Dangling bonds in doped amorphous silicon: Equilibrium, relaxation, and transition energies

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The phenomenology of the dangling-bond defect in doped hydrogenated amorphous silicon (*a*-Si:H) is analyzed in a thermodynamic equilibrium framework with use of positive correlation energy and defect relaxation energies taken from previous theoretical calculations. Good agreement is obtained between theoretical predictions and the optical absorption, luminescence, and deep-level transient spectroscopy energies from the experimental literature. Because the charge and hybridization of the dangling bond in doped *a*-Si:H are known, considerable information about dangling-bond energy levels and relaxations in *a*-Si:H is obtained. The controversy over an anomaly of about 0.9 eV in the sum of *n*-type and *p*-type films' optical-absorption-peak energies is largely resolved by recognizing that the optical transitions are vertical. A small residual anomaly is taken as evidence for a small (~ 0.2 eV) electronic-level deepening caused by dopant-defect pairing or potential fluctuations. Comparison of defect optical and luminescence energies suggests Stokes shifts of 0.3 and 0.4 eV for the dangling-bond levels of *n*-type and *p*-type *a*-Si:H, respectively.

I. INTRODUCTION

The threefold-coordinated Si defect or "dangling bond" is widely assumed[1] to dominate many of the transport and spectroscopic observations of hydrogenated amorphous silicon (*a*-Si:H) properties. In spite of the attention the dangling bond has received in recent years, considerable controversy remains concerning issues ranging from the position of its electronic levels in the mobility gap to the extent of atomic-position relaxations associated with changes of its charge state. Because the equilibrium charge state and hybridization of the dangling bond in doped *a*-Si:H are known, the interpretation of experiments is easier than in undoped *a*-Si:H. Consequently, much can be learned about the dangling bond. In this paper, I use calculated defect formation energies in *a*-Si:H (Ref. 2) and a thermal equilibrium model of charged defect concentrations[3] to interpret optical, luminescence, and other experiments on doped *a*-Si:H.

For example, the theoretical framework is used to address the controversy[4,5] over optical-absorption energies in doped *a*-Si:H. Subgap optical absorptions of about 1.1 and 1.3 eV have been observed in *n*-type and *p*-type *a*-Si:H, respectively. These are widely thought to correspond to $(-/0)$ and $(0/+)$ transitions of the dangling bond, respectively. With an *a*-Si:H optical band gap of 1.7, this result implies that the $(-/0)$ transition lies well below the $(0/+)$ transition and the effective correlation energy ($U_{\rm eff}$) of the dangling bond is negative.[4] However, most workers[1] favor a positive $U_{\rm eff}$ for the dangling bond, primarily because an equilibrium electron-spin-resonance (ESR) signal attributed to the neutral dangling bond is observed for a range of Fermi energy (E_F) positions near midgap.

Several resolutions of this puzzle have been proposed. Kocka[5] proposes that the electronic levels of charged dangling bonds shift about 0.5 eV deeper in doped *a*-Si:H by pairing with ionized dopants. Bar-Yam *et al.*[3] suggest that a disorder-induced distribution of transition energies and a small value of $U_{\rm eff}$ explain the data. Finally, Balagurov *et al.*[6] suggest that polaronic shifts of 0.25–0.4 eV between different configurations of the dangling bond, vertical optical transitions, and a gap energy of 2.0 eV resolve the controversy. In this paper, I address the issue by developing a theoretical treatment of transition energies based upon thermodynamics and defect formation energies. It is shown how differences among thermodynamic, optical, and luminescence energies of dangling bonds in *a*-Si:H may arise. The experimental literature of transition energies in doped *a*-Si:H is reviewed in detail and compared with the theory.

As first suggested by Balagurov *et al.*,[6] the controversy over the optical-absorption experiments is largely resolved by recognizing that optical transitions are vertical—no atomic relaxation occurs during the absorption. I find the observed absorption energies in *n*-type and *p*-type *a*-Si:H consistent with the band gap, assuming neither large negative correlation energy[4] nor large electronic-level deepening by dopant-defect pairing.[5] However, the analysis indicates a smaller electronic-level deepening of about 0.2 eV that may or may not be specific to doped *a*-Si:H, and models are discussed.

The review of the optical-absorption and luminescence data reveals Stokes shifts of 0.3 and 0.4 eV for the dangling-bond levels of *n*-type and *p*-type *a*-Si:H, respectively. Comparison with even larger relaxations predicted by total-energy calculations[2,7] suggests these Stokes shifts are partial relaxations constrained by the lattice from going to completion on experimental time scales.

Section II is a discussion of the dangling-bond defect based upon thermal equilibrium concepts. The theory of Bar-Yam *et al.*[3] for the defect structure of disordered materials is reviewed and a graphical representation of the E_F dependence of defect energies is presented. Par-

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ticular emphasis is placed upon dangling-bond relaxation and the differences among thermodynamic, optical, and luminescence transition energies. Section III is a review of the literature on optical-absorption and luminescence experiments that probe defect transitions in the doped films. Some experimental data that indicate a positive effective correlation energy for the dangling bond are also discussed. In Sec. IV, I interpret the available data in light of theory. The transition energies and the extent of relaxation of the dangling bond in various experiments are estimated. Models of electronic-level deepening are discussed. In Sec. V, I review my conclusions.

II. THEORY

A. Defect equilibrium

Although the structure and properties of *a*-Si:H obviously depend upon the growth technique and parameters, attempts to understand defects and doping in the material have often utilized thermodynamic concepts.[8] More recently, considerable evidence has developed[9–13] that equilibrium statistics, at least within a restricted ensemble of accessible structures, is a valuable tool for understanding the structure and properties of *a*-Si:H. The recent observation that the different growth techniques that produce device-quality *a*-Si:H yield films with nearly identical properties[14] also points to the primacy of thermodynamics in determining the structure of "good" *a*-Si:H.

In 1985, Smith and Wagner[9] first suggested that there is a cooling-rate-dependent temperature T^* above which the defect structure of *a*-Si:H remains in thermal equilibrium and below which the structure at T^* is frozen in. They also emphasized the role of carrier density in determining the equilibrium defect density above T^*. Street and co-workers provided more direct evidence for[10] T^* and for[11] the importance of E_F position and carrier concentration in determining equilibrium defect density in doped *a*-Si:H. At about the same time, Bar-Yam *et al.*[3] developed a comprehensive equilibrium model for defect concentrations in disordered materials which includes the effect of E_F on defect formation energies. In the remainder of this section, I examine the experimental transition energies of the dangling bond, using as a starting point the thermodynamic equilibrium theory of defects in *a*-Si:H.

B. Equilibrium defect concentrations

Shockley and Moll[15] pointed out in 1960 that the concentration of charged defects in equilibrium depends on E_F since these defects must donate an electron or hole to the Fermi sea. Bar-Yam *et al.*[3] used this observation to calculate defect concentrations and thermodynamic transition energies in amorphous solids and other workers[16] have applied it to crystalline solids.

Here, I focus on the threefold-coordinated Si dangling bond and its three charge states: T_3^0, T_3^-, and T_3^+. The formation energy of a defect is defined[3] as the change in total energy of an ideal random network when the defect is introduced. Because it is uncharged, the formation energy of T_3^0, $F[T_3^0]$, is independent of E_F. The formation energies of the charged states of T_3 are

$$F[T_3^+,E_F]=F[T_3^0]+E_F-E(0/+)\ , \tag{1a}$$

and

$$F[T_3^-,E_F]=F[T_3^0]+E(-/0)-E_F\ . \tag{1b}$$

$E(r/s)$ is the thermodynamic transition energy from charge state r to s, normally measured relative to a band mobility edge by thermal equilibrium experiments such as deep-level transient spectroscopy (DLTS) in which the defect is assumed to relax completely upon carrier emission or capture. By definition of the transition energy, when $E_F=E(r/s)$ the formation energies $F[T_3^r]=F[T_3^s]$, and a defect can convert freely between charge states r and s by exchanging an electron with the Fermi sea. However, when $E_F\neq E(r/s)$, a change of charge state of the defect entails a change of total system energy. The last two terms in Eq. (1a) represent the energy expended to ionize the neutral defect, relax the resulting positive defect completely, and deposit the electron at E_F. Similarly, the last two terms of Eq. (1b) represent the energy expended to remove an electron from E_F, deposit it on the neutral defect, and relax the resulting negative defect completely. Assuming that $T>T^*$ so equilibrium can be attained, and that the entropy term in the free energy is small, the concentration of T_3^q is

$$n(T_3^q,E_F,T)=n_{\mathrm{Si}}\exp[-F(T_3^q,E_F)/kT]\ , \tag{2}$$

where n_{Si} is the number of Si atoms at which a defect can form.

Figure 1(a) exhibits both the formation energy and the log concentration above T^* of T_3^0, T_3^+, and T_3^- defects as functions of E_F. The formation energy of the positively (negatively) charged dangling bond increases (decreases) linearly with E_F. As indicated on the right-hand axis, defect concentrations increase downward in Fig. 1(a) and are plotted in energy units after multiplying by kT. I have assumed that T_3 has two sharp thermodynamic transitions in the gap and that it is a positively correlated system. The effective correlation energy U_{eff} is

$$U_{\mathrm{eff}}=E(-/0)-E(0/+)>0\ . \tag{3}$$

At a given value of E_F, the defect with the lowest value of F is found in the greatest concentration. Note that when E_F is at the thermodynamic transition energy $E(r/s)$, equal concentrations of T_3^r and T_3^s are formed. As E_F moves to higher energy than $E(r/s)$, the more negative defect dominates. By Fig. 1(a), when the sample is n type, p type and intrinsic, the majority charge states are T_3^-, T_3^+, and T_3^0, respectively. The effective density of one-electron levels (assuming complete defect relaxation) for these cases is shown in Figs. 1(b)–1(d), respectively.

When the system temperature is lowered below T^*, structural relaxations are frozen out and the total number of dangling bonds prevailing above T^* is quenched in. Below T^*, the charge state of T_3 with the lowest formation energy is found at a concentration approximately equal[17] to its concentration in the sample at T^*. As a

function of E_F, the concentration of the lowest-formation-energy dangling bond is

$$n(T_3^q, E_F, T) \simeq n_{Si} \exp(-F[T_3^q, E_F]/kT^*) , \quad (4)$$

for $T < T^*$. This is pictured in Fig. 2. The observed increase of dangling-bond density with doping[18] is evident for both n-type and p-type doping.

C. Relaxation of defects

To this point, I have considered only fully relaxed T_3 defects. This is appropriate for computing equilibrium defect densities since growth takes place above T^* and full structural relaxation around a defect to the equilibrium configuration presumably occurs. Full relaxation of a defect is also usually assumed in interpreting DLTS experiments. Then $E_c - E(-/0)$ and $E_v - E(0/+)$ are the DLTS transition energies associated with electron emission from T_3^- in n-type and hole emission from T_3^+ in p-type a-Si:H, respectively. The observation of metastable T_3^0 centers in a-Si:H (Refs. 12 and 19) suggests, however, that total relaxation of T_3^0 below T^* may not occur on DLTS time scales. I return to this point in Sec. IV after considering the experimental data.

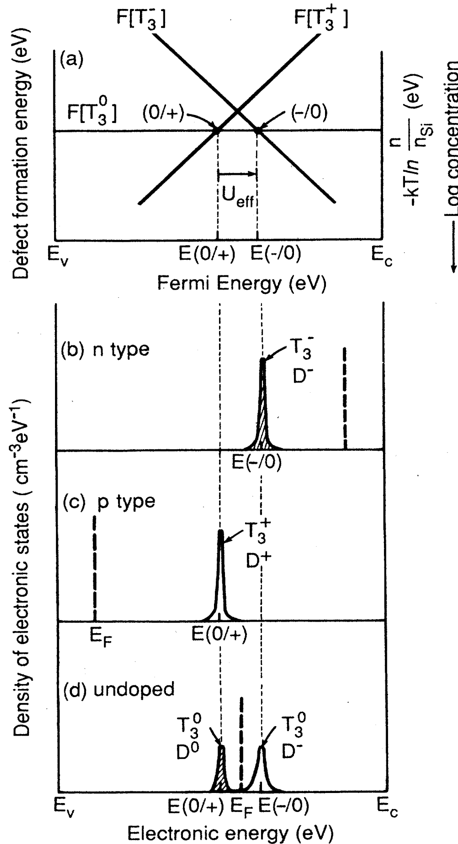


FIG. 1. (a) Formation energies and concentrations of relaxed dangling bonds as functions of E_F, for $T > T^*$. (b)–(d) Corresponding electronic density of states diagrams for n-type, p-type, and undoped a-Si:H. States are labeled T_3^+, T_3^0, or T_3^- according to the charge state of the defect (Ref. 21). The more usual labels (e.g., Ref. 5) of D^+, D^0, and D^- are also given. Filled states are shaded.

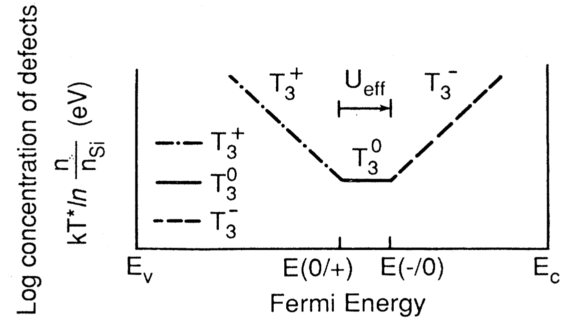


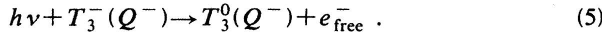
FIG. 2. log concentration of frozen-in dangling bonds as functions of E_F for $T < T^*$. A given defect type exists only at the values of E_F for which it is pictured.

According to the Franck-Condon principle, there is no relaxation of a defect's final state in either optical-absorption or luminescence experiments.[20] The initial states are assumed to be fully relaxed and the transitions instantaneous in both experiments. This gives rise to the well-known Stokes shift between the absorption and luminescence energies. To interpret these experiments, unrelaxed configurations of the dangling bond must be introduced into the theory.

D. Notation for unrelaxed defects

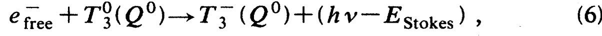
To discuss *unrelaxed* configurations of the dangling bond, a refinement of notation is required. Let Q^q represent the fully relaxed configuration of T_3^q. In this notation, the fully relaxed defects are denoted by $T_3^+(Q^+)$, $T_3^0(Q^0)$, and $T_3^-(Q^-)$. As suggested by Adler,[21] T_3^+, T_3^0, and T_3^- are isoelectronic with column-III, -IV, and -V atoms, respectively, and when relaxed each adopts the hybridization that its isoelectronic analog has in threefold-coordinated gas molecules. To a good approximation, Q^0 is an arrangement of the three neighboring atoms at the corners of a tetrahedron. This configuration arises from the sp^3 hybridization of electronic states that minimizes the total energy of T_3^0, Q^+ is an approximately planar, sp^2-hybridized, configuration with 120° bond angles that minimizes the energy of T_3^+. In Q^-, the bond angles are about 90°, reflecting the unhybridized s^2p^3 bonding. Total-energy calculations[2] confirm that distinct energy-minimizing configurations Q^+, Q^0, and Q^- do form in the solid, but suggest that the hybridization is not quite as complete as in the idealized configurations described above.

In general, $T_3^r(Q^s)$ denotes a dangling bond of charge r, in the configuration appropriate to the relaxed state of T_3^s. A T_3^- defect which loses an electron without relaxing is denoted by $T_3^0(Q^-)$. Optical absorption in n-type material by excitation of an electron out of a relaxed T_3^- by a photon of energy, $h\nu$, is represented by



$$h\nu + T_3^-(Q^-) \rightarrow T_3^0(Q^-) + e^-_{\rm free} \; . \qquad (5)$$

If the T_3^0 then relaxes to Q^0, the luminescence upon reabsorption of the electron is represented by



$$e^-_{\rm free} + T_3^0(Q^0) \rightarrow T_3^-(Q^0) + (h\nu - E_{\rm Stokes}) \; , \qquad (6)$$

where $E_{\rm Stokes}$ is the Stokes shift energy and $h\nu$ is the same energy as in Eq. (5). In Fig. 3, these optical and luminescence transitions are indicated by the solid vertical arrows at Q^- and Q^0, respectively.

E. Experimental energies

Experiments on doped *a*-Si:H are easier to interpret than those on undoped films for several reasons. First, each doped sample contains a single dangling-bond type of known hybridization: T_3^- (Q^-) and T_3^+ (Q^+) in *n*-type and *p*-type *a*-Si:H, respectively. An undoped *a*-Si:H sample may contain significant quantities of each of T_3^+, T_3^0, and T_3^-, due to a disorder-induced spread in thermodynamic transition energies.[3] Second, even if undoped *a*-Si:H contains only T_3^0 defects, competing transitions are observed in a given experiment. Optical absorption in undoped *a*-Si:H is due to both $T_3^0 \rightarrow T_3^+ + e^-$ and $T_3^0 \rightarrow T_3^- + h^+$. In *n*-type films, only $T_3^- \rightarrow T_3^0 + e^-$ is a single-photon process. Similarly, after sub-band-gap illumination, luminescence in *n*-type films must be from $e^- + T_3^0 \rightarrow T_3^-$. In undoped films, both $e^- + T_3^+ \rightarrow T_3^0$ and $h_3^+ + T_3^- \rightarrow T_3^0$ are possible luminescence transitions. Because of their relative simplicity, this paper focuses on the interpretation of experiments on doped *a*-Si:H.

Figure 4(a) shows the formation energies of the dangling-bond states relevant to experiments in *n*-type *a*-Si:H. The formation energies of the relaxed defects, $F[T_3^0(Q^0)]$ and $F[T_3^-(Q^-),E_F]$ are taken from Fig. 1(a). The total energy of an unrelaxed dangling bond is higher by the relaxation energy (about 0.2–0.3 eV). Table I defines the relaxation energies and lists values derived from total-energy calculations for the dangling bond. The relaxation energy of T_3^q in *n*-type (*p*-type) *a*-Si:H is denoted by Δ_q^n (Δ_q^p). In Fig. 4(a), Δ_0^n and Δ_-^n are shown and the formation energies of the unrelaxed defects, $F[T_3^0(Q^-)]$ and $F[T_3^-(Q^0),E_F]$, are plotted. To compute the relaxation energies, the pseudopotential density-functional theory calculation[2] embeds the defects in a *c*-Si supercell while the generalized valence-bond calculation[7] places them at a *c*-Si surface. The excellent agreement between relaxation energies computed by the different techniques suggests that these quantities may be quite accurate.

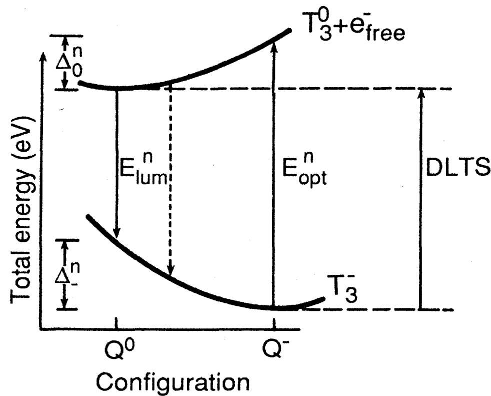


FIG. 3. Configuration-coordinate diagram of the dangling bond in *n*-type *a*-Si:H. The solid arrows represent optical, luminescence, and DLTS energies, assuming complete relaxation where appropriate. The dotted arrow represents the luminescence energy for incomplete initial-state relaxation.

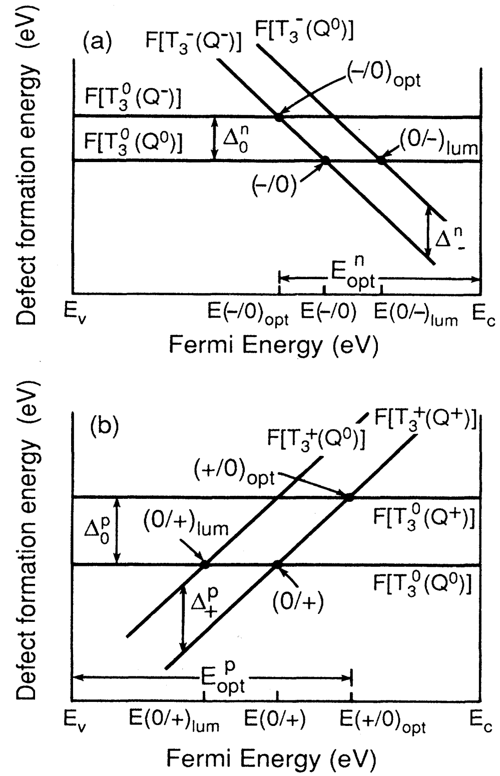


FIG. 4. Formation energies and transitions relevant to experiments in (a) *n*-type and (b) *p*-type *a*-Si:H. The charge states and configurations of both relaxed and unrelaxed defects are labeled. Note that the sum of optical transitions $E^n_{\rm opt} + E^p_{\rm opt} > E_g$ although $U_{\rm eff} > 0$.

The thermodynamic, optical, and luminescence transitions observed in experiments on *n*-type *a*-Si:H are labeled in Fig. 4(a) by $(-/0)$, $(-/0)_{\rm opt}$, and $(0/-)_{\rm lum}$, respectively. Their energies, $E(-/0)$, $E(-/0)_{\rm opt}$, and

TABLE I. Calculated relaxation energies of the dangling bond, taken from Refs. 2 and 7.

Relaxation energy	Definition	Ref. 2 (eV)	Ref. 7 (eV)
Δ_0^n	$F[T_3^0(Q^-)] - F[T_3^0(Q^0)]$	0.2	0.25
Δ_0^p	$F[T_3^0(Q^+)] - F[T_3^0(Q^0)]$	0.3	0.3
Δ_-^n	$F[T_3^-(Q^0)] - F[T_3^-(Q^-)]$	0.25	0.25
Δ_+^p	$F[T_3^+(Q^0)] - F[T_3^+(Q^+)]$	0.3	0.3

$E(0/-)_{\rm lum}$, are also shown, along with the conduction- and valence-band mobility edges E_c and E_v. The transition $(-/0)_{\rm opt}$ connects the initial state, $T_3^-(Q^-)$, and the final state, $T_3^0(Q^-)$, of the optical electronic excitation described by Eq. (5). To determine the optical-absorption energy for this electronic excitation, imagine E_F at $E(-/0)_{\rm opt}$ and split the event of Eq. (5) into a two-step process. The $(-/0)_{\rm opt}$ transition from $T_3^-(Q^-)$ to $T_3^0(Q^-)$ occurs without a change of total system energy. The excitation of the electron from E_F to the mobility edge requires $E_c-E(-/0)_{\rm opt}$. Thus, this optical transition requires $h\nu=E_c-E(-/0)_{\rm opt}$. Because the optical-absorption energy is independent of E_F, it is always $E_c-E(-/0)_{\rm opt}$ in n-type a-Si:H. From a similar argument, the luminescence energy is $E_c-E(0/-)_{\rm lum}$ for electron reabsorption into $T_3^0(Q^0)$ as described by Eq. (6). The predicted experimental energies in n-type a-Si:H are summarized in Table II. Complete relaxation is assumed in the DLTS measurement and in the initial states of optical absorption and luminescence. In Secs. IV B and IV C, this assumption will be examined further.

Figure 4(b) shows the formation energies of the fully relaxed defects $T_3^0(Q^0)$ and $T_3^+(Q^+)$ and of the unrelaxed defects $T_3^0(Q^+)$ and $T_3^+(Q^0)$ which are relevant to p-type material. The relaxation energies Δ_0^p and Δ_+^p are also shown. The thermodynamic, optical, and luminescence transitions are labeled by $(0/+)$, $(+/0)_{\rm opt}$, and $(0/+)_{\rm lum}$, respectively. The energy of each transition is indicated. DLTS measures $E(0/+)-E_v$, optical absorption measures $E(+/0)_{\rm opt}-E_v$, and luminescence measures $E(0/+)_{\rm lum}-E_v$, with the conventional assumptions about relaxation in these experiments. These energies are summarized in Table II.

III. REVIEW OF EXPERIMENTAL DATA

The optical and luminescence experimental energies are summarized in Table III. $E_{\rm opt}^n$ and $E_{\rm opt}^p$ are the experimental optical-absorption-peak energies observed in n-type and p-type a-Si:H, respectively, while $E_{\rm lum}^n$ and $E_{\rm lum}^p$ are the defect luminescence energies. In this section, I review the experimental literature and explain how I arrived at these values for the dangling-bond transitions. The effective correlation energy value is also discussed.

A. Optical absorption

Since 1980, there have been more than ten determinations[5,22–31] of the subgap optical-absorption-peak energy in n-type a-Si:H. There is general agreement that it is a broad peak which increases in magnitude with doping. Cohen *et al.*[32] use depletion-width-modulated ESR to demonstrate that the subgap DLTS transition at about 0.8 eV creates defects with the resonance at $g\simeq 2.0053$ that is characteristic[33] of T_3^0. They therefore conclude that DLTS probes the $(-/0)$ transition of T_3. This DLTS transition is likely the same transition as the dominant optical transition (see Sec. IV D). Further, Tajima *et al.*[34] show that reducing the optical excitation energy below the optical absorption-peak energy causes a dramatic drop in the 0.8-eV luminescence peak in n-type material, suggesting that the same defect causes both peaks. Street and Biegelsen[35] previously identified this 0.8-eV luminescence with the $e^-+T_3^0\rightarrow T_3^-$ transition by the similarity of its temperature and excitation energy dependence to those of the $g=2.0055$ light-induced ESR (LESR) signal. Together, these studies strongly suggest that the optical-absorption peak is due to a $T_3^-\rightarrow T_3^0+e^-$ transition, which has the energy $E_c-E(-/0)_{\rm opt}$.

Most workers fit their absorption data to an assumed density of states that includes a parabolic conduction band, an exponential conduction-band tail, and a gap state peak. All agree there is an optical gap of 1.7–1.8 eV. Cody[22] fits his optical transmission data from n-type a-Si:H with a peak centered 1.1 eV below E_c. Tanaka and Yamasaki[23] also find a peak at 1.1 eV below E_c by a detailed fit of their photoacoustic spectra. Various spectral photocurrent methods[5,24–27] place the peak at about the same energy. Wronski *et al.*[24] find a peak at 1.0–1.1 eV below E_c, using secondary photocurrent with a dc light bias to ensure constant trap filling. Inushima *et al.*[25] find 1.2 eV by a Fourier-transform ac photoconductivity measurement. The constant photocurrent method (CPM) is also used by the Prague group who first found 1.25 eV (Ref. 26) but later modified their estimate[5] to 1.0 eV below E_c. Their careful fitting procedure[5] yields a best fit at 1.0 eV with a full width at half maximum (FWHM) of the line of 0.24 eV. Fixing the FWHM at 0.3–0.4 eV, in agreement with the defect luminescence linewidth,[36] results in a best fit at 1.1–1.2 eV below E_c. Pierz *et al.*[27] use both CPM and photothermal deflection spectroscopy (PDS) to find a peak at 0.9–1.1 eV below E_c. Jackson and Amer[28] use PDS to measure the absorption and first fit their data with a peak at 1.3 eV below E_c. They later revised the PDS estimate[29,30] to about 0.8 eV, using a fitting procedure that involves raising the n-type absorption spectrum by a factor of 6 and shifting it until its shoulder matches that of an unshifted spectrum from undoped a-Si:H. Two separate photoemission studies[31] conclude that there is a density of states peak at about 1.3 eV below E_c. In this

TABLE II. Predicted experimental energies of the dangling bond in doped a-Si:H, assuming total relaxation of all DLTS states and of initial states in optical absorption and luminescence. There is no final-state relaxation in absorption and luminescence. The transition energies are pictured in Fig. 4.

Doping	Equilibrium dangling bond	Optical absorption	Luminescence	DLTS
n-type	$T_3^-(Q^-)$	$E_c-E(-/0)_{\rm opt}$	$E_c-E(0/-)_{\rm lum}$	$E_c-E(-/0)$
p-type	$T_3^+(Q^+)$	$E(+/0)_{\rm opt}-E_v$	$E(0/+)_{\rm lum}-E_v$	$E(0/+)-E_v$

TABLE. III. Summary table of experimental energies in doped a-Si:H. The superscript refers to the doping and the subscript to optical-absorption or luminescence experiments.

Experiment	Energy
$E^n_{\rm opt}$	1.1
$E^n_{\rm lum}$	0.8
$E^p_{\rm opt}$	1.3
$E^p_{\rm lum}$	0.9

paper, I take $E_c-1.1$ eV as the location of the optical transition $(-/0)_{\rm opt}$ in n-type a-Si:H, consistent with the optical transmission, photoacoustic, and photocurrent determinations.

Optical absorption in p-type films is less widely studied. A broad peak in the upper half of the gap is observed, and most workers assume it is associated with $T_3^+ \rightarrow T_3^0 + h^+$ excitation of an electron from the valence band. Another possible gap state in B-doped films is at the paramagnetic B_3^- center, and the optical absorption could be the transition $B_3^0 \rightarrow B_3^- + h^+$ by excitation of a valence electron.[37] The rapid increase of the absorption-peak magnitude with B doping does not distinguish between these two possibilities. The increase indicates either that the defect is associated with B or that it is a positively charged defect whose concentration increases exponentially with decreasing E_F (see Fig. 2). However, the observation of a LESR signal at $g=2.0055$ in p-type a-Si:H (Ref. 36) suggests that the dominant optical transition to a paramagnetic defect state is $T_3^+ \rightarrow T_3^0 + h^+$, not $B_3^0 \rightarrow B_0^- + h^+$. It is conceivable, however, that a short lifetime for the paramagnetic B_3^- state compared to T_3^0 could make it LESR invisible. Street and Biegelsen[35] did identify the 0.9-eV luminescence band in p-type material with T_3 by comparison of its temperature and excitation energy dependences with those of the T_3^0 LESR signal. In Sec. IV C, I argue that 0.9-eV luminescence is from the same defect as the optical absorption. From the evidence, I attribute the optical gap-state transition observed in p-type a-Si:H to the dangling-bond transition.

Inushima *et al.*[25] place the defect absorption in p-type a-Si:H at 1.3 eV above E_v by their ac photoconductivity measurements and Pierz *et al.*[27] also find this energy level from both PDS and CPM. The level appears consistent with the photoacoustic spectra of Yamasaki *et al.*,[38] though these authors do not compute the peak position. The Prague group first fit their data to a peak at 1.03 eV,[26] but later revise the estimate[5] to 1.27 eV above E_v. Thus, there is general agreement that $(+/0)_{\rm opt}$ lies about 1.3 eV above E_v.

B. Luminescence

The evidence that the defect luminescence bands in both n-type and p-type a-Si:H are due to the dangling-bond transitions from T_3^0 to the charged state[35] was reviewed in Sec. III A. Various workers[34,39–41] have found that this luminescence band in P-doped n-type a-Si:H peaks at the photon energy of 0.8 eV, and has a FWHM of 0.3–0.4 eV. Further evidence of the intrinsic nature of the defect responsible for the luminescence in n-type a-Si:H is the observation of 0.8-eV luminescence in Li-doped n-type a-Si:H.[42] In p-type a-Si:H, the defect luminescence is observed[40,41,43] at a photon energy of 0.9 eV, also with a FWHM of 0.3–0.4 eV.

C. Correlation energy

Since the effective correlation energy, $U_{\rm eff}$, is the difference between the *thermodynamic* transition energies $E(-/0)$ and $E(0/+)$, it is best determined by experiments that probe fully relaxed dangling bonds. From Fig. 2, it is evident that the dark ESR signal from T_3^0 at $g=2.0055$ will be observed if and only if E_F lies between the two thermodynamic transition energies $E(-/0)$ and $E(0/+)$. Analysis of the spin density, as a function of E_F position in the gap for a series of doped films should therefore yield $U_{\rm eff}$. A distribution of local environments may broaden both transitions, but an upper limit to $U_{\rm eff}$ can be obtained. $U_{\rm eff}$ estimates of 0.4 eV (Ref. 33) and 0.3 eV (Ref. 44) were made in this way. Stutzmann and Jackson[45] find $U_{\rm eff}=0.2\pm0.1$ eV from a more careful analysis of the ESR data, including its temperature dependence. It should be noted that a positive value of $U_{\rm eff}$ does not preclude the existence of charged dangling bonds in undoped a-Si:H if there is a distribution of thermodynamic transition energies.[3]

IV. DISCUSSION

A. Optical absorption

I now apply the theory of Sec. II for optical transition energies to the experimental data summarized in Table III. Note, first, that the sum of the defect optical transition energies in n-type and p-type a-Si:H significantly exceeds the band gap of 1.7 eV. This sum is $E^n_{\rm opt}+E^p_{\rm opt}=2.4$ eV. If the distinction between optical and DLTS transition energies is ignored, the relation

$$E^n_{\rm opt}+E^p_{\rm opt}=E_g-U_{\rm eff} \tag{7}$$

is easily derived from Fig. 1. Therefore, Adler[4] proposed that the data suggest a large negative correlation energy, for the dangling bond. The present data would imply that $U_{\rm eff}\sim -0.7$ eV. Kocka[5] proposes that the data, together with a positive correlation energy of 0.35 eV in undoped a-Si:H, imply that the electronic levels of charged dangling bonds are moved about 0.5 eV deeper in doped a-Si:H by spatial pairing with the oppositely charged ionized dopant. This accounts for the 1 eV anomaly they find between the positive $U_{\rm eff}$ and the sum of absorption energies.

Other authors[6,27] point out that the vertical nature of defect optical absorption helps resolve this apparent anomaly. This is evident in Fig. 4 which shows $E^n_{\rm opt}+E^p_{\rm opt}>E_g$ for $U_{\rm eff}>0$, without electronic-level deepening. The theory predicts (see Fig. 4)

$$E^n_{\rm opt}+E^p_{\rm opt}=E_g-U_{\rm eff}+\Delta_0^n+\Delta_0^p \; . \tag{8}$$

Substituting into Eq. (8) the relaxation energies of Ref. 2

from Table I, the experimental energies from Table III and the measured band gap of 1.7 eV yield

$$-U_{\text{eff}} \simeq E^n_{\text{opt}} + E^p_{\text{opt}} - E_g - \Delta^n_0 - \Delta^p_0 = +0.2 \text{ eV} . \quad (9)$$

Thus, $U_{\text{eff}} \simeq -0.2$ eV—close to the experimental value. The value $U_{\text{eff}} \sim 0$ can be obtained by stretching E_g to 1.8 eV (consistent with some measurements on n-type a-Si:H) and using slightly lower experimental values for E^n_{opt} and E^p_{opt}. The main point is that for a dangling-bond defect with small positive U_{eff} and significant relaxation energies associated with its different configurations, $E^n_{\text{opt}} + E^p_{\text{opt}} > E_g$ is *expected*. The experimental data cannot be taken as evidence for a large negative U_{eff}, nor for defect-dopant pairing that shifts dangling-bond energies 0.5 eV deeper into the gap of doped a-Si:H.

B. Electronic level deepening

There remains a smaller anomaly between $U_{\text{eff}} \simeq 0.2$ eV from spin-resonance experiments and $U_{\text{eff}} \simeq -0.2$ eV derived above from optical-absorption experiments. Evidently, the transition energies $E(-/0)_{\text{opt}}$ and $E(+/0)_{\text{opt}}$, taken together, are a total of about 0.4 eV deeper than is consistent with the assume value of U_{eff} and the relaxation energies. Neither a smaller value of U_{eff} nor larger values of Δ^n_0 and Δ^p_0 are attractive resolutions of this anomaly. The generally accepted value of U_{eff} is even greater than 0.2 eV; smaller values are unlikely. The relaxation energies of Refs. 2 and 7 are mutually consistent and yield[2] the low value of $U_{\text{eff}} = -0.2 \pm 0.2$ eV, which suggests that they may be too large. The remaining explanation of the anomaly is that electronic-level deepening (eld) occurs either only in the doped material as suggested by Kocka[5] or by a mechanism common to all a-Si:H. In either case, Eq. (8) becomes

$$E^n_{\text{opt}} + E^p_{\text{opt}} = E_g - U_{\text{eff}} + E^n_{\text{eld}} + E^p_{\text{eld}} + \Delta^n_0 + \Delta^p_0 , \quad (10)$$

when E^n_{eld} and E^p_{eld} are the magnitudes of the electronic-level deepening energies in n-type and p-type a-Si:H, respectively. Assuming $E^n_{\text{eld}} \approx E^p_{\text{eld}}$, level-deepening energies of about 0.2 eV are needed to explain the data.

The Kocka model[5] of T_3^--P_4^+ and T_3^+-B_4^- pairing could explain the small level deepening suggested by the optical-absorption data. Pairing of oppositely charged defects on nearest-neighbor sites can deepen the energy by about 0.5 eV.[21] It has been suggested that pairing reduces the system entropy compared to randomly distributed defects and is therefore unlikely.[46] However, deepening the transition energy by 0.2 eV requires oppositely charged pairs separated by 5–6 Å—approximately fourth-nearest neighbors in a-Si:H. This quite unrestrictive pairing represents much larger system entropy than nearest-neighbor pairing and is therefore more likely.

An alternative explanation of the level deepening, originally given by Bar-Yam *et al.*,[3] is a spread in thermodynamic transition energies of the defect. The total-energy calculations[2] show that dangling-bond thermodynamic transition energies are very sensitive to small distortions of the host lattice—much more so than is U_{eff}. The resulting spread in transition energies can also be interpreted as resulting from medium-range potential fluctuations,[47] and this approach is followed here.

Figure 5 illustrates the physics involved for n-type a-Si:H. The formation energies of $T_3^0(Q^0)$, $T_3^0(Q^-)$ and the mean energy of $T_3^-(Q^-)$ are shown by the solid lines and these are the same as in Fig. 4(a). Potential fluctuations $V(x)$ with a standard deviation of V_{sd}, cause a distribution of formation energies of T_3^- of FWHM equal to the full width, $2eV_{\text{sd}}$, of the fluctuations.[47] The distribution full width of $F[T_3^-]$ is indicated by the dashed lines. The dotted-dashed line represents the lowest formation energy T_3^- defects and these are the highest concentration defect in n-type a-Si:H. The dominant transition, $(-/0)^{\text{dom}}_{\text{opt}}$, observed in experiment is deeper than the mean transition, $(-/0)_{\text{opt}}$, by $E^n_{\text{eld}} = eV_{\text{sd}}$. The corresponding energy $E(-/0)^{\text{dom}}$ is pictured in Fig. 5. Similarly, the dominant optical transition is moved deeper in p-type a-Si:H by $E^p_{\text{eld}} \simeq eV_{\text{sd}}$. Together, Eqs. (9) and (10) imply

$$E^n_{\text{eld}} + E^p_{\text{eld}} - U_{\text{eff}} = 2 \text{ eV}_{\text{sd}} - U_{\text{eff}} \simeq 0.2 \text{ eV} . \quad (11)$$

Thus, if potential fluctuations cause the observed level deepening, their full width exceeds U_{eff}.[48]

Finally, it should be noted that the optical-absorption energies agree with the observed position of E_F in good quality undoped samples. Charge neutrality in a system where the only charged defects are dangling bonds requires that E_F lie at the crossing points of $F[T_3^-]$ and $F[T_3^+]$. If $\Delta^n_0 \sim \Delta^p_0$ and the level deepening is symmetric, $E_F = [E(-/0)_{\text{opt}} + E(0/+)_{\text{opt}}]/2$. Substituting from Table II, $E_c - E_F = (E^n_{\text{opt}} + E_g - E^p_{\text{opt}})/2$. The values of $E^n_{\text{opt}} = 1.1$ eV, $E^p_{\text{opt}} = 1.3$ eV, and $E_g = 1.7$ eV then put E_F at 0.75 eV below E_c in undoped a-Si:H. This agrees with the accepted value.

C. Luminescence

From the theory of Sec. II, a complete relaxation of T_3^0 in n-type a-Si:H after the optical excitation $T_3^- \rightarrow T_3^0 + e^-$ will result in a luminescence at

$$E^n_{\text{lum}} = E^n_{\text{opt}} - \Delta^n_0 - \Delta^n_- . \quad (12)$$

The predicted Stokes shift energy $\Delta^n_0 + \Delta^n_-$ is not affected by any possible electronic-level deepening, because both the luminescence and optical transition energies are deepened equally. Similarly, a Stokes shift of $\Delta^p_0 + \Delta^p_+$ is predicted for p-type a-Si:H. The predicted optical and luminescence transitions in n-type a-Si:H are shown by solid lines in the configuration coordinate diagram of Fig. 3. The relaxation energies Δ^n_0 and Δ^n_- that comprise the Stokes shift are indicated.

Stokes shifts of 0.3 and 0.4 eV are observed in n-type and p-type a-Si:H, respectively (see Table III). This conclusion is supported by the experiment of Tajima *et al.*[35] who showed directly a Stokes shift larger than 0.2 eV in n-type a-Si:H. The Stokes shifts are slightly smaller than the shifts of 0.45 and 0.6 eV that would be predicted by theory[4] for complete relaxation of the luminescence initial states in n-type and p-type a-Si:H, respectively (see Table I). The luminescence resulting from incomplete re-

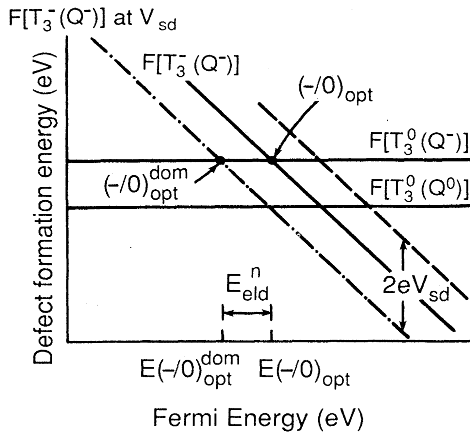


FIG. 5. Formation energies and transitions relevant to n-type a-Si:H with potential fluctuations. The dotted-dashed line represents $T_3^-(Q^-)$ defects at regions of high potential, $V=V_{sd}$. These are the dominant defect and their optical transition is labeled by $E(-/0)_{opt}^{dom}$. The electronic-level deepening, E_{eld}^n, is also shown.

laxation is indicated by the dotted line in Fig. 3. The final 0.15–0.2 eV of relaxation evidently cannot occur on the time scale of the luminescence. The configurational change associated with complete relaxation of the dangling bond requires cooperative motion of both neighboring and more distant atoms, particularly if configurations that break the axial symmetry of Q^+, Q^0, and Q^- lie higher in energy. This likely retards the relaxation. The incomplete relaxation also suggests the possibility of metastable dangling-bond states which cannot easily rehybridize.[49]

In both n-type and p-type a-Si:H, the linewidth of the defect luminescence is 0.3–0.4 eV. Assuming that the luminescence initial state always involves a carrier at the band mobility edge, the broadening results from a distribution of luminescence transition energies, and therefore potential fluctuations of width 0.3–0.4 eV. This width agrees with the value of $eV_{sd}>0.2$ eV that can be deduced from Eq. (11).

D. Other measurements

Comparison of DLTS and optical-absorption data is complicated by the different energy scales involved,[50] but I attempt it here. From Figs. 3 and 4, it is evident that the DLTS transition energy should be intermediate between the optical and luminescence energies. Workers have observed an electron-emitting transition from n-type a-Si:H at about 0.9–1.0 eV below E_c,[50,51] which is intermediate between the values in Table III. As in luminescence, it appears that only partial relaxation of the final state is possible on the DLTS time scale. Gelatos *et al.*[51] used photocapacitance to place an upper limit of 0.1 eV on the lattice relaxation of the final state in DLTS. Because the corresponding Stokes shift involves both initial and final states, it could be about twice as large as the DLTS relaxation energy. The observed Stokes shift of 0.3 eV in n-type material is consistent with the photocapacitance result.

V. CONCLUSION

I have analyzed the phenomenology of the dangling-bond defect in doped a-Si:H in a thermodynamic equilibrium framework using theoretical results[2,7] for the relaxation energies associated with its different charge states and assuming a positive effective correlation energy. The controversy over an anomaly of about 0.9 eV in the sum of optical-absorption energies in the doped films[4–6] is largely resolved by recognizing that optical transitions are to *unrelaxed* final states of the defect. The small anomaly of about 0.4 eV that remains can be explained by electronic-level deepening resulting from defect-dopant pairing[5] or a distribution of thermodynamic transition energies[4] that may result from potential fluctuations.[47]

Comparison of optical and defect luminescence energies suggests Stokes shifts of 0.3 and 0.4 eV in n-type and p-type a-Si:H, respectively. These represent an incomplete relaxation of the luminescence initial state and suggest that metastable configurations of the dangling bond may exist. The DLTS $(-/0)$ transition in n-type a-Si:H lies at an energy between that of luminescence and optical absorption, as predicted by theory. All the transition energy assignments are consistent with the known position of E_F in undoped a-Si:H. Considerable information about dangling-bond energy levels and relaxations in a-Si:H is obtained by examining transition energies in doped a-Si:H, for which the equilibrium charge and hybridization of the defect is known.

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