

Dependence of the saturated light-induced defect density on macroscopic properties of hydrogenated amorphous silicon

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We report a study of the saturated light-induced defect density $N_{s,sat}$ in 37 hydrogenated (and in part fluorinated) amorphous silicon [a -Si:H(F)] films grown in six different reactors under widely different conditions. $N_{s,sat}$ was attained by exposing the films to light from a krypton ion laser ($\lambda = 647.1$ nm). $N_{s,sat}$ is determined by the constant photocurrent method and lies between 5×10^{16} and 2×10^{17} cm⁻³. $N_{s,sat}$ drops with decreasing optical gap E_{opt} and hydrogen content c_H , but is not correlated with the initial defect density $N_{s,ann}$ or with the Urbach tail energy E_u . We discuss our results within the framework of existing models for light-induced defects.

The light-induced defect generation in hydrogenated amorphous silicon (a -Si:H) is a drawback for the application of this material to solar cells. Although the effect has been studied extensively, very little is known about the saturated light-induced defect density $N_{s,sat}$, mainly because of the difficulty of reaching saturation experimentally. Aside from its possible theoretical significance, saturation has two important practical aspects: one, it can be used as a descriptor of stability, and two, the knowledge of $N_{s,sat}$ may help predict the long-term cell performance. We recently introduced a method for reaching saturation of the light-induced defect density within a few hours by light soaking with light from a krypton ion laser ($\lambda = 647.1$ nm). We found that $N_{s,sat}$ near room temperature is independent of light intensity.¹ This finding provides a more reliable means for the evaluation of the stability of various a -Si:H materials than the rate of defect production. The rate of defect production depends on the product of a rate constant and the square of the volume carrier generation rate G , which is proportional to the light intensity. Extraction of the rate constant requires knowledge of the precise value of G which is difficult to obtain. Because saturation is independent of G , $N_{s,sat}$ can be used as a universal criterion for the stability against light soaking and as a vehicle in the search for stable material. We used this feature to study 37 a -Si:H (or a -Si:H,F) samples from five different laboratories. The purpose of this study is to find universal correlations between $N_{s,sat}$ and four macroscopic material parameters: the Tauc optical band gap E_{opt} , the hydrogen concentration c_H , the characteristic energy E_u of the Ur-

bach tail, and the annealed-state defect density $N_{s,ann}$. Such correlations on samples from many different sources will help identify the mechanism of the light-induced metastability and provide approaches to improving the stability of the material.

Deposition technique, key deposition conditions, and some properties for each group of samples are listed in Table I. The samples were deposited from a dc excited glow discharge (GD), from rf (13.6 or 70 MHz) excited glow discharges, or by dc magnetron sputtering. Special features of some samples include the use of fluorine, of a hot-wall reactor, or of an ultrahigh vacuum system. All samples were annealed at 170 °C for 90 min in N₂ gas before the experiment. E_{opt} values were determined from Tauc plots measured with the optical transmission method. The subgap absorption spectra were measured using the constant photocurrent method (CPM) in a coplanar electrode configuration. Photothermal deflection spectra and photoconductivities were also determined. We converted the integrated excess (above the extrapolated Urbach tail) subgap absorption to the defect density N_f using the empirical formula N_f (cm⁻³) = $1.9 \times 10^{16} \int \Delta\alpha_{CPM}$ (cm⁻¹) $\times dE$ (eV).² The Urbach tail energy E_u was taken from the CPM spectrum. The ranges of E_{opt} , $N_{s,ann}$, and E_u in our 37 samples were 1.61–1.83 eV, 1.1×10^{15} – 1.6×10^{16} cm⁻³, and 42–62 meV, respectively.

The Kr⁺ laser beam was broadened with a lens to produce an average carrier generation rate of $G = (5.0 \pm 0.5) \times 10^{22}$ cm⁻³ s⁻¹. During light soaking, the samples were cooled with liquid-nitrogen-cooled nitrogen gas. The sample temperature during light soaking, measured with an optical transmission method,¹ was 20–30 °C. The defect density N_f rises proportionally to $t^{-1/3}$ for 2–3 h, and then saturates at $\sim 10^{17}$ cm⁻³. Each sample was light soaked for at least 5 h. In a long-time test on one

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TABLE I. Deposition conditions and properties of the samples used in this study.

Deposition technique	Key features	Source	T_{sub}^a (°C)	c_{H}^b (at. %)	d^c (μm)	No. of samples
dc triode GD	Fluorinated $0.1 < c_{\text{F}}^d < 8$	$\text{SiF}_4 + \text{H}_2$	200,225,250 275,300	8–18	0.96–1.98	8
dc triode GD	Optimized deposition	SiH_4	300	< 10	1.20–1.97	4
rf GD (13.6 MHz)	Deposited under 0 V to –100 V substrate bias	SiH_4	200	n.a.	1.86–3.10	5
rf GD (13.6 MHz)	High T_{sub}	SiH_4	300,325 350	< 10	1.90–2.30	3
Hot wall rf GD (13.6 MHz)	Substrate temperature dependence	SiH_4	100,150 200,250 300	7.1–15.6	3.00–4.50	5
Ultrahigh vacuum rf GD (13.6 MHz)	Low impurity	SiH_4	180,350	12.6–21.7	0.70–1.52	3
rf GD (70 MHz)	High-freq. deposition	SiH_4	100,150 200,250	9.5–18.2	1.65–2.86	4
dc magnetron reactive sputtering	Sputtered	x-Si Ar, H ₂	200,230 300	11.3–28.0	0.80–2.0	5

^aSubstrate temperature.

^bHydrogen content from the integrated infrared Si-H absorption band at 630 cm^{-1} .

^cSample thickness.

^dFluorine content in at.% from the integrated sum of the Si-F, Si-F₂, Si-F₃, and Si-F₄ or (Si-F₂)_n infrared absorption bands between 830 and 1015 cm^{-1} .

sample, we found that N_{F} remained constant within a few percent during further light soaking up to 82 h. $N_{\text{F,sat}}$ can be annealed back to $N_{\text{F,ann}}$ by holding the samples at 180°C for more than 5 h.

The annealed-state ($N_{\text{F,ann}}$) and the saturated ($N_{\text{F,sat}}$) defect densities are plotted versus the Tauc gap in Fig. 1, and versus the Urbach energy in Fig. 2. $N_{\text{F,sat}}$ is of the order of 10^{17} cm^{-3} , consistent with values reported earlier.^{3,4} Figure 1 reveals that $N_{\text{F,sat}}$ drops exponentially from 2×10^{17} to $5 \times 10^{16} \text{ cm}^{-3}$ as E_{opt} decreases from 1.83 to 1.61 eV. No correlation is observed between $N_{\text{F,ann}}$ and E_{opt} . Figure 2 reveals no correlation between $N_{\text{F,sat}}$ and E_{U} ; the dip in $N_{\text{F,sat}}$ at $E_{\text{U}} = 50 \text{ meV}$ is also seen in a plot of E_{opt} vs E_{U} , suggesting that it is due to the dependence of $N_{\text{F,sat}}$ on E_{opt} shown in Fig. 1. Figure 2 also shows an exponential drop of $N_{\text{F,ann}}$ with decreasing E_{U} ; this observation agrees with the equilibrium theory of the dangling-bond density.⁵ The results of Figs. 1 and 2 suggest no correlation between $N_{\text{F,sat}}$ and $N_{\text{F,ann}}$. We have performed least-squares fits to the data with the approximation $\log[N_{\text{F,sat}}(\text{or } N_{\text{F,ann}})] = A + B[E_{\text{opt}}(\text{eV}) - 1.7] + C[E_{\text{U}}(\text{meV}) - 50]$, where A , B , and C are constants. These fits indicate that the term $C[E_{\text{U}}(\text{meV}) - 50]$ { or $B[E_{\text{opt}}(\text{eV}) - 1.7]$ } is not important for $N_{\text{F,sat}}$ (or $N_{\text{F,ann}}$, respectively), in agreement with the results in Figs. 1 and 2. These fits therefore yield the following empirical relations:

$$\log[N_{\text{F,sat}}(\text{cm}^{-3})] \approx 17 + 3.1[E_{\text{opt}}(\text{eV}) - 1.7], \quad (1)$$

$$\log[N_{\text{F,ann}}(\text{cm}^{-3})] \approx 15.6 + 0.044[E_{\text{U}}(\text{meV}) - 50], \quad (2)$$

in the ranges of E_{opt} and E_{U} of this study. The equilibrium

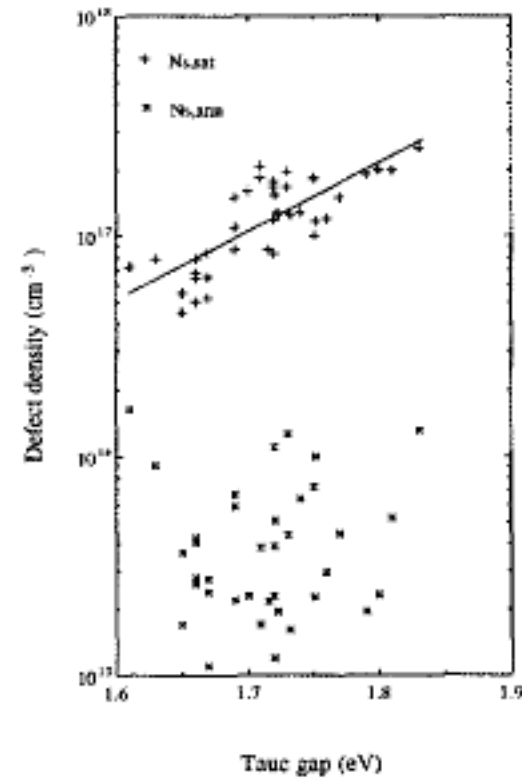


FIG. 1. Semilog plot of the saturated light-induced defect density $N_{\text{F,sat}}$ and the annealed-state defect density $N_{\text{F,ann}}$ vs the Tauc optical band gap E_{opt} . The solid line is the linear regression.

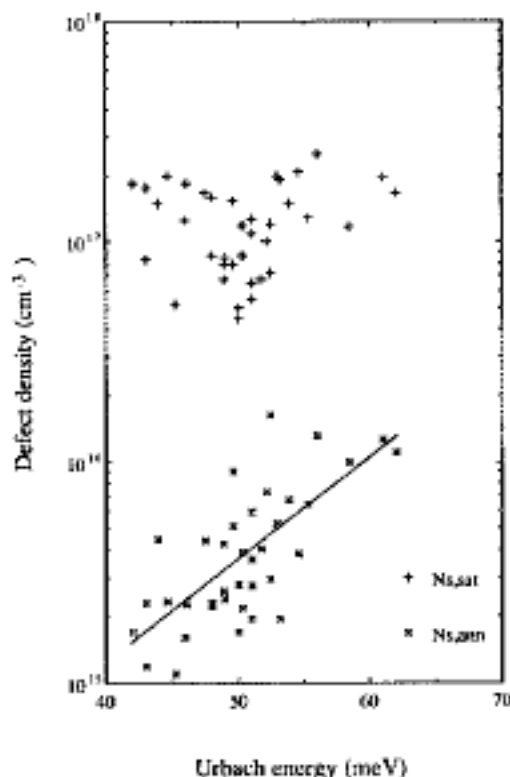


FIG. 2. Semilog plot of the saturated light-induced defect density $N_{s,sat}$ and the annealed-state defect density $N_{a,ann}$ vs the Urbach energy E_u . The solid line is the linear regression.

theory⁵ gives $\log[N_{a,ann} (\text{cm}^{-3})] \approx 15.9 + 0.069[E_u (\text{meV}) - 50]$ around $E_u = 50$ meV. The least-squares fits are shown as solid lines in Figs. 1 and 2.

The light-induced defect density may saturate either because of a balance between generation and annealing in steady state, or because of the depletion of convertible sites. Under the light soaking conditions of our study, thermal annealing cannot be important,⁶ but light-induced annealing is possible. Here we restrict our discussion to saturation due to the depletion of convertible sites. A widely cited model of the light-induced defect generation involves the breaking of a weak Si—Si bond by the recombination of photogenerated carriers, and subsequent stabilization of the broken bond by hydrogen bond switching.^{6,7} Following this model, the important material parameters influencing the number of convertible sites are the density of the weak bonds, the recombination energy, and the total hydrogen content c_H . The recombination energy is relevant because a higher recombination energy can break more bonds.⁸ The density of weak bonds, which constitute the valence-band tail states, is directly related to E_u . The recombination energy scales with E_{opt} ,⁹ c_H and E_{opt} are correlated, as shown in Fig. 3 for the 24 samples whose hydrogen content we know. Figure 3 also reveals a correlation between $N_{s,sat}$ and c_H ,¹⁰ which is consistent with the correlation observed between $N_{s,sat}$ and E_{opt} in Fig. 1. If the effect of the weak bond density on $N_{s,sat}$ dominates among the three parameters, a close correlation between $N_{s,sat}$ and E_u is expected. Our results do not show such a correlation, but instead one between $N_{s,sat}$ and E_{opt} (Fig. 1) and another between $N_{s,sat}$ and c_H (Fig. 3), consistent with the reported corre-

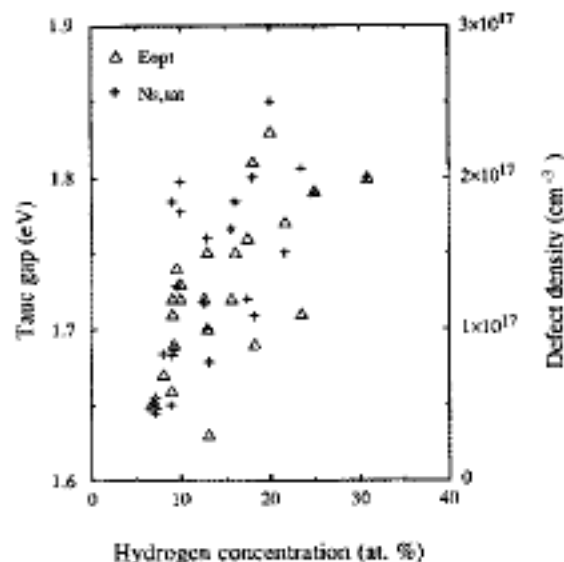


FIG. 3. Tauc optical band gap E_{opt} and the saturated light-induced defect density $N_{s,sat}$ vs the total hydrogen content.

lations between degradation rate and the optical band gap as well as the hydrogen content.^{8,11} Our observation suggests that the effect of the weak bond density is not dominant, at least for the samples we studied, which have E_u less than 65 meV. The correlation between c_H and E_{opt} makes it difficult to distinguish between the effects of these two parameters.

In conclusion, we saturated and measured the light-induced defect density in 37 α -Si:H(F) samples which had been grown in six different reactors over a range of conditions. These α -Si:H(F) samples have annealed-state defect densities in the range of 1.1×10^{15} – $1.6 \times 10^{16} \text{ cm}^{-3}$, Urbach energies of 42–62 meV, and Tauc optical band gaps of 1.61–1.83 eV. The saturated light-induced defect density, obtained by Kr⁺ laser light soaking ($\lambda = 647.1 \text{ nm}$), lies between 5×10^{16} and $2 \times 10^{17} \text{ cm}^{-3}$. This saturated defect density rises with increasing optical gap and total hydrogen content, but is not correlated with the Urbach energy or with the annealed-state defect density.

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¹⁰In the 24 samples whose densities of SiH₂ groups we know, we found no correlation between this density and $N_{s,sat}$.

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