

Direct Role of Hydrogen in the Staebler-Wronski Effect in Hydrogenated Amorphous Silicon

T. Su* and P. C. Taylor

Department of Physics, University of Utah, Salt Lake City, Utah 84112

G. Ganguly and D. E. Carlson

BP Solar, Toano, Virginia 23168

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We report a hydrogen-related defect that establishes the direct role of hydrogen in stabilizing the silicon dangling bonds created in the Staebler-Wronski effect in hydrogenated amorphous silicon. A specific NMR signal due to paired hydrogen atoms occurs only after optical excitation, exists at an intensity that is consistent with the density of optically induced silicon dangling bonds, and anneals at temperatures that are consistent with the annealing of the optically induced silicon dangling bonds. At this defect the hydrogen atoms are $2.3 \pm 0.2 \text{ \AA}$ apart.

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The interaction between hydrogen impurities and defects in crystalline and amorphous solids is of general interest in many diverse materials systems. In crystalline semiconductors, such as silicon, hydrogen can form a number of metastable complexes [1], including pairing with phosphorous or boron to passivate the dopants [2] or pairing with a second hydrogen to generate the metastable defect known as H_2^* [3]. In addition, in crystalline Si hydrogen can assist in the mobility of dislocations [4], influence the diffusion of impurities, and even aggregate along selected planes to produce "platelets" [5]. In crystalline Ge, hydrogen can actually activate neutral impurities such as carbon and oxygen [6]. The role of hydrogen in creating various defects and in stabilizing metastable defects is fairly well understood both experimentally and theoretically in crystalline Si [1,7], Ge [7,8], and in many III-V semiconducting materials [9–12].

The situation is very different in amorphous semiconductors. Despite over 25 years of effort, there has been no measurement that indicates the direct role of hydrogen in the production of the defects that produce the Staebler-Wronski effect [13], the most important metastability in the quintessential amorphous semiconductor, hydrogenated amorphous silicon (*a*-Si:H). Understanding the role of hydrogen in this well-studied case is an essential first step toward any general understanding for a wider class of amorphous materials. In addition, specific information concerning the role of hydrogen in amorphous semiconductors will greatly facilitate comparisons with the better known crystalline cases.

In *a*-Si:H, hydrogen has long been implicated in the Staebler-Wronski effect [13], which is characterized by a decrease in both the dark and photoconductivities after irradiation with visible light. These decreases are attributed to the production of approximately 10^{17} cm^{-3} of silicon dangling bonds, which are defects that serve as nonradiative recombination centers for carriers. Although hydrogen has long been implicated, no direct microscopic evidence exists to confirm this suspicion.

There are several reasons why previous experiments have not found any evidence for the direct role of hydrogen in stabilizing the silicon dangling bonds that produce the Staebler-Wronski effect. First, one needs a microscopic probe of the hydrogen, such as can be provided by electron spin resonance (ESR) or nuclear magnetic resonance (NMR). Although ESR is a technique that has been very valuable in examining the effects of hydrogen in crystalline semiconductors, extensive ESR experiments in *a*-Si:H over many years have failed to provide any evidence of sites related to hydrogen. Second, the densities of the defects produced in the Staebler-Wronski effect are much too small to be accessed by standard NMR experiments. For this reason, one must perform an NMR experiment that accentuates specific hydrogen environments, such as the one described below. One must also have a thin film that has been deposited very uniformly over a large area. Finally, one must use different halves of the same film for the comparison between irradiated and unirradiated conditions to avoid variations that can occur from sample to sample. Even if all of these conditions are met, we show below that the observed signal disappears above 10 K so that experiments at low temperatures are essential.

In this Letter we report the first direct evidence for optically induced changes in the local environment of a subset of the hydrogen atoms *at densities comparable* to those of the silicon dangling bonds that contribute to the Staebler-Wronski effect. After optical excitation, the ^1H NMR exhibits a hydrogen "doublet" that corresponds to a hydrogen configuration with two hydrogen atoms spaced approximately 2.3 \AA apart. This hydrogen "defect," whose density is between 10^{17} and 10^{18} cm^{-3} , can be thermally annealed with kinetics that generally match the annealing of the silicon dangling bonds. Although a detailed microscopic picture of this defect remains elusive, the direct tie to hydrogen is a critical first step that places severe constraints on existing microscopic models.

The film of *a*-Si:H employed in this study was made in a large area deposition system by dc plasma enhanced

chemical vapor deposition of silane (SiH_4). The pressure in the reactor was 0.5 Torr, the power density was $\sim 50 \text{ mW/cm}^2$, and the substrate temperature was about 200°C . These conditions represent those used in standard photovoltaic devices for which the electronic and optical properties are very well known. The film was deposited on Al foil and half of the area was irradiated with a solar simulator for 600 h. Two NMR samples were made from the irradiated (hereafter referred to as the light-soaked sample) and unirradiated (hereafter referred to as the as-grown sample) areas by dissolving away the Al foils in dilute hydrochloric acid and placing the cleaned powders in quartz tubes. The NMR measurements were made at 7 K, using a Jeener-Broekaert three-pulse sequence, on a standard pulsed spectrometer as described elsewhere [14]. Samples were annealed in a nitrogen environment at 170 and 200°C .

The Jeener-Broekaert three-pulse sequence probes the decay of dipolar order among the hydrogen nuclei in the sample [15]. The separations between the first and second pulses and the second and third pulses are denoted as τ_1 and τ_2 , respectively. A stimulated echo forms at a time τ_1 after the third pulse. Since the amplitude of the stimulated echo depends sensitively on the local environments of the hydrogen atoms or molecules, one can emphasize specific hydrogen sites by choosing the two pulse separations judiciously [14]. The echo intensity is proportional to $e^{-2\tau_1/T_2} e^{-(\tau_2/T_{1d})^{1/2}}$, where T_2 is the spin-spin relaxation time and T_{1d} is the dipolar spin-lattice relaxation time [14]. By monitoring the echo intensity as τ_1 and τ_2 approach zero, the relative concentration of a specific hydrogen site can be obtained.

In $a\text{-Si:H}$, T_{1d} is known to be the result of a cross relaxation between hydrogen nuclei and the paramagnetic electronic states, such as the silicon dangling bonds [14,16]. Therefore, large values of τ_2 emphasize any hydrogen site that interacts only weakly with silicon dangling bonds.

In Fig. 1 we show the Fourier transform of the stimulated dipolar echo, which represents the line shape in frequency space, in the two samples of $a\text{-Si:H}$ measured under various conditions. (We show the real transforms in Fig. 1 to improve the signal-to-noise ratios and eliminate small phase errors due to long term drift during signal averaging. The complex transforms exhibit the same features with slight asymmetries in the line shapes.) The bottom trace (d) is the line shape of the as-grown sample. This line shape contains the two standard features, a narrow Lorentzian line attributed to hydrogen bonded to silicon atoms in a dilute (essentially random) configuration and a broad Gaussian line attributed to hydrogen bonded to silicon in a clustered environment, such as might be obtained on the internal surfaces of microvoids. The top trace (a) is the line shape of the light-soaked sample. In addition to the two standard features, there exist two small peaks separated from the central frequency, which is labeled zero in Fig. 1, by about 8 kHz. (The features at $\pm 23 \text{ kHz}$ are artifacts due to an unknown, small interference with the NMR detection signal, which also occurs in the absence

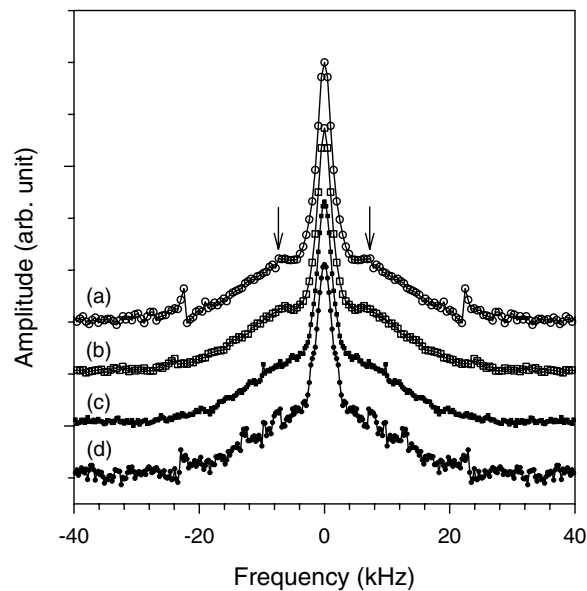


FIG. 1. ^1H Jeener-Broekaert stimulated echo spectra in $a\text{-Si:H}$. (a) light-soaked sample; (b) irradiated sample after annealing at 170°C for 4 h; (c) irradiated sample after annealing at 170°C for 4 h followed by annealing at 200°C for 4 h; (d) sample as grown. Arrows point to the appearance of a hydrogen doublet in the light-soaked sample. The peaks near $\pm 23 \text{ kHz}$ are artifacts. See text for details.

of a sample.) Trace (b) is the spectrum in the light-soaked sample after annealing at 170°C for 4 h. This procedure is known to partially anneal the Staebler-Wronski degradation observed in solar cells made from films of this type [17]. Trace (c) is the spectrum in the light-soaked sample after additional annealing at 200°C for 4 h. As shown in Fig. 2, the spectrum taken after annealing at 200°C and the spectrum in the as-grown sample are identical within experimental error.

Two conclusions are easily deduced from the data in Fig. 1. First, an extra feature appears in the ^1H NMR line

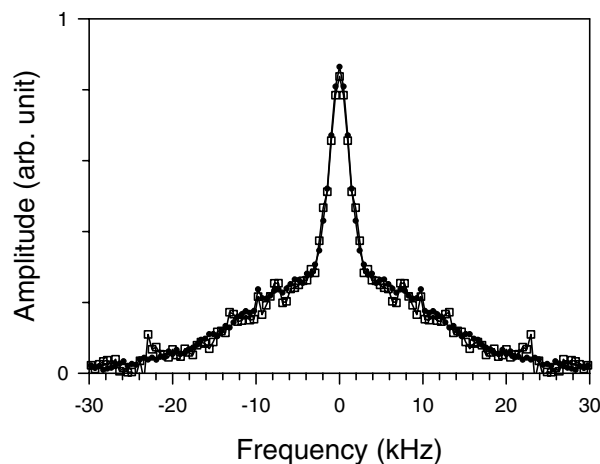


FIG. 2. ^1H Jeener-Broekaert stimulated echo spectra in $a\text{-Si:H}$. Data for the as-grown and annealed (200°C for 4 h) samples are represented by squares and circles, respectively. The two spectra are identical within experimental error.

shape of Fig. 1 after optical excitation. Second, this feature disappears after annealing at 200 °C. We have thus found a distinct hydrogen environment in *a*-Si:H that appears on optical excitation and disappears on annealing.

Further conclusions can be drawn, but they require progressively more interpretation. If we assume that the line shape change is indeed due to a doublet and not something more complicated, such as a triplet, then the spacing between the paired hydrogen atoms, R , can be estimated. Because the splitting depends inversely on R^3 , the separation can be estimated fairly accurately as $R_0 = 2.3 \pm 0.2$ Å. In addition, although this separation could in principle vary from site to site, there must be a well-defined maximum separation, which is also approximately R_0 .

A more detailed comparison of the NMR line shapes in the irradiated sample and in the same sample after annealing at 200 °C is shown in Fig. 3. By far the greatest difference in these two line shapes is the relatively smaller intensity of the narrow Lorentzian line. Although dramatic, this difference has a well-understood origin that is not of great interest for the present discussion. It is known [18] from previous T_{1d} measurements in doped and intrinsic *a*-Si:H that for a specific density of paramagnetic centers, in this case silicon dangling bonds, T_{1d} is shorter for the broad line than for the narrow line over the time scale shown in Fig. 3. Therefore, the broad line decays slightly more rapidly with pulse separation than the narrow line. We have confirmed that this is also the case for our sample of *a*-Si:H. Thus, as the number of dangling bonds increases after optical excitation, the T_{1d} of the broad line decreases more rapidly than that of the narrow line, and

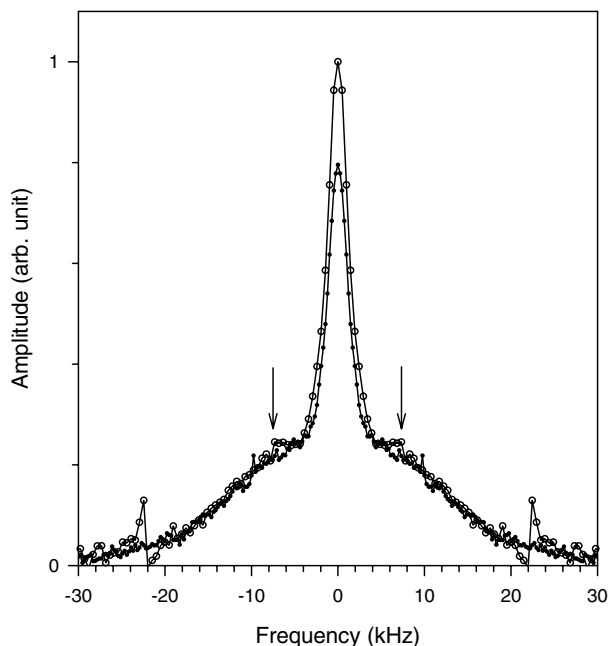


FIG. 3. ^1H Jeener-Broekaert stimulated echo spectra in *a*-Si:H. Data for the irradiated and annealed (200 °C for 4 h) samples are represented by open and solid circles, respectively. Arrows indicate the doublet in the irradiated sample.

at a constant pulse separation the relative intensity of the narrow line increases with respect to that of the broad line. This dependence on ESR spin density explains why the narrow Lorentzian line appears to grow relative to that of the broad Gaussian line after optical excitation. Therefore, the only intrinsic change in the line shape after optical excitation is the appearance of the doublet at ± 8 kHz in Figs. 1 and 3. Although we cannot completely rule out the possibility that changes in T_{1d} simply mask the doublet in the annealed and as-grown cases, this situation is very unlikely for the reasons discussed below.

One can also estimate the density of these optically induced hydrogen doublets. The relative densities of the two bonded hydrogen lines and the metastable doublet can be estimated by extrapolating the respective echo amplitudes to zero separation between the three pulses (as τ_1 and τ_2 both approach zero). There is considerable error in extrapolating the doublet signal as τ_2 approaches zero, and the behavior as τ_1 approaches zero is even more uncertain. Therefore, the density of these paired hydrogen atoms can only be estimated to be between 10^{17} and 10^{18} cm^{-3} . Although the error is 1 order of magnitude, this range encompasses the density of optically induced silicon dangling bonds as measured by ESR. This density, which itself is known only to within about a factor of 5, is 5×10^{16} cm^{-3} . The ESR signal is reduced by at least a factor of 3 on annealing at 170 °C and by more than a factor of 5 on subsequent annealing at 200 °C.

At first sight the annealing of the hydrogen doublet does not appear to coincide accurately with the annealing of the ESR because the doublet NMR signal is essentially the same intensity relative to the Gaussian and Lorentzian lines after annealing for 4 h at 170 °C while the ESR has decreased by about a factor of 3. However, the magnitude of the doublet depends not only on the number of hydrogen pairs but also on the value of T_{1d} for the doublet. Although the number of doublets decreases on annealing, the value of T_{1d} actually increases more rapidly than those for the Gaussian and Lorentzian components. These two effects counteract each other and make absolute determinations of the relative intensities on annealing very difficult. Nonetheless, it is clear that the hydrogen doublet signal is essentially gone after annealing for 4 h at 200 °C.

If the densities of silicon dangling bonds and hydrogen atoms contributing to the doublet are the same, this equality answers the long-standing question as to why the silicon dangling bonds that are stable (dark ESR signal) and those that are metastable (optically induced ESR signal) have identical line shapes. They are, indeed, the same, but one can anneal only up to a density that is twice the density of metastable hydrogen doublets.

The ^1H NMR experiments were performed at both 10 and 7 K. At 10 K the doublet is not observable either because of a smaller signal-to-noise ratio (due to the decrease of the Boltzmann factor) or because of a narrowing of the doublet due to local motion of the two hydrogen atoms. A detailed comparison of the two spectra at 7 and 10 K in

the region of the narrow line indicates a slight broadening at 10 K that is consistent with the latter interpretation.

Over the years many specific defects have been suggested for the metastable hydrogen complexes assumed to accompany the light-induced production of silicon dangling bonds. Two reviews are available in Refs. [19,20]. The present results place several restrictions on models for the Staebler-Wronski effect. First, the defect that stabilizes the silicon dangling bonds consists of two hydrogen atoms about 2.3 Å apart. These paired hydrogen atoms are isolated from other hydrogen clusters and from silicon dangling bonds. Finally, these paired hydrogen atoms may be free to rotate above about 10 K.

Stutzmann *et al.* first suggested that the silicon dangling bonds could emanate from the breaking of strained silicon-silicon bonds with subsequent hydrogen motion necessary to make the defects metastable [21]. In 1986 Carlson suggested that “vacancies” might play a role [22]. Zafar and Schiff [23] first suggested the presence of electrically inactive, paired hydrogen atoms. Branz has coupled the existence of paired hydrogen atoms to the Staebler-Wronski effect [24,25]. Given the present evidence, we can rule out most of the specific suggestions for the defects. Biswas and co-workers [26,27] have proposed the analog in *a*-Si:H of the H₂^{*} defect that occurs in crystalline silicon. We can rule out this specific example because the hydrogen atoms are too far apart. Recently, van de Walle and Tuttle [28] have suggested that molecular hydrogen (H₂) is the stabilizing defect. This example is ruled out because the hydrogen atoms are too close together. Very recently, Zhang and Branz [29] have suggested that a surface dimer at a fully hydrogenated multivacancy is the stabilizing defect, but this example is ruled out because there are too many hydrogen atoms in the cluster.

One specific hydrogen environment proposed by van de Walle and Tuttle [28], albeit as an intermediate state and not as the stabilizing defect, does fit the observed NMR doublet spacing. This site is a five-fold-coordinated silicon atom with two Si-H bonds. In the calculations of van de Walle performed on a crystalline cell, this defect is not stable enough to fit the annealing kinetics of the light-induced silicon dangling bonds. The stability must somehow be enhanced in the amorphous environment for this site to be consistent with the present results.

In summary, we have discovered a specific hydrogen configuration that may stabilize the silicon dangling bonds created in the Staebler-Wronski effect in *a*-Si:H. The paired hydrogen signal occurs only after optical excitation, exists at a density that is consistent with the density of optically induced silicon dangling bonds, and anneals at temperatures that are consistent with the annealing of the optically induced silicon dangling bonds.

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*Email address: tnsu@physics.utah.edu

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