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Persistent photoconductivity and field-enhanced conductivity in amorphous-silicon doping-modulated superlattices

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We have found both a large persistent photoconductivity and a remarkable field-enhanced conductivity (FEC) showing a three-orders-of-magnitude enhancement after application of low electric fields (20–100 $V cm^{-1}$) in *nipnip* $\cdots$ doping-modulated superlattices of amorphous hydrogenated silicon. The structures are up to ten times wider (1 cm) than previous structures. The dependence of the FEC on field and temperature shows it is caused by a relatively limited number of trap states.

Recent studies of layered structures of amorphous hydrogenated silicon *a*-Si:H, of different doping species, have reported and described the phenomenon of room-temperature persistent photoconductivity (PPC).[1-4] First tentatively ascribed[1,2] to light-induced carriers being trapped in the separate *n* and *p* layers according to simple theory,[5] it was soon shown[3] that predicted thermal effects and recombination rates were not consistent with the data. A recent suggestion[4] has been that light-excited carriers are trapped at phosphorus-boron complexes at *n-p* interfaces, and another[6] that excess holes create extra dangling-bond states of long lifetime.

In this Rapid Communication we present PPC for large structures and describe a remarkable new phenomenon which we call field-enhanced conductivity (FEC). We refer to the structures as superlattices because the band gaps of very thin *n*, *i*, and *p* layers are not identical.[7-9]

Previous samples[1-4] were 1 mm wide but we obtained all effects on samples 10 mm wide to a degree just as good as on narrow samples. This shows that the effects can occur in relatively large-area (1.7×1 cm^2) films and are not dependent on conditions obtainable only in small units. The structures were prepared by radio-frequency decomposition of silane doped with phosphine or diborane for *n* and *p* layers, respectively. The chamber was a 6-in.-diameter stainless-steel cross of the type described by Street, Knights, and Biegelsen[10] with a 2-in.-diam substrate heated uniformly to 220 °C by a contacting oil bath. Strong PPC was obtainable using appropriate conditions in a single chamber, confirming that separate chambers for the *n*- and *p*-layer depositions are not necessary[4] for large PPC effects. Figure 1 shows typical PPC from a structure. Values of *G*, defined as the ratio of the conductivity 10 min after a 20-sec light flash of 50 $mW cm^{-2}$ from a heat-filtered quartz-iodine lamp to the dark conductivity, ranged up to 300. The doped layers were produced with concentrations of approximately 0.01 at.% diborane and 0.1 at.% phosphine in silane. The *nipnip* $\cdots$ samples in the figures were all made with 6×66-Å *n* layers, 5×76 Å *i* layers, and 5×33 Å *p* layers.

It has previously been reported that the dark current changes with time in the case of *a*-Si:H–SiN_x:H layered structures,[11] saturating after periods of up to several hours. In the case of *a*-Si:H layered structures,[4] the dark current was also observed to change, settling to a lower equilibrium value in a few hours at a field of 10 $V cm^{-1}$.

The latter phenomenon was also observed in some of our samples. However, it is the prelude to a much larger and more significant effect. If larger fields are applied the current gradually begins to increase, as shown in Fig. 2, but eventually saturates at a value that can be orders of magnitude larger than the original current. Note that the higher the field, the sooner the attainment of saturation.

If the field is set at a given value and the experiment conducted at different temperatures (inside a vacuum oven) then the same saturation value is reached, but soon-

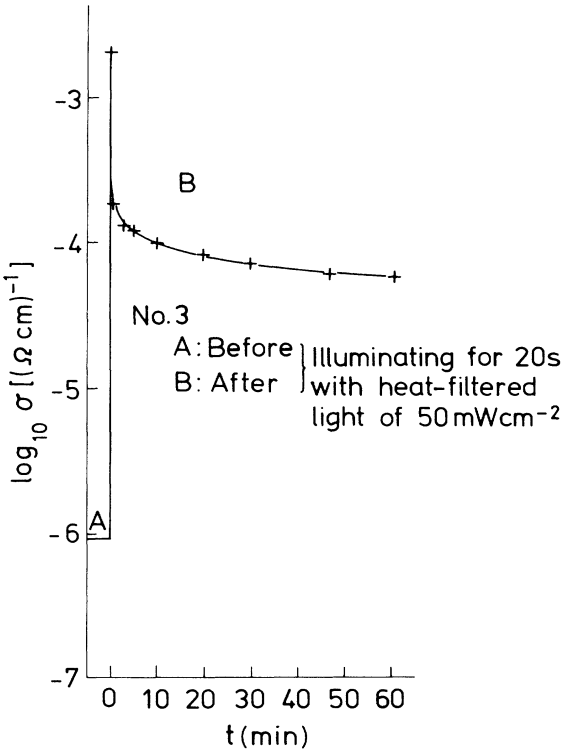

FIG. 1. Conductivity σ of 10-mm-wide structure after light flash (quartz-iodine lamp, 5-cm water filter) of 50 $mW cm^{-2}$ for 20 sec, showing strong PPC (enhancement 107 after 10 min).

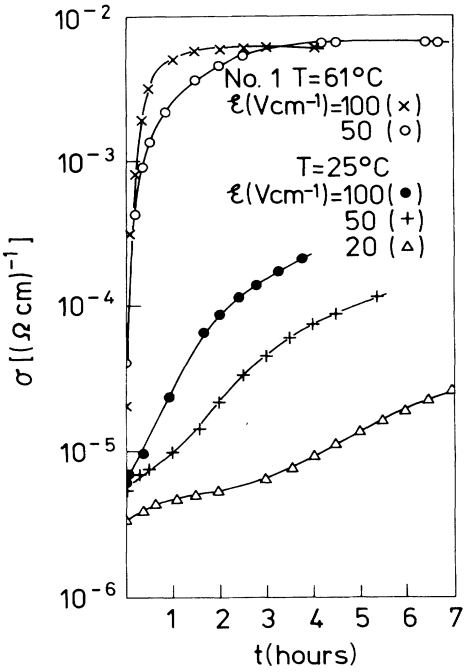

FIG. 2. Conductivity σ as function of time of application of longitudinal field with specimen in vacuum.

er in the case of higher temperatures, as shown in Fig. 3. Thus for a field of 100 $V\,cm^{-1}$, saturation occurs after about $2\frac{2}{3}$ h at 61 °C, $7\frac{1}{2}$ h at 46 °C, and 78 h at 23 °C, the conductivity being eventually enhanced by a factor of 850 at 23 °C for the sample shown. Times and enhancement factors differ somewhat for different temperatures and samples, but the general trends are the same.

We now consider an explanation of the various phenomena. As regards PPC, the original idea[5] of photoexcited carriers being separated into the n and p layers and there being impeded from recombining applies to crystalline superlattices at low temperatures,[12] but cannot account for room-temperature effects in a-Si:H structures. The reasons discussed by Hundhausen and Ley,[3] are principally that such separated carrier lifetimes are experimentally too low at 300 K and that thermal activation of the PPC state appears to be involved. The presence of hole traps was suggested[3] and a specific source for these was proposed by Agarwal and Guha[4] as being P-B complexes at n-p interfaces. Supporting evidence comes from failure to obtain PPC from *nini* $\cdots$ superlattices, a result which we generally corroborate, although in our case a very small effect ($G=1.1$) was sometimes obtainable. If the hole traps are located at energy E_t (say, 0.9 eV) below the conduction "band edge" E_c, the recombination lifetime τ_1 can be related to the normal recombination ("band-to-band") lifetime τ by

$$\tau_1=\tau[1+N_tN_c^{-1}\exp(E-E_t)/kT]\ , \tag{1}$$

using an expression of Rose.[13] With reasonable values of $\tau=10^{-9}$ sec, the conduction-edge density of states $N_c=10^{19}\ cm^{-3}$, the trap density $N_t=10^{17}\ cm^{-3}$, one obtains $\tau_1=10^4$ sec. Hence, if the assumptions behind Eq. (1) are justified, it is possible to explain long lifetimes by such hole traps, even neglecting activation barriers. However, it is found[3] that PPC (the parameter G) gets smaller at lower temperatures, an effect which we confirm for our high-G structures, which is contrary to Eq. (1). This indicates that the expression is oversimplified, and/or that the formation of the traps is thermally activated.

The conductivity σ of the samples rises from about 5×10^{-6} to about $5\times10^{-3}\ (\Omega\,cm)^{-1}$ at field saturation, Figs. 2 and 3. Measurements on individual layers of thickness 33 to 66 Å are complicated by high resistances comparable to the insulating substrate. However, n layers 420 Å thick gave a σ of $7\times10^{-6}\ (\Omega\,cm)^{-1}$ and p layers 160 Å thick gave $2\times10^{-6}\ (\Omega\,cm)^{-1}$. These thicknesses are the sums of the individual n and p layers. The values of σ are comparable to those of the structure.

It has been assumed in the past[1-4] that the *nipnip* or *nipi* structure has the usual alternating field structure expected from separate n, i, and p layers, with V^B, the p-n barrier, about 0.9 V. However, a calculation shows that this is not applicable to very thin layers. Take the case of a single n-p structure of p-layer width 33 Å and n-layer width 66 Å, as in our superlattice. One can obtain an expression for V^B from junction theory.[14] Taking the zero at the far edge of the p side, and assuming uniform charge density,

$$V^B=qN_aWW_p/2\varepsilon\varepsilon_0\ , \tag{2}$$

where q is the electron charge, N_a the positive charge concentration in the p side, taken as $1.24\times10^{20}\ m^{-3}$, W the total width of charged double layer (99 Å), W_p the p-layer width (33 Å), ε the dielectric constant taken as 11, and ε_0 the permittivity of free space. This gives 3.2×10^{-6} V, i.e., a negligible barrier. Hence the bands are essentially flat. The reason for this initially surprising result is that the layers are too thin to support a charge sufficient to create a large potential change. From Eq. (2), V^B is proportional to N_a. The value used corresponds to a p layer of conduc-

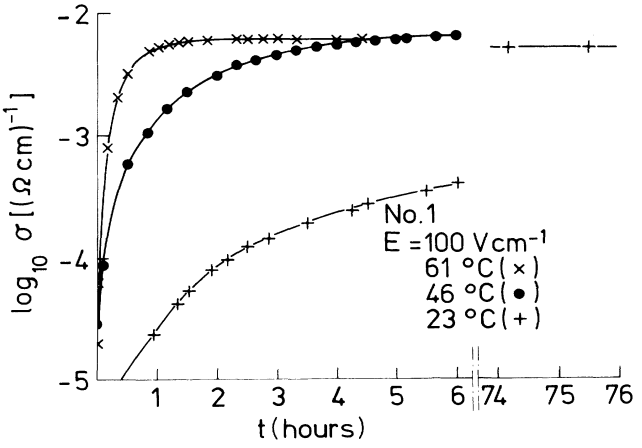

FIG. 3. As for Fig. 2. Same field, three different temperatures. Sample is annealed between treatments, hence starting conductivities may vary slightly.

tivity similar to that measured above for a separate layer. If one takes into account charge in the band gap, and assumes the total charge is as high as 10% of the B dopant during deposition, N is 10^{23} m^{-3}, yielding $V^B = 2.6\times10^{-3}$ V which is still negligible. In the case of the multiple layers in the superlattice, the theory is more complicated due to effects from nearby junctions but this will not alter the main result that the barriers are normally very small.

Hence, contrary to simple expectation, the whole structure behaves like a layer, slightly n type, with only a slight field modulation (see inset in Fig. 4). At very low temperatures (a few K) low values of V^B can keep carriers separated but such barriers are soon overcome as the temperature rises. Hence no junction-induced effects are expected. Indeed, at 80 K it has been reported that there was no PPC in a-Si:H superlattices, and above this (but below 300 K) the effect is weak, which we confirm in our structures. The question is then why PPC and FEC do occur at room temperature and above in p-n repeat structures.

A recent explanation[6] for PPC was that a fraction of light-excited holes could break bonds, causing extra dangling-bond states of positive charge D^+. These were presumed to remain unfilled because the photoinduced electrons were held in the n-type layers of the superlattice. In our thin structures the normal p-n barriers are of insufficient height to keep carriers separate, as explained above. Therefore, it is necessary to assume that there may be activation energy necessary before such extra dangling-bond states are filled, causing long lifetimes as discussed above in connection with Eq. (1).

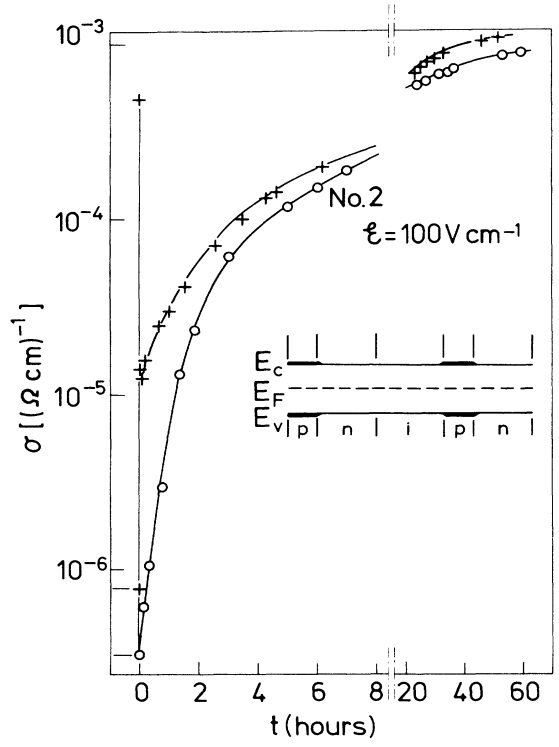

FIG. 4. Plot of conductivity σ vs time in cases where field of 100 V cm^{-1} is applied in dark (○), and 10 sec after cessation of light flash (+) (see Fig. 1). Inset shows band edges.

In the case of FEC, we suggest that the phenomena can be explained using the same concept of induced gap states, D^+. The fields used (10 V cm^{-1} and up) are too low to invoke avalanche effects (requiring at least 10^5 V cm^{-1} at 300 K) or defect-center polarization or other known high-field effects. Furthermore, the field is applied parallel to the layers so that possible ion drift from the interfaces into the layers is not promoted unless there are gross distortions in layer thickness. We have no evidence that such occur. Note that the energy gain by carriers accelerated by the field is very small. Taking a drift range $d = \mu\tau\mathcal{E}$ and assuming[15] $\mu\tau = 10^{-10}$ cm^{2}V^{-1}, then $d = 10^{-8}$ cm at 100-V-cm^{-1} field, and could not be more than two orders of magnitude greater. Thus the energy gain, even for $d = 10^{-6}$ cm, is only $qd\mathcal{E} = 10^{-4}$ eV, which is negligible compared with kT of 260×10^{-4} eV.

Thus the presence of majority-carrier flow along the layers cannot by itself cause a significant change to the population of filled traps. Therefore, we invoke the phenomenon of minority-carrier injection. It is extremely difficult to make perfectly noninjecting contacts in any semiconductor and even good contacts often have 5% minority-carrier injection, which we assume for the evaporated Al contacts here. The presence of excess minority carriers would not normally disturb the quasi-Fermi levels if the electrons and holes recombine, but if a fraction of holes cause bond breaking and long-lived dangling-bond states then effects will occur. As D^+ states are created and the charge density increases, the Fermi level approaches the band edges, thus causing the conductivity to increase. Eventually equilibrium is reached between the above process and recombination, leading to apparent saturation.

A quantitative check is possible. Consider the room-temperature FEC effect in Fig. 3. The conductivity rises from 5×10^{-6} to 1.5×10^{-4} (Ω cm)$^{-1}$ in 3 h. Assuming 5% of the injected current is holes, one can calculate that approximately 1.3×10^{15} holes are injected into the structure in the 3 h, giving a volume density of 8×10^{19} cm^{-3}. This may be compared with the charge density required to provide a conductivity of 1.5×10^{-4} (Ω cm)$^{-1}$, which is approximately 10^{15} cm^{-3}. Hence, if less than 1 in 10^4 of the injected holes is trapped in some way, e.g., by creating a new dangling-bond state, it is possible to account for the enhanced conductivity.

At higher temperatures the current is increased, leading to faster creation of D^+ states and, hence, faster saturation as shown in Figs. 2 and 3. Similarly at a given temperature, an increase in field causes higher currents and, hence, faster saturation, also in agreement with experiment.

On our present theory, the PPC after FEC has saturated should be very small since most possible D^+ states have already formed and so the light-excited carriers should recombine quickly. This was tested by applying the standard light flash to a field-saturated specimen. The value of G, which had been 7.2 in the dark, was now only 1.14, so that PPC was almost negligible. Furthermore, reversal of the above sequence should also show reduced effects. This was checked by applying a field of 100 V cm^{-1} to a

specimen, 10 sec after cessation of the standard light flash. As shown in Fig. 4, the conductivity saturated more rapidly, but reached a value similar to that achieved prior to illumination. Hence, this too is consistent with the concept of most possible D^+ states having already been formed by the light.

In conclusion, we have described the new phenomenon of field-enhanced conductivity in *a*-Si:H superlattices and suggest an explanation that is consistent with the data.

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