

# Reversible conductivity changes in discharge-produced amorphous Si<sup>a)</sup>

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A new reversible photoelectronic effect is reported for amorphous Si produced by glow discharge of SiH<sub>4</sub>. Long exposure to light decreases both the photoconductivity and the dark conductivity, the latter by nearly four orders of magnitude. Annealing above 150°C reverses the process. A model involving optically induced changes in gap states is proposed. The results have strong implications for both the physical nature of the material and for its applications in thin-film solar cells, as well as the reproducibility of measurements on discharge-produced Si.

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Amorphous Si produced by glow discharge of SiH<sub>4</sub><sup>1,2</sup> has been used to fabricate thin-film solar cells<sup>3,4</sup> with efficiencies as high as 5.5%.<sup>5</sup> The success of this material stems from its high optical absorption in the visible region of the spectrum,<sup>2,3,6</sup> its unusually good electronic properties<sup>7</sup> when deposited on substrates heated to 200–400°C,<sup>2,6,8</sup> and the ability to control its conductivity with dopants.<sup>1,3,8</sup> We report here, for the first time, a reversible photoelectronic effect not previously observed in this material. The effect involves (a) an optically induced decrease in both the photoconductivity and dark conductivity and (b) restoration to the original state by annealing above 150°C. Although similar in some respects to negative photoconductivity observed in other materials,<sup>9–11</sup> the effect reported here is unique in that enormous conductivity changes are involved, nearly four orders of magnitude in some cases, and the changes are stable at room temperature. The results have strong implications on both the physical nature of glow discharge amorphous Si and on its applications. In addition, it may be a significant factor in the scatter seen in previous studies of this material.

We have seen this effect, with interesting variations in detail, for samples prepared at different substrate temperatures using rf and dc discharge techniques, and in ones lightly doped with P, B, and As. Here we present results obtained from an *n*-type undoped sample. It was chosen because of the importance of this material in high-efficiency solar cells.<sup>3–5</sup>

The sample was deposited on a fused quartz substrate held at ~320°C in an rf glow discharge of SiH<sub>4</sub>. It was ~0.7 μm thick. All electrical measurements were made along the film plane, using a four-stripe Cr pattern deposited on the substrate. The stripe separation was 1 mm. To assure good Ohmic contact, a thin Sb film was deposited on the Cr pattern prior to the a-Si deposition. Voltages from 10 to 1200 V were applied to the outer two contacts to supply the current. The voltage across the inner two electrodes was monitored to verify that the contact properties did not change during the heating or optical exposures. Currents and

voltages were measured with Keithly 610A and 602B electrometers. Optical exposures were done with light from a tungsten source focused onto the film from above. The light was filtered to pass only the wavelength range 6000–9000 Å. Shorter wavelengths were avoided to ensure that the radiation was absorbed uniformly through the sample's thickness. The incident power was ~200 mW/cm<sup>2</sup>. Photoconductivity measurements were made with illumination from a tungsten-iodine lamp through a red filter (Corning 2-61).

The reversible effect begins with a sample in what could be considered a thermally stable state (hereafter called state A). It is reached by annealing the sample above 150°C and then cooling it to room temperature in the dark. Figure 1 shows what happens when such a sample is exposed to light at room temperature. Both the photoconductivity and the dark conductivity decrease. The photoconductivity is shown during the exposure and decreases by nearly a factor of 8 after 4 h. A more spectacular change is seen after the light is turned off. The dark conductivity is down by nearly four orders of magnitude from its initial value in state A. This new conductivity state (hereafter called state B) is stable at room temperature. It is not an equilibrium state, however, since it depends on the total exposure that the sample received. We have found that an exposure that produces the same photoconductivity will

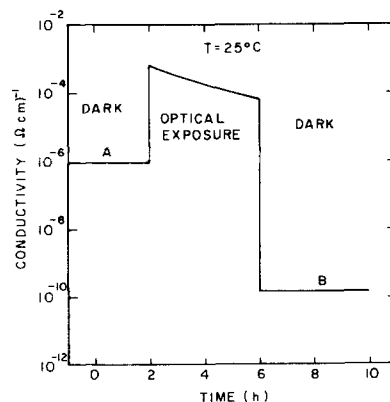


FIG. 1. Conductivity as a function of time before, during, and after exposure to ~200 mW/cm<sup>2</sup> of light in the wavelength range 6000–9000 Å.

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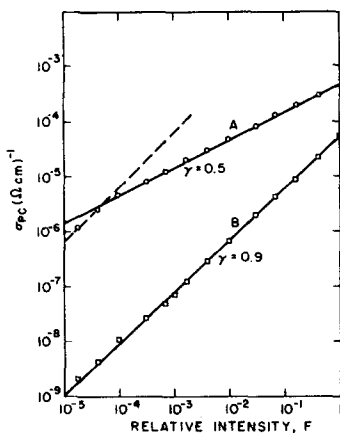


FIG. 2. Photoconductivity as a function of volume absorbed light intensity (curve A) before and (curve B) after the exposure shown in Fig. 1.

also decrease the conductivity at nearly the same rate, independent of the wavelength of the incident light. This was checked between 6000 and 9000 Å, a wavelength range where the photoconductivity per absorbed photon varies by an order of magnitude.<sup>6</sup> A check at -78 °C showed a similar dependence on photoconductivity. No change in the optical absorption nor photoconductivity spectrum was ever observed.

The exposure also changes the photoconductive behavior of the a-Si. Figure 2 shows the photoconductivity  $\sigma_{pc}$  of the two states plotted as a function of incident light intensity,  $F$ , from  $\sim 10^2$  to  $\sim 10^{-3}$  mW/cm<sup>2</sup>. Care was taken to prevent the film from changing during the measurement, particularly in state A. The dependence of  $\sigma_{pc}$  on  $F$  follows the relation  $\sigma_{pc} \propto F^\gamma$  where in state A  $\gamma = 0.5$  over nearly five orders of illumination, changing to  $\gamma \approx 0.9$  at values  $\sigma_{pc} \sim \sigma_D$  (dark conductivity). In state B,  $\gamma = 0.9$  over five orders of intensity, where  $\sigma_{pc} \gg \sigma_D$  even at the lowest intensities used. The difference in  $\gamma$  ( $\sim 0.5$  for state A,  $0.9$  for state B), reflects a dramatic difference in the recombination kinetics of the two states. Before exposure, the recombination has the bimolecular form; after exposure it is monomolecular. In addition, the change in  $\gamma$  accentuates the ratio between the  $\sigma_{pc}$  values of states A and B at low light levels; the ratio is  $\sim 500$  at  $10^{-3}$  mW/cm<sup>2</sup>. Since the photoconductivity in this material is due primarily to electrons,<sup>7</sup> this reflects a drastic reduction of the electron lifetime. In spite of these changes, the photoconductivities of both states exhibit approximately the same low activation energy of  $\sim 0.05$  eV between 0 and 100 °C.

The sample is returned to state A by heating it to about 150 °C. Figure 3 shows the dark conductivity as a function of temperature through this process. In state B, the conductivity increases with increasing temperature following the expression  $\sigma = \sigma_0 \exp(E_a/kT)$  with an activation energy  $E_a$  of 0.87 eV and a  $\sigma_0$  of  $\sim 10^5$  (Ω cm)<sup>-1</sup>. ( $k$  is Boltzmann's constant and  $T$  is the absolute temperature.) Below 150 °C, the sample is stable and can be repeatedly measured. Above this temperature, however, it relaxes within a few hours

or less back to state A. Upon cooling, the conductivity follows a smaller activation energy (0.57 eV) and a smaller  $\sigma_0$  [ $\sim 4 \times 10^3$  (Ω cm)<sup>-1</sup>], ending up at the original conductivity of Fig. 1. At that point, the whole procedure can be repeated with the same results. The same behavior is seen in either air or in a dry nitrogen atmosphere.

The relaxation time to state A is shown in the inset of Fig. 3 as a function of temperature. It varies according to  $\tau_R = \tau_0 \exp(E_r/kT)$  where  $E_r$ , the activation energy, is 1.52 eV and  $\tau_0$  is  $3.6 \times 10^{-15}$  sec. Extrapolation of this to room temperature predicts a relaxation time of  $3 \times 10^4$  years.

This general behavior, i.e., an optically induced increase of  $E_a$  and  $\sigma_0$  that anneals out above  $\sim 150$  °C, is also seen in lightly doped samples. Samples heavily doped with P or B show no change of any kind under optical exposure. In addition, none of these effects depend on the presence of an electric field during exposure.

We now discuss possible models. Phenomenologically, the effect of the optical exposure is to increase the density of gap states. The introduction of new gap states can result in shorter electron lifetimes, producing the observed lowering of photoconductivity. In addition, they can move the Fermi level away from the mobility edge for electrons, leading to the lower dark conductivity and the higher activation energy. This model is consistent with previous studies on discharge-produced films deposited at substrate temperatures below  $\sim 300$  °C.<sup>6,8</sup> In these studies, it was proposed that the changes in the a-Si properties caused by using a lower substrate temperature are associated with an increase in the density of gap states. Indeed, we find that such

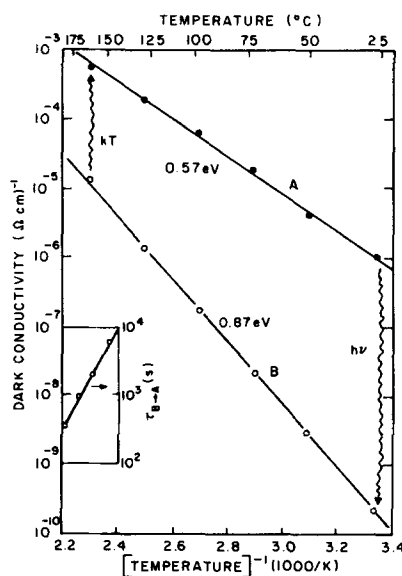


FIG. 3. Conductivity as a function of temperature for a sample in the thermally stable state (curve A) and in the metastable state produced by optical exposure (curve B). The inset shows the variation of relaxation time state B to state A with temperature. It has the same temperature scale as the main figure.

samples (e.g., those prepared at  $\sim 200^\circ\text{C}$ ) have dark conductivity and photoconductivity<sup>12</sup> properties, even in the annealed state, quite similar to the optically induced state, B, reported here (for a sample prepared at  $\sim 320^\circ\text{C}$ ). The introduction of new gap states is also consistent with studies on  $\text{He}^+$  bombardment of lightly doped samples.<sup>13</sup>

A specific mechanism by which light can introduce gap states is as yet not clear, but some general comments can be made. First we can rule out a gross structural or photochemical change of the material, since one would expect a corresponding change in the optical properties, and this is not observed. Second, a direct photoinduced change of a localized defect does not appear likely in view of the correlation of the effect with the photoconductivity. We find that light that produces a given photoconductivity also produces nearly the same change, irrespective of the photoconductivity per absorbed photon. A possible model is that a localized defect undergoes a metastable structural change (e.g., local bond reorientation) when it traps or acts as a recombination center for photogenerated charge carriers in extended states. A localized structural rearrangement has been observed in  $\text{SiO}_2$ ,<sup>14</sup> but it has not been reported to produce the type of effect reported here. In discharge-produced a-Si, however, where compensation of dangling bonds by hydrogen atoms is thought to play an important role,<sup>15,16</sup> a bond reorientation could have a large influence on the effective density of gap states. These films, in fact, contain 10–20 at. % of bonded hydrogen.<sup>12</sup> The hydrogen content, moreover, is stable at annealing temperatures below the deposition temperature.<sup>12</sup>

Previous explanations for negative photoconductivity have involved a different model.<sup>9–11</sup> The light transfers charge carriers to centers that are in poor communication with the rest of the material. Once there, they cannot contribute to the conductivity. Electric fields set up by the charge transfer may also decrease the mobility.<sup>17</sup> This model, however, requires an unlikely combination of trap properties.<sup>10,11</sup> Moreover, the specific way in which it could lead to our observed results, particularly the change in  $\gamma$ , is not clear. More experiments are required, particularly on the nature and distribution of the gap states, before we can make more definite statements concerning the relative merits of the models discussed here.

The influence of this effect on solar cell performance has not yet been fully evaluated, but we can point out some of our preliminary observations. First, the change in dark conductivity does not necessarily limit the performance because the bulk series resistance in

an operating cell is determined by the photoconductivity<sup>5,18</sup> and this does not change greatly under high illumination. Second, the cell collection efficiency is presently limited by the hole transport but nothing can be inferred about this from the photoconductivity changes reported here; they may be due entirely to electrons. Third, cells made with discharge-produced material show no degradation over extended operation under simulated AM1 illumination,<sup>5</sup> suggesting that the exposed material is still suitable for solar cell use. Research is continuing on the nature of the effect reported here and its impact on the performance of solar cells.

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