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Evidence for hydrogen motion in annealing of light-induced metastable defects in hydrogenated amorphous silicon

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The annealing of light-induced metastable defects, as measured by electron-spin resonance, exhibits a time dependence that is consistent with the kinetics of other metastable effects found in hydrogenated amorphous silicon (*a*-Si:H). The decay kinetics for these light-induced defects is related to the dispersive diffusion of hydrogen in *a*-Si:H providing strong support for the hypothesis that hydrogen motion is involved in the defect formation process. Mechanisms involving the motion of other defects motions, such as three- or fivefold coordinated silicon atoms, are found to be unlikely.

The microscopic origin of light-induced metastable defect creation is an important unsolved problem in the study of hydrogenated amorphous silicon (*a*-Si:H). Light-induced defects (LID's) are of great technological importance since the defect formation is one of the chief limitations for device performance. Despite intense activity over the past decade, the identity of the atoms involved and their rearrangements are the subject of much speculation. A major point of controversy is whether or not hydrogen motion is involved in the creation or annealing of light-induced defects. In this paper, time-dependent electron-spin-resonance (ESR) measurements are found to exhibit a characteristic decay with properties remarkably consistent with the hypothesis that hydrogen motion is involved in the annealing process.

Previous work has reported a number of important observations regarding the creation and annealing of LID's. Following the initial discovery of the phenomena,¹ it was found that the primary effect of illumination was to increase the electron-spin density of a defect associated with a *g* value of 2.0055.²⁻⁵ This *g* value is usually attributed to a trivalent dangling silicon bond defect;⁶ more recently, it has been suggested that the fivefold coordinated silicon atom is responsible for the *g*=2.0055 defect.⁷ Furthermore, ESR measurements as a function of temperature demonstrated that the annealing process is described by a distribution of annealing energies in a monomolecular process.⁸ Most of the other changes with illumination in other properties such as the decrease in photoluminescence intensity,⁹ photoconductivity,¹ and dark conductivity¹ can be attributed to this increase in dangling-bond density.¹⁰

The microscopic models developed to explain the metastable defect formation can be divided into two classes

—those which involve hydrogen motion and those which do not. The models without hydrogen motion postulate the breaking of weak silicon-silicon bonds,¹¹ the motion of characteristic defects such as the fivefold silicon defect,⁷ or defect conversion from one type to another.¹² The models involving hydrogen motion generally consider that a Si-H bond is either broken to form an interstitial hydrogen and a dangling bond or a Si-H bond is switched from one bonding configuration to another resulting in the formation of two dangling bonds.^{2,4} Subsequently, it has been proposed that other metastable changes in *a*-Si:H are caused by hydrogen diffusion¹³ which was studied in Refs. 14 and 15. Furthermore, there is evidence that the hydrogen exhibits "glasslike" behavior in that there is a characteristic temperature above which all memory of the sample's prior thermal history is lost.¹⁶

Recently, an important connection was made between the decay of thermally quenched band-tail carriers and hydrogen motion.¹⁷ The hydrogen diffusion was found to be dispersive exhibiting a time-dependent diffusion coefficient according to the relation $D(t) = D_0(\omega t)^{-\alpha}$ where D_0 is the diffusion coefficient at short times, ω is a phonon frequency, and α is the dispersion parameter. If the band-tail carriers are reduced from their quenched-in values by the change in the defect density due to hydrogen diffusion, then one would expect that for small changes in the band tail carrier density¹⁷

$$\frac{d\Delta n(t)}{dt} = -bD(t)\Delta n(t), \quad (1)$$

where *b* is a constant of proportionality. Substituting the observed time dependence $D(t)$ and integrating, yields the prediction that the excess band-tail carriers decay in time

according to the stretched exponential relation

$$\Delta n(t) = \Delta n_0 \exp[-(t/\tau)^\beta], \quad (2)$$

where the characteristic time, τ , exhibits an activated behavior, $\tau = \tau_0 \exp(E_a/kT)$, with $E_a \approx 0.9\text{--}1.0$ eV and $\tau_0 \propto (D_0)^{-(1/\beta)}$. The dispersion parameter $\beta = 1 - \alpha = T/T_0$, where T_0 is associated with the characteristic exponential width of the hydrogen hopping site energy distribution and T is the temperature. Thus, there is a simple relation between the power-law time decay of the hydrogen diffusion and the stretched exponential parameter β . If the LID's decay by hydrogen motion, then the defect decay kinetics should be consistent with other metastable phenomena and hydrogen diffusion—both of which have decays which may be fitted by a stretched exponential with consistent parameters. Consequently, in this paper we test whether hydrogen diffusion is involved in the annealing of dangling bonds by looking for the characteristic stretched exponential decay of the spin signal.

The LID's were generated by 16-h room-temperature illumination with white light of intensity 300 mW/cm^2 . The decay of the LID density at various temperatures was obtained using the double modulation method for ESR transient spectroscopy. The spin signal was measured in a Varian E201 spectrometer modulated at 100 kHz to yield the usual derivative spectra. A second coil is placed around the cavity and is modulated at 10 Hz. The 10 Hz modulation output of the 100-kHz detection is proportional to the spin density within the sample. The samples were placed in a nitrogen flow cryostat and the sample temperature was monitored with a thermocouple in contact with the sample (see Ref. 8 for further details). The samples consisted of plasma-deposited undoped α -Si:H and undoped deuterated amorphous-silicon films of thickness $3 \mu\text{m}$ deposited on 7059 glass substrates. Since no significant difference was found between deuterated and hydrogenated samples, the rest of the paper will discuss the hydrogenated samples. The substrate temperature during deposition was 230°C and low rf power was used to yield high-quality films.

The results for undoped α -Si:H are depicted in Fig. 1

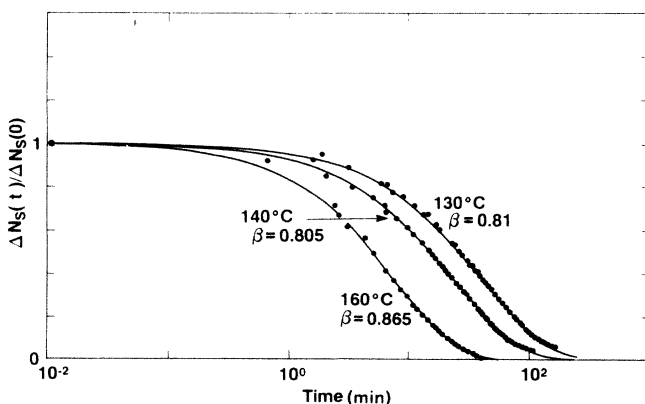


FIG. 1. Decay of the normalized light-induced dangling-bond density for various temperatures (points). A fit to Eq. (2) with the indicated values of β is given by the solid lines.

for three different temperatures. The background has been removed and the difference has been normalized by the initial spin density. The spin density decays much more rapidly for higher temperatures. Fits to the stretched exponential are superimposed on the data. We note that the stretched exponential yields a good fit over several orders of magnitude in time. Even more important is the agreement between the stretched exponential fitting parameters for these decays and those found for the decay of excess carriers in doped amorphous silicon induced by rapid thermal quenching.¹⁷ The values of τ obtained from these fits are plotted in Fig. 2 along with the values obtained for decays of excess carriers. The activation energy of τ is roughly 0.94 eV in good agreement with the activation energy of 0.95 eV found for the decay of excess carriers. The activation energy for the H diffusion is roughly 1.2–1.3 eV in rough agreement with the activation energy of τ . The value of τ is also significantly larger as expected from H diffusion. In Ref. 14, it was found that the H diffusion coefficient was roughly 25 times larger in 1 at.% P-doped films than in undoped films. Hence, since $\tau_0 \propto (D_0)^{-(1/\beta)}$, τ should be roughly a factor of 50 larger for the annealing of LID's in undoped amorphous silicon compared with the decay of excess carriers in 1 at.% P-doped material as is observed in Fig. 2. Since the H diffusion coefficient is even larger in heavily boron-doped material, we would expect that the annealing of LID's in boron-doped samples would be quite rapid. This result has also been observed in Refs. 18 and 19.

In Fig. 3, the values of β for the decays of LID's are plotted along with the values of β obtained from excess carrier relaxation. The value of T_0 is roughly 600 K for both the LID annealing and the decay of excess carriers indicating that the distribution of Si:H bonding energies is not strongly affected by doping. The values of β for LID annealing also agree with those values which can be obtained from H diffusion. Using the relation $\beta = 1 - \alpha$, the

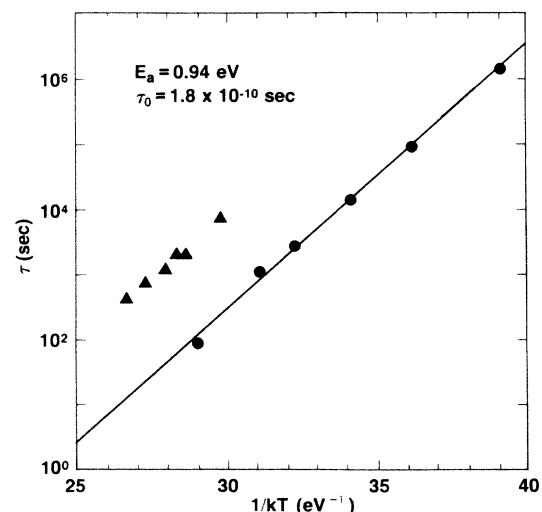


FIG. 2. The least-squares values of τ used to fit the time decay data to Eq. (2) vs $1/(kT)$ (triangles); the circles represent the corresponding values for decay of excess carriers in doped (1 at.% P) amorphous silicon due to rapid thermal quenching.

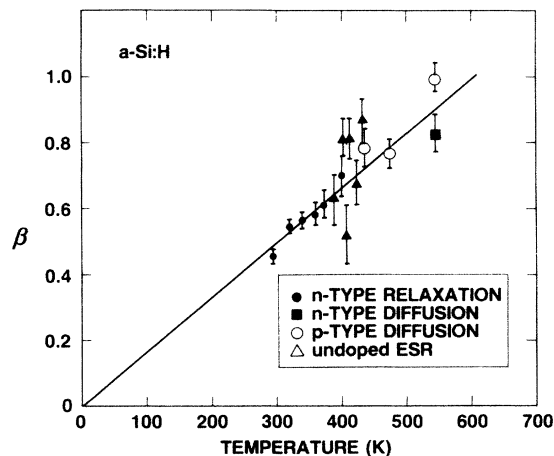


FIG. 3. The values of β used to fit the time data to Eq. (2) vs temperatures (triangles). The values of β for the decay of excess carriers are represented by the solid circles. The values obtained from dispersive hydrogen diffusion in *p*- and *n*-type *a*-Si:H are denoted with open circles and filled squares, respectively. The line represents $\beta = T/T_0$ with $T_0 = 600$ K.

H diffusion data of Ref. 14 can be used to estimate β (Fig. 3). The values of β obtained from H diffusion also are consistent with the annealing of LID's. We have obtained similar values of the stretched exponential parameters for other samples including deuterated amorphous silicon. In another publication,²⁰ we found that defect creation due to band-tail carriers in the accumulation region of *a*-Si:H field effect transistors also exhibit stretched exponential behavior with similar fitting parameters. In summary, the kinetics for at least three different metastable phenomena in *a*-Si:H is consistent with H motion.

The fact that the various metastable effects have such similar kinetics suggests that there is a single underlying mechanism, namely hydrogen motion. One may speculate that the motion of some other Si defect underlies both H motion and the annealing behavior of metastable defects. However, the spins in evaporated or sputtered amorphous-silicon films without hydrogen do not significantly anneal until 650°C (Ref. 21) while exposure of such films to atomic hydrogen greatly reduces the spin density throughout the entire film at much lower temperatures (400°C).²² This observation demonstrates that the low-temperature annealing of spins occurs only if hydrogen is present. Furthermore, it is unlikely that the kinetics are so similar to H motion in all the particular details for all of the different metastable effects. If another defect were responsible, one might expect that for some metastable effects, the defect creation kinetics would differ from that of H motion. Finally, since there is 10^6 more H than any other defect, then this Si defect would have to be 10^6 times more mobile than H, which is already highly mobile. Such a defect would rapidly move to internal voids or the surface of the film even at room temperature. This argues against the possibility that the common kinetics of the various phenomena and hydrogen motion is due to a distribution of local barriers to hydrogen and the

various metastable bonding rearrangements in the silicon lattice since this would occur in unhydrogenated silicon as well. Given the above arguments and the observation that the defect kinetics are consistent with hydrogen diffusion, the only reasonable possibility is that the kinetics of the various metastable phenomena are related to hydrogen motion¹³ and therefore the microscopic model for the metastable defect formation must involve hydrogen.

It should be pointed out that the conclusion that hydrogen is involved is independent of the stretched-exponential model. A more general approach which includes the stretched exponential as a special case is to explain the decays in terms of a distribution of annealing energies.⁸ The decays of the various metastable phenomena for different temperatures can be fitted by the same distribution of energies. The distribution of energies occurs as a result of a distribution of hopping energies for the hydrogen as it moves through the material. Because hydrogen motion underlies the various metastable phenomena, they have the same energy distribution. The stretched-exponential model has the conceptual advantage of fewer fitting parameters and provides a plausible connection between the decays and dispersive hydrogen diffusion.

Finally, we consider the implications of this agreement in the kinetics for the current picture of hydrogen motion through the material. Hydrogen can move through the material by either bond switching or via interstitial sites.^{13,14} In the course of its motion, the hydrogen can create new dangling bonds or cause existing dangling bonds to coalesce. The intrinsic disorder of the material will cause the sites that the hydrogen visits to be distributed in energy. If this energetic distribution of available sites is approximately exponential, then the hydrogen motion is dispersive (as is observed) and hydrogen atoms will slowly relax to lower-energy sites. Illumination causes some of the hydrogen atoms to become situated in higher-energy sites above their metastable equilibrium sites through the recombination of band-tail carriers, thereby creating new dangling bonds.⁸ These H atoms relax back towards equilibrium at elevated temperatures and remove excess dangling bonds. Since the light-induced creation process of recombination is a local one, we expect that the hydrogen does not move far upon creation of the defects. Consequently, the stretched exponential decay observed in this work is representative of one or at most a few hops and therefore may be quite close to the single hop distribution. The kinetics of H diffusion over longer distances would then be the cumulation of numerous hops, each of which has a distribution similar to the annealing of the light-induced defects. The slightly higher activation energy for H diffusion (1.2–1.5 eV) compared with 0.95 eV in Fig. 2 is therefore explained naturally as a consequence of the fact that H diffusion would be dominated by the higher-energy barriers during its motion. Much more work, both experimental and theoretical, is needed to fully investigate this picture.

In summary, we have found that the annealing of light-induced dangling bonds exhibits a time decay which can be characterized by a stretched exponential. This decay is very similar to decays of excess band-tail carriers in doped amorphous silicon and the creation of interface states due

to field-induced charge. This same decay behavior is quantitatively consistent with hydrogen diffusion data. These results provide strong support for the idea that hydrogen motion underlies the various metastable phenomena observed in hydrogenated amorphous silicon and tend to eliminate models suggesting that another defect is involved. Because of the local nature of the light-induced defect creation process, the decays of these defects

represent the characteristics of a few microscopic hops rather than the aggregate of many hops.

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