

## Doping and annealing effects on persistent photoconductivity in doping-modulated amorphous-silicon superlattices

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The effects of doping concentration and annealing on the persistent photoconductivity (PPC) in doping-modulated *npnp*. . . hydrogenated-amorphous-silicon (*a*-Si:H) multilayer structures and in compensated *a*-Si:H films have been studied. When the conductivity activation energy of the *p*-type layers was kept fixed at 0.53 eV and the activation energy of the *n*-type layers was varied from 0.31 to 0.52 eV by doping, the ratio of the excess conductivity to the annealed-state conductivity ( $\sigma_E/\sigma_A$ ) decreased from  $\sim 30$  to nearly zero in multilayer films. This result contradicts the usual models of *E* and *AX* centers. This argument is confirmed by the effect of annealing on the PPC in multilayer structures: the PPC for the multilayer structures deposited at 250°C is greatly reduced after 300°C annealing for 30 min. This annealing shows little change of the conductivity activation energy for the *p*-type layers. The annealing behavior of the PPC also rules out the dangling-bond model. We suggest that special centers of phosphorous, boron, and hydrogen complexes in the *p*-type layers near the *n*-*p* interfaces may explain the experimental results for the PPC of the multilayer structures.

### I. INTRODUCTION

Persistent photoconductivity (PPC) having a lifetime of the order of days has been observed in doping-modulated structures consisting of alternate layers of *n*- and *p*-type amorphous hydrogenated silicon (*a*-Si:H).<sup>1-5</sup> Several workers have reported that the PPC effect in doping-modulated multilayer structures depends on the specific details of the deposition conditions such as the substrate temperature, the degree of argon or helium dilution with silane, the layer thickness,<sup>2,3</sup> and the *p*-layer doping concentration.<sup>4,5</sup>

Most workers agree that the PPC effect in doping-modulated amorphous-silicon multilayer structures observed near room temperature cannot be accounted for solely through the charge separation of the photoexcited electron-hole pairs, which has been proposed as an interpretation of the PPC in crystalline doping superlattices<sup>6</sup> at low temperatures. The mechanism responsible for the PPC effect has not been established yet, although several plausible defect-center models<sup>4,5,7</sup> have been proposed to explain the origin of the effect. Kakalios<sup>4</sup> proposed a model of *E* centers which can trap the photoexcited holes in the *p*-type layers. Hundhausen *et al.*<sup>7</sup> suggested a model of *AX* centers which have strong lattice relaxation upon trapping holes in the *p*-type layers. Recently, Agarwal and Guha<sup>5</sup> reported PPC in compensated *a*-Si:H films as well as in multilayers. They argued that the PPC in both cases arises from special centers of phosphorous-boron complexes.

In this paper, we have investigated the effects of doping and annealing on the PPC in doping-modulated *npnp*. . . multilayers as well as in compensated *a*-Si:H films. The PPC for both cases decreases rapidly as the annealing temperature is raised above 250°C and the residual excess conductivity in the multilayers is nearly zero after 30-min annealing at 300°C. This annealing shows little change of the position of the Fermi levels both for the *n*- and *p*-type layers. The PPC in the multilayers depends on the position of the Fermi levels both for *n*- and *p*-type layers. Based on our experimental results, we compared the models proposed by Kakalios,<sup>4</sup> by Hundhausen *et al.*,<sup>7</sup> by Su *et al.*<sup>2,3</sup> and by Agarwal and Guha.<sup>5</sup> We conclude that *E*-center, *AX*-center, and dangling-bond models should be ruled out.

### II. EXPERIMENTAL DETAILS

The *a*-Si:H films were prepared on Corning 7059 glass substrates by rf glow-discharge decomposition of pure silane without argon. The stainless-steel electrodes were 5 cm in diameter with a separation of 2.5 cm. All samples were deposited at 250 °C and were 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. The silane gases mixed with phosphine (or diborane) by a mass-flow controller were used to prepare the *n*- (or *p*-) type *a*-Si:H films. The doping concentration in this paper represents the gas-phase concentration.

The multilayered samples were scratched with a diamond scribe before depositing electrodes (length 5 mm, separation 0.8 mm) of aluminum to assure that electrical contact was made to all individual layers for coplanar conductance measurements. The separation of the electrodes for unlayered  $\alpha$ -Si:H films was 0.4 mm. The conductivity data presented here were obtained using a voltage of 10 V which yielded linear  $I$ - $V$  characteristics for the unlayered films, but nonlinear characteristics for the layered ones.

The samples were first annealed in vacuum at 200 °C for 1 h to remove the surface adsorbates and the light-induced defects. They were then exposed to filtered light with a wavelength in the range between 6000 and 8000 Å from a tungsten-halogen lamp. The incident power density was 50 mW/cm<sup>2</sup> and the current-versus-time dependence was recorded using a microcomputer.

### III. EXPERIMENTAL RESULTS

#### A. Temperature and exposure-time dependences of persistent photoconductivity

Figure 1 shows an example of the temperature dependence of conductivity measured after a 2-min light exposure for a doping-modulated multilayer sample and a compensated film. The exposure was done at 300 K. As the temperature is increased, the conductivity follows the Arrhenius plot. However, when the temperature is raised above 360 K, the annealing effect starts to appear and the conductivity decreases. The PPC in the com-

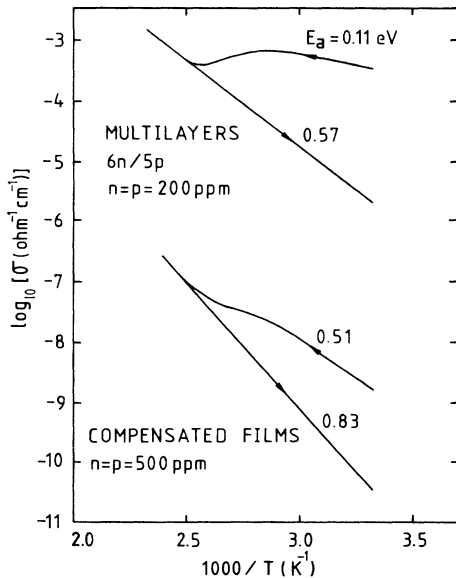


FIG. 1. Temperature dependence of dark conductivity after 2-min light exposure at 300 K for a multilayered sample with doping concentrations of 200 ppm each in both  $n$ - and  $p$ -type layers, and for a fully compensated film ( $[\text{PH}_3]/[\text{SiH}_4]=[\text{B}_2\text{H}_6]/[\text{SiH}_4]=500$  ppm). Both figures show the complete return to the annealed state after measured temperature reaches 400 K.

pensated film shows a similar behavior. The activation energies ( $E_a$ 's) for the annealed and the PPC states were 0.57 and 0.11 eV, respectively, in the multilayer, and 0.83 and 0.51 eV in the compensated film.

Figure 2 shows the ratio of the excess conductivity to the annealed-state conductivity ( $\sigma_E/\sigma_A$ ) measured at 300 K as a function of the exposure time ( $t_E$ ) for the same samples investigated in Fig. 1. We define the excess conductivity  $\sigma_E$  as the difference of the conductivity measured at 4 min after turning off the illumination and the annealed-state conductivity  $\sigma_A$ . The ratio  $\sigma_E/\sigma_A$  is the measure of the magnitude of the PPC. The magnitude of the PPC in the compensated samples is generally smaller than that observed in the layered ones at small  $t_E$ . Also, the saturation sets in after larger  $t_E$  than in the layered samples, as shown in Fig. 2. This is in agreement with the published results of Agarwal and Guha.<sup>5</sup>

The plot of the photoconductivity ( $\sigma_{\text{ph}}$ ) during the light exposure as a function of the exposure time at 300 K is shown in Fig. 3. The  $\sigma_{\text{ph}}$  in the multilayer saturates more rapidly than that in the compensated film, although the change of  $\sigma_{\text{ph}}$  with time in both cases is very small.

By exposing the samples for 2 min to light at elevated temperatures, we have found that the relaxation time ( $\tau_R$ ) of the PPC is thermally activated with an activation energy  $E_R$ . We define  $\tau_R$  as the time required for the conductivity measured at 4 min after illumination to decrease by half. As shown in Fig. 4, the activation energies for the multilayers and for the compensated films are 0.34 and 0.47 eV, respectively.

#### B. Doping concentration dependence of persistent photoconductivity

Table I shows a summary of the PPC for doping-modulated multilayers as a function of gas-phase doping

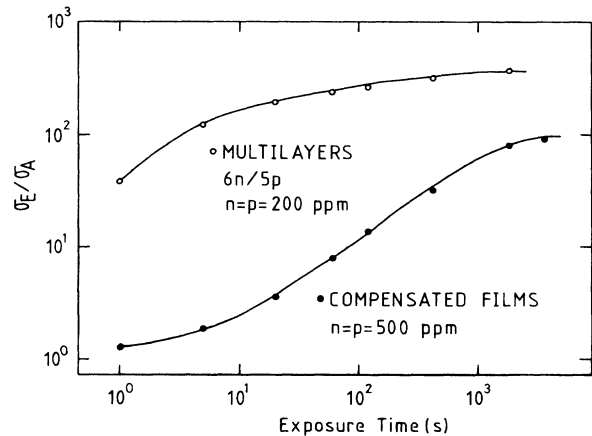


FIG. 2. Dependence of PPC ( $\sigma_E/\sigma_A$ ) at 300 K on the exposure time ( $t_E$ ) for the multilayered sample (200 ppm each layer) and the compensated film (500 ppm each).  $\sigma_E$  is defined as the difference between the conductivity measured 4 min after illumination and the annealed state conductivity ( $\sigma_A$ ).

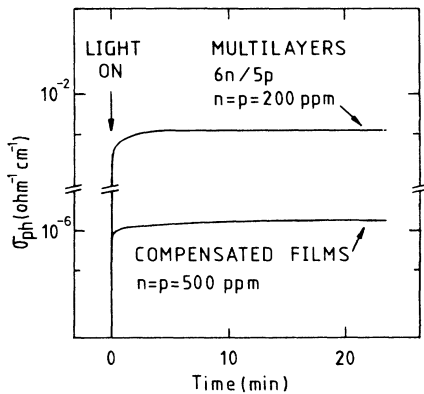


FIG. 3. Time dependence of photoconductivity ( $\sigma_{ph}$ ) at 300 K during light exposure for the multilayered sample (200 ppm each layer) and the compensated film (500 ppm each).

concentration. The temperature dependence of dark conductivity for the single-layer reference samples, made with the same deposition conditions as the doping-modulated multilayer films, was measured. The activation energy ( $E_a$ ) is  $(E_c - E_F)_0$  for  $n$ -type films and  $(E_F - E_v)_0$  for  $p$ -type ones. Here, subscript 0 denotes the temperature zero.

To test what kind of defect center is in the  $p$ -type regions we have made a series of samples where the phosphine concentration in the  $n$ -type layers was kept fixed at 200 ppm and the diborane concentration in the  $p$ -type layers was varied.  $\sigma_E/\sigma_A$  is the largest when

$(E_F - E_v)_0 = 0.65$  eV. We also made a series of samples where the diborane concentration in the  $p$ -type layers was kept fixed at 1000 ppm and the phosphine concentration in the  $n$ -type layers was varied from 200 to 2 ppm.  $\sigma_E/\sigma_A$  decreased with the decrease of the phosphine concentration in the  $n$ -type layers and we interpret the negative value of  $\sigma_E/\sigma_A$  at a phosphine concentration of 2 ppm to be due to the Staebler-Wronski effect.<sup>8</sup>

### C. Annealing temperature dependence of persistent photoconductivity

Figure 5 shows the effect of annealing on the PPC measured at 300 K for the multilayers ( $[\text{PH}_3]/[\text{SiH}_4] = [\text{B}_2\text{H}_6]/[\text{SiH}_4] = 200$  ppm). Annealing was carried out at different temperatures for 30 min in a vacuum of about  $10^{-7}$  torr in an ion-pumped system. After switching off the light, the conductivity of the unannealed sample deposited at 250 °C decays slowly and a large excess conductivity persists for a few days. The PPC, however, drastically decreases by annealing even at 275 °C.  $\sigma_E/\sigma_A + 1$  as a function of annealing temperature ( $T_A$ ) is shown in Fig. 6. As the annealing temperature is increased, the PPC decreases and for the multilayer films it shows a more abrupt change upon annealing than it does for compensated ones. It should be noted that the PPC in multilayers disappears at a much lower temperature (350 °C) than in compensated films. The experimental results for the effect of annealing on the PPC are summarized in Table II. We note that the sample qualities remain almost unchanged until the annealing temperature reaches about 300 °C, judging from the fact that the photoconductivities are affected little by this anneal.

## IV. DISCUSSION

We have observed large PPC's in compensated as well as in layered films. The magnitude of the PPC did not change even after etching the surface layers of the samples in 5% HF for 30 s. Hence, the PPC in compensated as well as in layered films is not due to the surface effect.<sup>9</sup> We have also found that the PPC in both cases depends on the concentrations of  $n$  doping as well as of  $p$  doping and is the largest when the concentrations of  $n$  and  $p$  doping are the same. In Secs. III A and III C, we listed the results for the fully compensated samples and multilayered films having the same P and B concentrations in  $n$ - and  $p$ -type layers. The fact that the PPC in both cases is the largest at equal doping concentrations of phosphorus and boron is interesting.

Amer *et al.*<sup>10</sup> showed that fully compensated  $a$ -Si:H films exhibit the smallest increase of dangling bonds after light exposure, i.e., the smallest Staebler-Wronski effect (SWE). We believe that the PPC in compensated film is the largest when the phosphorous and boron concentrations are equal because the SWE is the smallest for these films. The SWE and PPC effect are expected to occur in the multilayers as well as in the compensated films. We observed a small SWE in the multilayer film where the position of the Fermi level for the  $n$ -type layers is 0.52 eV below  $E_c$ . Since electrical conduction

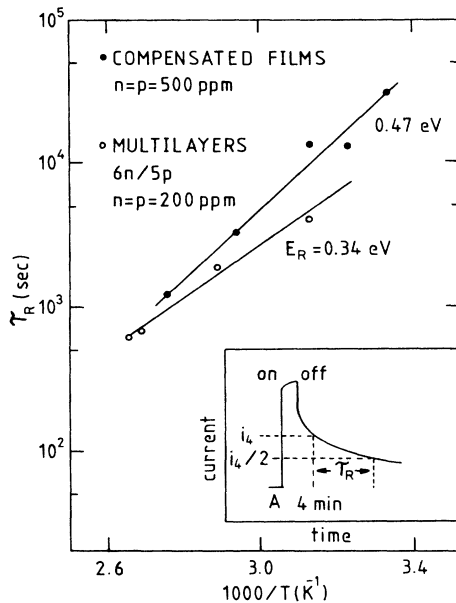


FIG. 4. Arrhenius plot of PPC relaxation time  $\tau_R$  for the multilayered sample (200 ppm each layer) and the compensated film (500 ppm each).  $\tau_R$  is defined as the time for the PPC current to decay by half after a 4-min waiting period as sketched in the inset.

TABLE I. Excess conductivity of *npnp* multilayers as a function of gas-phase doping concentration. The Ref.  $E_a(A)$  denotes the conductivity activation energy of annealed states obtained from the reference films of *n* and *p* type.

Sample	Doping conc. (ppm)		Ref. $E_a(A)$ (eV)		$\sigma_E/\sigma_A$
	<i>n</i>	<i>p</i>	<i>n</i>	<i>p</i>	
<i>npnp</i>	200	100	0.31	0.75	2.4
<i>npnp</i>	200	200	0.31	0.65	539.1
<i>npnp</i>	200	1000	0.31	0.53	29.7
<i>npnp</i>	50	1000	0.40	0.53	0.23
<i>npnp</i>	2	1000	0.52	0.53	-0.02

takes place through the *n*-type layers, it is important to know how large the SWE is in the *n*-type layers. It is expected that the shift of the Fermi level by light exposure decreases as  $(E_c - E_F)_0$  decreases from 0.52 to 0.31 eV, since the density of states at the Fermi level increases as the Fermi level moves toward the conduction band. It is likely that the SWE is slightly larger than the PPC effect in the last sample shown in Table I. However, in the other samples the PPC effect is dominant.

Recently, from the experimental results for the doping-modulated *a*-Si:H multilayers it is concluded that the room-temperature PPC is not purely due to a charge-separation effect, but due to the charge storage in novel defects requiring a strong lattice relaxation.<sup>4,7</sup> Kakalios<sup>4</sup> termed the novel defects *E* centers since they are responsible for the excess conductivity. The *E* centers can either trap a photoexcited hole with strong lattice relaxation, thereby preventing its recombination with an electron, or release an electron by optical excitation out of the center. Hundhausen *et al.*<sup>7</sup> ascribed the PPC

effect in amorphous *nipi* multilayers to charge trapping in acceptorlike defects which undergo strong lattice relaxations upon trapping holes in the *p* regions of the sample. They termed such defects *AX* centers.

Table I shows  $\sigma_E/\sigma_A$  for a series of the multilayer films where the phosphine concentration in the *n*-type layers is kept fixed at 200 ppm while the diborane concentration in the *p*-type layers is varied:  $(E_c - E_F)_0$  for the *n*-type layers is fixed at 0.31 eV and  $(E_F - E_v)_0$  of the *p*-type layers is varied from 0.53 to 0.75 eV. When  $(E_F - E_v)_0$  of the *p*-type layers is 0.65 eV, the maximum PPC is observed, agreeing with the results of Kakalios,<sup>4</sup> which caused him to claim that the *E* center is located in the *p*-type layers at 0.65 eV above the valence-band edge. On the other hand, when we fixed  $(E_F - E_v)_0$  of the *p*-type layers at 0.53 eV and increased  $(E_c - E_F)_0$  from 0.31 to 0.52 eV,  $\sigma_E/\sigma_A$  decreased from  $\sim 30$  to nearly zero and a small SWE appears when  $(E_c - E_F)_0$  is 0.52 eV. This result indicates that the PPC in the multilayers strongly depends on the  $(E_c - E_F)_0$  of the *n*-type layers.

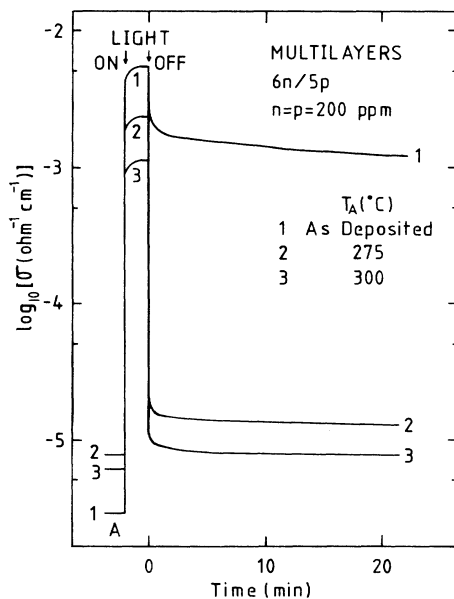


FIG. 5. Effect of annealing on the conductivity decay curves at 300 K after 2-min exposure for the multilayered sample (200 ppm each layer).

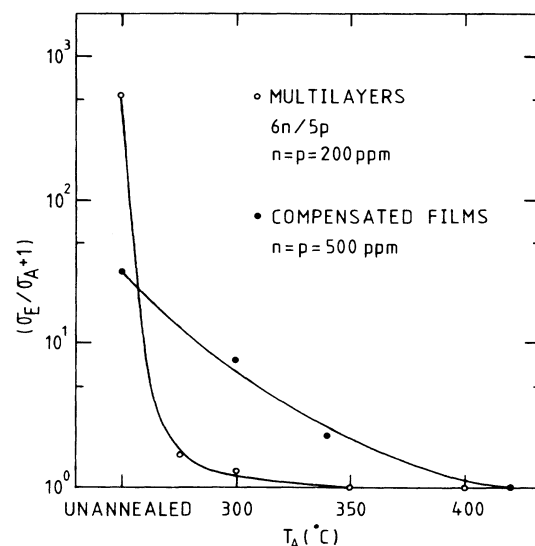


FIG. 6. Isochronal annealing curves for PPC ( $\sigma_E/\sigma_A$ ) at 300 K in the multilayered sample (200 ppm each layer) and the compensated film (500 ppm each).

TABLE II. Excess conductivity of *npnp* multilayers and compensated films as a function of annealing temperature.

Sample	Doping conc. (ppm)		$T_A$ (°C)	Ref. $E_a$ (A) (eV)		$\sigma_A$ ( $\Omega^{-1}\text{cm}^{-1}$ )	$\sigma_{ph}$ ( $\Omega^{-1}\text{cm}^{-1}$ )	$\sigma_E/\sigma_A$
	<i>n</i>	<i>p</i>		<i>n</i>	<i>p</i>			
<i>npnp</i>	200	200	as deposited	0.31	0.65	$3.64 \times 10^{-6}$	$5.41 \times 10^{-3}$	539.1
<i>npnp</i>	200	200	275	0.36	0.57	$7.94 \times 10^{-6}$	$2.11 \times 10^{-3}$	0.7
<i>npnp</i>	200	200	300	0.36	0.62	$6.14 \times 10^{-6}$	$1.04 \times 10^{-3}$	0.3
<i>npnp</i>	200	200	350	0.57	0.68	$1.54 \times 10^{-7}$	$2.81 \times 10^{-5}$	0
<i>npnp</i>	200	100	as deposited	0.31	0.75	$6.76 \times 10^{-4}$	$8.78 \times 10^{-3}$	2.4
<i>npnp</i>	200	100	300	0.36	0.65	$8.50 \times 10^{-6}$	$1.19 \times 10^{-3}$	0.7
<i>npnp</i>	200	100	350	0.57	0.70	$1.19 \times 10^{-7}$	$7.67 \times 10^{-6}$	0
Comp.	500	500	as deposited		0.83	$6.40 \times 10^{-11}$	$1.16 \times 10^{-6}$	30.6
Comp.	500	500	300		0.80	$5.97 \times 10^{-11}$	$5.65 \times 10^{-7}$	6.7
Comp.	500	500	340		0.82	$6.30 \times 10^{-11}$	$4.23 \times 10^{-7}$	1.3
Comp.	500	500	420		0.69	$1.92 \times 10^{-9}$	$1.62 \times 10^{-7}$	0

In doping-modulated multilayers, the built-in, internal field depends on the doping levels and the thickness of each layer. Charge transfer gives rise to the shift in Fermi level of each layer provided that the thickness of each layer is thin enough to have overlap in depletion regions between neighboring layers. On the other hand, when the thickness of individual layers is large enough to have an undepleted region between depleted regions, the Fermi level in the middle (undepleted region) of the layer will remain fixed and therefore barrier height due to the doping modulation in equilibrium is given by the difference in Fermi energies between *n*- and *p*-type layers. Only after illumination, the Fermi level in the midlayer region may be shifted due to the photoexcited carriers separated into the region causing the reduction in the barrier height (but not to zero).

It has been found that the largest PPC in doping superlattices is observed when the thickness of each layer (average layer thickness in the case of different *p*- and *n*-type layer thicknesses) is equal to the junction depletion width  $W$  ( $=W_n + W_p$ ).<sup>3</sup> This value of  $W$  was 275 Å for Kakalios<sup>4</sup> and 270 Å for Su *et al.*<sup>3</sup> The thickness of individual layers of all our samples is 360 Å, larger than  $W$ .

Now consider the case when the doping concentration in the *p*-type layers is fixed at 1000 ppm (which is much higher than the concentrations used by Kakalios and Su *et al.*, and consequently would give much shorter  $W_p$ ) while the doping concentration in the *n*-type layers is varied from 200 to 2 ppm as shown in the second column in Table I. Certainly there should exist undepleted, flat regions of sizable width in the *p*-type layers since  $W$  should be much shorter than 275 Å. As the doping level in the *n*-type layers is decreased from 200 ppm,  $W_n$  may increase but  $W_p$  will change little since the boron concentration in the *p* regions is kept fixed at a high value of 1000 ppm. Thus one would expect no drastic change in PPC by changing the position of  $E_F$  in the *n*-type region if the models of Kakalios and Hundhausen are the right ones because both  $E_F$  and  $W_p$  would not change much in the *p*-type regions, except possibly near the interface regions. Contrary to this expectation, our result (see Table I) shows drastic change

in PPC by changing phosphorus concentration of *n* regions from 200 to 50 ppm (change of reference  $E_F$  from 0.31 to 0.40 eV below  $E_c$ ).

Probably the most direct evidence against the *E*- and *AX*-center models comes from the following facts. Nobody observed PPC's of appreciable magnitude in *p*-type, unlayered films doped with boron only. On the other hand, in compensated, unlayered samples with both phosphorus and boron present, very large PPC was observed in several works (Mell and Beyer,<sup>11</sup> Agarwal and Guha,<sup>5</sup> our work). One may claim that the reason for not seeing PPC in B-doped film is due to the  $E_F$  lying below the *E* or *AX* centers so that they cannot trap any further holes. This is not true: We measured PPC in B-doped films with  $E_F$  lying above the *E*-center level (0.7 eV above  $E_v$ ) and observed no PPC in all films. For example, a 100-ppm B-doped film where  $E_F$  lies 0.75 eV above  $E_v$  exhibited no PPC at all. Agarwal and Guha<sup>5</sup> observed no PPC in an *ipip* . . . superlattice (40 ppm B doped, 360 Å each layer) where  $E_F$  in *p*-type layers was at 0.94 eV above  $E_v$ . Note that  $E_F$  near the interface could lie even higher. Note also that the largest PPC was observed when  $E_F$  lay at 0.65 eV above  $E_v$  in *p*-type layers (see Table I; see also the table on p. 210, Ref. 4).

All this evidence leads us to conclude that phosphorus impurities must take part in the cause of PPC together with boron atoms.

As annealing temperature is raised above the substrate temperature, the magnitude of the PPC in the multilayers decreases rapidly, as shown in Table II. The positions of the Fermi levels for *n*- and *p*-type layers do not change much by annealing up to 300°C. This result indicates that the change of the PPC effect by annealing is not related to the change of the position of the Fermi levels for each layer, and also contradicts the *E*- or *AX*-center model since the occupancy of those centers would remain unchanged by the 300°C anneal with such a little change in  $E_F$ . Moreover, there is no evidence that *E* or *AX* centers in the *p*-type layers will decrease by 300°C annealing. Thus, the results of the effect of annealing on PPC do not follow the *AX*- or *E*-center model.

Agarwal and Guha<sup>5</sup> argued that the PPC in layered as well as in compensated *a*-Si:H films was due to the spe-

cial centers composed of phosphorus-boron complexes, at the  $p$ - $n$  interfaces of the multilayer films or in the bulk of compensated films. On shining light upon them, they capture holes, leaving electrons behind to conduct. When the Fermi level is below the trapping levels of the special centers, these traps are nearly empty and are unable to trap the holes. When it is close to the conduction band above these trapping levels, the dark conductivity is large. Both these situations will give small  $\sigma_E/\sigma_A$ , which explains a maximum  $\sigma_E/\sigma_A$  plotted against the doping levels of the separate  $n$ - and  $p$ -type layers. The trapping of holes by these P-B complexes should depend on the position of the Fermi level in the compensated region. The Fermi level in the compensated region depends on the space charge transfer, which is largely influenced by doping concentrations of  $n$ - and  $p$ -type layers. When the doping concentration in the  $p$ -type layers is kept fixed at 1000 ppm and the doping concentration of the  $n$ -type layer is varied from 200 to 2 ppm, the Fermi level in the  $n$ - $p$  interface region will move toward the valence band and also the concentration of occupied special centers of P-B complexes will decrease, resulting in the decrease of the PPC as shown in Table I. Therefore, the results shown in Table I satisfy the special center model proposed by Agarwal and Guha.<sup>5</sup>

When we accept the P-B complex model for PPC in  $npnp$ ... multilayer structures, one may ask why PPC was also observed in  $nipi$ ... structures.<sup>7</sup> However, the values of PPC ( $\sigma_E/\sigma_A$ ) observed in  $nipi$ ... structures are much smaller than those in  $npnp$ ... structures: The value of PPC calculated from the results of Hundhausen *et al.* for  $nipi$ ...-type superlattices<sup>7</sup> is 6.8 after illumination of 300 mW/cm<sup>2</sup> for 20 s, which is much smaller than that of 539 observed by us in  $npnp$ ... structures after a comparable dose (50 mW/cm<sup>2</sup>, 2 min), that of 200 by Kakalios<sup>4</sup> with a smaller dose (50 mW/cm<sup>2</sup>, 30 s), and that of 320 by Agarwal *et al.*<sup>5</sup> with an even smaller dose (10 mW/cm<sup>2</sup>, 5 s). We also fabricated  $nipi$ ... multilayer structures ( $[PH_3]/[SiH_4]=[B_2H_6]/[SiH_4]=200$  ppm, 300 Å each layer) and observed a much smaller value of 3.9 (50 mW/cm<sup>2</sup>, 2 min) than for the  $npnp$ ...-type counterpart. Thus, the values of PPC in  $nipi$ ... multilayer structures are orders of magnitude smaller than those in  $npnp$ ... multilayer structures. The existence of PPC in  $nipi$ ... structures can be explained by the counter-contamination during the deposition and/or by the interdiffusion of dopants during the deposition.

Su *et al.*<sup>2,3</sup> proposed a model explaining the PPC in the multilayer films. They insist that the origin of the PPC is due to the dangling bonds in  $a$ -Si:H. By this model, the PPC effect should increase with the dangling-bond density in the  $p$ - and  $n$ -type layers. It is well established that the  $a$ -Si:H films deposited at 250 °C show little change of spin density by annealing up to 300 °C.<sup>12</sup> By annealing at a higher temperature, the spin density increases because of the evolution of hydrogen in the films.<sup>12</sup> It should be noted that the PPC in the multilayer films is removed almost completely by annealing at 300 °C (see Fig. 6). However, the spin density cannot be greatly reduced at this annealing temperature. Thus,

the results for the annealing effect on the PPC in the multilayers shown in Fig. 6 and Table II rule out the possibility that the dangling bonds are responsible for the PPC.

We have to worry about the increase of the compensated regions of the  $p$ - $n$  interfaces by the annealing. Matsumura *et al.*<sup>13</sup> have measured the diffusion constant of the boron atom from the boron-doped to undoped  $a$ -Si:H layer to be  $D \approx 10^{-16}$  cm<sup>2</sup>/s at 300 °C. This implies that during 30-min annealing some amounts of boron atoms have a chance to diffuse and form an intermixed region of 40 Å from the  $p$ - $n$  interface if we assume the diffusion constant of the boron atom in undoped and  $n$ -type  $a$ -Si:H films is the same. The compensated region of 40 Å is not large enough to affect the built-in potential between the layers appreciably.

It has been established that the bonded hydrogen to silicon in unlayered  $a$ -Si:H films deposited around 250 °C could not effuse out by the 300 °C annealing.<sup>14</sup> Hundhausen *et al.*<sup>7,15</sup> reported that the excess hydrogen exists near the  $i$ - $n$ ,  $i$ - $p$ , and  $n$ - $p$  interfaces by the measurements of hydrogen profile in the  $a$ -Si:H multilayers by SIMS (secondary ion mass spectrometry) measurements. When we deposit an  $inin$ ...  $a$ -Si:H multilayer, the excess hydrogen exists in the  $n$ -type layers near the  $i$ - $n$  interface, not  $n$ - $i$  interface. The diffusion coefficient of hydrogen in the  $i$ -type layer is much smaller compared with that in the  $n$ -type layers because the structure of  $i$ -type layer is more dense than in the  $n$ -type layers. The same argument is available at the  $n$ - $p$  interface in the  $npnp$ ... multilayers. The excess hydrogen exists in the  $p$ -type layers near the  $n$ - $p$  interfaces because the  $n$ -type layers are more dense than the  $p$ -type layers. The accumulated hydrogen atoms near the interface by the diffusion barrier are likely to be weakly bonded. These weakly bonded hydrogen atoms can be mostly effused out if the samples are annealed at 300 °C. Also the structure of  $p$  regions near the  $n$ - $p$  interfaces is likely to be more flexible and the trapped holes are able to have a strong lattice relaxation because these regions contain a large amount of weakly bonded hydrogen.

If we assume that the PPC in multilayer films is due to the special center made of phosphorus, boron, and hydrogen (P-B-H) complexes, our experimental results can be explained. It is likely that the special centers exist in the excess hydrogen region in the  $p$ -type layers near the  $n$ - $p$  interfaces. As the phosphine concentration in the discharge chamber increases during  $n$ -type layer deposition when the diborane concentration is fixed at 1000 ppm, the density of P-B-H complexes near the interfaces increases, so that the PPC increases as the doping concentration of the  $n$ -type layers is increased. The energy level of special centers may be 0.65 eV above valence-band edge because we have the largest PPC when the  $(E_F - E_v)_0$  is 0.65 eV. When the multilayer films are annealed at 300 °C, most of the excess hydrogen atoms near the  $n$ - $p$  interfaces are effused out because they are weakly bonded, resulting in the quenching of the PPC as shown in Table II. If the origin of the PPC is due to the  $E$  or  $AX$  centers in the bulk  $p$ -type layers containing no weakly bonded hydrogen, the PPC should not decrease

greatly because the electrical properties of *a*-Si:H films changes little by 300°C annealing.

In compensated films we also observed a decrease of the PPC by increasing the annealing temperature above the substrate temperature as shown in Fig. 4. However, the annealing effect is much slower than that in the multilayer films. We believe that the origin of the PPC in the compensated film is the same as that in the multilayer films. The increase of the conductivity during light exposure in compensated films is much slower than that in the multilayer samples because the charge separation effect does not occur in single-layered *a*-Si:H films. The hydrogen atoms in compensated films are not expected to be so weakly bonded as those in *n-p* interfaces of multilayer films because there are less excess hydrogen regions in single-layered samples. Therefore, the annealing effect on the magnitude of the PPC must be slower compared with the multilayer films as observed. However, the PPC is nearly absent when the annealing temperature is 500°C, because most of the hydrogen atoms in P-B-H complexes are effused out.

The reversible change of the PPC may be due to the movement of hydrogens in the P-B-H complexes. Further experimental and theoretical works on the role of the hydrogen in the multilayers as well as in the compensated films should be done to study the microscopic origin of the PPC in *a*-Si:H.

## V. CONCLUSIONS

We have investigated the PPC effect in *nnp*. . . *a*-Si:H multilayer films as functions of *n*- and *p*-type layer doping concentrations. It is found that the PPC depends greatly on doping concentrations of *n*-type layers as well as of *p*-type layers. As  $(E_c - E_F)_0$  in *n*-type layers increases from 0.31 to 0.52 eV, with  $(E_F - E_v)_0$  in *p*-type layers fixed at 0.53 eV, the  $\sigma_E/\sigma_A$  for the multilayer films decreases from  $\sim 30$  to nearly zero. This result contradicts *E*-center and *AX*-center models. This contradiction was confirmed by the effect of annealing on the PPC for multilayer films. The PPC's for multilayers nearly disappear after 300°C annealing, while the  $(E_F - E_v)_0$  for *p*-type layers is changed little. This annealing behavior of the PPC in the multilayer also excludes the dangling-bond model. It is likely that the PPC in the multilayer films is related to the weakly bonded excess hydrogen in the *p* layers near the *n-p* interface. The phosphorus, boron, and hydrogen complexes in the excess hydrogen region may be an origin of the PPC in the *nnp*. . . multilayer films.

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