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Thermal quenching of the minority-carrier lifetime in *a*-Si:H

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While the phenomenon of thermal quenching of the photoconductivity (i.e., the decrease of the majority-carrier mobility-lifetime product with increasing temperature) is well known, the thermal quenching of the minority-carrier mobility-lifetime product has not been reported thus far for any photoconductor. In this paper, we report such an effect in ''device-quality'' hydrogenated amorphous silicon, *a*-Si:H. It is shown that this unusual phenomenon can be accommodated within the framework of available models suggested for intrinsic *a*-Si:H. [S0163-1829(97)51624-9]

One of the most well-known phenomena in photoconductors is the decrease or saturation of the photoconductivity $\sigma_{\rm ph}$ with increasing temperature, known as the thermal quenching of the photoconductivity.[1,2] The observed thermal quenching (TQ) of $\sigma_{\rm ph}$ can arise from many scenarios and is of importance from the device physics point of view because of its close relationship to the sensitization phenomenon.[1,2] The most known[1,2] scenario of TQ arises in the presence of two recombination levels, such that the increase of temperature changes the one which dominates the recombination. The photoconductivity is related to the microscopic properties of the solid via the majority-carrier (assumed here to be the electron) mobility-lifetime, $\mu\tau$, product by the relation[2,3] $(\mu\tau)_e = \sigma_{\rm ph}/qG$, where q is the electronic charge and G is the electron-hole pair-generation rate which is proportional to the illumination intensity. The illumination intensity dependence of $\sigma_{\rm ph}$ is usually characterized then by the power low $(\mu\tau)_e \propto G^{\gamma_e - 1}$ where γ_e is known as the light intensity exponent of the photoconductivity.[1,3] Hence the ''electron thermal quenching'' $({\rm TQ})_e$ is a result of the decrease or the saturation.[1,2,4] of $(\mu\tau)_e(T)$. This phenomenon is also known to be accompanied by a simultaneous cusp in $\gamma_e(T)$, which in most cases[1,2] attains a value of $\gamma_e > 1$.

The mobility-lifetime product of the minority carrier (hereafter assumed to be the hole), $(\mu\tau)_h$, is usually[5] derived experimentally from the measurement of its diffusion length L and the use of the Einstein relation[6] $(\mu\tau)_h = qL^2/kT$, where kT is the thermal energy. The corresponding light-intensity dependence is characterized then by the exponent γ_h, which is defined by $(\mu\tau)_h \propto G^{\gamma_h - 1}$. We are unaware of previous determinations of the temperature dependence of γ_h, in spite of the fact that other dependences of γ_h have been shown to reveal significant information regarding the recombination level structure in photoconductors.[3,7]

One of the most intensively studied photoconductors in recent years is hydrogenated amorphous silicon, *a*-Si:H. For this system the phenomenon of $({\rm TQ})_e$ has been reported by many authors.[8–11] On the other hand, in the works in which the $(\mu\tau)_h(T)$ dependence has been measured, this quantity was found to increase monotonically with temperature.[10,11]

In this paper we report an observation of thermal quenching of the minority carrier's $\mu\tau$ in a photoconductor. For the material studied here, i.e., *a*-Si:H, this is by no means the universal behavior of $(\mu\tau)_h$, but we found it to occur in materials of ''device quality.''[12] This may indicate that the presence of this phenomenon has also some predictive power regarding the ''quality'' of the material for photoelectronic applications. From the basic physics point of view, the important question is whether such a behavior is specific to the materials on which we report here or is it a manifestation of the richness of the behaviors which can be expected for intrinsic *a*-Si:H (see below). To answer this rather fundamental question, we ran simulations of ''accepted'' models of *a*-Si:H and compared their results with our experimental data. In turn, this procedure yielded information on the recombination process in this material. We should emphasize that while *a*-Si:H has been extensively studied in the last 20 years[8,11,13] and the behavior of its minority carriers has been investigated in numerous studies in the last 10 years,[10–15] the behavior found here has not, as far as we are aware, been discovered experimentally or predicted theoretically before.

In our study we have measured five sets of device-quality *a*-Si:H samples which were deposited by decomposition of silane on a 7059 Corning glass. The first set was deposited by a rf glow discharge at a frequency of 13.6 MHz, while the substrate temperature T_s was 250 °C, resulting in films which had a thickness d of 1.3 μm. The second set was prepared using the hot-wire technique,[13] with $T_s = 510$ °C and $d = 2.8$ μm. Since the temperature dependences of the phototransport properties of these two sets were qualitatively similar, we will show here only the results obtained on the first set, hereafter set A. The third and fourth sets of samples were deposited[12] by dc glow discharge. The third set was deposited at $T_s = 260$ °C, while the fourth set was deposited at $T_s = 210$ °C with a 10:1 hydrogen dilution of the silane. For these two sets, d was 1 μm. The fifth set was prepared by the hot-wire technique,[13] but with $T_s = 300$ °C, yielding films with $d = 1.1$ μm. Again, since the results on the last three sets were qualitatively similar, we will show here only the results obtained on the fourth set, hereafter set D. We will use then the results obtained on the samples of set A as representing the $({\rm TQ})_e$ behavior and those obtained on

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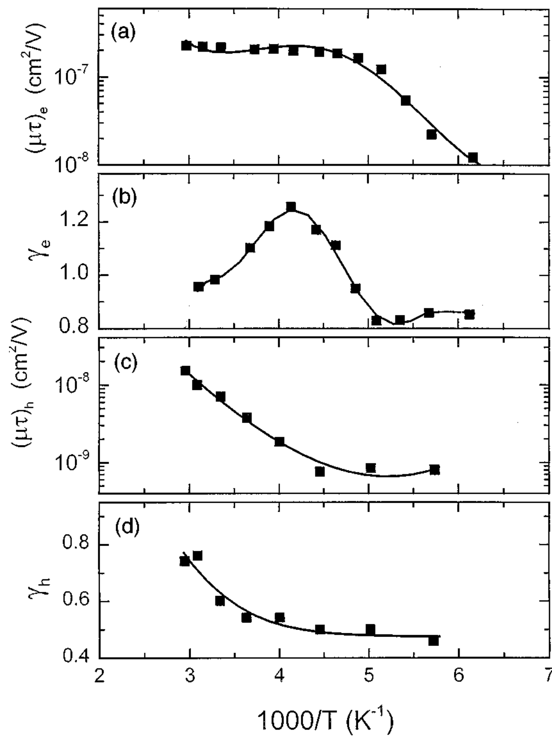

FIG. 1. The most common behavior of the temperature dependence of the four phototransport properties in intrinsic a-Si:H films. These results were obtained here on samples which were prepared by rf glow discharge decomposition of silane.

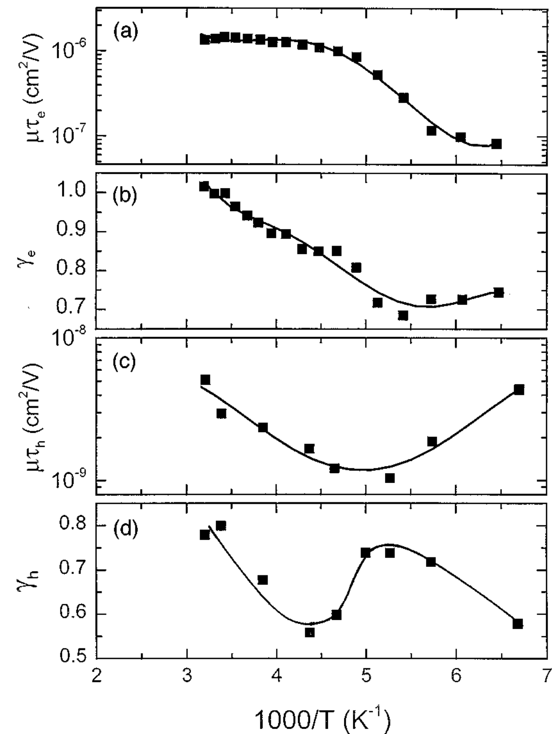

FIG. 2. Observation of the temperature dependences of the four phototransport properties in films of intrinsic a-Si:H. These films were prepared by dc glow discharge decomposition of silane.

samples of set D as representing the (TQ_h) behavior.

Coplanar NiCr contacts, with a separation of 0.4 mm, were deposited on top of the films to enable the transport measurements.[7] The phototransport properties were determined using the photocarrier grating technique, which has been described in detail previously.[14,15] The light source in our measurements[7,15] was a He-Ne laser, which yielded a maximum photogeneration rate of $G = 10^{20}\ \mathrm{cm}^{-3}\ \mathrm{sec}^{-1}$. The exponents γ_e and γ_h were determined over the range $3\times 10^{18} \leqslant G \leqslant 10^{20}\ \mathrm{cm}^{-3}\ \mathrm{sec}^{-1}$. The samples were placed in a cryostat operating in the temperature range of 160–350 K.

We have started our experimental study by measuring the dark conductivity as a function of temperature. Using values of the dark conductivity in the regime at which it is thermally activated and considering the suggested[16] microscopic prefactor of the room-temperature conductivity to be 150 $(\Omega\ \mathrm{cm})^{-1}$, we derived the position of the Fermi level E_F with respect to the conduction band edge E_C. For set A we found that $E_C - E_F \approx 0.75$ eV, while for set D we found that $E_C - E_F \approx 0.60$ eV.

Turning to the phototransport properties, we present in Fig. 1(a) the temperature dependence of $(\mu\tau)_e$ and in Fig. 1(b) the temperature dependence of γ_e, as measured on samples of set A. We can see that at low temperatures $(\mu\tau)_e$ increases significantly with temperature, but then (at about 210 K) it saturates. This appearance of the $(TQ)_e$ is accompanied by a cusp in $\gamma_e(T)$ as expected[11,17] and found in many previous studies[8,9,17] of a-Si:H. The monotonic increase of $(\mu\tau)_h(T)$, shown in Fig. 1(c), has been observed experimentally and is well accounted for by accepted models.[10,11] For completeness, we present in Fig. 1(d) our corresponding observations of $\gamma_h(T)$. The important characteristic of these minority-carrier behaviors is the monotonic increase of $(\mu\tau)_h$ and γ_h with temperature, i.e., the absence of a TQ-like behavior.

In Fig. 2 we present the temperature dependences of the phototransport properties in the samples of set D. We see in Fig. 2(a) that $(\mu\tau)_e$ increases monotonically (first sharply and then weakly) with temperature, until at about 300 K it starts showing a beginning of a $(TQ)_e$. In Fig. 2(b) we see the temperature dependence of γ_e, which appears to exceed unity at the onset of this $(TQ)_e$. The temperature dependences of the hole phototransport properties, presented in Figs. 2(c) and 2(d), exhibit behaviors that are very different from those measured on set A. As can be seen in Fig. 2(c), $(\mu\tau)_h$ first decreases with T (by nearly one order of magnitude) and then (above about 200 K) it increases back at a similar pace. In view of the above discussion, this is a *thermal quenching of the minority carriers'* $(\mu\tau)_h$, which we denote here by $(TQ)_h$. Such a behavior has not been observed experimentally or been predicted theoretically for photoconductors in general and for a-Si:H in particular. In Fig. 2(d) we show the corresponding $\gamma_h(T)$. Its most significant feature for the present discussion is the peak observed in $\gamma_h(T)$. The fact that this peak is located at about 200 K, i.e., that it corresponds to the "deep" observed in $(\mu\tau)_h$, establishes the conclusion (see above) that indeed we see here a thermal quenching of the mobility-lifetime product of the minority carrier. This correlation rules out the possibility that the observed decrease of $(\mu\tau)_h$ in Fig. 2(c) is due to a mobility variation effect, since the exponents γ_e and γ_h are associated only with the kinetics of the recombination process.[1–3] As discussed below, further convincing support

for this interpretation comes from our computer simulations, which assume temperature-independent mobilities and still yield the observed $(TQ)_h$ and the corresponding cusp in $\gamma_h(T)$.

Beyond the fact that the above results show a TQ for the minority carriers, the question arises whether this behavior is inherent to intrinsic a-Si:H. In principle, the nonuniversality of the observed $(TQ)_h$ may arise due to some peculiar defects which are unique to our materials. On the other hand, it may signal that differences between different a-Si:H materials are only due to variations in the relative concentrations of well-defined defects. The fact that we have observed the $(TQ)_e$ in materials which were prepared by different deposition methods (note that such a behavior has also been reported for materials prepared using the dc glow discharge method[10]) and the fact that we have observed here the $(TQ)_h$ behavior for materials prepared by different methods of deposition support the latter option.

In order to prove conclusively that the $(TQ)_h$ is inherent to intrinsic a-Si:H materials and that it is a manifestation of the richness of their phototransport behaviors, we have carried out a comprehensive simulation study of the simplest accepted models that describe these materials. This was done by computing the predictions of such models for the above four phototransport properties. A detailed discussion of this study will be given elsewhere. Here we concentrate on the predictions of these models concerning the $(TQ)_h$, i.e., on the behaviors shown in Figs. 1(c) and 2(c). The first model we consider is the so called ''standard'' model. For the present purpose we used a recent version of this model which was presented by Tran.[17] This model is composed of dangling bonds, the energy of which lies around midgap, and a valence-band tail that has a width which is almost twice that of the conduction-band tail. We have applied Tran's model using exactly his parameters (case B1 of Ref. 17), finding that the results are not sensitive to E_C-E_F around our experimentally found 0.75 eV value. The results obtained for $(\mu\tau)_h$ using this model are presented in Fig. 3(a). The monotonic increase of $(\mu\tau)_h(T)$ is in qualitative agreement with the behavior shown in Fig. 1(c). We should also emphasize that the qualitative behaviors of all other three phototransport properties, i.e., $(\mu\tau)_e$, γ_e, and γ_h, were found to be the same as those shown in Fig. 1. In addition, we found that using the various capture cross section combinations, considered in Ref. 17 yielded the same qualitative behaviors. The reader should note that we deliberately used only parameters which have been suggested previously. This is because we concentrate in this paper on the TQ phenomenon and not on the derivation of the parameters which will yield a quantitative fit to our experimental data.

Following the qualitative agreement between the results shown in Figs. 3(a) and 1(c), the question arises which parameter within the above model should be varied to yield the $(TQ)_h$ behavior. To find this parameter we were guided by the analysis of Tran[17] for the $(TQ)_e$. In principle, there are three different recombination channels: The valence-band tail, the conduction-band tail, and the dangling bonds. The recombination rates through these channels are denoted by G_{vt}, G_{ct}, and G_{db}, respectively. Tran has shown (using a few series of parameters) that as long as the density of states at the valence-band edge, N_{vt}, is about the same as that at

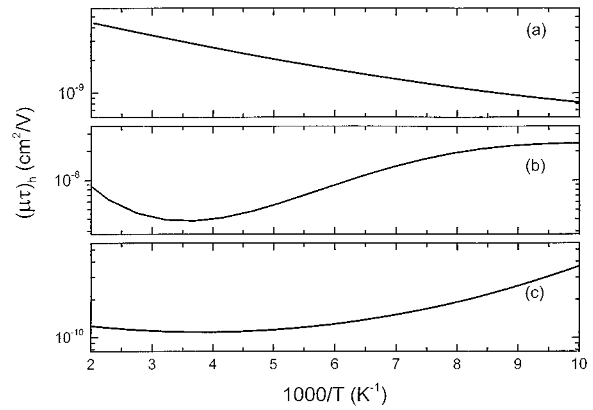

FIG. 3. Computed temperature dependence of $(\mu\tau)_h$ for three models. Tran's ''standard'' (B1) model with $E_C-E_F=0.75$ eV. Tran's ''standard'' (B1) model but with $E_C-E_F=0.6$ eV and $N_{vt}=10^{19}$ cm^{-3} eV^{-1}. (c) A simple defect pool model (see Ref. 19) which is composed of three dangling bond levels at $E_C-E_1=1.05$ eV, $E_C-E_2=0.7$ eV, and $E_C-E_3=0.55$ eV. The correlation energy is taken to be 0.3 eV, and the charged-to-neutral dangling-bond-capture cross sections ratio is 100. The corresponding dangling-bond concentrations are $N_1=10^{17}$, $N_2=10^{13}$, and $N_3=10^{16}$ cm^{-3}. The band-tail widths are $E_{ct}=0.025$ eV and $E_{vt}=0.045$ eV, and the corresponding band-tail densities of states are $N_{ct}=N_{vt}=10^{21}$ eV^{-1} cm^{-3}.

the conduction band tail, N_{ct}, one would get that $G_{vt}>G_{ct}$ for all temperatures. He further showed that at low temperatures the recombination is dominated by G_{vt} and at high temperatures by G_{db} and that the $(TQ)_e$ occurs at the temperature for which these two recombination rates are about the same.

Considering this analysis, it appeared reasonable to expect that the $(TQ)_h$ will occur when $G_{ct}\approx G_{vt}$. Since this does not happen within the framework of the Tran model, a modification of this model is required so that G_{vt} will be lowered. We have obtained the effect by lowering N_{vt}. (As above, we found that the results were insensitive to E_C-E_F around 0.6 eV.) In order to get the $(TQ)_h$ while keeping all other parameters as in Ref. 17, we had to use the (probably exaggerated) low value of $N_{vt}=10^{19}$ eV^{-1} cm^{-3}. The results of these simulations are shown in Fig. 3(b). It is seen that, qualitatively, the behavior found resembles the experimental data of Fig. 2(c). Our computations of G_{ct}, G_{vt}, and G_{db} in this case have revealed that indeed, at low temperatures, the G_{ct} dominates and that the observed $(TQ)_h$ takes place at the temperature for which G_{vt} equals G_{ct}. The conclusion from these calculations is that the novel $(TQ)_h$ phenomenon must indicate that at low temperatures (sometimes up to 250 K) it is the conduction-band tail that controls the recombination kinetics.

Is the above low value of N_{vt} the only plausible explanation for the $(TQ)_h$? Since within the simplest ''standard'' models considered (cases B, B1, C, and C1 of Ref. 17) we were unable to obtain a $(TQ)_h$ without reducing N_{vt}, we turned also to the ''defect pool'' model[18] of a-Si:H, using its simplest version.[19]

In this version there are three sets of discrete dangling-bond levels. We thus carried out our simulations using parameters which are common to such simulations[19] and ob-

tained behaviors which were reported before,[10] i.e., results which are qualitatively similar to those shown in Figs. 1 and 3(a). Following the above conclusion—that the $(TQ)_h$ occurs due to the reduction in the concentration of the holes trapped in the valence-band tail—we have chosen a somewhat higher concentration (10^{17} cm^{-3}) of the low-lying dangling bonds. These states, which are negatively charged in equilibrium, have a high tendency to capture holes and thus serve at low temperatures as ''safe hole traps.'' We found that this model yields results which are in good qualitative agreement with all the data shown in Fig. 2. In particular, as we show in Fig. 3(c), we found that a $(TQ)_h$ behavior is obtained and that the reduction of E_C-E_F from 0.75 to 0.60 eV enhances the $(TQ)_h$ effect. Hence the $(TQ)_h$ phenomenon not only enables us to obtain information regarding the density of the various defects within the material, but also to assess the role of these defects in the recombination processes. We note that such an analysis for the ''defect-pool'' mode has not been carried out thus far in the same detailed manner as Tran has analyzed the standard model.

From the qualitative agreement between the results shown in Figs. 3(b) and 3(c) and those shown in Fig. 2(c), one can further argue that both the standard and the defect-pool models reproduce the main features of the data. The defect-pool model makes it, however, with assumptions which are more compatible with the known concentrations of defects in intrinsic a-Si:H. We found then that the $(TQ)_h$ phenomenon is a result of a relatively low N_{vt} and/or a relatively high state concentration in the energetically low-lying band of dangling bonds. In the present context of a-Si:H, the important message is that the results of Figs. 3(b) and 3(c) demonstrate that the $(TQ)_h$ phenomenon, just like the $(TQ)_e$ phenomenon, is a ''natural'' behavior of a-Si:H and that the very rich ensemble of temperature dependences of the phototransport properties reported for a-Si:H is simply due to diffrent concentrations of the various defects which are known to exist in this material. In a broader context the present work indicates that sensitizaiton of the minority-carrier properties should be looked for in other semiconductors in order to better understand recombination processes, as well as for the improvement of the efficiency of bipolar photoelectronic devices.

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