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Microscopic origin of light-induced changes in hydrogenated amorphous silicon

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Light-induced changes in the stretching mode absorption of Si-H and Si-H₂ have been studied for hydrogenated amorphous silicon (*a*-Si:H) films. The absorption below 2000 cm⁻¹ decreases greatly, but a small change has been observed above 2100 cm⁻¹. The magnitude of the overall change increases as the substrate temperature is lowered and little change is observed for *a*-Si:H films deposited at above 200 °C. The change in boron-doped *a*-Si:H is small compared with the undoped film deposited at the same substrate temperature. Based on experimental results, it is suggested that the hydrogen in the bulk of *a*-Si:H diffuses to the microvoids during light illumination.

The light-induced effect in hydrogenated amorphous silicon (*a*-Si:H) is one of the most important problems in technical applications as well as basic research. The spin density increases, the conductivity decreases, the photoluminescence intensity decreases, and the solar cell efficiency decreases after light soaking. However, it is still controversial whether the vibrational absorption of Si-H and Si-H₂ changes. The electronic properties of device-quality *a*-Si:H change greatly by the creation of dangling bonds of 10¹⁷ cm⁻³ after light soaking. However, the same amount of change in Si-H_{*n*} (*n* = 1 or 2) bonds cannot be detected by IR (infrared) vibrational absorption. Therefore, it is necessary to find samples showing large photocreated spin densities in order to check the light-induced change in vibrational absorption of Si-H and Si-H₂.

The following summarizes the effect of deposition parameters on the light-induced changes: (1) the light-induced change increases as the substrate temperature is lowered,^{1,2} (2) the change increases as the doping concentration is increased,³ (3) the change increases as the deposition rate is increased,⁴ (4) the change increases as the impurity (O or C) concentration is increased above 10²⁰ cm⁻³,^{5,6} (5) the effect is very small for fully compensated films. In this work, the changes in the stretching mode absorptions of Si-H_{*n*} in undoped, B-doped, P-doped, and compensated films have been investigated.

Hydrogenated amorphous silicon films were deposited on Corning 7059 glass plates and on high-resistivity (100 Ω cm) silicon wafers by rf glow discharge decomposition of silane mixed with hydrogen in a capacitatively coupled plasma reactor. For the preparation of doped and compensated *a*-Si:H films, premixed gases are used. The thicknesses of all films were around 1 μm.

The light soaking was done using three 250-W General Electric ELH tungsten lamps. The sample temperature was controlled during illumination by using an IR absorbing filter and a water-cooled sample holder. The sample temperature was kept below 60 °C during the illumination. The in-

frared spectra were measured by a Nicolet MX-3600 Fourier transform IR spectrophotometer.

Figure 1 shows the changes in absorption coefficients of Si-H_{*n*} stretching modes after light soaking for undoped *a*-Si:H films deposited at 100 °C. The illumination light intensity was 800 mW/cm². The absorption below 2100 cm⁻¹ initially decreases rapidly and then gradually. However, the absorption above 2100 cm⁻¹ increases slightly until 8 h and then decreases gradually. The change above 2100 cm⁻¹ is much smaller than that below 2000 cm⁻¹. The final soaked spectrum did not change after annealing at 90 °C for 4 h.

It is believed so far that the light-induced effect in *a*-Si:H is an intrinsic, bulk property. This means that the microscopic model to explain the effect should involve only silicon

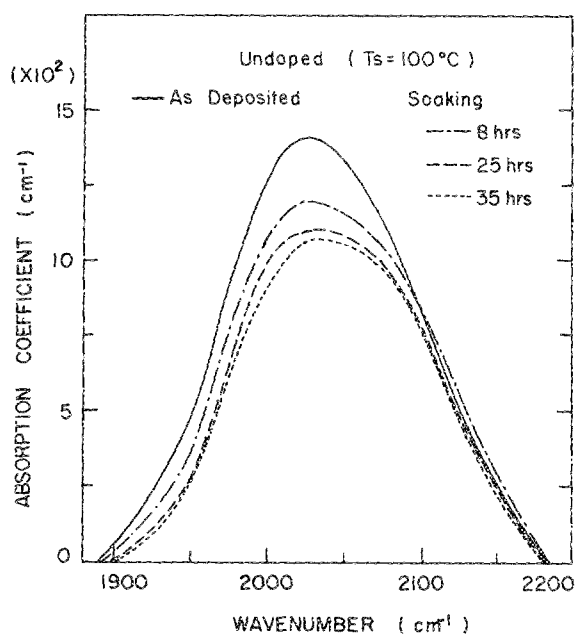


FIG. 1. Changes in the absorption coefficient of Si-H_{*n*} stretching modes by light soaking under 800 mW/cm² for undoped *a*-Si:H films deposited at 100 °C.

and hydrogen. We observed a 28% decrease in the peak absorption for *a*-Si:H deposited at 100 °C. For this low substrate temperature sample we cannot check the reversibility, which is a general feature of the Staebler–Wronski effect, since the light-induced effect can be annealed at above 150 °C for undoped *a*-Si:H films.

As the deposition temperature is lowered, the 2090 cm^{-1} peak increases. This peak is controversial whether it is due to the Si-H₂ or the hydrogens in the internal walls of microvoids. The hydrogen on the crystal silicon surface shows a silicon hydrogen mode near 2100 cm^{-1} independent of the presence of Si-H or Si-H₂ species.^{7,8} Accordingly, the 2090 cm^{-1} peak is likely to be the stretching modes of hydrogen atoms on the internal surfaces of microvoids independent of Si-H and Si-H₂.^{9,10} Therefore, it is assumed, for the present work, that the 2090 cm^{-1} peak is due to the hydrogen atoms bonded to silicon in the internal surfaces of microvoids independent of Si-H or Si-H₂.

Figure 2 shows the changes in the peak absorption coefficient for various undoped *a*-Si:H films. The peak absorption coefficients of Si-H_n stretching modes are plotted as a function of illumination time under 800 mW/cm^2 . The peak for the low substrate temperature (100 °C) sample initially decreases rapidly and then gradually saturates. However, the change in the peak value as well as absorption spectrum around 2000 cm^{-1} for undoped *a*-Si:H films deposited at above 180 °C was not detected. The 2090 cm^{-1} peak increases with an increasing deposition rate. So, it might be possible to observe a change in the IR absorption of *a*-Si:H films deposited with a high rate. However, for our undoped *a*-Si:H film deposited with a relatively high deposition rate of 6 Å/s, it does not show any change in vibrational absorption after light soaking.

The microstructure of *a*-Si:H changes with substrate temperature for more microvoids are incorporated at a lower temperature, creating more internal surface areas. We believe that the motion of hydrogen near the internal surfaces of microvoids is a probable mechanism to explain the changes in the Si-H_n stretching modes. It is suggested that the hydrogen in Si-H bonds near the internal surfaces in the

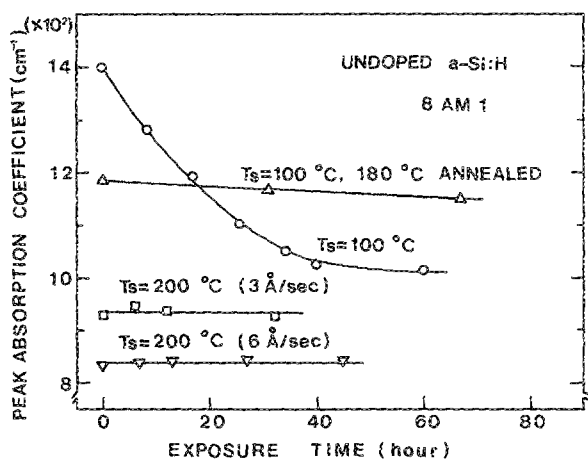


FIG. 2. Changes in the peak absorption coefficient of Si-H_n stretching modes by light soaking under 800 mW/cm^2 for various undoped *a*-Si:H films.

bulk can be induced to move to form Si-H_n in the internal surfaces of microvoids by recombination or by trapping of holes. Thus, light soaking appears to increase the hydrogens inside microvoids, explaining the initial change in the absorption spectrum; the absorption above 2100 cm^{-1} increases after 8 h light soaking.

Since the hydrogen content increases and the volume fraction of microvoids increases as the substrate temperature decreases one would expect that the light-induced effect should decrease as the substrate temperature increases. Ohsawa *et al.*¹¹ have shown that the concentration of metastable centers is proportional to the concentration of weakly bonded hydrogen from hydrogen evolution experiments. The concentration of weakly bonded Si-H_n will be larger at the internal surfaces of microvoids.

The great decrease in overall absorption coefficients shown in Fig. 1 suggests that through the diffusion of hydrogen near the microvoids in the bulk the hydrogens collect on the insides of microvoids, where they can combine to form H₂ in low substrate temperature samples. This phenomenon can be checked by calorimetry.

Figure 3 shows the changes in the Si-H_n stretching mode absorption after light soaking and after annealing at 90 °C for 4 h. Because the 2000 cm^{-1} peak for a 0.1% boron-doped *a*-Si:H is much smaller than that for an undoped film (compare Figs. 1 and 2), the smaller change in the absorption peak of 0.1% boron-doped films was obtained.

Figure 4 shows the changes in the peak absorption coefficient for doped and compensated *a*-Si:H films. The continuous decrease in the peak value for 0.1% boron-doped films can be seen. But the sample deposited at 180 °C shows a smaller change compared with that deposited at 100 °C. However, the change in the peak value was not observed for P-doped and compensated *a*-Si:H films deposited at and above 200 °C. These results indicate that only low substrate temperature samples show a change in absorption coefficients around 2000 cm^{-1} .

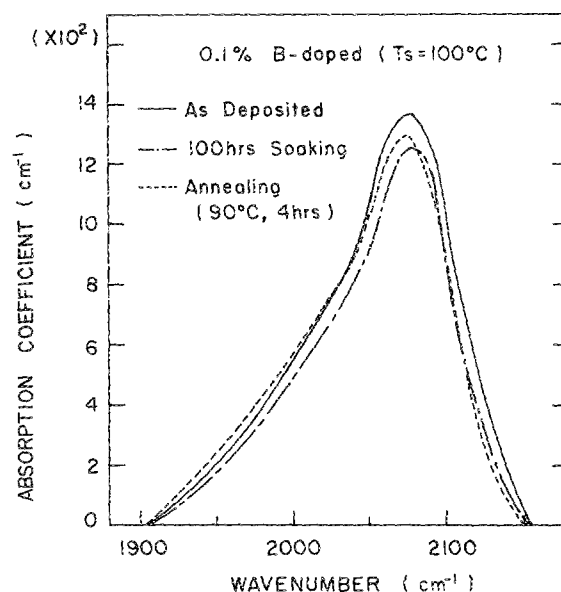


FIG. 3. Light soaking and annealing effects on absorption coefficient of Si-H_n stretching modes for 0.1% boron-doped *a*-Si:H films, deposited at 100 °C. Annealing was done at 90 °C for 4 h.

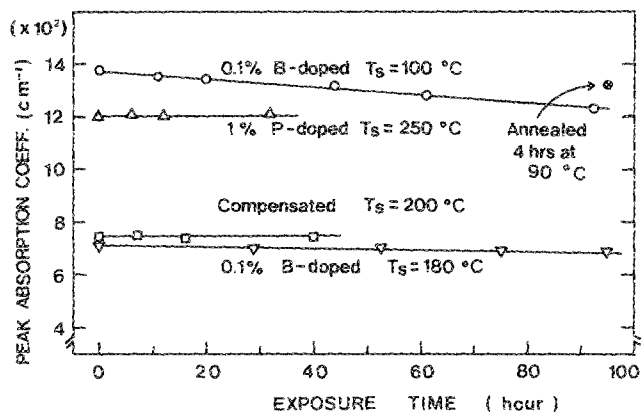


FIG. 4. Changes in the absorption peak of Si-H_n stretching modes for doped and compensated α -Si:H films. The compensated film was deposited with a gas mixture $[PH_3]/[SiH_4] = [B_2H_6]/[SiH_4] = 0.1\%$.

From the photothermal deflection spectra, it is shown that the incorporation of boron or phosphorus into α -Si:H increases the light-induced changes. So, it is possible to expect that the doped α -Si:H films show the change in stretching modes of Si-H_n even though the deposition temperature is above 200 °C. However, experimental results indicate that only low substrate temperature samples show a decrease in Si-H_n vibrational absorption.

The changes in 0.1% boron-doped α -Si:H deposited at 100 °C show that the decrease in absorption below 2000 cm⁻¹ can be recovered, but little recovery is seen above 2100 cm⁻¹, suggesting that the decrease in Si-H modes in the bulk can be recovered, but the change in the inside walls of microvoids cannot be recovered. We expect, therefore, that the irreversible light-induced change can exist, and it will be particularly large in low substrate temperature samples. The reversible change is likely to be due to the hydrogen diffusion from the bulk to the inside walls of microvoids, and the irreversible change is due to the creation of H₂ by collection of H inside walls of microvoids.

Because the α -Si:H films deposited at above 200 °C have a small volume fraction of microvoids, the change in the IR vibrational absorption was not detected for our samples until 100 h soaking under 800 mW/cm². Hong and Hwang¹² reported a clear decrease in the IR absorption after 400 h light soaking for the α -Si:H film deposited at 250 °C.

The change for the boron-doped film deposited at 100 °C shows quite a different behavior compared with the undoped sample deposited at the same substrate temperature. Incorporation of boron into α -Si:H gives rise to an increase in the volume fraction of microvoids and to the increase in the diffusion coefficient of hydrogen.¹³

From the changes in absorption spectra for the samples deposited at 100 °C, it is found that the decrease in the undoped α -Si:H is large and the decreasing rate decreases as the exposure time is increased, whereas the decrease is small and the decreasing rate is constant for a 0.1% boron-doped film. These results can be explained by the differences in the absorption peak at 2000 cm⁻¹ and in the diffusion coefficient of hydrogen. The absorption peaks at 2090 cm⁻¹ are large for both undoped and boron-doped α -Si:H films, whereas, the peak at 2000 cm⁻¹ is large in the undoped film and small in the B-doped film as shown in Figs. 1 and 3. It is expected, therefore, that the change in the hydrogen content transferring to the internal walls of microvoids will be smaller in the boron-doped film. Since the diffusion of hydrogen in the boron-doped α -Si:H is faster than that in the undoped film and the volume fraction of microvoids is larger, the transferring of hydrogen from the bulk to the microvoids is easy and thus the decreasing rate will be nearly constant in the boron-doped α -Si:H.

In summary, the decrease of the absorption peak of Si-H_n stretching modes after light soaking has been observed for low substrate temperature α -Si:H samples. The decrease in absorption below 2000 cm⁻¹ is large compared with that above 2100 cm⁻¹, and the change is small for the boron-doped α -Si:H film compared with the undoped α -Si:H. Based on the experimental results, it is suggested that the hydrogen in the bulk diffuses to the internal walls of microvoids during light soaking in α -Si:H.

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¹J. Jang and C. Lee, AIP Conf. Proc. No. 120, 280 (1984).

²Y. Uchida and H. Sakai, Materials Research Society Proc. No. 70, 577 (1986).

³A. Skumanich and N. M. Amer, Phys. Rev. B 31, 2263 (1985).

⁴J. Xi, R. Hollingsworth, P. Bhat, and A. Madan, AIP Conf. Proc. No. 157, 158 (1987).

⁵D. E. Carlson, A. Catalano, R. V. D'Aiello, C. R. Dickson, and R. S. Oswald, AIP Conf. Proc. No. 120, 234 (1984).

⁶A. Morimoto, H. Yokomichi, T. Atoji, M. Kumeda, I. Watanabe, and T. Shimizu, AIP Conf. Proc. No. 120, 221 (1984).

⁷Y. J. Chabal, Phys. Rev. Lett. 50, 1850 (1983).

⁸T. Satou and A. Hiraki, Jpn. J. Appl. Phys. 24, L491 (1985).

⁹H. Wagner and W. Beyer, Solid State Commun. 48, 585 (1983).

¹⁰H. Richter, J. Trodani, and M. Cardona, J. Non-Cryst. Solids 59&60, 181 (1983).

¹¹M. Ohsawa, T. Hama, T. Akasaka, T. Ichimura, H. Sakai, S. Ishida, and Y. Uchida, Jpn. J. Appl. Phys. 24, L838 (1985).

¹²C. S. Hong and H. L. Hwang, Appl. Phys. Lett. 49, 645 (1986).

¹³R. A. Street, J. Kakalios, C. C. Tsai, and T. M. Hayes, Phys. Rev. B 35, 1316 (1987).