Persistent photoconductivity in compensated amorphous silicon

Byueng-Su Yoo, Yoon-Ho Song, and Choochon Lee
Department of Physics, Korea Advanced Institute of Science and Technology,
P.O. Box 150, Cheongryang-ni, Seoul 130-650, Korea

Jin Jang
Department of Physics and Research Institute for Basic Sciences, Kyung Hee University,
Dongdaemoon-ku, Seoul 131-701, Korea
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Persistent photoconductivity (PPC) in compensated amorphous silicon (*a*-Si:H) has been investigated. Single-carrier injection was performed with use of Schottky-barrier structures. Only hole injection can give rise to the PPC in compensated *a*-Si:H, with the result that the PPC is not a recombination-enhanced effect. A close correlation between the magnitude of the PPC and the defect density obtained from the constant photocurrent method was observed. On the basis of the experimental results, we discuss the existing models and propose a new model for the PPC in compensated *a*-Si:H films.

I. INTRODUCTION

Several laboratories have recently reported the persistent photoconductivity (PPC) in compensated[1,2] as well as in doping-modulated amorphous silicon (*a*-Si:H) superlattice films.[2–7] The PPC in these films manifests itself as an enhanced dark conductivity by several orders of magnitude after a brief white-light exposure, which decays very slowly at room temperature over a few days.

Agarwal and Guha[2] found the similarities of the PPC behaviors observed in compensated and in *npnp* multilayered *a*-Si:H films. Thus they explained their results in terms of special hole traps (P-B complex centers), which do not act as recombination centers.

On the other hand, Kakalios and Street[8] suggested the faster equilibration rate of boron-doped *a*-Si:H and the layering, which spatially separates the photogenerated electrons and holes, as the origin of PPC in *npnp* multilayered *a*-Si:H films. Then they also indicated that the PPC in compensated *a*-Si:H films is identical in origin to the PPC in *npnp* multilayers by assuming the microscopic *n*-*p* junction field in compensated films.

Although several laboratories have agreed that the carrier separation by built-in *n*-*p* junction field in *npnp* multilayers might enhance the PPC, the origins of the PPC in compensated and multilayered films are still controversial. In this work, we observed that the PPC in compensated films is limited by the injected hole density, not electron-hole pair density, and then we found a strong correlation between the PPC and the subband gap optical absorption. From these results, we propose a new model for the PPC in compensated films, which is different from the origin in *npnp* multilayers.

II. EXPERIMENTS

The compensated *a*-Si:H films were deposited on 7059 Corning glass for coplanar structure and on the indium tin oxide (ITO) –coated glass substrates for Schottky-barrier (SB) structure by rf glow-discharge decomposition at 250 °C. To ensure an Ohmic or low-resistance contact in SB, the 500-Å-thick P-doped (n^+-type) *a*-Si:H layers were deposited on ITO-coated glass substrates before the deposition of compensated films. All compensated films reported in this work have doping concentrations of $[PH_3]/[SiH_4]=[B_2H_6]/[SiH_4]=500$ ppm. The SB contacts were formed by evaporating semitransparent Pd electrodes of 1 mm^2 area on the *a*-Si:H surface, giving a [transparent conducting oxide (TCO)]/(n^+/compensated *a*-Si:H)/Pd structure. The total thickness of *a*-Si:H was about 1 μm.

Before measuring conductance, the films were heated up to 180 °C in a vacuum of 10^{-6} Torr for 30 min to remove the effect of prior light exposure. Electron-hole–pair generation and single-carrier injection were carried out by the exposure of a band-gap light ($6000<\lambda<8000$ Å) and blue light ($3000<\lambda<5000$ Å), respectively, through filters from a tungsten-halogen lamp.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the dark current-voltage (*I*-*V*) characteristics for a compensated film in SB structure. The dark *I*-*V* characteristics after illumination are also shown. Using band-gap light, electron-hole (*e*-*h*) pairs are generated in the bulk of compensated film. The light intensity is about 1 mW/cm^2. After illumination, both the forward and reverse currents increase and the increase of forward currents is much more pronounced. After 1 h exposure, the conductance increases by about one order of magnitude of annealed value. These changes can be reversed by thermal annealing. Because the built-in voltage in this SB is less than 1 V, the forward current at above 1 V may be due to the bulk conductance. Thus the increase of the forward current over 1 V is attributed

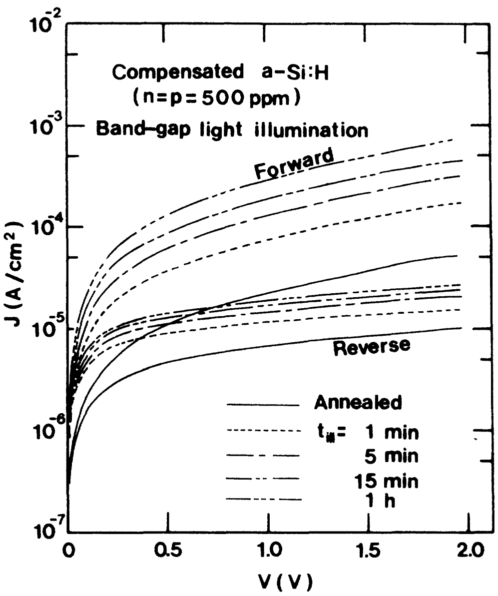

FIG. 1. The effect of light illumination through the Schottky metal on the dark current-voltage characteristics for compensated a-Si:H Schottky diode at room temperature. Band-gap light ($6000 < \lambda < 8000$ Å) was used for illumination.

to the increase of conductivity of compensated film, showing the bulk property of the PPC. And the increase in reverse current may be due to the change of the defect density such as dangling bonds in SB region near Pd.

Figure 2 shows the dark I-V characteristics after hole injection. Single-carrier injection was performed with blue light. For hole and electron injections, blue light is illuminated though the n^+-layer and the Pd in SB structure, respectively. The light intensity is fixed to 1 mW/cm^2, which is the same light intensity to band-gap light illumination. After hole injection, the increase of forward current is dominant and the magnitude of the PPC is nearly the same as the value of band-gap light illumination, as compared with Fig. 1. The absorption depth of blue light in this compensated film is less than 1000 Å. Most electron-hole pairs are generated near the n^+-type region and only the holes pass through the bulk of compensated a-Si:H. As shown in Figs. 1 and 2, the magnitude of the PPC is similar for electron-hole generation and hole injection cases. From these results we can infer that the PPC effect is limited by the excess hole and the magnitude is closely related to the density of injected holes.

After hole injection, however, the reverse current increases very slightly, much less than the band-gap light illumination. As previously mentioned, the reverse current change may be related to the creation of defects. The hole injection may be less efficient to the creation of defects than in electron-hole–pair generation. Therefore the change of reverse current is probably small in the hole injection case, as shown in Fig. 2.

Electron injection effects are indicated in Fig. 3. The change of forward current is small but the reverse current is comparable to the band-gap light illumination case. Because e-h pairs are generated in the SB region near Pd in this case, the change of SB properties is large. From the small change of forward current by electron injection only, we can argue that the PPC effect depends on the ex-

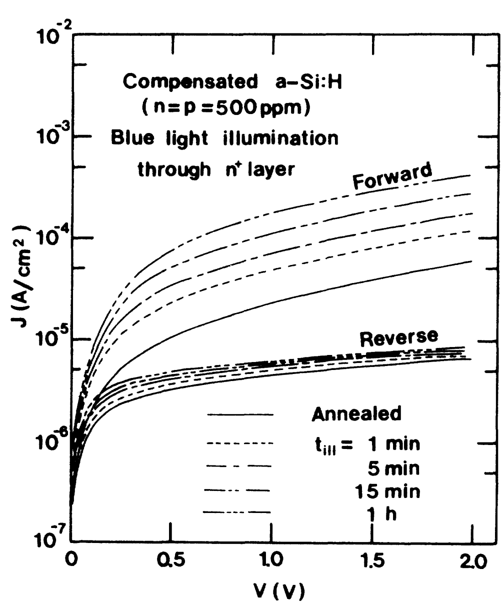

FIG. 2. The dark current-voltage characteristics for compensated a-Si:H Schottky diode at room temperature, after hole injections. Hole injection was carried out by blue-light ($3000 < \lambda < 5000$ Å) illumination through an n^+-type layer.

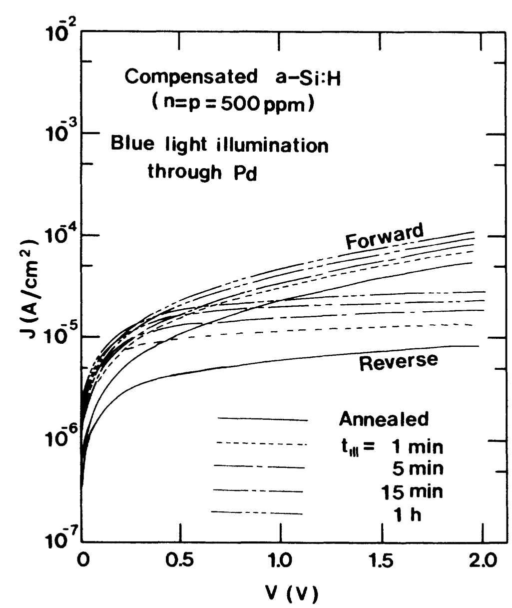

FIG. 3. The dark current-voltage characteristics for compensated a-Si:H Schottky diode at room temperature, after electron injections. Electron injection was performed by blue-light illumination through Pd.

cess hole density, not on the photogenerated electron-hole pair or excess electron density in the films. Hence the PPC is not the recombination-enhanced effect, but is limited by the excess hole density.

From these results, therefore, we can consider two possible mechanisms for the PPC in compensated films.

One is the special hole trap center models, which have already been proposed by several laboratories for the explanation of the PPC in *npnp* multilayers as well as in compensated films.[2–6] In a hole injection experiment, the electrons can also be injected, even though the density is less than 10^{-3} of injected hole density, which can contribute to the PPC. Because only the excess electrons, whose density is the same as the trapped holes at special hole centers, remain without recombination and contribute to excess conductance, the trapping of hole in the special centers can limit the PPC. Thus the injected hole density determines the magnitude of the PPC.

Another is hole injection-induced changes. If excess hole can change some electronic structure in a direction of increasing doping efficiency, the PPC, limited by excess hole density, can be explained. In doped *a*-Si:H several experimental results, showing the change of doping efficiency by various treatments, have been reported.

Street *et al.*[9] observed the thermal quenching and depletion bias annealing effects of electronic properties, which were explained by the increase of doping efficiency. And illumination-induced doping efficiency changes are also reported in electrical conductivity,[10,11] electron spin resonance (ESR), and photoinduced absorption experiments.[12,13] Branz[14] proposed a pair of charge-trapping defect reactions in order to unify the analysis of quenching, illumination, and depletion bias annealing experiments, which take place at an ensemble of bistable defects. In compensated films there are both dopants P and B, and so the change in doping efficiency can be possible as an origin of the PPC.

To check this possibility, we measure a correlation between the defect density and the magnitude of the PPC. The defect density was measured using the constant-photocurrent method (CPM) in coplanar structure. Figure 4 shows the plots of the excess dark conductivity and the excess defect density against illumination time at room temperature. For illumination, the white light of ~ 60 mW/cm^2 intensity was used with IR absorbing filter. The excess conductivities and defect densities are normalized by annealed value and measured at 1 h after turning off the illumination. The defect density is obtained from the integration of subband gap absorption, subtracting the contribution of the absorption due to exponential band tail,[15] and the exponential part of the optical-absorption coefficient determined by CPM is fitted to the transmittance data.[16]

During illumination, the dark conductivity and defect density increase monotonously up to 35 h. After 35 h illumination, the sample was rested in the dark for 54 h at room temperature and then annealed for 1 h at 100 °C. We obtained a very important result from this experiment. We measured a correlation between the magnitude of the PPC and the excess defect density, as shown in Fig. 4. The resting and annealing give rise to the decrease of

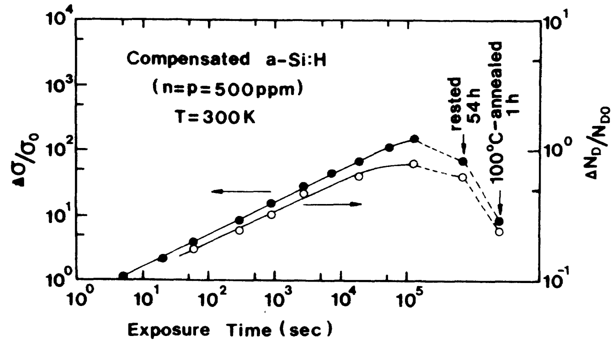

FIG. 4. Dependence of the excess conductivity ($\Delta\sigma$, solid circles) and of the excess defect density (ΔN_D, open circles) normalized by annealed values σ_0 and N_{D0}, respectively, on the exposure time for compensated *a*-Si:H at room temperature. The effects of resting for 54 h at room temperature and 100 °C annealing for 1 h, after 35 h exposure, are also shown. The defect density is obtained from subband gap absorption.

both the excess defect density and the PPC by exactly the same proportion (Fig. 4). These results strongly suggest that the defect creation is closely related to the PPC. In compensated film, dangling-bond creation by light exposure is small[17] compared with doped *a*-Si:H films, so that the defect creation by illumination may be small.

From the correlation between the PPC and the defect creation, we now consider several models for the PPC in compensated films.

In the case of the special hole trap model,[2,6] the lifetime of photoexcited carriers increases by hole traps, since the hole traps are in poor communication with the bulk. The hole trapping has to be accompanied by the creation of defects from our results, which is hardly expected.

Kakalios and Street[8] introduced the charge separation effects in compensated films by the inhomogeneities of counterdoping which will produce internal potential fluctuations, as in *npnp* multilayers. By this model, the conduction takes place through the *n* layers, and the PPC is due to the defect creation or charge trapping in the *p* layers.[8,18] Accordingly the defect density measured by CPM must show the defects in *n*-type layers, since the CPM is using the photocurrent. On the contrary, our data, which show a close correlation between the defect density in *n* region and the magnitude of the PPC, cannot be explained by this model.

In this paper, we want to propose a new model for the PPC in compensated films. Injected holes are trapped in dopants or weak silicon bonds near dopants and these hole trappings cause the creation of dangling bonds as well as the change of doping efficiency, resulting in the excess conductivity after illumination. Accordingly, the following reactions are possible:

$$h^+ + \mathrm{Si}_4^0 + \mathrm{P}_3^0 \rightleftarrows \mathrm{Si}_3^0 + \mathrm{P}_4^+ , \tag{1}$$

or

$$h^+ + \mathrm{Si}_4^0 + \mathrm{B}_4^- \rightleftarrows \mathrm{Si}_3^0 + \mathrm{B}_3^0 , \tag{2}$$

where h is an injected hole. These reactions are previously introduced by Branz,[14] as a class of bistable charge-trapping defects in doped a-Si:H. If one of these reactions takes place by illumination, the correlation of defect density with the magnitude of the PPC can be explained.

Kakalios and Street[8] proposed earlier a similar reaction to (2) as one of the possible mechanisms of the PPC for doping-modulated and compensated a-Si:H, in terms of the thermal equilibration model. In their model, internal potential fluctuations which can spatially separate photoexcited carriers are considered. And then these separated holes are equilibrated into the localized state distribution and are immobile. Thus excess unrecombined electron density can persist after illumination. In our model, however, the excess unrecombined electron and the internal potential fluctuation are not essential to the PPC in compensated films. The injection of excess hole without excess electron can create the PPC by the doping efficiency changes. These doping efficiency changes should be followed by dangling-bond formation, such as reaction (1) or (2).

The solid line in Fig. 5 illustrates the numerical calculation of the correlation between the excess defect density ($\Delta N_D/N_{D0}$) and the PPC ($\Delta\sigma/\sigma_c$). According to reaction (1), the dangling bonds (Si_3^0) and the active dopants (P_4) increase simultaneously. On the other hand, by reaction (2), the density of Si_3^0 increases, but the density of B_4 decreases by hole injection. So far as the effect on PPC is concerned, there is no difference between reactions (1) and (2). The solid circles in Fig. 5 denote the experimental results, which agree closely with the calculated values (solid line).

In this calculation, we assume a linear energy dependence of the density of states in the region of band tail down to 0.1 eV below the mobility edge, from which the exponential density of states started. The inverse slope (E_0) of exponential tail states was assumed to be 0.027 eV. We also used Gaussian shape for the dangling bonds and donor band with a width of 0.15 and 0.05 eV and a peak position of 0.94 and 0.1 eV from conduction band edge (E_c), respectively. The effective correlation energy of dangling bonds was taken as 0.4 eV. The Fermi-level position for the annealed state was 0.65 eV below E_c, which was obtained from the temperature dependence of conductivity. From the subband gap absorption,[15,16] annealed state defect density was observed to be about 2.2×10^{16} cm^{-3}, but the variation of the intrinsic defect density up to 4.4×10^{16} cm^{-3} gave little effect on the calculated values of Fig. 5. All parameters used for the calculation do not affect the results greatly, but the peak position of dangling bonds is sensitive to the results.

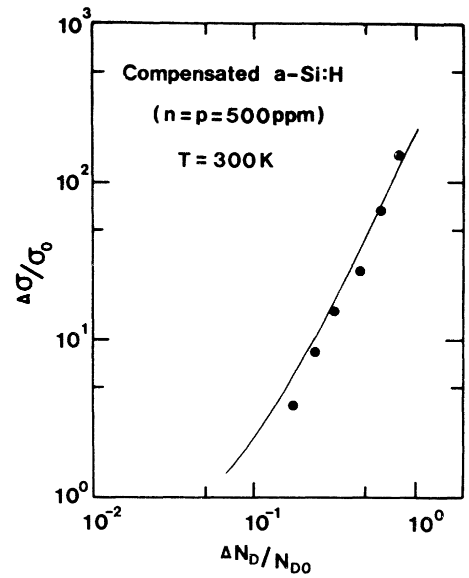

FIG. 5. Dependence of the excess conductivity at room temperature on the excess defect density for the experimental results (solid circles) and the numerical calculation (solid line) in compensated a-Si:H.

Because the Fermi level is near midgap in compensated films, the dark conductivity may be sensitively dependent on the change in doping efficiency. But by these results, we cannot determine which reaction between (1) and (2) is predominant. The created defect density by illumination, estimated from Figs. 4 and 5, is of the order of 10^{16} cm^{-3} and this value is similar to the light-induced changes in doped a-Si:H: $10^{16}-10^{17}$ cm^{-3} (Ref. 12). Thus these changes may be possible in compensated films.

IV. CONCLUSION

In conclusion, we demonstrated that the PPC in compensated a-Si:H is limited by injected hole density and has a strong correlation with the created defect density. From these results, we propose a hole-induced doping efficiency change as the origin of the PPC in compensated films.

ACKNOWLEDGMENTS

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