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Origin of the spectral dependence of the nonradiative efficiency in hydrogenated amorphous silicon

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Measurements of the excitation kinetics and model calculations of the wavelength dependence of the room-temperature nonradiative efficiency in hydrogenated amorphous silicon (*a*-Si:H) are described. The nonradiative efficiency, defined as the ratio of the heat released per absorbed photon, is measured using photopyroelectric spectroscopy and displays a fairly sharp minimum when the *a*-Si:H is illuminated with near-band-gap photons. The results reported here indicate that this minimum arises from the variation in the amount of heat generated by free-carrier thermalization with incident photon energy.

A powerful method for measuring the sub-band-gap absorption coefficient α of thin-film amorphous semiconductors involves detecting the temperature rise of the material resulting from the nonradiative recombination of the photoexcited charge carriers. Bolometric techniques such as photothermal deflection spectroscopy[1] (PDS) and photopyroelectric spectroscopy[2–5] (PPES) have much greater sensitivity than conventional transmission spectroscopy, and enable determinations of small absorptances down to $\alpha d > 10^{-5}$ and $\alpha d > 10^{-3}$, respectively, for films of thickness d. An implicit assumption in the analysis of PDS and PPES data is that the nonradiative efficiency η, defined as the ratio of the thermal energy released per absorbed photon, is independent of the wavelength of the incident light at room temperature. Support for this assumption is provided by the very small efficiency for radiative recombination, as indicated by the weak room-temperature photoluminescence signal in amorphous semiconductors.[6]

The recent observation of a fairly sharp minimum in plots of η against incident photon energy, obtained from absorptance data using PPES when a hydrogenated amorphous silicon (*a*-Si:H) film is illuminated with photons of near-band-gap energy is therefore quite surprising.[4,5] Extensive investigations indicate that this minimum in η is not an experimental artifact of the PPES technique and rather reflects the bulk properties of the *a*-Si:H.[5,7] There is no increase in the radiative efficiency for band-gap illumination in *a*-Si:H, presenting a challenge to account for this "missing heat." In this paper we describe measurements of the excitation kinetics of η in *a*-Si:H and model calculations which indicate that the spectral dependence of η reflects the variation in the amount of heat released by free-carrier thermalization as the incident photon energy is varied.

The procedure for measuring the spectral dependence of η using photopyroelectric spectroscopy is briefly reviewed below; detailed descriptions of the experimental setup and data analysis have been published previously.[7] Monochromatic light is mechanically chopped (typical chopper frequency $\omega \sim 13$ Hz), and then focused onto the *a*-Si:H film, which is physically clamped next to a commercially available pyroelectric polymer polyvinylidene difluoride[8] (PVDF). The temperature rise in the *a*-Si:H leads to thermal diffusion toward the PVDF detector, inducing a voltage V_t across the polymer which is amplified and then detected using a lock-in, with the chopper frequency serving as the reference signal. The transmitted light also induces a voltage in the polymer and consequently a signal is generated even when the sample is not in thermal contact. The detected signal in this configuration, termed the nonthermal contact voltage V_{nt} is directly proportional to the transmission coefficient T_{Si} of the *a*-Si:H film. By combining measurements when the *a*-Si:H film is in thermal and nonthermal contact configurations, one obtains[9]

$$V_t - V_{\text{nt}} = C I_0 A_{\text{Si}} \eta g \ , \tag{1}$$

where C is an instrumental and geometric factor, I_0 is the incident light intensity, the nonthermal contact voltage is given by $V_{\text{nt}} = C I_0 T_{\text{Si}} A_p \eta_p$ ($A_p \eta_p$ the product of the polymer absorbance and signal efficiency), A_{Si} is the silicon absorptance, and g represents the thermal coupling between the *a*-Si:H and the PVDF polymer. In the strong absorption regime, that is, for photon energies greater than 1.6 eV, the absorption coefficient can be obtained from conventional transmission spectroscopy measurements and consequently $A_{\text{Si}} = 1 - \exp[-\alpha d]$ is a known quantity. Equation (1) can therefore be used to measure the product of the nonradiative efficiency η and the thermal coupling factor g in the strong absorption regime, assuming that g is independent of photon energy.

The samples studied here are 1 μm thick and were grown in rf glow discharge deposition reactor, at a substrate temperature of 250 °C and an incident rf power of 2 W. The data reported here are for an n-type doped *a*-Si:H film (gas phase doping level of 10 ppm PH_3); identical results are found for p-type and undoped *a*-Si:H. The absorption spectra measured with the PPES technique are very similar to those obtained using PDS (Refs. 7 and 10) and yield an optical gap E_{gap} of 1.75 eV. As shown in Fig. 1, η is nearly constant for photon energies much greater than E_{gap}, but has a sharp minimum near 1.75 eV, and then increases with sub-band-gap illumination. Lacking a precise knowledge of the thermal coupling factor g in Eq. (1), the values η obtained are relative, and have consequently been arbitrarily normalized to unity at

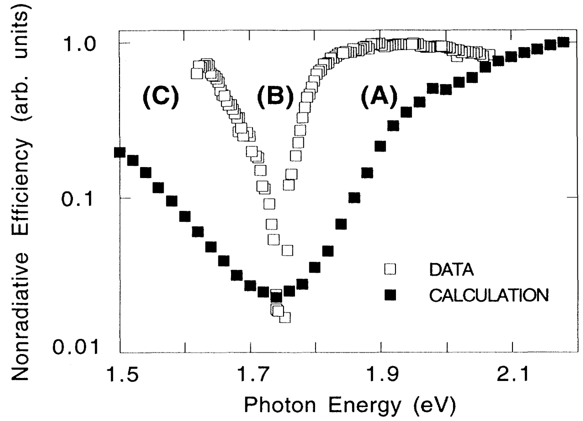

FIG. 1. Spectral dependence of the room-temperature nonradiative efficiency of *n*-type *a*-Si:H. The filled squares curve is the result of model calculations described in the text.

$h\nu=1.9$ eV. While a minimum in η is always observed over a wide range of doping levels for *n*-type, *p*-type, and undoped *a*-Si:H, as well as for *a*-Si:H films deposited by rf sputtering, the minimum is not always as sharp nor as deep as that in Fig. 1.[5]

The heat generated following photoexcitation of electron-hole pairs is due to (i) free-carrier thermalization as charge carriers excited into extended states move toward localized band tail states and (ii) nonradiative recombination. The amount of energy released in the first process is wavelength dependent, in that it depends on how far into the extended states the charge carriers are promoted, while the energy released by recombination is set by the energy separation of the localized band-tail states in which the charge carriers reside,which to first order is independent of the excitation energy. As indicated in the sketch of the electronic density of states in Fig. 2, absorption of photons with $h\nu > E_{\text{gap}}$ $(=E_c-E_v)$, represented by the arrow labeled *A* in Fig. 2 yields electrons and holes in extended states which then thermalize to localized band-tail states. Similarly lower-energy photons (arrow *C* in Fig. 2) produce *either* a free electron *or* a free hole, which then thermalizes to the band tail. In contrast photons with energy such that the maximum absorption occurs near the band edges (arrow *B*) create charge carriers at or very near the band-tail states, and the free-carrier thermalization energy is very small in this case. These three absorption regions are also labeled on Fig. 1.

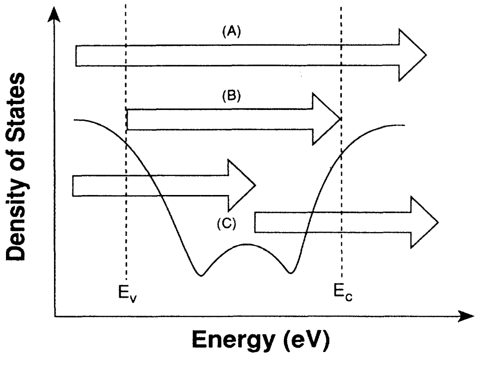

FIG. 2. Sketch of the density of states of *a*-Si:H. The arrows *A*, *B*, and *C* indicate the absorption of light with energy greater than, comparable to, and less than the optical band gap $(E_{\text{gap}}=E_c-E_v)$, respectively.

Preliminary model calculations of the thermalization energy as a function of incident photon energy are indicated by the solid squares in Fig. 1. The calculation assumes an energy-independent matrix element connecting final and initial states and sums over all possible transitions for a given photon energy. For a given incident photon, charge carriers are excited to and from energy states for which the absorption is largest, and then release thermalization energy determined by their location from the mobility edges. The heat detected is then this thermalization energy. These calculations reproduce the observed minimum but with a broader line shape. The qualitative agreement between calculation and experiment supports the proposal that photons with $h\nu \sim E_{\text{gap}}$ are absorbed primarily near the band edges and do not contribute significant thermalization energy. The sensitivity of the model calculations to variations in the density of states is described elsewhere.[11]

The heat released following light absorption is due to both recombination and thermalization processes and must always equal the energy of the absorbed photon, if no radiative or Auger processes occur. However the heat *detected* per absorbed photon by the PVDF polymer is

$$\eta=(E_{\text{therm}}+fE_{\text{rec}})/h\nu\ ,\quad 0<f\le 1\ , \tag{2}$$

where E_{therm} is the thermalization energy, E_{rec} is the heat released by nonradiative recombination, and f represents the fraction of E_{rec} that is detected during the time determined by the inverse of the chopper frequency ω^{-1}. The time required for free-carrier thermalization is on the order of psec,[12] consequently all of E_{therm} will be transmitted to the PVDF during a measurement cycle. In contrast, the nonradiative recombination time τ is longer than the inverse of the chopper frequency used to measure the PPES signal, that is $\tau > \omega^{-1}$. It has long been known that τ in *a*-Si:H becomes longer at low light intensities.[13–17] As shown in Fig. 3, measurements of the photoconductivity rise and decay times[18] are indeed on the order of 1 sec for the generation rates G used in the PPES measurements $(G \sim 10^{16}\ \text{cm}^{-3}\,\text{sec}^{-1})$, which is longer than the inverse chopper frequency $\omega^{-1}=77$ msec. When illumination is stopped, for an exponentially decaying density of photoexcited charge carriers $n(t)=n(0)\exp[-t/\tau]$ it can be easily shown that

$$f=1/(1+\omega\tau)\ \text{ for }\ \omega\tau>1\ . \tag{3}$$

Consequently not all of the recombination heat is detected by the PVDF polymer but all of the thermalization energy is recorded; in this case $\eta<1$ and will have the same spectral dependence as the thermalization energy.

If the model described above is correct then f and

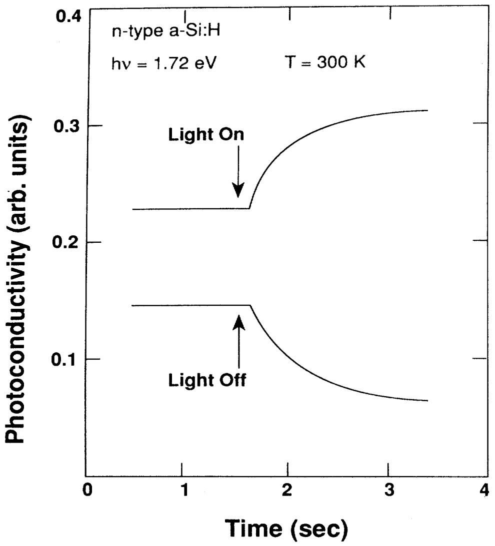

FIG. 3. Rise and decay time traces of the dc photoconductivity for an n-type a-Si:H film at 300 K illuminated with 1.72-eV light with a generation rate of 10^{16} cm^{-3} sec^{-1}.

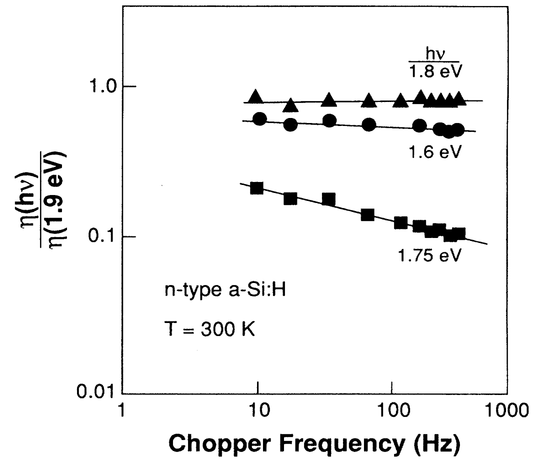

FIG. 4. Log-log plot of the normalized nonradiative efficiency η against chopper frequency for illumination with 1.8-, 1.75-, and 1.6-eV light for an n-type a-Si:H film at room temperature.

hence η will be a sensitive function of the excitation kinetics, that is of the incident light intensity (through the variation of τ with G) and chopper frequency. For sub- and above-band-gap illumination, E_{therm} is comparable to fE_{rec}; a significant fraction of the heat detected by the PVDF polymer will therefore be independent of G and ω. The excitation dependence of f will be most readily observed for near-band-gap illumination, for which the energy detected due to free-carrier thermalization is minimal.

It is difficult to directly verify the generation rate dependence of τ in Eq. (3). The light intensity is not easily varied, since we are presently operating the light source at its maximum setting and decreasing the light intensity would further reduce an already small signal. Preliminary measurements of the generation rate dependence of η do find that at the minimum f does increase with G in reasonable agreement with the above model. In contrast, increasing the chopper frequency should deepen the minimum in η by reducing the proportion of heat detected due to recombination. Figure 4 shows a log-log plot of η against ω for three different incident photon energies, where the η values have been normalized by their values at 1.9 eV. For above- and below-band-gap illumination η is independent of chopper frequency, consistent with the proposal that a significant fraction of the heat detected by the PVDF polymer for these photon energies results from free-carrier thermalization. The depth of the minimum in η at 1.75 eV does indeed increase as ω is raised from 10 to 400 Hz, with an approximate power-law dependence on frequency, that is, $\eta \propto \omega^{-\zeta}$ where $\zeta \sim 0.25$. While the results of Fig. 4 are in qualitative agreement with our model, the power-law exponent is lower than expected from Eq. (3). A complete description of the frequency and excitation dependence of η will be published separately.[11]

If the observed minimum in η results from τ being longer than ω^{-1}, then other bolometric techniques such as PDS should also observe a decrease in the amount of heat detected for near-band-gap illumination. No "missing heat" has been reported for PDS data, even though typically $\omega \sim 13$ Hz in PDS measurements as well.[10] One possible explanation for this discrepancy may be the variation of τ with generation rate. If the light intensity used in PDS experiments is only one order of magnitude larger than that used here, then τ would be <0.1 sec (Refs. 14 and 15) (that is, $\tau < \omega^{-1}$) and all of the heat released by nonradiative recombination processes would be detected. In that case there would be no minimum in a corresponding plot of η against $h\nu$. Comparisons of PDS and PPES spectra as a function of light intensity would be an important test of the proposed model for the minimum in the nonradiative efficiency.

In summary, we have argued that the spectral dependence of the nonradiative efficiency of a-Si:H measured using photopyroelectric spectroscopy reflects the variation of the heat released by free-carrier thermalization as the incident photon energy is decreased. The thermalization energy is independent of chopper frequency but depends on the excitation wavelength, while the amount of nonradiative energy detected at the low incident light intensities used here is independent of photon energy, but does depend on the chopper frequency. Measurements of the nonradiative efficiency as a function of the chopper frequency, along with model calculations, are consistent with the above proposal.

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[9] While Eq. (1) deals only with the magnitudes of the thermal and nonthermal contact voltages, in fact these signals have both a magnitude and a phase. The heat generated in the amorphous semiconductor must diffuse through the thin film in order to be detected by the PVDF polymer; the resulting thermal lag will be reflected in a phase difference between V_t and V_{nt}. This phase change as the incident photon energy is reduced would explain a decrease in the amount of heat detected, though of course not the subsequent rise for sub-band-gap illumination. Direct measurements of the phase difference between V_t and V_{nt} find that the phase change is very minor and gradual in the region of 1.8 to 1.7 eV where the nonradiative efficiency changes by up to two orders of magnitude, which justifies using only the magnitudes of V_t and V_{nt} in Eq. (1). A complete description of the phase difference measurements will be published separately (see Ref. 11).

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[18] Strictly speaking, the time τ inferred from Fig. 3 is the photoconductivity response time, which at room temperature is the relevant time scale for determining whether all of the heat released is detected within a time set by the inverse of the chopper frequency.