Charge Redistribution Process on Gap States in Hydrogenated Amorphous Silicon

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The charge relaxation in an electron capture process on the continuously distributed gap states in *a*-Si:H has been analyzed. It is shown that a process of charge redistribution among the gap states occurs during a filling pulse, causing the thermal emission energy of the trapped electrons to shift deeper into the mobility gap. For an exponential distribution of gap states, an electron's thermal emission time is proportional to the filling pulse width. These results provide a natural explanation for the recently reported results on a junction capacitance transient experiment, which were attributed to a novel defect relaxation process.

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Defects in the energy gap of hydrogenated amorphous silicon (*a*-Si:H) have been investigated extensively in the past decade due to their role in controlling electronic properties of this material. However, controversy over the origin and nature of these gap states continues. For example, it is not clear whether the difference in the distribution of gap states in *n*-type material compared to intrinsic material is caused simply by the Fermi-level position [1,2], or whether it is due to the formation of intimate dopant-defect pairs in doped material [3,4]. In an attempt to study the role of the Fermi-level position in the creation of the deep defects, Cohen, Leen, and Rasmussen recently studied gap states in lightly *n*-doped samples using junction capacitance transient measurements and depletion-width-modulated electron spin resonance measurements [5]. The charge transients, $N_Q(t)$, were measured for various filling pulse widths, t_p, and were found to obey a power law. The most striking feature observed in their study is that for short filling pulses, the thermal emission rate of a trapped electron is inversely proportional to its occupation time in the defect and is nearly temperature independent. In the long filling pulse limit, the emission rate reaches a saturation limit which depends on temperature as defined by an activation energy. In addition, a scaling law was found to describe the charge transients such that when $t_p \rightarrow \alpha t_p$, then $N_Q(t) \rightarrow N_Q(\beta t)$ with $\beta \approx \alpha$ for the short pulse regime [5]. The above results were concluded to result from a new type of defect relaxation process which occurs upon a change of charge state of the defect. Cohen, Leen, and Rasmussen speculated that a D^- defect creates a positive polarization cloud in its vicinity that deepens the potential well for the trapped electron. However, a quantitative connection between the postulated polarization and the observed scaling-law dependence of the emission was not made. The purpose of this Letter is to show that the novel charge transient behavior observed in the junction capacitance experiment can be fully understood without invoking any kind of defect relaxation. It will be shown that the deepening of the emission energy is merely a consequence of charge redistribution among the continuously distributed gap states through the mechanism of multiple trapping. Both the observed scaling-law dependence and the temperature dependence are explained by charge redistribution.

The phenomenon of charge redistribution has been observed in Si-doped $Al_xGa_{1-x}As$ [6], where the *DX* center (a distorted configuration of the donor state) can trap two electrons due to its negative-*U* characteristics. In principle, a charge redistribution process can occur in any multiple-energy-level system having more trap states than total free carriers. Thus, the charge redistribution process can occur in *a*-Si:H because of the large number of gap states compared to the free carriers provided by the dopants. In this Letter, the redistribution process is analyzed for *a*-Si:H, where the deep defect levels are distributed continuously. An analytical expression of the defect charge transient is derived in the short-pulse-width and long-pulse-width limits. Numerical calculations are made that include the whole range of filling conditions. It will be shown that the charge redistribution process provides a simple and accurate description of the previous experimental results.

In the junction capacitance experiment, at any time t, during and after a filling pulse, the defect charge concentration, i.e., the total trapped charge in the gap states, is simply the integral over the band gap of the product of the distribution of gap states, $g(E)$, and the occupation function, $f(E,t)$, where E is the energy with the zero point chosen at the conduction band edge. Assuming a constant value of capture cross section for all the gap states considered, and because $g(E)$ usually changes less rapidly with energy than the Boltzmann tail of the Fermi-Dirac distribution, the occupation function can be approximated by a step function. In this case, the trapped charge during the filling pulse is given by

$$N_Q(t) = f \int_{E_F}^{E_d} g(E)\,dE\,, \tag{1}$$

where E_F is the Fermi level in the *space charge* region *before* the beginning of the filling pulse, E_d is a demarkation energy which separates the empty states and the par-

tially occupied states, and f is the fractional occupation number for states between E_d and E_F. During the fill pulse, f varies from 0 to 1 and E_d varies from E_c to E_F^n (the Fermi level in the neutral region). After the end of the fill pulse, f is constant while E_d approaches E_F as the carriers are thermally emitted. Because of the high density of gap states, most of the free electrons can be captured almost immediately after the filling pulse begins [7]; thus, $N_Q(t)$ can be approximated as a constant, n_{c0}, for t within the filling pulse, where n_{c0} is the free electron concentration at the beginning of the filling pulse. Note that n_{c0} is not the same as the free carrier concentration in the neutral region. Using this approximation and assuming an exponential distribution of gap states in the upper half of the band gap, given by

$$g(E)=g_0\exp(E/kT_0)\,,$$

where g_0 and T_0 are constants, the relationship between f and E_d can be obtained by integrating Eq. (1). Using this relationship, the defect charge following a filling pulse with length t_p reduces to

$$N_Q(t)=n_{c0}\exp\{[E_d(t)-E_d(t_p)]/kT_0\}\quad(\text{for } t>t_p),\quad(2)$$

where N_Q has been simplified by neglecting the term $\exp(E_F/kT_0)$. Equation (2) implies the scaling law described in Ref. [5].

In the case of a short filling pulse, a large fraction of the states below E_d are unoccupied for the whole period of filling pulse. Thus, the electrons that are released from the states near E_d can be effectively recaptured by the deeper states. In such a case, the time dependence of the demarkation energy is approximately determined by the thermal release rate of the shallowest occupied levels, i.e., t^{-1}. Thus $E_d(t)=-kT\ln(\nu_n t)$, where ν_n is the attempt-to-escape frequency, and t is the time from the beginning of a filling pulse. Defining time t' as the time after the fill pulse and substituting $E_d(t')$ into Eq. (2) gives $N_Q(t')=n_{c0}(1+t'/t_p)^{-c}$, where $c=T/T_0$. Using the definition for the characteristic emission time t_e for a transient as the time for half of the trapped charge to be emitted, the characteristic emission time is $t_e=t_p(2^{1/c}-1)$. Thus, in the short-pulse-width limit, the characteristic emission time is proportional to the duration of the filling pulse, consistent with the experimental results of Ref. [5]. For a constant width of filling pulse, the emission time is only weakly temperature dependent in this regime.

During a long filling pulse, once the demarkation energy approaches the Fermi energy in the neutral region, E_F^n, it becomes nearly constant. Under these conditions the time dependence of the demarkation energy *after* the completion of the pulse can be written as

$$E_d(t')=-kT\ln[\nu_n(t_s+t')]\,,$$

where $t_s=\exp(-E_F^n/kT)/\nu_n$. Replacing t_p from the short pulse limit with t_s for the long pulse limit gives the characteristic emission time $t_e=(2^{1/c}-1)\exp(-E_F^n/kT)/\nu_n$. In the long pulse limit, t_e is independent of the filling pulse duration and the temperature dependence of t_e is now defined by an activation energy, $E_a=kT_0\ln 2-E_F^n$, again in agreement with the experimental results.

In order to find the exact solution of the charge redistribution in a general case, the rate equations that govern the capture and emission kinetics on the gap states must be solved numerically. The distribution of trapped electrons in the space charge region evolves in time according to

$$\frac{dn_t(E,t)}{dt}=\sigma\langle v\rangle n_c(t)[g(E)-n_t(E,t)]-\nu_n e^{E/kT}n_t(E,t)\,,\quad(3)$$

where $n_t(E,t)$ is the total charge distribution at time t, σ is the electron capture cross section, $\langle v\rangle$ is the mean velocity of free electrons, and $n_c(t)$ is the time-dependent free electron concentration in the conduction band, which is given by $n_{c0}-N_Q(t)$ during the filling pulse and is zero after the completion of the filling pulse. Equation (3) can be solved numerically using the following parameters: $g_0=2\times10^{21}$ cm^{-3}eV^{-1}, $\nu_n=10^9$ s^{-1}, $T_0=1000$ K, $N_c=10^{21}$ cm^{-3}eV^{-1}, $n_{c0}=5\times10^{17}$ cm^{-3}, and $E_F=-0.85$ eV.

The calculated occupation function for different times during a filling pulse is shown in Fig. 1. The results confirm the validity of the approximate expression of the occupation function used in the earlier analytic calculations. The demarkation energy shifts toward midgap and the filling fraction increases as the filling pulse duration increases, as expected. As shown in Fig. 2, the charge distribution in gap states evolves with the filling time. The charge has a peaked distribution which shifts toward midgap with increasing filling time.

The calculated defect charge transients at 340 K for various filling pulse widths are shown in Fig. 3. The power-law dependence for short filling pulses is clearly

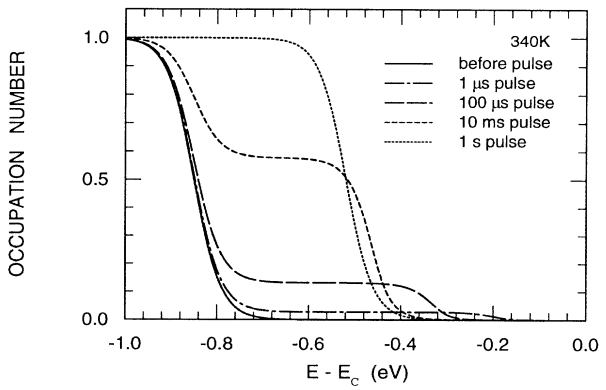

FIG. 1. The filling time dependence of the occupation function at $T=340$ K, calculated from Eq. (3) with parameters described in the text.

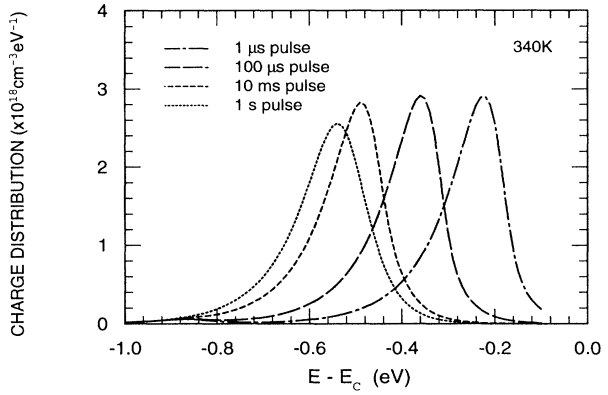

FIG. 2. Evolution of charge distribution on the gap states during a filling pulse.

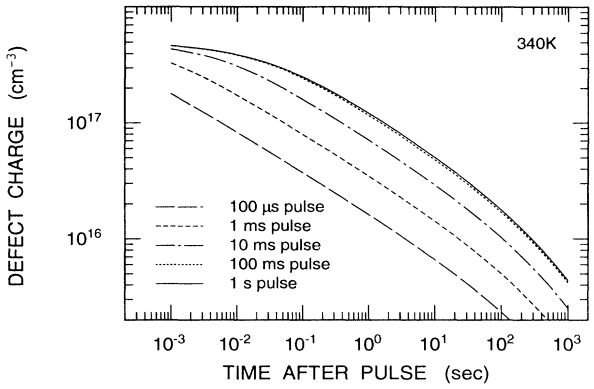

FIG. 3. The calculated charge emission transients for various filling pulse widths.

seen. The general shape of the curves for long filling pulses is in excellent agreement with the data in Fig. 1 of Ref. [5]. The calculations are based on reasonable assumptions for the appropriate parameters involved and do not represent a best fit to the experimental data. The characteristic emission time as a function of filling pulse width is shown in Fig. 4. These calculations show the direct dependence of the emission time on the length of the filling pulse for short filling times. For long filling pulses the emission is independent of the filling time and has a temperature dependence that corresponds to a thermally activated process. These calculations are again in excellent agreement with the previously reported experimental data. The calculated activation energy is equal to 0.57 eV, which is slightly smaller than the experimentally measured value (0.74 eV) [5]. The values of t_e in the short-pulse-width limit exhibit a weak temperature dependence which is consistent with the experimental results, considering the experimental uncertainty in this range.

In the deep level transient spectroscopy (DLTS) experiment [8], the attempt-to-escape frequency is found to be 10^{12}–10^{13} s^{-1}, with the assumption that ν_n is independent of energy and temperature. In the isothermal capacitance transient spectroscopy (ICTS) experiment [9], however, ν_n is determined to be only 10^9 s^{-1}. The discrepancy in the value of ν_n and in turn the discrepancy in the energy location of the gap states have been main controversial issues in the study of a-Si:H [9–11]. Interestingly, it is found from the present analysis that $\nu_n = 10^9$ s^{-1} is the only value consistent with the fact that the charge redistribution process endures for about 1 s for samples with a Fermi energy of 0.5 eV as was observed in Ref. [5]. If ν_n were equal to 10^{13} s^{-1}, the charge redistribution process would be completed in about 10 μs and could not be observed by the capacitance transient experiment. The small value of ν_n has been interpreted by Okushi [9] as an evidence for the multiphonon emission mechanism for the doubly occupied states. In fact, the smaller activation energy obtained from Fig. 3 than the measured value may suggest a capture barrier of about 0.1 eV, resulting in a temperature dependence of ν_n. This capture barrier also reconciles the large optical energy threshold observed in a photocapacitance experiment [12].

It may be questioned why the charge redistribution effect has not been observed in the earlier junction capacitance measurements, since it is a general effect for a system with a large number of distributed energy states. The present results show that the charge redistribution process completes within a time near $\exp(-E_F^n/kT)/\nu_n$. If the Fermi energy is 0.2 eV, a typical value for samples in the early junction capacitance measurements, then the completion time is only 1 μs at 300 K, shorter than the filling pulses usually used in junction capacitance experiments. Therefore, the charge redistribution process can only be observed in samples prepared such that the Fermi energy is around 0.5 eV.

Although an exponential distribution of gap states has often been used to describe the results of the time-of-

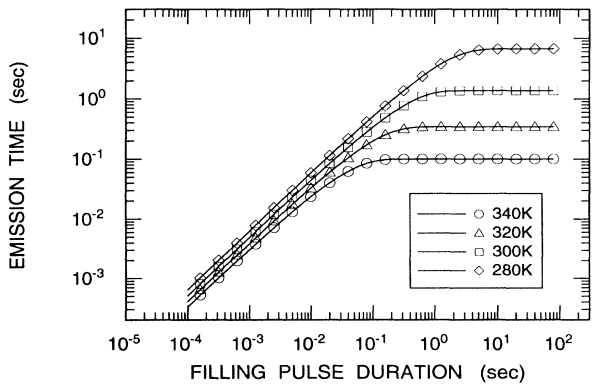

FIG. 4. Plot of the thermal emission time as a function of the filling pulse width for several temperatures.

flight [13,14] and photoconductivity decay experiments [15,16], only the band tail states are effective for these experiments. In fact, the gap state distribution determined from many experiments, such as DLTS and ICTS, usually exhibits a peak structure. However, an exponential distribution of gap states is actually a direct result of the power-law dependence of the charge emission transients. In the numerical calculations, several other possible distributions of gap states were used and only the exponential distribution can satisfactorily produce the proportional relationship between the thermal emission rate and filling pulse width. It appears that the exponential gap state distribution (effectively from 0.2 to 0.8 eV below E_c) is a peculiar characteristic for the annealed light-soaked state of the samples in Ref. [5].

In conclusion, the charge redistribution process on the continuously distributed gap states in a-Si:H has been analyzed. It is found that the experimentally observed scaling-law dependence for the charge emission transients is accounted for in a natural way. The charge redistribution model also fully describes the filling-pulse-width dependence of the emission time of the trapped electrons. Therefore, it is not necessary to invoke a "novel" defect relaxation to account for the new observations.

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