

Chemical-Equilibrium Description of the Gap-State Distribution in *a*-Si:H

K. Winer

Xerox Palo Alto Research Center, Palo Alto, California 94304

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A pool of potential energies at which defect states can be created is incorporated into a simple chemical-equilibrium description of defect formation in *a*-Si:H. For a wide enough defect-pool distribution, D^- lies deeper in the gap than D^0 , in agreement with recent photoemission results, even though the correlation energy is positive. Bonded hydrogen is proposed as the physical origin of the defect pool.

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Although many uncertainties regarding the defect structure of hydrogenated amorphous silicon (*a*-Si:H) remain, the temperature independence of the electron-spin-resonance signal in undoped *a*-Si:H below 300 K is a clear and unambiguous signature of defects with a positive correlation energy U , which is the extra energy required to place a second electron on a singly occupied localized defect level.^{1,2} It is, therefore, puzzling that several recent experiments have shown that the negatively charged defect band peak (D^-) in *n*-type *a*-Si:H lies ~ 0.1 eV below the neutral defect band peak (D^0) in undoped *a*-Si:H.³⁻⁵ Such a distribution is incompatible with both a positive correlation energy and a fixed set of defect energy levels where only the occupation of these states varies with doping. Because the experimental evidence for $U > 0$ is strong, any explanation of this defect energy ordering must abandon the notion of fixed defect energy levels.

Two possible explanations along these lines have been proposed. The first proposes an intimate pairing of dopants and defects whereby D^- in *n*-type *a*-Si:H lies deeper in the gap than D^0 in undoped *a*-Si:H due to the extra energy $-V_{\text{Coul}} > U$ from the mutual Coulombic attraction between dopant (in this case P) and defect.³ There are several problems with this explanation. The degree of pairing should depend on the particular dopant chemistry and, therefore, cannot explain the observation of deep lying D^- levels in interstitially Li-doped *a*-Si:H,⁶ near activated-oxygen-covered *a*-Si:H surfaces,⁷ or in metal-insulator *a*-Si:H device structures under voltage bias⁸ where either the dopant chemistry is substantially different from that of substitutional P or dopants are absent altogether. Also, the intimate pairing of virtually all dopants with defects unrealistically restricts their entropic contribution to the system free energy, which is not compatible with the observation of dopant, but not defect, equilibration in *n*-type *a*-Si:H.⁹

The second explanation proposes the existence of a pool of defect sites from which the system can choose to create or destroy defects in order to minimize the system free energy.¹⁰⁻¹² This proposal has yet to be fully realized in the form of a theory of the distribution of defect states in *a*-Si:H due to the lack of a suitable framework within which to incorporate it. In such a framework, de-

fects would be treated as chemical species whose charge state and concentration are governed by a defect chemical potential in analogy with the description of point defects (vacancies and interstitials) in crystalline silicon (*c*-Si).¹³ However, unlike *c*-Si where translational symmetry leads to single, fixed defect-state energies, the broad distribution of defect states in *a*-Si:H would also depend on the defect chemical potential and, therefore, on the Fermi energy. Such a chemical-equilibrium framework has the advantage that it is independent of any particular dopant chemistry and it explicitly takes entropy into account in a straightforward way. In addition, recent experimental studies have verified that this approach accurately describes the temperature dependence of the neutral defect concentration above 500 K observed in undoped *a*-Si:H.¹⁴

Starting with the proposition that *a*-Si:H can achieve a chemical equilibrium between coordination defects and weak Si-Si bonds, the defect-pool concept is employed to derive a formal expression for the distribution of defect states in the gap at equilibrium. This distribution is shown to be governed by a simple relation between the distribution of weak Si-Si bonding (valence-band tail) states and the standard deviation σ of the defect-pool distribution. Evidence for the validity of this approach lies in its main result, that for a wide enough defect-pool distribution, D^- in *n*-type *a*-Si:H lies deeper in the gap than D^0 in undoped *a*-Si:H even though U is positive.

In *c*-Si, Frenkel defects (Si vacancies V and interstitials I) are generated according to the reaction



When the defects achieve equilibrium with the lattices, their concentration is given by the law of mass action:

$$[I] = [V] = ([V][I])^{1/2} \approx ([N_{\text{Si}}][N_{\text{Int}}])^{1/2} \times \exp(-E_I/2kT), \quad (2)$$

where E_I (~ 4 eV) is the energy required to form an interstitial-vacancy pair.¹³

In analogy with Frenkel defect formation in *c*-Si, we can model neutral defect formation in undoped *a*-Si:H

by the following reaction:¹⁴



where SiH are hydrogen atoms ($[\text{SiH}] \approx [\text{H}] \sim 0.1[\text{Si}]$) bonded to Si whose motion enables the equilibration, SiSi are weak Si-Si bonds that make up the valence-band tail of localized states, D^0 are neutral coordination defects ("dangling bonds") in the band gap, and SiHSi are H trapped at a weak bond site. The application of the law of mass action is straightforward but requires some care because of the exponential distribution of defect formation energies introduced by the valence-band tail. The contribution to the defect concentration at E^* from H atoms trapped at weak bond states in the interval between E and $E + dE$ is

$$\delta[D^0] = \delta[\text{SiHSi}]dE = \frac{[\text{H}][\text{SiSi}] - \delta[\text{SiHSi}]\exp(-E_{\text{form}}/kT)}{[D^0]}dE, \quad (4)$$

where $[\text{SiSi}] = N_0 \exp[(E_{v0} - E)/E_0]$ represents the valence-band tail density of states of slope E_0 and $E_{\text{form}} = E^* - E$ is the formation energy of a single SiHSi- D^0 pair (ionic and multielectronic effects are ignored).¹¹ The resulting concentration of neutral defect states between E^* and $E^* + dE^*$ for a δ -function defect distribution at equilibrium is

$$\frac{d[D^0]}{dE^*} = \int_{E_{v0}}^{\infty} \frac{N_0 \exp[(E_{v0} - E)/E_0]dE}{1 + ([D^0]/[\text{H}])\exp[(E^* - E)/kT]} \delta(E^* - E_{D^0}), \quad (5)$$

where $E_{v0} \equiv 0$ is taken as the reference energy, E_{D^0} is the single defect gap-state energy (restricted by the δ function), and the integral is over all valence-band tail state energies E . The integral expresses the defect concentration at $E^* = E_{D^0}$ as the number of weak bonds occupied by hydrogen, in analogy with Fermi occupation statistics where the neutral defect chemical potential $\mu_{D^0}(E^*) \equiv E^* + kT \ln([D^0]/[\text{H}])$ plays the role of the Fermi level. The numerical solution of Eq. (5) leads to a temperature dependence of $[D^0] \{-\partial \ln[D^0]/\partial(1/kT) \approx 0.15 \text{ eV for } T \geq 500 \text{ K}\}$ that agrees well with experiment.¹⁴ The temperature dependence of $[D^0]$ clearly demonstrates the essential role of entropy in α -Si:H defect formation, which strongly depends on the specific reaction considered. However, the defect-state distribution is only weakly dependent on temperature so that reaction (3) is sufficiently general for the forthcoming analysis. The point so far is that defect formation in α -Si:H is well

described by a formalism based on the chemical equilibrium between coordination defects and weak (i.e., localized) bonds.

The δ function in Eq. (5) represents the distribution of all possible ("virtual") defect-state energies at which the system can choose to create defect states in order to minimize the system free energy. In this particular case, the equilibrium defect distribution and the distribution of virtual states are identical, and the system free-energy minimum is determined by a balance between the entropy produced via defect creation and the enthalpy cost of transferring H from bond terminating sites to weak bond trapping sites. However, if we replace the δ function in Eq. (5) with a more general Gaussian distribution of virtual defect energies (i.e., a defect pool), the system free energy can be further reduced through a lowering of the transfer enthalpy. The defect density becomes

$$\frac{d[D^0]}{dE^*} = \left[\frac{N_0 E_0 kT}{E_0 - kT} \right] \left\{ \frac{E_0}{kT} \exp \left[\frac{-\mu_{D^0}(E^*)}{E_0} \right] - \exp \left[\frac{-\mu_{D^0}(E^*)}{kT} \right] \right\} \frac{1}{(2\pi\sigma)^{1/2}} \exp \left[\frac{-(E^* - E_p)^2}{2\sigma^2} \right], \quad (6)$$

where the integral in Eq. (5) has been explicitly evaluated with the restriction that $\mu_{D^0}(E^*) \geq 0$, σ is the standard deviation of the Gaussian defect-pool distribution, and E_p is the energy of the most probable defect configuration, i.e., the defect-pool maximum. A candidate for the physical manifestation of the defect pool, according to reaction (3), is the large concentration of bonded hydrogen, where the variable backbond strain gives rise to the broad distribution of potential defect sites. Thus, σ should be a characteristic measure of disorder in α -Si:H as has been proposed for E_0 ,¹¹ both of which might be described by a single disorder parameter such as the average bond-angle deviation.

The maximum of the defect distribution can be calculated by extremizing Eq. (6) with respect to E^* , which

for $kT < E_0$ gives $E_{D^0} \equiv E_{\text{max}}^* = E_p - \sigma^2/E_0$. This is just what is required to cancel out the first (second when $kT > E_0$) exponential in Eq. (6) which results in an observed defect distribution $d[D^0]/dE^*$ that is Gaussian with width σ and a peak at $E_p - \sigma^2/E_0$ ($E_p - \sigma^2/kT$ when $kT > E_0$). The shift is due to the balance between a defect formation energy reduction ($\propto E^* - E_p$) for defect states formed in the low-energy tail of the defect-pool distribution and an addition [$\propto (E^* - E_p)^2$] due to the increased distortion energy for states formed far from the defect-pool maximum, which results in a system free-energy change $\Delta F \approx -\sigma^2/E_0$. Therefore, introducing a distribution of defect energies (a defect pool) into a simple chemical-equilibrium description of defect

formation results in the creation of the majority of neutral defects not at an energy where potential defect sites are least distorted due to backbond strain and most numerous (i.e., at E_p), but where it costs the system the least free energy (i.e., at $E_p - \sigma^2/E_0$). The effect of the electron chemical potential (the Fermi energy) on the defect distribution is next considered.

The presence of electrons in n -type a -Si:H, say from donor ionization, changes the equilibrium point of reaction (3). Consider the additional reaction,



which describes the capture of an electron from (or release to) the conduction band by a neutral defect. An increase in the number of electrons in the system pushes the equilibrium point of reaction (7) and, as a consequence, reaction (3) to the right, which results in a larger defect concentration. This process is independent of the origin of the extra electrons and can result from applied fields, light exposure, doping, or activated gas adsorption, all of which can change the position of the Fermi energy. However, a shift in the Fermi energy to fill or empty defect states will not lead to a change in their distribution if the probe time is much less than the characteristic equilibration time τ at a given temperature ($\tau \approx 10^6$ s at 300 K and ≈ 60 s at 400 K in n -type a -Si:H).⁹ The results presented here apply only to fully equilibrated material.

The increase in the defect concentration comes about because the enthalpic cost to form a defect is reduced by the energy gained in dropping an electron from the Fermi level onto the defect level (i.e., by $E^* - E_F$) plus the extra cost U of having two electrons occupy the same localized defect state. Thus, the distribution of charged defects in n -type material at equilibrium is given by Eq. (6) with the neutral defect chemical potential $\mu_{D^0}(E^*) = E^* + kT \ln([D^0]/[H])$ replaced by the Fermi-energy-dependent chemical potential

$$\mu_{D^-}(E^*) = 2E^* + U - E_F + kT \ln([D^-]/[H]) .$$

Also, the defect-pool maximum E_p in Eq. (6) must be replaced by $E_p + U$. This becomes obvious in the limit that $\sigma \rightarrow 0$, where the single D^- defect level must lie above the single D^0 defect level by an energy U . More generally, we could include the energy dependence of U in the formalism as has been attempted elsewhere.¹⁵

The maximum of the resulting defect distribution in n -type a -Si:H (D^-) at equilibrium occurs at $E_{D^-} \equiv E_{\max}^* = E_p + U - 2\sigma^2/E_0$. At equilibrium, D^0 in intrinsic a -Si:H is separated from D^- in n -type a -Si:H by an amount $\Delta E^{-/0} \equiv E_{D^-} - E_{D^0} = U - \sigma^2/E_0$. In the limit that $\sigma \rightarrow 0$ we recover the result $\Delta E^{-/0} = U$ expected for a single correlated defect level. It can be similarly shown that the shift between D^- in n -type and D^+ in p -type a -Si:H at equilibrium is given by $\Delta E^{-/+} \equiv E_{D^-} - E_{D^+} = U - 2\sigma^2/E_0$. Taking reasonable values for σ ,

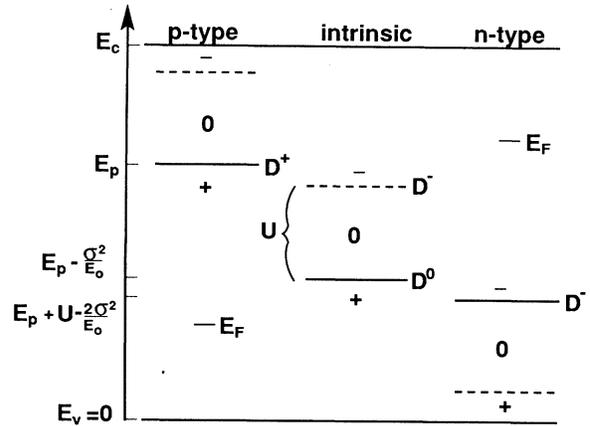


FIG. 1. Schematic ordering of defect transition energies in a -Si:H. +, 0, and - refer to the charge state of the majority of the defects when the Fermi energy is momentarily shifted below, in between, or above the two correlated levels, respectively. The 0/+ transition corresponds to the D^+ defect band peak in p -type, the 0/+ transition to the D^0 defect band peak in undoped, and the -/0 transition to the D^- defect band peak in n -type a -Si:H at equilibrium.

E_0 , and U we can estimate the magnitudes of these shifts. E_0 is well determined from photoemission and optical-absorption data to be 0.045 eV.^{5,16} The full width at half maximum of the defect band is generally found to be ≈ 0.3 eV so that $\sigma \approx 0.13$ eV.^{3-5,17} U has been estimated to be 0.25 eV.¹⁸ These result in shifts $\Delta E^{-/0} \approx -0.13$ eV and $\Delta E^{-/+} \approx -0.50$ eV, which are in reasonable agreement with the results of recent photoemission ($\Delta E^{-/0} = -0.15$ eV and $\Delta E^{-/+} \approx -0.7$ eV)^{5,7} and optical-absorption ($\Delta E^{-/0} = -0.1$ eV and $\Delta E^{-/+} = -0.5$ eV)^{3,4} measurements. The resulting ordering of 0/+ and -/0 defect transition energies for p -type, intrinsic, and n -type a -Si:H is shown schematically in Fig. 1. The resulting equilibrium defect distributions calculated from Eq. (6) compare well with the experimentally determined distributions as shown in Fig. 2. The main result is that for a wide enough defect-pool distribution ($\sigma > 0.1$ eV), D^- in n -type a -Si:H lies deeper than D^0 in undoped a -Si:H at equilibrium even though the correlation energy is positive.

This important result resolves the apparent contradiction between electron-spin-resonance data, which require a positive correlation energy, and equilibrium gap-state spectra, which show D^- in n -type a -Si:H to lie below D^0 in undoped a -Si:H as might be expected for negative- U defects with fixed defect energies. The ideal experiment to further test this idea would involve shifting the Fermi level of an equilibrated a -Si:H film, say through a voltage bias in a metal-insulator-semiconductor sandwich, and monitoring the resulting change in the defect distribution as the film reequilibrates. Although the precision of the input parameters in the model could be improved

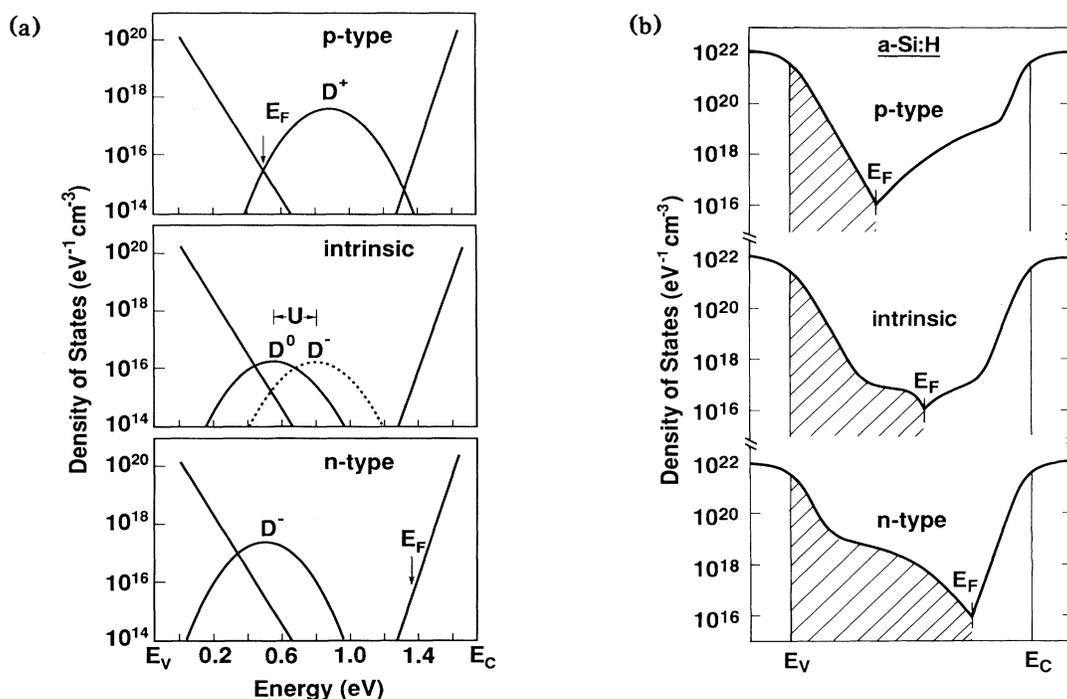


FIG. 2. (a) Gap-state defect distributions for *n*-type, intrinsic, and *p*-type *a*-Si:H calculated using Eq. (5) with the corresponding D^- , D^0 , and D^+ chemical potentials and the following parameters (see Ref. 19): $N_0 = 2 \times 10^{20} \text{ eV}^{-1} \text{ cm}^{-3}$, $[H] = 5 \times 10^{21} \text{ cm}^{-3}$, $E_0 = 0.045 \text{ eV}$, $U = 0.25 \text{ eV}$, $\sigma = 0.125 \text{ eV}$, and $E_p = 0.9 \text{ eV}$. (b) Gap-state defect distributions for *n*-type, intrinsic, and *p*-type *a*-Si:H inferred from total yield photoelectron and photothermal deflection spectroscopy measurements. Shaded areas correspond to states whose distribution is directly measured by total yield (Refs. 5 and 12).

with better experiments, its success in resolving this perplexing contradiction makes clear the usefulness of a chemical-equilibrium framework for understanding the physics of *a*-Si:H.

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¹⁹The lower bound on the integral in Eq. (5) was shifted to -0.7 eV for the *n*-type calculation to deal with the negative defect chemical potential that occurs over a limited range in this case. This deficiency in the model can be corrected with smaller values for U and σ .