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Thermal activation energy of steady-state photoconductivity in undoped amorphous silicon and silicon-germanium alloys

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The physical origin of the commonly observed small thermal activation energy of the steady-state photoconductivity in undoped hydrogenated amorphous silicon (*a*-Si:H) and silicon-germanium alloys (*a*-Si,Ge:H,F) is identified as the strong temperature dependence of the quasi-Fermi level for electrons. Using the Simmons-Taylor steady-state statistics [J. G. Simmons and G. W. Taylor, Phys. Rev. B **4**, 502 (1971)], we have derived *analytical* expressions for the activation energy and the temperature derivative of the electron quasi-Fermi energy. The result agrees with the experimental data for *a*-Si:H and *a*-Si,Ge:H,F alloys.

Steady-state photoconductivity is one of the most extensively used tools in the study of transport and recombination processes in hydrogenated amorphous silicon [*a*-Si:H(F)] and its alloys. The interpretation of photoconductivity, like that of other transport properties, however, is not straightforward. An outstanding question has been the physical origin of the relatively small thermal activation energy E_a^{ph} of the photoconductivity. E_a^{ph} is about 0.1–0.2 eV, while the quasi-Fermi energy for electrons (which dominate photoconductivity) lies about 0.3–0.5 eV below the conduction-band edge (see Table I). Does the relatively small E_a^{ph} imply any special gap states around an energy level lying E_a^{ph} below the conduction-band edge, or can it be explained in the model of exponential band tails plus defect states? The question must be answered to understand transport and recombination processes in *a*-Si:H(F) and its alloy under illumination. An early model proposed by Spear, Loveland, and Al-Sharbaty[1] invokes recombination between localized states and relates the activation energy to an energy level E_A which lies about 0.2 eV below the conduction-band edge.[2] In the region of temperature and generation rate in which we are interested in this paper, this model equates E_a^{ph} to the difference between the conduction-band edge and E_A. More recently, numerical calculations have been carried out[3] based on the Simmons-Taylor steady-state statistics[4] in semiconductors with continuously distributed gap states. Such numerical calculations have proven helpful but the question of E_a^{ph} addressed above remains unsolved.

In this paper we use the steady-state statistics of Simmons and Taylor to derive an analytical expression for the thermal activation energy. We will also show that the temperature coefficient (derivative) of the quasi-Fermi level is much larger than those of the other relevant energy levels, i.e., the conduction-band mobility edge and the Fermi energy in dark. The results identify the physical origin of the relatively small thermal activation energy of the photoconductivity as the large temperature dependence of the quasi-Fermi energy. To explain the small thermal activation energy E_a^{ph}, there is no need for a special energy level which lies E_a^{ph} below the conduction-band edge, or for recombination paths between the localized states. Our theoretical results agree well with experimental data on undoped *a*-Si:H and *a*-Si,Ge:H,F alloys.

The photoconductivity σ_{ph} is defined as the conductivity under illumination minus the dark conductivity. We will restrict ourselves to the region of temperature and generation rate where the photoconductivity is larger than the dark conductivity.[5] *a*-Si:H(F) and *a*-Si,Ge:H,F without intentional doping are slightly *n* type. At high enough temperature, the contribution of the hopping conduction is negligible. Therefore the free electrons make the major contribution to photoconductivity. That is, $\sigma_{\mathrm{ph}}=\mu_0 en$, where μ_0 is the mobility of the free electrons, e the absolute value of the electronic charge, and n the concentration of free electrons. We take μ_0 to be independent of temperature. Then, σ_{ph} and n are equivalent within a constant factor. n is given by

$$n=N_C\exp\left[\frac{-(E_C-E_{Fn})}{kT}\right], \tag{1}$$

where N_C is the effective density of states in the conduction band, E_C the energy of the mobility edge of the conduction band, E_{Fn} the quasi-Fermi energy for the free electrons, k the Boltzmann constant, and T the absolute temperature. We will neglect the weak temperature dependence of N_C. Equation (1) actually is the definition of E_{Fn}.

The Simmons-Taylor statistics is general.[4] For simplicity and without loss of physical significance, we will make several assumptions and simplifications. (1) Electronic transitions between gap states (which are localized) are neglected. (This assumption is included in the Simmons-Taylor statistics.) (2) The optical excitation energy is larger than the optical band gap so that the hole-electron pairs are mainly generated by transitions between the extended states. (3) Only one species of gap states is considered. By this we mean that the ratio of the capture cross section of the gap states for free electrons, $s_n(E)$, to the capture cross section of these states for free holes, $s_p(E)$, is independent of the energy of the gap states. With this assumption we can define the quasi-Fermi energy for the trapped electrons, E_{tn}, and the quasi-Fermi energy for the trapped holes, E_{tp}. In what follows, we further regard s_n and s_p as constants for simplicity. (4) The material is undoped or only slightly n type so that the energy level E_{da} which separates the donorlike gap states and the acceptorlike gap states lies near the middle of the gap. (5) The increase of the density of the gap states above E_{Fn} with E is not faster than that of the inverse Boltzmann factor $\exp(E/kT)$. (At the end of the paper, we will discuss the failure of this assumption.) (6) $np \gg n_0 p_0$ and $s_n n \gg s_p p$, where n and p are the concentration of free electrons and free holes under illumination, respectively, and n_0 and p_0 are their counterparts without illumination. The condition $s_n n \gg s_p p$ enables us to equate E_{Fn} to E_{tn} at the last stage of the simplification. With these assumptions, we have[3,4,6]

$$n = G\tau_n \ , \tag{2}$$

$$\tau_n^{-1} = vs_n \int_{E_{da}}^{E_{Fn}} N(E)dE \ , \tag{3}$$

where G is the generation rate, τ_n the recombination lifetime of the free electrons, v the thermal velocity of the free electrons, and $N(E)$ the density of gap states as a function of energy. Equations (1)–(3) are our basic equations. This set of equations is also called the Rose model.[7]

The thermal activation energy of the photoconductivity at any temperature is defined as

$$\begin{aligned} E_a^{\text{ph}}(T) &\equiv -\frac{d\ln(\sigma_{\text{ph}})}{d[1/(kT)]} \\ &= (E_C - E_{Fn}) - T\frac{d(E_C - E_{Fn})}{dT} \ . \end{aligned} \tag{4}$$

We note that there are two contributions to the thermal activation energy: The first term in Eq. (4) originates in the Boltzmann statistics and the second term in the temperature dependence of E_C and E_{Fn}. We can also define the following quantities:

$$E_{C0}(T) \equiv E_C(T) - T\frac{dE_C}{dT} \ , \tag{5a}$$

$$\delta(T) \equiv -\frac{1}{k}\frac{dE_C}{dT} \ ; \tag{5b}$$

$$E_{Fn0}(T) \equiv E_{Fn}(T) - T\frac{dE_{Fn}}{dT} \ , \tag{6a}$$

$$\theta(T) \equiv -\frac{1}{k}\frac{dE_{Fn}}{dT} \ . \tag{6b}$$

We call δ and θ the temperature coefficient of E_C and E_{Fn}, respectively. Minus signs are used in the definitions of both $\delta(T)$ and $\theta(T)$ to make the values of these two quantities positive. Note that $E_{C0}(T)$ is generally not the value of E_C at $T = 0$ K, unless E_C varies with T linearly from 0 K to T. The same comment applies to E_{Fn0}. E_{C0} usually is independent of temperature and $\delta \approx 2.5$, in a large range of T around 300 K (Ref. 8). With Eqs. (5) and (6), $E_a^{\text{ph}}(T)$ can be expressed in several forms:

$$E_a^{\text{ph}}(T) = (E_C - E_{Fn}) + \delta kT - \theta kT \ . \tag{7a}$$

Substitution by Eqs. (5a) and (6a) results in

$$E_a^{\text{ph}}(T) = (E_{C0} - E_{Fn}) - \theta kT \tag{7b}$$

$$= E_{C0}(T) - E_{Fn0}(T) \ . \tag{7c}$$

Equation (7a) implies that the temperature dependence of E_C, given by δ (>0), increases E_a^{ph} above $E_C - E_{Fn}$. Therefore, to explain the experimental observation that $E_a^{\text{ph}} < E_C - E_{Fn}$, we turn our attention to the temperature dependence of E_{Fn}, given by θ.

It will be clear later that θ and E_a^{ph} are best expressed in terms of the exponent γ of the power dependence of the photoconductivity on the generation rate. We therefore first derive the expression for γ. γ is defined as

$$\gamma \equiv \frac{d\ln(n)}{d\ln(G)} \ . \tag{8}$$

We now derive the exponent γ and the thermal activation energy from Eqs. (1)–(3). These equations contain two independent variables: the temperature T and the generation rate G. n and E_{Fn} are functions of T and G, while E_C depends on T only. E_{da} is a constant by definition. We assume that N_C, vs_n, and $N(E)$ are independent of temperature. From Eq. (1) we obtain

$$\frac{d\ln(n)}{d\ln(G)} = \frac{1}{kT}\frac{dE_{Fn}}{d(\ln G)} \ . \tag{9}$$

Equations (2) and (3) give

$$\frac{d\ln(n)}{d\ln(G)} = 1 - \tau_n vs_n N(E_{Fn})\frac{dE_{Fn}}{d(\ln G)} \ . \tag{10}$$

Combination of Eq. (9) with Eq. (10) yields

$$\gamma = \frac{T_0}{T_0 + T} \ , \tag{11}$$

where T_0 is in general a function of E_{Fn} and is defined by

$$kT_0 \equiv \frac{1}{N(E_{Fn})}\int_{E_{da}}^{E_{Fn}} N(E)dE \ . \tag{12}$$

This general expression for γ is useful in discussing the dependence of γ on E_{Fn} if $N(E)$ is given. When the density of gap states depend exponentially on the energy between E_{da} and E_{Fn}, T_0 and thus γ are constant, and Eqs. (11) and (12) reduce to the result of the well-known Rose model for a constant γ.[7]

The temperature coefficient θ of E_{Fn} is derived by starting with Eq. (1),

$$\frac{1}{k}\frac{d\ln(n)}{dT} = \frac{1}{(kT)^2}(E_{C0} - E_{Fn}) - \frac{\theta}{kT} \ . \tag{13}$$

Note that δ is incorporated in E_{C0}. Equations (2) and (3) lead to

$$\frac{1}{k}\frac{d\ln(n)}{dT} = vs_n\tau_n N(E_{Fn})\theta \ . \tag{14}$$

With Eqs. (8), (10), (13), and (14) we obtain

$$\theta=\gamma\frac{E_{C0}-E_{Fn}}{kT} . \tag{15}$$

Because $\gamma>0$, $\theta>0$. That is, E_{Fn} decreases with T [Eq. (6b)]. Substitution of Eq. (15) to Eq. (7b) yields the thermal activation energy

$$E_a^{\mathrm{ph}}=(E_{C0}-E_{Fn})(1-\gamma) . \tag{16}$$

Equation (16) gives a relation between the activation energy, the quasi-Fermi energy, and γ. Since the observed values of γ lie between 0.5 and 1, one can immediately see from Eq. (16) that E_a^{ph} is about half or less of $E_{C0}-E_{Fn}$, in agreement with experiment. In Table I, we list the experimental data of E_a^{ph} and the calculated values of E_a^{ph} and θ for *a*-Si:H and *a*-Si,Ge:H,F alloys, together with other relevant properties of the samples. In this table, samples 1 and 2 were prepared by dc excited glow discharge and samples 3 and 4 were prepared by rf excited glow discharge. Sample 1 is *a*-Si:H grown from SiH_4; the other samples are *a*-Si,Ge:H,F alloys grown from SiF_4, GeF_4, and H_2. Samples 1, 2, 3, and 4 correspond to our laboratory sample labels GP70, GP47, RC102, and RC97, respectively. σ_{ph} is the photoconductivity when an almost uniform generation rate of about 10^{20} $\mathrm{cm}^{-3}\,\mathrm{sec}^{-1}$ is applied by illuminating the sample with band-pass filtered light. Table I shows satisfactory agreement between the experimental E_a^{ph} and the calculated $E_{a\,\mathrm{cal}}^{\mathrm{ph}}$. We will discuss the difference between E_a^{ph} and $E_{a\,\mathrm{cal}}^{\mathrm{ph}}$ for sample 1 later in some detail. The calculated values of the temperature coefficient θ in E_{Fn} are equal to or more than 10, much larger than those of E_C (≈ 2.5) (Ref. 8) and the dark Fermi energy E_F (≈ 1.4) (Ref. 9).

Within the assumptions we made, our derivation does not depend on the form of the density of gap states. In particular, the gap states at energies above E_{Fn} have no effect. States above E_{Fn} (including the extended states in the conduction band) are approximately in thermal equilibrium. Each of these gap states has the same capture and emission rates for free electrons. Therefore these states do not contribute to the net recombination rate. As shown below, the contribution of these states to the net recombination rate can be neglected only under assumption (5): their density does not increase with energy faster than the inverse Boltzmann factor. In *a*-Si:H and its alloys, E_a^{ph} is much smaller than $E_{C0}-E_{Fn}$ (Table I), i.e., E_{Fn0} is much closer to E_{C0} than is E_{Fn} [Eq. (7c)]. This is not because of a peculiar gap state density near E_{Fn0}, but because the density of the gap states between E_{da} and E_{Fn} is such that the temperature coefficient of E_{Fn} becomes large.

In general, E_a^{ph} and γ vary with measurement temperature and generation rate and are defined differentially [Eqs. (4) and (8)]. Equation (16) must be compared with experimental data measured at the same temperature and generation rate. For example, Eq. (16) agrees at least qualitatively with the observation[3] of anomalous thermal quenching of photoconductivity. Within the temperature region in which the thermal quenching is observed, E_a^{ph} is negative and γ is larger than 1; beyond this region, E_a^{ph} is positive and γ is smaller than 1; at both ends of the region, $E_a^{\mathrm{ph}}=0$ and one may expect that $\gamma=1$. In this case, Eq. (3) for τ_n may need to be modified to allow another species of defect states with a different capture cross section.[3,7] But we may still have $\tau_n=f(E_{Fn}(T,G))$, where f represents a function. With this expression of τ_n, Eqs. (15) and (16) can be derived similarly.

We now discuss the consequence of dropping assumption (5). While this assumption is valid for *a*-Si,Ge:H,F (see Ref. 11 and Table I), there are some experimental data for *a*-Si:H which suggest the existence of a conduction-band tail sharper than the inverse Boltzmann factor.[2] If such tails states exist, Eq. (3) should be replaced by the more general form[6]

$$\tau_n^{-1}=vs_n\int_{E_{da}}^{E_C}\frac{N(E)}{1+\exp[(E-E_{Fn})/kT]}dE . \tag{17}$$

The contribution by the states in $E_{Fn}<E<E_C$ to the recombination rate is reduced by the Boltzmann factor $\exp[-(E-E_{Fn})/(kT)]$ compared with that by the states in $E_{da}<E<E_{Fn}$. With Eqs. (1), (2), and (17) as the basic equations, we again can derive the expressions for γ, θ, and E_a^{ph}. γ still can be expressed formally by Eq. (11), but now T_0 is defined by

$$kT_0\equiv\frac{\displaystyle\int_{E_{da}}^{E_C}\frac{N(E)}{1+\exp[(E-E_{Fn})/kT]}dE}{\displaystyle\frac{1}{kT}\int_{E_{da}}^{E_C}\frac{N(E)}{4\cosh^2[(E-E_{Fn})/2kT]}dE} , \tag{18}$$

TABLE I. Experimental values for optical gap E_g, inverse slope of the conduction-band tail $E_u(T)$ measured at T by time of flight, photoconductivity σ_{ph}, photosensitivity $kT\ln(\sigma_{\mathrm{ph}}/\sigma_d)$ where σ_d is dark conductivity, activation energies E_a^d of σ_d and E_a^{ph} of σ_{ph}, and photoconductivity exponent γ. $E_{C0}-E_{Fn}$ is equal to $E_a^d-kT\ln(\sigma_{\mathrm{ph}}/\sigma_d)-(kT)dE_F/d(kT)$, where E_F is the dark Fermi energy and $dE_F/d(kT)$ is taken to be 1.4 (Ref. 9). The experimental data for samples 3 and 4 are from Ref. 10. Also listed are calculated values for the activation energy $E_{a\,\mathrm{cal}}^{\mathrm{ph}}$ of σ_{ph} from Eq. (16), and for the temperature coefficient θ_{cal} of E_{Fn} from Eq. (15). $T=300$ K unless otherwise specified. Sample 1 is *a*-Si:H and the other samples are *a*-Si,Ge:H,F alloys.

Sample no.	E_g (eV)	$E_u(T)$ (eV)	σ_{ph} (S/cm)	$kT\ln(\sigma_{\mathrm{ph}}/\sigma_d)$ (meV)	E_a^d (eV)	E_a^{ph} (eV)	γ	$E_{C0}-E_{Fn}$ (eV)	$E_{a\,\mathrm{cal}}^{\mathrm{ph}}$ (eV)	θ_{cal}
1	1.65		9.8*E*-6	230	0.590	0.038	0.80	0.324	0.065	10
2	1.47		3.8*E*-5	218	0.620	0.079	0.77	0.366	0.084	11
3	1.32	0.05 (364 K)	2.1*E*-6	106	0.63	0.15	0.77	0.49	0.11	15
4	1.28	0.05 (383 K)	5*E*-7	59	0.56	0.15	0.73	0.47	0.13	13

$$\theta=\frac{1}{kT}[\gamma(E_{C0}-E_{Fn})+(E^*-E_{Fn})(1-\gamma)] \ , \qquad (19)$$

$$E_a^{\mathrm{ph}}=(E_{C0}-E^*)(1-\gamma) \ , \qquad (20)$$

where $E_{C0}-E^*$ is a weighted mean of $E_{C0}-E$ and is defined by

$$E_{C0}-E^*\equiv\frac{\displaystyle\int_{E_{da}}^{E_C}\frac{N(E)}{4\cosh^2[(E-E_{Fn})/2kT]}(E_{C0}-E)dE}{\displaystyle\int_{E_{da}}^{E_C}\frac{N(E)}{4\cosh^2[(E-E_{Fn})/2kT]}dE} \ . \qquad (21)$$

The function $\{4\cosh^2[(E-E_{Fn})/2kT]\}^{-1}$ peaks at $E=E_{Fn}$ and reduces to an exponential function when $|E-E_{Fn}|>2kT$. With this in mind, one can see that these more general results reduce to Eqs. (12), (15), and (16), when the assumption is made that the density of the gap states in $E_{Fn}<E<E_C$ does not increase faster than the inverse Boltzmann factor.

Equation (21) implies that in general $(E_{C0}-E^*)\leq(E_{C0}-E_{Fn})$. Therefore, $\theta\geq\gamma(E_{C0}-E_{Fn})kT$ and $E_a^{\mathrm{ph}}\leq(E_{C0}-E_{Fn})(1-\gamma)$. That is, the contribution to the recombination rate from the gap states in $E_{Fn}<E<E_C$ makes the temperature coefficient of the quasi-Fermi energy larger and the activation energy smaller. This effect on E_a^{ph} explains the larger relative discrepancy between E_a^{ph} and $E_{a\,\mathrm{cal}}^{\mathrm{ph}}$ for *a*-Si:H (sample 1) in Table I, because the conduction-band tail in *a*-Si:H may be sharper than the inverse Boltzmann factor. We note that even if the density of the trapped electrons at E_A dominates[2] so that $E^*\approx E_A$, the activation energy is not $E_{C0}-E_A$ (Ref. 1) but $(E_{C0}-E_A)(1-\gamma)$.

In summary, we have calculated the temperature dependence of the photoconductivity of *a*-Si:H and related semiconductors. We have demonstrated that the low activation energy is due to a strong temperature dependence of the electron quasi-Fermi energy and that it is not necessary to invoke a special energy level which lies E_a^{ph} below the conduction-band edge, or recombination paths between localized states to explain the observed low activation energy. The calculated values agree with experiment.

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[1] W. E. Spear, R. J. Loveland, and A. Al-Sharbaty, J. Non-Cryst. Solids **15**, 410 (1974).

[2] In the model of Ref. 1, E_A is the peak position of the density of trapped electrons in the conduction-band tail, at which the slowly decreasing density of states turns to a tail with a characteristic temperature less than the measurement temperature (which is the room temperature). See W. E. Spear and P. G. LeComber, J. Non-Cryst. Solids **8-10**, 727 (1972). Such a sharp tail may exist in *a*-Si:H but not in *a*-Si,Ge:H,F. See, for example, Ref. 11.

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[4] J. G. Simmons and G. W. Taylor, Phys. Rev. B **4**, 502 (1971); G. W. Taylor and J. G. Simmons, J. Non-Cryst. Solids **8-10**, 940 (1972).

[5] At high temperature or small generation rate, where the photoconductivity is smaller than the dark conductivity, the photoconductivity shows a negative activation energy (Refs. 1 and 3). While the Simmons-Taylor statistics may still be applicable to this case (Ref. 3), some of the simplifying assumptions preceding Eq. (2) are not valid.

[6] J. Z. Liu (unpublished).

[7] Albert Rose, *Concepts in Photoconductivity and Allied Problems* (Krieger, Huntington, NY, 1978).

[8] The temperature coefficient δ of E_C can be approximated as half of that of the optical gap E_g. $dE_g/d(kT)\approx 5$ around room temperature for *a*-Si:H and *a*-Si,Ge:H,F alloys with E_g from 1.7 to 1.25 eV. See R. Schwarz, K. Dietrich, S. Goedecker, J. Kolodzey, D. Slobodin, and S. Wagner, in *Amorphous Silicon Semiconductors—Pure and Hydrogenated,* Mater. Res. Soc. Proc. No. 95, edited by A. Madan, M. Thompson, D. Adler, and Y. Hamakawa (MRS, Pittsburgh, 1987), p. 353, and the references therein.

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