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# Microstructure and the light-induced metastability in hydrogenated amorphous silicon

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Using a parameter obtained from infrared measurements of the silicon-hydrogen stretch mode, the amount of light-induced degradation in hydrogenated amorphous silicon (*a*-Si:H) has been explored as a function of the amount of microstructure present in our samples. We find that samples with more microstructure, and also more bonded hydrogen, show an increased light-induced effect. At the same time, the volume density of states in the initial (annealed) state remains virtually unchanged. We discuss how the present results relate to existing models proposed to describe the light-induced effect.

The reversible light-induced degradation in hydrogenated amorphous silicon (*a*-Si:H) has drawn considerable attention in recent years. Though numerous experimental results have added to our understanding of the effect, a complete picture has yet to emerge.<sup>1</sup> There have been various models proposed to explain the creation of the light-induced defects. The bond breaking model was first proposed by Pankove and Berkeyheiser<sup>2</sup> and Dersch *et al.*,<sup>3</sup> and was later developed by Stutzmann *et al.*<sup>4</sup> Adler<sup>5</sup> suggested a model for the light-induced effect in terms of redistribution of charges among the charged and neutral dangling bonds. Carlson<sup>6</sup> has suggested a mechanism for the light-induced degradation involving the motion of hydrogen on the surfaces of microvoids in the material. In this letter we report our investigation on the correlation of the light-induced effect with the amount of microstructure present in the material.

The *a*-Si:H films used in this study were grown in a capacitively coupled glow discharge apparatus using 100% silane. State-of-the-art *a*-Si:H can be produced in this system using a substrate temperature of 250 °C, a radio frequency (rf) power of 50 mW/cm<sup>2</sup>, and a silane flow rate of 60 sccm. In this letter, since our main interest was in varying the amount of microstructure present in our material, we have grown the films used in this study at higher rf powers and/or lower substrate temperatures.<sup>7,8</sup> The films were typically 1 to 2 μm thick and were grown simultaneously on glass and crystalline Si substrates to enable a correlation of the amount of light-induced degradation with the initial kind of H bonding in the films (as inferred from infrared measurements).

The microstructure in the films was determined from infrared (IR) absorption measurements. In *a*-Si:H the amount of microstructure can be inferred<sup>9,10</sup> from the ratio of the integrated band intensity of the IR mode centered at 2070 cm<sup>-1</sup> to the sum of the integrated band intensities of modes centered at 2070 cm<sup>-1</sup> and 2000 cm<sup>-1</sup>. This ratio is proportional to that fraction of hydrogen bonded in some sort of microstructure (typically hydrogen multibonded to a single atom, or singly bonded hydrogen on an internal surface).<sup>11</sup> We thus define a microstructure fraction  $R$  ( $0 < R < 1$ ) as

$$R = \frac{[2070]}{[2000] + [2070]}$$

where the brackets denote the integrated band intensities of the respective modes. We make no claims about the exact shape or nature of the microstructure (multivacancies, small voids, columnar growth morphology, etc.)<sup>12</sup> *except* that an increase in  $R$  contributes to a larger density deficiency. In particular,  $R$  has been correlated<sup>9</sup> with a void fraction (or density deficiency) by film density measurements using the flotation method; in that work, the reduction in film density compared to crystalline silicon was taken to be the void fraction, and a direct relation between  $R$  and the void fraction was observed for values of  $R < 0.8$ . Note that the effects observed here are significantly outside the range of the error bars estimated for each of these measurement techniques (3% accuracy in  $R$ , due to the determination of the baselines of the absorption peaks, and 1% accuracy in density, as estimated from successive density determinations of a crystalline silicon sample). For example, for films with the largest  $R$  values studied in the present paper (0.6–0.7), the void fractions are 8–10%, which correspond to measured film densities of 2.15–2.10 g/cm<sup>3</sup>. Film densities of similar magnitude (containing H contents similar to the present samples) have been reported elsewhere.<sup>13</sup>

Photothermal deflection spectroscopy (PDS) measurements were done to monitor the light-induced changes in the films. The films were annealed at 160 °C in vacuum for an hour before the measurements were initiated (state *A*). They were then light soaked for 22 h under an ELH lamp calibrated to 100 mW/cm<sup>2</sup> and remeasured (state *B*). The volume density of states in each case was obtained by integrating the excess absorption from an energy equal to half the optical gap to where the low-energy shoulder in the PDS curve meets the Urbach tail,<sup>14</sup> an energy interval of about 0.6 eV. This range of integration was kept constant for all samples. Table I lists the values of the optical gap,  $R$ , hydrogen content [obtained from the integrated absorption strength of the silicon-hydrogen bending (rocking) mode centered at 630 cm<sup>-1</sup>], an estimate of the amount of H bonded in the SiH 2000 cm<sup>-1</sup> mode, the Urbach tail width ( $E_0$ ), the volume density of states in state *A* ( $N_A$ ) and the excess volume density of states after light soaking ( $\Delta N = N_B - N_A$ ), for these samples. Figure 1(a) shows a plot of  $\Delta N$  versus the microstructure fraction  $R$ . We find that  $\Delta N$  increases by a factor of 4 as the microstructure fraction  $R$  increases from 0.15 to 0.60. In Fig. 1(b), we show the same  $\Delta N$  values, but this time

TABLE I. Some properties of the  $\alpha$ -Si:H samples used in these measurements.

| Sample | $R$  | $E_{opt}$ (eV) | $E_g$ (mV) | $[H]_{630}(\%)^a$ | $[H]_{2000}(\%)^b$ | $N_A^c$ | $\Delta N^c$ |
|--------|------|----------------|------------|-------------------|--------------------|---------|--------------|
| 1      | 0.15 | 1.72           | 49         | 8.0               | 6.8                | 2.60    | 0.77         |
| 2      | 0.22 | 1.76           | 56         | 11.6              | 9.0                | 2.23    | 1.84         |
| 3      | 0.25 | 1.71           | 48         | 6.8               | 5.1                | 1.12    | 0.93         |
| 4      | 0.35 | 1.75           | 60         | 10.0              | 6.5                | 1.78    | 1.05         |
| 5      | 0.39 | 1.75           | 57         | 6.8               | 4.1                | 1.31    | 0.62         |
| 6      | 0.44 | 1.78           | 58         | 12.8              | 7.1                | 2.20    | 1.40         |
| 7      | 0.56 | 1.76           | 67         | 16.8              | 7.4                | 2.10    | 3.10         |
| 8      | 0.56 | 1.79           | 69         | 13.5              | 5.9                | 2.10    | 1.58         |
| 9      | 0.62 | 1.80           | 71         | 18.0              | 6.8                | 3.60    | 2.30         |
| 10     | 0.63 | 1.74           | 77         | 15.5              | 5.7                | 7.95    | 2.15         |

<sup>a</sup> The total hydrogen content is obtained from an integration of the SiH 630  $\text{cm}^{-1}$  rocking-bending mode.

<sup>b</sup> These values were obtained from the formula  $[H]_{2000} \sim (1 - R) [H]_{630}$ .

<sup>c</sup> The numbers in these columns are in units of  $10^{16}$  states/ $\text{cm}^3$ .

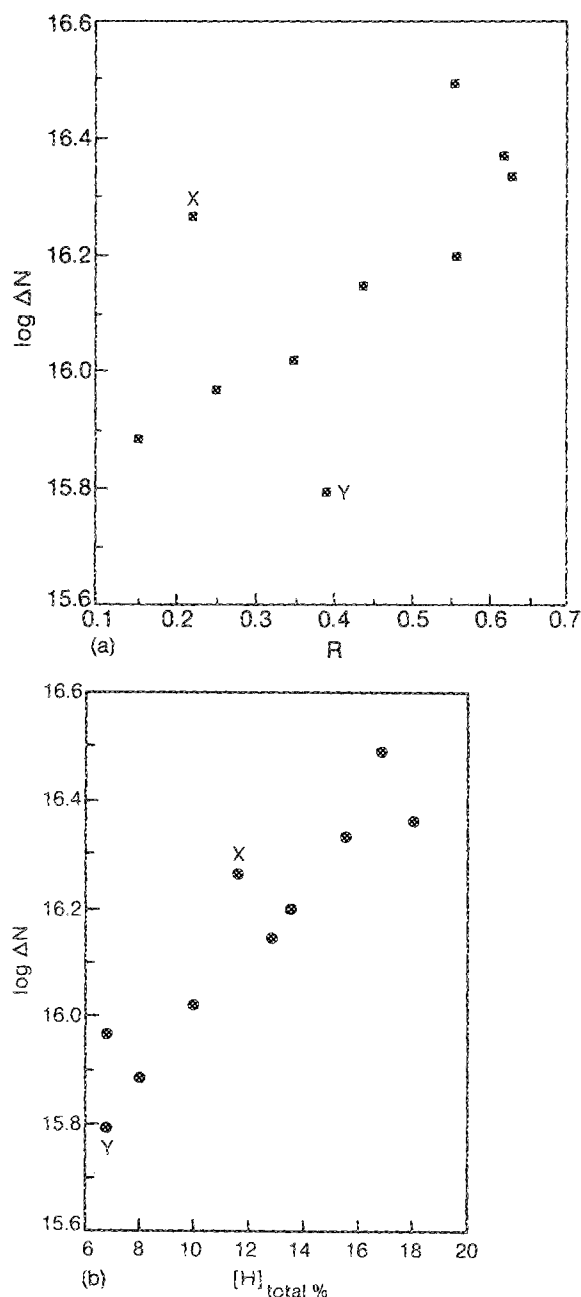


FIG. 1. Logarithm of excess volume density of states ( $\Delta N = N_B - N_A$ ) after light soaking vs (a) microstructure fraction  $R$ , and (b) total hydrogen content  $[H]_{total}$  for different  $\alpha$ -Si:H samples.

plotted versus the total H content of the films. Again, we see a well-defined correlation. However, since previous nuclear magnetic resonance work (correlated with infrared measurements) has noted a saturation in the amount of distributed H (H bonded in the 2000  $\text{cm}^{-1}$  infrared mode),<sup>15</sup> the excess H must therefore be bonded either in the  $(\text{SiH}_2)_n$  (or  $\text{SiH}_2$ ) configuration, or as singly bonded H on the internal surfaces of voids, both of which contribute to the infrared 2070  $\text{cm}^{-1}$  mode.<sup>11</sup> Therefore, since an increase in the 2070  $\text{cm}^{-1}$  mode (which contributes to an increase in  $R$ ) has been shown to correlate with an increased void fraction, we suggest that the increased amount of microstructure is the cause of the increased light-induced effect in our samples. The exact mechanism which produces the excess absorption upon light soaking cannot be discerned from the present experiments, but we believe the present results present the first *direct* confirmation of the model of Carlson linking hydrogenated microstructure with the light-induced degradation.

Ohsawa *et al.*<sup>16</sup> have studied the effect of hydrogen concentration on the light-induced effect by monitoring the changes in the electron spin resonance signal. From hydrogen evolution experiments they found a correlation between the light-induced effect and the amount of hydrogen which evolves at the lower (300–400 °C) evolution temperature. This evolution is believed to be due to the release of clustered hydrogen from either the SiH or  $\text{SiH}_2$  bonding configurations. Although the trend of this data is in agreement with the present work, especially that of Fig. 1(b), important differences should be noted. In particular, we correlated our results directly with a void fraction. We do not think this is obvious from Ohsawa's results, since even though the IR frequency of clustered SiH has been seen to occur at 2070  $\text{cm}^{-1}$ , clustered hydrogen can also appear in films showing no 2070  $\text{cm}^{-1}$  peak.<sup>17</sup> In addition, Ohsawa's results also show a much larger light-induced effect than ours. We believe this is because their samples show not only a higher overall H concentration than the present samples, but also more H bonded in the SiH 2000  $\text{cm}^{-1}$  infrared mode. We suggest this for the following reason. In particular, in Fig. 1(a) of the present paper, two data points (labeled X and Y) fall significantly outside the range of the other samples whose trend we have observed. These samples we claim have H contents in the 2000  $\text{cm}^{-1}$  mode outside the range of the

other samples. We are unable to determine quantitatively how much H is bonded in either the  $2000\text{ cm}^{-1}$  mode or the  $2070\text{ cm}^{-1}$  mode due to confusion over which values of the parameter  $A$  to use for the different bonding modes.<sup>15,18</sup> However, a determination of the total H content from an integration of the SiH  $630\text{ cm}^{-1}$  rocking-bending mode (denoted as  $[H]_{630}$ ) is universally accepted as being an accurate determination due to an independent calibration procedure.<sup>19</sup> Therefore, if we assume that the amount of H bonded in the  $2000\text{ cm}^{-1}$  mode is proportional to the factor  $[H]_{2000} \sim (1 - R)[H]_{630}$ , then all the other points in Figs. 1(a) and 1(b) contain 5.0 at. %  $< [H]_{2000} < 7.5$  at. %. However, points X and Y in Fig. 1 contain respectively 9.0 at. % and 4.1 at. % H bonded in the  $2000\text{ cm}^{-1}$  mode, and exhibit a much larger and smaller (respectively) light-induced effect than samples having a similar amount of microstructure, but having an  $[H]_{2000}$  content within the previously stated range. Note that the  $[H]_{2000}$  values for Ohsawa's samples lie in the range 10–14 at. %. Therefore, following the model of Carlson, one can speculate that even singly bonded H (in the  $2000\text{ cm}^{-1}$  mode) can to a certain extent move and cause the light-induced effect. This has been discussed in a recent paper by Jang *et al.*<sup>20</sup>

Finally, we comment on the relevance of the present results as they relate to the bond breaking model of the light-induced effect,<sup>2-4</sup> which suggests that the breaking of strained bonds by the energy released during recombination of photogenerated electron-hole pairs is the cause of the degradation. These strained bonds are believed to be deep band tail states,<sup>21</sup> which would give rise to broader Urbach tails.<sup>22</sup> However, a direct relationship between microstructure ( $R$ ) and the Urbach edge ( $E_0$ ) has been observed for  $a\text{-Si:H}$  as well as for  $a\text{-SiC:H}$  and  $a\text{-SiGe:H}$ .<sup>23</sup> These authors have attributed the broadening of  $E_0$  beyond the nominal 50 mV value as being due entirely to the presence of an increased microstructure in their material, and we see the same increase in  $E_0$  with an increase in  $R$  for our samples (see Table I). From this correlation, we suggest that the strained bonds (which manifest themselves in a broader Urbach tail), which break upon electron-hole recombination, may lie almost entirely on the interior surfaces of the microstructure, and that, therefore, the bond breaking model can indirectly involve microstructure as well. It is important to note at this point that we do not need to invoke an increase in  $N_A$ , the initial gap state density in the material, to explain an increase in  $\Delta N$ . In particular, from the results in Table I, the values of  $\Delta N$  and  $N_A$  can be seen; except for the last sample (#10),  $\Delta N$  has increased significantly while  $N_A$  has remained relatively constant. Therefore, we have not significantly degraded the quality of our bulk material (by increasing  $N_A$ ). Rather, we have just increased the amount of microstructure, and this is what we claim causes the increased light-induced effect observed here.

In conclusion, we find that there is a net increase in the light-induced excess volume density of states ( $\Delta N$ ) as the amount of microstructure increases. There is also a direct correlation between the total hydrogen content and the amount of the light-induced degradation. On the other hand, almost no increase in the initial gap state density is observed while  $\Delta N$  increases. We believe that these results support the model of Carlson for light-induced degradation involving the motion of hydrogen near the internal surfaces of microvoids, and can also be an (indirect) explanation for the bond breaking model proposed by Dersch and others.

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<sup>18</sup>See M. Cardona, *Phys. Status Solidi B* **118**, 463 (1983). In particular, depending on whether the H contributing to the  $2070\text{ cm}^{-1}$  mode is bonded as  $(\text{SiH}_2)_n$  or as SiH on microstructure surfaces, the parameter  $A$  can vary by as much as a factor of 2. Cardona discusses the accuracy of the parameter  $A$  values.

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