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Model for the temperature dependence of photoluminescence in a-Si:H and related materials

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We develop a model which interprets the temperature dependence of the intensity of the photoluminescence peak near 1.4 eV observed in a-Si:H and related materials in terms of a distribution of activation energies for nonradiative recombination. We find that the width and energy position of the maximum of the distribution correlates well with the spectral width of the luminescence and the activation energy for the drift mobility of photoproduced carriers. This correlation holds for sputtered and glow discharge a-Si:H, and a-Si:O, a-Si:H:O, a-Si:H:F, and $a\text{-Si}_{1-x}\text{Ge}_x$:H. Consistent differences between the distributions for sputtered and glow discharge a-Si:H, and between a-Si:H and a-Si:H:O are obtained. We conclude that changes in the luminescence spectral width and temperature-quenching behavior among these materials reflect changes in the distribution of localized states below the conduction-band edge.

I. INTRODUCTION

The temperature dependence of the intensity of the photoluminescence peak near 1.4 eV in a-Si:H has been employed in an attempt to obtain information about the electronic structure of glow discharge (GD) and sputtered thin films.[1] It is plausible to suggest that the photoluminescence intensity I as a function of temperature T in the low intensity limit of purely geminate recombination follows the expression

$$I(T) \propto \frac{p_r}{p_r + p_0 \exp(-\epsilon/kT)} , \qquad (1)$$

where p_r is the (temperature-independent) probability of radiative recombination, ϵ is an activation energy for nonradiative recombination (assumed to be the same for all radiative centers), and p_0 is an attempt probability.[2] Equation (1) appears to describe observed data with two different values of ϵ, $\epsilon_1 \sim 0.05$ eV for the range $60 < T < 125$ K and $\epsilon_2 \sim 0.2$ eV for $T > 150$ K.[3–5] It has been suggested that ϵ_1 and ϵ_2 represent the average energy necessary to dissociate thermalizing and thermalized pairs, respectively.[5]

Another approach is to assume different activation energies for different radiative centers. We define a distribution, $g(\epsilon)$, representing the number of radiative centers with an activation energy between ϵ and $\epsilon + d\epsilon$ that are occupied in the limit of low T,

$$I(T) \propto \int_0^\infty d\epsilon\, g(\epsilon) \left[1 + \frac{p_0}{p_r} \exp\left[\frac{-\epsilon}{kT}\right] \right]^{-1} . \qquad (2)$$

In our case, it is assumed that nonradiative recombination occurs when an electron is activated from the radiative center to the conduction-band edge, an energy ϵ above it (see Ref. 2).

Kastner[6] has suggested that the functional form of $I(T)$ often observed in chalcogenide systems, $I(T) \propto e^{-T/T_0}$, is consistent with Eq. (2) using $g(\epsilon) \propto \exp(-\epsilon/\epsilon_0)$. We shall obtain, in a similar manner, the corresponding $g(\epsilon)$ for a-Si:H and related materials using the functional form

$$I(T) \propto [1 + A \exp(T/T_0)]^{-1} \qquad (3)$$

observed for sputtered and GD a-Si:H.[7] We shall conclude that the resulting $g(\epsilon)$ is consistent with the activation energy for trap-limited drift mobility and is also consistent with measurements of the photoluminescence spectral width. We shall also draw upon these consistencies to infer the shape of the distribution of localized states in the conduction-band tails of a-Si:H, a-Si:H:O, a-Si:H:F, and $a\text{-Si}_{1-x}\text{Ge}_x$:H prepared by different techniques.

II. EXPERIMENTAL

The preparation of most of the samples used in this study has been described elsewhere. Samples of a-Si:H were prepared by sputtering[8] and rf[9] or dc[10] anode or cathode plasma decomposition of

SiH_4. Samples of a-$Si_{1-x}Ge_x$:H were prepared by sputtering Si in an atmosphere of Ar, H, and GeH_4, or by dc cathode GD using a mixture of SiH_4 and GeH_4.[10] Samples of a-Si:H:F were prepared by dc cathode GD using SiF_4 and H_2 or SiH_4 and F_2.[10] a-Si:O was prepared by sputtering.[11] The details of photoluminescence measurements are also described elsewhere.[5,7]

III. RESULTS AND DISCUSSION

We have verified that Eq. (3) is applicable in the regime of geminate recombination, that is, when the excitation intensity is given by

$$I_{\rm PL} \propto I_{\rm exc}^{1+\alpha}, \quad |\alpha| \leq 0.03$$

at all temperatures of measurement, where $I_{\rm PL}$ and $I_{\rm exc}$ are the luminescence and excitation intensities, respectively. Since Eq. (3) accurately represents the temperature dependence of the photoluminescence intensity in samples of a-Si:H for which recombination is geminate, we can equate Eq. (2) and Eq. (3). In addition we shall make a simplifying assumption and replace p_0/p_r by a suitable average constant, B:

$$\left[1+A\exp\left[\frac{T}{T_0}\right]\right]^{-1} \propto \int_0^\infty d\epsilon\, g(\epsilon)\left[1+B\exp\left[\frac{-\epsilon}{kT}\right]\right]^{-1} . \quad (4)$$

Thus the factor on the right is an approximate step function of width kT. If we take the first term of the Sommerfeld expansion of the right side of Eq. (4) and differentiate both sides with respect to T, we obtain

$$g(\epsilon) \propto \frac{e^{-\epsilon/\epsilon_0}}{(e^{-\epsilon/\epsilon_0}+A)^2} \quad (5a)$$

with

$$\epsilon_0 \equiv kT_0 \ln B .$$

This distribution exhibits a maximum at an energy given by

$$\epsilon_{\rm max} = -kT_0 \ln A \ln B \quad (5b)$$

and a full width at half maximum (FWHM) of

$$\Delta\epsilon = 3.5kT_0 \ln B . \quad (5c)$$

Both $\epsilon_{\rm max}$ and $\Delta\epsilon$ are proportional to T_0, the temperature which defines the slope of the high-temperature asymptote in Eq. (4).

Intuitively we might expect that the peak in the distribution of activation energies, $\epsilon_{\rm max}$, should approximately equal the activation energy of the drift mobility. We have typically found values of ~ 0.2 eV for sputtered samples prepared under a wide range of deposition conditions from experiments on both photoconductivity and time of flight of injected pulses.[12] Using this value and the experimental parameters $A \sim 0.01$ and $T_0 = 25$ K, we obtain $\ln B = 21$. From this we obtain $\epsilon_0 = 0.04$ eV and $\Delta\epsilon = 0.15$ eV. We propose that in the large-ϵ tail, $g(\epsilon)$ is proportional to the density of states below the conduction-band edge, $N_c(\epsilon)$. Thus, $N_c(\epsilon) \propto \exp(-\epsilon/0.04\ {\rm eV})$, a plausible result for a band tail. The above value of $\Delta\epsilon = 0.15$ eV, interpreted as the contribution to the spectral width of the photoluminescence from states in the conduction-band tail, compares with the spectral FWHM of 0.32 eV observed in sputtered a-Si:H prepared under a wide range of deposition conditions (see Ref. 1, Paul and Anderson). In the low-ϵ tail we find that $g(\epsilon) \propto \exp(\epsilon/\epsilon_0)$. Since the shape of this tail is determined by the shape of $I(T)$ near the low-T saturation, we place little confidence in the accuracy of our derivation at low ϵ. This will not influence any of the conclusions of this study. Independent of the occupancy factors for the localized states at low ϵ, we expect that $g(\epsilon)$ must *decrease* with decreasing ϵ as ϵ approaches the lowest-lying conducting levels.

Next we shall examine a larger group of samples

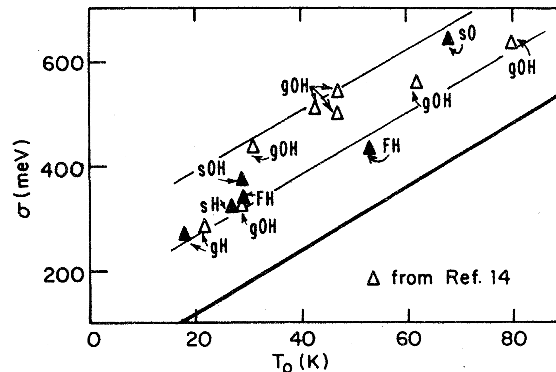

FIG. 1. Spectral width σ of the photoluminescence peak plotted vs T_0 obtained from the temperature dependence of the luminescence intensity for several samples of a-Si using combinations of various compensators H, F, and O. Data from Ref. 14 are also included. Bold solid line indicates result expected from Eq. (5c) assuming $\sigma = \Delta\epsilon$. Key: gOH=GD a-Si:O:H, FH=GD a-Si:H:F, sH=rf sputtered a-Si:H, gH=GD a-Si:H, sO=sputtered a-SiO_x, sOH=sputtered a-Si:H:O.

of a-Si:H and related materials to test the trends suggested by Eqs. (5b) and (5c). The values of T_0 presented for different samples are obtained by the technique outlined in Ref. 7.[13] Figures 1 and 2 display the FWHM, σ, of the luminescence spectrum of a given sample at 77 K plotted against the value of T_0 obtained from the temperature dependence of the photoluminescence measured on the same sample. Figure 1 exhibits results for a-Si using combinations of various compensators H, F, and O. Extensive data of Street and Knights for a-Si:O:H are also included.[14] Figure 2 exhibits comparable results on a finer scale for a-Si:H and a-Si$_{1-x}$Ge$_x$:H prepared by different techniques. Thus the trends in Figs.1 and 2 indicate that the FWHM of the photoluminescence peak includes a contribution which decreases monotonically as the density-of-states distribution below the conduction-band edge inferred from T_0 becomes steeper. This implies that the FWHM may be used as a relative indicator of this state-density distribution. We also include in Figs. 1 and 2 the result expected from Eq. (5c) assuming that $\ln B$ is sample independent and that the only contribution to the spectral width arises from the width of $g(\epsilon)$. Obviously there must also be a significant contribution to the spectral width due to the spread in energies of the holes. Since these contributions are not additive, the fact that, on the wider scale of Fig. 1, the hole contribution can be represented by an approximately constant additive factor, 0.15 eV, does not imply that this contribution is independent of sample.

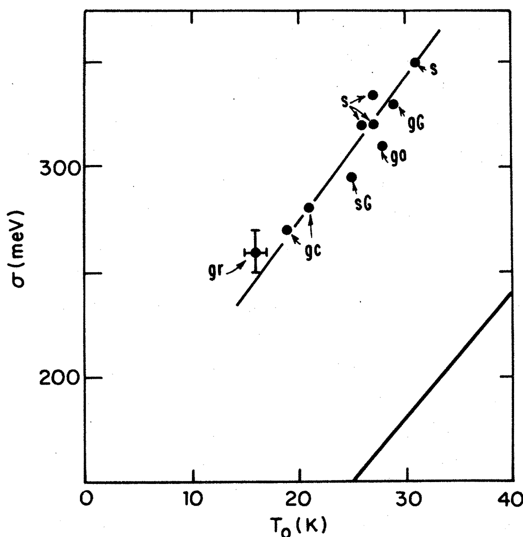

FIG. 2. Spectral width of the luminescence peak vs T_0 for several samples of a-Si:H and a-Si$_{1-x}$Ge$_x$:H. Solid line at lower right indicates result expected from Eq. (5c) assuming $\sigma=\Delta\epsilon$. Key: s =rf sputtered a-Si:H, sG=sputtered a-Si$_{1-x}$Ge$_x$:H, gG=GD a-Si$_{1-x}$Ge$_x$:H, and gc =dc cathode GD a-Si:H, ga =dc anode GD a-Si:H, gr =rf GD a-Si:H.

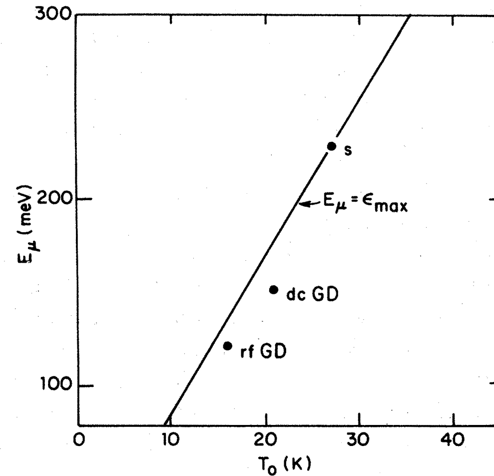

FIG. 3. Value of T_0 vs E_μ for three samples of a-Si:H prepared by rf GD, dc cathode GD and rf sputtering. Solid line indicates result expected from Eq. (5b).

In Fig. 3 we exhibit additional confirmatory evidence suggesting that T_0 provides a measure of the slope of the density-of-states distribution below the conduction-band edge. Here we plot T_0 for a small group of samples versus E_μ, the activation energy for electron drift mobility obtained from photoconductivity measurements as described elsewhere (see Ref. 12, Moddel *et al.*). Also included in Fig. 3 is the expected value of E_μ from Eq. (5b) assuming $\epsilon_{\max}=E_\mu$ and that $\ln A \ln B$ is independent of sample. The quantity A describes the approach to saturation in $I(T)$ at low temperature, and although there exist sample to sample variations in A, no regular trends are observed. The reasonable fit to the data again implies internal consistency and suggests that it is at least appropriate to suppose $\epsilon_{\max}$ proportional to E_μ and perhaps even appropriate to equate the two quantities. The deviation of the plasma-deposited samples from the behavior predicted by Eq. (5b) may be a result of the observation that the measured T_0 value for these samples is an upper limit to the actual value due to a nongeminate component. (See Ref. 13.)

We shall now briefly discuss Figs. 1 and 2 in terms of the electronic state distribution of a-Si:H and related materials prepared by different methods. More detailed discussions are found else-

where.[11,12] Figure 1 suggests that using O as a compensator in sputtered a-Si instead of H results in much greater band-tail broadening. This is also evident from an obviously shallower absorption edge for this material.[11] We believe that the increased spectral width of the photoluminescence of the a-Si:O:H samples as reported by Street and Knights can be explained in this way rather than by invoking changes in electron-phonon coupling with O content.[14] Similar band-tail broadening has been observed with the incorporation of F in dc cathodic GD a-Si:H. It is possible that the changes in spectral width and T_0 arise from indirect effects of F caused by changes in the chemistry of plasma deposition due to SiF_4 involvement.

Next we shall turn our attention to the finer-scale trends of Fig. 2. Sputtered a-Si:H samples prepared under a wide range of conditions that result in low-temperature luminescence quantum efficiencies varying from 0.1% to 50%, with H contents from 5 at.% to 25 at.% and Fermi-level density-of-state magnitudes[15] from 10^{18} to 10^{16} $eV^{-1}cm^{-3}$, exhibit only $\sim 10\%$ variations in T_0 and spectral width. Clearly hydrogen content does not strongly influence the distribution of states in the conduction-band tail. Incorporation of Ge into a-Si:H results in ambiguous behavior depending on the preparation technique. We have found that incorporating Ge into sputtered a-Si:H by adding GeH_4 to Ar and H_2 in the plasma results in a narrower distribution of tail states than in sputtered

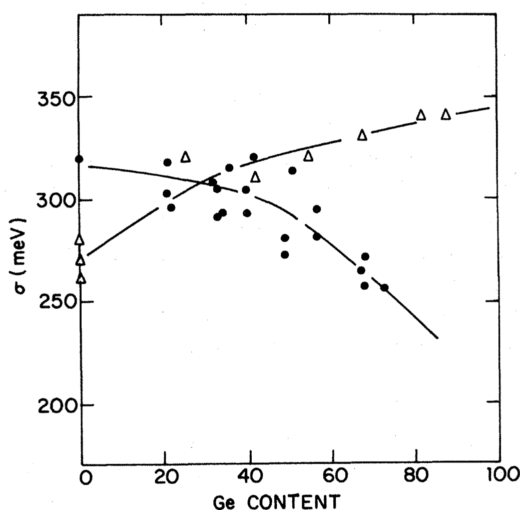

FIG. 4. Spectral width of the luminescence peak as a function of atomic percentage Ge content for samples of sputtered a-$Si_{1-x}Ge_x$:H (closed circles) and dc cathode GD a-$Si_{1-x}Ge_x$:H (open triangles).

a-Si:H, whereas incorporating the same amount of Ge into a glow-discharge sample of a-Si:H by adding GeH_4 to SiH_4 in the glow-discharge plasma results in a broader distribution of tail states than in glow discharge a-Si:H. To illustrate this, in Fig. 4 we show the spectral width of the photoluminescence peak as a function of Ge content for a group of sputtered and GD a-$Si_{1-x}Ge_x$:H alloys. Obviously the resulting tail-state distribution is not determined by the alloy composition of the sample but by structural and chemical differences that are presumably linked to the physics and chemistry of the plasma and its interaction with the growing film.

More noticeable in Fig. 2 is the difference between samples of a-Si:H prepared by GD (both rf and dc cathode samples) and by sputtering. Several aspects of this difference are discussed elsewhere.[12] The tail-state distribution for the sputtered samples seems to be consistently broader. We note that dc anodic GD a-Si:H exhibits a tail-state distribution similar to the sputtered samples, although the low-temperature luminescence quantum efficiency is comparable to the dc cathodic samples. This may suggest that sputtered samples as well as dc anodic GD samples during growth may be subjected to electron bombardment from the plasma and result in samples with broader tail-state distributions.[16] We believe, however, that the actual differences may be caused by a rather complex interplay of plasma physical mechanisms and leave a detailed discussion with the necessary correlation with ir and structural properties to future research.

Before concluding, we shall make a brief comment concerning Fig. 2 and its relation to solar-cell devices fabricated from the different types of material depicted there. The solar-cell efficiency depends critically on the lifetimes for both electrons and holes, which, in turn, are sensitive to the *overall* distribution of recombination centers and trapping states. Thus, everything else being equal, we might expect the quality of device material to scale as the magnitude of the low-temperature photoluminescence efficiency of the material, since this magnitude at 77 K is inversely related to the magnitude of the density of states near midgap.[17] In fact, from comparison of the PL efficiencies and device performances of the material discussed here and material kindly given us for measurement by RCA Laboratories,[18] it is clear that there is not a one-to-one correlation. It is our belief that a low density of (filled) states in and above the valence-

band tail is essential if rapid trapping of photoexcited holes and consequent poor photovoltaic performance are to be avoided.

The present data have some bearing on this. Thus, we suggest that, for a given low-temperature luminescence efficiency, solar-cell devices fabricated from material at the lower left of the plot in Fig. 2 should be more efficient. The argument is that the lower T_0 of these samples denotes fewer disorder-induced intrinsic tail states, and fewer defect or microstructure-related extrinsic localized states of the same energy. Furthermore, such conditions imply that the state density in the valence-band tail and in the lower half of the band gap will also be low, and it is just such a low overall density of states in the gap which can give solar-cell devices of long electron and hole lifetimes.

We are presently attempting to establish a more direct connection between T_0 and solar-cell efficiencies through measurement, on the samples studied here, of parameters more directly related to device performance. An example of such a parameter is the surface photovoltage.[19]

In conclusion we have developed a model which employs the quenching of the photoluminescence band at 1.4 eV in deriving a distribution of activation energies for nonradiative recombination in *a*-Si:H prepared by glow discharge and sputtering, and in *a*-Si:O, *a*-Si:H:O, *a*-Si:H:F, and *a*-$Si_{1-x}Ge_x$:H. Consistent differences between the distributions for sputtered and GD *a*-Si:H are observed, and regular trends are obtained with O incorporation. The derived distributions for *a*-$Si_{1-x}Ge_x$:H and *a*-Si:H:F depend sensitively on the preparation technique possibly due to extrinsic effects such as microstructure, rather than intrinsic disorder. For these samples, the width and maximum in energy of this distribution is consistent with independent measurements of the spectral width of the photoluminescence and the photoconductivity drift-mobility activation energy, respectively. We have suggested that the width of the distribution of activation energies is related to the distribution of localized tail states that are intimately involved in phototransport mechanisms. Finally, we have discussed possible inferences from these results concerning the efficiency of solar cells.

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[2]See, for example, R. A. Street, Adv. Phys. 25, 397 (1976). Strictly, Eq. (1) is valid when the activation process occurs between two discrete levels separated by an energy ϵ. It is more realistic, however, to suggest that radiative recombination is quenched when one carrier is excited from a localized radiative center into the continuum of states above the band edge. Under these circumstances, assuming a constant-matrix element for all transitions and a constant density of states in the continuum, the activation term in the denominator of Eq. (1) should be written $CkT\exp(-\epsilon/kT)$, where C is $\sim 10^{13}-10^{14}\ \mathrm{eV^{-1}s^{-1}}$. We shall use the conventional form since the results we derive are not sensitive to the presence of the kT factor.

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[13]Measurement of T_0 using high excitation intensity data may introduce minor errors of 3 K maximum for most samples and thus are used when low-intensity data are not available. One group of a-Si:H samples, however, consisting of those prepared by rf and dc GD exhibits significant nongeminate recombination at the lowest excitation intensities of measurement. For these samples, the value of T_0 is obtained from data measured at the lowest possible intensity, and even so this represents an upper limit of the actual value.

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[18]We thank J. Dresner of the RCA Corporation for kindly supplying these samples.

[19]J. Dresner, D. J. Szostak, and B. Goldstein in Ref. 12, p. 312.