Photodilatation Effect of Undoped *a*-Si:H Films

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A photodilatation effect of undoped *a*-Si:H films has been discovered by a differential dilatometric method. The film thickness has been found to increase instantaneously when the sample is exposed to light. The dilatation weakens with illumination time, following a stretched exponential law, and finally reaches a saturation value. The dilatation disappears when light is off. The results unambiguously show that the whole structure of the film becomes less compact and less stable under light exposure. The metastable change (Staebler-Wronski effect) could be a redistribution of different configurations after this photodilatation in the *a*-Si:H films. [S0031-9007(97)04609-7]

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With the accumulation of data, more and more people have recognized that the light-induced metastable change of *a*-Si:H [Staebler-Wronski effect (SWE)] [1] cannot be accounted for by any simple model which associates the effect only with the change of individual bonds. NMR experiment [2] shows that most of the hydrogen atoms take part in the light-induced enhancement of local motion. An experiment on the effect of post hydrogenation proves that an increase of Si:H(D) bonds by as much as $\sim 3 \times 10^{21}$ cm^{-3} was at the cost of decreasing all kinds of Si-Si bonds with equal probability instead of only weak Si-Si bonds [3]. The x-ray photoemission spectra of *a*-Si:H exhibit a reversible shift of the Si 2*p* peak between annealed state (state *A*) and light-soaked state (state *B*), indicating some long-range structural rearrangements of the amorphous network [4]. A direct evidence of light-induced increase of Si-H bonds has been given by tracing the change of Si-H stretching mode absorption at 2000 cm^{-1} [5]. It would be difficult to imagine the process without a structural change of the Si network [6]. Fritzsche even argued that the finding in Ref. [5] could be caused by mere structural change [7].

Although many experiments imply a possible light-induced structural change in *a*-Si:H, two difficulties prevent drawing a final conclusion from these results. First, since SWE is a colorful phenomenon, manifesting itself in various properties, the experimental results on SWE can often be understood in different ways, and light-induced structural change is not the only answer. Second, even though some measurements were more closely related to the structure than to the electron system, the results usually were not enough to answer whether the whole structure of the amorphous network or only some local configurations were changed. To find a deterministic answer to the problem one needs to investigate the behavior of a physical property which depends only directly on the structure no matter how the other properties of the sample change. We notice that one of the suitable quantities is the film thickness. This quantity is directly related to the structure of the sample and may have a detectable change when the whole amorphous network undergoes some rearrangement. However, the possible light-induced thickness change could be very small. Therefore, if we want to trace such a possible subtle change special attention should be paid to the stability of the measurements and to ensure that only the change of film thickness related to photoeffect is detected. To meet these requirements, we have developed a specially designed differential dilatometric method. By using this method a surprising photodilatation effect has been discovered in undoped *a*-Si:H films. The effect gives unambiguous and direct evidence of some light-induced instability of the Si network. Staebler-Wronski effect could be a posteffect of this instability.

The differential dilatometric method is schematically shown in Fig. 1. The essence of the method is that the thickness change of an *a*-Si:H film is detected by a capacitance sensor C_1 outside the sample. Thus, any internal process which does not cause a structural change in the film will not influence the value of C_1. A reference capacitor C_2 enables drawing out only the light-induced change. This was realized in the following way. An electrode covered the surface of the *a*-Si:H sample (Fig. 1). Two electrodes, e_1 and e_2, were separately evaporated on two identical etched pits in the quartz substrate q_2. The pits were made by photolithography to a homogeneous depth of $l = 10.9$ μm. When the sample was pressed on q_2 as shown in Fig. 1, electrode e_1 formed the capacitive sensor C_1 with half of e and e_2 formed sensor C_2 with the other half of e. The whole set was mounted to a thermostat in a vacuum chamber which had an optical window allowing only the half of *a*-Si:H film faced by e_1 to be exposed to light. During the whole measurements the thermostat was kept at 310 K except for annealing the sample. The temperature fluctuation was less than ±5 mK in both light-on and light-off states. A computer-controlled relay allowed the capacitances of C_1 and C_2 to

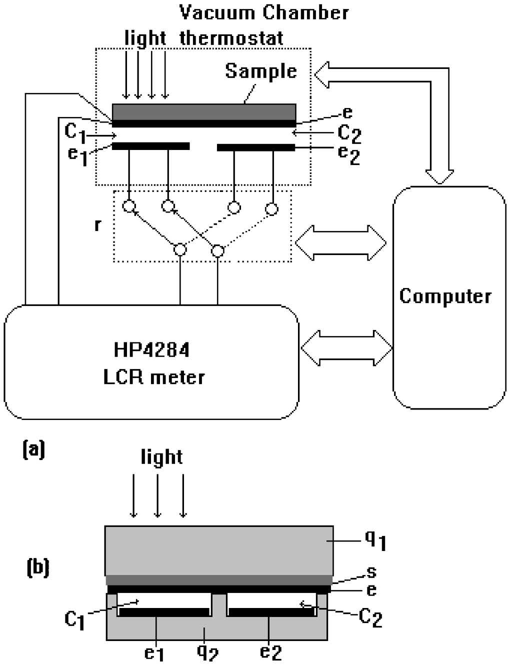

FIG. 1. (a) Schematic diagram of the differential dilatometric method. C_1—sensor of photodilatation; C_2—reference sensor; r—relay. (b) The structure of the sensors; q_1, q_2—quartz substrates; s—a-Si:H film; e, e_1, e_2—electrodes.

be measured alternately in time sequence by a HP 4284A precision LCR meter in four-leads configuration. In an ideal case C_1 and C_2 as well as their time drifts should be exactly the same when the light is off, so their ratio, $k = \frac{C_1}{C_2}$, should be close to unity and time independent. If there exists a thickness change caused by a light-excited structure rearrangement, C_1 should change when the light is on. The relative change of sample thickness reads

$$\frac{\Delta d}{d} = \frac{l}{d}\frac{\Delta k}{k}, \tag{1}$$

where Δk is the light-induced change of k, and d is the thickness of the a-Si:H sample. We see that Eq. (1) only picks up the change caused by illumination, and the changes caused by the factors common to C_1 and C_2 have been eliminated.

The undoped a-Si:H films were deposited on quartz substrate at 200 °C by rf glow discharge decomposition of $SiH_4 + H_2$ mixture in 1:4 ratio. The thickness of the samples were 4.8 μm. One sample was investigated in detail and another sample was measured briefly to be sure that the phenomenon observed here was reproducible. The samples were annealed at 430 K for 3 h before measurements to ensure the measurements starting from state A.

Before illumination, the sample was kept at 310 K, and C_1 and C_2 were continuously measured for long enough time (20 h) to check the stability of the readings. It turned out that the k value in state A was stable to 10^{-5}. Then a white light of 70 mW/cm^2, passing through a water filter to minimize infrared heating, was put on the C_1 side of the a-Si:H sample. A surprising photodilatation effect appeared when the light was on. Figure 2 presents the relative change of film thickness with illumination time. First, let us discuss the possibility that the phenomenon was caused by some parasite effects, especially heating effect. The possibility was checked in several ways. A very small thermocouple was placed across the a-Si:H film and the body of the thermostat, showing that the temperature inhomogeneity was always less then 0.1 K during both light-off and light-on states. Another experiment was that by putting a cutoff filter in the optical pass, allowing only infrared light through, we found no detectable change in k value. We also traced the change in C_1 and C_2 in the annealing process. Increasing the temperature to 430 K caused decreases of C_1 and C_2 by less than 1%, which means a temperature fluctuation of 1 K only brings an uncertainty in C_1 and C_2 less than 10^{-4}. Furthermore, the photodilatation shown in Fig. 2 is in the opposite direction compared to the heating effect. Since the quartz substrate had a thickness of 1.5 mm which was comparable to the distance from the center of illumination area to the edge of heat sink (~3 mm), the possible bending effect due to some local heating should be negligibly small. Especially, the most pronounced dilatation occurred at the beginning of illumination, in a time interval less than 0.2 s (see below), a simple estimation shows that in this time interval the local temperature increase is only ~60 mK. Later we will see that when illumination starts from the annealing state the dilatation behavior is remarkably different from that when illumination starts from the light-soaking state, though the heat flow pattern of the setup is essentially independent of which film state the process

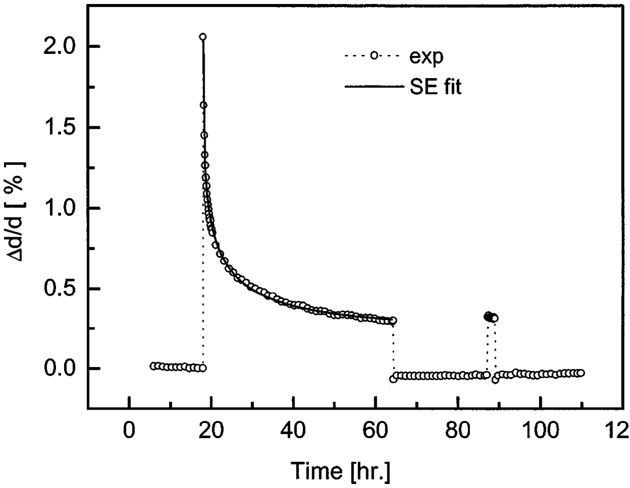

FIG. 2. The relative thickness change of the a-Si:H film with illumination time. The base line around $\Delta d/d = 0$ corresponds to the light-off state. The slow decay of the dilatation can be fitted to a stretched exponential rule Eq. (2) with the parameters: $\frac{\Delta d_0}{d} \sim 2\%$, $\Delta d_s/d = 0.24\%$, $\tau = 2.1$ h, and $\beta = 0.38$.

starts from. This fact provides a conclusive evidence that the phenomenon reported here is by no means a heating effect.

It is obvious from Fig. 2 that two time scales are involved in the photodilatation effect: a transient expansion followed by a slow decay in the process. The present experiment could not give an accurate answer as to how fast the transient response is. From the readings of 4284A we estimate that the process should be substantially quicker than the sampling time of the instrument (0.2 s). The transient photodilatation can be as large as $\sim 2\%$. The transient expansion then slowly decays according to a stretched exponential law (dotted line in Fig. 2). By fitting the data to

$$\frac{\Delta d}{d} = \frac{\Delta d_s}{d} + \frac{\Delta d_0 - \Delta d_s}{d} \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \quad (2)$$

where Δd_s is the saturation value of Δd after prolonged illumination and Δd_0 is the transient expansion at the starting of illumination, we find that the relaxation time $\tau \sim 2.1$ h, the dispersive factor $\beta \sim 0.38$, $\frac{\Delta d_0}{d} \sim 2\%$, and $\frac{\Delta d_s}{d} \sim 0.24\%$. We do not think that these values are intrinsic to the effect. Our measurements show that these parameters were sample dependent, which is understandable, considering the inhomogeneity always existing in a-Si:H samples. As we shall see later, even for the same sample, these parameters change by repeated annealing-illumination cycle.

Since the dilatometric method only feels the macroscopic volume change of the samples, the present discovery provides a direct and unambiguous evidence that the whole network of the a-Si:H films becomes unstable under light exposure. The Staebler-Wronski effect discovered about two decades ago could only be a posteffect of this light-excited structural instability. Any model, relating the SWE with the change of individual bonds, cannot be compatible with the photodilatation effect reported here. It has been a long-lasting dispute how the energy barriers between different configurations could be overcome to give rise to the light-induced defect formation in a-Si:H. Now we see that under illumination the initial expansion of the films can be as large as 1%–2%. This expansion would certainly lower the energy barriers and facilitates the transformation between different configurations. It is not a fortuity that the photodilatation from state A decays following similar stretched exponential rule observed in many other light-induced metastable changes of a-Si:H films [5,8].

To further confirm that the decay of photodilatation is related to a structural change in a-Si:H films and the change survives when light is off after the first prolonged illumination, the sample was kept at 310 K in light-off state for 23 h, and then switched to the light-on state again. This time we find that the transient photodilatation was still there, but the slow decay process almost disappeared (Fig. 2). The amplitude of the transient dilatation matched the value at the end of the last illumination. This is a strong evidence that the structures in state A and in state B are not identical.

The experiment of photodilatation was completed by annealing the sample again to 430 K for 6 h to see if the slow process could be recovered. After the heating treatment the film was kept at 310 K for another 20 h. Then the sample was exposed to light again. Indeed, the slow decay of the photodilatation reappeared after annealing (Fig. 3). This means that the main features of the photodilatation effect are reversible. However, some obvious differences exist: The amplitude of the initial thickness expansion upon light exposure is not as large as that observed in the first illumination, and the dilatation decays slower in the new cycle of experiment. The decay can be fitted to Eq. (2) by choosing the parameters as $\frac{\Delta d_0}{d} = 1.5\%$, $\frac{\Delta d_s}{d} = 0.38\%$, $\tau = 4$ h, and $\beta = 0.46$. We see that the structure of the a-Si:H film after repeated annealing-illumination treatment is not identical with the initial structure even when both are in state A. The result again proves that some structural change takes place during both illumination and annealing processes. The photodilatation effect is not fully reversible in the sense that after illumination of an a-Si:H sample you can never make its structure be an exact replica of its initial structure.

Since our experiments only measure the average dilatation of the sample, we cannot directly answer whether the effect is caused by some changes of inhomogeneous local structures (e.g., voids or clusters) and then spreading to the whole sample, or the whole network simultaneously responds to the light. As we mentioned earlier, the photodilatation effect involves two processes: a transient response and a slow decay. The slow process exists only when the sample goes from state A to state B,

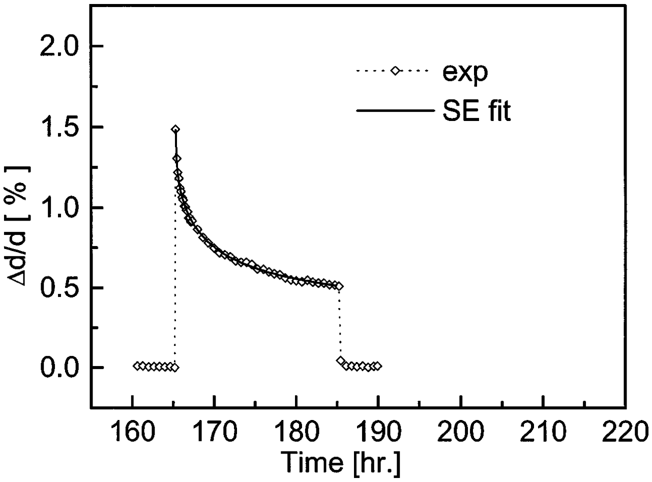

FIG. 3. The relative change of the sample thickness with illumination time after the sample was reannealed. The slow decay here can also be fitted to Eq. (2) but with different parameters: $\frac{\Delta d_0}{d} \sim 1.5\%$, $\Delta d_s/d = 0.38\%$, $\tau = 4$ h, and $\beta = 0.46$.

while the transient process occurs in both states. It is reasonable to think that the transient process corresponds to the response of the whole sample, while the slow process may involve the migration of atoms for some distance and hence resulting in more drastic structural changes in the sample.

Finally, we should say a few words about the mechanism of the surprising photodilatation effect. The effect is so new that at present we do not have enough information to make a clear microscopic picture. One possible origin is some internal "chemical pressure" or "dynamical pressure" which is photoactivated (e.g., the photoenhancement of hydrogen motion). Further investigation is needed to fully understand the phenomenon observed here.

In summary, we have discovered a photodilatation effect in undoped a-Si:H films. The effect unambiguously proves the light-induced structural change of the sample. The metastable change (Staebler-Wronski effect) could be a posteffect of this photodilatation which gives rise to a redistribution of different configurations in a-Si:H films. The present results not only are helpful to understand SWE, but the photodilatation effect is itself a very interesting phenomenon for further investigation as well.

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