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Metastable changes of the electronic spin-lattice relaxation time in hydrogenated amorphous silicon

Martin Stutzmann*
Xerox Palo Alto Research Center, Palo Alto, California 94304

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Reversible changes in the electronic spin-lattice relaxation time T_1 are observed in the case of the dangling-bond defect in hydrogenated amorphous silicon. These changes occur during prolonged illumination with intense light and are completely reversible upon annealing at elevated temperatures in the dark. A possible connection with metastable quenching of localized vibrational modes is discussed.

The breakdown of translational symmetry in amorphous materials leads to several characteristic differences between the crystalline and amorphous phases. The most general and intriguing difference is the existence of additional low-energy vibrational modes in amorphous solids, originally observed through anomalies in the thermal properties at temperatures below ≈ 10 K.[1] It was first believed that these modes only occur in typical glass-forming materials with low average coordination of the individual atoms (Se, SiO_2, chalcogenides)[2-4] permitting sufficient topological disorder. However, it is now well established that the same low-temperature anomalies are also present in topologically overconstrained amorphous solids, especially amorphous Si and Ge,[5,6] and even in crystalline solids with only orientational disorder.[7,8] As far as the microscopic structure of these additional low-energy excitations is concerned, little is known in detail as of now, but two general properties follow from the experimental results: (1) The weak (linear) temperature dependence of the specific-heat contribution due to the low-energy excitations implies that their density of states $D(E)$ is approximately constant.[9] Thus, the additional vibrational modes in amorphous solids are distinct from the long-wavelength phonons with a Debye density of states, $D_{\mathrm{ph}}(E) \propto E^2$. (2) The observation of phonon echoes in amorphous solids[10] provides conclusive evidence that in at least some cases the additional excitations are restricted to two energetic levels. Because of this, the name "two-level systems" is often used to refer to these vibrational modes. However, so far similar phonon-echo experiments have not been performed for amorphous silicon, so that the two-level nature of the low-energy modes in this material remains to be established.

There is a second difference, of a more quantitative nature, between amorphous semiconductors and their crystalline counterparts. This is the possibility of creating a significant density of metastable defects in the mobility gap of the amorphous material by prolonged illumination with light. These defects are metastable in the sense that short anneals at elevated temperatures restore the properties of the sample before the illumination. Examples for these reversible structural changes are the photodarkening observed in amorphous chalcogenides[11] and, especially, the Staebler-Wronski effect in hydrogenated amorphous silicon (*a*-Si:H). This latter effect has been explained by the reversible creation of dangling-bond states via recombination-induced breaking of weak Si-Si bonds. Since these dangling bonds act as recombination centers in *a*-Si:H, the Staebler-Wronski effect has quite far-reaching consequences for the application of this material. For more details, see Ref. 12, and references therein.

In this article I will report on a different, quite surprising aspect of light-induced metastable changes in hydrogenated amorphous silicon; namely, the observation of a reversible increase of the electronic spin-lattice relaxation time, T_1. This spin-lattice relaxation time is the characteristic time constant with which the spin system reaches thermal equilibrium with the phonon bath. It is known that, due to changes in the density of vibrational states, additional relaxation paths exist in the disordered solid phase, leading to relaxation times which are very different from what is typically observed in crystalline materials.[13-16] Not only is T_1 in the disordered material usually orders of magnitude shorter than T_1 for the same spins in the corresponding crystalline case, but, in addition, the temperature dependence of T_1 can no longer be described within the context of the otherwise successful crystalline relaxation theories based on single or multiple phonon processes.[17,18]

A similar situation occurs also in hydrogenated amorphous silicon. The existence of two-level systems or other localized vibrational modes in this material and their influence on the spin-lattice relaxation time have been reported previously,[5,19,20] and interested readers are referred to these articles for further details. The samples used in the present study were deposited by low-power rf glow discharge of undiluted silane, and are comparable to typical state-of-the-art *a*-Si:H as far as hydrogen content and microstructure are concerned. The density of dangling-bond defects after deposition, as measured by electron spin resonance (ESR), was 5×10^{15} cm^{-3}. For the transformation of the samples into the metastable, light-soaked state prolonged illumination with ir-filtered white light from a tungsten lamp was carried out at controlled temperatures between 20 and 150 °C. The spin-lattice relaxation times were measured by use of the passage technique described in more detail in Ref. 19.

Figure 1 summarizes the measured temperature dependence of the spin-lattice relaxation time for the Si dangling-bond defect ($g = 2.0055$) in various states of an *a*-Si:H sample. For the as-deposited sample (dashed-dotted curve), a $T^{-2.3}$ dependence of T_1 is observed over the entire accessible temperature range (10–300 K), as reported before.[19] When this sample is illuminated for an extended period at a temperature of 90 °C, T_1 at low temperatures ($T < 100$ K) becomes significantly longer, e.g., by an order of magnitude

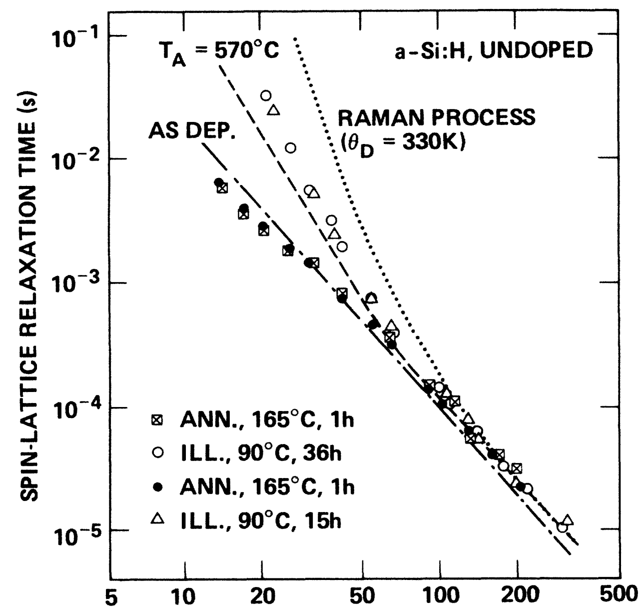

FIG. 1. Spin-lattice relaxation time T_1 for the dangling-bond defect in a-Si:H as a function of temperature. Open circles and triangles refer to the metastable, illuminated state, all other symbols to the annealed state of a-Si:H. The dashed-dotted line shows the relaxation time observed in an as-deposited sample, the dashed curve indicates the relaxation time after an anneal at 570 °C. The dotted line shows the calculated temperature dependence of T_1 in the case of a two-phonon Raman process (Debye temperature: 330 K).

at 20 K. Surprisingly, annealing of the illuminated sample at 165 °C for about one hour restores the original value of T_1 to within a factor of < 1.5 at all temperatures. This shows the reversible nature of the changes in the spin-lattice relaxation time. Indeed, the illumination-annealing cycle can be repeated with great reproducibility, as shown by the additional data points in Fig. 1.

Two more curves are shown in Fig. 1. The dashed curve gives the temperature dependence of the dangling-bond T_1 in a sample which has been annealed to a point just before crystallization ($T_A = 570\,°\mathrm{C}$), and again the increase of T_1 at lower temperatures is observed. However, in this case the change is not reversible. Finally, the dotted curve shows the theoretical predictions for $T_1(T)$ due to a phonon Raman process with a Debye temperature $\theta_D = 330$ K, a value obtained from heat-capacity measurements in a-Si:H.[5]

The illumination process employed for inducing the T_1 changes in Fig. 1 also leads to a metastable increase of the dangling-bond spin density itself. Therefore, a possible explanation for the experimental results in Fig. 1 could be provided by a different (longer) relaxation time for these light-induced defects. Such a situation would have been difficult to detect within the ESR passage measurements used to obtain the data in Fig. 1. To clarify this point, a time-resolved measurement had to be performed in order to insure that all dangling-bond spins are characterized by the same value of T_1, irrespective of their stable or metastable nature. The required time resolution is conveniently provided by transient electron nuclear double resonance (ENDOR) measurements. Details of these measurements will be published elsewhere.[21] For the present case it is sufficient to say that the ENDOR response caused by the magnetic hyperfine interaction between dangling-bond electronic spins and the nuclear spins of nearby protons in a-Si:H decays with a time constant equal to the spin-lattice relaxation time of the electronic spin system. Therefore, in order to obtain the required time resolution, transient ENDOR signals have been recorded in the annealed (stable) and the light-soaked (metastable) state of a-Si:H. The transients shown in Fig. 2 demonstrate the time decay of the ENDOR signal after application of a saturating rf pulse satisfying the nuclear resonance condition ($\nu = 13.88$ MHz for protons in a magnetic field of $H_0 = 3.26$ kG), with the ESR spectrometer tuned to the dangling-bond resonance. The point of interest here is that in both cases single exponential decays are obtained to within experimental accuracy. Since, in the case of Fig 2, the illumination conditions had been chosen such as to create approximately the same density of stable and metastable dangling bonds ($\approx 1\times 10^{16}$ cm^{-3} each), it is clear that spin-lattice relaxation times differing by more than $\approx 50\%$ for stable and metastable dangling bonds would have led to a noticeable deviation of the transient ENDOR decay in Fig. 2 from a single exponential. Instead, the same time constant ($T_1 = 25$ ms at $T = 22$ K) is observed for stable and for metastable dangling bonds.

As mentioned before, the electronic spin-lattice relaxation time in a-Si:H is anomalously short and, moreover, shows a temperature dependence which cannot be explained by the conventional crystalline theories. It has been proposed, therefore, that the spin-lattice relaxation in a-Si:H, as in most other amorphous solids, is determined by a coupling of the spins to vibrational modes characteristic of the amorphous network (for example, two-level systems).[19,20] Then the experimental results presented here clearly indicate that either the density of such disorder modes in a-Si:H is reduced in a metastable way by the illumination process, or that the coupling between *all* electronic spins and these modes is diminished reversibly. Note in this context that the observed temperature dependence of T_1 in the il-

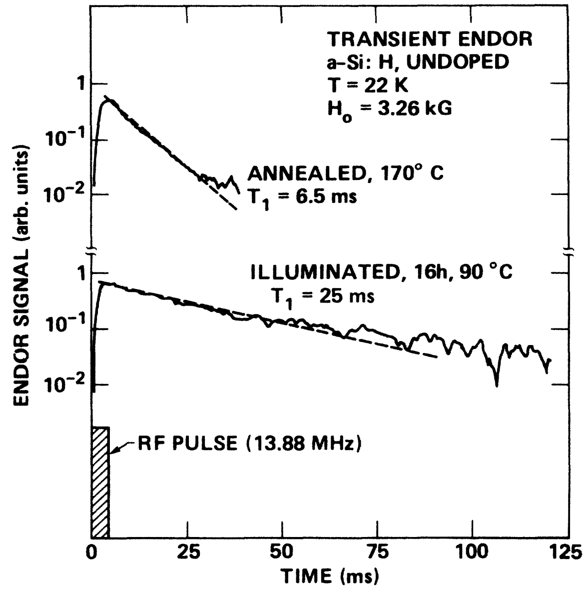

FIG. 2. Transient ENDOR decay in the annealed and the light-soaked state of undoped a-Si:H at $T = 22$ K. See text for details.

luminated state approaches that of a two-phonon Raman process characteristic of crystalline materials (dotted line in Fig. 1). A definitive decision between the two possible explanations mentioned, i.e., reversible changes of either the vibrational density of states or of the spin-lattice coupling strength, could be obtained by specific-heat measurements, which only probe the spectral density of vibrational states.

It is also interesting to note that a similar effect of illumination on the density of two-level systems has been observed by microwave echo experiments in a more typical glass-forming material As_2S_3,[22] which also shows the light-induced creation of gap states similar to the metastable dangling bonds in *a*-Si:H. It is, therefore, quite conceivable that the illumination process in *a*-Si:H leads to a reversible quenching of those disorder modes which determine the magnitude of the spin-lattice relaxation time in this material. However, this question cannot be answered by spin-resonance measurements alone.

Rather than speculating further on this point, I would like to report a different experimental result which concerns the dependence of the magnitude of the observed metastable T_1 changes on the sample temperature maintained during the illumination process. The experimental data are shown in Fig. 3(b), where the spin-lattice relaxation time at $T = 20$ K in both the annealed state and after prolonged illumination is plotted as a function of the illumination temperature. For all illumination temperatures, T_1 in the illuminated state is at least a factor of 2 longer than in the annealed state. A pronounced resonancelike behavior, however, is observed in a narrow region around the illumination temperature 90 °C. Very probably, the decrease in the magnitude of the metastable changes at illumination temperatures above 100 °C is caused by annealing, which will occur at these temperatures even during illumination. The increase of the effect with an illumination temperature up to 90 °C, on the other hand, could indicate that the transition into the metastable state is thermally assisted. Another interesting experimental result is that the metastable changes observed for the dangling-bond T_1 do not correlate with the metastable increase of the dangling-bond density. As shown in Fig. 3(a), the density of dangling bonds in the illuminated state has been kept approximately constant [$N(B) \approx 1.5 \times 10^{16}$ cm^{-3}, open triangles], by adjusting illumination time and intensity. Therefore, the concentration of metastable dangling bonds, $N(B) - N(A)$, is always similar to the density of stable dangling bonds observed in the annealed state [$N(A) \approx 1 \times 10^{16}$ cm^{-3}, filled triangles]. On the other hand, T_1 under these conditions shows the pronounced changes seen in Fig. 3(b). This again confirms the fact that the changes in the spin-lattice relaxation time are the same for all dangling bonds, independent of their stable or metastable character.

A last comment concerns possible microscopic explanations for the disorder modes in *a*-Si:H and the reversible changes in their density or coupling. Klinger has recently proposed a general model in which tunneling modes arise from anharmonicities of the interatomic potential.[23] In *a*-Si:H, these anharmonic potentials can, for example, occur at the sites of weak (or strained) bonds known to exist in this material with densities of about 10^{18}–10^{19} cm^{-3}. Furthermore, strained bonds or strain in general play an important role in the creation of metastable dangling bonds.[12,24] The obvious similarities between the creation of these metastable dangling bonds and the reversible changes of the disorder modes could then suggest that the latter are caused by light-induced local structural changes which are not as extreme as bond breaking, but large enough to produce changes in the anharmonicity of a weak bond. Note, however, that these structural changes are not a secondary effect of the dangling-bond formation (cf. Fig. 3). Finally, it has also been suggested that the disorder modes strongly interact with each other and with the phonons via static and dynamic strain.[25] This could provide the homogeneity in the relaxation mechanism necessary to explain the observation of the same well-defined T_1 for all dangling bonds.

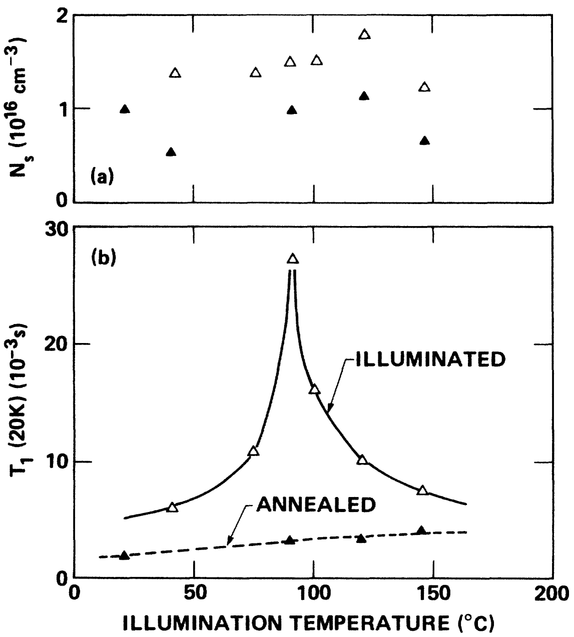

FIG. 3. (a) Dangling-bond spin density and (b) spin-lattice relaxation time at $T = 20$ K in the annealed (filled triangles) and illuminated state (open triangles) as a function of illumination temperature.

In conclusion, reversible changes of the spin-lattice relaxation time of the dangling-bond defect in *a*-Si:H are observed. These changes occur at temperatures $T < 100$ K and are linked to a corresponding metastable decrease of the density of or the coupling to vibrational modes responsible for the anomalous relaxation rate in this material. Extended illumination of *a*-Si:H with intense light results in a homogeneous increase of the relaxation time by an order of magnitude at 20 K. This increase can be reversed by an annealing of the sample in the dark.

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*Present address: Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany.

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