Energy dependence of electron-capture cross section of gap states in *n*-type *a*-Si:H

H. Okushi, Y. Tokumaru, S. Yamasaki, H. Oheda, and K. Tanaka
Electrotechnical Laboratory, 1-1-4 Umezono, Sakura-mura, Niihari-gun, Ibaraki 305, Japan
(Received 11 December 1981)

Isothermal capacitance transient spectroscopy has been employed for the measurement of the capture cross section of continuously distributed trap levels in *a*-Si:H, and the energy dependence of the electron-capture cross section of gap states has been determined for the first time. Experimental results indicate that an electron-capture cross section of a localized level decreases exponentially with an energy depth measured from the mobility edge of the conduction band, suggesting that the multiphonon emission predominates in the electron-capture process at the deep gap states in *a*-Si:H.

Detailed information on the nature of gap states of hydrogenated amorphous silicon (*a*-Si:H) has been required for understanding the electronic properties of the material. The capture cross section of the gap states for electrons and holes is one of the most important parameters in recombination and trapping kinetics. The DLTS (deep level transient spectroscopy[1]) has been considered as a useful method for determining the energy level and the capture cross section of continuously distributed trap levels,[2] but this method inherently involves a temperature scanning process. This causes the difficulty for separating a temperature dependence from an energy dependence of capture cross section of continuously distributed trap levels.

In earlier works we proposed the ICTS (isothermal capacitance transient spectroscopy) for a system of continuously distributed trap levels and reported the initial data on the energy-distribution of gap-state density in lightly P-doped *a*-Si:H.[3,4] The ICTS is a variation of capacitance transient spectroscopy in which, in contrast to DLTS,[1] a transient junction capacitance is measured in a time domain under an isothermal condition. Therefore, it can cover a wide span of time constants involved in the transient capacitance without varying temperature, which is one of the advantages compared with the conventional DLTS when applied to the system of continuously distributed trap levels.

In this paper, we present a new method for determining the capture cross section of continuously distributed trap levels using the ICTS, and give the first measurement on the energy distribution of electron-capture cross section of gap states in *n*-type *a*-Si:H.

In the ICTS a main quantity is expressed by

$$S(t) \equiv t\frac{df}{dt} \ , \tag{1}$$

with

$$f(t) = C^2(t) - C^2(\infty) \ , \tag{2}$$

where $S(t)$ is an ICTS signal defined, t time, and $C(t)$ a junction capacitance, respectively.[3,4] The ICTS signal $S(t)$ is experimentally obtained from the time dependence of $C(t)$ of the p-n junction or the Schottky barrier diode after removing a voltage pulse superimposed on a steady reverse voltage V_R. As shown in Fig. 1, a height (V_p) of the voltage pulse is always kept the same as $|V_R|$. For a system of continuously distributed trap levels, the relationship between the ICTS signal $S(t)$ and the density-of-states distribution $g(E)$ for electron traps is given as[3]

$$g(E) = -\left[\frac{1}{kTB}\right]S(t) \ , \tag{3}$$

and

$$E_c - E = kT\ln[\nu(E)t] \ , \tag{4}$$

where $B = q\epsilon A^2/2(V_D + V_R)$, q the electronic charge, ϵ the dielectric constant of the material, A the junction area, V_D the effective diffusion potential at the junction, $\nu(E(t)) = N_c\,\sigma_n(E(t))\,v_{\rm th}$ the attempt-to-escape frequency of the electron, $\sigma_n(E(t))$ the electron-capture cross section, $v_{\rm th}$ the electron thermal velocity, N_c the effective density of states in the

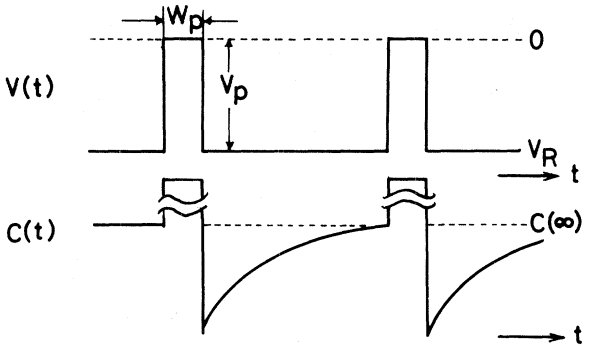

FIG. 1. Voltage and capacitance transient during ICTS measurement.

conduction band, and E_c the mobility edge of the conduction band.

As is clear from Eqs. (3) and (4), $g(E)$ is determined directly from $S(t)$ if an energy dependence of $\nu(E)$ is given. In the derivation of Eq. (3) it is assumed that a voltage pulse width (W_p) is long enough to fill up every trap below the Fermi level with carriers. However, when W_p decreases, $S(t)$ should decrease in proportion to a decrease in the number of carriers at energy level $E(t)$ trapped during a voltage pulse application. We can therefore determine the electron-capture rate at energy level $E(t)$ as a function of W_p by using the following equation:

$$S(t,W_p)=S(t,\infty)\left[1-\exp\left[-\frac{W_p}{\tau(E(t))}\right]\right], \quad (5)$$

where $\tau(E(t))=1/n\sigma_n(E(t))v_{\text{th}}$, $S(t,\infty)$ the value of $S(t,W_p)$ at $W_p=\infty$, and n the density of free electrons. Equation (5) is based on the assumption that the electron-emission process can be neglected compared with the electron-capture process within the duration of the voltage pulse application, i.e., Eq. (5) is valid when $W_p \ll t=1/e_n$, where e_n is the electron emission rate.

From the measurement of $S(t,W_p)$ for different W_p's, $\tau(E)$ is experimentally obtained using Eq. (5). Then $\nu(E)$ is determined from the relation $\nu(E)=N_c/n\tau(E)$, since N_c/n is independently estimated from the activation energy of the dark conducitivity. Thus we can determine the energy dependence of the attempt-to-escape frequency $\nu(E)$, and automatically that of the capture cross section $\sigma_n(E)$ in the system of continuously distributed trap levels.

The specimen used in the present experiment was prepared by the glow-discharge technique.[5] P-doped (0.01 at.%) a-Si:H film was deposited on a crystalline Si (n^+, 0.01 Ωcm) under the condition described earlier.[3] The optical gap of the specimen is 1.7 eV, being determined using the empirical relation $\sqrt{ah\nu} \propto h\nu-E_0$, and the activation energy of its dark conductivity is 0.21 eV. The Schottky diode was fabricated by evaporating Au on the film with an area of 1.96×10^{-3} cm^2. The present diode shows a good rectifying I-V characteristic with a diode quality factor close to unity and the $1/C^2$-V characteristic satisfies approximately a linear relation. Equation (3) can be therefore applied for the analysis of the present diode.[3]

The capacitance signal $C(t)$ after the majority-carrier introduction was measured under the isothermal condition (297 K) in the time range from 10^{-3} to 10^3 sec. The signal was led to a minicomputer system which performed a detailed calculation of $S(t,W_p)$ as well as a derivation of $g(E)$ from $S(t,\infty)$.

Figure 2 shows the ICTS signals for different W_p's

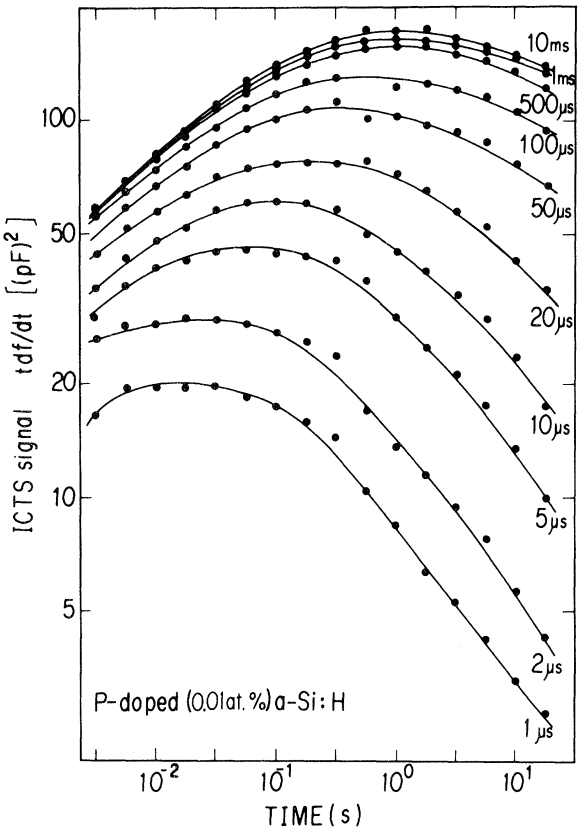

FIG. 2. ICTS signals of P-doped (0.01 at.%) a-Si:H Schottky diode for various pulse widths (W_p's) of voltage pulse.

under the condition of $V_p=1$ and $V_R=-1$ V. As shown in the figure, the ICTS signals increase with an increase of W_p and saturate for $W_p \gtrsim 5$ msec in the time range between $10^{-2.5}$ and $10^{1.5}$ sec. It is noted, as mentioned above, that the density-of-states distribution $g(E)$ corresponds to the saturated ICTS signal $S(T,\infty)$. Figure 3 shows a semilog plot of $S(t,\infty)-S(t,W_p)$ vs W_p for four different values of t, where we took the value of $S(t,W_p=10$ msec) as $S(t,\infty)$.

From these data, both $\tau(E(t))$ and $\nu(E)$ were determined using Eq. (5) and the relation $\nu(E)=N_c/n\tau(E)$. The results are shown in Figs. 3 and 4. The calculated values of $\tau(E(t))$ are given in Fig. 3 for four different values of t. Figure 4 shows an energy dependence of the attempt-to-escape frequency $\nu(E)$ as well as a corresponding electron-capture cross section $\sigma_n(E)$ calculated under $N_c=10^{20}$/cm^3 and $v_{\text{th}}=10^7$ cm/sec which are assumed usually in a-Si:H.[6–8] It should be noted that each obtained numerical value of $\nu(E)$ is accurate within the experimental errors, while that of $\sigma_n(E)$ involves another ambiguity originated in the estimation of N_c and v_{th}.

As shown in the figure, $\nu(E)$ or $\sigma_n(E)$ decrease exponentially with an increase in the depth of energy

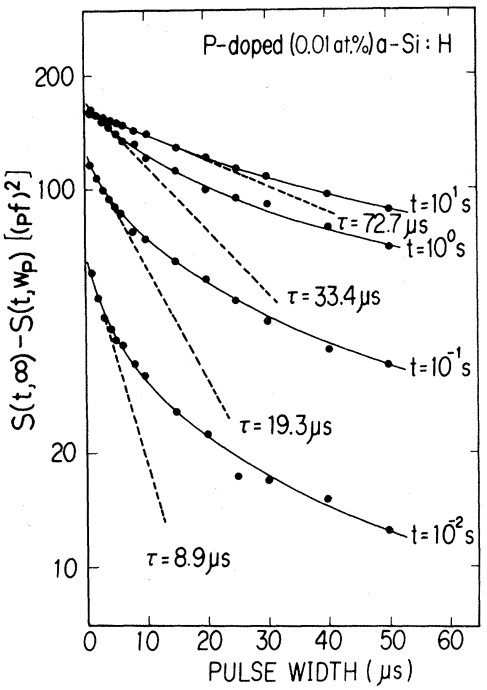

FIG. 3. $S(t,\infty)-S(t,W_p)$ vs W_p for four different values of t obtained from the data of Fig. 2.

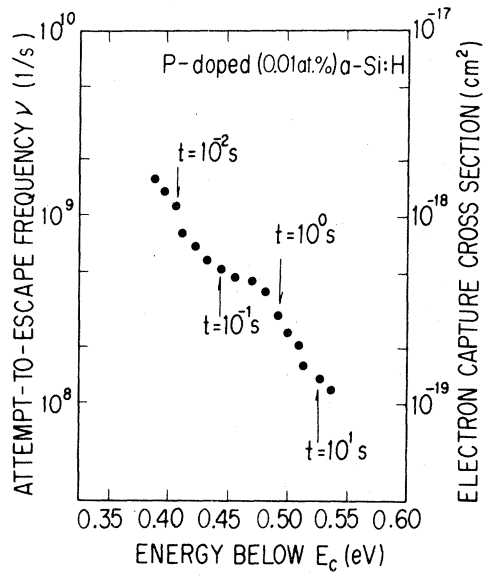

FIG. 4. Energy dependence of the attempt-to-escape frequency $\nu(E)$ and the electron-capture cross section $\sigma_n(E)$ in P-doped (0.01 at.%) a-Si:H.

level from the mobility edge of the conduction band. This fact gives us important information on the electron-capture process at the gap states in a-Si:H.

In the present experiment, the observed gap states lie deeply in the energy range from 0.35 to 0.55 eV below E_c, as shown in Fig. 4. Judging from the emission spectra of photoluminescence on a-Si:H,[9] a nonradiative transition might be dominant in the electron-capture process at these deep gap states. In general, the following mechanisms have been proposed for the nonradiative transition: (1) the Auger process,[10] (2) the cascade-phonon process,[11] and (3) the multiphonon process,[12] respectively. The Auger process usually occurs through the direct interaction of carriers, which is, therefore, not likely the mechanism in the present system with a relatively low density of free or trapped carriers. In the cascade phonon process, a carrier diffuses down the spectrum of Coulomb excited states emitting one phonon at a time. This mechanism is dominant for trapping of carriers at a shallow and ionized impurities in semiconductors, but, as pointed out by Lax,[11] it does not work for the capture of the carrier into deep levels where the lowest states are separated by more than a few phonon energy.

From the above argument it appears that the multiphonon process is the most probable mechanism for the capture of the carrier into the deep gap states. In this process, the electron-lattice coupling is essential, and the coupling is strong in an ionic bonding system while it is very weak in a covalent bonding system such as a crystalline Si. Even in the covalent bonding system, however, the electron-lattice coupling becomes relatively strong in the amorphous phase compared with the crystalline counterparts, which has been considered to be a general trend of disordered system.[13] In the a-Si:H system such a trend could be enhanced because of the flexibility of its structure by the presence of Si:H bonds.[14]

The multiphonon-emission process has been studied by several groups in a variety of insulators.[15,16] In a weak-coupling case, a multiphonon transition rate is theoretically given by[15,17]

$$W \propto \exp(-\gamma E_a/\hbar\omega) \ , \tag{6}$$

where E_a is the energy gap between the free-carrier states and trap level, γ a constant, and $\hbar\omega$ the energy of the phonon. This energy dependence of W is known as the energy-gap law and has been verified experimentally in a variety of system such as rare-earth compounds.[15,16]

The result shown in Fig. 4 indicates that Eq. (6) approximately holds in the present system, which means that the multiphonon-emission process with a weak coupling prevails in the electron-capture process at the deep gap states in the a-Si:H system. This conclusion is not so unrealistic if an electron transition between gap states is a minor process compared to the transition between the conduction band and gap states. We believe that this result is the first confirmation of the energy-gap law associated with the multiphonon-emission process through a weak coupling obtained in one identical amorphous materi-

al involving a continuous distribution of trap level within the energy gap.

Concerning the magnitude of the electron-capture cross section of deep gap states, the present result appears considerably smaller than the conventional value usually assumed.[18] But, our recent experiment on PAS (photoacoustic spectroscopy) and ESR[19] suggests that the bump of the gap states observed in the present work or those of gap states for various P-doped samples[20] could possibly originate from the doubly-occupied dangling bond states ($D2$). This speculation is compatible with the model for the gap-state profile reported by Street on the basis of PL and LESR (light-induced ESR),[9] where the $D2$ state is predicted to lie at 0.6 eV below E_c. Morigaki *et al.* also pointed out independently from their ODMR (optical detection of magnetic resonance) experiment that the $D2$ state is located at a similar energy depth from E_c.[21] It is quite reasonable to consider that an electron-capture cross section of such a state should be small because of a Coulomb repulsion of bare electrons.

In summary, we have presented a new method for determining the capture cross section of continuously distributed trap levels by isothermal capacitance transient spectroscopy (ICTS) and have given the first measurement on the energy dependence of electron-capture cross section of the gap states in *a*-Si:H. In P-doped *a*-Si:H (n type, $E_f = 0.21$ eV), the electron-capture cross section decreases exponentially (from 2×10^{-18} to 1×10^{-19} cm^2 for $N_c = 10^{20}$/ cm^3 and $v_{th} = 10^7$ cm/sec) with an increase in the depth of the energy level measured from E_c (from 0.35 to 0.55 eV).

ACKNOWLEDGMENTS

We would like to thank H. Sumi of Tsukuba University and T. Simizu of Kanazawa University for fruitful discussions. We acknowledge our colleagues of the amorphous materials section of ETL, A. Matsuda, N. Hata, H. Kawai, Y. Yamamoto, T. Yoshida, and K. Takakuwa for stimulating discussions. We are also indebted to M. Hidezima and A. Motoki for their experimental assistance.

[1]D. V. Lang, J. Appl. Phys. 45, 3023 (1974).
[2]T. Katsube, K. Kakimoto, and T. Ikoma, J. Appl. Phys. 52, 3504 (1981).
[3]H. Okushi, Y. Tokumaru, S. Yamasaki, H. Oheda, and K. Tanaka, Jpn. J. Appl. Phys. 20, L549 (1981).
[4]H. Okushi, Y. Tokumaru, S. Yamasaki, H. Oheda, and K. Tanaka, in *Proceedings of the 9th International Conference Amorphous and Liquid Semiconductors, Grenoble, 1981* (in press).
[5]K. Tanaka, K. Nakagawa, A. Matsuda, M. Matsumura, H. Yamamoto, S. Yamasaki, H. Okushi, and S. Iizima, Jpn. J. Appl. Phys. Supp. 20-1, 267 (1981).
[6]W. E. Spear, P. G. LeComber, and A. T. Snell, Philos. Mag. B 38, 303 (1976).
[7]J. Beichler, W. Fuhs, H. Mell, and H. M. Welsch, J. Non-Cryst. Solids 35/36, 587 (1980).
[8]P. Viktrovitch and D. Jousse, J. Non-Cryst. Solids 35/36, 569 (1980).
[9]R. A. Street, Adv. Phys. 30, 593 (1981).
[10]P. T. Landsberg, C. Phys-Roberts, and P. Lal, Proc. Phys. Soc. 80, 915 (1964).
[11]M. Lax, Phys. Rev. 119, 1502 (1960).
[12]A. M. Stoneham, Philos. Mag. 36, 983 (1977).
[13]D. Emin, in *Electronic and Structural Properties of Amorphous Semiconductors,* edited by P. G. Lecomber and J. Mort (Academic, London, New York, 1973), p. 201.
[14]R. Fisch and D. C. Licciardello, Phys. Rev. Lett. 41, 889 (1978).
[15]L. A. Riseberg and H. W. Moss, Phys. Rev. 174, 429 (1968).
[16]M. J. Weber, Phys. Rev. B 8, 54 (1973).
[17]A. M. Stoneham, *Theory of Defects in Solids* (Oxford University Press, New York, 1975).
[18]For example, H. Fritzsche, Sol. Energy Mater. 3, 447 (1980).
[19]S. Yamasaki, T. Hata, T. Yoshida, H. Oheda, A. Matsuda, H. Okushi, and K. Tanaka, in Ref. 4.
[20]See Fig. 4 in Ref. 4, where we have done energy scaling by assuming a constant $\nu(E) = 3 \times 10^{13}$ /sec, therefore, the bump of the gap-state spectra is located at 0.8 eV below E_c. But, using the present result of $\nu(E)$ in Fig. 4, we rescaled energy axis, which has produced the bump at 0.5 eV below E_c.
[21]K. Morigaki, Y. Sano, and I. Hirabayashi, Solid State Commun. 39, 947 (1981).