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Intrinsic dangling-bond density in hydrogenated amorphous silicon

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Recently proposed models for the recombination-induced creation and thermally activated annealing of dangling bonds in hydrogenated amorphous silicon are discussed. While these models were proposed to explain dangling bonds produced by the recombination of electron-hole pairs created by optical generation or electrical injection, we propose that intrinsic-carrier recombination processes can produce the same effect. The dynamic equilibrium between this generation process and thermal annealing determines an intrinsic dangling-bond density. This intrinsic dangling-bond density is shown to be negligible at room temperature but may be sizable at growth temperatures commonly employed. We show that typical cooling rates after film growth could lead to a "freeze-in" of dangling-bond densities in the range 10^{15}–10^{16} cm^{-3}. Furthermore, we show that this process can be used to explain the enhancement in performance observed when solar cells are annealed under reverse bias.

I. INTRODUCTION

As the materials technologies involved in the growth and characterization of hydrogenated amorphous silicon (a-Si:H) mature, the central importance of the density of dangling silicon bonds becomes increasingly clear. Carrier-recombination centers associated with the neutral dangling bond have been shown to determine carrier lifetime in undoped a-Si:H.[1] In devices using undoped a-Si:H, such as p-i-n solar cells, the density of dangling bonds N_s controls device performance.[2] The degradation of a-Si:H solar-cell performance by exposure to light or forward bias current,[3] and the light-induced[4] or electron-irradiation-induced[5] changes in photoconductivity (the Staebler-Wronski effect[6]) have been identified with the increase of N_s as determined by electron-spin-resonance (ESR) measurements.[7] Recently, the kinetics of the growth of N_s with light exposure and its reduction with thermal annealing has been studied and several models have been proposed.[8,9]

Yet nagging questions remain. It is widely accepted that the role of hydrogen in a-Si:H is to saturate dangling silicon bonds otherwise present in a-Si; experiments involving dehydrogenation and then rehydrogenation[10] have shown that hydrogen can diffuse freely in and out of the a-Si "matrix" at elevated temperatures, lowering the ESR signal from 10^{19} cm^{-3} to the range 10^{15}–10^{16} cm^{-3}.[11] The spin density of the best-quality a-Si:H films produced by all groups falls in this range as well. In experiments involving the Staebler-Wronski effect, most workers have chosen to subtract this "baseline" spin density in order to model the light-induced component, as annealing does not remove it. What is the origin of this baseline? Why is it not lower? If hydrogen moves so freely through the material, why can it not saturate these 10^{15} spins?

Until recently, it has been common to ascribe this baseline to impurities; however, current research indicates little correlation between impurity concentration and either material stability or initial defect density, as long as concentrations are kept below alloy levels ($<1\%$).[12] Admittedly, questions remain as to the importance of the local environment of incorporated impurities, rather than their bulk concentration. Instead, we consider the possibility that recombinations of thermally generated carriers create defects at high temperatures which are frozen in by normal cooling rates. The magnitude of this effect will depend on the models chosen for creation and annealing of dangling bonds.

II. KINETICS OF GROWTH IN SPIN DENSITY

Since the observation that passing a forward-bias current through a-Si:H solar cells produces the same degradation as light exposure,[13,14] it has been widely understood that the Staebler-Wronski effect is a recombination-induced process, i.e., the light exposure used in early experiments simply served to generate electron-hole pairs which recombine and produce the defect. Several models have been proposed to explain the effect in a-Si:H, as reviewed by Fritzsche;[15] we follow the approach of Stutzmann, Jackson, and Tsai.[16]

In the Stutzmann model, dangling bonds are produced by some small fraction c_{SW} of band-to-band (or band-tail-to-band-tail) recombinations. Thus, the rate of increase in dangling-bond density is

$$\frac{dN_s}{dt} = c_{\mathrm{SW}} r_t np \ , \tag{1}$$

where n and p are the free-electron and -hole concentrations and r_t is the rate constant for nonradiative band-to-band transitions. Using the observation that associated with dangling bonds are the recombination centers which determine carrier lifetime,[1] such that $\tau_n = 1/r_n N_s$ and $\tau_p = 1/r_n N_s$ (with $r_{n,p}$ the appropriate rate constants), an expression is derived for the growth of dangling-bond density under light exposure:

$$N_s^3(t) - N_s^3(0) = \alpha G^2 t \ , \tag{2}$$

where G is the carrier generation rate and $\alpha = 3c_{\mathrm{SW}} r_t / r_n r_p$. After long times,

$$N_s(t) \cong \alpha^{1/3} G^{2/3} t^{1/3} \ . \tag{3}$$

III. ANNEALING KINETICS

Once the spin density has been increased by an amount N_{ind} by light exposure, the kinetics of the annealing process can be explored. The simplest model for annealing would

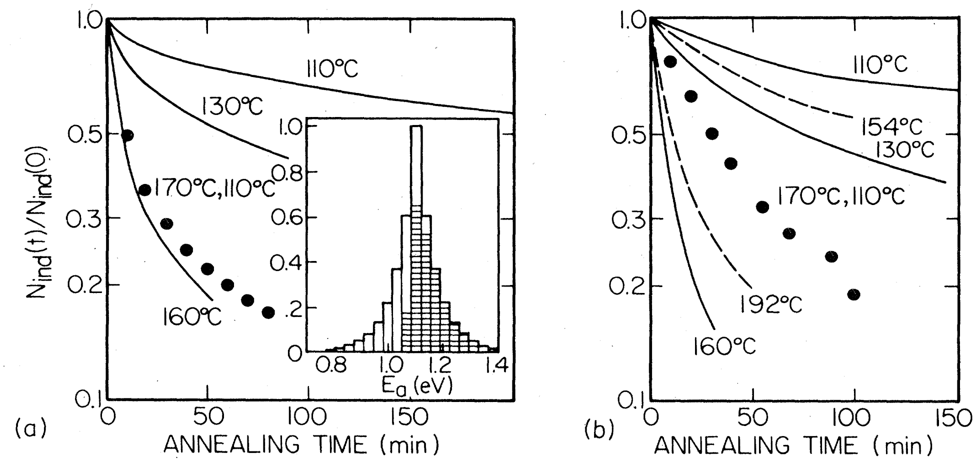

FIG. 1. Density of light-induced neutral dangling bonds as a function of annealing time $N_{\rm ind}(t)$ for various annealing temperatures. (a) shows the values predicted assuming a distribution of annealing activation energies centered on 1.1 eV (see inset) and monomolecular annealing kinetics. Closed circles represent points for a sample annealed for 200 min at 110 °C, annealing out the shallow end of the distribution (resulting in the shaded distribution), and then subsequently annealed at 170 °C. Parameters for (a) chosen for best fit of the data of Stutzman *et al.* (Ref. 9), displayed in (b) using solid lines. Data of Lee *et al.* (Ref. 8) are displayed for comparison using dashed lines.

assume a temperature-activated process with

$$\frac{dN_{\rm ind}}{dt} = -\nu e^{-E_A/kT} N_{\rm ind} , \qquad (4)$$

where ν is an anneal-attempt frequency (expected to be on the order of the phonon frequency, 10^{12} s^{-1}) and E_A is the activation energy for annealing. Thus, plots of $\log[N_{\rm ind}(t)/N_{\rm ind}(0)]$ vs t should yield straight lines; as the experimental data[8,9] yield lines with some curvature, two modifications to this model have been offered. Lee *et al.*[8,17] propose a bimolecular annealing process:

$$\frac{dN_{\rm ind}}{dt} = -\gamma N_{\rm ind}^2 , \qquad (5)$$

where $\gamma = \gamma_0 \exp(-E_A/kT)$ and $N_{\rm ind}(0)$ is the spin density after light soaking, but before annealing. The integral of this equation implies that

$$\left[\frac{N_{\rm ind}(t)}{N_{\rm ind}(0)}\right]^{-1} = 1 + \gamma N_{\rm ind}(0) t . \qquad (6)$$

They show that their data produce the straight lines predicted by Eq. (6), and their plot of the slopes of these lines versus $1/T$ yields $E_A = 1.04$ eV, $\gamma_0 = 3.2\times 10^{-8}$ $cm^3 s^{-1}$. Alternately, Stutzmann, Jackson, and Tsai[9] propose a distribution of activation energies with monomolecular kinetics:

$$\frac{dN_{\rm ind}}{dt} = -\nu \int N_{\rm ind} f(E) e^{-E/kT} dE , \qquad (7)$$

where $f(E)$ is a distribution function, as yet undetermined. We have fitted the data in Ref. 9 with either a Gaussian distribution or with exponential tails centered on a given activation energy E_{A0}, finding relatively little difference in the quality of the fit. The best fit yields $E_{A0} = 1.1$ eV, a characteristic energy width of $\sigma_E = 0.07$ eV, and $\nu = 1\times 10^{10}$ s^{-1} (see Fig. 1); reasonable fits are possible over the range 0.95 eV $< E_{A0} < 1.2$ eV, 0.05 eV $< \sigma_E < 0.13$ eV, and 10^8 s^{-1} $< \nu < 5\times 10^{11}$ s^{-1}.

One test of these models is to plot the data of the first group with the model of the second, and vice versa. We do this in Figs. 1(b) and 2. Within the published error limits, the Stutzmann data fit the Lee model with approximately

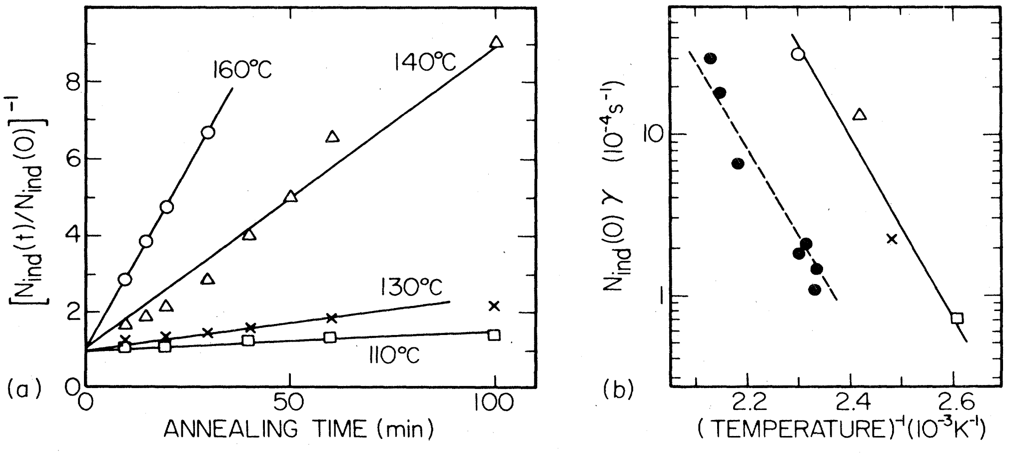

FIG. 2. Annealing behavior of light-induced neutral dangling bonds plotted assuming bimolecular kinetics. (a) Data of Stutzmann *et al.* (Ref. 9). (b) Slopes of lines in (a) plotted vs inverse of annealing temperature; slope data of Lee *et al.* (Ref. 8) are plotted using closed circles in (b) for comparison.

the same E_A, but with a different $\gamma_0 N_{\text{ind}}(0)$; given the light-soaking conditions specified, our analysis indicates that the difference cannot be attributed entirely to different $N_s(0)$. Likewise, the Lee data fit the Stutzmann model with a different ν. At this stage, we can make no conclusive choice between these models.

IV. INTRINSIC SPIN DENSITY

In the model for dangling-bond generation developed above, there is nothing which requires the carrier concentrations to be *excess* concentrations. We propose that the thermal-equilibrium intrinsic-carrier concentrations could produce dangling bonds as well:

$$\frac{dN_s}{dt} = c_{\text{SW}} r_t n_0 p_0 = c_{\text{SW}} r_t n_i^2(T) \ . \tag{8}$$

The value of $c_{\text{SW}} r_t$ reported in Ref. 9 is 1.5×10^{-15} cm^{3}s^{-1}; its dependence on temperature is sufficiently weak[18] that we assume it to be constant for this discussion. A value for $n_i(T)$ is, unfortunately, less well established. In computer modeling of p-i-n a-Si:H solar cells, Swartz[19] found empirically that the value $n_i(300\text{ K}) = 5\times10^7$ cm^{-3} produced the best agreement between the model and the observed cell characteristics. Another, admittedly crude, estimate can be made from the observed dark conductivity of undoped a-Si:H films as a function of temperature $\sigma_d(T)$. If the conduction in these films is truly intrinsic (i.e., without substantial impurity contributions), then $\sigma_d(T) = e(\mu_n + \mu_p) n_i(T)$, where the relevant mobilities μ are the conductivity mobilities, commonly assumed to be approximately an order of magnitude larger than the more easily measured drift mobilities,[20] and so $\mu_n + \mu_p \cong 10$ cm^{2}V^{-1}s^{-1}. This value is consistent with that predicted by the minimum metallic conductivity theory postulated by Mott.[21] Our analysis of the $\sigma_d(T)$ data of Dersch, Schweitzer, and Stuke[5] yields $n_i(300\text{ K}) = 2\times10^7$ cm^{-3}, while a similar analysis of the data of Staebler and Wronski[22] yields $n_i(300\text{ K}) = 1\times10^{10}$ cm^{-3}. Taken together, these various estimates establish a range of values on $n_i(300\text{ K})$ of 10^7–10^{10} cm^{-3}.

Using this range of values, an upper bound of the room-temperature growth rate in spin density due to intrinsic-carrier recombination of 10^5 cm^{-3}s^{-1} is established; this would not be observable against the commonly found $N_s \geq 10^{15}$ cm^{-3}. However, at higher temperatures the growth rate given by Eq. (8) would become sizeable due to $n_i(T)$; at these temperatures thermally activated annealing also becomes significant, and the net growth or reduction in N_s is determined by the competition between these processes. When these processes balance, a dynamic equilibrium value N_s^{eq} is established. For an unilluminated sample,

$$\frac{dN_s}{dt} = c_{\text{SW}} r_t n_i^2(T) - c_A(m,T) N_s^m \ , \tag{9}$$

$$N_s^{\text{eq}} = [c_{\text{SW}} r_t n_i^2(T)/c_A(m,T)]^{1/m} \ , \tag{10}$$

where $m=1$ for monomolecular and $m=2$ for bimolecular annealing kinetics, with the appropriate form of $c_A(m,T)$ as implied by Eqs. (5) and (7). As long as n_i^2 rises more quickly with T than c_A, this equilibrium spin density will rise with T.

Consider the situation at some elevated temperature where equilibrium has been established. If the temperature is abruptly lowered by some small amount, the annealing term in Eq. (9) overpowers the generation term and drives the system towards the new equilibrium. But the magnitude of the annealing term drops with temperature; thus if the sample is cooled faster than equilibrium can be reestablished, a higher-than-equilibrium spin density is frozen in. This is illustrated in Fig. 3. In Fig. 3(a), we have assumed bimolecular annealing kinetics with the rate constants from Ref. 17, and $n_i(300\text{ K})$ from the low end of the possible range; in 3(b) we assume monomolecular kinetics with constants as shown in Fig. 1(a), and $n_i(300\text{ K})$ closer to the upper end of the range. Both show freeze-in of spin densities above 10^{15} cm^{-3} when samples are cooled from 240 °C at commonly used cooling rates. Therefore, we propose that, at this stage of research, the densities of dangling

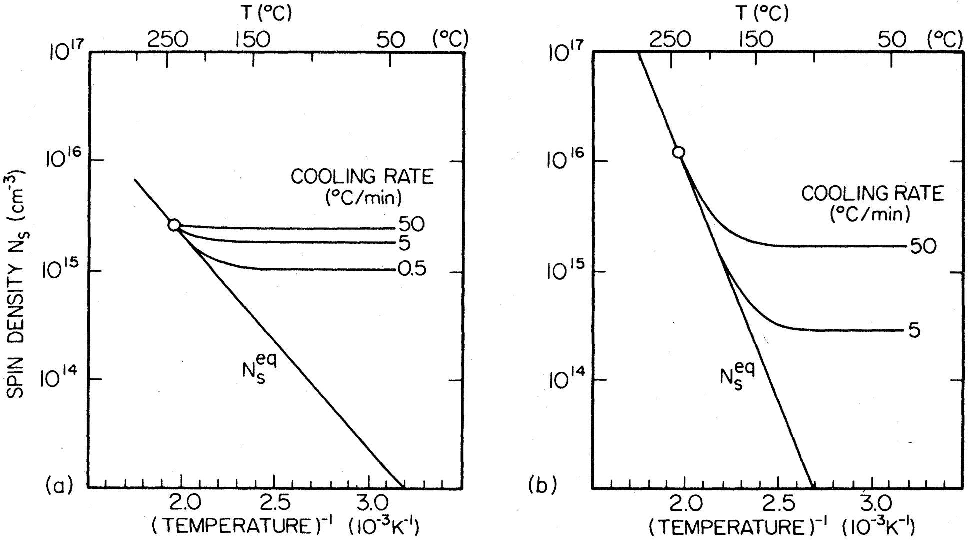

FIG. 3. Density of neutral dangling bonds N_s as a function of temperature resulting from the competition between generations by intrinsic carrier recombination and thermal annealing. (a) Assumes bimolecular annealing kinetics, $n_i(300\text{ K}) = 5\times10^7$ cm^{-3}; (b) assumes monomolecular annealing kinetics with a distribution of activation energies, as in Fig. 1(a), and $n_i(300\text{ K}) = 1\times10^9$ cm^{-3}.

bonds commonly observed in the best a-Si:H may be attributable to the freeze-in of dangling bonds generated by intrinsic carrier recombination.

Since most a-Si:H films are grown by the glow-discharge method, it is appropriate to ask whether the optical emission of the discharge is light-soaking the film during growth. Indeed, it has been reported that films grown with the homogeneous chemical-vapor-deposition technique (for which there would be much less optical emission) exhibit slightly lower spin density than their glow discharge counterparts.[23] From measurements of the optical power output of a silane discharge over the visible wavelengths (400–700 nm) and comparison with optical emission spectra[24] over the full wavelength range (200–700 nm), we can set an upper limit on the discharge illumination of approximately 1 mW/cm^2, or a maximum photon flux of 10^{15} cm^{-2}s^{-1}. (The fact that much of this irradiation is in the ultraviolet is not important, because the efficiency of defect generation does not depend on photon energy[15]). Following the light-soaking kinetics of Eqs. (2) and (3), this illumination appears to be far too weak to be responsible for a significant fraction of the observed spin density.

It might appear that the only way to produce a-Si:H with lower dangling-bond densities would be to use extremely slow cooldown rates after growth, leading to impractically long cooldown times. This is not necessary. In fact, we would argue that a more efficient procedure has already been unwittingly developed. Over the past few years, several groups[25,26] have reported enhancement of p-i-n a-Si:H solar-cell performance by the so-called reverse-bias anneal technique. In this process, cells are heated to 200 °C and then cooled down under a reverse bias of, typically, 5 V. The original intent of this process was to apply the field-induced conductivity enhancement reported by Lang, Cohen, and Harbison[27] to improve the open circuit voltage (V_{OC}) of solar cells. In fact, some small ($\cong 3\%$) improvement in V_{OC} was observed, but even more significant (4–13%) improvements in fill factor (FF) and modest gains in short-circuit current density (J_{SC}) were observed as well. Enhancement of the doping efficiency in the p and n layers yielding such small gains in V_{OC} would not be expected to improve the FF and J_{SC} so significantly. Swartz[25] reported that measurements of the current-voltage characteristics of the cells treated with the reverse-bias anneal process indicated an improvement in the i-layer mobility-carrier lifetime product ($\mu\tau$) of as much as 50%. As Street[1] has established that τ is inversely proportional to N_s, it would appear that the reverse-bias anneal technique reduces the density of dangling bonds in the i layer. It is interesting to note that Swartz repeatedly stresses the importance of *maintaining the reverse bias during cooldown.* In light of the present model, the explanation is that the np product in a reverse-biased p-i-n diode is, of course, less than n_i^2; this lowers the value of N_s^{eq} at the anneal temperature, and by maintaining the reverse bias during cooldown, this lowered value is frozen in. Using a model for FF and J_{SC} in which N_s enters explicitly,[3] we would predict that a 10% improvement in FF due to a reduction in N_s should result in a 3.8% improvement in J_{SC}, in excellent agreement with the values listed in Ref. 25.

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