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Metastable paramagnetism in hydrogenated amorphous silicon: Evidence for a new class of defects in tetrahedrally bonded amorphous semiconductors

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After rapid cooling from 483 K, the characteristic electron-spin-resonance (ESR) signal in hydrogenated amorphous silicon (*a*-Si:H) has been observed to grow with time at room temperature. This increased ESR signal anneals at temperatures above ~370 K. These results have a significant effect on our understanding of the electronic states in *a*-Si:H.

Ever since the first successful doping experiments in hydrogenated amorphous silicon (*a*-Si:H) the nature of the electronic states in this prototype tetrahedrally bonded amorphous semiconductor has been a subject of much debate. Currently, the most commonly accepted models suggest that the only important electronic defect with a state deep in the gap is a silicon "dangling bond." This defect, denoted by D^0, is thought to lie about 1.0 ± 0.2 eV below the conduction-band edge and to have a negatively charged (doubly occupied) state (D^-) which lies ~0.2 to 0.4 eV higher in energy. The most direct evidence for this positive electron-electron correlation energy (positive U) is the existence of a dark electron-spin-resonance (ESR) signal that indicates a spin density n_s which is essentially independent of temperature and never less than about 10^{15} spins cm^{-3}.

This Rapid Communication describes ESR data which directly challenge the simple picture as just presented. We have observed around room temperature an ESR signal in undoped *a*-Si:H which, after relatively rapid cooling from 483 K (210 °C), grows with time. The growth rates for this ESR signal are not strongly dependent on the temperature for temperatures below about 343 K (70 °C). We will show that these observations and others suggest one of three possible scenarios.

In the first scenario, defects can be created or annihilated by some mechanism. The most likely possibility is that a subset of the hydrogen atoms in *a*-Si:H diffuses at room temperature and through some unspecified mechanism generates an increase in the dangling-bond density. The diffusion of hydrogen has been suggested as an explanation for time-dependent changes in the defect structure in doped[1] samples of *a*-Si:H. Because the temperature dependence which we observe for the increase in the ESR signal is weak ($\Delta E < 0.6$ eV if the process is thermally activated), this explanation is not without some problems since the activation energy for diffusion of hydrogen in undoped *a*-Si:H is greater than 1.4 eV.[1-3]

In the second scenario the Fermi level changes with time via the rearrangement of charge into D^0 states from paramagnetic states, which for some reason are not observed in ESR, but which are essentially isoenergetic with some of the D^0 states. In this scenario the present data would provide strong experimental evidence for at least a second important type of paramagnetic deep-gap state in *a*-Si:H in addition to the silicon dangling bond.

In the third scenario, only silicon dangling-bond states are important, but positive (D^+) and negative (D^-) configurations of the silicon dangling bond are converted in time into D^0 states. This explanation requires that the U for this subset of states be very small and positive. Because a broad distribution of U's is unlikely to end precisely at $U = 0$, the third scenario implies that a subset of the dangling bonds in *a*-Si:H exists with negative effective U's as has been suggested by some authors.[4]

Several recent experiments in *a*-Si:H have detected changes in the electronic density of states (or in the occupancy of localized electronic states) either as a function of quenching rate[5] or with time[1] for temperatures below some characteristic temperature, T_x. Above T_x thermal equilibrium occurs rapidly, but below T_x the thermodynamic equilibrium characteristic of this temperature is frozen into the amorphous solid. Below T_x, the approach to thermodynamic equilibrium occurs exponentially more and more slowly. In our case the approach to equilibrium depends very weakly on temperature below a characteristic temperature in the range of 375 K.

Figure 1 shows the growth of the ESR signal at 295 and 315 K in *a*-Si:H after cooling from 483 K. The open squares are simultaneous measurements of an *a*-Si:H/SiO$_2$ interface signal which is related to the classic E' defect in SiO$_2$ and has been described elsewhere.[6] This interface signal, which is in the same sample as the silicon dangling-bond signal and is constant in time, provides a fiducial mark to account for any long-term instabilities in the ESR spectrometer. The open circles and diamonds in Fig. 1 are plotted for the mean measurement time after cooling the samples from 483 K.

It is apparent from Fig. 1 that there is an increase in the ESR signal with time. This increase is further documented in Fig. 2, which presents histograms of the data taken immediately after cooling from 483 K and of the data taken after greater than 50 h in the dark at 295 or 315 K. (Figure 2 contains data not plotted in Fig. 1.) Immediately after cooling from 483 K the average ESR signal amplitude shown in Fig. 2 is 8.2 (in arbitrary units) with a standard deviation of 1.2. After storage at 295 or 315 K in the dark for greater than 50 h the average intensity is 11.6 with a standard deviation of 0.7. The intensities of the corresponding E'-type interface signals are 5.8 ± 0.7 and 6.2 ± 0.6, respectively. It is therefore quite certain that there exists an increase in the dark of the ESR signal at-

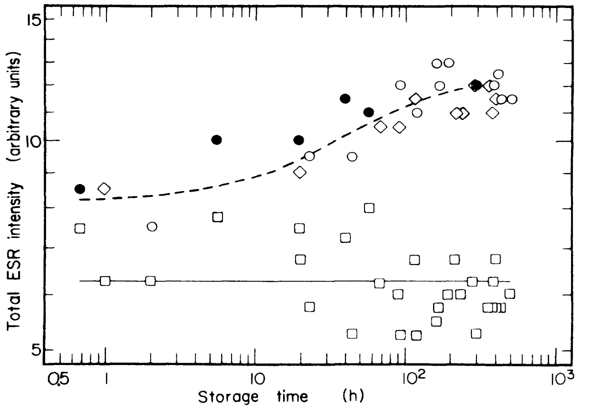

FIG. 1. Total ESR intensity as a function of time. Lines are guides to the eye. The open circles and diamonds and the solid circles are data for the Si dangling-bond line in 3-μm-thick films of undoped *a*-Si:H that have been kept in the dark after cooling from 483 K. The open and closed circles represent a cooling rate whose order of magnitude is 1000 K/s and the open diamonds a rate of approximately twice as fast. The open circles and diamonds are data for those stored at 295 K and the solid circles for those at 315 K. The squares are data for the E'-type center. All ESR spectra are measured at 295 K. The vertical scale is normalized so that 10 corresponds to $\sim 4\times10^{15}$ ESR centers/cm^3. The normalization applies only to the dangling-bond line because the E'-type center was over modulated during the measurement.

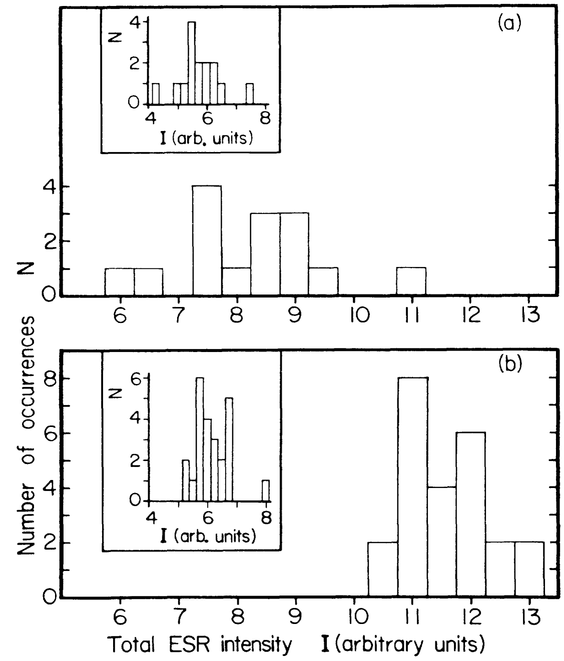

FIG. 2. Distribution of the total ESR intensity in *a*-Si:H as measured (a) immediately after quenching from 483 K and then (b) after at least 50 h of storage in the dark. The insets show the distributions of the corresponding E'-type center. The horizontal scale is normalized so that 10 corresponds to $\sim 4\times10^{15}$ ESR centers/cm^3. The normalization does not apply to the E'-type center.

tributed to a silicon dangling bond in *a*-Si:H after rapid cooling from elevated temperatures. This increase corresponds to $\sim 10^{15}$ spins/cm^3.

This increase in the ESR signal represents a real increase in the spin density and is not due to a change in the spin-lattice relaxation rates (change in the microwave saturation behavior) before and after storage in the dark. Stray light is also not responsible for this effect. Even deliberate exposure of the samples to doses of room light ($\sim$0.3 mW/cm^2) which were at least 1000 times greater than background irradiation doses over the course of the experiments did not produce an increase in the ESR signal as great as that shown in Figs. 1 and 2.

Although detailed experiments as a function of sample thickness are difficult because of the weak signals, the increase of the ESR signal in the dark in films of *a*-Si:H and in *p-i-n* structures based on *a*-Si:H appears to be at least partially a bulk effect. In a series of layers of *a*-Si:H the change in the ESR after storage in the dark at 295 K increased by a factor of $\sim$2 when the thickness varied from 3000 to 30000 Å. In a separate set of *p-i-n* structures where the *i*-layer thicknesses were varied, the change in dark ESR signal increased by a factor of $\sim$3 when the thickness varied from 2000 to 10700 Å.

There is evidence that the increase in the ESR signal after storage in the dark at 295 K does not scale with the initial quenched-in dark spin density. Experiments performed on samples of *a*-Si:H with an initial dark spin density of greater than 10^{16} spins/cm^3 did not show any increase with time at 295 K after quenching from 413 K. Although there could have been an increase on a scale of $\sim 10^{15}$ spins/cm^3 as was observed for the films in Figs. 1 and 2, there was no increase on a scale of $\sim 10^{16}$ spins/cm^3.

The ESR, which grows while the samples are stored in the dark at 295 K, can be annealed at temperatures above $\sim$370 K. In Fig. 3 the filled data points represent annealing of the increase in the ESR after storage at 295 K for about 500 h. The three annealing curves were run sequentially, and to the extent that there is no discernible decay of the ESR for annealing at 340 K, the data at 370 K represent the isothermal decay at 370 K. The data for 400 K were taken after the annealing at 370 K. For the data shown in Fig. 3 all the ESR spectra were taken at 300 K.

The open symbols in Fig. 3 represent data taken after optical excitation at $\sim$300 K with $\sim$1.3 W/cm^2 of white light from a tungsten source. Although the two kinds of annealing experiments as indicated by the open and solid data points in Fig. 3 are not identical, comparison of the solid triangles at 370 K and the open triangles at 390 K indicates that, at least qualitatively, the spins generated in the dark anneal faster at a given temperature than those which are optically induced.

The change with time in the ESR signal in *a*-Si:H at 295 K after rapid quenching from elevated temperatures can be explained by the creation of additional defects at elevated temperatures (first scenario). Recent investigations[1,5,7] have suggested that the defect structure in *a*-Si:H is in thermal equilibrium at elevated temperatures, but that departures from thermal equilibrium are frozen-

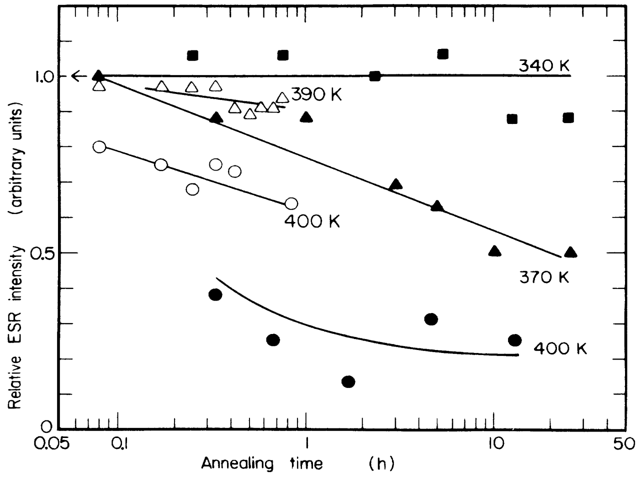

FIG. 3. Isothermal annealing of the increased ESR line in *a*-Si:H. The annealing temperatures are as shown. Lines are guides to the eye. The open symbols are data for the optically induced ESR with an initial net spin density Δn_s of $\sim 7\times 10^{15}$ cm^{-3}. The solid symbols are data for the ESR centers which have an an initial Δn_s of $\sim 2\times 10^{15}$ cm^{-3} after storage in the dark. The initial Δn_s in both cases is normalized to 1, as indicated by the arrow.

in during cooling below some characteristic temperature T_X. From sweep out and other experiments on doped samples of *a*-Si:H Street, Kakalios, and Hayes[1] have suggested that diffusion of bonded hydrogen may play an important role in the approach to equilibrium at temperatures below T_X. On the other hand, Smith and Wagner[5] have suggested that defect formation is induced by recombination of carriers (generated thermally in the dark) and that the annealing is governed by thermally activated reexcitation of electrons out of the (dangling-bond) defect states. Both of these interpretations suggest that the activation energy for the approach to thermal equilibrium is ~1.4 to 1.6 eV. However, the present results in Fig. 1 show that the approach, if activated, has an activation energy of no greater than about 0.6 eV. In fact, within experimental error the data of Fig. 1 are independent of temperature which would imply that a tunneling, rather than a diffusion, process may be responsible for the effect.

The growth of an ESR signal with time as shown in Fig. 1 is unexpected. Because the paramagnetic silicon dangling bond, or D^0 state, is commonly thought to be the only important defect deep in the gap, most model interpretations of metastabilities in *a*-Si:H suggest that during departures from equilibrium one should freeze-in paramagnetic dangling bonds which can subsequently be annealed. The optically induced increases seen in the ESR in *a*-Si:H (Staebler-Wronski effect) exhibit this behavior. There is also evidence from other experiments[5] that the room-temperature below-gap absorption is larger immediately after rapid quenching from elevated temperatures. This absorption is thought to scale with the ESR signal. Since the experimentally observed behavior of Fig. 1 is exactly the opposite, it may be difficult to formulate models which explain with the same mechanism both the optically induced increase in the ESR signal and the decrease in the dark ESR signal upon rapid quenching. If one assumes, for example, that hydrogen diffusion is responsible for the growth of the ESR signal in the dark, then one must account not only for the small upper bound on the activation energy but also for a hydrogen diffusion process which both creates dangling bonds (dark ESR of Fig. 1) and removes dangling bonds (light-induced ESR) when driven toward equilibrium. One can perhaps circumvent the first problem by assuming a distribution of activation energies for hydrogen diffusion in *a*-Si:H, but the second problem seems to be more formidable. One encounters the same difficulty in explaining consistently both the optically induced and thermally driven changes in the ESR by defects induced upon carrier recombination.

If one assumes that there exists a second kind of paramagnetic defect which is essentially isoenergetic with the D^0 states but whose ESR signature is not observed (second scenario), then the thermally driven changes in the ESR signal can also be explained. In this case no new defects are formed, but the quasi-Fermi level moves toward equilibrium with time. This explanation has the difficulty that there is little corroborative evidence for such defects, although there is some evidence for the involvement of a second state deep in the gap from transient capacitive measurements[8] and the involvement of a second state in the optically induced changes in the density of states from photoconductivity experiments.[9]

Finally, one could assume that the effective U for the dangling bond defects cover a wide range of values from $U=0.2-0.4$ eV down to zero, and presumably negative as well (third scenario). This explanation has the advantage that the optically induced measurements would be sensitive to large positive (or negative) values of U, while the thermal quenching experiments would not. The difficulty with this explanation is that small or negative values of U are not expected in a predominantly tetrahedrally coordinated solid such as *a*-Si:H. Also, this explanation may imply a temperature dependence to the dark ESR for which there is currently no convincing evidence.

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