Light-induced perturbation of the high-temperature equilibrium in phosphorus-doped a-Si:H

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We observed light-induced deviations from the high-temperature defect equilibrium in phosphorus-doped hydrogenated amorphous silicon (a-Si:H). These deviations rise and decay much slower than the dark equilibration times. The light-induced deviations from equilibrium result in an excess conductivity at high temperatures and a decrease photoconductivity of the rapidly quenched state at room temperature. We suggest that these phenomena result from a light-induced increase in the doping efficiency associated with an increase in dangling-bond defects according to the reaction $P_{(3)}^0 + Si_{(4)}^0 \rightarrow P_{(4)}^+ + Si_{(3)}^-$.

I. INTRODUCTION

It was recently discovered[1,2] that the distribution of electronic states in hydrogenated amorphous silicon is governed by thermal equilibrium of particular structural configurations that involve the density of silicon dangling bonds (DB) and the electron concentration. The equilibration rate has been associated with the diffusion rate of hydrogen bonded to silicon.[2] Since the diffusion decreases rapidly with decreasing temperature the distribution of electronic states becomes essentially frozen below a certain temperature T_E. Analogous to the glass transition temperature the value of T_E depends on the time scale of the chosen experiment. For phosphorus-doped a-Si:H the defect equilibrium occurs within minutes at $T_E = 130\,°C$. The equilibrium states above T_E can be studied by rapidly quenching samples from $T > T_E$ and investigating the electronic properties at lower temperatures. The temperature dependence of the dc dark conductivity and the density of electrons and holes in band tail states have been studied in this manner.[1,2]

This paper addresses the question whether the high-temperature $T > T_E$ equilibrium states can be disturbed by strong light illumination. We expect this to be the case because the equilibrium reactions of the DB defects involve the carrier concentrations. For this purpose we established equilibrium at $T > T_E$ with and without strong illumination. The dark and photoconductivity of the quenched states are compared to determine changes in the density of recombination centers and the position of the Fermi level.

II. EXPERIMENTAL DETAILS

About 1-μm-thick a-Si:H films were deposited at 520 K in an rf plasma reactor from pure SiH_4 containing 5–100 ppm PH_3. Evaporated NiCr contacts, 0.6 cm long and separated by 0.2 cm, were used for coplanar conductivity measurements. They were found to be Ohmic up to 200 V, the largest bias applied. The electron-hole generation rate was 4×10^{20} photons/cm^{3}s for strong illumination and 2×10^{15} photons/cm^{3}s for weak illumination. All

measurements were carried out in an oil-free vacuum after annealing at 180 °C for 30 min.

III. RESULTS

Figure 1 shows the dark conductivity $\sigma_D(T)$ while heating the sample slowly at a rate of 0.05 °C/s after a quench (about 20 °C/s) from different temperatures T_Q to 0 °C. The annealed state A was obtained by slowly cooling the sample at a rate of 0.1 °C/s.

These results and the value $T_E = 130\,°C$ agree with those of Street and co-workers.[1,2] In Fig. 2 we plotted σ_D and the photoconductivity σ_P at 0 °C as a function of T_Q. For σ_P we used the weak light to avoid photoinduced creation of metastable defects by the Staebler-Wronski effect.[3] It appears that the position of the Fermi level E_F at 0 °C lies higher and that the concentration of recombination centers is smaller for the higher T_Q states. Below T_E these parameters remain essentially constant because of the very long equilibration times. We observe, howev-
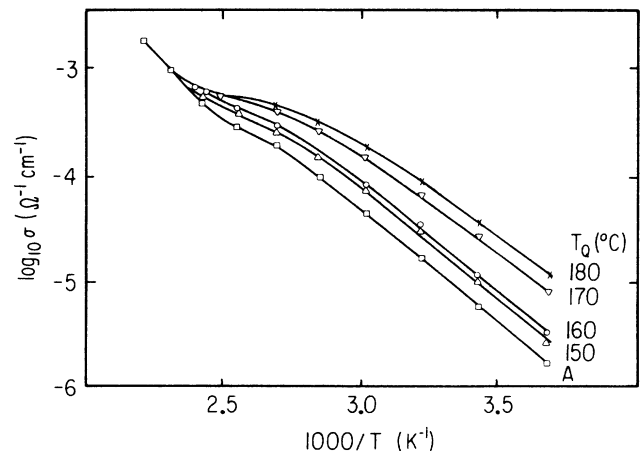

FIG. 1. Conductivity curves measured while heating after rapid quenching from various temperatures T_Q. State A is obtained after slow cooling. Sample doped with 5 ppm PH_3.
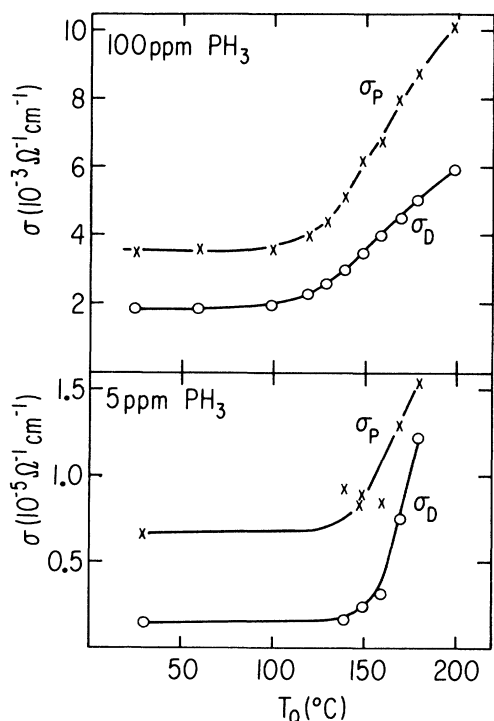
LIGHT-INDUCED PERTURBATION OF THE HIGH- . . .

FIG. 2. Photoconductivity σ_P and dark conductivity σ_D at 0 °C after quenching from T_Q.

er, the very slow relaxation toward the A state reported by Kakalios and Street.[4]

We now turn to the perturbations of the high-temperature equilibrium states by strong illumination. The sample was allowed to equilibrate at $T > T_E$ while it was exposed to strong illumination for a time t_i. After turning off the light and a certain delay time t_d the sample was rapidly quenched to 0 °C as before. The new state is denoted by IQ. Figure 3 shows $\sigma_D(T)$ of the Q and IQ

states obtained with $T_Q = 180$ °C and $t_i = 30$ min as well as of the annealed state A. These data were taken during slow heating after resting the sample for 10 min at 0 °C to ascertain electronic equilibrium. At lower temperatures σ_D of the IQ state is lower, but above 80 °C it is higher than σ_D of the Q state. Surprisingly it remains higher even at temperatures above T_E where one should expect very short equilibration times. It takes about 1 h at 180 °C before σ_D of the IQ state relaxes to that of the equilibrium state. The slow decay of the IQ state is accompanied by a slow rise at 180 °C. Figure 4 for example shows how σ_D and σ_P of the IQ state at 0 °C depends on the illumination time t_i at 180 °C. Both parameters decrease from their values in the Q state and saturate between $30 < t_i < 60$ min. These data were obtained with nearly zero delay time t_d. Because of the slow decay of these light-induced perturbations the results are not changed much by $t_d < 10$ min.

One might argue that these light-induced changes in the high-temperature equilibrium state might be associated with Staebler-Wronski defects (SW). It has been reported that SW defects require higher annealing temperatures when they are created at higher temperatures.[5] However, those experiments never exceeded 140 °C. In order to resolve this question we measured the time dependence of σ_D at 140 °C after a strong illumination for $t_i = 10$ s and 10 min. The results are shown in Fig. 5. After shutting off the light σ_D is below the value of the A state shown by the horizontal dashed line. One expects this from the SW effect because metastable DB states shift E_F toward the gap center. The recovery of σ_D at 140 °C overshoots the A-state value and finally decreases slowly over a period of several hours to the equilibrium value. The initial rapid rise, which may be the recovery of the SW effect, is too fast to be noticeable at higher temperatures. The very slow decrease of the light-induced excess conductivity at $T > T_E$ suggests the presence of a new light-induced metastable state in P-doped a-Si:H that is different from the SW effect. This new metastable state has, after quenching to 0 °C (IQ state), a lower photoconductivity than the Q state and hence more defects. At
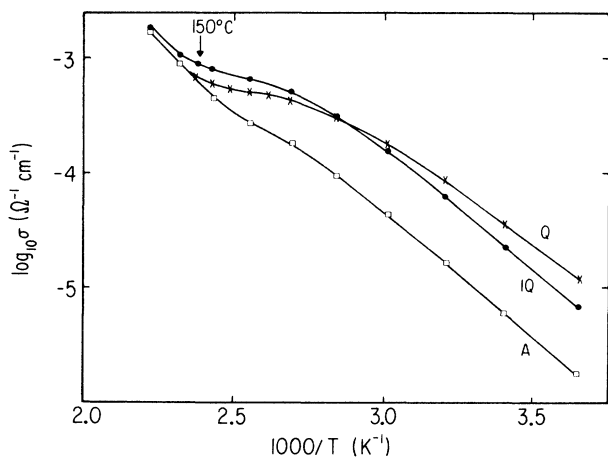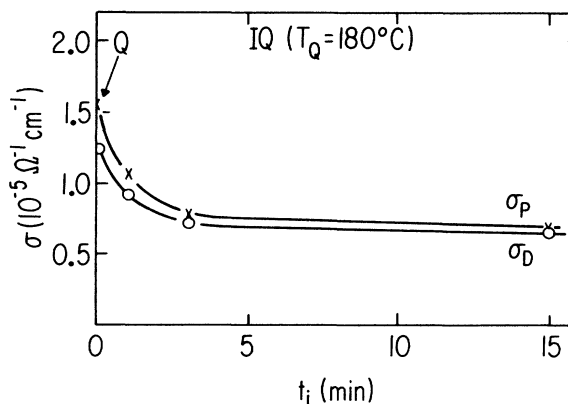

FIG. 3. Dark conductivity curves measured while heating after slow cooling (state A), rapid quenching from 180 °C (state Q), and rapid quenching from the strongly illuminated state at 180 °C (state IQ). Sample doped with 5 ppm PH_3.

FIG. 4. Photoconductivity and dark conductivity of IQ state at 0 °C as a function of exposure time to 4×10^{20} photons/cm^{3}s at 180 °C before quenching. Sample doped with 5 ppm PH_3.
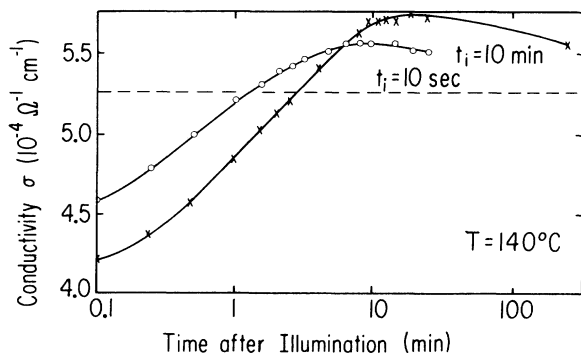
FIG. 5. Time dependence of dark conductivity at 140 °C after strong illumination for 10 s and 10 min. Sample doped with 5 ppm PH_3.

high temperatures it exhibits an excess conductivity that persists for hours rather than the typical short equilibration times for $T > T_E$. In order to eliminate perturbations of the IQ state by the SW effect we used a delay time t_d before quenching such that σ_D was near the maximum value of the curve in Fig. 5.

IV. DISCUSSION

As pointed out by Street, Kakalios, and Hayes[1] n_{BT}, the concentration of carriers in tail states, and n, the free-carrier concentration which determines σ_D of the quenched state, increase with increasing $T_Q > T_E$. This may result either from an increase in donor concentration, the fourfold coordinated phosphorus ions $P_{(4)}^+$, or from a decrease in the number of negatively charged DB defects D^-, or a combination of the two effects. Our observation of an increase of the photoconductivity with increasing T_Q indicates a decrease in the D^- concentration. This argument is based on the widely accepted view that the D^- states are the main recombination centers in n-type a-Si:H.

Even though it seems counterintuitive that a sample quenched from a higher T is less defective than one quenched from a lower T, one may argue that this should be expected from the known defect reactions. Let us consider an n-type sample at 200 °C. Because of charge neutrality the Fermi level should be somewhere between the D^- and the $P_{(4)}^+$ states. We now assume that the sample is rapidly cooled to say 150 °C. First, E_F will move up into the exponentially rising band tail distribution because electronic equilibration proceeds much faster than a change in defect concentration. This is the well-known

statistical shift of E_F. As a consequence more antibonding states of weak Si bonds will be occupied. Because of the small correlation energy some will be doubly occupied. If that happens it is energetically favorable to form two D^- defects[6] instead which move E_F down again. As a consequence the equilibrium state at 150 °C has more defects than the one at 200 °C. This equilibration process slows down rapidly below $T_E = 130$ °C because hydrogen motion facilitates the changes in local bonding. We now try to explain the observations associated with the new metastable state that is produced by strong illumination at $T > T_E$. We have to explain the excess conductivity at high T, the very long rise and decay times of this metastable state, and the lower photoconductivity of the IQ state compared to that of the Q state. We tentatively suggest that one is dealing here with a light-induced increase in $P_{(4)}^+$ combined with an increase in D^-. The increase in donor concentration might result from a conversion of threefold coordinated $P_{(3)}^0$. This might occur by photo-ionization

$$P_{(3)}^0 \xrightarrow{h\nu} P_{(3)}^+ + e^- \qquad (1)$$

and subsequent bond rearrangement which creates a donor and a dangling bond

$$P_{(3)}^+ + Si_{(4)}^0 \rightarrow P_{(4)}^+ + D^0 . \qquad (2)$$
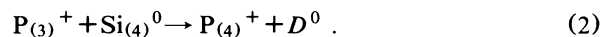
Because of the position E_F above the D^0 band, the DB will become negatively charged so that the total reaction is

$$P_{(3)}^0 + Si_{(4)}^0 \xrightarrow{h\nu} P_{(4)}^+ + D^- . \qquad (3)$$
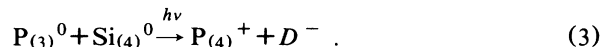
The slow decay of this metastable state suggests that the metastable $P_{(4)}^+$ are more difficult to anneal than other metastable defects. Since the excess D^- of Eq. (3) is associated with the excess $P_{(4)}^+$, its decay is linked with that of $P_{(4)}^+$. The excess conductivity at high temperatures results then from the higher doping concentration or an upward shift of E_F caused by the increased number of D^- states. The latter is responsible for the lower photoconductivity of the IQ state relative to the Q state.

We observed these phenomena only in lightly P-doped a-Si:H. Our failure to find these effects in more strongly doped a-Si:H is probably due to the fact that our light intensity was insufficient to obtain a significant photoconductivity at high temperatures.

ACKNOWLEDGMENTS

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