicon dihydride line shape exhibits the well-known "Pake" doublet form resulting from a dipole interaction between two protons. We simulate the line shape using the relevant Hamiltonian and broadening effects known to occur in this amorphous system. The sets of simulation parameters that reproduce the experimental data render an approximate realization of the hydrogen's local bonding environment (i. e. hydrogen-hydrogen separation, nearest neighbor distances). A unique parameter set cannot be determined from the magnetic resonance data alone. However, it is possible to extract the upper and lower limits by considering the extreme cases for known hydrogen bonding environments—the true parameter set being somewhere in between these values.

Of particular importance is the hydrogen-hydrogen separation since the dihydride site is a possible candidate for the metastable defect mediating the Staebler-Wronski effect. We compare our results with a previous study that links a metastable paired hydrogen site to the effect.

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Summary

We have fitted the experimental Pake doublet for stable SiH_2 with line shape simulations whose fitting parameters reflect the possible local environments and variation in the hydrogen-hydrogen separation. It is found that that an accurate fit is obtainable when the hydrogen-hydrogen separation in SiH_2 is 1.8 Å. Isotropic broadening due to neighboring atoms and variations in the separation distance allow for satisfactory fit, but cannot be uniquely determined from the NMR spectra alone.

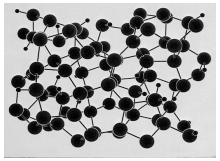
The significant deviation from the previous result of 2.3 ± 0.2 Å suggests that the metastable site may not be SiH_2. However, it is difficult to rule out SiH_2 since a detailed line shape for the metastable site in device-grade material has not been possible to date.

The study of a-Si:H is driven primarily by two factors:

Technological Applications

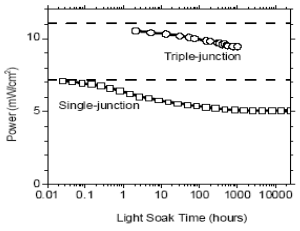
The optical and electronic properties make a-Si:H a useful material for photovoltaic devices. Compared to the cells made from the crystalline counterpart, uniform, monolithic a-Si:H thin film solar cells can be produced inexpensively.

Basic Science



a-Si:H is the prototypical system for studying the effects of disorder. The degree of disorder, or departure from the tetrahedral crystalline form, where the electronic and optical properties can be readily calculated, can be tailored using growth techniques. Therefore, a-Si:H is a proving ground for theoretical and computational models of departures (i.e. point defects, micro-voids, strained bonds etc.) from the crystalline phase. The above picture is a cartoon of the hydrogenated amorphous silicon system.

The Problem with a-Si:H



The a-Si:H system suffers from the Staebler-Wronski Effect (SWE) which is metastable degradation in the energy conversion efficiency after long illumination times. The figure demonstrates the SWE for a single and triple junction a-Si:H solar cell, made at United Solar Systems Corp, for increasing exposure to sunlight [1,2]. A full understanding of the SWE has remained elusive for nearly thirty years.

1. Guha S, in *Technology and Applications of Amorphous Silicon*, 252-305, edited by Street R A, Springer, Berlin (1999).

2. Guha S, Yang J, Banerjee A, Glatfelter T, Hoffman K, Xu X, *Technical Digest - 7th International Photovoltaic Science and Engineering Conference, Nagoya, Japan (PVSEC-7)*, p. 43 (1993).

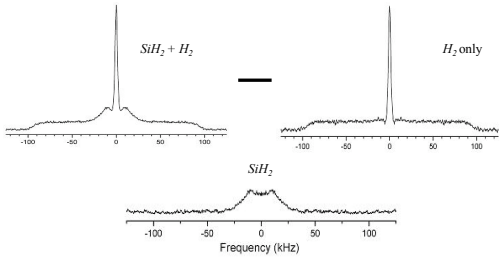
Hydrogen's Role in the SWE

Recent proton (^{1}H) nuclear magnetic resonance (NMR) experiments have linked a specific metastable, "paired" hydrogen site, in which the hydrogen pair is separated by 2.3 ± 0.2 Å, to the SWE [3]. The observed NMR signal can be created via light soaking and annealed in accordance with the metastable defect thought to produce the SWE. Silicon dihydride (SiH_2) is a possible candidate for this site since calculations using the conventional tetrahedral silicon structure give 2.4 Å as the hydrogen separation [4]. Observation of the SiH_2 NMR line shape allows for a an indirect evaluation of the hydrogen-hydrogen separation that can be compared to the previous study.

3. T. Su, P.C. Taylor, G. Ganguly, and D.E. Carlson, Phys. Rev. Lett. 89, 015502 (2002).

4. Tesfaye A. Abtew, D. A. Drabold, and P. C. Taylor, Appl. Phys. Lett. 86, 241916 (2005).

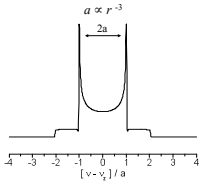
Silicon Dihydride Bonding $(SiH_2)_n$ in High Defect Density a-Si:H: NMR Evidence



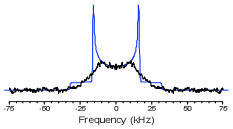
Hydrogen-Hydrogen Separation From Line Shape Analysis

The (SiH_2) line shape exhibits a well-known form resulting from a dipole interaction between the two hydrogen protons. An analytic expression of the intensity of this so-called "Pake doublet" line shape can be expressed in terms of the coupling strength, and hence the hydrogen-hydrogen separation, r. It is therefore possible to extract r by fitting simulated line shapes to the experimental data.

Theoretical Line Shape (ν, a in frequency units):



Experimental Line Shape with Pake doublet $r = 1.8$ Å



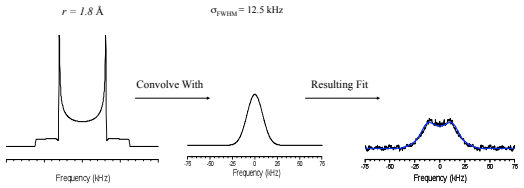
Bonding Environments

In the case where modulations to the local field exist, due to nearby hydrogen nuclei, the pure Pake doublet is broadened by an amount related to the proximity and number of surrounding nuclei. This "isotropic" broadening effect, which is Gaussian for clustered arrays, can be taken as a fitting parameter in simulations.

Broadening of the pure Pake doublet may also result from a distribution of proton-proton separations. The distribution can also be taken as a fitting parameter whereby the resulting broadened spectrum is a summation of Pake doublets

Simulation I: Clustered $(SiH_2)_n$ Sites

It is well known that some SiH sites form in small groups, or clusters. The participating hydrogen atoms experience a net local field that is different from site to site depending on the neighbor's proximity. The line shape broadening due to this clustering is well modeled by convoluting the frequency space spectra with a Gaussian whose full width at half maximum, σ_{FWHM}, is related to the cluster geometry.



Simulation II: Isolated $(SiH_2)_n$ Sites

By assuming the sites are isolated from other hydrogen atoms, the broadening mechanism must result almost entirely from the distribution in r. We assume a Gaussian distribution with mean separation, $r_0 = 1.8$ Å and full width half max parameter $\sigma_{FWHM} = 0.54$ Å. The resulting spectrum is the superposition of weighted Pake doublets. As a reference, the weighted spectra for $r = 1.8$, *2.03*, and *1.53* Å are drawn below.

It is well known that the line shape due to the most isolated SiH suffers a ~ 1 kHz isotropic broadening due neighboring protons. Therefore we include a 1 kHz broadening along with the superposition broadening.