Comments

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Comment on "Excitation-energy dependence of optically induced ESR in *a*-Si:H"

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The infrared light-induced electron-spin-resonance (LESR) data of Ristein *et al.* [Phys. Rev. B **40**, 88 (1989)] are reinterpreted. A model of undoped hydrogenated amorphous silicon (*a*-Si:H) including more *charged* than *neutral* dangling-bond defects yields a natural explanation of the experimental results. These LESR data are the most direct experimental evidence to date for the existence of bulk charged dangling bonds in undoped *a*-Si:H at electronic equilibrium.

In a recent paper, Ristein *et al.*[1] present experimental studies of red and infrared (ir) light-induced electron-spin resonance (LESR) of undoped hydrogenated amorphous silicon (*a*-Si:H). Because ir excitation precludes one-photon band-to-band carrier excitations, this important experiment permits observation of LESR due to defect absorption. It therefore affords a crucial test of models of point-defect statistics in *a*-Si:H.

Previously, Shimizu *et al.*[2] published white-light LESR evidence for charged dangling-bond defects which outnumber neutral dangling-bond defects in the bulk of undoped *a*-Si:H. This evidence was obtained by deconvoluting three LESR lines, two of which have similar g values, widths, and line shapes. In this Comment, I propose that Ristein *et al.*[1] have obtained additional, more direct, experimental evidence for the existence of copious charged dangling bonds in bulk undoped *a*-Si:H at electronic equilibrium.

Ristein *et al.*[1] use a model of bulk *a*-Si:H that includes only neutral threefold-coordinated Si "dangling bonds" (T_3^0) and band tails as defects giving rise to localized electronic states. To fit the ir-LESR data, these authors require that two-step optical-absorption processes are important in the bulk and that very large numbers of surface and near-surface states (up to 10^{14} cm^{-2}) dominate the observed spectra, even in an 8-μm-thick sample. Instead, I fit the data with a model that includes only one-step optical excitations from large numbers of equilibrium charged dangling-bond defects (T_3^+ and T_3^-) formed in the bulk due to sample inhomogeneity. The model predicts a 3:1 ratio of narrow ir-LESR spin density to broad ir-LESR spin density. This simple prediction agrees with the data for thick samples but must be modified to include surface effects in the thinnest sample.

Ristein *et al.*[1] measured samples from two different glow-discharge (GD) deposition systems, *A* and *B*. Relevant characteristics and ESR results from Ref. 1 are found in Table I. Broad and narrow LESR lines can be distinguished. The broad line at $g \simeq 2.011$ is a hole resonance associated with states located in the valence-band tail. The narrow line is a composite of a T_3^0 resonance at $g \simeq 2.0055$ and an electron resonance associated with states located in the conduction band tail with $g \simeq 2.0048$. Unlike Shimizu *et al.*,[2] Ristein *et al.*[1] do not separate these narrow resonances. Charged dangling bonds, T_3^+ and T_3^-, are spinless.

Red light excitation ($\sim$2 eV) yields equal broad (n_b) and narrow (n_n) spin densities in LESR.[1] Electrons and holes excited into the tail resonances mask the light-induced change in dangling-bond spin density. Table I shows the experimentally observed[1] narrow and broad components of the LESR signal under illumination at 40 K by 53 W/cm^2 of ir-laser (1.17 eV) intensity. All spin densities are computed under the assumption of uniform-

TABLE I. Sample characteristics, dark and ir-light-induced ESR data (from Ref. 1).

Sample	Total thickness (μm)	Number of films stacked	Dark ESR ($g \sim 2.0055$) (cm^{-3})	ir-LESR n_n (cm^{-3})	ir-LESR n_b (cm^{-3})
A(8)	8.0	1	1.5×10^{16}	1.8×10^{17}	6×10^{16}
B(0.3)	0.9	3	2×10^{15}	1.5×10^{17}	none
B(3)	9.0	3	2×10^{15}	3.2×10^{16}	1.6×10^{16}

ly absorbed light and uniformly distributed spins.

There are several models of a-Si:H that suggest the bulk undoped material contains T_3^+ and T_3^- defects in addition to T_3^0 defects.[3-5] In each model, material inhomogeneity causes the coexistence of all three dangling-bond charge states. Most recently, Branz and Silver[5] assumed positive U_{eff} and modeled the disorder as electrostatic potential fluctuations. They demonstrated that large numbers of T_3^+ and T_3^- are formed, respectively, in regions of low and high potential whenever the peak-to-peak magnitude of the fluctuations exceeds U_{eff}. In each model,[3-5] charge neutrality ensures that T_3^+ and T_3^- defect densities are equal if no other charged defects or impurities are present.

The resulting density of electronic states is as sketched in Fig. 1. Figure 1(a) (adapted from Ref. 1) shows only the neutral dangling bonds. These, of course, have the $(-/0)$ ionization level from T_3^- to T_3^0 above the Fermi energy (E_F) and the $(0/+)$ level below E_F. Figure 1(b) shows the charged dangling bonds. Each T_3^- defect has a $(-/0)$ level below E_F while each T_3^+ defect has a $(0/+)$ level above E_F. In the model of Ref. 5, the charged defects are formed in regions of large potential fluctuation.

I suggest (see Table II) that surface states are negligible in the 8-μm sample $A(8)$ and consider only bulk transitions to explain its ir-LESR spectra. One-step bulk transition processes are marked by solid arrows in Fig. 1. ir illumination at 1.17 eV cannot excite the band-to-band transition of process 1, which would result in one broad (b) and one narrow (n) spin. Process 4 transitions from tail-to-tail or tail-to-band also result in one broad and one narrow spin ($b+n$), but tail state densities are too low to account for 6×10^{16} cm^{-3} broad LESR spins or an even greater density of narrow spins. Process 2, which excites an electron from the T_3^0 defect to the paramagnetic state located in the conduction band tail is more likely but has no observable effect on either the broad or narrow LESR magnitude. Process 3 results in creation of a broad spin and destruction of a narrow (T_3^0) spin ($b-n$). Until an electron deexcites back into the T_3^+ defect, process 2 may be followed by 2'; the two-step process produces a broad and a narrow spin ($b+n$). Similarly, process 3' ($2n$) can follow process 3 ($b-n$) to produce a broad and a narrow spin ($b+n$). As pointed out in Ref. 1, *none of these processes can account for a larger narrow line than broad line.* To model LESR spectra having $n_n > n_b$ [e.g., sample $A(8)$], with bulk dangling-bond processes, charged dangling bonds must be considered.

Figure 1(b) shows process 5, in which an electron is exited out of a T_3^- defect. This produces two narrow spins ($2n$). Process 6 is excitation of a hole out of a T_3^+ defect ($b+n$). Equal steady-state spin densities due to the one-step processes 5 and 6 result in production of three narrow spins for each broad spin ($3n+b$). Ristein *et al.*[1] observed this 3:1 ratio for sample $A(8)$ (see Table I), suggesting there are *at least* 6×10^{16} cm^{-3} of both T_3^+ and T_3^- defects in this undoped a-Si:H compared to only 1.5×10^{16} T_3^0 defects. This agrees with the prediction of Ref. 5 that charged defects outnumber neutral defects in a-Si:H.

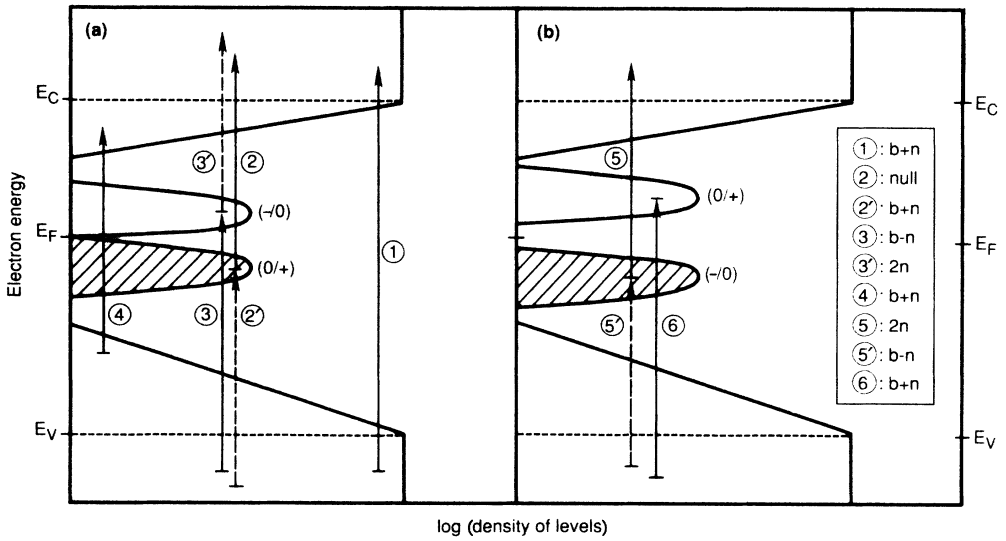

FIG. 1. Schematic diagram of the density of ionization levels for (a) neutral and (b) charged dangling bonds in undoped a-Si:H. Levels filled with an electron are shaded. Single-photon light-induced excitations are marked by solid arrows and the second step of two-step excitations by dotted arrows. The excitation-induced changes in narrow (n) and broad (b) spin resonances are indicated. (a) T_3^0 levels in homogeneous a-Si:H with $U_{\text{eff}} > 0$ (after Ref. 1). (b) Additional T_3^- and T_3^+ levels proposed in inhomogeneous a-Si:H. Shaded and unshaded levels are for equilibrium T_3^- and T_3^+ defects, respectively.

TABLE II. Division of observed LESR lines between surface and bulk in the present model and that of Ref. 1.

	Present model			Model of Ref. 1		
Sample	Surface narrow line (cm^{-2})	Bulk n_n (cm^{-3})	Bulk n_b (cm^{-3})	Surface narrow line (cm^{-2})	Bulk n_n (cm^{-3})	Bulk n_b (cm^{-3})
$A(8)$	4.5×10^{12}	1.74×10^{17}	6×10^{16}	9.6×10^{13}	6×10^{16}	6×10^{16}
$B(0.3)$	4.5×10^{12}	none	none	4.5×10^{12}	none	none
$B(3)$	4.5×10^{12}	1.7×10^{16}	1.6×10^{16}	4.5×10^{12}	1.7×10^{16}	1.6×10^{16}

Samples B are thinner and have a smaller number of T_3^0 defects, so surface effects are likely to be more important than in sample A. As suggested in Ref. 1, LESR of sample $B(0.3)$ measures the surface contribution to the spectra from near the quartz interfaces. A surface accumulation layer would have only T_3^- defects and would be dominated by process 5 ($2n$). If the accumulation layer is uniform and 1000 Å thick,[1] 4.5×10^{12} cm^{-2} narrow spins corresponds to a T_3^- density of about 2.3×10^{17} cm^{-3} in the surface region. The density is therefore larger than the density of bulk defects, at least in a portion of the accumulation layer. Such a high density of T_3^- defects is consistent with the thermodynamic equilibrium theory of defect density since accumulation raises E_F at the surface during growth.[6]

While a thin layer of a-Si:H such as sample $B(0.3)$ need not be charge neutral, thicker layers of a-Si:H [e.g., sample $B(3)$] should be nearly neutral. Charge in the quartz substrate induces electron accumulation in the a-Si:H, but the wide quartz band gap likely prohibits charge transfer to or from the a-Si:H. For films with only dangling bonds and band-tail defects and with E_F near midgap, charge neutrality means equal numbers of T_3^+ and T_3^-, regardless of their spatial distribution. In the first approximation, a 3:1 ratio of n_n:n_b is therefore expected in sample $B(3)$ in spite of the sizable surface T_3^- component. The observed 2:1 ratio (see Table I) agrees qualitatively. Deexcitation rates of T_3^0 defects to T_3^- by recombination with electrons are likely to be higher in the accumulation layer than in normal bulk material due to an electric field which concentrates the excited electrons near the surface. Elevated deexcitation rates of process 5 can explain the reduced (2:1) ratio of n_n:n_p in sample $B(3)$ compared to the expected 3:1 ratio.

The "Present model" columns of Table II summarize my division of the observed spins between surface and bulk states. I assume simply that the surface of sample $A(8)$ has the same spin density as that of sample B. Ristein *et al.*[1] require that $n_n \simeq n_b$ in the bulk of each film. This leads them to conclude that sample $A(8)$ has 9.6×10^{13} cm^{-2} surface LESR spins, *twenty times more per unit area* than samples B. This corresponds to 4.8×10^{18} cm^{-3} T_3^- defects at the surface of sample A, assuming a uniform accumulation layer 1000 Å thick. While sample A may have many more surface-layer states than samples B, I prefer to assume that the surfaces are similar and sample $A(8)$ has a larger LESR signal because of its greater bulk layer thickness.

The assumption of Ristein *et al.*[1] that $n_n \simeq n_b$ in the bulk is also problematic. They require that two-step processes are important in the bulk while ignoring two-step processes at the film surface. In the bulk, only the two-step processes $2+2'$ or $3+3'$ could account for an ir-LESR signal with $n_n \sim n_b$. However, the interpretation of ir-LESR results on sample $B(0.3)$ by Ristein *et al.*[1] suggests that two-step processes are unimportant. No broad line due to hole excitation (process 5′) is observed in sample $B(0.3)$ through the ir-LESR signal is attributed[1] to process 5 in a surface layer of T_3^- defects. If two-step processes occur, the broad line should be observed. Recombination (geminate or otherwise) after excitation from T_3^- or T_3^+ defects should be less rapid than after excitation from T_3^0 because there is no Coulomb attraction between the photogenerated carriers and a defect that is neutral after ionization. Two-step processes involving equilibrium charged defects should be *more* likely than those involving equilibrium T_3^0 defects. In short, if two-step processes involving the T_3^- defect in sample $B(0.3)$ are weak (unobserved), two-step processes involving bulk T_3^0 defects should be even weaker due to Coulomb-assisted recombination.[7]

In conclusion, I propose an alternative explanation of the ir-LESR data of Ref. 1 based upon copious bulk charged defects in undoped a-Si:H. My model does not require large and extremely sample-dependent numbers of surface T_3^- defects. Equal numbers of bulk T_3^+ and T_3^- defects are predicted to yield a 3:1 ratio of broad-to-narrow ir-LESR spins. This is observed in the thickest (8-μm) sample. Spectra of thinner samples are explained by T_3^- defects in an accumulation layer and charge neutrality in the 3-μm a-Si:H layers. The bulk of sample $A(8)$ contains 1.5×10^{16} cm^{-3} neutral dangling bonds and a *minimum* of 6×10^{16} cm^{-3} of each type of charged dangling bond (T_3^+ and T_3^-). The ir-LESR data of Ristein *et al.*[1] and the white-light LESR data of Shimizu *et al.*[2] support models of a-Si:H which predict that charged dangling-bond defects outnumber neutral dangling-bond defects in bulk undoped a-Si:H.[3-5]

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[7]M. Silver (private communication) suggests the 1.2-eV luminescence observed under ir illumination [J. Ristein and P. C. Taylor, J. Opt. Soc. Am. B **6**, 1003 (1989)] may be due to recombination of an electron excited from T_3^- (process 5) and a hole excited from T_3^+ (process 6).