Steady-state photoconductivity and recombination process in sputtered hydrogenated amorphous silicon

E. Arene and J. Baixeras
Laboratoire de Génie Electrique de Paris (Laboratoire No. 127 associé au Centre National de la Recherche Scientifique), Ecole Supérieure d'Electricité, Université de Paris VI et Université de Paris, Plateau du Moulon, F-91190 Gif-sur-Yvette, France
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Steady-state photoconductivity has been studied on *a*-Si:H films prepared either by diode rf or triode dc sputtering in order to determine the predominant recombination process of free carriers acting in these materials. The experimental results have been compared with the predictions of the two currently used models proposed, respectively, by Spear *et al.* and by Rose. In all of the investigated samples, in agreement with Rose's model, the recombination process involves a continuum of localized states obeying Shockley-Read statistics. The photoconductivity has then been calculated using the formal approach of Taylor and Simmons. The theoretical equations allow one to obtain basic information about localized states around the Fermi level from the dependence of the photoconductivity on photon flux intensity. The characteristic parameters determined in this way have been used to calculate the variation of the photoconductivity as a function of the temperature: A very good agreement with the experimental variation has been observed. Although the recombination process is the same either for the diode-rf- or the triode-dc-sputtered samples, the behavior of the photoconductivity can be quite different for these two materials. An explanation involving the capture cross section of the traps is proposed.

I. INTRODUCTION

The study of photoconductivity in hydrogenated amorphous silicon (*a*-Si:H) is a valuable tool in achieving a good understanding of the recombination processes and in obtaining basic information on the localized states which control the recombination of free carriers in this material.[1] However, in spite of extensive studies,[2] the interpretation of experimental data remains difficult and engenders controversy. Indeed, in some cases the photoconductivity of the bulk material may be obscured by surface effects[3] or may be affected by light-induced changes in the density of states.[4,5] Moreover, different processes of recombination are likely to occur simultaneously, leading to complex variations of the photoconductivity as a function of the temperature or of the light intensity.

Until now, two main models of recombination of free carriers have been proposed in order to explain the experimental behavior of the photoconductivity. Spear, Loveland, and Al Shabarty[6] proposed a simple model in which essentially three groups of localized states are associated with the recombination of excess carriers: states at E_A acting as shallow electron traps and situated at 0.18 eV below the bottom of the conduction band E_c, states near the Fermi level E_F, and states E_y situated at about 1.1 eV below E_c where a local maximum of the density of states $N(E)$ occurs. It is important to note that the recombination paths in this model involve transitions between the three groups of localized states. The positions of these groups may be derived from the experimental dependence of the photoconductivity with the temperature. The second recombination model was first proposed by Rose[7] to explain the behavior of the photoconductivity in semiconductors or insulators with an arbitrary distribution of localized states $N(E)$ in the mobility gap. Starting from the traditional Shockley-Read equations[8] for the recombination of free carriers through one discrete trapping level, Rose extended the Shockley-Read process to the case of distributed trapping levels. He neglected the transitions between localized states and, using a semiquantitative approach, introduced the crucial distinction between shallow traps and deep recombination centers. The model is based on the physical idea that the recombination of free carriers occurs through deep states near the Fermi level. In this way, simple expressions of the free-carrier lifetimes have been obtained which can be used to obtain information about the density of states near the Fermi level from experimental data.

These two models of recombination have been widely used[1,9,10] in order to explain the photoconductive properties of *a*-Si:H, but often without real confirmation of the validity of the assumed recombination mechanism. In this paper we report an extensive study of the photoconductivity in sputtered undoped and doped *a*-Si:H films. The dependence of the photoconductivity as a function of incident-light intensity and temperature has been measured in order to investigate the predominant recombination process acting in our material. As the experimental results seem to be in agreement with the predictions of Rose's model, we have carried out a calculation of the photoconductivity using the formal approach of Simmons and Taylor[11,12] in the case of an arbitrary distribution of traps with distinct capture cross sections for electrons and holes. Then we focused our attention on *n*-type materials for which the quasi Fermi level of trapped electrons coincides with the quasi Fermi level of free electrons. We

have demonstrated that in this case, the shape of the density of states above the Fermi level and the product $v\sigma_n N(E_F)$ [v being the thermal velocity, σ_n being the capture cross section of localized states for electrons, and $N(E_F)$ being the density of states at the Fermi level] can be determined from the experimental dependence of the photoconductivity with the incident-light intensity. Then, by comparing the theoretical variation of the photoconductivity as a function of the temperature (calculated using these two parameters) with the experimental one, we are able to discuss the validity of the proposed recombination model.

II. THEORY

In this section we first recall the basic equations describing the recombination of free carriers through a continuum of trapping levels. According to Shockley-Read statistics,[8] the recombination rates for electrons and holes, U_n and U_p, respectively, through a single trapping level at the energy E, are given by

$$U_n = v\sigma_n\{n\mathcal{N}(E)[1-f(E)] - n_1\mathcal{N}(E)f(E)\} ,$$
$$U_p = v\sigma_p\{p\mathcal{N}(E)f(E) - p_1\mathcal{N}(E)[1-f(E)]\} , \quad (1)$$

where v is the thermal velocity, σ_n and σ_p are the capture cross sections of the trap for electrons and holes, respectively, $\mathcal{N}(E)$ is the density of traps per unit volume at the energy E, $f(E)$ is the probability of occupation of the trapping level, and n and p are the free-electron and free-hole densities, respectively:

$$n_1 = N_c\exp\left[\frac{E-E_c}{k_BT}\right], \quad p_1 = N_v\exp\left[\frac{E_v-E}{k_BT}\right] ,$$

with N_c and N_v being the equivalent densities of states of conduction and valence bands. In the nonequilibrium steady state, $U_n = U_p$, and hence, the probability of occupation of the trapping level can be written as[8]

$$f(E) = \frac{v\sigma_n n + e_p}{v\sigma_n n + v\sigma_p p + e_n + e_p} , \quad (2)$$

where

$$e_n = v\sigma_n N_c\exp[(E-E_c)/k_BT] ,$$
$$e_p = v\sigma_p N_v\exp[(E_v-E)/k_BT] .$$

Now consider the case of a continuous distribution of traps, $N(E)$ per unit volume and per unit energy, throughout the gap. If one neglects the electronic transitions between localized states, the steady-state recombination rate for free carriers, $U = U_n = U_p$, can be deduced from Eq. (1):

$$U = \int_{E_v}^{E_c} v\sigma_n(E)\{nN(E)[1-f(E)] - n_1N(E)f(E)\}dE . \quad (3)$$

It can be shown[11] that the steady-state probability of occupation $f(E)$ of a trapping level at the energy E is given by Eq. (2), i.e., the statistics are the same as in the case of a single trapping level. Inserting the expression for $f(E)$ in Eq. (3), we obtain

$$U = \int_{E_v}^{E_c} N(E)\frac{v^2\sigma_n(E)\sigma_p(E)(np-n_0p_0)}{v\sigma_n(E)n + v\sigma_p(E)p + e_n(E) + e_p(E)}dE , \quad (4)$$

n_0 and p_0 being the equilibrium densities of free electrons and holes, respectively. Equation (4) is a quite general expression for the recombination rate of free carriers under steady-state conditions taking into account a distribution of traps $N(E)$ and a distribution of capture cross sections $\sigma_n(E)$ and $\sigma_p(E)$. Now we assume that the capture cross sections are independent of the energy:

$$\sigma_n(E) = \sigma_n, \quad \sigma_p(E) = \sigma_p, \quad E_v \le E \le E_c .$$

In this case, according to Simmons and Taylor,[11] we can define the quasi Fermi levels for trapped electrons and holes, E_{tn} and E_{tp}, respectively, by the relations

$$\sigma_n N_c\exp\frac{E_{tn}-E_c}{k_BT} = \sigma_n n + \sigma_p p ,$$
$$\sigma_p N_v\exp\frac{E_v-E_{tp}}{k_BT} = \sigma_n n + \sigma_p p . \quad (5)$$

With the use of these definitions, Eq. (4) can be rewritten in the form

$$U = \frac{v^2\sigma_n\sigma_p(np-n_0p_0)}{v\sigma_n n + v\sigma_p p}\int_{E_v}^{E_c}\left[N(E)\Big/\left[1+\frac{e_n(E)+e_p(E)}{v\sigma_n n + v\sigma_p p}\right]\right]dE ,$$

so that

$$U = \frac{v^2\sigma_n\sigma_p(np-n_0p_0)}{v\sigma_n n + v\sigma_p p}\int_{E_v}^{E_c}\left[N(E)\Big/\left[1+\exp\frac{E-E_{tn}}{k_BT}+\exp\frac{E_{tp}-E}{k_BT}\right]\right]dE .$$

If we assume, moreover, that the distribution of traps $N(E)$ varies with the energy slower than the Boltzmann function, we can use the classical low-temperature limit.[12] Thus we obtain

$$U = \frac{v\sigma_n\sigma_p(np-n_0p_0)}{\sigma_n n + \sigma_p p}\int_{E_{tp}}^{E_{tn}} N(E)dE . \quad (6)$$

Equation (6) shows that only the states lying between the quasi Fermi levels E_{tp} and E_{tn} are active in the recombination process. Therefore, these levels mark the boundary between shallow traps and recombination centers. We report in Fig. 1 the approximate positions of the quasi Fermi levels in the case of an n-type material. Simmons and Taylor[11] have shown that the quasi Fermi levels E_{tp} and E_{tn} are, respectively, not far from the demarcation levels E_{dp} and E_{dn} used by Rose to distinguish shallow

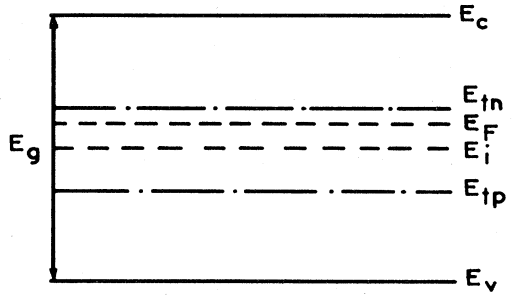

FIG. 1. Typical positions of the quasi Fermi levels E_{tn} and E_{tp} for trapped electrons and holes, respectively, in an n-type material. E_F is the Fermi level, E_c is the bottom of the conduction band, E_v is the top of the valence band, E_g is the optical gap, and E_i is the "intrinsic level" positioned at the middle of the gap.

traps from recombination centers.[7]

A second basic equation is given by the charge-neutrality condition[12]

$$\int_{E_v}^{E_f} N(E)[1-f(E)]dE + p = \int_{E_F}^{E_c} N(E)f(E)dE + n \ ,$$

with E_F being the equilibrium Fermi level. It is well known that in a-Si:H, the charge due to free carriers is many orders of magnitude less than the charge due to trapped carriers. Therefore, the charge-neutrality condition can be written as

$$\int_{E_v}^{E_F} N(E)[1-f(E)]dE - \int_{E_F}^{E_c} N(E)f(E)dE \simeq 0 \ .$$

From the general expression of $f(E)$ given by Eq. (2) and by using the definitions of the quasi Fermi levels for trapped carriers and the low-temperature limit, a simple expression of the charge-neutrality condition can be obtained:[12]

$$\sigma_n n \int_{E_F}^{E_{tn}} N(E)dE = \sigma_p p \int_{E_{tp}}^{E_F} N(E)dE \ . \tag{7}$$

Since in n-type material, $np \gg n_0 p_0$, Eqs. (6) and (7) then lead to a simple expression of the steady-state recombination rate of free carriers,

$$U = v\sigma_n n \int_{E_F}^{E_{tn}} N(E)dE = v\sigma_p p \int_{E_{tp}}^{E_f} N(E)dE \ , \tag{8}$$

with

$$E_{tn} = E_F + k_B T \ln\left[\frac{\sigma_n n + \sigma_p p}{\sigma_n n_0}\right] ,$$
$$E_{tp} = E_F - k_B T \ln\left[\frac{\sigma_n n + \sigma_p p}{\sigma_p p_0}\right] . \tag{9}$$

Equations (8) and (9), first proposed by Simmons and Taylor, are the two basic equations describing the recombination process. The expressions of the hole and electron lifetimes τ_p and τ_n, respectively, can be deduced from Eq. (8):

$$\tau_n = \left[v\sigma_n \int_{E_F}^{E_{tn}} N(E)dE\right]^{-1}$$

and

$$\tau_p = \left[v\sigma_p \int_{E_{tp}}^{E_F} N(E)dE\right]^{-1} .$$

Moreover, using the steady-state condition $U=G$, G being the electron-hole—pair generation rate, these equations lead to a general expression of the photoconductivity, which can be calculated numerically if the density of states between E_{tp} and E_{tn} and the capture cross sections σ_p and σ_n are known. However, these calculations are not very convenient to interpret the experimental results and do not lead to a clear determination of physical parameters of the material.

Therefore, we further assume that $\sigma_p p \ll \sigma_n n$. This inequality can be reasonably proposed for our material provided the capture cross section for holes did not exceed the capture cross section for electrons by more than 2 orders of magnitude. We have indeed determined the mobility lifetime products $\mu_n\tau_n$ and $\mu_p\tau_p$ for free electrons and holes, respectively, from the photoconductivity and spectral response of Schottky diodes. The results have been published elsewhere[13] and show that the electron lifetime τ_n is more than 3 order of magnitude greater than the hole lifetime τ_p in our samples. With this new assumption, Eq. (9) can be rewritten as

$$E_{tn} = E_F + k_B T \ln\frac{n}{n_0}, \quad E_{tp} = E_F - k_B T \ln\frac{\sigma_n n}{\sigma_p p_0} \ . \tag{10a}$$

The quasi Fermi level for free electrons E_{Fn} is defined by

$$n = N_c \exp[(E_{Fn} - E_c)/k_B T] \ . \tag{10b}$$

The equilibrium electron density is given by

$$n_0 = N_c \exp[(E_F - E_c)/k_B T] \ . \tag{10c}$$

Therefore, it appears from Eqs. (10) that the quasi Fermi level for trapped electrons, E_{tn}, coincides with the quasi Fermi level for free electrons, E_{Fn}. Therefore the two electronic populations are in thermal equilibrium. Moreover, Eqs. (10) show that the quasi Fermi levels E_{tp} and E_{tn} are about symmetrical with respect to the middle of the gap.

Now, the steady-state photoconductivity σ_{phot} can easily be calculated. We have pointed out before that, in our material, the hole lifetime is much smaller than the electron lifetime. The photoconductivity can therefore be expressed as

$$\sigma_{\text{phot}} = q\mu_n(n - n_0) \ , \tag{11}$$

where μ_n is the true mobility of the electrons in the conduction band and has been taken to be equal to 5 $\text{cm}^2/\text{V s}$, a value commonly admitted for these materials.[14] The electron density is determined from steady-state conditions: The recombination rate U is equal to the photogeneration rate[9]

$$G = \eta_q(1-R)F\frac{1-\exp(-\alpha d)}{d} \ ,$$

F being the incident-photon flux, R being the reflectivity of the a-Si:H film ($R=30\%$ for our samples), d being the

thickness of the sample, α being the optical-absorption coefficient, and η_q being the quantum efficiency of photogeneration which we assume to be equal to unity according to previous work.[15] Therefore the electron density n is given by

$$\frac{F(1-R)[1-\exp(-\alpha d)]}{v\sigma_n d}=n\int_{E_F}^{E_{tn}}N(E)dE\ . \qquad (12)$$

The photoconductivity can be numerically obtained from Eqs. (11) and (12) for a given photon-flux intensity F and temperature T. However, two unknown physical parameters appear in the equations: the capture cross section for free electrons σ_n and the density of states $N(E)$ between E_F and E_{tn}. Now we will show that these parameters can be unambiguously deduced from experimental data.

At a given temperature, we determine the experimental variation of the total current under illumination, I_T, as a function of the photon flux F. From Eqs. (10) the position of the quasi Fermi level E_{tn} under flux F can be deduced:

$$E_{tn}=E_F+k_BT\ln\frac{n}{n_0}=E_F+k_BT\ln\frac{I_T}{I_0}\ , \qquad (13)$$

I_0 being the dark current. In this manner we obtain the experimental variation of $E_{tn}-E_F$ with the photon flux F. Evidently, $E_{tn}-E_F$ is an increasing function of F. On the other hand, Eq. (12) shows that the quantity F/I_T is proportional to the number of electron recombination centers,

$$\frac{F}{I_T}=A\int_{E_F}^{E_{tn}}N(E)dE\ . \qquad (14)$$

Thus, we are able to experimentally determine the dependence of $A\int_{E_F}^{E_{tn}}N(E)dE$ as a function of the photon flux F. Then, from the two functions $A\int_{E_F}^{E_{tn}}N(E)dE=f(F)$ and $E_{tn}-E_F=g(F)$, we deduce the dependence of the number of recombination centers as a function of the position of the quasi Fermi level E_{tn}:

$$A\int_{E_F}^{E_{tn}}N(E)dE=h(E_{tn}-E_F)\ .$$

Now the calculation of $N(E)$ is straightforward,

$$N(E)=A^{-1}\{d[h(E_{tn}-E_F)]/dE_{tn}\}_{E_{tn}=E}\ .$$

Therefore, the experimental procedure described above allows us to determine (i) the shape of the density of states between the equilibrium Fermi level E_F and the maximum value of the quasi Fermi level $(E_{tn})_{\max}$ obtained for the highest value of the photon flux used in the experiment, and (ii) the quantity $AN(E_F)$ from which we can deduce the value of the product $v\sigma_nN(E_F)$.

The experimental variation of the total current under illumination as a function of the light intensity at a given temperature gives very basic information on the deep-gap states acting as recombination centers for electrons. However, it is then essential to verify the validity of these results, i.e., to confirm the validity of the recombination model. For this purpose, we introduce, in the theoretical equations (11) and (12), the shape of the density of states above the Fermi level and the value of the product $v\sigma_nN(E_F)$ previously determined, and we calculate the theoretical dependence of the photoconductivity σ_{phot} as a function of temperature for a given photon-flux intensity. The comparison between theoretical and experimental dependences will then provide a genuine test of the validity of the recombination model. Indeed, it appears from Eq. (12) that the photoconductivity is essentially controlled by the position of the quasi Fermi level E_{tn}. Moreover, the quasi Fermi level E_{tn} can be moved in two ways: by changing the temperature or the light intensity. According to Eqs. (10), increasing the temperature has the same effect as decreasing the light intensity. Therefore, if this theoretical correspondence between temperature and flux intensity is experimentally observed, we can be quite confident that the recombination process in our material is well described by the model of Rose. However, we must be more cautious about the validity of the information on the deep-gap states. Indeed, the shape of the density of states as well as the value of $v\sigma_nN(E_F)$ can be influenced in an unobvious way if the theoretical assumptions used for their determination are not entirely verified. We will discuss this point further in Sec. IV.

III. EXPERIMENTAL METHODS

The a-Si:H films were deposited by triode dc sputtering or by diode rf sputtering of an "electronic-grade" monocrystalline silicon target on Pyrex glass substrates held at a temperature of 550 K. The plasma was formed by a mixture of argon and hydrogen.

The a-Si:H layer is either intrinsic or n doped by introducing a small partial pressure of PH_3 in the argon-hydrogen mixture. The investigated n-doped samples have been prepared by triode dc sputtering at a total plasma pressure of 5 mTorr and a partial pressure of hydrogen of 0.4 mTorr.

The photoconductivity was measured in a gap cell geometry using back-surface electrodes formed by evaporated Cr-Sb layers. We have verified the Ohmic behavior of these contacts. The electrodes are 5 mm long and separated by 1 mm. The thickness of a a-Si:H films is about 1 μm.

The electrode gap was illuminated with continuous monochromatic light delivered by a helium-neon laser. The wavelength of the incident light is 633 nm, corresponding to an absorption coefficient of about 10^4 cm^{-1}. The intensity of the light was varied by means of a series of filters. The photon-flux intensity F, measured with a calibrated detector, ranges from 10^{12} to 10^{16} cm^{-2}s^{-1}.

A constant bias of 50 V was applied across the electrodes and the dark and light currents were measured with a 616-type Keithley electrometer. The sample was mounted in a vacuum cryostat (the residual pressure was about 10^{-6} Torr), and its temperature, ranging from 230 to 470 K, was measured using a platinum resistance thermometer in good thermal contact with the sample. The samples were initially annealed at 470 K in vacuum in order to obtain reproducible measurements. No Staebler-Wronski effect has been observed in our samples.

TABLE I. Elaboration conditions of diode-rf-sputtered samples (total pressure, P_T, and molecular percentage of hydrogen in the plasma, mol % H_2) and physical parameters deduced from experimental data: optical gap E_g, dark-conductivity activation energy $E_c - E_F$, product $v\sigma_n N(E_F)$ [v is the thermal velocity, σ_n is the capture cross section for electrons, and $N(E_F)$ is the density of states at the Fermi level], and the parameter E_0 characterizing the shape of the density of states.

Sample no.	P_T (m Torr)	H_2 content (mol %)	$E_C - E_F$ (eV)	E_g (eV)	$v\sigma_n N(E_F)$ ($s^{-1}eV^{-1}$)	E_0 (eV)
4.0282	20	6	0.67	1.65	5×10^6	0.10
11.0282	22	6.8	0.63	1.66	1×10^7	0.10
30.0182	12	4.4	0.57	1.59	3×10^5	0.07

IV. EXPERIMENTAL RESULTS AND DISCUSSION

We first study the undoped films prepared by diode rf sputtering. Three samples have been investigated. In Table I we have reported the conditions of sputtering (total pressure of the gas mixture, P_T, and molecular percentage of hydrogen in the plasma, mol % H_2) and some characteristic parameters of the films: dark conductivity, activation energy ($E_C - E_F$), and optical gap E_g.

Figure 2 shows a typical dependence of the photocurrent I_{phot}, difference between the dark current I_0, and the total current under illumination I_T, as a function of the photon flux F, at a temperature of 80 °C. We observe that the dependence of I_{phot} on F has the mathematical form, $I_{phot} \sim F^{\beta}$,[13] with $\beta = 0.78$ for this sample in the entire explored photon-flux range ($10^{12} \leq F \leq 10^{16}$ photons/cm^{2}s. Such a behavior has often been observed[2,9] and sometimes explained in the framework of Spear's model:[6] Recombination through states at E_A and E_V is bimolecular and recombination through states near the Fermi level is monomolecular, hence the relation $I_{phot} \sim F^{\beta}$, with $0.5 \leq \beta \leq 1$, can be explained by the mixture of these two recombination processes. However, if this explanation was correct, the parameter β would not remain constant but would vary with photon-flux intensity, the relative importance of the two recombination processes being dependent on this intensity. Therefore, the experimental dependence $I_{phot} \sim F^{\beta}$ observed in our samples when the photon flux varies by 4 orders of magnitude cannot be taken into account by Spear's model. On the contrary, we will now show that a quite satisfactory interpretation is given by Rose's recombination model.

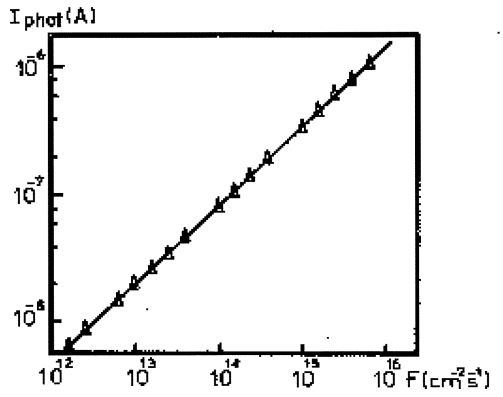

FIG. 2. Typical variation of the photocurrent I_{phot} versus the photon flux F at a temperature of 80 °C for an undoped sample prepared by diode rf sputtering. A variation of the form $I_{phot} \sim F^{0.78}$ is observed in this figure over the entire photon-flux range.

As previously reported in Sec. II, using the dependence of the total current I_T as a function of the photon flux F, we have determined the shape of the density of states above the Fermi level. For all of the investigated samples, the distribution of the density of states is found to be exponential:

$$N(E) = N(E_F)\exp[(E - E_F)/E_0] . \tag{15}$$

The parameter E_0 characterizing the shape of $N(E)$ has been calculated for each sample. The maximum value of E_0, obtained for $F = 10^{16}$ photon/cm^{2}s, being equal to $E_F + 0.3$ eV in these samples, the determination of the shape of $N(E)$ is relevant only in the energy range $E_F \leq E \leq E_F + 0.3$ eV.

The values of the product $v\sigma_n N(E_F)$ have been also experimentally determined. The corresponding results for the three studied samples appear in Table I.

As explained in the theoretical section the variation of I_{phot} versus F is entirely controlled by the shape of the density of states above the Fermi level. Therefore, the parameter β is necessarily linked to E_0. A simple relation between these two parameters can be obtained by introducing in Eq. (12) a distribution of localized states such as that given by Eq. (15). As expected, the calculation leads to a variation of I_{phot} versus F of the form $I_{phot} \sim F^{\beta}$, β being given by

$$\beta = E_0/(E_0 + k_B T) . \tag{16}$$

This result is only valid for conditions sufficiently far from equilibrium, i.e., $n \gg n_0$; if not, I_{phot} varies linearly with F.

This relation between β and E_0 was first proposed by Rose and was subsequently widely used[16,9] in order to explain the behavior of the photoconductivity as a function of the light intensity. It is noteworthy that the value of β obligatorily lies between 0.5 and 1, because the theoretical model only applies if the exponential density of states $N(E)$ varies with the energy slower than the Boltzmann factor, i.e., if $E_0 > k_B T$.

The values of E_0 determined from the experimental data and reported in Table I show that this last condition is well verified for our samples; therefore we can be confi-

dent in the exponential variation of $N(E)$.

The capture cross section for electrons can also be evaluated from the value of $v\sigma_n N(E_F)$. The density of states at the Fermi level in these samples is unknown but we can take a typical value obtained on rf-sputtered materials by means of capacitance and conductance measurements on Schottky diodes:[17] $N(E_F)=10^{17}$ cm^{-3}eV^{-1}. Therefore, with an approximate value of 10^7 cm/s for the thermal velocity, we obtain

$$\sigma_n = 10^{-18} - 10^{-17} \text{ cm}^2 .$$

Such small values of electron-capture cross sections, generally associated with Coulomb repulsive centers,[7] are in contrast with some values of the order of $\sigma_n \simeq 10^{-15}$ cm^2 previously reported.[18,19] This discrepancy is apparently due to the different determinations of the total number of recombination centers. Indeed, Street,[18] measuring the density of dangling bonds by ESR, has found values of the order of $N_s = 10^{16}$ cm^{-3} and has taken this value for the number of recombination centers. Moreover, it is noteworthy that for the determination of the electron lifetime, Street has used a trap-limited mobility, the value of which is difficult to obtain with some precision. On the other hand, Moustakas *et al.*[19] have determined the hole lifetime and the density of states close to the Fermi level from collection efficiencies and capacitance-voltage measurements on Schottky diodes. These authors have further supposed that the density of states does not vary in an energy range of 1 eV below the Fermi level and have determined in this way a capture cross section valid only for holes.

More generally, the knowledge of the density of states in a wide range of energy around the Fermi level is needed in order to obtain a good determination of the free-carrier capture cross sections. In our mind, the dc-photoconductivity experiments are well adapted to this problem.

We now proceed to examine the dependence of the photocurrent as a function of $10^3/T$ (see Sec. II). With the use of the experimental values of $v\sigma_n N(E_F)$ and of E_0, we have calculated the dependence of the photocurrent as a function of $10^3/T$ at a given photon flux. In Fig. 3 we report the theoretical and experimental curves at a photon flux of 9.3×10^{14} cm^{-2}s^{-1} for sample no. 4.0282. A very good agreement between the two curves is observed for this sample, as well as for the other samples, confirming that the recombination model is, for these samples, consistent with all the experimental data.

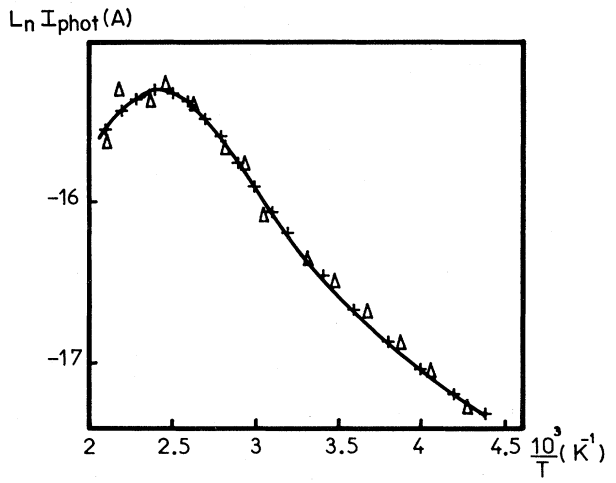

FIG. 3. Typical variation of the photocurrent I_{phot} versus $10^3/T$ at a photon flux of 6.3×10^{14} photons/cm^{2}s for an undoped sample prepared by diode rf sputtering. △ represents the experimental points and + represents the calculated curve.

We observe in Fig. 3 that a maximum and then a decrease of the photocurrent occur in the high-temperature region. The theoretical equations show that this behavior corresponds to a situation near equilibrium ($n \simeq n_0$). It can be shown, moreover, that in this case the photocurrent has a linear dependence as a function of the light intensity. Such a behavior has been experimentally observed; nevertheless it does not appear in Fig. 2, because for the experimental conditions ($T=80$°C and $F \geq 10^{12}$ photons/cm^{2}s) the inequality $n \gg n_0$ always prevails. Some n-doped films prepared by triode dc sputtering have also been studied. The activation energies $E_\sigma = E_c - E_F$ of the dark conductivity have been reported in Table II. The behavior of the photoconductivity is the same for the three doped samples. Therefore, the results obtained on a particular sample, no. 237, will now be presented and discussed.

In Fig. 4 we report the experimental dependences of the photocurrent I_{phot} as a function of the photon flux F, at two temperatures, $T=30$ (△) and -29°C (□). At $T=-29$°C (□), a variation of I_{phot} versus F of the form $I_{\text{phot}} \sim F^{0.55}$ is observed in the entire photon-flux range. On the other hand, at $T=30$°C (△) the photocurrent presents a more complex variation. We will show later that these different behaviors are well explained by the theoretical model.

TABLE II. n-doped triode-dc-sputtered samples: dopant content in the plasma, dark-conductivity activation energy $E_c - E_F$, product $v\sigma_n N(E_F)$ [v is the thermal velocity, σ_n is the capture cross section for electrons, and $N(E_F)$ is the density of states at the Fermi level], and the parameter E_0 characterizing the shape of the density of states.

Sample no.	PH_3 content (mol ppm)	$E_C - E_F$ (eV)	E_0 (eV)	$v\sigma_n N(E_F)$ (s^{-1}eV^{-1})
237	25	0.41	26×10^{-3}	5×10^5
236	50	0.32	21×10^{-3}	10^6
235	100	0.32	20×10^{-3}	4×10^6

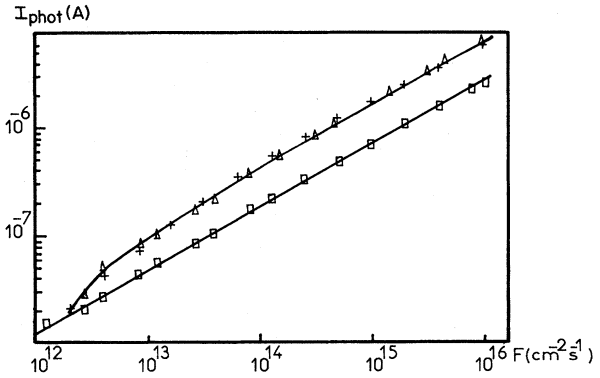

FIG. 4. Variations of the photocurrent I_{phot} versus the photon flux F for the doped sample no. 237 prepared by triode dc sputtering. □ represents the experimental points at $T=-29\,^{\circ}\text{C}$, △ represents the experimental points at $T=30\,^{\circ}\text{C}$, and + represents the calculated curve at $T=30\,^{\circ}\text{C}$.

Using the curve $I_{\text{phot}}(F)$ at $T=-29\,^{\circ}\text{C}$, we have determined (see Sec. II) the variation of the quantity $A\int_{E_F}^{E_{tn}} N(E)dE$ versus $(E_{tn}-E_F)$. This curve is shown in Fig. 5. We first remark that the maximum distance between E_{tn} and E_F (obtained for $F=10^{16}$ cm^{-2}s^{-1} at $T=-29\,^{\circ}\text{C}$) is equal to 0.12 eV for this sample. This value is much smaller than the value obtained for undoped samples [$(E_{tn}-E_F)_{\max}=0.3$ eV, typically]. Indeed,

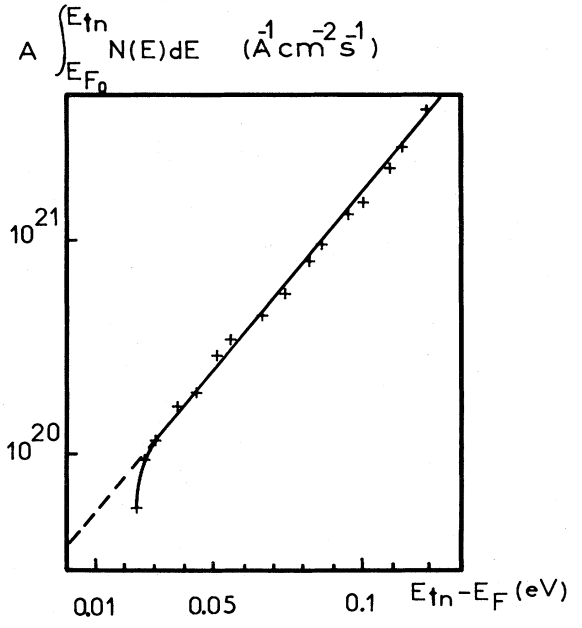

FIG. 5. Dependence of the quantity $A\int_{E_F}^{E_{tn}} N(E)dE=F/I_T$ as a function of $E_{tn}-E_F$ for the doped sample no. 237 prepared by triode dc sputtering where E_F is the Fermi level, E_{tn} is the quasi Fermi level for trapped electrons, F is the photon flux, and I_T is the total current under illumination. This curve has been deduced from the variation of the photocurrent I_{phot} versus the photon flux F at $T=-29\,^{\circ}\text{C}$ reported in Fig. 4.

the definition of E_{tn} [se Eqs. (10)] shows that the distance $E_{tn}-E_F$ decreases, for given conditions of temperature and light intensity, when the Fermi level is moved up towards the conduction band by the doping, due to the increase of the equilibrium electron density n_0. From the curve shown in Fig. 5, we are now able to determine the shape of $N(E)$ in the energy range

$$E_F \le E \le E_F+0.12 \text{ eV} .$$

As in the previously investigated samples, the distribution of localized states is found to be exponential:

$$N(E)=N(E_F)\exp(E-E_F)/E_0 ,$$

with

$$E_0=26\times10^{-3} \text{ eV} .$$

The product $v\sigma_n N(E_F)$ is also determined,

$$v\sigma_n N(E_F)=5\times10^5 \text{ s}^{-1}\text{eV}^{-1} .$$

These parameters have been determined from the experimental curve $I_{\text{phot}}(F)$ at $T=-29\,^{\circ}\text{C}$. Nevertheless, their values must by no means vary significantly with the temperature. Therefore, in order to ensure the validity of the theoretical model, we compare the experimental curve $I_{\text{phot}}(F)$ at $T=30\,^{\circ}\text{C}$ with the theoretical curve calculated with the preceding values of E_0 and $v\sigma_n N(E_F)$. These two curves are shown in Fig. 4. A very good agreement is observed confirming the validity of the recombination model in these n-doped samples.

The variation of the photocurrent versus F at the temperature of 30 °C (Fig. 4) is particularly interesting, as it indeed points out two regimes predicted by the theoretical equations: when $n\simeq n_0$ (near equilibrium), a linear dependence of I_{phot} versus F is expected; a tendency to this behavior is effectively observed for $F<5.10^{12}$ photons/cm^2 s, and when $n\gg n_0$ (far from equilibrium), the theoretical variation of I_{phot} versus F is given by

$$I_{\text{phot}}\sim F^{\beta},\quad \beta=E_0/(E_0+k_BT) ,$$

and this behavior is experimentally observed for high photon fluxes ($F>10^{15}$ photons/cm^2 s).

In the same manner as we calculated the $I_{\text{phot}}(F)$ function, we now proceed to determine the I_{phot} $(10^3/T)$ variation at a given photon flux in order to compare it with the experimental results. Figure 6 shows the experimental and theoretical curves for a photon flux $F=10^{16}$ photons/cm^2 s. The agreement between the two curves is quite satisfactory for temperatures less than about 40 °C. For higher temperatures, a maximum of the photocurrent followed by a rapid decrease occurs experimentally while the theoretical photocurrent continues to increase. This disagreement can easily be explained. We pointed out before that the theoretical equations are valid only if the condition $E_0>k_BT$ is verified. From the experimental value $E_0=26.10^{-3}$ eV, it appears that this inequality no longer prevails when the temperature is greater than 40 °C and the theoretical model does not apply. The rapid decrease of I_{phot} at high temperatures can be explained by the influence of localized states lying between E_{tn} and E_c. Indeed, their contribution to the recombination process

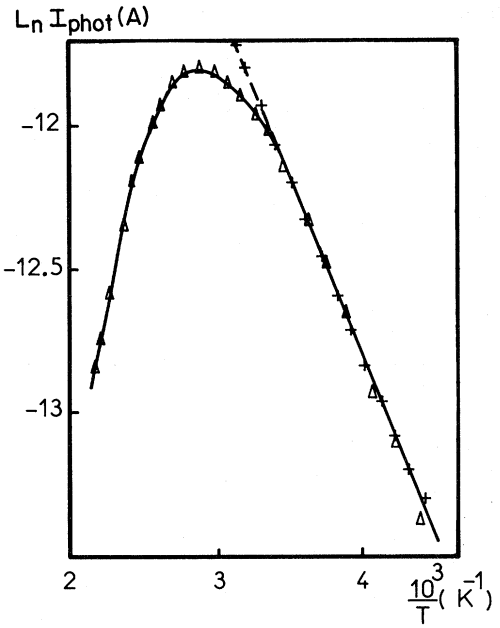

FIG. 6. Dependence of the photocurrent I_{phot} as a function of $10^3/T$ at a photon flux of 10^{16} photons/cm^{2}s for the doped sample no. 237 prepared by triode dc sputtering. △ represents the experimental points and + represents the calculated curve.

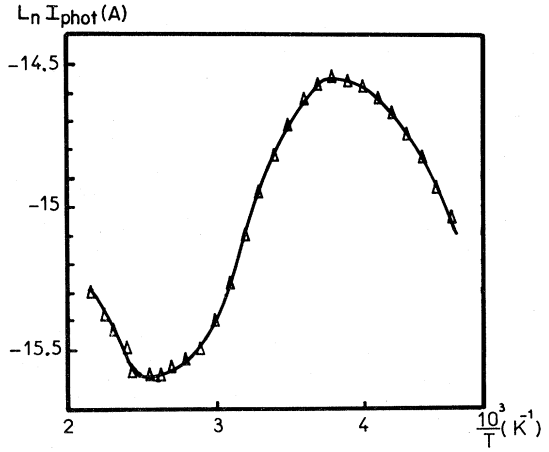

FIG. 7. Typical variation of the photocurrent I_{phot} as a function of $10^3/T$ at a photon flux of 10^{15} photons/cm^{2}s for an undoped sample prepared by triode dc sputtering. This curve points out the thermal quenching of the photoconductivity between 260 and 400 K.

cannot be neglected when the density of states varies with the energy faster than the Boltzmann factor [see Eqs. (4) and (6)].

The results obtained for the n-doped samples have been reported in Table II. The values of E_0 show that the density of states is a very rapidly increasing function of the energy near the conduction band. The determination of the shape of the density of states (characterized by the parameter E_0) is relevant for these samples in an energy range of about 0.1 eV above the Fermi level. It is, moreover, interesting to compare the values of the product $v\sigma_n N(E_F)$ obtained for the three samples. According to Anderson and Spear,[1] if we assume that the density of states and the capture cross section for electrons are unaltered by doping, the results obtained on samples with increasing dopant content might allow an exploration of the distribution of localized states on a wide energy range. From the characteristic parameters of sample no. 237, $v\sigma_n N(E_F)=5\times10^5$ s^{-1}eV^{-1}, $E_C-E_F=0.41$ eV, and $E_0=26\times10^{-3}$ eV, we are able to calculate the quantity $v\sigma_n N(E)$ corresponding to $E=E_c-0.32$ eV:

$$v\sigma_n N(E_c-0.32\text{ eV})=1.6\times10^7\text{ s}^{-1}\text{eV}^{-1}\,.$$

This value is much greater than the value of the product $v\sigma_n N(E_F)$ determined for the sample nos. 236 and 235 for which the Fermi level is situated 0.32 eV from the conduction band. According to previous work,[2] this seems to indicate that the results obtained for our samples with different dopant content cannot be directly compared, i.e., that the doping leads to a significant alteration of the density of states 0.4–0.3 eV from the conduction band.

Lastly, undoped films prepared by triode dc sputtering have been investigated. A typical variation of the photoconductivity as a function of the temperature is shown in Fig. 7. A quite different behavior is now observed, the curve $I_{\text{phot}}(10^3/T)$ exhibits a low-temperature peak (at about 260 K) and a broad valley with a minimum at 400 K. The measurements are quite reproducible, ruling out an accidental pollution of the sample as a cause of this phenomenon. Such results have already been observed for undoped a-Si:H films prepared by glow discharge[20,21] or by sputtering.[2] The prominent feature of the observed behavior is the decrease of the photoconductivity with increasing temperature, i.e., a thermal quenching of the photoconductivity. It seems at first that such a phenomenon cannot be explained in the framework of our recombination model; indeed Eqs. (10) and (12) show that, far from equilibrium, the photoconductivity must be an increasing function of the temperature. However, it is possible to show that the basic process of recombination remains the same as in the previous sample. Indeed, a plausible explanation of the thermal quenching of the photoconductivity was first proposed by Rose[7] using a two-level model. Suppose that two sets of states are present in the gap: (i) hole traps, "states 1," situated in the lower half of the gap and having a small capture cross section for electrons σ_{1n}, and (ii) electron traps, "states 2," lying near the Fermi level, with a larger capture cross section for electrons $\sigma_{2n}\gg\sigma_{1n}$. Now consider first the situation in which the quasi Fermi level for free holes E_{Fp} lies between states 1 and 2: states 2 act as recombination centers and control the recombination kinetics. Then, as the temperature is lowered, E_{Fp} moves down into states 1, leading to a transfer of holes from states 2 to states 1. Since $\sigma_{2n}\gg\sigma_{1n}$, this transfer results in an increase of the photoconductivity. The thermal quenching of the photoconductivity can thus be qualitatively explained. Moreover, as discussed in Sec. II, an increase of the light intensity has a similar effect on the position of the quasi Fermi

levels for trapped carriers as a decrease of the temperature. Thus, the thermal quenching of the photoconductivity is theoretically associated with a supralinear variation of the photoconductivity as a function of the light intensity in the framework of Rose's model. These two behaviors have actually been simultaneously observed for our samples, confirming the validity of the interpretation of our experimental results in light of Rose's model.

Nevertheless, quantitative information about the localized states are difficult to infer from experimental data. Certainly, a general calculation of the photoconductivity in the case of several species of traps (a species being defined by the capture cross sections σ_n and σ_p) could be made from the basic equation (4) and the charge-neutrality condition. However, in this case we must define two quasi Fermi levels E_{tp} and E_{tn} for each species of traps,[11] and this formal approach is too complex to provide a clear interpretation of the experimental results. However, a crude estimate of the position in energy of states 1 (with small capture cross section) can be obtained using the quasi Fermi level for free holes, E_{Fp}. Indeed, we observe in Fig. 7 that the thermal quenching of the photoconductivity occurs in the temperature range $260 < T < 400$ K, i.e., when the quasi Fermi level for free electrons E_{Fn} defined by Eqs. (10) lies between E_F and $E_F + 0.25$ eV. The quasi Fermi level for free holes, E_{Fp}, is almost symmetrical to the quasi Fermi level for free electrons, E_{Fn}, with respect to the middle of the gap. From the conductivity activation energy, $E_c - E_F = 0.66$ eV, and the optical gap, $E_g = 1.7$ eV, for this sample, we deduce that the thermal quenching occurs when $E_v + 0.4 < E_{Fp} < E_v + 0.65$ eV. This energy range corresponds approximately to the position of states 1.[21] Similar results have been previously obtained on samples prepared by glow discharge[21,22] and explained in the same way. A great number of undoped triode-dc-sputtered samples have been investigated. The thermal quenching of the photoconductivity has always been observed. Thus, the existence of localized states with relative small capture cross section for electrons situated 0.4—0.65 eV above the valence band seems to be a common feature of these samples. However, the presence of more than two species of traps in this material cannot be excluded. Indeed, as previously reported by Persans,[22] a third species of traps may exist but cannot be detected by dc photoconductivity.

Capacitance measurements as a function of the frequency of Schottky diodes prepared on undoped triode-dc-sputtered a-Si:H have also been carried out in our laboratory.[13] This experiment is used for the determination of the density of states near the Fermi level and gives, moreover, information on the trapping kinetics of free electrons. The results pointed out that some states lying below the Fermi level exhibit very slow trapping kinetics of free electrons due to a small capture cross section for electrons. The correlation between these experimental results and the behavior of the photoconductivity seems to confirm the previous interpretation satisfactorily.

The previous study of n-doped triode-dc-sputtered films have shown that the thermal quenching of the photoconductivity does not occur in these samples. Therefore, now the question is how to explain the disappearance of the thermal quenching of the photoconductivity as an effect of the n-doping. This phenomenon has already been observed[20,21] and a plausible explanation can be proposed in light of our experimental results. The thermal quenching of the photoconductivity in undoped samples disappears when the temperature is less than 260 K (see Fig. 7), i.e., when the quasi Fermi level for free holes, E_{Fp}, is situated at less than 0.4 eV from the valence band. In this case, we consider that the states 1 are completely filled; therefore the transfer of trapped holes between states 1 and 2 no longer occurs and the thermal quenching of the photoconductivity cannot appear. If we now consider the n-doped samples, we remark that the quasi Fermi level for free holes is always situated at less than 0.4 eV from the valence band at any temperature and any light intensity ($E_C - E_F \leq 0.41$ eV and $E_g = 1.7$ eV for the n-doped samples). Thus, the states 1 are always filled and the thermal quenching of the photoconductivity is inhibited. However, one must bear in mind that the determination of the product $v\sigma_n N(E_F)$ can be doubtful in a material containing different species of traps.

This remark raises the following question: Can we verify clearly the validity of our recombination model, i.e., can we be confident in the basic informations obtained on the deep gap states, even if the data are very consistent with the model as for the undoped rf-diode- and doped dc-triode-sputtered samples? The assumptions made in the calculation in order to obtain a simple expression of the photoconductivity are clearly verified *a posteriori* by the fit between theoretical and experimental curves, except for the following hypothesis: The capture cross sections for electrons and holes are independent of the energy, i.e., there is only one species of traps. Indeed, the presence of different species of traps can clearly be detected if the thermal quenching of the dc photoconductivity is observed (as for our undoped triode-dc-sputtered samples), but various species of traps may exist in some materials and influence the behavior of the photoconductivity in a less obvious way without thermal quenching. In this case, the basic information on deep-gap states inferred from the experimental data [the product $v\sigma_n N(E_F)$ and the shape of $N(E)$] are doubtful. Our recombination model is not as unique: different distributions of densities of states and capture cross sections may fit the data. Further experiments, such as deep-level transient spectroscopy, seem essential in order to verify and possibly to complete our recombination model, and to therefore obtain more precise information on deep-gap states which control the recombination process in our material.

V. CONCLUSIONS

We have measured the temperature and photon-flux dependences of the steady-state photoconductivity for a large number of sputtered a-Si:H films. The experimental results can be interpreted satisfactorily on the basis of a model first proposed by Rose involving a continuous distribution of localized states in the gap. Therefore, we can conclude that the predominant recombination process in our material is well described by the Shockley-Read statistics extented to a continuous distribution of traps without

interpretation between them.

The photoconductivity has been calculated using the formal approach of Simmons and Taylor and we have shown that the experimental data give directly basic information about the localized states lying near the Fermi level. The main results obtained are the following.

(i) The capture cross sections for electrons and holes in undoped diode-rf-sputtered *a*-Si:H seem to be independent of the energy of the localized state. An order of magnitude of the capture cross section for electrons is $\sigma_n = 10^{-18} - 10^{-17}$ cm^2. We have shown, moreover, that in this material the distribution of localized states is exponential in an energy range of 0.3 eV above the Fermi level with a characteristic parameter E_0 equal to about 0.1 eV.

(ii) The undoped triode-dc-sputtered films exhibit a thermal quenching of the photoconductivity. This phenomenon has been explained by the presence in the gap of two species of traps having very different capture cross sections for electrons. The species with the smallest capture cross section lies at about 0.4—0.65 eV from the valence band.

(iii) The thermal quenching of the photoconductivity disappears when the triode-dc-sputtered films are *n* doped. The distribution of localized states in the *n*-doped samples has again been found to be exponential in an energy range of 0.1 eV above the Fermi level with a characteristic parameter E_0 equal to about 25×10^{-3} eV, indicating that the density of localized states increases with the energy very quickly at less than 0.4 eV from the conduction band. Moreover, our results seem to indicate that the density of states in this energy range is significantly altered by the *n* doping.

It is noteworthy that the results are quite different for rf diode or dc triode sputtering. This emphasizes the great importance of the method of preparation in determining the detailed nature of the material, and could explain the diversity of behaviors observed for the photoconductivity in *a*-Si:H.

ACKNOWLEDGMENTS

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