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# Density-of-State Distribution for Undoped a-Si:H and a-$Si_{1-x}Ge_x$:H Determined by Transient Heterojunction-Monitored Capacitance Method

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A novel technique has been proposed for determining the density-of-state (DOS) distribution in the mobility gap of highly resistive amorphous semiconductors, using amorphous/crystalline heterojunction structures. This technique has been tested and applied on undoped hydrogenated amorphous silicon (a-Si:H) films and silicon-germanium alloy (a-$Si_{1-x}Ge_x$:H) films, covering the optical gap range ($E_0$) of 1.55 eV to 1.76 eV. For undoped a-Si:H ($E_0$=1.76 eV), the peak of the mid-gap DOS distribution has been located at 0.85 eV below the conduction band mobility edge, with a value of $5.6\times10^{15}$ cm$^{-3}$eV$^{-1}$.

**KEYWORDS:** mid-gap density-of-state distribution, undoped a-Si:H, undoped a-$Si_{1-x}Ge_x$:H, transient heterojunction-monitored capacitance

## §1. Introduction

The electronic properties of hydrogenated amorphous silicon (a-Si:H) films and hydrogenated amorphous silicon-germanium alloy (a-$Si_{1-x}Ge_x$:H) films are critically linked with the density and distribution of localized states in the mobility gap. Prior to this letter, the densities of mid-gap states for undoped a-Si:H and undoped a-$Si_{1-x}Ge_x$:H had been obtained from steady-state heterojunction-monitored capacitance (HMC) methods[1,2] and they had been found to be densities of singly-occupied dangling bonds.[2]

Transient capacitance methods like isothermal capacitance transient spectroscopy[3] (ICTS) and deep level transient spectroscopy[4] (DLTS) are tested techniques for determining the density-of-state (DOS) distribution, $g(E)$, in phosphorus-doped a-Si:H. However, these methods are limited in their application to samples of low resistivity. For high resistivity materials, such as undoped or compensated a-Si:H films, the dielectric relaxation times are too long for the measurement of the capacitance which can reflect the depletion width of the junction.

In this letter, it has been demonstrated that the $g(E)$ below the Fermi level ($E_F$) of undoped a-Si:H and undoped a-$Si_{1-x}Ge_x$:H can be determined from the experimental results of transient HMC measurements.

## §2. Theory of Transient Heterojunction-Monitored Capacitance Method

The capacitance (heterojunction-monitored capacitance, $C_{HM}$) of undoped (i.e., *n*-type) a-$Si_{1-x}Ge_x$:H (or a-Si:H)/*p*-type crystalline silicon (*p* c-Si) heterojunctions, which is measured at 2 MHz, is expressed by the relation[1,2]

$$1/C_{HM}=1/C_1+1/C_2 \tag{1}$$

where $C_1$ is the capacitance ($\varepsilon_{s1}/W_1$) in the *p* c-Si and $C_2$ is the capacitance ($\varepsilon_{s2}/L$) in the amorphous film, since 2 MHz is much higher than $1/2\pi\varepsilon_{s2}\rho_2$. Here $\varepsilon_{s1}$ and $\varepsilon_{s2}$ are the semiconductor permittivities for c-Si and the amorphous film, respectively, $W_1$ is the width of the depletion region in the *p* c-Si, $L$ is the thickness of the amorphous film, and $\rho_2$ is the resistivity of the amorphous film. The width of the depletion region in the *p* c-Si is given by

$$W_1^2=\varepsilon_{s1}^2(1/C_{HM}-1/C_2)^2 \tag{2}$$

$$=2\varepsilon_{s1}\varepsilon_{s2}N_1(V_B-V_R)/qN_A(N_A\varepsilon_{s1}+N_1\varepsilon_{s2}) \tag{3}$$

according to the abrupt heterojunction model.[1,2] Here $q$ is the magnitude of the electron charge, $V_B$ is the built-in potential, $V_R$ is the bias voltage, $N_A$ is the acceptor density in the *p* c-Si, and $N_1$ is the effective density of donor-like states in the amorphous film.[1,2]

In order to estimate $g(E)$, the transient HMC is considered after $V_R$ is applied to the sample over the zero-

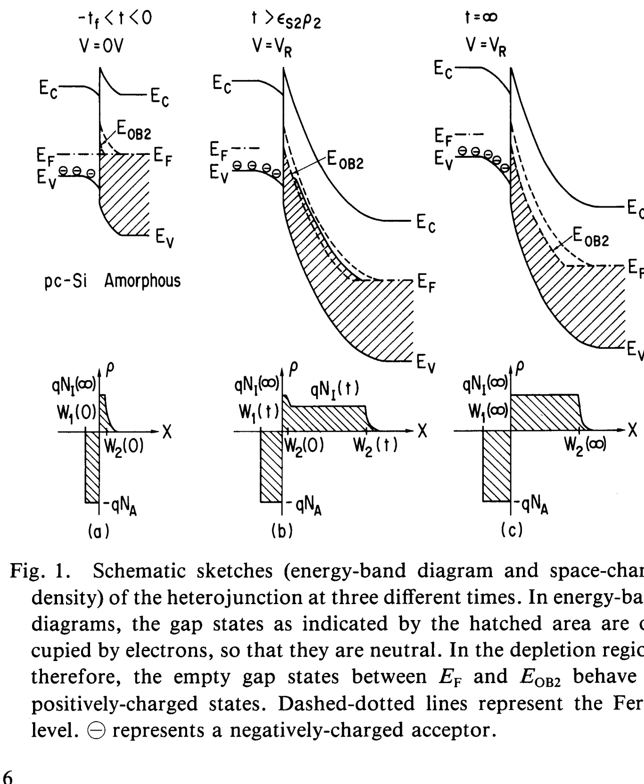


Fig. 1. Schematic sketches (energy-band diagram and space-charge density) of the heterojunction at three different times. In energy-band diagrams, the gap states as indicated by the hatched area are occupied by electrons, so that they are neutral. In the depletion region, therefore, the empty gap states between $E_F$ and $E_{OB2}$ behave as positively-charged states. Dashed-dotted lines represent the Fermi level. ⊖ represents a negatively-charged acceptor.

bias condition, as shown in Fig. 1. Electrons trapped at shallower states at $t<0$ get thermally emitted into the conduction band. After $V_R$ has been on for the dielectric relaxation time ($\varepsilon_{s2}\rho_2$) of the amorphous film, the space charge in the vicinity of the heterojunction will redistribute itself in response to the applied potential, as shown in Fig. 1(b). The data of $C_{HM}(t)$ after the dielectric relaxation time can be analyzed from eqs. (2) and (3), and $N_I$ at a time of $t$ can be expressed as

$$N_I(t)=\varepsilon_{s1}V_c(t)N_A/\varepsilon_{s2}(V_B-V_R-V_c(t)) \quad (4)$$

with

$$V_c(t)=qN_A W_1^2(t)/2\varepsilon_{s1} \quad (5)$$

and

$$W_1(t)=\varepsilon_{s1}(1/C_{HM}(t)-1/C_2) \quad (6)$$

where $W_1(t)$ is the depletion width at time $t$ and $V_c(t)$ is the voltage across the depletion region of c-Si at $t$. In order to make the above analysis feasible, the absolute value of $V_R$ has to be necessarily much higher than $V_B$, so that the relation $(N_I(t)W_2(t)\gg N_I(\infty)W_2(0))$ is valid and the average value of $N_I$ over the depletion region at $t$ is close to $N_I(t)$. This condition also suggests that interface states do not affect the measurement of HMC.

The function $H(t)$ is defined as

$$H(t)\equiv -t(d(N_I(t)-N_I(\infty))/\mathrm{d}t), \quad (7)$$

and the measured $H(t)$ is obtained from transient $C_{HM}$ using eqs. (4)–(7). The values of $V_B$ and $C_2$ are obtained from steady-state HMC measurements.[2]

On the other hand, $H(t)$ is theoretically derived as[3]

$$H(t)=\int_{E_V}^{E_C}(f(E)-F_\infty(E))g(E)t(e_n(E)+e_p(E)) \times \exp(-(e_n(E)+e_p(E))t)\,\mathrm{d}E \quad (8)$$

with

$$f(E)=1/(1+\exp((E-E_F)/kT)), \quad (9)$$

$$F_\infty(E)=e_p(E)/(e_n(E)+e_p(E)), \quad (10)$$

$$e_n(E)=\nu_n\exp((E-E_C)/kT), \quad (11)$$

and

$$e_p(E)=\nu_p\exp((E_V-E)/kT). \quad (12)$$

Here $\nu_n$ and $\nu_p$ are the attempt-to-escape frequencies for electrons and holes, respectively, $E_C$ is the conduction band edge, and $E_V$ is the valence band edge. The $g(E)$ from which $H(t)$ of eq. (8) can be obtained to fit the measured $H(t)$ is determined.

Under the conditions that $e_p(E)\ll e_n(E)$ and $f(E)\sim 1$ (i.e., for the gap states between $E_F$ and $E_{OB2}$*), the relations

$$g(E(t))=H(t)/kT \quad (13)$$

and

$$E_C-E(t)=kT\ln(\nu_n t) \quad (14)$$

*In the depletion region, the gap states above $E_{OB2}$ are vacant of electrons, where $E_{OB2}$ is given by $E_{OB2}=E_C-E_{g2}/2+(kT/2)\ln(\nu_p/\nu_n)$. Here $E_{g2}$ is the mobility gap of the amorphous film.

are obtained, which are similar to the relations obtained from the ICTS analysis.[3]

## §3. Sample Preparation

Undoped a-Si:H films have been deposited using a diode-type glow discharge reactor from pure $SiH_4$, and undoped a-$Si_{1-x}Ge_x$:H films have been prepared using a triode-type glow discharge reactor from $GeH_4/SiH_4$ gas mixture. Good quality films can be obtained from these techniques.[5]

The heterojunctions have been fabricated by depositing the amorphous films onto $p$ c-Si substrates ($N_A=1\times10^{16}$ cm$^{-3}$) heated to 250°C and then evaporating magnesium (Mg) on an area (0.785 mm$^2$) of those films at room temperature. Mg forms an ohmic contact with those amorphous films.[6] All the heterojunctions have exhibited good rectifying properties.

## §4. Results and Discussion

The signals of $H(t)$ get saturated at a filling time $t_f$ (under the zero-bias condition) longer than 1 s. Therefore, $H(t)$ has been measured at $t_f=50$ s.

Figure 2 shows the reverse-bias dependence of $H(t)$ for the a-$Si_{1-x}Ge_x$:H ($E_0=1.55$ eV)/$p$ c-Si heterojunction. The signals of $H(t)$ for $-5\text{ V}\le V_R\le -3\text{ V}$ have been found to be independent of $V_R$. Since the relation $(N_I(t)W_2(t)\gg N_I(\infty)W_2(0))$ is invalid for the reverse biases of $-1$ V and $-2$ V, these $H(t)$ include information on interface besides bulk. Therefore, $H(t)$ has been measured at $V_R=-4$ V.

The temperature dependence of $H(t)$ is shown in Fig. 3 for the a-$Si_{1-x}Ge_x$:H ($E_0=1.63$ eV)/$p$ c-Si heterojunction, and the temperature dependence of the time ($t_p$) at which the signal of $H(t)$ becomes maximum is inserted in the figure. A good leaner relation between ln ($t_p$) and $1/T$ has been obtained, and values of $\nu_n=1\times10^{12}$ s$^{-1}$ and $E_C-E_{peak}=0.78$ eV have been estimated from eq. (14).

Figure 4 shows the measured $H(t)$ and the $H(t)$ calculated from eq. (8) with $\nu_n=1\times10^{12}$ s$^{-1}$ under the assumption ($\nu_p=1\times10^8$ s$^{-1}$).** Here $g(E)$ for $E_0=1.63$ eV as shown in Fig. 5 has been used. The calculated $H(t)$ have been found to fit the measured $H(t)$ very well at each temperature.

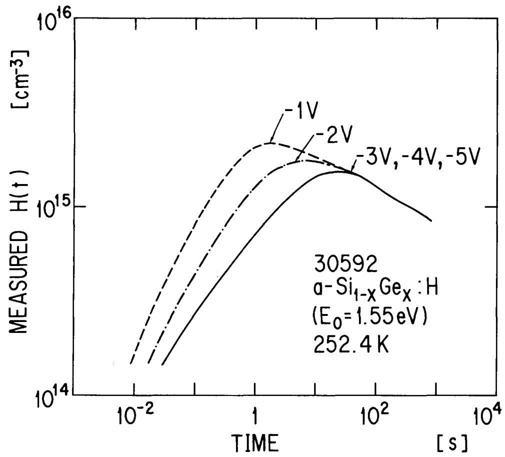


Fig. 2. Reverse-bias dependence of $H(t)$. ($t_f=50$ s)

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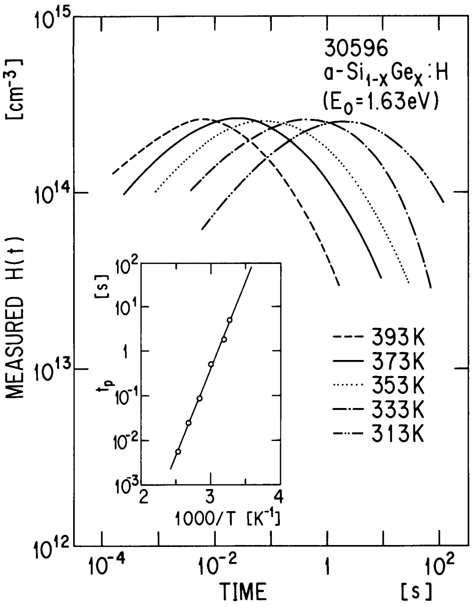


Fig. 3. Temperature dependence of $H(t)$. The temperature dependence of $t_p$ is inserted. ($t_f$=50 s and $V_R$=−4 V)

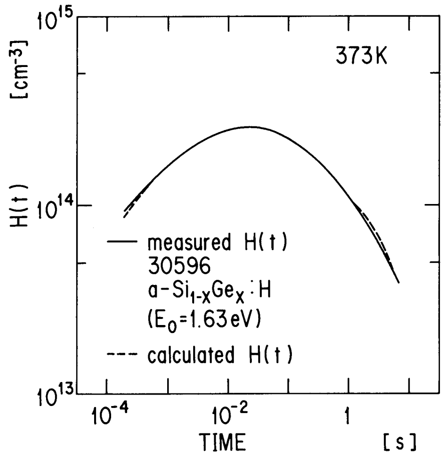


Fig. 4. Comparison between the measured $H(t)$ and the calculated $H(t)$.

All the $g(E)$ obtained from the fitting procedure are shown in Fig. 5. The values of $\nu_n$ obtained from the temperature dependence are $4\times10^{12}$, $8\times10^{11}$, and $4\times10^{11}$ s$^{-1}$ for $E_0$=1.55, 1.70, and 1.76 eV, respectively. These $g(E)$ are correlated with singly-occupied dangling bonds, as is clear from the results of steady-state HMC measurements.[2]

Tsutsumi *et al.*[7] first determined the energy location of singly-occupied dangling bonds in a-$Si_{1-x}Ge_x$:H, while Mackenzie *et al.*,[8] Skumanich *et al.*,[9] and Aljishi *et al.*[10] discussed it in relation with their own experimental results. The data shown in Fig. 5 coincide quantatively with the data reported by Tsutsumi *et al.* Using the transient HMC method, however, the magnitude as well as

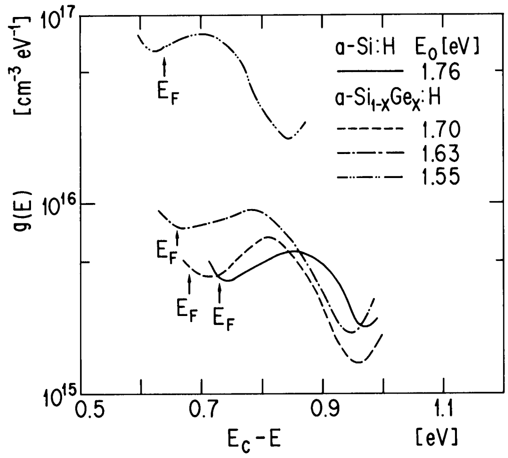


Fig. 5. DOS distribution for undoped a-Si:H and undoped a-$Si_{1-x}Ge_x$:H.

the location have been determined for the first time.

## §5. Summary

The DOS distribution for undoped a-Si:H and undoped a-$Si_{1-x}Ge_x$:H have been determined by transient heterojunction-monitored capacitance measurements which have been proposed in this letter. This technique can be applied to highly resistive thin-film semiconductors.

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## References

1) H. Matsuura, T. Okuno, H. Okushi and K. Tanaka: J. Appl. Phys. **55** (1984) 1012.
2) H. Matsuura: Jpn. J. Appl. Phys. **27** (1988) L513.
3) H. Okushi: Philos. Mag. **B52** (1985) 33.
4) D. V. Lang, J. D. Cohen and J. P. Harbison: Phys. Rev. **B25** (1982) 5285.
5) A. Matsuda, M. Koyama, N. Ikuchi, Y. Imanishi and K. Tanaka: Jpn. J. Appl. Phys. **25** (1986) L54.
6) H. Matsuura and H. Okushi: J. Appl. Phys. **62** (1987) 2871.
7) Y. Tsutsumi, S. Sakata, K. Abe, Y. Nitta, H. Okamoto and Y. Hamakawa: *Proc. 12th Int. Conf. on Amorphous and Liquid Semiconductors, Prague 1987*, J. Non-Cryst. Solids **97 & 98** (1987) 1063.
8) K. D. Mackenzie, J. R. Eggert, D. J. Leopold, Y. M. Li, S. Lin and W. Paul: Phys. Rev. **B31** (1985) 2198.
9) A. Skumanich, A. Frova and N. M. Amer: Solid State Commun. **54** (1985) 597.
10) S. Aljishi, Z. E. Smith, D. Slobodin, J. Kolodzey, V. Chu, R. Schwarz and S. Wanger: *Mater. Res. Soc. Symp. Proc.* **70** (1986) 269.