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Evidence for potential fluctuations in compensated amorphous silicon

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Measurements of the electron and hole drift mobilities and the optical-absorption edge in compensated hydrogenated amorphous silicon are reported. The mobilities of both carriers decrease with increasing doping and converge to similar values for gas-phase doping levels greater than one part per thousand. The mobility and optical-absorption data are not consistent with disorder-induced band-tail broadening, but agree with the predictions of a model of long-range potential fluctuations originating from charged donor and acceptor states.

I. INTRODUCTION

Electron and hole transport in hydrogenated amorphous silicon (*a*-Si:H) involves multiple trapping in localized band-tail states.[1] The drift mobility therefore reflects the band-edge density-of-states distribution. Undoped *a*-Si:H is modeled by approximately exponential band tails, with characteristic slopes kT_C and kT_V for the conduction and valence bands, respectively. Such band tails give a dispersive drift mobility (μ_{DE} for electrons and μ_{DH} for holes) at temperatures below T_C or T_V, with the time dependence

$$\mu_{DE,H} \sim \mu_0 t^{\alpha-1}, \quad \alpha = T/T_{C,V} . \tag{1}$$

Confirmation of at least one exponential band tail in undoped *a*-Si:H is obtained from measurements of the optical-absorption coefficient, which also depends exponentially on energy. Analysis of the hole mobility, using the multiple trapping model, gives roughly the same characteristic slope as the absorption edge,[2] and both are identified with the shape of valence-band-tail density-of-states distribution.

The electrical transport is sensitive to the doping concentration in *a*-Si:H. The minority-carrier lifetime is decreased by two to three orders of magnitude in material doped by only a few ppm, which is caused by the introduction of deep traps by charged dangling-bond defects.[3] The majority-carrier drift mobility decreases slightly with doping as a result of an apparent shift of the mobility edge, which was tentatively attributed to potential fluctuations.[4] The drift mobility of compensated *a*-Si:H is much more sensitive to doping than singly doped material, decreasing by several orders of magnitude.[5-7] Allen, LeComber, and Spear interpreted the low mobility as hopping in donor levels, but reported a second trap-controlled mechanism.[5] Marshall, Street, and Thompson explained the rapid drop in μ_{DE} and μ_{DH}, and their increased activation energy, in terms of a broadening in energy of the band-tail states, possibly due to boron-phosphorus complexes.[6] Recent measurements by Goldie, Spear, and Liu reproduce the low activation energy found by Allen, LeComber, and Spear, and show that the different results of Marshall, Street, and Thompson are attributable to a different deposition condition.[7] Goldie, Spear, and Liu propose that the decrease in mobility is due to potential fluctuations.

Long-range potential fluctuations in *a*-Si:H have also been invoked to explain the difference between the thermopower and conductivity activation energies, and several other electronic properties.[8-10] Coulombic potential fluctuations arise from random electrical charges which are not fully screened by free carriers. The statistical deviation in the average charge within a volume of material is the origin of the spatially varying potential. Other possible sources of potential fluctuations are structural inhomogeneities such as voids, clustered hydrogen bonds, etc. In singly doped or compensated material, most of the donor and acceptor states are ionized and therefore charged.[11] These random charges therefore add to any potential fluctuations that are present in undoped *a*-Si:H. Singly doped material has a low doping efficiency and also a high carrier concentration which tends to screen the fluctuations. Compensated *a*-Si:H has a larger concentration of ionized donors and acceptors because the doping efficiency is believed to be high, and reduced screening because the carrier concentration is very low. The compensated material is therefore anticipated to have particularly large potential fluctuations.

This paper investigates the presence of potential fluctuations in compensated hydrogenated amorphous silicon, by comparing data on the mobility of both electrons and holes with the optical-absorption edge. We report a drop in electron mobility of six orders of magnitude and in hole mobility of four orders of magnitude over a range of gas-phase doping levels (of both boron and phosphorus) from 1 to 10 000 ppm. Furthermore, at doping levels of greater than 1000 ppm the mobilities of the two carriers become similar to within one order of magnitude. Measurements of the optical-absorption edge show almost no change at low compensation, but extensive broadening is observed in the heavily compensated material.

The observed reduction in mobility in compensated material is analyzed within the context of two different models. The first is that of spatially invariant band-edge broadening in which the boron and phosphorus dopants contribute to the formation of additional localized states which broaden the energy distribution of the band tail. A

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reduction of mobility is expected as a consequence of the carriers interacting with the broader distribution of the band-edge traps, according to the multiple trapping model. A second possible explanation is that the charged donor and acceptor atoms present in compensated material give rise to long-range potential fluctuations throughout the material. In this case, a reduction in mobility is expected as the carriers experience larger potential wells with increased compensation. The comparison of transport and optical data is used to distinguish the two models.

II. MEASUREMENTS

The compensated a-Si:H samples were made by plasma deposition of SiH_4 using equal volume concentrations of B_2H_6 and PH_3. Samples were made having the following concentration ratios of B_2H_6 and PH_3 to SiH_4 in the deposition gas: 10^{-6}, 10^{-5}, 10^{-4}, 3×10^{-4}, 10^{-3}, 3×10^{-3}, 10^{-2}. The doping levels used throughout this paper refer to these concentrations. The solid-phase concentration was not measured, but is known from previous work to be 3–5 times larger than the gas-phase concentration.[12] The samples used had nominal thickness of 1 and 5 μm, but uncontrolled variations in growth rate resulted in some samples measuring up to 10 μm thick. The actual thickness of each sample run was determined by viewing the cross section in a scanning electron microscope. Details of the sample deposition,[13] time-of-flight (TOF) measurement technique,[14] and photothermal deflection spectroscopy (PDS) measurement technique,[15] are provided elsewhere.

A. Electron and hole drift mobility

Electron and hole drift mobilities were obtained using TOF transient photocurrent measurements over a range of applied fields. The variation of charge collection with electric field was recorded to ensure that the transit time data were taken in a region of full charge collection. The transit times were identified from the change in slope of the time dependence of the current, and were confirmed by the dependence of the transit time on applied field. Figure 1 shows typical examples of the dispersive transients at different applied electric fields together with the identified transit time. Examples of the hole transients are shown in Fig. 2 for different levels of compensation, illustrating the large range in transit times.

The variation in electron and hole mobility with doping is shown in Fig. 3. The electron mobility drops from about 1 $cm^2/V\,s$ in undoped a-Si:H to 3×10^{-6} $cm^2/V\,s$ at high doping levels, with the largest change occurring at doping levels between 10^{-4} and 10^{-3}. Although the electron and hole mobilities differ by two orders of magnitude in undoped a-Si:H, they approach similar values in heavily compensated material having a gas-phase dopant concentration of 10^{-3} or greater. This behavior suggests that the mechanism suppressing the mobility affects both signs of carrier in a similar manner.

The temperature dependence of μ_{DE} and μ_{DH} was measured on some samples. Samples with the lower mobilities gave a higher activation energy as expected from multiple trapping, with values of about 0.6 eV at the highest doping levels. The results are consistent with those of Marshall, Street, and Thompson, but we do not find the reduced activation energy in heavily doped material reported in Refs. 5 and 7.

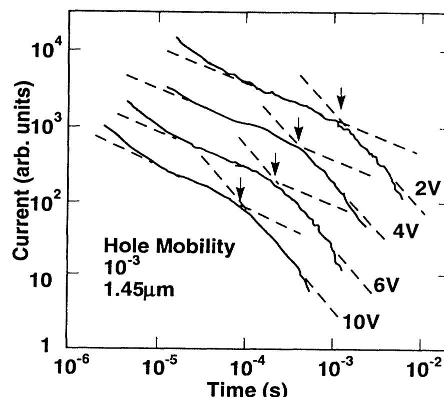

FIG. 1. Examples of the hole photocurrent transients in compensated a-Si:H at a doping level of 10^{-3}, showing the variation of the transit time with applied electric field.

B. Optical absorption

The absorption edge was measured using optical transmission for energies above 1.6 eV and photothermal deflection spectroscopy (PDS) for energies between 0.7 and 2.0 eV. The optical-absorption edges for several different doping levels are shown in Fig. 4, which plots the absorption coefficients α_A against energy. The exponential region of the absorption edge at low compensation is almost identical to that for undoped material, showing very little change until the dopant concentration exceeds 10^{-4}. A large shift in the absorption edge is observed in samples having dopant concentrations greater

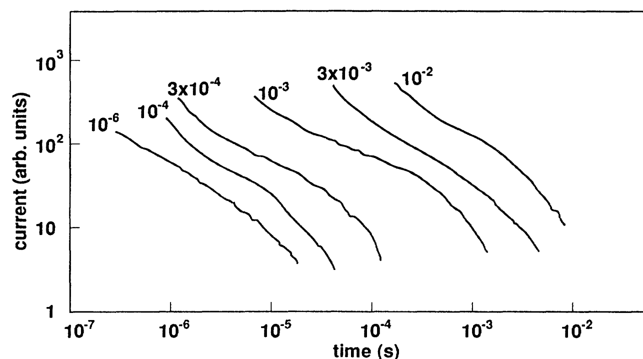

FIG. 2. Examples of photocurrent transients obtained during TOF measurement of hole mobility in compensated a-Si:H. Each curve corresponds to a different gas-phase dopant concentration as indicated. Sample thicknesses range from 1 to 4 μm.

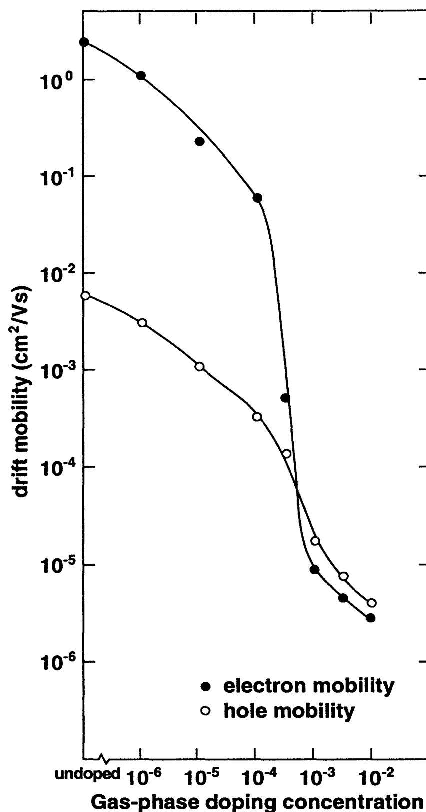

FIG. 3. Dependence of electron and hole drift mobilities on the compensation level in a-Si:H. Mobilities were measured at room temperature using TOF techniques. Fields applied during TOF ranged between 2×10^3 and 5×10^4 V/cm. Shown here is an average mobility for each compensation level.

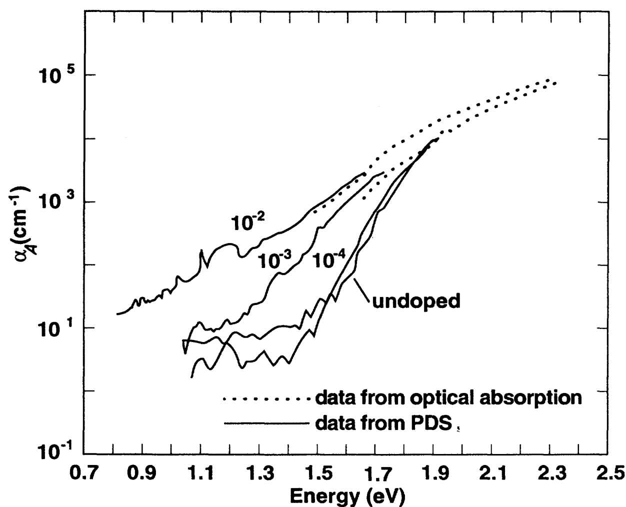

FIG. 4. The optical-absorption coefficient α_A, as a function of photon energy for various compensated a-Si:H samples. The gas-phase dopant concentration is indicated on each curve. Note that the slope of the absorption edge is virtually unchanged for doping levels up to 10^{-4}, but shows large changes for higher compensation.

than 10^{-4}. The broadening of the absorption edge is expressed in terms of the slope of the exponential edge E_0,

$$\alpha_A = \alpha_0 \exp(E/E_0) , \tag{2}$$

where α_A is the absorption coefficient. The value of E_0 reaches 130 meV for compensation of 10^{-2} but remains around 55 meV for compensation up to and including 10^{-4}.

C. Defect density and conductivity

The density of paramagnetic states in the compensated samples was investigated using electron-spin resonance. Very few spins were detected, indicating a maximum neutral dangling-bond density of about 10^{16} cm^{-3}, consistent with previous measurements.[12] The low defect density is also confirmed by charge collection measurements in the TOF experiments which were in the range 10^{-7}–10^{-8} cm^2/V, corresponding to a low-defect density,[12] and also consistent with earlier measurements.[6]

Measurements of the dc conductivity found low values, confirming that the samples were compensated. The conductivity activation energy was about 0.6 eV at the high dopant levels.

III. DISCUSSION

The decrease in drift mobility and the related increase in activation energy is due to trapping of carriers in states with increasing binding energy. Two alterative explanations for the traps are considered here; broadening of the band-tail distribution and the presence of long-range potential fluctuations. While it is difficult to distinguish between these models from the mobility data alone, they give different predictions for the shape of the optical-absorption edge. The band-tail distribution is reflected in the absorption edge, which is expected to have the same slope as the broader of the valence and conduction bands. Long-range potentials do not broaden the absorption edge because the optical transition is spatially localized. The absorption is modified only when the period of the fluctuations is comparable with the wave-function extent of the electron and hole. These two models are considered in detail below.

A. Model of band-tail broadening

In this model the decrease in carrier mobility is a result of trapping by a broadened distribution of band-tail states in the compensated material, which arise either from dopants or disorder. Increased compensation is assumed to introduce deeper traps, which progressively reduce the carrier mobility. In the multiple trapping model of dispersive transport, the mobility is related to the slope of the exponential band tail.[1] The value of kT_V derived from hole mobility data should agree with the slope of the band edge E_0, observed directly in optical-absorption measurements. Figure 5 plots the slope of the band tail against increasing dopant concentration. Curve (a) shows the change in the band-edge slope as measured directly from the slope of the optical-absorption tail. Curve (b) is

calculated from the measured hole mobility using the relationship derived by Tiedje and Rose,[1]

$$t_T=\frac{1}{\omega_0}\left[\frac{\omega_0}{2(1-\alpha)}\right]^{1/\alpha}\left[\frac{L}{\mu_0 E}\right]^{1/\alpha}, \tag{3}$$

where t_T is the carrier transit time, ω_0 is the attempt-to-escape rate ($\simeq 10^{12}$ s^{-1}), L is the sample thickness, E is the electric field applied during TOF measurement, μ_0 is the free-carrier mobility, and α is related to the slope of the band edge kT_V, through Eq. (1). The value use for the free-carrier mobility was 10 cm^2/V s.

The two measurements of the band-tail slope in Fig. 5 are inconsistent for the compensated samples, and suggest that the band-tail broadening model does not apply. Undoped *a*-Si:H has an absorption slope of 55 meV and a value of 45 meV from time-of-flight measurements. This difference *is* consistent with the band-tail model, because of the experimental uncertainty in both measurements, and because the absorption is slightly broader than the valence-band tail, since it is a convolution of the valence and conduction bands. The optical-absorption data show that the band-tail slope is unchanged in compensated *a*-Si:H for dopant concentrations up to 10^{-4}, but rapidly broadens at higher compensation. In contrast, the mobility data when analyzed within the model of band-edge broadening suggests that the valence-band tail becomes broader with increasing compensation, even at low doping levels when there is no change in absorption.

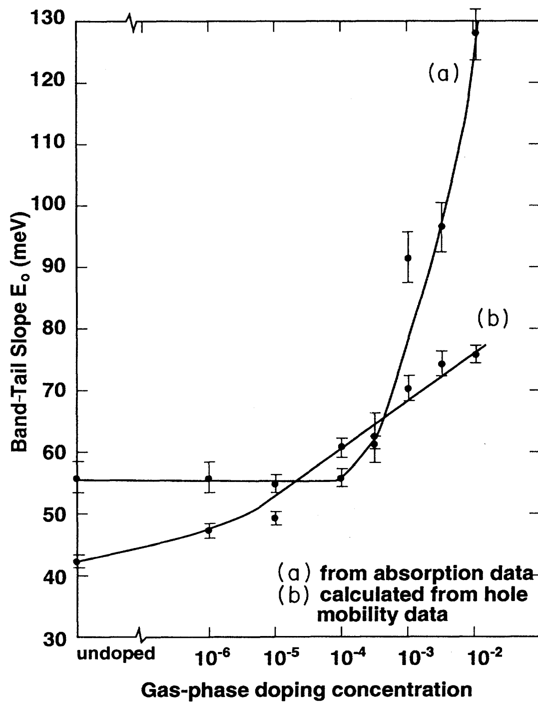

FIG. 5. Dependence of the optical-absorption edge slope E_0, on compensation level in *a*-Si:H. Data for the curve marked (a) was taken directly from optical-absorption measurements. Points on the curve marked (b) were calculated using the formula given in text, from measured hole mobilities. Both sets of data would be expected to follow the form of curve (b) if band-edge broadening occurs with compensation.

A second discrepancy is seen when examining the defect density from the perspective of a band-edge broadening model. Stutzmann has observed a correlation between the broadening of an exponential band tail and the density of dangling-bond defects in undoped *a*-Si:H,[16] which is explained by defect equilibration.[17] If the decrease in mobility in compensated material is to be explained within the model of band-tail broadening, then an increase in defect density with doping should also be observed. At the highest doping levels, a defect density of $>10^{18}$ cm^{-3} is expected from the Stutzmann data, compared with measured values of about 10^{16} cm^{-3}.

Thus, the data are not consistent with a model that explains the decrease in mobility in compensated *a*-Si:H as a consequence of spatially invariant band-tail broadening. The concept of long-range potential fluctuations is a more appropriate model under which to examine this data.

B. Model of potential fluctuations

The dopant atoms in compensated material give rise to local charge centers because both the donors and acceptors are ionized. When the compensation level is high enough, the number of free carriers available in the material is not sufficient for complete screening, and the random charge centers act as sources of long-range potential fluctuations. The reduction in mobility with compensation is explained by the confinement of the carriers in the potential wells of the fluctuations, as indicated in Fig. 6. Raising the doping concentrations increases the voltage swing of the fluctuations, and reduces their average separation. Eventually the potential fluctuations reach nearly half the band-gap energy and can increase no more, limit-

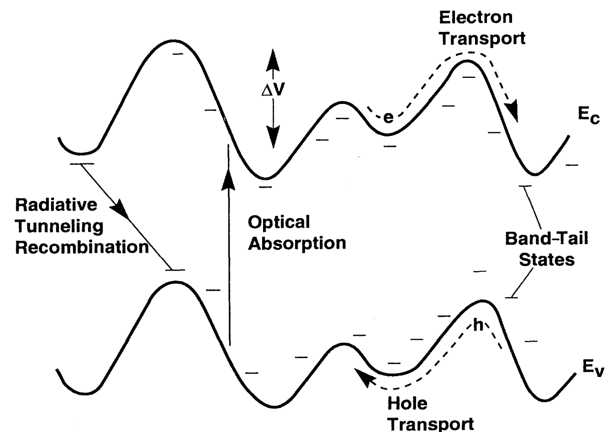

FIG. 6. The model of long-range potential fluctuations, illustrating the magnitude of the fluctuations ΔV, the electron and hole transport paths, the vertical optical-absorption transition, and the tunneling radiative recombination transition.

ing the decrease in mobility, which changes little at doping concentrations greater than 10^{-3}. The electron and hole mobilities converge to similar values because the potential fluctuations are of sufficient strength to dominate over other trapping mechanisms and influence both electrons and holes in a similar manner. The spacing between the fluctuations decreases at high doping levels and results in a high internal field. We show that this field accounts for the broadening of the optical-absorption edge.

These qualitative arguments are supported by estimates of the electrostatic field which may be expected to arise as a result of potential fluctuations in compensated material, following the approach used by Overhof and Beyer.[9] Within a volume L^3, the statistical fluctuation in charge is given by $(NL^3)^{1/2}$, where N is the total number of ionized dopant atoms per unit volume. The potential fluctuation $\pm\Delta V$ arising due to this fluctuation in charge is given by

$$\Delta V \simeq \frac{(NL^3)^{1/2}}{4\pi\epsilon\epsilon_0 L} . \quad (4)$$

The magnitude of the fluctuations are limited by the screening length L_s, so that

$$\Delta V \simeq \frac{N^{1/2}L_s^{1/2}}{4\pi\epsilon\epsilon_0} . \quad (5)$$

Normal screening by free carriers is weak because of the low conductivity of compensated *a*-Si:H. Instead, screening occurs when the potential fluctuations are sufficiently large that the Fermi energy approaches one of the band tails and there is locally a high carrier concentration. In this situation the magnitude of the potential fluctuations changes little with doping level, having a value ΔV_{max}, approaching half the band-gap energy,

$$\Delta V_{max} = \pm\tfrac{1}{2}(E_G - \Delta E_G - \Delta E_V) \approx \pm 0.5\text{–}0.6 \text{ eV} , \quad (6)$$

where ΔE_C and ΔE_V are the energies between the Fermi energy and the mobility edges at the peak of the fluctuations, determined by the need to provide sufficient carriers to screen the fluctuations. We estimate that $\Delta E_C \simeq 0.2$ eV and $\Delta E_V \simeq 0.4$ eV, and note that these energies change little with doping because of the steep increase in the band-tail density of states. These values agree with the activation energy of the drift mobility at high doping levels.

When the fluctuations have reached their maximum voltage range, constrained by the band edges, the main doping dependence is in the spatial period of the fluctuations. The average period L_p is given from Eq. (5),

$$L_P \simeq \frac{(\Delta V_{max} 4\pi\epsilon\epsilon_0)^2}{N} . \quad (7)$$

Assigning the upper limit on the magnitude of potential fluctuations to be 0.5 eV, we calculated the period of the fluctuations L_p for each compensation level. From the period and the maximum magnitude of potential fluctuations, the average internal electric field $\Delta V_{max}/L_p$ was obtained. The results of these calculations are presented in Table I.

TABLE I. Calculations of the average fluctuation period, internal electric field, and broadening of the absorption edge, derived from Eqs. (7) and (8).

Dopant concentration	Fluctuation period L_P (Å)	Average field (V/cm)	Absorption shift (meV)
10^{-6}	1.25×10^6	40	8×10^{-3}
10^{-5}	1.25×10^5	400	8×10^{-2}
10^{-4}	1.25×10^4	4×10^3	8×10^{-1}
3×10^{-4}	4×10^3	1.2×10^4	2.4
10^{-3}	1.25×10^3	4×10^4	8
3×10^{-3}	400	1.2×10^5	24
10^{-2}	125	4×10^5	80

At low levels of compensation, the field arising from the potential fluctuations is small. The fluctuations are weak traps and the mobility is not strongly affected because the internal field is smaller than the externally applied field. At a dopant concentration of 10^{-4} the field due to potential fluctuations becomes comparable to the fields applied during the TOF measurements. At doping levels greater than 10^{-4}, the field due to potential fluctuations becomes dominant and exceeds the field applied during TOF by up to two orders of magnitude. As seen from Fig. 3, this regime correlates with the region where the electron and hole mobilities converge.

The observed behavior of the optical-absorption edge is understandable in terms of potential fluctuations. Optical absorption is a vertical transition in real space, as shown schematically in Fig. 6. Long-range potential fluctuations therefore do not broaden the absorption because the local band gap is unchanged. Thus the absence of a doping dependence of the absorption edge at low doping levels in Fig. 5 is readily understood. The rapid increase in absorption slope at high doping levels is explained by an electric-field-induced reduction of the gap through the Franz-Keldysh effect. The electric field arising from potential fluctuations tilts the band edges, as shown in Fig. 6. The average reduction in band gap is the product of the field due to potential fluctuations and the spatial extent of the electron wave function in amorphous silicon R_0,

$$\Delta E_0 \simeq \frac{R_0 \Delta V_{max}}{L_p} = \frac{N R_0}{\Delta V_{max}(4\pi\epsilon\epsilon_0)^2} . \quad (8)$$

The distribution of values of ΔE_0 due to the random fluctuations leads us to associate ΔE_0 with the broadening of the optical-absorption edge. The shift is proportional to the doping concentration, and is only significant at the highest doping levels. An estimate of the absorption edge shift is given in Table I. R_0 is taken to be on the order of 20 Å for states near the mobility edge. The change in absorption becomes significant compared to the absorption edge slope of undoped material ($\simeq 50$ meV) at doping levels of 3×10^{-4} and greater. This corresponds to the level of compensation at which the large change in the absorption edge was observed. The sudden broadening of the

optical-absorption edge for compensation concentrations greater than 10^{-4} is consistent with a model of potential fluctuations in which sufficiently high fields allow tunneling transitions of lower energy to occur.

Finally, the potential fluctuations also account for the luminescence of compensated *a*-Si:H. The luminescence peak shifts rapidly to low energy at gas-phase doping levels above 10^{-4}, but the luminescence linewidth is unchanged.[12] Low-temperature recombination in *a*-Si:H occurs by tunneling over a distance that is large compared with the localization length R_0, as illustrated in Fig. 6.[18] In the presence of potential fluctuations, we expect that the electrons and holes thermalize into low-energy fluctuations and recombine by tunneling. Thus, the energy of recombination is more affected by the fluctuations than of absorption.

IV. SUMMARY

The observed mobility, optical absorption, and defect density data for compensated material are not consistent with a model of band-edge broadening as a consequence of compensation. The data are understandable in the context of potential fluctuations in the material as a result of unscreened charge centers.

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