

Evidence for Light-Induced Increase of Si-H Bonds in Undoped *a*-Si:H

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The light-induced change of Si-H bonds in undoped *a*-Si:H has been investigated by tracing the change of the absorption coefficient related to the Si-H stretching mode, using a specially designed differential method. The results unambiguously show that the Si-H bonds increase with the illumination time, following the same stretched exponential rule as the dangling bonds. The change of the Si-H bonds can be reversed by annealing. These findings bear out a close correlation between the changes of the Si-H bonds and the dangling bonds under illumination.

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Shortly after the discovery of the effective doping of hydrogenated amorphous silicon (*a*-Si:H) [1], it was found that the material suffered from certain light-induced metastable changes (Staebler-Wronski effect) [2], which seriously affects its fruitful application. Since then a great deal of effort has been made to improve the stability of the material as well as to understand the mechanism of the effect. Various models to account for the effect have been proposed, most of which associate the effect with an active role of hydrogen [3–7]. This is supported by some recent work showing a close relation between the metastability and hydrogen diffusivity [6]. However, it is not clear from these experiments if the active role of hydrogen results in changes of Si-H bonds after light soaking. We believe that this can be a key issue for deciding on the validity of a proposed model. So we have been making efforts to determine reliably whether there are changes of Si-H bonds in *a*-Si:H subject to illumination.

The Si-H bonds can be detected, by the infrared absorption, by their characteristic vibration modes. Previous efforts in trying to detect the light-induced change of Si-H bonds have not been successful [8]. As we usually have $\sim 10^{21}$ cm⁻³ Si-H bonds in *a*-Si:H, and if we compare this with the fact that light-induced defects hardly exceed 10^{18} cm⁻³ [9], we are facing a change less than one-thousandth of the background Si-H bonds, which is substantially below the resolution limit of the usual ir spectrometers. To overcome this difficulty, we have developed a specially designed differential method which was described in detail elsewhere [10]. The essence of the method is that, in an absorption measurement setup, by rotating a sample half of which is in the annealing state (state *A*) and the other half in the light-soaked state (state *B*), a detector behind the sample, combined with a lock-in amplifier, only picks up the metastable change signal if the inhomogeneity of the sample is neglected. In the present Letter we report our measurements on the light-induced changes in the Si-H bond absorption in undoped *a*-Si:H samples using this method. Our results unambigu-

ously show a light-induced increase of Si-H bonds. The close relation of this increase with the defect creation is clearly shown by the closely parallel changes of the Si-H bonds with that of the dangling bonds.

The undoped *a*-Si:H samples were deposited on high-resistivity crystalline Si substrates at 200 °C by rf glow discharge decomposition of SiH₄ + H₂ mixture in 1:4 ratio. On the side of the substrate where *a*-Si:H was deposited, the surface was unpolished to eliminate possible interference effect. Three samples, *I719*, *I404a*, and *I404b*, with thicknesses of 14.4, 20, and 20 μm, respectively, were measured; they gave similar results. That the observed light-induced change is caused by the increase of absorption rather than changes in reflection has been verified by the thickness dependence and the fact that the results are not sensitive to which side the monochromatic light is incident on. The data presented here were taken with the light incident on the substrate side.

We have focused our measurements on the Si-H stretching mode, and the absorption spectra were scanned from 1900 to 2200 cm⁻¹. The background signal was recorded when the whole sample was in state *A*. The results showed that the contribution from the sample inhomogeneity was about 1% of the absorption peak. Therefore, great care had been taken during the light-soaking process in order not to disturb the whole system, especially the sample position. The light-induced change was then traced after every step of successively illuminating the same half of the sample with white light of 400 mW/cm². The absorption coefficient α , and its change with illumination time $\Delta\alpha$, as a function of wave number ω for sample *I404b*, are presented in Figs. 1(a) and 1(b). We see a systematic increase of α with light soaking, in contrast to some earlier reports [8]. While the light-induced increases for our undoped *a*-Si:H samples always peak at 2000 cm⁻¹, which evidently corresponds to the change of Si-H stretching mode, the spectra can actually be resolved into three bands, with one main band peaked at 2000 cm⁻¹ and two subsidiary bands developing simultaneously with the main band. The band resolution for the absorption change after 342 h light

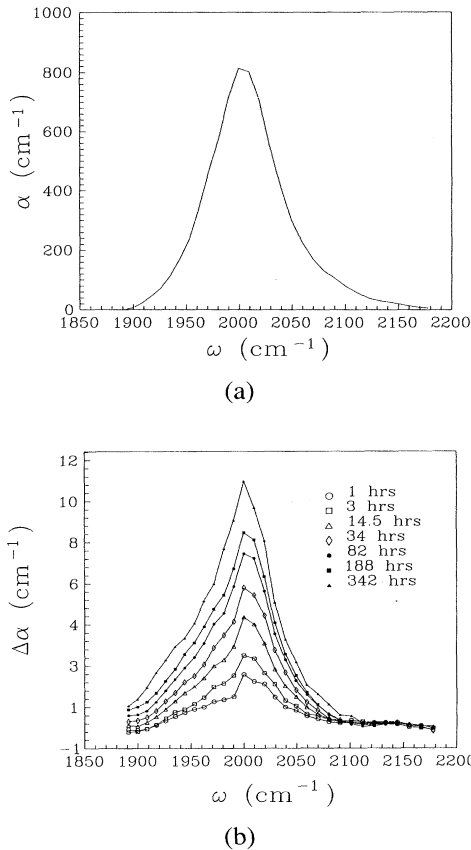


FIG. 1. (a) The absorption spectrum at Si-H stretching mode for undoped *a*-Si:H sample *I404b*. (b) The light-induced increment of absorption coefficient $\Delta\alpha$ for different light-soaking times indicated in the figure.

soaking is shown in Fig. 2. The positions of the two subsidiary bands are somewhat sample dependent. In Fig. 2 we see that the left band peaks at 1940 cm^{-1} and the right band peaks at 2064 cm^{-1} for sample *I404b*. The identities of these two subsidiary bands need to be clarified by further investigation.

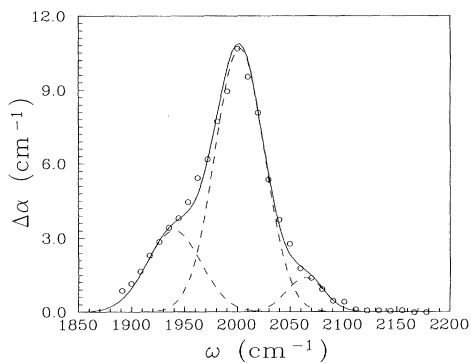


FIG. 2. The deconvolution into three bands of the change of absorption coefficient $\Delta\alpha$ after light soaking for 342 h. A Gaussian distribution is assumed for each band.

Since the change of the oscillator strength cannot be so large as to account for the increase of absorption (see the later discussion), our results present clear evidence of the light-induced increase of Si-H bonds. This fact implies that there is always some hydrogen available in the form which can be transformed into Si-H bonds by light soaking. We can estimate the light-induced increase of Si-H bonds, ΔN_H , by the integral

$$\Delta N_H = A \int \Delta\alpha/\omega d\omega, \quad (1)$$

taking the coefficient $A = 9 \times 10^{19}\text{ cm}^{-2}$ [11]. Many experiments confirm that both the increase of dangling bonds with time under illumination and their decrease by annealing observe a stretched exponential behavior [12]. If we use this functional dependence to fit our data of ΔN_H , which give

$$\Delta N_H = \Delta N_{HS} \{1 - \exp[-(t/\tau)^\beta]\}, \quad (2)$$

where ΔN_{HS} is the saturated value of ΔN_H , τ is the relaxation time, and β is the dispersive factor, then we find that our data fit well with Eq. (2), giving $\Delta N_{HS} \sim 9 \times 10^{19}\text{ cm}^{-3}$, $\beta \sim 0.32$, and $\tau \sim 1450\text{ h}$ (Fig. 3). It is interesting to note that when $t \ll \tau$ Eq. (2) reduces to a power law t dependence of ΔN_H , with the exponent $\beta = 0.32$, very close to the $t^{1/3}$ dependence found by Stutzmann *et al.* for the change of dangling bonds under illumination [3]. The density of the total Si-H bonds estimated from the absorption of the stretching mode 2000 cm^{-1} is about $4.0 \times 10^{21}\text{ cm}^{-3}$ for sample *I404b*. Therefore, the light-induced increase of Si-H bonds can be as large as 1% of the total number. This finding is striking as the change of Si-H bond number is much larger than that of dangling bonds, yet they evolve with time by the same rule.

To confirm the close relation of the Si-H bond change with the dangling bond change, we have also measured the subband absorption for sample *I404b*. From the absorption coefficient at 1.2 eV, we can estimate the change of

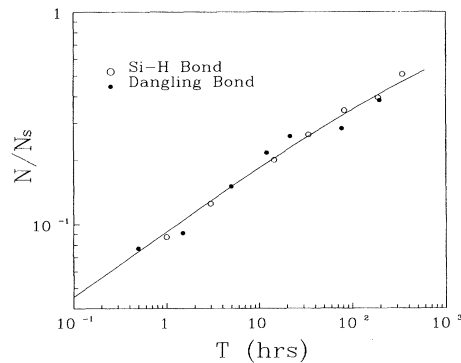


FIG. 3. The light-induced increases of Si-H bond number and dangling bond number as a function of time. The two sets of data are well scaled.

dangling bond density ΔN_D [13]. Again, by fitting with the stretched exponential formula

$$\Delta N_D = \Delta N_{DS} \{1 - \exp[-(t/\tau)^\beta]\}, \quad (3)$$

where ΔN_{DS} is the saturated value of dangling bonds, we find that the change of dangling bonds is fairly well scaled with the change of Si-H bonds. This can clearly be seen from Fig. 3 where the data for ΔN_H and that for ΔN_D (both normalized) are fairly good approximated by a single curve, i.e., the same τ (~ 1450 h) and β (~ 0.32) are obtained for ΔN_H and ΔN_D , though ΔN_{DS} ($\sim 3.6 \times 10^{18} \text{ cm}^{-3}$) is more than an order lower than ΔN_H .

Since the Staebler-Wronski effect is a reversible phenomenon, to complete our experiments we should see if the light-induced increase of Si-H bonds can be eliminated by annealing. This is a very difficult task, because we must keep the sample position unperturbed during the whole process of experiments. The same source for light soaking was used in the annealing experiment, but in the latter case the high energy photons were blocked by a filter. The temperature reached with this method was 75°C as estimated by a simulation experiment. This was not a very effective way, but the result did show that the Si-H bonds decreased after annealing at 75°C for 56 and 284 h (Fig. 4).

Now we should discuss an alternative possibility in the explanation of our results. From Eq. (1) we see that the absorption coefficient α depends on the number of Si-H bonds as well as constant A . After illumination the value of A may also change through the effective charge e^* [14], if some rearrangement of the environment of a Si-H bond occurs. The most important change of the environment could be the appearance of a dangling bond on or near a Si-H bond. However, since the density of dangling bonds is less than one-thousandth of the Si-H bond density, and the chance they meet together is even less, the effect of the dangling bonds can be neglected [15]. Moreover, recent investigation shows that the value of A does not depend on the details of sample preparation [11], which means that A is not sensitive to the variations of a -Si network. The same A value is applicable even to the samples bombarded by heavy He^+ ion [11,16]. Therefore it is unlikely that

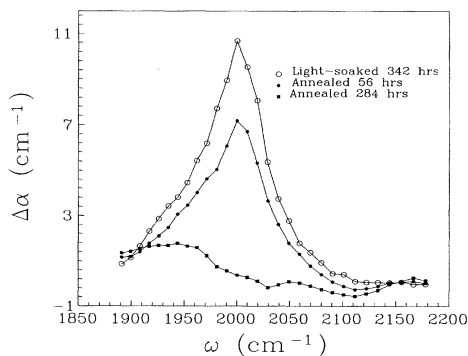


FIG. 4. The reverse change of absorption coefficient $\Delta\alpha$ of sample I404b after annealing for 56 and 284 h at 75°C .

the increase of α around 2000 cm^{-1} is due to the decrease of A .

Our findings present a serious challenge to existing models. Since the increase of Si-H bonds by light soaking is much higher (an order of magnitude) than that of dangling bonds, it seems reasonable to think that the former may be the main process responsible for the metastable change in a -Si:H. It is plausible that most of the dangling bonds created under illumination are passivated by hydrogen, while the resultant defects usually detected are only a small fraction of them. This would explain why the defect creation efficiency seems very low (the rate of defect creation is approximately 10^{-5} defects/recombination event) [9]. It remains to be further clarified whether the changes of Si-H bonds and dangling bonds are two aspects of a single process, or if they are two processes happening in parallel, but correlated closely to each other. In any case, a reasonable model should explain how the Si-H bonds and the dangling bonds are simultaneously changed.

In summary, by using a specially designed technique, we have been able to measure effectively the light-induced change of Si-H bonds in a -Si:H. The experiments provide unambiguous evidence for an increase of Si-H bonds in undoped a -Si:H under illumination, and the effect can be reversed by annealing. The observed scaled behavior of the Si-H bond change with that of the dangling bond can be used as an important criterion for judging the validity of a model to account for the Staebler-Wronski effect.

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- [1] W.E. Spear and P.G. LeComber, *Solid State Commun.* **17**, 1193 (1975).
- [2] D.L. Staebler and C.R. Wronski, *Appl. Phys. Lett.* **31**, 292 (1977).
- [3] M. Stutzmann, W.B. Jackson, and C.C. Tsai, *Phys. Rev. B* **32**, 23 (1985).
- [4] L.E. Mosley, M.A. Paesler, and I. Shimizu, *Philos. Mag. B* **51**, L27 (1985).
- [5] W.B. Jackson, *Phys. Rev. B* **41**, 10257 (1990).
- [6] R.A. Street, *Physica (Amsterdam)* **170B**, 69 (1991).
- [7] G.G. Qin and G.L. Kong, *Philos. Mag. Lett.* **57**, 117 (1988).
- [8] Fritzsche, Kakalios, and Dernstein [H. Fritzsche, J. Kakalios, and D. Dernstein, in *Optical Effects in Amorphous Semiconductors—1984*, edited by P.C. Taylor and S.G. Bishop, AIP Conf. Proc. No. 120 (AIP, New York, 1984), p. 229] did not find any light-induced change of the Si-H absorption modes in a series of a -Si:H samples. There were also some reports claiming either a large increase or a large decrease of Si-H vibration modes under illumination [P.X. Zhang, C.L. Tan, Q.R.

- Zhu, and S.Q. Peng, *J. Non-Cryst. Solids* **59 & 60**, 417 (1983); D.E. Carlson *et al.*, *Solar Cells* **9**, 19 (1983); D.E. Carlson, *Solar Energy Mater.* **8**, 129 (1982); C.S. Hong and H.L. Hwang, *Appl. Phys. Lett.* **49**, 645 (1986); J. Jang, L.G. Lee, S.C. Park, and C.C. Lee, *Appl. Phys. Lett.* **51**, 1673 (1987)].
- [9] H. Fritzsche, in *Optical Effects in Amorphous Semiconductors* (Ref. [8]), p. 478.
- [10] G.L. Kong, D.L. Zhang, Y.P. Zhao, G.S. Sun, G.Q. Pan, and X.B. Liao, *J. Non-Cryst. Solids* **164-166**, 211 (1993).
- [11] A.A. Langford, M.L. Fleet, B.P. Nelson, W.A. Langford, and N. Maley, *Phys. Rev. B* **45**, 13 367 (1992).
- [12] J. Kakalios, R.A. Street, and W.B. Jackson, *Phys. Rev. Lett.* **59**, 1037 (1987).
- [13] N. Nyrsch, F. Finger, J.J. McMahon, and M. Vanecek, *J. Non-Cryst. Solids* **137 & 138**, 347 (1991).
- [14] M. Cardona, *Phys. Status Solidi (b)* **118**, 463 (1983).
- [15] For the Si-H stretching mode at 2000 cm^{-1} , $e^* = 0.44e$ (see, e.g., Ref. [11]), where e is the free electron charge. Even if a nearby dangling bond can increase e^* to the maximum value allowed ($\approx e$), it contributes to the increase of α no more than 0.1% as can be estimated from the formula in Ref. [14].
- [16] Suha Oguz, D.A. Anderson, William Paul, and H.J. Stein, *Phys. Rev. B* **22**, 880 (1980). In this work a large increase of α by He-ion bombardment was observed in the 2000 cm^{-1} stretching mode, and was explained in terms of changes in oscillator strength. However, such a large increase of oscillator strength should result in a noticeable shift of ω_0 [up to several tens cm^{-1} according to Eqs. (10) and (16) in Ref. [14]], which was not found in the experiments. Therefore, these experiments actually support that e^* is not sensitive to the structure change.