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Persistent photoconductivity in doping-modulated multilayers and compensated thin films of hydrogenated amorphous silicon

S. C. Agarwal* and S. Guha
Energy Conversion Devices, Inc., 1675 West Maple Road, Troy, Michigan 48084

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Persistent photoconductivity (PPC) has been studied in doping-modulated (*npnp* . . .) hydrogenated amorphous silicon (*a*-Si:H) multilayers as well as compensated *a*-Si:H films. The built-in field in the multilayers is varied by changing the dopant concentrations. It is concluded that charge separation in this built-in field alone cannot explain PPC in these *npnp* . . . structures. Experimental evidence is presented to argue that PPC in layered as well as compensated films arises from special centers made of phosphorous-boron complexes, which are in poor communication with the rest of the material.

There has been a great deal of interest in the study of layered structures of amorphous silicon alloys.[1-5] An interesting persistent photoconductivity effect (PPC) has recently been observed[4] in the doping-modulated structures consisting of alternate layers of *n*- and *p*-type amorphous hydrogenated silicon alloy (*a*-Si:H). PPC in these structures manifests itself as an enhanced dark conductivity parallel to the layers after a brief exposure to light, which decays very slowly.

Such PPC effects are known to occur[6] in crystalline GaAs doping superlattices at ≈ 4 K, and have been understood[7] in terms of the increased lifetime of carriers, resulting from their separation in the built-in field. There are important differences, however. In doping-modulated *a*-Si:H, PPC is not restricted to low T, but is observed even at 300 K or higher. Further, in the crystalline doping superlattices of GaAs, the enhanced lifetime of carriers results in a large photoconductivity enhancement.[7] In contrast, the *npnp* . . . layers of *a*-Si:H show no significant increase in photoconductivity,[4] although the PPC effect is much larger.

In this connection, it is interesting to note that Mell and Beyer[8] found that their compensated *a*-Si:H samples, having no layered structure, showed an enhanced dark conductivity upon exposure to light at room temperature. The length of exposure required here is, however, about an order of magnitude larger. The similarities in the PPC observed in the two cases are nevertheless striking, and one wonders whether PPC in the *a*-Si:H *npnp* . . . multilayers is the result of charge separation alone, in the built-in fields between the *n* and *p* layers.

In this Rapid Communication, we present our studies of PPC on *a*-Si:H *npnp* . . . multilayers and also on compensated unlayered samples, in which the dopings are varied over a large range. We show that PPC is primarily caused by the presence of phosphorous-boron (P-B) complexes and charge separation alone cannot explain PPC in these structures.

The films are grown by the glow discharge method. The substrate is Corning 7059 glass which is kept at 275 °C during the deposition. All samples are about 4000 Å thick. The layered samples consist of six *n*-type and five *p*-type layers of thickness ≈ 360 Å each, deposited alternately, by switching gases in a single chamber system. PPC on *npnp* . . . structures, in which *n* and *p* layers are deposited in separate chambers, is found to be similar to those prepared in the single chamber system.[9]

Graphite electrodes ≈ 1 mm apart in a coplanar geometry are used to measure electrical conduction. Layered samples are scratched before applying the contacts, to ensure contact to all the layers. The unlayered compensated films are Ohmic up to the highest measuring electric fields $\approx 10^3$ V/cm. But the layered films are non-Ohmic, even for the smallest field used (≈ 10 V/cm). Further, upon application of this low field in dark (after heat drying in vacuum at 200 °C for 30 min), the current is found to be large initially. It settles to a smaller equilibrium (i_d) value in a few hours. We believe that this effect, which is similar to that found in the *a*-Si:H/*a*-SiN$_x$:H heterostructures,[10] has to do with heterogeneities and states at the interface.

To measure PPC, the sample is first heat dried, in dark, at 200 °C for about 30 min to erase the effect of any prior exposure to light. After cooling, a field of 10 V/cm is applied. Upon reaching a steady-state dark current i_d the sample is exposed to a band-gap light of intensity ≈ 10 mW/cm^2 from a tungsten halogen lamp (6000 Å $\leq \lambda \leq$ 8000 Å).

Both compensated as well as layered samples show PPC, in agreement with the published results.[4,8]

Figure 1 shows the PPC results for four layered samples, in which the *n*-layer doping is kept fixed at 80 ppm, and the

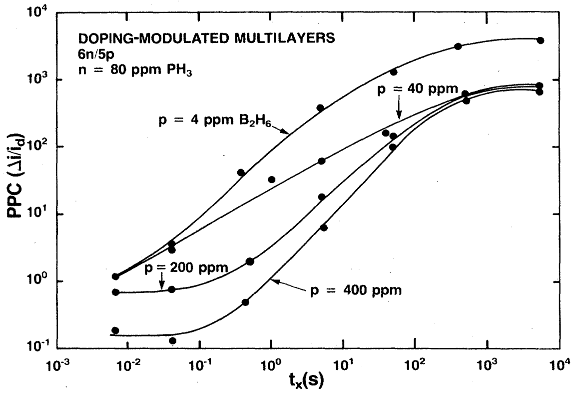

FIG. 1. Dependence of PPC ($\Delta i/i_d$) on the exposure time (t_x) for doping-modulated layered samples consisting of alternately deposited six *n*-type and five *p*-type layers. The *n*-layer doping is fixed at PH$_3$/SiH$_4$ = 80 ppm. The *p*-layer doping is varied by changing the ratio B$_2$H$_6$/SiH$_4$ between 4 and 400 ppm.

p-layer doping is varied between 4 and 400 ppm. We call PPC, to be the ratio of the excess current (Δi) measured after 10 min of switching off the light, to the steady-state dark current (i_d) in the unexcited state. A smaller boron content in the p layer results in a larger PPC (i.e., $\Delta i/i_d$) for any given exposure. It is, however, interesting to note that a sample having zero boron content in the p layer (i.e., *nini* . . .) shows no PPC at all.

The variation of PPC with different levels of phosphorous doping shows similar trends. For the diborane level fixed at 40 ppm, a decrease in the phosphine concentration for the n layer from 2000 to 80 ppm results in an increased PPC. Also, as before, for the sample in which the n layer is replaced by the undoped intrinsic layer, (i.e., *ipipi* . . .) no PPC is found. This is in agreement with the published results of Sakata, Hayashi, Yamanaka, and Satoh,[11] who also did not observe any PPC in their *pip* structures.

The doping-level dependence of PPC in our compensated samples is shown in Fig. 2. Here, we have kept the p doping fixed at 40 ppm and varied the n doping. We see that $n = 800$ ppm gives the maximum PPC. Freshly made boron-doped samples show no PPC, but a small PPC is sometimes observed after storing them in air for a few days. It is probably related to the presence of a surface oxide layer in these samples,[12] as it disappears upon etching. In contrast, PPC in our compensated samples does not go away upon similar etching treatment. Figure 2 also shows the effect of decreasing the p-level doping. As p doping is lowered from 40 to 20 ppm, we observe a smaller PPC. A sample having no boron doping shows no PPC at all. These trends are qualitatively similar to those of the layered samples. The details do not match quantitatively, however. For example, the exact doping levels for which maximum PPC is observed in the two cases differ. Further, the magnitude of PPC in compensated samples is generally smaller than that observed in the layered ones, especially at small exposure times (t_x). Also, the saturation sets in for $t_x > 10^4$ s, which is about 10 times larger than the layered samples.

Now we compare our results on the compensated samples with the findings of Mell and Beyer[8] (Fig. 3). In our samples, PPC is largest when the Fermi level is ≈ 0.6 eV away from the conduction band. For the data of Mell and Beyer it occurs at ≈ 0.7 eV. Considering the fact that the absolute doping concentrations are not exactly matched in the two cases, the agreement is fair.

Once again, there are similarities between these and the observations obtained from the layered samples. A quantitative comparison is not possible because, as noted before, the layered samples are usually non-Ohmic. However, we have observed that the layered structures that show a large PPC have a negative thermopower, near room temperature. This agrees with the result on the compensated samples, where the samples that show a large PPC are also n type.

The observation that the PPC effect is larger in the layered samples as compared to the unlayered compensated ones might appear to suggest that charge separation enhances PPC. If we try, however, to increase the built-in field by increasing the separation between the Fermi levels of the n and p layers, we get a smaller PPC. Table I shows the results for samples with n-layer doping fixed at 80 ppm and a variable p doping, so that the separation between the Fermi levels ΔE_F^{n-p} varies from 0.58 to 1.12 eV. The sample with the smallest ΔE_F^{n-p} ($=0.58$ eV) has the largest PPC. This sample also has the smallest doping concentrations and, therefore, the smallest built-in field. As the p-layer doping is increased, ΔE_F^{n-p} and the built-in field increase, but PPC is found to decrease. This is contrary to what one would have expected, if charge separation in the built-in field between the layers alone were responsible for PPC.

These considerations and the similarities between the layered and the compensated samples indicate that the PPC in the two cases might have the same origin.

Mell and Beyer[8] have suggested the possibility of the excess conductivity arising from the slow trapping in "isolated centers" in their compensated samples. Since PPC is maximum when the Fermi level lies in the upper half of the gap (Fig. 3), these centers may be situated in the upper half of the gap. Thus, they are filled with electrons when the Fermi level is above them. On shining light, they capture holes, leaving electrons behind to conduct. When the Fermi level is below them these traps are empty, and when it is too close to the conduction band, the dark current is large. Both these situations will give smaller PPC, which qualita-

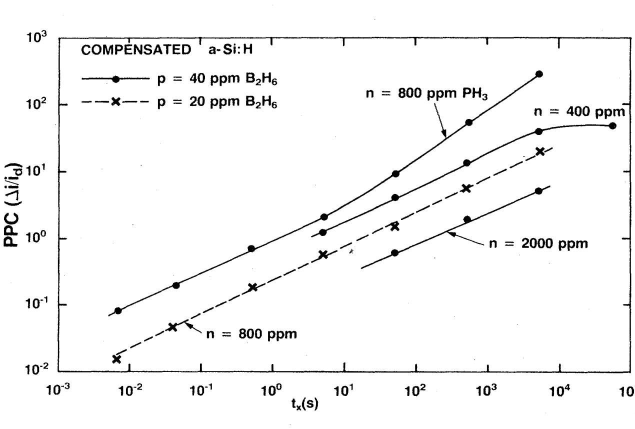

FIG. 2. Dependence of PPC ($\Delta i/i_d$) on the exposure time (t_x) for compensated samples. Dots are for samples in which B_2H_6/SiH_4 doping is kept fixed at 40 ppm and PH_3/SiH_4 doping is varied between 800 and 2000 ppm. Crosses denote data for a compensated sample in which PH_3/SiH_4 is 800 ppm and B_2H_6/SiH_4 is decreased to 20 ppm.

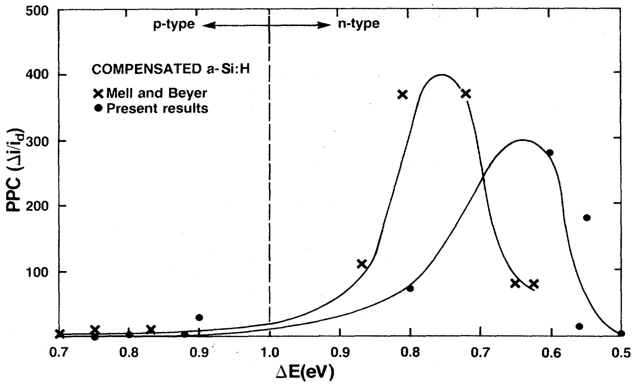

FIG. 3. PPC ($\Delta i/i_d$) as a function of activation energy (ΔE) of dark conductivity in the heat-dried state. The mobility gap is chosen to be 2.0 eV. The dots represent our data and the crosses are from the data of Mell and Beyer (Ref. 8).

TABLE I. PPC observed after 10 min, after a 5-s exposure to band-gap light, for layered samples with six n-type layers containing PH_3 doping of 80 ppm by volume of SiH_4 and five p-type layers of varying B_2H_6 doping concentrations, as shown. The activation energy is measured on a separate 3000-Å-thick calibration sample for each layer and is $\Delta E_{Fn} \approx 0.18$ eV for the n layer. The mobility gap is assumed to be 2.0 eV.

p-layer doping B_2H_6/SiH_4 (ppm)	Activation energy ΔE_{Fp} (p layer) (eV)	Difference in Fermi levels $\Delta E_F^{n-p} \approx 2.0-(\Delta E_{Fp}+\Delta E_{Fn})$ (eV)	PPC ($\Delta i/i_d$)
4	0.86 (n type)	0.58	320
40	0.94	0.78	50
200	0.75	0.97	17
400	0.70	1.02	6
1000	0.60	1.12	<1

tively explains the observed peak in Fig. 3. In view of the long time constants, however, they must have extremely small cross sections, or have barriers.

Since the undoped films or those having only one dopant (B or P) do not show PPC, we think that these centers might result from the formation of P-B complexes in these compensated films.

In the layered samples, such complexes can certainly be formed at the interfaces. In addition, since the samples are made at a high substrate temperature, the dopants are likely to diffuse from one layer to the other, and the possibility of formation of such complexes well inside the layers is also quite high. Matsumura, Maeda, and Furukawa[13] have measured the diffusion constant of B atoms from a doped to an undoped a-Si:H layer to be $D \approx 10^{-16}$ cm^2/s at 275 °C. This implies that during deposition (i.e., more than $\frac{1}{2}$ h) significant amounts of dopants have a chance to diffuse and intermix in at least about $\sim$100-Å layer adjacent to the interface.

There are difficulties, however. The effect of light exposure in our present model is to raise the Fermi level in the compensated material, thus making more electrons available for conduction. Since only a fraction of a layered sample can be expected to have compensated regions, the PPC in the layered samples should have been smaller. It is, however, important to recognize that the detailed nature of the transport process in the layered structures is quite different from that in the compensated material. In the former, current tends to flow through the low-resistance field-free region, the thickness of which is determined by the doping levels and the width of the individual layers. In the case of compensated material, on the other hand, current flows through the bulk. In addition, because of interdiffusion of dopants, the layered samples are likely to have a gradient of P and B concentrations. This is likely to result in a less uniform distribution of P-B complexes than expected in the compensated material. It is therefore not surprising that PPC in the two cases is not identical.

Let us now look at the saturation of PPC with t_x in the two cases. We find that at high temperatures ($T > 400$ K), in both cases, PPC for shorter exposure times is larger than PPC for longer exposures.[9] This indicates that the observed "saturation behavior" at room temperature is not a simple saturation, but results from two opposing effects: (i) a PPC effect which enhances the dark conductivity, and (ii) the light-induced Staebler-Wronski effect,[14] which usually reduces the dark conductivity.

Thus, our model explains, at least qualitatively, the observed behavior of PPC. A more quantitative discussion is not possible now, because this would require the knowledge of the compositional variation of the film as one moves from one layer to the other and of the changes in the depletion widths upon exposure to light.

At present, however, we cannot entirely rule out alternative explanations. Centers located in the upper half of the mobility gap in the Borne doped layers can also explain our results. The absence of PPC in the *ipipi* . . . multilayers and the unlayered Borne doped films can then be explained because the Fermi level in these layers is below the centers, thus making them empty. In addition, we cannot rule out the light-induced creation or annihilation of other defects. These must be created, in the regions where both phosphorous and boron can be found, because no PPC is observed in singly doped films. Finally, the carrier separation in built-in n-p fields might enhance PPC in the layered structures, although it does not seem to be the main cause of PPC.

In conclusion, we have studied the PPC effect as a function of the built-in field in the *npnp* . . . multilayers. It is found that there is no positive correlation between PPC and the built-in field. Charge separation due to built-in field alone cannot therefore explain PPC in the layered films.

Based on experimental evidence, it is argued that PPC in layered, as well as compensated, films arises from special centers which are most probably P-B complexes, which are in poor communication with the rest of the material. It has been pointed out that the observed saturation of PPC with exposure time is most likely a combination of two opposing effects: (i) PPC effect, which increases dark conductivity, and (ii) the Staebler-Wronski effect, which tends to decrease it. The differences in the detailed behavior of PPC in the compensated and layered samples are explained in terms of different conduction mechanisms in the two cases.

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[*] On leave from the Department of Physics, Indian Institute of Technology, Kanpur 208 016, India.

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