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Citation: Applied Physics Letters **51**, 1804 (1987); doi: 10.1063/1.98528
View online: http://dx.doi.org/10.1063/1.98528
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Increase of doping efficiency by light soaking in boron-doped hydrogenated amorphous silicon

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(Received 11 June 1987; accepted for publication 30 September 1987)

Boron-doped hydrogenated amorphous silicon deposited at 100 °C exhibits a decrease of dark conductivity and an increase of doping efficiency, simultaneously, during band-gap light illumination. We prove that these two effects are bulk effects and that their origins are different. The decrease in dark conductivity is due to the creation of dangling bonds. On the other hand, the increase in doping efficiency anneals out with an activation energy of 1.66 eV. The increase in stretching mode absorption of boron-hydrogen has been observed after light soaking for the amorphous silicon-boron alloy film, and this appears to be related with the increase in doping efficiency of boron.

The decrease of conductivity during band-gap light exposure is the well-known Steabler–Wronski effect in hydrogenated amorphous silicon (*a*-Si:H).[1] Recently, the increase of dark conductivity after illumination, called persistent photoconductivity, has been observed for doping modulated *a*-Si:H *npnp*... superlattices[2] and in compensated films.[3] On the other hand, dark conductivity at 20 °C for doped *a*-Si:H films depends on the speed at which they are quenched from the thermal equilibrium value[4]; fast cooling results in a higher conductance. All of these effects in conductivity disappear completely after heating the samples at ~180 °C for 30 min.

We report here the first experimental verification of the increase of doping efficiency of boron during illumination in boron-doped *a*-Si:H. Our samples are boron-doped *a*-Si:H films deposited at 100 °C by glow discharge decomposition. For boron-doped *a*-Si:H the optical absorption edge becomes steeper and the light to dark conductivity ratio increases[5] as the substrate temperature is lowered from 350 down to 100 °C. It appears, therefore, that boron-doped *a*-Si:H deposited around 100 °C has a low density of states in the gap and a high photosensitivity compared with that deposited at ~250 °C. It should be noted that the optimum substrate temperature to deposit undoped *a*-Si:H is ~250 °C.

The conductivity data presented here were obtained with use of an electric field of 2.5×10^3 V/cm, for which the samples exhibited ohmic current-voltage characteristics. Before the coplanar conductivity was measured, the *a*-Si:H films were annealed in vacuum at 180 °C for 4 h to remove the surface adsorbates and the residual light-induced effects. The conductivity was measured by a programmable electrometer (Keithley model 617) interfaced to an Apple II microcomputer.

Figure 1 shows the effect of light exposure to 100 mW/cm^2 heat-filtered ($h\nu\geqslant1.6$ eV) white light from a tungsten halogen lamp on the annealed state of 100 ppm boron-doped *a*-Si:H film. The film displays a photoconductivity decay at all temperatures; the photoconductivity continues to decrease during light illumination, this is known as the Steabler–Wronski effect and is due to the creation of dangling bonds.

On the other hand, the dark conductivity decreases rapidly until 1 min illumination, and after 1 min it starts to

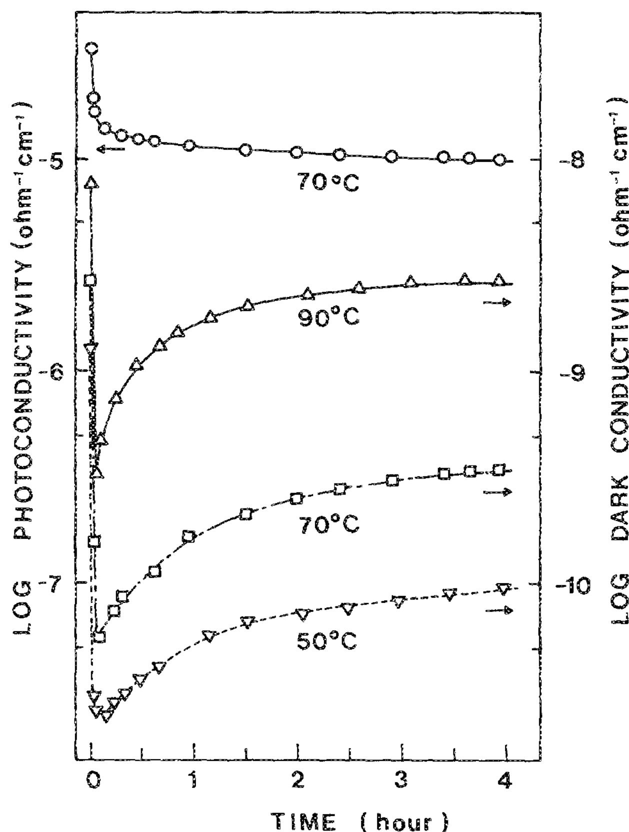

FIG. 1. Changes in dark conductivity and photoconductivity of 100 ppm boron-doped *a*-Si:H film, deposited at 100 °C and annealed at 180 °C for 1 h, as results of successive light exposures under AM1 (100 mW/cm^2). The temperature below the line indicates measurement temperature.

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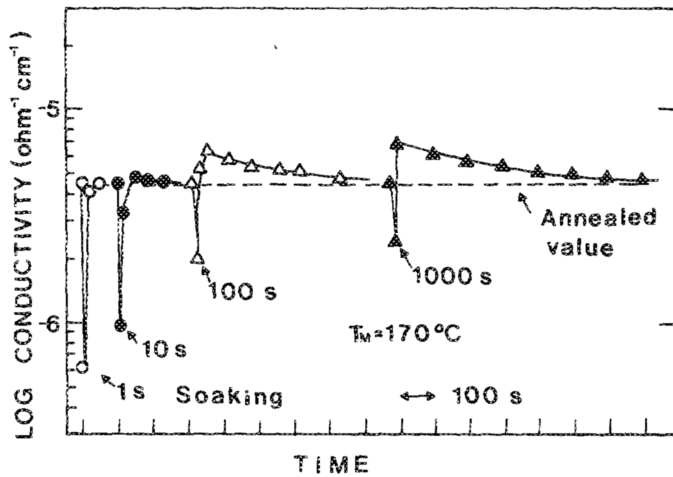

FIG. 2. Change in dark conductivity with time for 100 ppm boron-doped a-Si:H film as results of 1, 10, 100, and 1000 s light exposures at 170 °C. The soaking was done under 100 mW/cm^2 on annealed state for all cases.

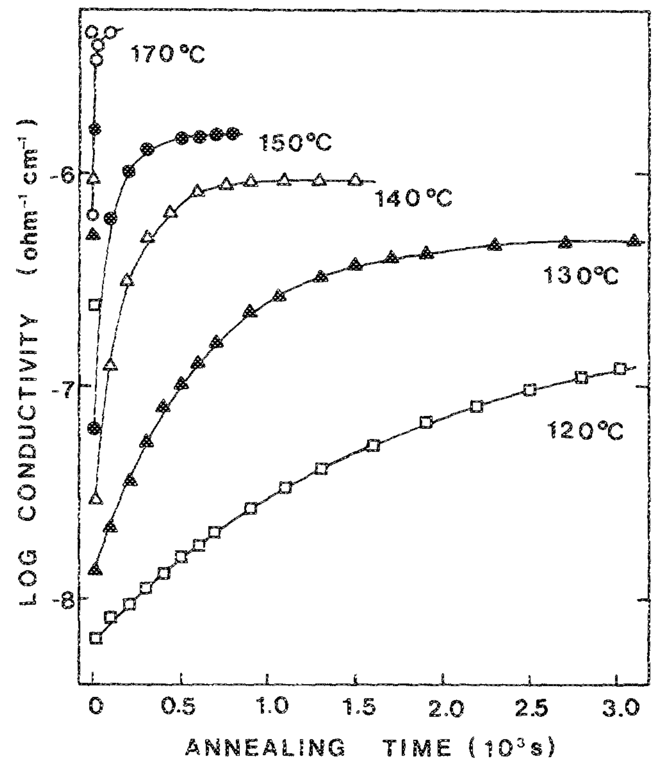

FIG. 3. Dark conductivity plotted against annealing time after 1 s light exposure for 100 ppm boron-doped a-Si:H at different temperature.

increase as shown in Fig. 1. The increasing rate accelerates as the sample temperature is raised. After removing the surface oxide layer of this sample by diluted HF solution, a similar behavior as shown in Fig. 1 was obtained. Furthermore, the early decrease and late increase in dark conductivity with exposure time have been observed in a-Si:H p^+-p-p^+ structures.[6] Therefore, the conductivity change shown in Fig. 1 is a bulk property of boron-doped a-Si:H. Accordingly, the increase in dark conductivity during light illumination should be explained as the increase in the doping efficiency of boron.

Figure 2 shows the changes in dark conductivity for 100 ppm boron-doped a-Si:H film as results of 1, 10, 100, and 1000 s light exposures at 170 °C. The light soaking was done on the annealed state for all cases. Upon 1 s illumination, the dark conductivity drops to ~1/7 of its original (annealed) value, and then conductivity starts to increase rapidly with time and goes to its annealed value within 100 s.

After 10 s illumination on the annealed state, the recovery in conductivity is similar to that of 1 s illumination, but the conductivity goes up above the original value and then starts to decrease slowly to the annealed value, as can be seen in Fig. 2. The magnitude of this excess (maximum-original) conductivity increases as the exposure time is prolonged. So we conclude that the annealing process is different between the two kinds of changes. The annealing process of the increase in conductivity is much slower than the decrease in conductivity and results in higher conductivity than the original value during the heating. From these annealing behaviors we conclude that the origins of the two kinds of changes are different. One is due to the creation of dangling bonds and the other is the increase of doping efficiency of boron during illumination. The changes in conductivity were completely annealed out within 1 h heating at 170 °C.

Figure 3 shows the temperature dependence of conductivity change with time after 1 s light exposure. In order to decrease the effect of the increase in conductivity on the light-soaked state, we limited the exposure time to 1 s. The fast annealing was obtained at the elevated temperature. From the recovery of conductivity with time we defined the relaxation time τ_R as the time required to anneal half of the change in conductivity as shown in the inset of Fig. 4.

The activation energy of annealing, obtained from 1 s light exposure, is 1.40 eV, and this value is higher than that of the Steabler–Wronski effect in boron-doped a-Si:H.[7,8] The conductivity change after light soaking can be annealed out at 100 °C, and the activation energy of annealing is 1.1 eV for 100 ppm boron-doped a-Si:H.[7] Even though we limited the exposure time to 1 s, the light-soaked state would involve both effects of dangling bond creation and the increase in doping efficiency. Therefore, the activation energy of 1.40 eV is somewhat overestimated as the true annealing activation energy of photocreated dangling bonds in boron-doped a-Si:H.

We also measured the activation energy of annealing for the increase of doping efficiency. As shown in the inset of Fig. 4, we define the relaxation time τ'_R as the time required to decrease half of the excess conductivity. We fixed the exposure time to be 1000 s. The observed activation energy is 1.66 eV, and this value is higher than that (1.50 eV) of the Staebler–Wronski effect in undoped a-Si:H. It is concluded, therefore, that the annealing process of the increase in doping efficiency is much slower than that of photocreated dangling bonds in boron-doped a-Si:H.

Now, let us discuss the microscopic picture of the increase in doping efficiency during light illumination in boron-doped a-Si:H. Tanielian *et al.*[9] reported that the conductivity of slightly n- or p-type a-Si:H films, whose conductivity activation energies are around 1 eV, increases after light illumination. We observed the early decrease and late increase of conductivity during illumination (see Fig. 1) for boron-

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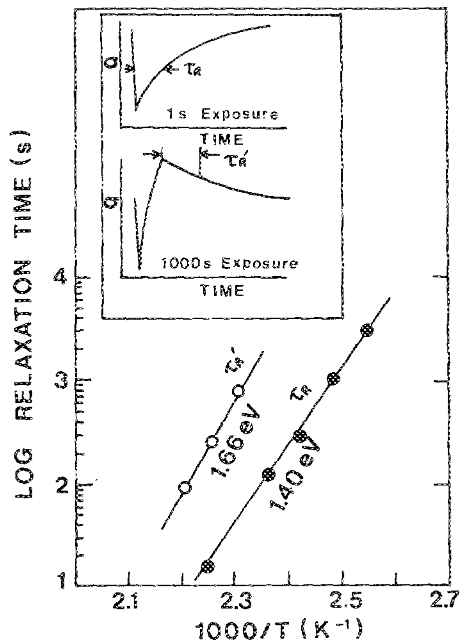

FIG. 4. Time necessary to reach a given level of dark conductivity vs $1/T$. Also plotted is the relaxation time which is defined as the time required to recover half of the decrease (τ_R) and of the increase (τ_R') as shown in the inset.

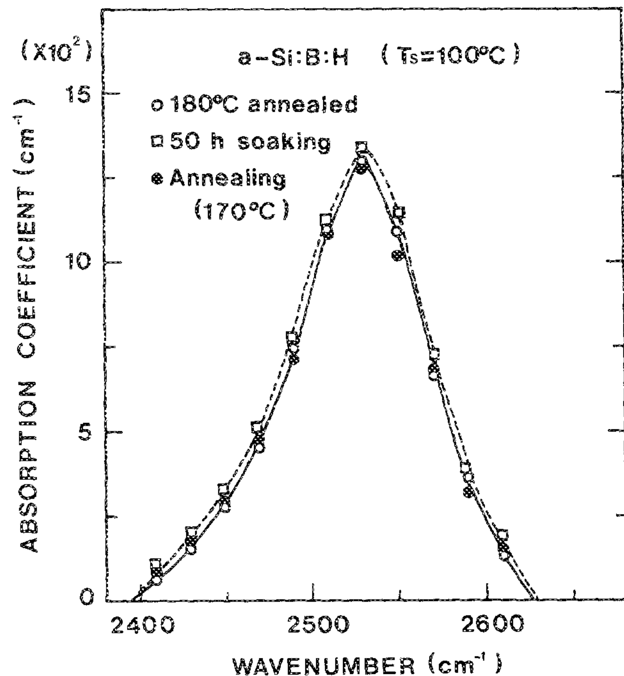

FIG. 5. Changes in IR absorption coefficient of B-H stretching modes in amorphous silicon-boron alloy film deposited with a gas mixture ($[B_2H_6]/[SiH_4] = 0.5$). The light soaking was done under 800 mW/cm^2 for 50 h. The annealing was done at 170 °C for 1 h.

doped a-Si:H films whose doping concentration ranges between 20 and 1000 ppm, and conductivity activation energy between 1.0 and 0.51 eV. However, this anomalous behavior as shown in Fig. 1 disappears after annealing the samples at above 250 °C. Therefore, the increase in conductivity is a general behavior of boron-doped a-Si:H deposited at low substrate temperature and annealed at less than 180 °C.

Acceptor activity of boron in p-type silicon can be neutralized by exposure to atomic hydrogen.[10] The deactivation requires a reaction that leaves the acceptor atom threefold coordinated with its neighbors. The existence of a Si–H bond near the neutralized boron atom has been found.[11] It is possible that there are many silicon–hydrogen bonds deactivating the boron acceptors in boron-doped a-Si:H because the conductivity of heavily boron-doped amorphous silicon can be decreased greatly by hydrogenation.[12] These hydrogens will attempt to bond covalently with borons during illumination because H-B-Si is likely to be a metastable configuration for a hydrogen atom.[13] If this interpretation is exact, the increase in boron-hydrogen (B-H) modes after light exposure will be obtained. For 100 ppm boron-doped a-Si:H films, the stretching mode absorption of B-H modes cannot be measured by a Fourier-transform infrared (IR) spectrophotometer because the concentration of B–H bonds is less than the detection limit. For our boron-silicon alloy film prepared with a gas mixture of $[B_2H_6]/[SiH_4] = 0.5$, the reversible change in absorption coefficient of B-H stretching modes has been obtained as shown in Fig. 5. The absorption of B-H stretching mode increases after light soaking and the increase in IR absorption can be completely reduced by heating the films at 170 °C for 1 h. Therefore, the increase in doping efficiency for boron-doped a-Si:H appears to be due to the transfer of hydrogen from Si-H to B-H during light exposure. Note that the increase in dark conductivity as well as the increase in B-H stretching modes can be removed after heating at 170 °C for 1 h.

In conclusion, we have demonstrated that the doping efficiency of boron increases during illumination in boron-doped a-Si:H. We prove that this effect is a bulk property and that the origin is different from the creation of dangling bonds during illumination. The increase in doping efficiency anneals out with an activation energy of 1.66 eV, and it may be related with the increase in B-H stretching mode absorption after light soaking.

This work was supported by the Korea Science and Engineering Foundation.

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