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Model for persistent photoconductivity in doping-modulated amorphous silicon superlattices

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Doping superlattices prepared by depositing successively 105-Å-thick layers of n-type, intrinsic, and p-type amorphous hydrogenated silicon (n-i-p-i structures), exhibit persistent photoconductivity at room temperature. Persistent photoconductivity (PPC) is the excess dark conductivity that remains after the sample has been exposed to white, heat-filtered light and that decays on a time-scale of hours or days. We prove that PPC is a bulk effect and that the amount of light necessary to induce a certain level of PPC decreases exponentially with temperature. This temperature dependence corresponds to an activation energy of ~ 0.4 eV for the creation of "state PPC"; a slightly higher activation energy (~ 0.7 eV) for the quenching of PPC is deduced from the annealing behavior. Above around 400 K the sample can be transformed into a second metastable state C, which does not exhibit PPC. The fact that the generation of PPC is thermally activated is incompatible with an explanation of this effect simply in terms of metastable carriers which are spatially separated in the space-charge fields of the n-i-p-i structure. We propose instead that holes are trapped in acceptorlike centers, AX, in the p regions of the sample, whereas the balancing concentration of electrons, confined to the n layers by the n-i-p-i fields and thus prevented from recombining with the holes, are responsible for PPC. The AX centers possess, in analogy to the DX centers in $Ga_{1-x}Al_xAs$, a strong electron-lattice coupling which accounts for the thermal activation energies of hole capture and ionization.

I. INTRODUCTION

The recombination kinetics of optically generated carriers in doping-modulated amorphous hydrogenated silicon (a-Si:H) has recently been investigated in the low- ($T < 50$ K) and high- ($T \geq 300$ K) temperature regimes.[1,2] In both cases excess carrier concentrations were observed after the end of the illumination period with lifetimes that exceeded those found in unstructured material by many orders of magnitude. At room temperature these long-lived carriers contribute to an excess nonequilibrium dark conductance which is referred to as persistent photoconductivity (PPC).[2] This PPC exceeds the equilibrium dark conductance by about 2 orders of magnitude under the experimental conditions of Ref. 2 and decays on a time scale of the order of hours. In the low-temperature work of Hundhausen, Ley, and Carius (Ref. 1), the photogenerated carriers are trapped in tail states and are detected through their contributions to an infrared- (ir) induced photoconductivity transient. The recombination kinetics of the excess carriers were followed by varying the dark time between the end of the photocarrier creation and their reexcitation by ir light. As in the PPC experiments of Kakalios and Fritzsche[2] lifetimes in excess of 10^3 sec could be observed.

The long lifetimes were in both cases attributed to the spatial separation of electrons and holes in the electric fields that exist in the amorphous doping superlattices, as originally suggested by Döhler,[3] although Kakalios and Fritzsche suggested alternative explanations as well. The situation is schematically sketched in Fig. 1 for a n-i-p-i superlattice, i.e., one where alternating layers of n- and p-doped a-Si:H are separated by layers of intrinsic material. The regular alternation in the type of doping results in a periodic modulation of the band-edge energies with an amplitude $e\Delta U$ in the direction perpendicular to the sample surface [see Fig. 1(a)], whereas the material is homogeneous and isotropic in the plane parallel to the surface. The electric fields accompanying the band-edge modulation separate electrons and holes which accumulate in the band extrema: electrons in the n layers and holes in the p layers. Even for the smallest mobility-lifetime product $\mu\tau$

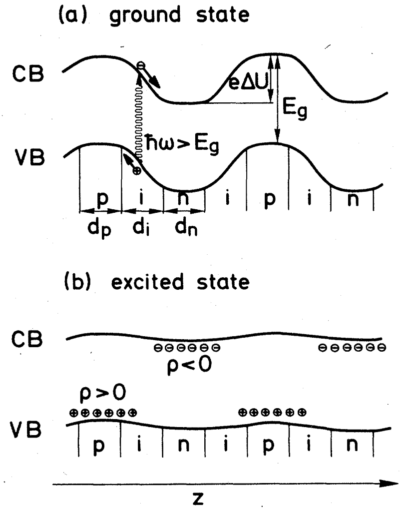

FIG. 1. Schematic real-space band diagram of an n-i-p-i structure: (a) equilibrium; (b) with a concentration of spatially separated photoexcited carriers sufficient to reduce the band modulation.

of 10^{-10} cm^2/V measured[4] in *a*-Si:H and for quite moderate internal fields of $E=10^5$ V/cm a drift length of 1000 Å is achieved. This is sufficient to separate electrons and holes in superlattices with periods of less than 500 Å and thereby reduce their recombination probability. It could indeed be shown in Ref. 1 that the lifetime of the excess carriers increased exponentially with superlattice period as expected when recombination proceeds via tunneling to carriers of opposite sign or to a recombination center.

Another characteristic aspect of Döhler's model is the saturation in the concentration of spatially separated carriers. Due to their long lifetimes electrons and holes accumulate in the *n* and *p* regions, respectively, and set up space charges which reduce the modulation amplitude $e\Delta u$ of the band energies and thereby the magnitude of the electric fields [see Fig. 1(b)] until no further carrier separation occurs. Our studies[1] at low temperatures showed that the maximum concentration of spatially separated carriers and the way this concentration depends on the superlattice period agrees with this model. As we shall show in Sec. III A, the initial probability for the spatial separation of photogenerated carriers is close to unity. In contrast to this result, much higher photon fluxes (10^{21} cm^{-2}sec^{-1} compared to $\sim 10^{17}$ cm^{-2}sec^{-1} at $T=5$ K) turned out to be necessary to achieve saturation of PPC according to Ref. 2.

The samples used in Ref. 2 were *n-p-n-p* multilayers deposited in a two-chamber system whereas the specimens in Ref. 1 were of the *n-i-p-i* variety prepared in a continuous plasma by switching between different gases. Past experience has shown that the properties of *a*-Si:H depend often critically on preparation conditions. We therefore considered it necessary to investigate light-induced conductivity changes in our samples as well, in order to establish whether high-temperature PPC is an intrinsic effect of amorphous doping superlattices in general or peculiar to the preparation conditions employed in Ref. 2. As it turned out, high-temperature PPC is also observed in our samples and we consequently widened the scope of our investigation in an attempt to shed further light on this phenomenon. To this end we measured the temperature dependence of PPC in *n-i-p-i* superlattices and established that a thermal barrier for the creation of PPC exists. This result sets PPC clearly apart from Döhler's model of charge separation where no such barrier exists.

These and further measurements of light-induced effects in *n-i-p-i* structures are presented in Sec. III after a short description of sample preparation and experimental conditions is given in Sec. II. The results are discussed in the light of PPC in crystalline materials in Sec. IV and a novel mechanism for the excess dark conductivity in amorphous doping superlattices is proposed. A short summary concludes the paper.

II. EXPERIMENTAL

The experiments were almost exclusively performed on an *n-i-p-i* multilayer (sample 61) consisting of 22 periods. The *n*, *i*, and *p* layers have identical widths of 105 Å resulting in a total thickness of 0.9 μm. This particular sample was selected because it showed in our earlier experiments at $T=5$ K the highest density of spatially separated nonequilibrium carriers.[1] This sample—as well as others—was prepared by the glow-discharge decomposition of SiH_4 in a computer-controlled continuous rf plasma on quartz substrates held at a temperature of 350 °C. rf power density and gas pressure were maintained at 0.08 W/cm^2 and 0.25 Torr, respectively. Doping was achieved by adding alternately 100 ppm PH_3 (*n*-type layer) or B_2H_6 (*p*-type layer) to SiH_4. The activation energies of unmodulated samples with the same doping were 0.16 eV (*n* type) and 0.65 eV (*p* type), respectively. The discharge vessel, pumps, valves, and seals were designed and maintained according to ultrahigh-vacuum standards.

Chromium contacts were evaporated onto the samples after deposition either as two strips with a gap of 1×10 mm^2 or as intermeshed electrodes with an effective gap of 0.4×70 mm^2. Both gave Ohmic curves with 10 V applied voltage. We verified that the measured conductance was representative for the bulk of the multilayer structures and not just the top layer by illuminating the sample with strongly absorbed blue light ($h\nu=3.1$ eV, $\alpha\simeq 5\times 10^5$ cm^{-1}) from the front and through the substrate. The same photoconductivity was observed in both cases. We also compared our contacts with those prepared according to the method employed by Kakalios and Fritzsche,[2] i.e., we scratched the sample surface before applying the contacts and found no difference. These tests indicate that the resistance perpendicular to the layers is small compared to that parallel to the layers as a result of the geometrical advantage of large-area contacts.

All measurements were performed in an oil-free vacuum of 10^{-4} Torr.

III. RESULTS

A. Persistent photoconductivity

Figure 2 illustrates PPC in our amorphous *n-i-p-i* superlattice. The initial state *A* corresponds to a sample that has been annealed at 500 K in the dark and under vacuum for about 30 min. The sample is then illuminated with heat-filtered light ($h\nu\geq 1.4$ eV) from a quartz iodine lamp with a power density of 300 mW/cm^2 for various periods of time while the conductivity σ is monitored. The results of these measurements may be summarized as follows. (i) The sample exhibits a photoconductivity of $\sigma_{\text{ph}}=2\times 10^{-3}$ Ω^{-1}cm^{-1} during illumination which is comparable to unstructured *a*-Si:H. (ii) The conductivity decays nonexponentially on a timescale of 10^2 sec after the end of the illumination and reaches a value σ_{PPC}, the persistent photoconductivity, which exceeds σ_A, the conductivity in state *A*. The PPC decays on a much longer time scale of the order of hours and days. (iii) The value of σ_{PPC} increases with increasing illumination times as illustrated in Figs. 2(b) and 2(c) for additional illumination periods of 5 and 60 sec, respectively.

When plotted against the illumination time as in Fig. 3 a saturation of σ_{PPC} appears to manifest itself in the bending-over of σ_{PPC} versus *t* around $t=10\,000$ sec. This

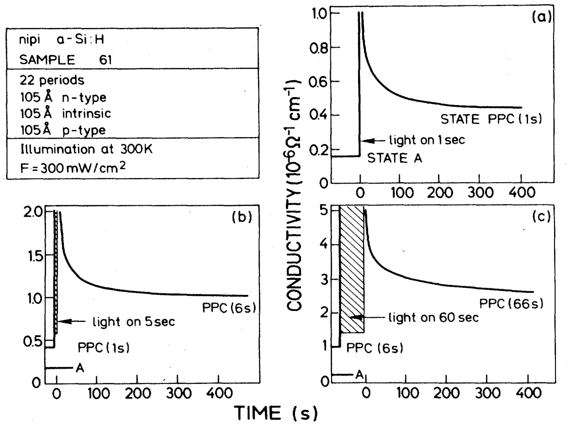

FIG. 2. Conductivity of an *a*-Si:H *n*-*i*-*p*-*i* superlattice after annealing (state *A*) and after (a) 1, (b) 5, and (c) 60 sec illumination with 300-mW/cm^2 heat-filtered light at $T=300$ K. Time zero corresponds to the end of the illumination. Notice the different conductivity scales of the three frames.

time corresponds to a total density of absorbed photons of about 10^{26} cm^{-3}. On the left-hand side of Fig. 3 we have plotted for the same sample the concentration of spatially separated excess carriers at $T=5$ K as a function of absorbed photon density. The carrier concentrations were determined according to Ref. 1 from the amplitude of the infrared-induced photoconductivity transient. The carrier concentration is initially proportional to the density of absorbed photons.[5] Extrapolating the initial slope to the highest possible density of excess carriers [see Fig. 1(b)] as determined in Ref. 1 yields a photon density of 2.3×10^{18} cm^{-3}. This photon density is 8 orders of magnitude less than necessary to approach saturation of PPC at $T=300$ K.

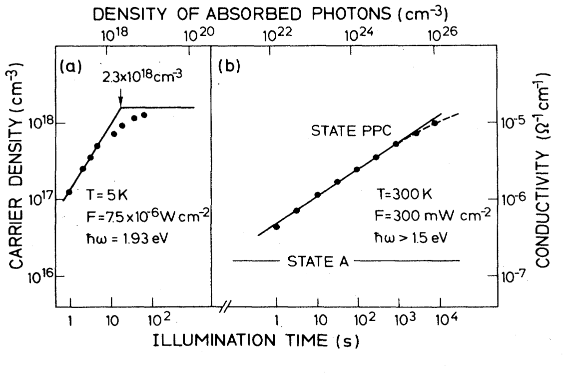

FIG. 3. (a) Concentration of spatially separated carriers at $T=5$ K as determined by the method of Ref. 1 as a function of illumination time. (b) Buildup of persistent photoconductivity, $\sigma_{\rm PPC}$, at $T=300$ K as a function of illumination time. $\sigma_{\rm PPC}$ is measured 5 min after the end of the illumination. Irradiation times have been expressed in terms of absorbed photon densities (upper abscissa) on the basis of an average photon energy of 2.0 eV and a corresponding absorption coefficient of 2.5×10^4 cm^{-1}.

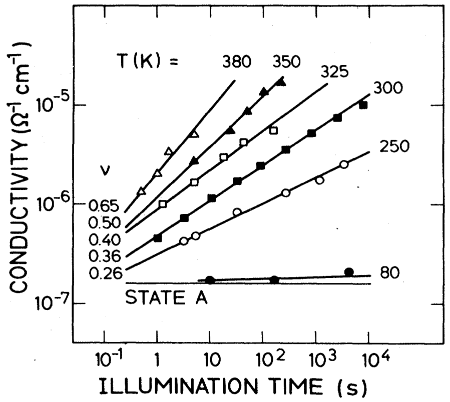

FIG. 4. Persistent photoconductivity, measured at room temperature, $\sigma_{\rm PPC}(300)$, as a function of irradiation times, *t*. Parameter is the temperature during irradiation. Straight lines represent the relationship between $\sigma_{\rm PPC}(300)$ and *Ft* according to $\sigma_{\rm PPC}(300)\propto(Ft)^{\nu}$, where *F* is the illumination density.

The influence of the temperature during illumination on $\sigma_{\rm PPC}$ (measured at $T=300$ K) is illustrated in Fig. 4. It turns out that with increasing temperature fewer photons are necessary to achieve a given level of $\sigma_{\rm PPC}$. At $T=80$ K virtually no PPC could be induced even after a total of 3000 sec of illumination at a level of 300 mW/cm^2. For a given temperature the relationship between $\sigma_{\rm PPC}$ and the product of illumination time and power density F is well described by a power law $\sigma_{\rm PPC}\propto(Ft)^{\nu}$ with an exponent that varies between $\nu=0.26$ for $T=250$ K and $\nu=0.65$ for $T=380$ K.

Conversely, we might ask what irradiation time τ is necessary to reach a PPC state characterized by a value of $\sigma_{\rm PPC}=x\sigma_A$. Arrhenius plots of τ versus $1/T$ in Fig. 5 suggest that the transition from state A to state PPC in-

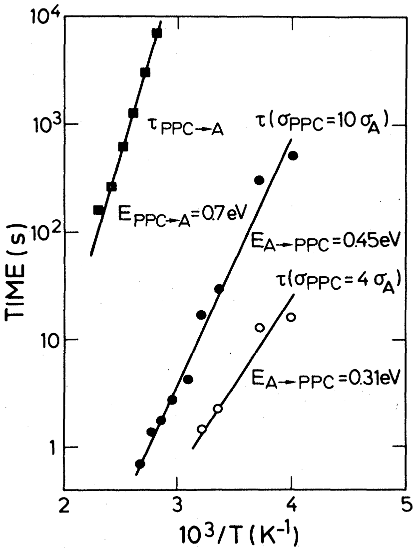

FIG. 5. Time necessary to reach a given level of $\sigma_{\rm PPC}$ vs $1/T$. Also plotted is the relaxation time $\tau_{{\rm PPC}\rightarrow A}$ which is defined as the time after which PPC is reduced by a factor of 2 from its value 4 min after the end of the illumination.

volves a thermally activated step. The activation energies $E_{A\rightarrow \mathrm{PPC}}$ derived from linear regressions to the data points of Fig. 5 depend somewhat on x, the choice made for σ_{PPC}. We obtain $E_{A\rightarrow \mathrm{PPC}}=0.31$ eV for $x=4$ and $E_{A\rightarrow \mathrm{PPC}}=0.45$ eV for $x=10$.

The relaxation of state PPC proceeds also faster with increasing temperature and we derive an activation energy $E_{\mathrm{PPC}\rightarrow A}=0.7$ eV (see Fig. 5).

B. State *C*

We expect, according to Fig. 5, that the state PPC corresponding to $\sigma_{\mathrm{PPC}}=10\sigma_A$ is established in less than 0.1 sec at $T=480$ K $[(1000\text{ K})T=2.1]$. This expectation is indeed borne out by Fig. 6(a) where PPC is fully established after 2 sec of illumination followed by the relaxation of PPC to state A. As a corollary we do not anticipate any changes in σ for illumination times longer than 1 sec. This is, however, not the case as illustrated in Fig. 6(b) for an irradiation period of 130 sec. The conductivity rises initially with a time constant of 0.1 sec (from Fig. 5) to a value which is the sum of σ_{PPC} and σ_{ph}, the normal photoconductivity. The conductivity drops during illumination from this value with an initial time constant $\tau_{\mathrm{PPC}\rightarrow C}$ of 20 sec and approaches a level that is equal to the photoconductivity of the sample (see Sec. III C). As the light is switched off at $t=0$, σ drops instantaneously to a value *below* σ_A and recovers subsequently over a period of several hundred seconds to its dark value $\sigma_A(480\text{ K})$. The sample is obviously transformed during the illumination into a new state C that is characterized by a dark conductivity σ_C *smaller* than σ_A in contrast to the excess conductivity in state PPC. The generation of C, *during* illumination, which is accompanied by the decrease in conductivity proceeds with a time constant $\tau_{\mathrm{PPC}\rightarrow C}$ as indicated in Fig. 6(b). It turns out that $\tau_{\mathrm{PPC}\rightarrow C}$ decreases with increasing temperature, according to $\tau_{\mathrm{PPC}\rightarrow C}=\tau_{0,\mathrm{PPC}\rightarrow C}\exp(E_{\mathrm{PPC}\rightarrow C}/kT)$ with an activation energy $E_{\mathrm{PPC}\rightarrow C}=0.8$ eV as shown by the Arrhenius plot of Fig. 7. The prefactor $\tau_{0,\mathrm{PPC}\rightarrow C}$ depends, of course, on the light intensity. We establish, however, that the product of time constant and the asymptotic photoconductivity $\tau_{\mathrm{PPC}\rightarrow C}\sigma_{\mathrm{ph}}$ is independent of the illumination intensity at a given temperature. The relaxation time $\tau_{C\rightarrow A}$ which characterizes the return to equilibrium state A after the end of the illumination is also thermally activated with an activation $E_{C\rightarrow A}=0.8$ eV as demonstrated in Fig. 7 as well.

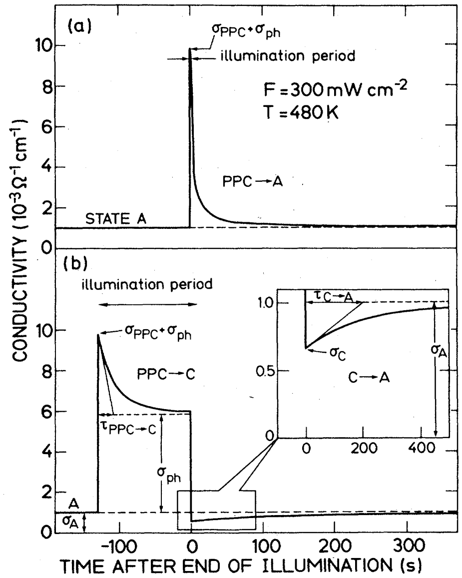

FIG. 6. Conductivity of an amorphous n-i-p-i superlattice as a function of time at $T=480$ K for different irradiation periods. Power density of the heat-filtered light is 300 mW/cm^2. (a) Irradiation time 2 sec. Sample shows the decay of PPC on a time scale of ~50 sec. (b) Irradiation time 130 sec. Transformation from PPC to C during illumination and subsequent decay of state C into A.

Since the relaxation time from $C\rightarrow A$ is comparatively long and steeply activated it should, in principle, be possible to "freeze-in" state C at room temperature. State C, prepared at $T=450$ K $[(1000\text{ K})/T=2.2]$, relaxes into state A with a time constant of 500 sec at this temperature. Cooling the sample with a rate of 20 K/min down to room temperature allows us to quench-in the now metastable state C with minimal relaxation into A. While samples in states A and C differ only marginally in their room-temperature dark conductivity they are readily distinguished owing to their very different sensitivity to illumination. This is demonstrated in Fig. 8 where we plot the room-temperature dark conductivity of an n-p-n-p sample in states A and C after increasing illumination times. The illumination was performed with 300-mW/cm^2 heat-filtered light at a slightly elevated temperature ($T=360$ K) corresponding to $(1000\text{ K})T=2.8$ because according to Fig. 5 briefer irradiation periods are sufficient for the creation of persistent photoconductivity than at room temperature. The sample in state A shows indeed the expected buildup of PPC. Saturation with a 50-fold increase in σ is achieved after about 100 sec. A

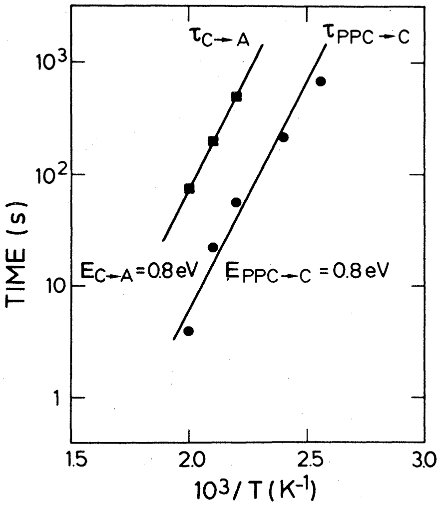

FIG. 7. Arrhenius plots of the time constants for the observed transformations between states A, PPC, and C. Corresponding activation energies are indicated.

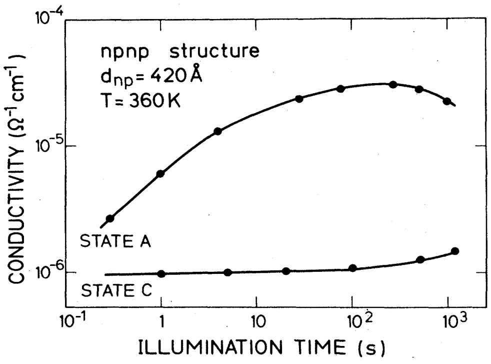

FIG. 8. Dark conductivity vs illumination time for an *n-p-n-p* superlattice starting from states *A* and *C*.

further increase in PPC is limited by the creation of state *C* as indicated by the drop in dark conductivity for illumination times beyond 100 sec. The sample previously brought into state *C* is, on the other hand, virtually insensitive to light exposure and can no longer be transformed into state PPC as illustrated by the lower curve of Fig. 8.

C. Conductivity activation energies

Figure 9 shows Arrhenius plots of the dark conductivities in states *A*, PPC (1000 sec), and *C* of our *n-i-p-i* superlattice. The conductivities are activated in all three cases with an activation energy of 0.62 and 0.64 eV in states *A* and *C* and similar σ_0 values of 3500 $\Omega^{-1}\text{cm}^{-1}$ and 4000 $\Omega^{-1}\text{cm}^{-1}$, respectively. The higher conductivity in state PPC is mainly the result of a reduced activation energy of 0.54 eV, whereas σ_0 is 5000 $\Omega^{-1}\text{cm}^{-1}$. Longer illumination times reduce E_{PPC} further and this results in a correspondingly higher σ_{PPC}. Since *C* and PPC are metastable the three conductivity curves merge around $T=500$ K [(1000 K)/$T=2$] when approached from below.

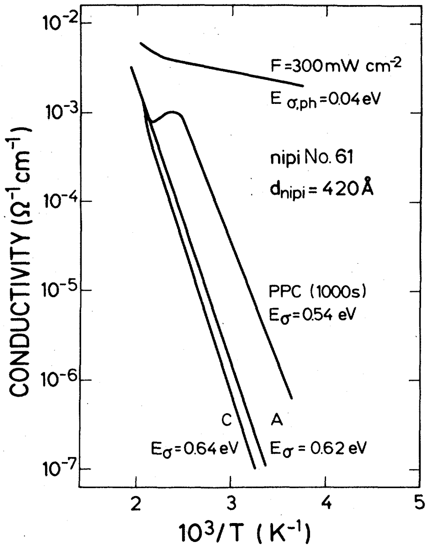

FIG. 9. Arrhenius plots of the photoconductivity (upper curve) and the dark conductivities in states *A*, PPC, and *C*.

The creation of states PPC and *C* is intimately related to the presence of photocarriers. As we have seen, the times necessary to establish *C* are, for example, inversely proportional to the photoconductivity. It is thus conceivable that the thermal activation energies connected with these transitions are largely due to the activation energy of photoconductivity. That this is not the case is demonstrated by the temperature dependence of the photoconductivity of our sample in Fig. 9. The measurements were performed with the same light intensity of 300 mW/cm^2 used throughout this investigation. The activation energy of 0.04 eV is clearly substantially lower than any of the activation energies observed for the light-induced transformations.

D. Is PPC a surface effect?

PPC has been observed for unstructured *a*-Si:H samples in three instances.[6–8] In one case, that of slightly boron-doped *a*-Si:H, the occurrence of PPC could be traced to the presence of an oxide surface layer.[6] This raises the question as to whether PPC is truly a bulk property of modulation-doped *a*-Si:H. We have therefore measured PPC in our *n-i-p-i* sample before and after a 1 min etch in 5% HF and found no difference. A compensated sample, prepared in the same deposition system, also exhibits PPC, a result that is in agreement with Ref. 7. When subjected to the same treatment as the *n-i-p-i* sample, however, it showed a reduction in PPC by an order of magnitude. We conclude therefore that PPC in *n-i-p-i* structures is a true bulk effect, whereas it is related to the surface in all other cases.

IV. DISCUSSION

A. State PPC

PPC is a phenomenon that is observed in a wide variety of crystalline semiconductors.[9,10] In many instances PPC can be traced to the spatial separation of photogenerated carriers by macroscopic barriers which leads to an increase in carrier lifetime as a result of their reduced recombination probability. A well-documented example is that of a thin epitaxial layer of *n*-type GaAs on an insulating GaAs substrate.[11,12] The carriers are separated in the field of the *n-i* junction. The holes diffuse into the substrate where they are trapped in deep traps and are thus rendered immobile. The excess electrons remain mobile and contribute to an excess dark conductivity after the light has been switched off. The relaxation of this PPC occurs through the recombination of increasingly distant pairs of electrons and holes which leads to the characteristic nonexponential decay of PPC (Ref. 12) that is also found in our case.

An analogous explanation has been given for PPC in weakly *p*-type *a*-Si:H where the barrier responsible for the carrier separation is formed by a surface oxide which induces a hole accumulation layer and traps the excess electrons.[6]

Doping superlattices with their periodic arrangement of *p-n* junctions are expected to exhibit PPC as well. Ploog and Künzel[13] indeed observed an increase in the lifetime of photocarriers by 12 orders of magnitude in a crystalline GaAs doping superlattice compared to unmodulated GaAs. It is thus not surprising that the original observation of PPC in *n-p-n-p* *a*-Si:H superlattices[2] was associated with the charge separation by the internal barrier fields as suggested by Döhler. Our results presented here corroborate that PPC is a bulk phenomenon that occurs generally in doping multilayers of *a*-Si:H independent of details in preparation (one- versus two-chamber deposition) or structure (*n-p-n-p* versus *n-i-p-i*). We argue, nevertheless, that PPC in doping superlattices of *a*-Si:H cannot be explained straightforwardly by Döhler's model for the following reasons.

Our earlier experiments in Ref. 1 and the results of Fig. 3(a) show that it is possible to store excess photocarriers in the *n* and *p* regimes of an *n-i-p-i* superlattice in accordance with Döhler's model with an efficiency of about one at $T=5$ K. The density of these excess carriers in our *n-i-p-i* sample was calculated to be 1.6×10^{18} cm^{-3}. It is thus natural to assume that the same carriers are responsible for the observed room-temperature PPC. As it turns out, however, the spatially separated charges are only stable at temperatures below ~10 K, i.e., as long as they remain trapped in the valence- and conduction-band tails. Under these circumstances the lifetime of the carriers depends exponentially on their separation according to $\tau=\tau_0\exp(-2R/R_0)$ where R_0 is a characteristic radius of the carrier wave function of the order of 10 Å, and R, the average separation of the carriers from each other or from a recombination center, increases with increasing superlattice period.[1] The lifetime of the carriers is rapidly reduced if they are excited either thermally or by infrared radiation above their respective mobility edges. This process is depicted in Fig. 10 where we plot the concentration of spatially separated excess carriers in our *n-i-p-i* sample as a function of temperature. The specimen originally in state *A* was loaded with excess carriers by band-gap illumination at $T=5$ K. After annealing at a given temperature for four minutes the sample was again cooled to 5 K and the carrier concentration determined from the amplitude of the ir photoconductivity transient as described in Ref. 1. It is evident that at $T=80$ K only 5% of the original carrier concentration remains and this value is likely to be further reduced at room temperature and above. Any remaining spatially separated carriers are not responsible for PPC because PPC is not observed in specimens that were in state *A* before the low-temperature loading. On the other hand, a sample that has been brought into state PPC exhibits the transient ir photoconductivity at low temperature *only* after it has experienced additional band-gap illumination that fills the band extrema. The same sample when brought up to room temperature is still in state PPC with unchanged conductivity in spite of the fact that the excess carriers stored at low temperatures have recombined during the warm-up period as illustrated in Fig. 10.

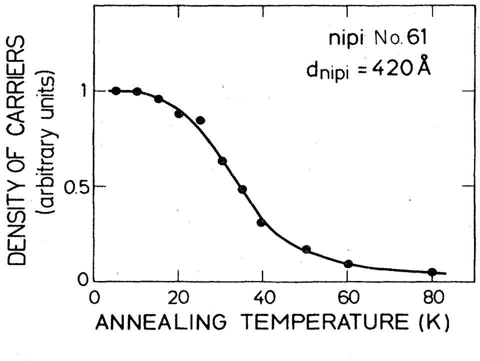

FIG. 10. Density of separated carriers at $T=5$ K that remain after annealing at increasing temperatures.

We are thus led to the conclusion that the PPC observed in *n-i-p-i* or *n-p-n-p* superlattices cannot be explained simply in terms of Döhler's model, a model that clearly applies to the low-temperature storage of excess charges. The low-temperature effect and PPC are obviously quite independent of each other. Furthermore, the fact that thermal energy is *required* to establish PPC implies the presence of barriers in one of the microscopic steps that are responsible for PPC. In Döhler's model such barriers exist only for the *recombination* of separated carriers in the form of potential barriers. But they are certainly absent if we were to describe the *creation* of PPC in terms of this model.

We have, at present, no satisfactory microscopic description to explain PPC in *n-i-p-i* or *n-p-n-p* structures. We can make, however, a few clarifying remarks concerning possible mechanisms. First, recall that PPC in doping superlattices is a bulk effect and not due to surface fields as in compensated or *p*-type samples. Secondly, thermopower measurements indicate that PPC is due to electrons.[14] That implies that holes are trapped thus raising the quasi-Fermi-level of electrons, E_F, due to the lack of recombination partners. The increase in conductivity in state PPC over that in *A* corresponds to a lowering of the activation energy by about 0.08 eV (see Fig. 9). The number of electrons necessary to accomplish this shift in E_F is approximately 10^{15} cm^{-3} assuming a density of states of 10^{16} cm^{-3}eV^{-1} near the equilibrium position of E_F. This is only one thousandth of the excess carrier concentration that can be stored in the same *n-i-p-i* sample below 10 K.

The buildup of PPC may then be envisaged as follows. Photogenerated electrons and holes drift during illumination towards the *n* and *p* regions, respectively, and maintain excess carrier densities which are determined by the balance between creation and recombination rates. With the end of the illumination most carriers recombine (drop of photoconductivity) except for a small fraction of holes which has been trapped during illumination in special traps in the *p* regions. The balancing number of electrons remain in the *n* regions and are responsible for the persistent photoconductivity

The hole traps are of a special kind in that they have to be thermally sensitized with an activation energy of about

0.4 eV and a slightly higher barrier has to be overcome for their ionization (see Fig. 5). The latter barrier renders the hole in these traps rather immobile compared to the majority of holes which are trapped in shallow centers and are obviously able to recombine with electrons even at temperatures as low as 80 K as we have seen in Fig. 10. Thus the recombination mechanism of Fig. 10 requires that *both* electrons and holes are mobile to be able to drift to a recombination center with an energy close to midgap and situated at the boundary between *n* and *p* regions. A temperature of 80 K is clearly insufficient to overcome the potential barriers that separate electrons and holes in *n-i-p-i* structures.[15] The spatial separation of the holes immobilized in the centers of the *p* regions and the balancing electrons kept in the *n* regions by the *n-i-p-i* potentials is thus responsible for the reduced recombination rates which give rise to the long-lived PPC.

The special hole traps are, in our opinion, not peculiar to doping superlattices but are present also in unstructured *a*-Si:H. This raises the question why PPC is not generally observed in unstructured amorphous silicon. The reason is that the electrons which balance the trapped holes are free to move towards the holes and recombine in unstructured material. Band bending as a result of space-charge layers at surfaces can act in the same way as the *n-i-p-i* fields. This explains the observed surface-sensitive PPC of oxidized and compensated samples.[6,7]

B. The *AX* center

An electron trap that requires thermal energy in order to be filled is the so-called *DX* center that has been identified in Te-doped $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ ($x \simeq 0.4$).[16,17] It is believed that the *DX* center consists of a donor (Te)-vacancy complex. The electron capture is thermally activated with an activation energy of ~ 0.2 eV due to a strong electron-lattice coupling which raises the donor level above the conduction-band edge once the electron has been released. The resulting barrier leads to a low-temperature PPC in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ because electrons (the majority carriers) cannot recombine with their donors once they have been generated by sub-band-gap illumination with an energy sufficient to ionize the donors.

We propose that an analogous trap is responsible for PPC in amorphous doping superlattices. The center—we call it *AX* because it has the character of an acceptor—traps holes and reduces thereby the recombination probability of electrons which cause the persistent photoconductivity. In analogy to the *DX* center, we postulate that a strong electron-lattice interaction at the site of *AX* is responsible for the thermal barrier of $\simeq 0.4 \text{ eV} \equiv E_{A\rightarrow\mathrm{PPC}}$. Note that the roles of the activation energies for the neutralization of *DX* and *AX* centers are reversed: in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ (*DX*) they reflect the barrier against the *quenching* of PPC whereas it is the barrier against the *creation* of PPC in the *n-i-p-i* structures that requires thermal energy. A different activation energy is necessary for the ionization of *AX* which is, of course, identical with the activation energy for the quenching of PPC: $E_{\mathrm{PPC}\rightarrow A} \cong 0.7$ eV.

Once we accept the existence of *AX* centers several avenues are open to explain PPC as a bulk property of amorphous *n-i-p-i* and *n-p-n-p* structures. We can assume that the *AX* are not recombination centers, i.e., holes that are trapped in an *AX* are no longer available for recombination even if they coexist in regions of high electron concentrations. In this case *AX* centers have to be related to the special preparation procedure of *n-i-p-i* or *n-p-n-p* multilayers because otherwise unstructured *a*-Si:H would also exhibit bulk PPC and that is not the case. Alternatively, it is conceivable that *AX* centers are located at the interfaces between the layers. We have indeed evidence from hydrogen profiles that the *n-p* interface has an excess hydrogen concentration. The observation of PPC in the structure of Ref. 2 which were prepared entirely different from the samples discussed here and in unstructured specimens[6–8] leads us to the conclusion that *AX* centers are not specific to *n-i-p-i* or *n-p-n-p* superlattices. This leaves only the scenario already sketched above. *AX* centers are dispersed throughout the material. They can act as recombination centers and this prevents PPC from occurring in unstructured material. Only the spatial separation of free electrons and trapped holes in doping-modulated *a*-Si:H makes PPC possible.

The strong electron-lattice interaction ascribed to *AX* comes as little surprise for an amorphous system; it is indeed at the heart of the small-polaron theory of transport in *a*-Si:H (Ref. 18) and responsible for the 0.4-eV Stokes shift of the 1.4-eV luminescence band.[19] The lowest unoccupied level of *AX* in its charged state is pushed into the valence-band continuum by the electron-lattice interactions. Once neutralized by the capture of a hole the lattice around *AX* relaxes towards a different equilibrium such that the energy of AX^0 is above the valence-band edge.

The quenching of PPC, i.e., the transition from AX^0 to AX^-, requires an activation energy of about 0.7 eV and the binding energy E_0 of the AX^0 is thus ~ 0.3 eV, the difference between $E_{A\rightarrow\mathrm{PPC}}$ and $E_{\mathrm{PPC}\rightarrow A}$. This means that AX^0 lies in the valence-band tail of *a*-Si:H.

C. State *C*

The second light-induced state of the amorphous *n-i-p-i* structures, state *C*, is also thermally activated. Owing to its higher activation energy of 0.8 eV compared to the transition from *A* to PPC, state *C* can only be reached by passing through state PPC after prolonged irradiation at elevated temperatures. This raises the question of whether *C* is a state *sui generis*, i.e., unrelated to PPC, or whether the changes that take place in state *C* affect the *AX* centers directly and are thus responsible for the loss of PPC. The creation of new deep-lying defects or the thermally activated trapping of the excess electrons in *DX* centers could, for instance, force the quasi-Fermi-level of electrons from that in state PPC back towards its value in state *A* and thus eliminate the excess dark conductivity. Such a model would fall under the first alternative. Its relationship to the Staebler-Wronski effect (SWE) is obvious. We are quick to ascertain, however, that we are dealing *not* with the Staebler-Wronski effect here. The high activation energy for the creation of *C* makes it impossible to establish C at room temperature where the Staebler-Wronski effect is readily achieved in our samples. The creation of SWE is not thermally activated in contrast to creation of state C.

In favor of the second alternative, namely that the transition PPC$\rightarrow C$ affects the AX centers, is the observation that state C appears to be identical to A except for the loss of PPC. Any further speculations about the nature of state C are entirely premature and must await further experiments. It is nevertheless reasonable to state that the observation of a maximum PPC level does not establish a saturation of PPC but rather a limitation through the interference of state C.

V. SUMMARY AND CONCLUSIONS

We have established room-temperature persistent photoconductivity with decay times of hours and days in *n-i-p-i* doping superlattices based on amorphous hydrogenated silicon. PPC in *n-i-p-i* structures is a bulk effect and not related to surface properties as in compensated material. The creation and quenching times of PPC are both thermally activated with activation energies of ~ 0.4 and 0.7 eV, respectively. This excludes an explanation of PPC along the lines suggested by Döhler[3] as due to carriers which are spatially separated in the *n-i-p-i* fields because there exists no barrier for this process. We could demonstrate, in fact, that the two phenomena are mutually exclusive in the sense that charge separation according to Döhler's model is stable only below ~ 10 K whereas PPC cannot be established below ~ 80 K.

We suggest that PPC in *n-i-p-i* and *n-p-n-p* structures is caused by the trapping of holes in AX centers in the p-type regions which leaves long-lived electrons in the n regions that contribute to an excess dark conductivity after illumination. The AX centers are acceptorlike and we postulate a strong electron-lattice coupling that allows small thermal barriers against ionization and neutralization (~ 0.7 eV) while keeping the corresponding vertical energies (i.e., without lattice relaxation) prohibitively large. The carrier concentration responsible for PPC is in this model orders of magnitude smaller than the maximum concentration of excess carriers that can be stored due to the band modulation at low temperatures.

A third state C can be induced after prolonged illumination at elevated temperatures that eventually supersedes state PPC. Since C exhibits no PPC, it limits the maximum observable persistent photoconductivity. Creation and quenching of C are also thermally activated and it is argued that changes involving the AX centers are possibly involved in the transition from PPC to C.

The present work is, of necessity, a detailed account of the new light-induced phenomena that are distinctive features of the doping-modulated superstructure based on *a*-Si:H. Their microscopic origin is to a considerable extend delineated by what they are not: namely Staebler-Wronski effect or a mere charge separation as observed earlier at temperatures below 10 K. The postulated AX center with its strong electron-lattice coupling is speculative as yet but appears to be the only reasonable explanation for the persistent photoconductivity.

Note added. Possible candidates for the AX defect are dangling bonds which are present in sufficient concentrations. In order to examine this possibility we have illuminated the sample at 80 K with 300 mW/cm^2 white light for 1 h. This treatment is known to rise the density of dangling bonds by about a factor of 4 through the so-called Staebler-Wronski effect,[20] without inducing PPC (compare Fig. 4). The creation of PPC at room temperature was not affected by this treatment, however, which makes it unlikely that dangling bonds are the centers responsible for PPC.

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