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Temperature dependence of electron-capture cross section of localized states in a-Si:H

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A temperature dependence of the electron-capture cross section $[\sigma_n(E,T)]$ of the gap states in *a*-Si:H was determined for the first time by isothermal capacitance transient spectroscopy. A bump was observed on the gap-state profile of lightly P-doped *a*-Si:H and $\sigma_n(E,T)$ increases as temperature increases. From this temperature dependence as well as the energy dependence of $\sigma_n(E,T)$ reported previously, it is concluded that the bump of gap-state profile is located approximately 0.5 eV below the conduction-band mobility edge and multiphonon emission predominates in the electron-capture process at the gap states near the bump. It is strongly suggested that the bump structure originates from doubly occupied dangling-bond states.

In our earlier work,[1] we reported the first data on the energy dependence of the electron-capture cross section $[\sigma_n(E)]$ of the gap states in n-type *a*-Si:H determined by the isothermal capacitance transient spectroscopy (ICTS) method.[2,3] σ_n of each state has been found to decrease exponentially with an increase in energy depth measured from E_c. Taking into account this energy dependence of $\sigma_n(E)$ we also determined a precise energy distribution of the gap-state density $g(E)$. A bump of $g(E)$ was estimated to lie approximately 0.5 eV below the conduction-band mobility edge E_c in lightly P-doped *a*-Si:H,[1] and its origin suggested to be a doubly occupied dangling-bond state D^-. On the other hand, the deep-level transient spectroscopy (DLTS) analysis of Lang *et al.*[4] determined the bump of $g(E)$ to be located at about 0.85 eV below E_c. Using this value, Cohen *et al.* reported the identification of the dangling-bond states in *a*-Si:H by observing the change in the dark absorption ESR signal.[5] Their assignment is compatible with our suggestion except for the difference in the energy location of the gap-state bump. These conflicting values might come from a difference in the estimation method for an attempt-to-escape frequency ν, a preexponential factor of the thermal-emission rate, by which the energy position E is determined through the relationship

$$E_c - E = kT\ln(\nu t) \ , \qquad (1)$$

where T is the absolute temperature and t the reciprocal of the thermal-emission rate. In the DLTS measurement[5] ν is assumed to be independent of both temperature and energy. With this assumption, Lang *et al.* obtained a value of $\nu = 10^{13}\ \mathrm{s}^{-1}$. On the other hand, in the ICTS measurement, taking the energy dependence of ν into account, we obtained a value of ν at the center of the bump to be approximately equal to $10^9\ \mathrm{s}^{-1}$ at 297 K.

In this paper, we report temperature as well as energy dependence of ν and σ_n of the gap-state bump determined by the ICTS method. The results give the first confirmation of the energy-gap law associated with the multiphonon-emission process with a weak electron-lattice coupling suggested in our earlier paper[1] and also give a possible explanation for the apparent incoincidence in energy position of the bump between DLTS and ICTS.

P-doped (0.001 at.%) *a*-Si:H film was deposited on a crystalline Si(n^+, 0.01 Ω cm) substrate by the glow-discharge technique and the Au Schottky barrier diode fabricated under the same condition as described earlier.[1] The optical gap of the specimen is 1.7 eV and activation energy of its dark conductivity is 0.30 eV. The Schottky diode shows a good rectifying I-V characteristic with a diode quality factor of 1.18. C-V characteristics of the diode for the bias voltage ranging from 0 to -1.2 V reveal the junction to be abrupt for such low-bias voltage.[2,6] The transient capacitance of the diode, $C(t)$, was measured at several different temperatures in the time range from 10^{-3} to 10^3 s.

The ICTS signal is defined as $S(t) = t\,df/dt$ with $f(t) = C^2(t) - C^2(\infty)$, where $C(\infty)$ is the depletion layer capacitance of the diode under a dc reverse-bias voltage V_R and $C(t)$ the transient capacitance after applying a voltage pulse V_p superimposed on the steady-state reverse-bias voltage. A height of the voltage pulse V_p is always kept the same as $|V_R|$.

Figure 1 shows the temperature dependence of the ICTS spectrum in the present specimen measured under the condition of $V_p = 1$ V and $V_R = -1$ V. The value of -1 V was selected for the following reasons: (1) -1 V is the highest reverse-bias condition of the present Au Schottky diode for obtaining reliability and reproducibility of the ICTS data. (2) A reverse bias higher than $|-1.5\ \mathrm{V}|$ causes a non-negligible change in I-V and C-V characteristics of the diode, and sometimes an irreversible degradation occurs. (3) -1 V is large enough to avoid a band-bending effect on the voltage-pulse-width dependence of ICTS

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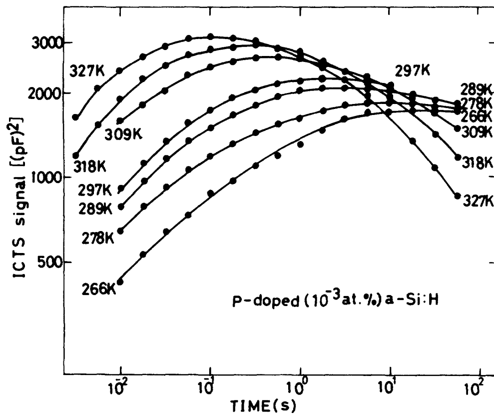

FIG. 1. ICTS (electron-emission) spectra of P-doped (10^{-3} at.%) a-Si:H Schottky diode traced for various temperatures.

spectra covered by the present work, as described later. As shown in the figure, each curve has a peak, corresponding to the bump of $g(E)$, and the peak position moves towards shorter time constants as temperature increases. This tendency is similar to that of a discrete level in crystalline semiconductors. Figure 2(a) shows the relationship between the time constants (t_{peak}) at the peak position of the bump plotted against reciprocal temperature, from which the activation energy of 0.69 eV was obtained. This value should correspond to the energy depth of the bump measured from E_c if ν and σ_n are assumed to be independent of temperature. It should be noted that the value of 0.69 eV is closer to that obtained by the DLTS measurement[4] rather than that obtained from voltage–pulse-width dependence of ICTS spectra.[1]

Figure 3 shows the ICTS traces for a variety of voltage pulse widths (W_p's) measured at two different temperatures, $T=$ (a) 278 and (b) 325 K, respectively. By replotting the data of Fig. 3, we obtain the ICTS signal dependence on W_p's for each t, and

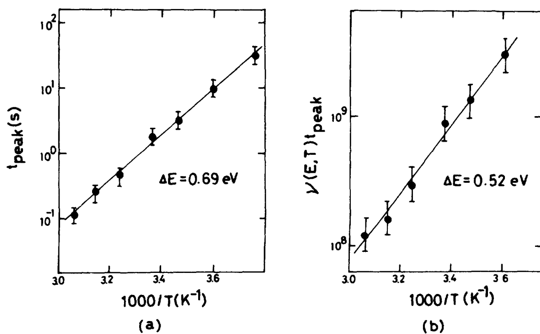

FIG. 2. (a) The thermal emission time at the peak (t_{peak}) of the ICTS spectrum vs the inverse temperature, and (b) $\nu(E,T)t_{\text{peak}}$ vs the inverse temperature.

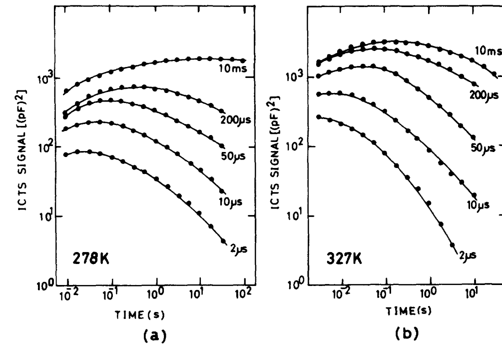

FIG. 3. ICTS spectra of P-doped (10^{-3} at.%) a-Si:H Schottky diode for various voltage pulse widths (W_p's); (a) $T=278$ K and (b) $T=327$ K.

eventually, the energy dependence of the electron-capture time constant $\tau(E)$ for two different temperatures. $\tau(E,T)$ is related to the emission parameters, i.e.,

$$\frac{1}{\tau(E,T)}=\sigma_n(E,T)v_{\text{th}}n=\frac{n}{N_c}\nu(E,T) \ , \quad (2)$$

where n is the free-electron density at a neutral bulk region. Another well-known relationship holds between n and N_c, represented by

$$n=N_c\exp[-(E_c-E_F)/kT] \ , \quad (3)$$

where E_F is the Fermi energy. From Eqs. (1)–(3) the following equation is obtained:

$$E_F-E=kT\ln[t/\tau(E,T)] \ . \quad (4)$$

It must be pointed out that we determined the band-bending effect for -1-V reverse bias used in the present experiment. Zylbersztejn[7] pointed out that for small-bias voltages the trap filling during the zero-bias voltage pulse is not in neutral material but the edge region of the depletion region where the carrier concentration is lower than the bulk. Our results using a simple quadratic band-bending diagram show that -1-V reverse bias causes no serious band-bending effect for the localized gap states located in the energy range of $E-E_F\lesssim 0.3$ eV, where E_F is the Fermi energy. Since our results in the present paper are associated with the gap states located nearly 0.5 eV below E_c on a P-doped specimen with $E_F=0.30$ eV, therefore the present results are almost free from errors originating in the band-bending effect. This has also been confirmed by the experimental results on the reverse-bias dependence of the voltage–pulse-width data of the present specimen.[8] The experimental results for the reverse-bias voltage in the range between -0.5 to -1.2 V indicate that the time constant τ decreases with an increase in bias voltage and is almost saturated in the range of $-0.8\sim-1.2$ V. This is quite consistent with the

simple analysis mentioned above.

Figure 4 shows a temperature dependence of the peak energy, $E_F - E_{peak}$, calculated using Eq. (4) from the data of $\tau(E,T)$ obtained for several different temperatures. The result in the figure implies two alternative possibilities; one is the case where E_F is temperature-dependent while E_{peak} stays constant, and the other the case when E_{peak} is temperature dependent. For the case of doped semiconductors, in general, E_F is expected to vary with temperature and, actually, Jones *et al.* have indicated through their thermoelectric power measurement that E_F moves towards the midgap in P-doped *a*-Si:H when temperature rises.[9] On the other hand, it is unlikely that E_{peak} has a temperature dependence, since E_{peak} is associated with a particular electronic configuration (probably a defect termed D^-) and any dilation effect on E_{peak} might be negligibly small within a temperature range scanned in the present measurement. Thus it is quite reasonable to consider that a decrease in $E_F - E_{peak}$ when temperature increases should be attributed to an increase in $E_c - E_F$.

The above argument leads us to an exact determination of energy and temperature dependences of $\sigma_n(E,T)$ and $\nu(E,T)$. Figure 5 shows $\sigma_n(E)$ and $\nu(E)$ for several different temperatures, determined under the condition of E_F shifting and E_{peak} constancy. As shown in the figure, $\sigma_n(E,T)$ and $\nu(E,T)$ increase with an increase of temperature. The peak energy of 0.69 eV derived under the assumption of constant σ_n and ν [see Fig. 2(a)] was corrected into 0.52 eV, which was deduced from the Arrhenius plot of $\nu(E,T)t_{peak}$, as shown in Fig. 2(b). This value coincides with that determined from the voltage–pulse-width experiment of the ICTS spectrum within the experimental margin of error.

Lang *et al.*[4] have reported the DLTS electron-emission spectra with a bump at about $T = 350$ K for the emission time constant of 100 ms. On the other hand, the bump observed in the ICTS spectra takes a maximum value at $t = 100$ ms when $T = 327$ K.

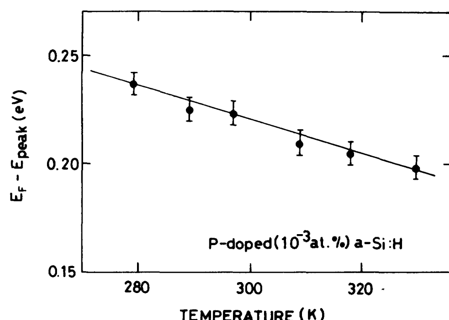

FIG. 4. Energy difference between Fermi and peak energy in the ICTS spectrum of P-doped (10^{-3} at.%) *a*-Si:H as a function of temperature.

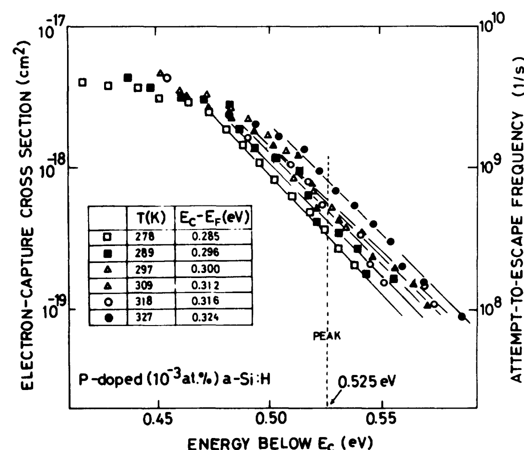

FIG. 5. Energy dependence of the electron-capture cross section and the attempt-to-escape frequency in P-doped (10^{-3} at.%) *a*-Si:H for various temperatures.

Judging from these results, to a first approximation, it is clear that the origin of the bump observed in the DLTS spectra is the same as that in the ICTS spectra. In spite of that, as mentioned above, there exists a considerable difference in the energy location of the bump between DLTS and ICTS. As is clear from Figs. 2 and 5, this apparent discrepancy should be ascribed to the assumption of constant ν and σ_n adopted in DLTS. Consequently, the values of ν and σ_n at the center of bump are accurately estimated to be 10^9 s^{-1} and 10^{-18} cm^2 for $N_c = 10^{20}$/cm^3 and $v_{th} = 10^7$ cm/s at 297 K, respectively, and the bump is located nearly 0.5 eV below E_c.

In our previous work,[1] the multiphonon-emission process was suggested as a dominant mechanism in the electron-capture process at the localized states around the bump. Theoretically, the temperature dependence of the transition probability for the multiphonon-emission process with a weak electron-lattice coupling is given as[11]

$$W_T = W_{T=0}(1 + n_{ph})^p \ , \tag{5}$$

where n_{ph} is the expectation value for the number of phonons in a single configuration coordinate mode at temperature T and p is the number of phonons released by the electron deexcitation. $W_{T=0}$ is the transition probability at absolute zero temperature and obeys the energy-gap law,[10] i.e.,

$$W_{T=0} \propto \exp(-\gamma E_a/\hbar\omega) \ , \tag{6}$$

where E_a is the energy gap between the free carrier states and the trap states, γ a constant, and $\hbar\omega$ the energy of the phonon. According to Eq. (5) W_T should show a weak temperature dependence, namely, W_T increases as temperature increases. The relation experessed by Eqs. (5) and (6) is qualitatively satisfied in the present system, which is clear in the

result shown in Fig. 5.

From these facts it is concluded that the multiphonon-emission with a weak electron-lattice coupling predominates in the electron-capture process at the gap-state bump located around 0.5 eV below E_c.

Morigaki *et al.*[12] and Street *et al.*[13] have independently shown through the optically detected magnetic resonance and the time-resolved photoluminescence that nonradiative recombination occurs via dangling-bond states (D^-) located approximately 0.6 eV below E_c. Their results are compatible with our conclusion, in the sense that the present work provides direct evidence for the nonradiative process termed "multiphonon emission." Concerning the assignment of the localized states to the dangling bonds, Cohen *et al.* have presented the first direct experimental result as mentioned above.[5]

In summary, we have presented the temperature dependence of $\sigma_n(E,T)$ at the localized states in a-Si:H for the first time by the ICTS method. Experimental results indicate that $\sigma_n(E,T)$ increases as temperature increases. Energy as well as temperature dependence of $\sigma_n(E,T)$ leads us to a conclusion that the multiphonon emission with a weak electron-lattice coupling predominates at the states near the bump of $g(E)$ originating from doubly occupied dangling-bond states approximately 0.5 eV below E_c.

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