Modulated Electron-Spin-Resonance Measurements and Defect Correlation Energies in Amorphous Silicon

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We show that thermal modulation of the spin density is determined primarily by the defect correlation energy in intrinsic amorphous semiconductors, and is fairly insensitive to Fermi level position. We present temperature-dependent electron-spin-resonance (ESR) measurements for intrinsic hydrogenated amorphous silicon indicating a correlation energy of about 0.3 eV in low-defect-density material. We discuss the previous interpretation of depletion-width-modulated ESR in intrinsic *a*-Si:H as indicating a correlation energy of 0.0 eV.

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Ever since the discovery that defects in chalcogenide glasses such as Se and As_2Se_3 can have *negative* effective correlation energies U—that is, ever since the discovery that charge exchange between identical defects

$$D^0+D^0+U\rightarrow D^+ +D^-$$

can be *exothermic*—it has been clear that experimental constraints on U are crucial to the interpretation of defect experiments [1-4]. The original puzzle in chalcogenides was that the large densities of gap states detected electrically gave no corresponding signal in electron-spin-resonance (ESR) measurements. The puzzle is neatly solved by a negative correlation energy: Only neutral defects are detected by ESR, but with a negative U essentially all defects are charged in equilibrium (half positively and half negatively).

The discovery of negative U in chalcogenide glasses was probably delayed by the absence of experimental techniques which directly address its value and sign. Research on hydrogenated amorphous silicon (*a*-Si:H) benefited from a novel, depletion-width-modulated (DWM) ESR technique developed in 1982 by Cohen, Harbison, and Wecht [5] to probe correlation energies. These "DWM-ESR" measurements were done on phosphorus-doped *a*-Si:H. Initially, the D centers were negatively charged due to doping; spins were created by "depleting" the specimen of electrons, thereby creating spins (neutral D^0 defects). The measurements were consistent with a substantial, positive correlation energy $U>0.2$ eV.

One might expect that the properties of D centers in doped *a*-Si:H and intrinsic (not intentionally doped) *a*-Si:H should be the same, and indeed some early experimental estimates of U were based on this premise. However, it now appears that the optical [6,7] and spin-relaxation [8] properties of the D center vary significantly between specimens, presumably reflecting the relatively large range of configurations possible for a given type of defect in a noncrystalline material. A systematic difference between doped and intrinsic *a*-Si:H is possible and even probable. The first DWM-ESR measurements in intrinsic *a*-Si:H were reported only fairly recently [9]. They were interpreted as evidence for a zero correlation energy, thereby suggesting that most defects in intrinsic *a*-Si:H are charged and undetected by ESR. A summary of the evidence favoring the generalized "charged-defect" view for *a*-Si:H has been given recently [10]. Specifically at issue are the microscopic interpretation of the defect density of states, and the use of ESR measurements for absolute calibration of optical and electrical defect spectroscopies.

In this paper we first discuss further the general relationship of modulated electron-spin-resonance measurements and effective correlation energies. We evaluate both thermal-modulated and depletion-modulated ESR for a conventional model of defects in amorphous semiconductors. The model incorporates both the correlation energy of the defects and also the Fermi level, which may be affected by dopants or by other defects not included in the model. As expected from previous work [5,9], depletion-modulated ESR is quite sensitive to the correlation energy, but it proves to be quite sensitive to the Fermi level as well. Thermal modulation is primarily sensitive to the correlation energy, and is remarkably independent of the Fermi level. We therefore propose that temperature-dependent ESR should be used to estimate U in amorphous semiconductors, and that depletion modulation should be used in conjunction to gauge the doping level.

We then present temperature-dependent ESR measurements for intrinsic *a*-Si:H prepared under a wide range of conditions. These appear to be the first such measurements to be published [11]; we believe that our measurements are sufficiently accurate to detect 1% deviations from Curie-law behavior in the temperature range 77-350 K. We interpret these measurements as indicating a correlation energy of 0.3 eV for the D center in intrinsic *a*-Si:H, and we reinterpret the DWM-ESR data as indicating essentially no inadvertent doping of the specimen.

The principle of the two modulation techniques is illustrated in Fig. 1 for a conventional model [6,7,9] of de-

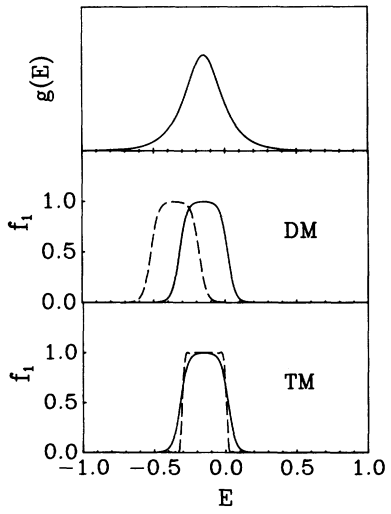

FIG. 1. Calculation of spin densities for a density-of-states model. The upper panel illustrates the density of states $g(E)$. The function $f_1(E)$ in the middle and lower panels is the probability that a defect labeled by E is occupied by one electron for an effective correlation energy $U_{\text{eff}}=+0.3$ eV. The middle panel illustrates $f_1(E)$ for two values of the total electron density n; the lower panel illustrates $f_1(E)$ for two temperatures and a constant value of n.

fects in a-Si:H. The density of states $g(E)$ corresponding to the transition $D^+ + e^- \rightarrow D^0$ is illustrated in the top panel. The density of spins N_s is determined in this model using the probability $f_1(E)$ that a defect is singly occupied: $N_s = \int g(E) f_1(E) dE$. $f_1(E)$ is evaluated using textbook statistical mechanics for sites D^+, D^0, and D^- charge states [12]:

$$f_1(E) = \{1 + \tfrac{1}{2}\exp[\beta(E-\mu)] + \tfrac{1}{2}\exp[-\beta(E-\mu+U)]\}^{-1}. \quad (1)$$

μ is the electronic chemical potential (or Fermi level) determined by the total density of electrons n; $\beta \equiv 1/k_B T$. We assume that defects have a common correlation energy U despite the distribution of level positions E. The solid curve in the middle panel of Fig. 1 illustrates the function obtained for $\mu = 0.0$ eV and $U = +0.3$ eV. The upper cutoff in this curve is at μ, as for ordinary Fermi statistics. The lower cutoff is at $\mu - U$. Levels lying deeper than $\mu - U$ are doubly occupied, and hence f_1 declines to zero.

In an ideal depletion-modulation experiment, the chemical potential μ would be lowered by depleting the total density of electrons n. The new function $f_1(E)$ which might result is illustrated by the dashed curve of the middle panel; there is of course a corresponding change in spin density. Lowering the specimen temperature can also affect the spin density; the lower panel of Fig. 1 illustrates the effects of changing temperature while leaving the electron density n constant. The cutoffs in f_1 become sharper at lower temperature. There is also a change in μ, although this effect is not obvious in the illustration.

We found it simplest to study the depletion and thermal effects in this model using numerically evaluated partial derivatives of $N_s(n,T)$. We define the depletion modulation of the spin density $\text{DM} \equiv \partial N_s/\partial n$, and we define the thermal modulation $\text{TM} \equiv (\partial N_s/\partial T)/N_s$. We used the density of states illustrated in Fig. 1:

$$g(E) = (N_D/\pi\Delta E)\,\text{sech}[(E-E_0)/\Delta E]. \quad (2)$$

N_D is the total density of defects; note that TM and DM are independent of N_D. We chose a value for ΔE which yields a FWHM width of 0.3 eV; this value is consistent with the optical measurements [6,7], and was used in the previous work on depletion modulation [9].

In Fig. 2 we illustrate how DM and TM depended upon the density of electrons $(n-N_D)/N_D$ near 360 K. If no dopants or other defects are present, the ratio $(n-N_D)/N_D$ is zero; doping or other defects cause $(n-N_D)/N_D$ to vary between -1 and $+1$. Consider first an empty defect system with $(n-N_D)/N_D = -1$. When $U = 0.3$ eV, adding an electron increases the mean number of spins by almost 1.0 (DM = 0.9). As the electron density n increases, DM declines to zero because of the increasing population of D^- states. DM is an odd function of $(n-N_D)/N_D$; for a nearly full system $[(n-N_D)/N_D = +1]$, adding an electron decreases the spin density. As illustrated, DM also falls substantially as U

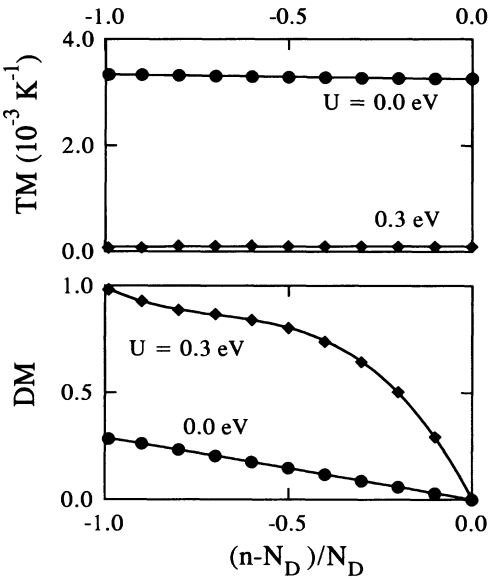

FIG. 2. Dependence of depletion-modulated ESR $\text{DM} \equiv \partial N_s/\partial n$ and thermal-modulated ESR $\text{TM} \equiv (\partial N_s/\partial T)/N_s$ upon the excess electron occupancy $(n-N_D)/N_D$ due to doping effects. The points were computed numerically from the defect model of Fig. 1; the curves are guides. Results for two correlation energies U are plotted.

decreases; for negative U essentially no spins are present for any Fermi level.

Thermal modulation exhibits a dependence upon U which is nicely complementary to that of depletion modulation. For $U=0.0$ eV TM is of order $1/T$, and it declines to nearly zero for $U=0.3$ eV. On the other hand, TM *hardly depends upon the Fermi level at all.* This feature makes TM simpler to use than DM when doping levels are poorly known.

We now discuss experimental determination of TM in a-Si:H. In Fig. 3 we have presented temperature-dependent measurements of the product $S(T)T$ of the absorption susceptibility $S(T)$ (measured using electron spin resonance) and the specimen temperature T. This product eliminates the $1/T$ Curie-law temperature dependence of the susceptibility anticipated for isolated spin $=\frac{1}{2}$ defects, and hence is interpretable as the temperature-dependent spin density $N_s(T)$. Since we are only interested in the form of $N_s(T)$, we have normalized the data so that the apparent $T=0$ K intercept is 1.0.

The various symbols correspond to different a-Si:H specimens, as explained in the caption. The specimens were deposited using a commercial plasma deposition system (Plasma Technology, Inc. "Plasmalab") operating with 200 mtorr of SiH_4. Specimens with widely varying spin densities were obtained by varying the substrate temperature during deposition, and by subsequent thermal quenching and annealing treatments in some cases. ESR measurements were done with a commercial spectrometer (Varian, Inc. model E-9; 100 kHz magnetic-field modulation). Temperature-dependent measurements were performed with the specimen inside a quartz insert in the microwave cavity; only the insert and the specimen were cooled using flowing nitrogen gas. We determined the effects of changing the insert temperature upon the cavity Q using a high-sensitivity microwave reflectivity technique. We found about a 4% change in Q as the insert temperature changed between 300 and 77 K. We checked this calibration using a ruby (0.1% Cr^{3+}), which exhibited a 2% deviation from Curie behavior between 77 and 300 K. Further details of our procedures are given elsewhere [13].

It is crucial to use low microwave power for temperature-dependent measurements to avoid microwave saturation effects. We chose a power of 0.004 mW, based on previous studies [8,14]. We subsequently discovered that the uppermost curve of Fig. 3 was slightly saturated below 150 K, which accounted for the deviation from linear behavior for this curve. This specimen was deposited at 150°C; the anomalous saturation behavior largely disappeared upon annealing at 220°C (data presented as open circle symbols).

We also explored the role of interface states on these Curie-law deviations by studying the effects of specimen thickness for specified deposition and annealing conditions. For the two upper curves in Fig. 3 the areal spin density (spins per cm^2 of specimen) was accurately proportional to the specimen thickness, confirming that these data are characteristic of the specimen bulk. For better specimens we measured an interfacial spin density of 2×10^{12} cm^2. The lowest curve in Fig. 3 is thus entirely due to interfacial states, and we concluded from these data that there is no significant non-Curie behavior for interfacial spins.

We estimated the thermal-modulation parameter TM $=(\partial N_s/\partial T)/N_s$ from the slopes of the linear temperature dependence, as indicated in Fig. 3. For specimens with areal spin densities comparable to the interfacial density of 2×10^{12} cm^{-2} we calculated the slopes after subtracting a (temperature-independent) interfacial spin density 2×10^{12} cm^{-2} to estimate the bulk spin density N_B. We did not explicitly measure the temperature dependence of the entire thickness series in these specimens.

In Fig. 4 we show the correlation of TM with the bulk spin density N_B; the error bars indicate the statistical un-

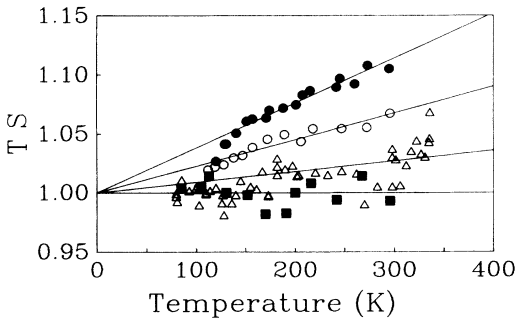

FIG. 3. Temperature-dependent measurements of the resonant absorption susceptibility $S(T)$ for four specimens of a-Si:H. The vertical axis is the product $S(T)T$, which compensates for the Curie-law dependence of $S(T)$; the measurements for each specimen were normalized so that the $T=0$ K limit is 1.0. The average spin densities and the thicknesses of the specimens were ●: 1.4×10^{19} cm^{-3}, 8.1 μm; ○: 1.2×10^{18} cm^{-3}, 8.1 μm; △: 5×10^{16} cm^{-3}, 3.0 μm; ■: 1.1×10^{16} cm^{-3}, 1.6 μm.

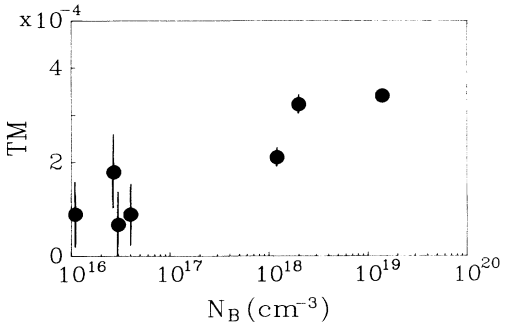

FIG. 4. Correlation of the thermal modulation (TM) of the spin density with the bulk spin density N_B for seven specimens of a-Si:H. TM was evaluated using straight-line fits such as shown in Fig. 3; a correction for interfacial spins was applied to the specimens with $N_B < 10^{17}$ cm^{-3}. The error bars indicate the standard deviation of independent thermal cycles.

certainties in the slope estimates. We estimate that "bulk spins" in a-Si:H of typical device quality exhibit a thermal modulation of $(1-2)\times10^{-4}$ K^{-1}, which corresponds to a deviation from Curie dependence of (2-4)% between 100 and 300 K. Poorer specimens exhibit a thermal modulation of nearly 4×10^{-4} K^{-1}. Such a systematic variation appears compatible with other inhomogeneities in D center effects noted in the introduction; a microscopic interpretation is probably premature. It surprised us that interfacial spins gave no detectible Curie-law deviation, since we might assume that these spins should be characteristic of poor a-Si:H. Presumably the surface and bulk microstructures in a-Si:H leading to defects in the two regions are different.

We shall interpret these measurements using the conventional model presented in Figs. 1 and 2. A "device-grade" material with TM of 10^{-4} K^{-1} corresponds to $U=0.3$ eV; this fitting is essentially independent of the measurement temperature between 77 and 400 K. "Poor-quality" a-Si:H corresponds to a lower value $U=0.2$ eV. A better way to describe the implications of the TM data is to estimate the ratio N_s/N_D of the spin density to the total defect density N_D. This ratio depends less strongly on the particular parameters of $g(E)$; we obtained $N_s/N_D\sim0.75$ when TM $=10^{-4}$ K^{-1}. Thus these temperature-dependent ESR data agree broadly with earlier estimates of U based on interpretations of infrared absorption measurements [6,7], and they support the widespread use of the spin density N_s as an estimate for the total density of deep levels in a-Si:H.

We now discuss the relationship of these TM measurements and the earlier DWM-ESR work. Essick and Cohen [9] reported a depletion effect $\Delta N_s/\Delta n\sim0.14$ for the five different "light-soaking" states of the specimen. They proposed that $U\sim0.0$ eV using a similar correlation energy model and density of states to that used here. Their estimate for U reflects their assumption about the Fermi level. They chose the value $(n-N_D)/N_D=-0.5$ [15], corresponding to a nominal degree of inadvertent doping of the specimen. Equating $\Delta N_s/\Delta n=+0.14$ =DM, their value $U=0.0$ eV obtains from Fig. 2. Essick and Cohen argued that, if the specimen were truly undoped and had a larger U, it would be unlikely that the five light-soaking states (with five different spin densities) should have yielded essentially the same value for $\Delta N_s/\Delta n$. Light soaking presumably modifies $(n-N_D)/N_D$, and thereby DM.

We interpret these measurements as follows. The temperature-dependent measurements establish U fairly unambiguously given a basic density-of-states model. DWM-ESR can then be used to estimate the inadvertent doping level in intrinsic a-Si:H; for $U\sim0.25$ eV we found [16] that $(n-N_D)/N_D$ is indistinguishable from zero based on Essick and Cohen's data.

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[1] P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).

[2] R. A. Street and N. F. Mott, Phys. Rev. Lett. **35**, 1293 (1975).

[3] M. Kastner, D. Adler, and H. Fritzsche, Phys. Rev. Lett. **37**, 1504 (1976).

[4] D. Adler and E. Yoffa, Phys. Rev. Lett. **36**, 1197 (1976).

[5] J. D. Cohen, J. P. Harbison, and K. W. Wecht, Phys. Rev. Lett. **48**, 109 (1982).

[6] J. Kocka, M. Vanacek, and F. Schauer, J. Non-Cryst. Solids **97&98**, 715 (1987).

[7] Z. Vardeny, T. X. Zhou, H. A. Stoddart, and J. Tauc, Solid State Commun. **65**, 1049 (1988).

[8] Sufi Zafar and E. A. Schiff, in *Amorphous Semiconductor Technology-1989*, edited by Arun Madan *et al.* (Materials Research Society, Pittsburgh, 1989), p. 113.

[9] J. M. Essick and J. D. Cohen, Phys. Rev. Lett. **64**, 3062 (1990).

[10] Howard M. Branz and Marvin Silver, Phys. Rev. B **42**, 7420 (1990).

[11] Some work has been done by other groups on temperature-dependent spin densities, but was not published; see M. Stutzmann and W. B. Jackson, Solid State Commun. **62**, 153 (1987); and F. Finger, Ph.D. thesis, Phillips Universität, Marburg, 1988 (unpublished). We believe this work to be consistent with our measurements.

[12] N. W. Ashcroft and N. David Mermin, *Solid State Physics* (Holt, Rinehart, and Winston, New York, 1976), p. 586.

[13] J.-K. Lee, Ph.D. thesis, Syracuse University, 1991 (unpublished).

[14] M. Stutzmann and D. K. Biegelsen, Phys. Rev. B **28**, 6236 (1983).

[15] J. M. Essick, Ph.D. thesis, University of Oregon, 1989 (unpublished).

[16] J.-K. Lee and E. A. Schiff, in *Amorphous Silicon Technology-1991*, edited by A. Madan, Y. Hamakawa, M. Thompson, P. C. Taylor, and P. G. LeComber (Materials Research Society, Pittsburgh, 1991), p. 605.