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SATURATION BEHAVIOR OF THE LIGHT-INDUCED DEFECT DENSITY IN HYDROGENATED AMORPHOUS SILICON

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ABSTRACT

Using a Kr ion laser ($\lambda = 647.1$ nm), we have saturated the light-induced defect generation in hydrogenated (and fluorinated) amorphous silicon (a-Si:H(F)) at a carrier generation rate G of 3 x $10^{20}cm^{-3}s^{-1}$, within a few hours near room temperature. The defect generation rate scales with $1/G^2$, but the saturation defect densities $N_{s,sat}$ are independent of G. The saturation is not due to thermal annealing. We have measured $N_{s,sat}$ in 37 a-Si:H(F) films grown in six different reactors by different techniques. In these films $N_{s,sat}$ lies between 5 x 10^{16} and 2 x $10^{17}cm^{-3}$. $N_{s,sat}$ drops with decreasing optical gap and hydrogen content. $N_{s,sat}$ is not correlated with the initial defect density or with the Urbach energy.

INTRODUCTION

The light-induced defect generation in hydrogenated amorphous silicon (a-Si:H(F)) is an important issue for its photovoltaic applications. Because of the difficulty of reaching saturation under commonly employed illumination intensities, little is known about the saturated light-induced defect density $N_{s,sat}$, mainly because of the difficulty of reaching saturation experimentally under commonly employed illumination conditions. Aside from its theoretical significance, saturation can also be used as a practical descriptor of stability. We recently introduced a method for reaching saturation within a few hours illumination near room temperature by using light from a krypton ion laser ($\lambda = 647.1$ nm) [1]. First we found that $N_{s,sat}$ near room temperature is essentially independent of light intensity [1]. Then we measured 37 a-Si:H (or a-Si:H,F) samples grown in six different reactors at five different laboratories, in an attempt to correlate $N_{s,sat}$ with four macroscopic material parameters: the Tauc optical band gap E_{opt}, the Urbach energy E_u, the annealed-state defect density $N_{s,ann}$, and the hydrogen concentration c_H. Such correlations on samples from many different sources may help identify the mechanism of the light-induced metastability and provide approaches to improving the stability of the material. Here we report the results of our work done to date on $N_{s,sat}$.

EXPERIMENTAL CONDITIONS

Deposition technique, key deposition condition, 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 nitrogen gas before the experiment. E_{opt} values were determined from Tauc plots measured with the optical transmission method. The subgap optical absorption spectra were measured using the constant photocurrent method (CPM) in a coplanar configuration of chromium electrode. 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_s using the empirical formula $N_s\ (cm^{-2}) = 1.9 \times 10^{15} \int \Delta\alpha_{CPM}\ (cm^{-1})\ dE\ (eV)$ [2]. The Urbach 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 x 10^{15} - 1.6 x $10^{16}cm^{-3}$, and 42-62 meV, respectively.

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)	Number of samples
DC triode GD	Fluorinated $0.1 < c_F^{(d)} < 8$	SiF_4+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 0V to - 100V 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 (13.6MHz)	Substrate temperature dependence	SiH_4	100,150 200,250 300	7.1-15.6	3.00-4.50	5
Ultrahigh vacuum RF GD (13.6MHz)	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	Sputtered	x-Si Ar,H_2	200,230 300	11.3-28.0	0.80-2.0	5

(a) Substrate temperature.

(b) Hydrogen content from the integrated infrared Si-H absorption band at 630 cm^{-1}.

(c) Sample thickness.

(d) Fluorine content in at.% from the integrated sum of the Si-F, $Si-F_2$, $Si-F_4$ and $Si-F_3$ or $(Si-F_2)_n$ infrared absorption bands between 830 and 1015 cm^{-1}.

Nearly uniformly absorbed light of low and high intensities was used. The low-intensity light (denoted LIS) was produced by passing the light from a tungsten-halogen lamp through a 650 ± 35 nm bandpass filter. This light source yields an average carrier generation rate of $G = 5 \times 10^{20} cm^{-3} s^{-1}$. The high-intensity light source (denoted HIS) was the Kr ion laser beam broadened with a lens to produce an average carrier generation rate of $G = 3 \times 10^{22} cm^{-3} s^{-1}$. Particular attention was paid to keeping the sample temperature during the illumination near room temperature, so that thermal annealing was unimportant. During the LIS soaking, the sample was mounted on a water-cooled copper plate and cooled with blown nitrogen gas. We estimate that the sample temperature during the LIS light soaking was below 35 °C. During HIS soaking, the nitrogen gas was chilled by passing it though liquid nitrogen. The sample temperature during the HIS soaking, average over the sample thickness, was monitored with an optical transmission method. We calibrated the transmittance versus temperature by passing a He-Ne laser beam ($\lambda = 632.8$ nm) through a sample located in a temperature-controlled oven. Because of the temperature dependence of the optical absorption edge, the transmittance of the laser light decreases nearly two orders of magnitude as the sample temperature increases from room temperature to 180 °C. The typical sample temperature measured with the optical transmission method was 20 - 30 °C.

SATURATION OF LIGHT-INDUCED DEFECT GENERATION

The defect density over the entire duration of the LIS and HIS soaking of two samples is shown in Fig. 1. The sample thickness and optical band gap of these two samples are 1.7 μm and 1.71 eV (a-Si:H,F), and 1.9 μm and 1.67 eV (a-Si:H), respectively. Saturation under HIS illumination is obvious. The LIS soaking also shows the onset of saturation. After LIS illumination, the samples were exposed to the HIS light for 10 hours. The additional HIS illumination resulted in the last data points on the right side in Fig. 1. These two data points lie at the asymptotic value of the LIS curves and are nearly the same as the saturation values in HIS soaking. Therefore, the saturation value is essentially independent of the illumination intensity for generation rates which differ by a factor of 60. Furthermore, the duration of illumination to the onset of the saturation in Fig. 1 is approximately inversely proportional to the square of the carrier generation rate.

The existence of saturation near room temperature cannot be explained by the model of Stutzmann, Jackson, and Tsai [3]. This model predicts saturation only at illumination temperatures above about 100 °C, where the saturation results from the balance between the light induced generation and the thermal annealing. Such saturation value will scale with $1/G^{2/3}$. Our observation that the saturation values are independent of G indicates that the saturation we observed is not due to thermal annealing.

Both the existence of saturation near room temperature and the observation that the time to reach the onset of saturation is approximately proportional to $1/G^2$ can be explained by the model of Redfield and Bube [4]. Part of the LIS data (up to 1000 hours) for a-Si:H,F sample in Fig. 1 was fitted to the model with $N_{s,sat} = 3 \times 10^{17} cm^{-3}$ [4]; and indeed, the observed $N_{s,sat}$ in Fig. 1 is $1.8 \times 10^{17} cm^{-3}$, suggesting a good fit to the model over the entire illumination time. In this model, the saturation near room temperature results from a balance between the light-induced generation and the annealing of defects. The time constant of defect generation in this model is proportional to $1/G^{1/\beta}$, which is $1/G^{2.2}$ using $\beta = 0.45$ [5]. Since saturation could also be reached because precursor sites are depleted, however, the mere observation of saturation cannot be used as an evidence of the light-induced annealing process [1].

Fig. 1 shows that the saturation values $N_{s,sat}$ lie at $\sim 10^{17} cm^{-3}$, in rough agreement with reports from other groups [6-8]. In a long-time test of the saturation on one sample, we found that the defect density N_s, reached after an initial five hours of HIS soaking, remained constant within a few percent during further light-soaking up to 82 hours. Furthermore, $N_{s,sat}$ can be annealed back to $N_{s,ann}$ by holding the samples at 180 °C for longer than five hours.

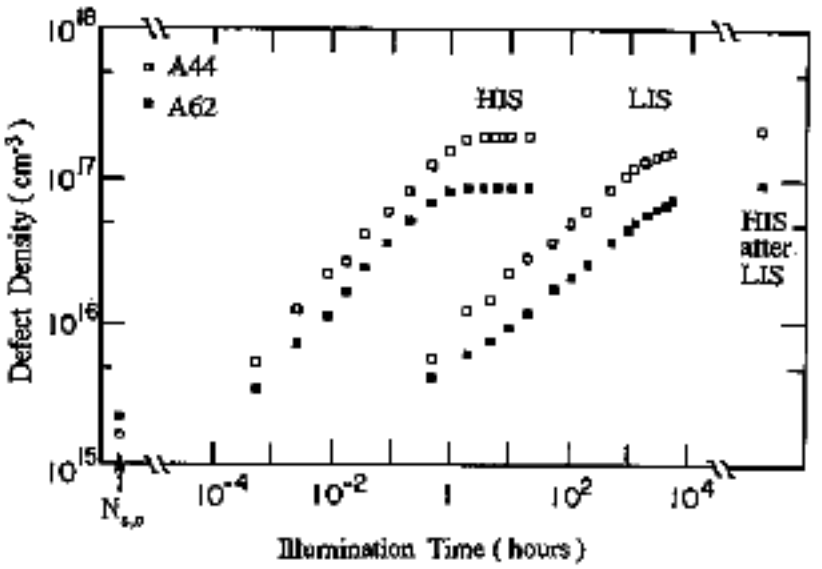

Fig. 1: Semi-log plot of the defect density versus the illumination time under low-intensity (LIS) and high-intensity (HIS) light soaking, for two samples. The two points on the right side were taken after 10 hours of high-intensity light-soaking, following low-intensity soaking.

CORRELATION OF THE SATURATION VALUE WITH MACROSCOPIC PARAMETERS

Now that saturation can be reached within a few hours of laser light soaking, we can study the dependence of the saturation value on macroscopic parameters in a large number of samples. We have measured 37 a-Si:H (or a-Si:H,F) samples from five different laboratories and attempted to correlate $N_{s,sat}$ with the Tauc optical band gap E_{opt}, the Urbach energy E_u, the annealed-state defect density $N_{s,ann}$, and the hydrogen concentration c_H. Each sample was light-soaked with the Kr ion laser (HIS) for at least five hours.

The annealed-state ($N_{s,ann}$) and the saturated ($N_{s,sat}$) defect densities of these 37 samples are plotted versus the Tauc gap in Fig. 2, and vs. the Urbach energy in Fig. 3. Figure 2 reveals that $N_{s,sat}$ rises exponentially from 5×10^{15} to $2 \times 10^{17} cm^{-3}$ as E_{opt} increases from 1.61 to 1.83 eV. No correlation is observed between $N_{s,ann}$ and E_{opt}. Fig. 3 reveals no correlation between $N_{s,sat}$ and E_u; the dip in $N_{s,sat}$ at $E_u = 50$ meV is also seen in a plot of E_{opt} versus E_u, suggesting that it is due to the dependence of $N_{s,sat}$ on E_{opt} shown in Fig. 2. Fig. 3 also shows an exponential rise of $N_{s,ann}$ with increasing E_u; this observation agrees with the

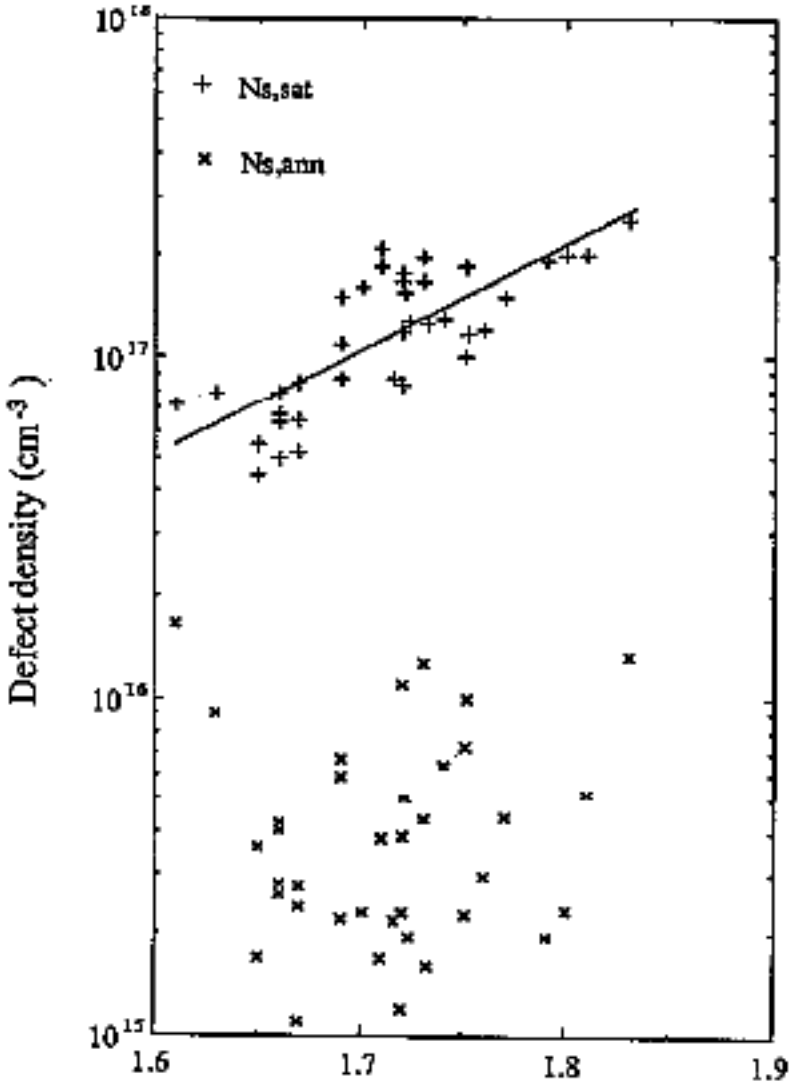

Fig. 2: Semi-log plot of the saturated light-induced defect density $N_{s,sat}$ and the annealed-state defect density $N_{s,ann}$ versus the Tauc optical band gap E_{opt}. The solid line is the linear regression.

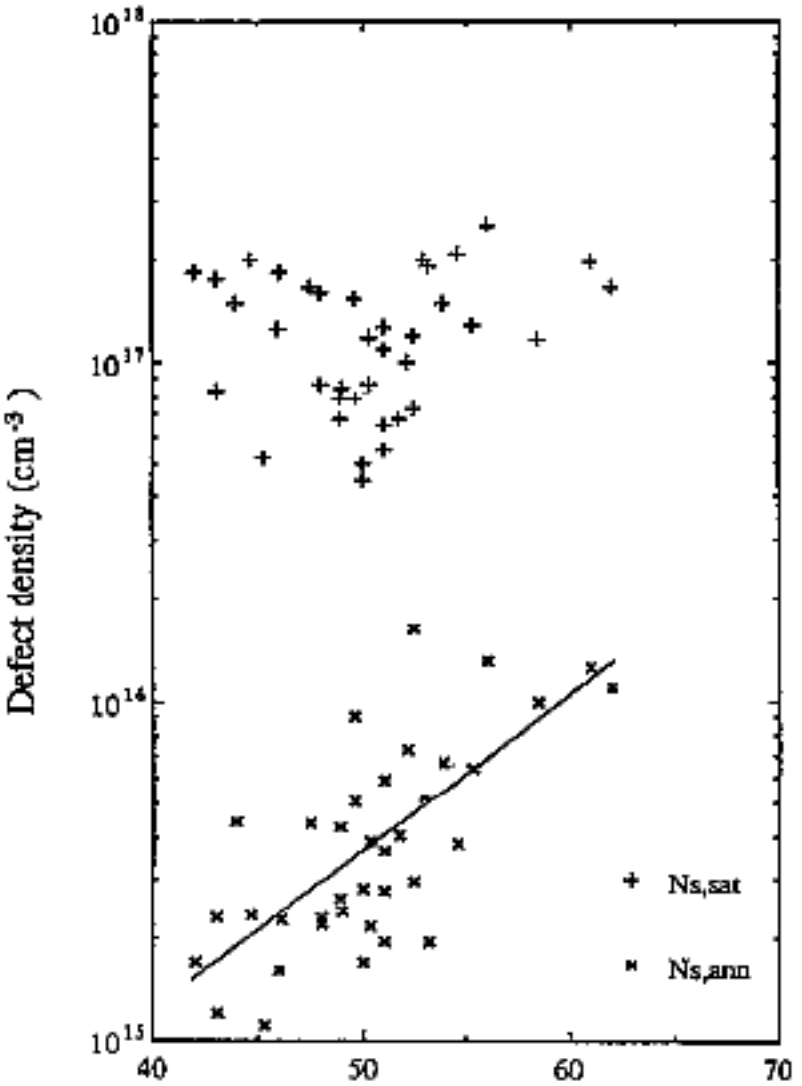

Fig. 3: Semi-log plot of the saturated light-induced defect density $N_{s,sat}$ and the annealed-state defect density $N_{s,ann}$ versus the Urbach energy E_u. The solid line is the linear regression.

equilibrium theory of the dangling-bond density [9]. The results of Figs. 2 and 3 suggest no correlation between $N_{s,sat}$ and $N_{s,ann}$. We made least-square fits to the data with the approximation $\log[N_{s,sat}\ (\text{or } N_{s,ann})] = A + B[E_{opt}\ (\text{eV}) - 1.7] + C[E_u\ (\text{meV}) - 50]$, where A, B and C are constants. These fits indicate that the term $C[E_u\ (\text{meV}) - 50]$ {or $B[E_{opt}\ (\text{eV}) - 1.7]$} is not important for $N_{s,sat}$ (or $N_{s,ann}$, respectively), in agreement with the results of Figs. 2 and 3. The fits therefore yield the following empirical relations:

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

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

in the ranges of E_{opt} and E_u of this study. The equilibrium theory [9] gives $\log[N_{s,ann}(\text{cm}^{-3})] \approx 15.9 + 0.069\ [E_u\ (\text{meV}) - 50]$ around $E_u = 50$ meV. The least-square fits are shown as solid lines in Figs. 2 and 3.

As mentioned earlier, the light-induced defect density may saturate either because of a balance between generation and annealing in a steady-state, or because of the depletion of convertible sites. 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 [3,10]. Following this model, the important material parameters influencing the

number of convertible sites are the density of weak bonds, the recombination energy, and the total hydrogen content c_H. The recombination energy is relevant because a higher recombination energy could break more bonds [11]. 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} [12]. c_H and E_{opt} are correlated, as shown in Fig. 4 for the 24 samples whose hydrogen content we know. Fig. 4 also reveals a correlation between $N_{s,sat}$ and c_H [13], which is consistent with the correlation observed between $N_{s,sat}$ and E_{opt} in Fig. 2. 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. 2) and another between $N_{s,sat}$ and c_H (Fig. 4), consistent with the reported correlations between degradation rate and the optical bandgap as well as the hydrogen content [11,14]. Our observation suggests that the effect of the weak bond density is not dominant, at least for the samples we studied, with 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.

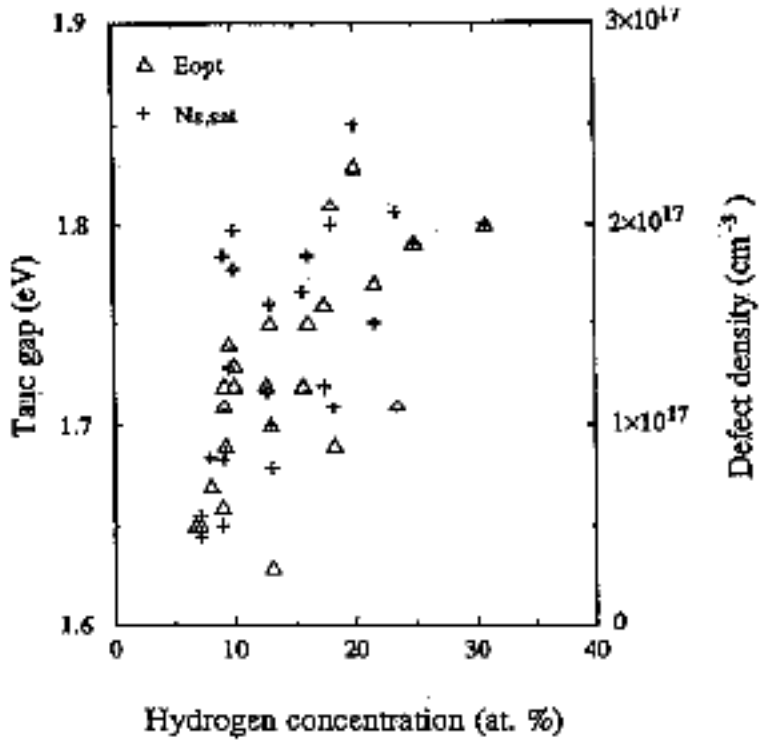

Fig. 4: The Tauc optical band gap E_{opt} and the saturated light-induced defect density $N_{s,sat}$ versus the total hydrogen content.

CONCLUSION

We saturated the light-induced generation of defects in a-Si:H(F) by a few hours of illumination with Kr ion laser light soaking (λ = 647.1 nm) near room temperature. The time to reach saturation scales roughly with $1/G^2$, but the saturation value is essentially independent of the illumination intensity. Therefore, the saturation is not due to thermal annealing. We measured the saturation values of the light-induced defect density in 37 a-Si:H(F) samples which had been grown in six different reactors over a range of conditions. These a-Si:H(F) samples have annealed-state defect densities in the range of 1.1 x 10^{15} - 1.6 x 10^{15}cm^{-3}, Urbach energies of 42-62 meV, and Tauc optical band gaps of 1.61 to 1.83 eV. The saturation value rises from 5 x 10^{15} to 2 x 10^{17}cm^{-3} 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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