

Observation of a Novel Relaxation Process Associated with Electronic Transitions from Deep (D) Defects in Hydrogenated Amorphous Silicon

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Junction capacitance transient measurements were employed to study the thermal emission of electrons trapped in deep (D) defects in lightly n -doped a -Si:H samples. We conclude that a novel defect relaxation process occurs upon a change of charge state of the defect such that an electron's thermal release rate is inversely proportional to its residence time in the defect. Supplemental spin transient measurements indicate that both D^-/D^0 and D^0/D^+ transitions must be involved. A good fit to our data is obtained if we assume a non-Markovian process for the D^0/D^+ transition.

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The dominant deep defect (D) in the mobility gap of hydrogenated amorphous silicon (a -Si:H) has received enormous attention in efforts to understand the electronic properties of this material. Initially identified through ESR spectroscopy [1], this center was subsequently shown to give rise to a band of thermal [2,3] and optical [4,5] transitions near midgap. Important aspects of the structure of this defect have remained unresolved: for example, why the different charge states of this defect (D^+, D^0, D^-) appear to occur at different energies in doped versus intrinsic samples, and whether the correlation energy between the two electron transitions (D^-/D^0 and D^0/D^+) is significantly positive (≥ 0.2 eV [3,6,7], or fairly small (< 0.1 eV) [8,9].

In this Letter we report recent studies of thermally excited electronic transitions from this defect using junction-capacitance-based charge transient measurements [2] and spin transient measurements obtained from depletion-width-modulated electron spin resonance (DWM ESR) [3,9]. Both methods were applied to the same lightly n -doped samples encompassing a wide range of Fermi-level positions. We hoped to identify an intermediate case between the defect's apparent different electronic structures in n -type versus intrinsic material and thus distinguish between two proposed reasons for this difference: (1) The "defect pool model," in which the Fermi-level position affects the manner (and energy distribution) over which D defects will form [10,11]; and (2) the possible predominance of intimate dopant-defect pairs in doped material, altering the behavior of those D defects compared to intrinsic material [12,13]. Instead, we found conclusive evidence for a new type of defect relaxation process which results in a change in the D defect's thermal energy within the gap following a change in its charge state. We believe that it is this relaxation process that provides the correct explanation for the apparent differences in defect properties noted above.

Samples for both DWM ESR and capacitance measurements were deposited simultaneously on identical p^+ c -Si substrates by the glow discharge method from PH_3/SiH_4 gas mixtures diluted 1:1 with argon. Schottky diodes needed for both techniques were obtained by evaporating semitransparent Pd contacts onto the amorphous

layer. Two samples, with 10 and 19 volppm (parts per million by volume) PH_3/SiH_4 ratios, were studied in detail and gave qualitatively identical results.

Fermi-level positions quoted for our samples were obtained by measuring the activation energies of the dark conductivity. We varied these Fermi energies E_F in each sample using light soaking [14] followed by a sequence of partial anneal treatments at increasing temperatures. We found that E_F could be accurately manipulated over a range of several tenths of eV in this manner due to the metastable activation and deactivation of phosphorus dopants [15]. It was found most informative to position E_F deep enough to avoid the participation of conduction band tail states, yet shallow enough to ensure the complete filling of the D defect band; i.e., $0.6 \text{ eV} \geq E_C - E_F \leq 0.4 \text{ eV}$.

Charge emission from deep gap states was studied using voltage-filling-pulse capacitance transient measurements [2]. We estimate the release of trapped defect charge, $N_Q(t)$, from the capacitance emission transient, $C(t)$, using the depletion width approximation: $N_Q(t) \propto C^2(\infty) - C^2(t)$. For n -type samples this expression agrees with a more detailed numerical analysis [16] within a few percent. Representative trapped charge transients for a series of filling pulse widths, t_p , are shown in Fig. 1 for the 420-K anneal state of the 19-volppm sample ($E_F \approx 0.50$ eV). Assuming a typical emission rate prefactor ν of 10^{13} s^{-1} [2], the five decades of emission time displayed correspond to a range of thermal activation energies from about 0.7 to 1.0 eV.

Because all the transients seem to approach the same limiting value of junction capacitance at short times, we conclude that the same number of electrons are being captured into deep defects even for filling pulses of less than 1 ms duration. Therefore, the marked variation of the resultant transients with filling pulse is not due to a change in the *fraction* of defects capturing electrons, but to a change in the *time scale* of the subsequent thermal emission. The characteristic emission time for each transient, defined as the time for the defect to lose 50% of its captured charge, is plotted as a function of t_p for several temperatures in Fig. 2. This figure indicates that a well-defined activation energy for the thermal release rate ex-

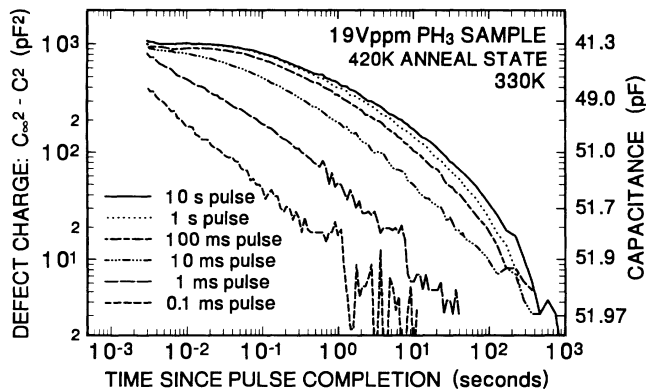


FIG. 1. Charge emission transients derived from 10-kHz capacitance transients for the 420-K anneal state of the 19-volppm PH₃-doped sample. These data were obtained at 330 K with a -2-V bias and pulsing to 0 V with the pulse widths indicated. The asymptotic capacitance value, C_∞, is 52.0 pF and the total trapped defect charge at t = 0 is approximately 5 × 10¹⁷ cm⁻³.

ists in the long-filling-pulse limit; however, the emission rate appears nearly temperature independent for short filling pulses.

The above variation of emission times implies a change in the thermal emission energy for trapped electrons on each defect, indicating some form of configurational relaxation. This conclusion is corroborated by our previously published work showing that, in similar anneal states of our lightly doped samples, the optical energy threshold for the release of trapped charge from these defects can be much larger (~1.3 eV) than the corresponding thermal energy (~0.8 eV) [17]. On the other hand, the observed behavior is unusual compared to known examples of deep defect configurational relaxation in crystalline semiconductors, since it displays a nearly continuous range of emission rates.

Complementary information is obtained on the spin of the emitting defects by examining DWM ESR spin transients. Figure 3 shows two spin transients for the 420-K anneal state of our 10-volppm sample. The intermediate part of these transients is spin creating, and thus indicates

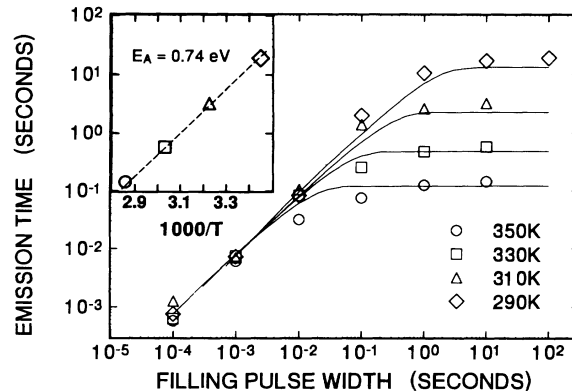


FIG. 2. The dependence of the thermal emission time with filling pulse width for the 420-K anneal state of the 19-volppm PH₃-doped sample for several temperatures. The thin solid lines indicate results of calculations based on our defect relaxation model. Inset: The variation of the saturation values with temperature.

a predominance of D⁻/D⁰ defect transitions. At longer times the defect spin remains fairly constant in spite of continued charge loss from the defects. This indicates a combination of D⁻/D⁰ and D⁰/D⁺ transitions. Also, when the filling pulse width is increased from 30 to 300 ms the time scale for the spin transient is increased by roughly a factor of 2, exactly the same as for the corresponding capacitance transients. Finally, for the 30-ms pulse we observe that the initial portion of the transient is spin annihilating, indicating D⁰/D⁺ transitions.

These data imply that the emission rate of electrons from the defect to the conduction band decreases as the occupation time of the electron in the defect increases. Moreover, the charge transients are very nearly identical when shifted horizontally on the logarithmic time axis (see Fig. 1). That is, to a good approximation: t_p → at_p implies N_Q(t) → N_Q(βt) with β ≈ a for the short pulse regime. This general scaling law appears to be obeyed over a large range of temperatures and for most metastable states of both our 10- and 19-volppm PH₃-doped samples.

While the duration of the filling pulse sets the average

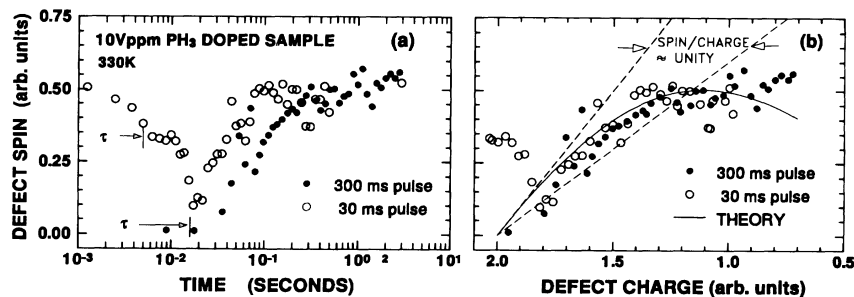


FIG. 3. (a) Spin transients for the 420-K anneal state of the 10-volppm PH₃-doped sample for two different filling pulses. (Each transient represents over 200 h of signal averaging.) The arrows indicate the instrumental time constants τ. Thus, only the data points at longer times represent the actual spin behavior. (b) The same spin transient data plotted against the defect charge obtained by concurrent capacitance transient measurements. The dashed lines indicate the range of a 1:1 spin-to-charge ratio consistent with our calibration procedure. The solid line is the spin behavior predicted using our defect relaxation model.

time of electronic occupation before the emission phase begins, we believe that the emission rate continues to decrease as long as the defects hold onto their electrons. This continued relaxation thus accounts for the very nonexponential, nearly power-law decays exhibited in Fig. 1. Indeed, a power-law decay is a necessary consequence of the stated scaling law itself since if we write

$$\frac{dN_Q}{dt} = -r(t)N_Q \quad (1)$$

to indicate that the emission rate $r(t)$ depends on the total occupation time of the defect, then the scaling law implies that

$$\int_{t_p^{\text{eff}}}^{t+t_p^{\text{eff}}} r(t') dt' = \int_{at_p^{\text{eff}}}^{a(t+t_p^{\text{eff}})} r(t') dt', \quad (2)$$

where t now indicates the elapsed time since the end of the filling pulse, and where t_p^{eff} is equal to t_p for short pulses, and is defined more generally such that $r(t_p^{\text{eff}})$ is equal to the initial emission rate at the end of the filling pulse. Equation (2) can be satisfied for arbitrary a if and only if $r(t) = c/(t+t_p^{\text{eff}})$ for some constant c . This form of $r(t)$ together with Eq. (1) implies the power-law dependence for N_Q ; specifically, $N_Q(t, t_p^{\text{eff}}) \propto (1+t/t_p^{\text{eff}})^{-c}$.

Thus the time for an electron to be emitted is proportional to the residence time of the electron in the defect. This type of behavior suggests a hierarchical relaxation process of a general type proposed for glassy systems [18]. A plausible physical picture is that a D^- defect creates a positive polarization cloud in its vicinity (due perhaps to the flexibility of bonds in the amorphous network or to mobile, charged H species). This deepens the potential well for the trapped electron in a manner that proceeds more and more slowly with time. To account for our observations, the spatial extent of the cloud would

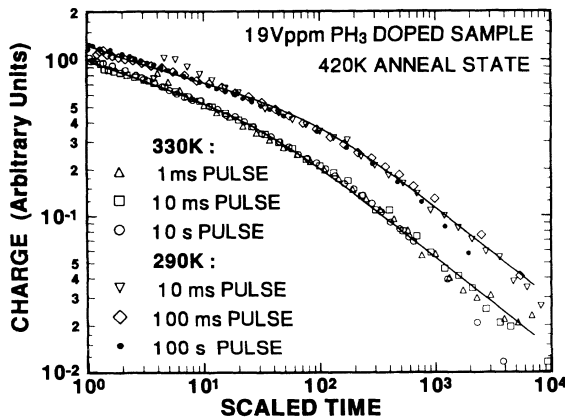


FIG. 4. The charge emission data for the 420-K anneal state, 19-volppm PH_3 sample vs the rescaled time: $x = 1 + t/t_p^{\text{eff}}$. The data for two measurement temperatures have been offset vertically for display purposes. The overlap of the data points obtained for different pulse widths at each temperature demonstrates a scaling law. The solid lines are fits to these data calculated from our defect relaxation model with $c=0.58$, and $c/d=4$ (330 K) or 8 (290 K).

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coalesce to $\sim 30 \text{ \AA}$ in the vicinity of the defect at long times.

In Fig. 4 we have plotted the data of Fig. 1, plus that taken at a second temperature, against the rescaled time, $1 + t/t_p^{\text{eff}}$. These data do indeed follow the scaling property quite well, but actually seem to exhibit *two* distinct power-law regimes with different slopes. This is actually *inconsistent* with Eq. (1) which can only lead to a single power law. This implies that $r(t)$ must also depend on N_Q , the average occupation of the defects. However, due to the low defect concentration ($\sim 10^{17} \text{ cm}^{-3}$) an N_Q dependence cannot arise from interactions between defects; rather, it must result from changes in occupation of each defect independently. This can happen if a substantial fraction of defects undergo *two* successive emission events: D^-/D^0 and D^0/D^+ . The spin transient data of Fig. 3 confirm this.

We thus attempted to model $N_Q(t)$ using the coupled equations:

$$\frac{dN_2}{dt} = -r_2(t)N_2, \quad \frac{dN_1}{dt} = r_2(t)N_2 - r_1(t)N_1, \quad (3)$$

where N_2 denotes the number of doubly occupied defects, N_1 the number of singly occupied defects, and $N_Q = 2N_2 + N_1$. The form $r_2(t) = c/(t+t_p^{\text{eff}})$ is again required by the previous argument, and we examined a number of cases for $r_1(t)$ consistent with the scaling law [19]. However, none of these gave reasonable fits.

We then surmised that $r_1(t)$ might depend on the extent of the polarization cloud that had developed during the period that the defect had been in its doubly occupied state. In such a case the process describing the D^0/D^+ transition would be *non-Markovian*, possessing a memory of the duration, t_2 , of the D^- state, and implying that $r_1 = r_1(t, t_2)$. The mathematics describing such a simple non-Markovian process are straightforward, but require reformulating Eqs. (3) in terms of integral equations.

A fairly general form for r_1 was examined,

$$r_1(t, t_2) = \frac{d}{t_2 + t_p^{\text{eff}}} \left(\frac{t + t_p^{\text{eff}}}{t_2 + t_p^{\text{eff}}} \right)^\eta, \quad (4)$$

which yields an exact solution for $N_Q(t)$. Equation (4) includes one Markovian case ($\eta = -1$) plus the case where the polarization cloud becomes frozen after the emission of the first electron ($\eta = 0$). We obtain

$$N_Q(x) = 2x^{-c} + x^{-c} \frac{c}{\eta+1} \left[\frac{\eta+1}{d} \right]^{c/(\eta+1)} \times \int_{d/(\eta+1)}^{x^{(\eta+1)d/(\eta+1)}} p^{-[1-c/(\eta+1)]} e^{-p} dp, \quad (5)$$

where $X = 1 + t/t_p^{\text{eff}}$ and the integral may be expressed in terms of incomplete gamma functions. The two terms on the right-hand side of Eq. (5) correspond to the number of electrons in doubly and singly occupied defects, respectively.

Reasonably good fits to the data could be obtained for $0 \geq \eta \geq -0.5$. The solution assumes a simpler form with

only two free parameters when $\eta = c - 1$ and still provides quite satisfactory fits to the data as shown in Fig. 4. Physically, the ratio c/d is related to the local effective correlation energy, U_{eff} , between the one- and two-electron states of the defect [perhaps $U_{\text{eff}} = k_B T \ln(c/d)$], and c itself depends on the relative rates between emission and relaxation of the electrons in the defect. Good fits were obtained for temperatures from 290 to 350 K and indicate that d increases with T , while c is constant or increases slightly. In all cases we found the ratio c/d to be 10 or less, implying $U_{\text{eff}} < 0.1$ eV.

Further verification of this analysis is provided by our spin transient data. For the 10-volppm PH_3 -doped sample, we fitted the 330 K charge transient data in the same manner as in Fig. 4. This fit then predicts the dependence of the spin on the defect charge with no additional adjustable parameters. This prediction is shown as the solid line in Fig. 3(b) with only a slight adjustment in its overall magnitude as allowed by the $\pm 25\%$ experimental uncertainty in the spin/charge calibration. The agreement with the spin data is fairly compelling. We also tried to observe the predicted decrease of the spin signal at longer emission times but, due to the low spin signal levels, were unable to verify this unambiguously. We should note that the observed similar emission rates for D^-/D^0 and D^0/D^+ do not alone totally preclude a larger value of U_{eff} [20]. However, with the small correlation energy suggested, our analysis explains how the early phase of charge emission can exhibit a nearly 1:1 spin/charge ratio while, in a later regime, yield a very small value. Thus we can account for DWM ESR results previously published for n -doped and intrinsic samples [3,9].

A final aspect of our proposed defect relaxation process is demonstrated in the fits to the data of Fig. 2. If the D^-/D^0 emission rate decreases during the time the defect holds two electrons due to formation of a positive polarization cloud, then this polarization cloud must disperse when the defect loses an electron. This implies that the D^-/D^0 transition rate (if the defect again captures a second electron) will have *increased* during the time the defect was in its D^0 state. During the filling pulse, defects continually capture and re-emit electrons eventually reaching a dynamic equilibrium which determines the thermal emission rate in the long-filling-pulse limit. We know the decrease in emission rate for the D^- state from $r_2(t)$, but must guess the dependence of the reverse process. This introduces two parameters which are chosen once to produce all the fits shown in Fig. 2. The details of this calculation are to be presented elsewhere.

Recent modulated photocurrent studies on intrinsic samples suggest that the prerelaxed D^- center can exhibit a D^-/D^0 thermal transition energy as shallow as 0.55 eV [21], while the same transition from the fully relaxed D^- state exceeds 0.8 eV [2]. Our model of the relaxation process also implies that the thermal equilibrium energy of the D^-/D^0 transition will become deeper as E_F

becomes shallower, a characteristic generally taken to support the defect pool model [10,11]. Our results thus suggest that this is caused by defect *relaxation* rather than changes in the defect *formation* process. Indeed, the time scale of the relaxation process reported here is 10^4 to 10^5 faster than that observed in metastable creation and annealing of defects [22]. Nonetheless, an intimate connection between these two aspects of defect dynamics in a -Si:H is quite likely and is an important area of future study.

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