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Kinetics of the metastable optically induced ESR in *a*-Si:H

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The kinetics of a metastable, optically induced increase in the ESR in *a*-Si:H have been examined between 77 and ~500 K. Isothermal annealing (decay) and inducing (growth) curves indicate that the decay is bimolecular and thermally activated with an activation energy of ~1 eV, and the growth is relatively temperature independent. These kinetics are more easily explained through the optical rearrangement of charge in existing dimagnetic (negative-*U*) defects and less easily in terms of the optical creation of additional, paramagnetic localized states in the gap.

I. INTRODUCTION

After prolonged exposure to band-gap light, metastable changes in both the transport and optical properties of hydrogenated amorphous silicon (*a*-Si:H) are well known. The first, and perhaps best known, metastable change in the transport properties is a decrease in the photoconductivity which was first observed by Staebler and Wronski.[1] Since this original experiment a myriad of metastable changes in various transport properties has been observed.[2] A metastable increase in absorption below the gap has also been measured.[3]

A metastable, optically induced increase in the electron-spin resonance (ESR) signal from *a*-Si:H was first observed at 300 K by Dersch *et al.*[4] These authors observed a doubling of the ESR response over that which existed before irradiation. Within experimental accuracy the metastable line shape was the same as that observed before irradiation and attributed to a "dangling bond" on a silicon atom.[5,6] Irradiation with x rays also produces an increase in the ESR line attributed to silicon dangling bonds.[7] In both the optically induced and x-ray irradiated samples, the increase in the ESR can be annealed by cycling to elevated temperatures.[8] This annealing parallels[8] that of an optically induced decrease, or fatigue, of the photoluminescence (PL) intensity at 1.2 eV.

There is an additional low-temperature component to the metastable optically induced ESR. This component, which decays thermally above approximately 80 K, was first observed by Street *et al.*[9] and later by other authors.[10,11] This ESR can be induced by low-level light intensities (~50 mW cm^{-2}). At higher light intensities, low-temperature metastable ESR centers can be generated which anneal only above about 300 K.[12,13] It is clear that, even as far as the ESR is concerned, there are several different metastable contributions depending on such parameters as the temperature and the power density of the inducing light.

In order to understand better the microscopic details of the traps or defects which cause these metastable increases in the ESR, we have examined the temperature dependence of the annealing and inducing processes in several samples of *a*-Si:H. Two types of experiments have been performed to determine the kinetics for formation and decay of the optically induced gap states. In the first experiment, the isothermal decay of the increase in the ESR is monitored at various temperatures between 300 and 500 K. In a complementary set of experiments the increase in the ESR response is monitored as a function of irradiation time over the same temperature range.

II. EXPERIMENTAL DETAILS

Films of *a*-Si:H between 1 and 3 μm thick were deposited on 250-°C (523-K) substrates using standard glow-discharge techniques. Most samples were deposited on aluminum foil, but in selected cases, samples were deposited on aluminum foil and quartz substrates in the same run. The samples on aluminum foil were removed from the substrates using dilute hydrochloric acid. The resulting "flakes" were washed in distilled water, thoroughly dried, and sealed in evacuated quartz tubes. The high-temperature experiments were performed mainly on the powdered samples, but selected experiments were also performed on samples on quartz substrates. The ESR spin densities n_s of both kinds of samples before irradiation were $\leq 5\times10^{15}$ spins/cm^3.

Irradiation was performed with a tungsten source at power densities over the approximate range from 0.3–3 W/cm^2. The incident power density on any flake of the sample, however, is less than that incident on the quartz tube due to scattering or absorption by other flakes and the quartz tube. The quartz tubes containing the powdered samples were rotated in a horizontal position during irradiation in order to illuminate all the flakes evenly. Elevated temperatures were obtained with a nitrogen-gas-flow system. Samples were annealed at 480 K for 20 min upon completion of each experiment.

The ESR experiments were performed using a Varian Associates model no. V4500 spectrometer with Varian Associates model no. V4012 12-in. electromagnet. When necessary, signal enhancement was accomplished with a Nicolet model no. 1070 signal averager.

III. RESULTS

The isothermal decays in time of the optically induced portions of the ESR intensities are shown in Fig. 1 for a sample of a-Si:H supplied by Brookhaven National Laboratory (BNL). These data were taken after irradiation with $\sim 1\ \mathrm{W\,cm^{-2}}$ at 300 K for 90 min. (During irradiation the temperature of the powdered sample is greater than 300 K because of poor thermal contact with the quartz tube.) The decay curves cannot be described by simple exponentials, but are in fact best fit by second-order kinetics (bimolecular decay). If these kinetics are appropriate, then a plot of the reciprocal of the ESR intensity increase should vary linearly with time as is seen for the various annealing temperatures in Fig. 1 for times longer than 5 min. The kinetics at short times cannot be determined accurately because of experimental limitations.

If the decay is governed by second-order kinetics, then the density of optically induced ESR spins n_s is given by

$$\frac{dn_s}{dt} = -\gamma n_s^2 \ . \tag{1}$$

The bimolecular decay rate γ depends on the temperature and is well fit by the thermally activated form

$$\gamma = \gamma_0 \exp(-E_a/kT) \tag{2}$$

where the prefactor γ_0 is the infinite-temperature intercept, E_a is the activation energy, k is Boltzmann's constant, and T is the temperature.

The solution to Eq. (1) is

$$(n_s/n_0)^{-1} = 1 + n_0\gamma t \ , \tag{3}$$

where n_0 is the saturated density of metastable ESR spins after long-time irradiation at low temperatures (≤ 300 K). Hence, the slopes of the decay curves of Fig. 1 yield values for the product $n_0\gamma$ where the temperature dependence is due to γ [Eq. (2)].

The temperature dependence of $n_0\gamma$ is shown in Fig. 2. The circles are data from the BNL sample and the diamonds data from a sample supplied by ARCO Solar, Inc. (ARCO). The solid line in Fig. 2 corresponds to $E_a = 1.1$ eV and $n_0\gamma_0 = 6.4\times 10^8\ \mathrm{sec^{-1}}$.

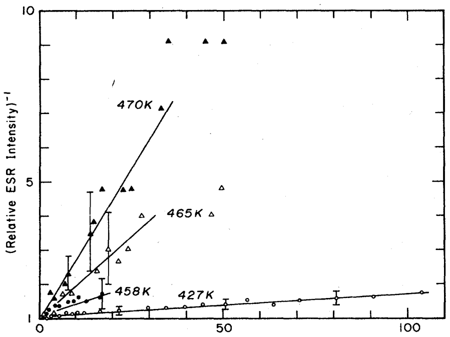

FIG. 1. Inverse of the optically induced ESR intensity in a-Si:H as a function of annealing time at various temperatures. Data at temperatures of 470, 465, 458, and 427 K are indicated by solid triangles, open triangles, solid circles, and open circles, respectively. Details of the optical excitation are described in the text.

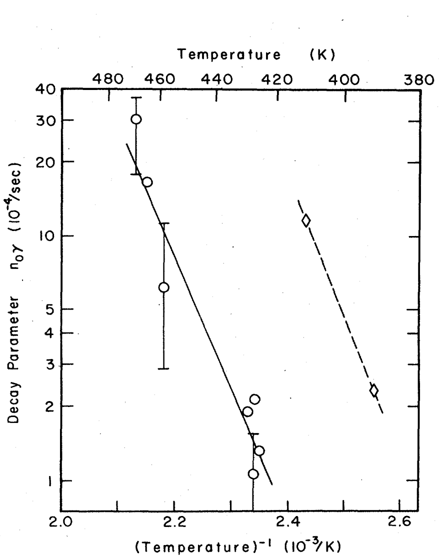

FIG. 2. Temperature dependence of the decay rate γ of the metastable optically induced ESR in a-Si:H. The parameter n_0 is the saturated density of metastable ESR spins after long-time irradiation at low temperatures ($T \leq 300$ K). Circles and diamonds are data for the BNL and ARCO samples, respectively. The solid line is a fit to the data with $E_a = 1.1$ eV. See text for details.

The kinetics of the optically induced effects are further tested by observing the growth in time of the optically induced portion of the ESR intensity at several selected temperatures. The ESR intensities measured at 77 K as functions of time after irradiation at 297 and 405 K are plotted in Fig. 3 for the same sample as indicated by the diamonds in Fig. 2. The trend which is the most apparent from these data is the existence of a long-time asymptote in the ESR intensity and the decrease of this asymptotic or saturated value with increasing irradiation temperature. Qualitatively, this trend is the result of a competition between the inducing rate and the decay rate at the elevated temperatures. In Fig. 4 are plotted the saturated ESR intensities at various irradiation temperatures. Although no

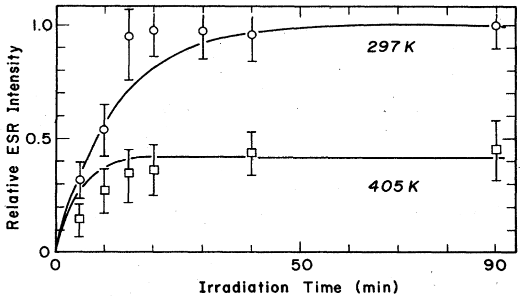

FIG. 3. Metastable, optically induced ESR intensity as a function of irradiation time at two representative temperatures. The irradiation was performed with a tungsten source with $\sim 3\ \mathrm{W\,cm^{-2}}$ incident on the quartz tube containing the sample. Circles and squares are data at 297 and 405 K, respectively. The solid lines are model fits to the data as described in the text.

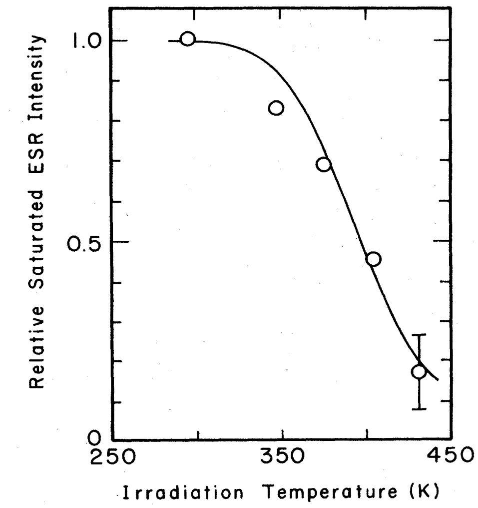

FIG. 4. Saturated (long-time) values of the metastable, optically induced ESR intensity as a function of irradiation temperature for the irradiation conditions of Fig. 2. The solid line is a model fit to the data as described in the text.

detailed measurements were performed, inducing experiments at 77 K on the powdered samples indicate that the inducing rates are similar to those at 300 K, and the saturated intensities are the same, within experimental error (±10%), as those observed at 300 K.

It is difficult to tell the difference between saturation and very slow growth at long times, but two tests were performed to check for saturation. First, the powdered samples were irradiated for 18 h and checked against the induced ESR responses after ~2 h. These two ESR intensities were found to be the same within experimental error (±10%). Second, the film sample on a quartz substrate was irradiated for 12 h and the ESR intensity compared to that measured after ~2 h. Again no detectable difference was observed within experimental error (±15%). These two experiments suggest that if there is a slow growth process, then at these light intensities (0.3—3 W/cm^2 incident on the quartz sample tube) the growth rate constant is less than 10^{-5} sec^{-1} as compared to $\sim 10^{-3}$ sec^{-1} for the rapid growth shown in Fig. 3.

IV. DISCUSSION

In analyzing the data of Figs. 3 and 4 we make several simplifying assumptions. First, we assume an exponential (monomolecular) generation rate which is sufficiently slowly varying with temperature in comparison with the thermally activated recombination (or decay) rate that it may be considered to be temperature independent. We do not address the question of the intensity dependence of either the generation rate or the saturated density of metastable ESR spins. Second, we assume that, at least at short times and high generation rates (high light intensities), the metastable ESR centers can decay by activated recombination with conduction-band (or band-tail) electrons or valence-band (or band-tail) holes. This second assumption is not necessary to determine the activation energy consistently between the annealing and inducing experiments, but it is required if one wishes to fit the absolute values of the growth and decay consistently at all temperatures. In other words, there is an additional contribution to the thermally activated decay of the induced spin density in the presence of large densities of optically excited electrons and holes.

With these two approximations the equation governing the time dependence of the spin density at a given light intensity becomes

$$\frac{dn_s}{dt} = (n_0 - n_s)\alpha - n_s^2\gamma - n'n_s\gamma \ . \tag{4}$$

In this equation n_0 is the low-temperature, saturated density of metastable ESR spins, α is the net (temperature-independent) growth rate constant, and n' is the density of optically generated electrons or holes which are effective in the recombination process ($n' \gg n_s$). Our philosophy in the development of Eq. (4) has been to consider the simplest and most general assumptions which are capable of explaining the bulk of the data. We note that Eq. (4) introduces a monomolecular term to the decay, but this term should rapidly become unimportant after the exciting light is removed (i.e., n' decays quickly at temperatures of 300 K and above). Hence, on the time scale of the present isothermal annealing experiments ($t \geq 2$—3 min) this term will be unobservable.

The solution of Eq. (4) yields the relative ESR intensity n_s/n_0 as a function of irradiation time t:

$$\frac{n_s}{n_0} = \{\beta + (x+\beta^2)^{1/2}\coth[(x+\beta^2)^{1/2}\alpha t]\}^{-1} \tag{5}$$

where

$$\beta = \tfrac{1}{2}(1+Kx) \ ,$$

$$x = n_0\gamma/\alpha \ ,$$

and

$$K = n'/n_0 \ .$$

At short times Eq. (5) is approximately $n_s/n_0 \simeq \alpha t$ so that α can be determined from the initial growth rate. In practice α is best determined at the lowest temperatures where the growth process dominates ($n_0\gamma \ll \alpha$). From the short-time behavior of the 297-K data of Fig. 3 we estimate that $\alpha \simeq 10^{-3}$ sec^{-1} for incident intensities of ~ 3 W cm^{-2}.

At long times the asymptotic value of Eq. (5) is given by

$$\left[\frac{n_s}{n_0}\right]_\infty = [(x+\beta^2)^{1/2} - \beta]/x \ . \tag{6}$$

With α determined by the short-time behavior of the isothermal inducing curves such as those in Fig. 3, the long-time asymptotes determine the temperature dependence of γ fairly accurately. For the ARCO sample on which both isothermal annealing and isothermal inducing measurements were taken, the activation energies obtained by the two experiments are consistent. The comparison between the two experiments is by no means precise, but the values of E_a are constrained to lie between 0.5 and 1.0 eV by this analysis.

The requirement that the inducing and annealing experiments yield the same values for γ at any given temperature fixes the remaining constant K. The agreement between the data extracted from the inducing and annealing curves is shown in Fig. 5 for $K=3$. These data were taken at an incident-light intensity of $\sim 3\ \mathrm{W\,cm^{-2}}$. Although as already mentioned, these data do not determine the three parameters (E_a,γ_0,K) with a high degree of accuracy, reasonable choices do provide consistent fits to the experimental curves. For example, the solid line in Fig. 5 is drawn for $E_a=0.63$ eV, $n_0\gamma_0=4.3\times10^4$ Hz, $K=3$, and $\alpha=1.4\times10^{-3}$ Hz. These parameters also yield the solid curves in Figs. 3 and 4, in good agreement with experiment.

The values of these parameters differ considerably from those quoted earlier for the isothermal decay of the BNL sample. Because of the accuracy of the data and the limited temperature range over which to determine an activation energy, the difference (0.6 vs 1.1 eV in E_a) may not be significant. Certainly the values of $n_0\gamma_0$ are very inaccurate because they involve considerable extrapolation of a line whose slope is inaccurately determined.

The important point concerning the present model is not the exact values of the parameters but rather the consistent framework within which to explain the most important aspects of the kinetics. These aspects are the bimolecular nature of the isothermal decay and the rapid (thermally activated) temperature dependence of the decay rate.

At least one experimental detail is not reproduced by the simple approximations discussed so far. This detail is the simplifying assumption in Eq. (4) that there is no intensity dependence to the saturated value $(n_s/n_0)_\infty$ (i.e., $n_0=\mathrm{const}$). Experimentally, the saturated ESR intensity is dependent on the incident-light intensity. Although no detailed experiments were performed, the amplitude of the long-time ESR ($\sim$18 h) depends only weakly on the incident-light intensity (sublinear). One would have to invoke a more complicated growth mechanism (n_0 dependent on intensity) in Eq. (4) to account for this fact. We emphasize that this complication does not alter the basic conclusions in any substantive way.

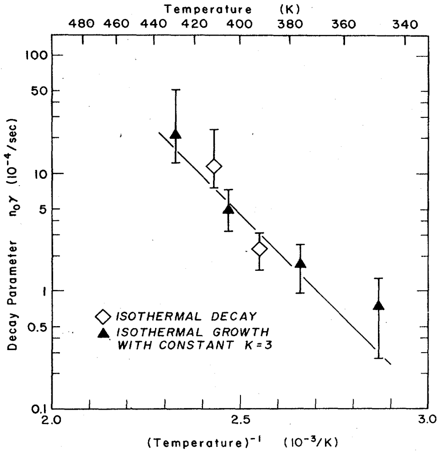

FIG. 5. Agreement between values of $n_0\gamma$ extracted from isothermal decay (diamonds) and growth (triangles) experiments using Eqs. (3) and (6), respectively, with $K=3$. The solid line is drawn with an activation energy E_a of $\sim$0.6 eV. See text for details.

The analysis embodied in Eq. (4) was motivated primarily by phenomonological considerations and was developed essentially without regard for the microscopic nature of the metastable centers. However, the conclusions resulting from the analysis have definite ramifications for any microscopic description. Currently there are two classes of models which have been invoked to explain metastable changes in the electronic and optical properties of a-Si:H. One type of model suggests that there is an increase in the density of silicon dangling bonds when "weak bonds" are broken optically.[4,14,15] A second class of model assumes that the metastable changes result from an optical rearrangement of electrons and holes in existing diamagnetic (negative-U) defects.[16–18]

The bimolecular nature of the isothermal decay of the optically induced ESR is easier to explain on the basis of the rearrangement of charge in existing, negative-U defects than it is on the basis of creating new defects. One would expect a change[4] in the ESR line shape if neither of the two electrons involved in the broken bond can diffuse, and we do not observe any difference in the ESR line shapes for irradiation at 77 K. This fact implies that the bond-breaking hypothesis requires the "diffusion" of one of the formerly bonded electrons to a distant trapping site. Diffusion is also required in order to obtain the second-order decay kinetics. Such a mechanism has in fact been proposed where the diffusion of bonded hydrogen atoms provides the intermediary.[4]

The major difficulty with the hydrogen-diffusion model is that we observe similar growth curves and saturated spin densities for irradiation at either 77 or 300 K, and it is difficult to imagine a diffusion process which is independent of temperature over this range. The hydrogen-diffusion model requires thermally activated generation and annealing processes, whereas the observed ESR results only exhibit significant thermal activation in the annealing process.

The data are more naturally explained if negative-U defects are postulated. In this case there should be little difference in the optically induced ESR at low temperatures since one is merely rearranging electrons in existing defects via optical excitation. (One must, however, invoke some interaction with the lattice to obtain the long decay times above 300 K.) Also, the bimolecular nature of the isothermal annealing arises naturally from the assumed random locations of the existing defects.

There is one piece of evidence which, on the face of it, favors the creation of additional defects on light soaking. We find that the optical creation and thermal annealing are not completely reversible processes. After many cycles ($\geq$30–50) the annealed value of the "dark" spin density increases and the magnitude of the saturated optically induced spin density decreases to the point where the optically induced effect is difficult to observe. A process involving hydrogen diffusion provides a natural explanation of this effect if there is a possibility that the hydrogen can form H_2 and diffuse out of the sample. On the other hand, there may be any number of other secondary effects which are not completely thermally reversible and can eventually degrade the material.

In addition to the ESR results of the present paper, there is other evidence for a bimolecular annealing process for metastabilities in the properties of localized electronic states in *a*-Si:H. Art and Brodsky[19] found an increase in the dark conductivity σ at 300 K in samples which were rapidly quenched from $T \geq 200\,^{\circ}\mathrm{C}$ (473 K). The annealing of this "excess" conductivity was found to be bimolecular with an activation energy of $E_n \simeq 0.9$ eV. This effect is not exactly the same phenomenon as that probed by the annealing of the light-induced increase in the ESR, but the parallels are striking.

From correlations between changes in σ and E_a, Ast and Brodsky[19] deduced that the quenching-induced effects could be explained entirely as a change in E_F of about 0.02 eV. There was no necessity to suppose an increase in the density of electronic states below the gap. Studies as a function of sample thickness demonstrated that the effect was indeed in the bulk. Since comparable metastable increases in σ could be induced by quenching slowly in the presence of an electric field, these authors suggested that the process does not involve the motion of hydrogen, which is presumably insensitive to the presence of the electric field.

Recently the results of some additional transport experiments, such as deep-level transient spectroscopy, have been explained in terms of optically induced shifts of the Fermi level without recourse to the creation of new defects.[20,21] Other transport experiments, such as time-resolved photoconductivity and spin-dependent photoconductivity, have been interpreted in terms of the creation of additional states in the gap.[14,22] There is currently no single defect which describes all the metastabilities observed in transport experiments in *a*-Si:H.

As the transport results indicate, the general situation with regard to metastable electronic effects in *a*-Si:H is more complicated than the present ESR results would suggest. Evidence has been mounting for some time that the light-induced metastable effects in *a*-Si:H involve a broad range of states in the gap and not just a single state.[23–25] In particular, Han and Fritzsche[24] have found that at least two states are necessary to explain the generation and annealing behavior of optically induced changes in the photoconductivity of *a*-Si:H. One type of state affects carrier lifetime and the other produces an increase in the below-gap absorption.

By irradiating samples at different temperatures, Guba *et al.*[25] have found that the annealing behavior of photoconductivity in *a*-Si:H depends on the temperature at which the samples were initially exposed to light. These authors have found that the room-temperature photoconductivity decreases much less after irradiation at 160 K than it does after irradiation at 300 K. In addition, the changes produced at 300 K are much more stable than those produced at 160 K. This behavior has a parallel with the fatigue of the 1.2-eV PL peak and the growth of the 0.9-eV peak.[15,26,27] The magnitudes of the photoconductivity and PL effects appear to peak for irradiation at about 300 K and decrease at higher and lower temperatures. In this sense these particular effects may well be better understood in terms of a model which invokes the hydrogen-assisted diffusion of a broken bond. At temperatures below 300 K the hydrogen diffusion is inhibited and at temperatures about 300 K the defects anneal. At the very least one can say that the correlation which exists between the isothermal annealing of the optically induced 0.9-eV PL (or fatigue of the 1.2-eV PL) and the ESR (Ref. 8) does not imply that these two effects are directly related. Because the low-temperature behavior of these two effects is very different, more than one localized electronic state must be invoked in any complete explanation of both the PL and ESR results.

Similar conclusions can be drawn from comparisons with other experiments, such as below-gap optical absorption,[3,28] optically detected magnetic resonance,[10] and time-resolved photoconductivity.[14] Consistent explanations for these experiments and the PL and ESR results appear to require optically induced changes in more than one type of below-gap electronic state in *a*-Si:H. Future experiments must tackle the task of better characterizing these states and their inter-relationships.

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