CHAPTER V TRANSIENT HMC METHOD

\[ H(t_m) \approx [f(E_m) - F_\infty(E_m)]g(E_m) \int_{E_V}^{E_C} D(E, t_m) dE \]

\[ \approx [f(E_m) - F_\infty(E_m)]g(E_m) \int_0^\infty D(E, t_m) dE \]

\[ = [f(E_m) - F_\infty(E_m)]g(E_m)kT \]  \hfill (5-17)

where \( E_m \) is the energy at which \( D(E, t) \) has a maximum value when

\[ e_n(E_m)t_m = 1 \]  \hfill (5-18)

Therefore, the relation between \( E_m \) and \( t_m \) is derived from Eqs. (5-12) and (5-18):

\[ E_C - E_m = kT \ln(\nu n t_m) \]  \hfill (5-19)

In a more general form, this equation can be expressed as

\[ E_C - E(t) = kT \ln(\nu nt) \]  \hfill (5-20)

Under the conditions that \( e_n(E) \) is much higher than \( e_p(E) \) [i.e., \( F_\infty(E) = 0 \)] as well as that \( f(E) \) is close to unity for the gap states between \( E_F \) and \( E_{OB} \), the relation between \( H(t) \) and \( g(E) \) is generally obtained from Eq. (5-17) as

\[ g(E) = H(t)/kT \]  \hfill (5-21)

Therefore, the \( g(E) \) around the middle of the energies between \( E_F \) and \( E_{OB} \) can be easily estimated from the measured \( H(t) \) using Eqs. (5-20) and (5-21).

5-4. Transient HMC Measurements

Undoped a-Si:H films were deposited by the rf glow-discharge decomposition of pure SiH₄, and undoped a-Si₁₋ₓGeₓ:H films were prepared by the rf glow-discharge decomposition of
CHAPTER V TRANSIENT HMC METHOD

**Fig. 5.3.** Reverse-bias dependence of measured $H(t)$.

**Fig. 5.4.** Set of two measured $H(t)$ corresponding to (111) and (100) surfaces of p c-Si for undoped a-Si$_{1-x}$ Ge$_x$:H ($E_D=1.44$ eV).
Chapter V Transient HMC Method

GeH₄/SiH₄/H₂ gas mixture. Good quality films could be obtained by those techniques. The optical gap (E₀) was determined by the Tauc plots of $(\alpha h\nu)^{1/2} \sim B_1(h\nu - E₀)$, where $\alpha$ is the optical absorption coefficient, $h\nu$ is the photon energy, and $B_1$ is a constant. The heterojunctions were fabricated by depositing the amorphous films onto p c-Si substrates ($N_A=1.0x10^{16}$ or $3.5x10^{16}$ cm⁻³) heated to 250 °C and then evaporating Mg on an area (0.785 mm²) of those films at room temperature in a vacuum of $7\times10^{-7}$ Torr. Thicknesses of amorphous films were kept between 0.8 and 1.2 μm. Mg formed a good Ohmic contact with those amorphous films. All the heterojunctions exhibited good rectifying properties.

Transient HMC measurements were carried out at 2 MHz for various temperatures. Only signals of $H(t)$ at time longer than the dielectric relaxation time are valid as mentioned in Section 5-3. The signals of $H(t)$ get saturated at a filling time $\tau_f$ (under the zero-bias condition) longer than 1 s. In the following measurements, $H(t)$ has been measured at $\tau_f=50$ s under the zero-bias condition.

Figure 5.3 shows the reverse-bias dependence of $H(t)$ for an a-Si₁₋ₓGeₓ:H(E₀=1.55 eV)/p c-Si heterojunction. The signals of $H(t)$ for $-5 \leq V_R \leq -3$ V are found to be independent of the reverse bias $V_R$, while the signals for $V_R$ of -1 V and -2 V depend on $V_R$, indicating that the relation, that $N_I(t)W_2(t)$ is much larger than $N_I(\infty)W_2(0)$, is invalid for the reverse biases of -1 V and -2 V. As described in Section 5-3, these $H(t)$ include information not only on the bulk but also on the interface. Since the $g(E)$ in the bulk is necessary, $H(t)$ has been measured at $V_R=-4$ V.

In order to check to what extent the interface states can affect the signal of $H(t)$, the signals of $H(t)$ with different surfaces of c-Si are compared, as shown in Fig. 5.4. The (111) surface of c-Si has the largest number of available bonds per cm², and the (100) surface has the smallest. According to the experimental results from Si/SiO₂ systems, the interface-state density for the (100) surface is reported to be lower by a factor of 10 compared to that for the (111) surface. In the
Fig. 5.5. Set of five measured $H(t)$ corresponding to five different measuring temperatures for undoped $a$-$Si_{1-x}Ge_x$:H/p $c$-$Si$:H ($N_A=1.0 \times 10^{16}$ cm$^{-3}$) heterojunction.

Fig. 5.6. Temperature dependence of time ($t_p$) at which $H(t)$ becomes maximum for undoped $a$-$Si_{1-x}Ge_x$:H/p $c$-$Si$ ($N_A=1.0 \times 10^{16}$ cm$^{-3}$) heterojunction.
present work, however, \( H(t) \) has not shown any significant variation with surface orientation, as is clear from Fig. 5.4. Thus, \( H(t) \) is considered to be unaffected by the interface states in the present heterojunctions. From the figure, moreover, \( H(t) \) is considered to be independent of the resistivity of p c-Si, which is considered to be natural since \( N_I \) obtained from the steady-state HMC method is independent of the p c-Si resistivity as discussed in Chapter III.

In order to calculate \( H(t) \) using Eq. (5-14), only \( \nu_n \) and \( \nu_p \) are necessary. Here, an undoped \( aSi_{1-x}Ge_x:H/p \) c-Si heterojunction with \( N_A=1.0\times10^{16} \text{ cm}^{-3} \), as shown in Fig. 5.5, is considered in order to estimate the values of \( \nu_p \) and \( \nu_n \). The electron thermal-emission rate \([e_n(E)]\) for a particular gap state at a depth \((E_C-E)\) from the conduction band is given by Eq. (5-12), and the time, which is required for a trapped electron to be thermally re-emitted, is \( 1/e_n(E) \). Under the assumption that the gap states corresponding to the peak of \( H(t) \) is located between \( E_F \) and \( E_{OB} \), the \( g(E_p) \) is obtained as \( H(t_p)/kT \) from Eq. (5-21). Therefore, the value of \( \nu_n \) can be approximately estimated from the temperature dependence of the time \((t_p)\) at the peak of \( H(t) \). Then,

\[
t_p = \frac{1}{e_n(E_p)} = \frac{1}{\nu_n}\exp\left[\frac{(E_C - E_p)/kT}{\nu_n}\right]
\]

if \( \nu_n \) is independent of temperature and energy. Figure 5.6 shows the temperature dependence of \( t_p \), and from the intercept on the vertical axis in the figure using Eq. (5-22) the value of \( \nu_n \) is found to be \( 2\times10^{13} \text{ s}^{-1} \). Next, a maximum value of \( \nu_p/\nu_n \) is estimated as follows. Figure 5.7 shows the calculated \( H(t) \) for different \( \nu_p \) with \( g(E)=1\times10^{17} \text{ cm}^{-3}\text{eV}^{-1} \) and \( \nu_n=2\times10^{13} \text{ s}^{-1} \). The measured \( H(t) \) at 1.4 s (T=306.6 K) is about \( 5\times10^{14} \text{ cm}^{-3} \) from Fig. 5.5, while in the case of \( \nu_p/\nu_n=1 \) using \( E_g = E_0 = 1.52 \text{ eV} \) the calculated one is about \( 10^8 \text{ cm}^{-3} \) from Fig. 5.7, suggesting that the value of \( g(E) \) corresponding to 1.4 s should attain an unreasonable value of \( 5\times10^{23} \text{ cm}^{-3}\text{eV}^{-1} \) simply because

91
Fig. 5.7. Set of three calculated $H(t)$ corresponding to three different attempt-to-escape frequencies for holes with $g(E) = 1 \times 10^{17} \text{ cm}^{-3}\text{eV}^{-1}$ and $\nu = 2 \times 10^{13} \text{ s}^{-1}$ for $E_g = E_0 = 1.52 \text{ eV}$. 

$g(E) = 1 \times 10^{17} \text{ cm}^{-3}\text{eV}^{-1}$
$E_g = 1.52 \text{ eV}$
$E_0 = 0.66 \text{ eV}$
$T = 306.6 \text{ K}$

- $\nu_n = 2 \times 10^{13} \text{ sec}^{-1}$
- $\nu_p = 0 \text{ sec}^{-1}$
- $\nu = 2 \times 10^{13} \text{ sec}^{-1}$
- $\nu_p = 2 \times 10^{13} \text{ sec}^{-1}$
\( g(E) : 1 \times 10^{17} = 5 \times 10^{14} : 10^8 \)

From the above consideration, the value of \( \nu_n \) and the maximum value of \( \nu_p \) are taken as \( 2 \times 10^{13} \) and \( 2 \times 10^9 \) s\(^{-1} \), respectively. The calculated \( H(t) \) was approached to the measured \( H(t) \) by changing \( g(E) \), and then the \( g(E) \) shown in Fig. 5.8 made the calculated \( H(t) \) fit in with the measured \( H(t) \) very well, as shown in Fig. 5.9. Here, it is assumed that the mobility gap coincides with \( E_0 \). Figure 5.10 shows the temperature dependence of the calculated \( H(t) \) which fits in with the measured \( H(t) \) at each temperature.

The \( g(E) \) for undoped a-Si:H, estimated from the measured \( H(t) \) in Fig. 5.11, is shown in Fig. 5.12 using \( \nu_n = 1 \times 10^{11} \) s\(^{-1} \), \( \nu_p = 1 \times 10^8 \) s\(^{-1} \), and \( E_g = E_0 = 1.70 \) eV. Density-of-state distributions for other amorphous silicon-based alloys will be discussed in Chapter VI.

The distribution \( g(E) \) obtained here is found to be the bulk DOS distribution unaffected by interface states. This appears to be the first systematic effort to electrically estimate the \( g(E) \) below the Fermi level for undoped amorphous materials. Therefore, the following part of this section considers the validity of this transient HMC method in more detail. The following pertinent questions could arise, viz.:

1. Is the assumption that \( \nu_n \) and \( \nu_p \) are independent of temperature and energy correct?
2. Are the values obtained for \( \nu_n \) and \( \nu_p \) reasonable?
3. To what degree does tunneling affect \( g(E) \)?

There has been a controversy in opinion regarding the answers to (1) and (2) mainly on the basis of results obtained from DLTS\(^1,5,6\) and ICTS\(^2,7\). These techniques have mainly been applied to P-doped a-Si:H, but no data exist for undoped a-Si:H and undoped a-Si\(_{1-x}\)Ge\(_{x}\):H.

If \( \nu_n \) has a temperature dependence of the form

\[
\nu_n = \nu_{n0} T^2 \exp(-\Delta E_{\nu}/kT),
\]

where \( \nu_{n0} \) and \( \Delta E_{\nu} \) are constants independent of \( T \), Eq. (5-22)
**Fig. 5.8.** Density-of-state distribution for $a$-$\text{Si}_{1-x}\text{Ge}_x$:H ($E_0=1.52$ eV).

**Fig. 5.9.** Comparison between measured $H(t)$ for $a$-$\text{Si}_{1-x}\text{Ge}_x$:H ($E_0=1.52$ eV) and calculated $H(t)$ with $E_g=1.52$ eV, $\nu_n=2\times10^{13}$ s$^{-1}$ and $\nu_p=2\times10^{9}$ s$^{-1}$. 
Fig. 5.10. Set of five calculated $H(t)$ corresponding to five different temperatures for $E_g = 1.52 \text{ eV}$ with $\nu_n = 2 \times 10^{13} \text{ s}^{-1}$ and $\nu_p = 2 \times 10^9 \text{ s}^{-1}$. 
Fig. 5.11. Set of five measured H(t) corresponding to five different measuring temperatures for undoped a-Si:H/p c-Si \(N_A=1.0\times10^{16} \text{ cm}^{-3}\) heterojunction.

Fig. 5.12. Density-of-state distribution for a-Si:H \(E_0=1.70 \text{ eV}\) which can fit measured H(t) with calculated H(t) using \(E_g=1.70 \text{ eV}\), \(\nu_n=1\times10^{11} \text{ s}^{-1}\), and \(\nu_p=1\times10^8 \text{ s}^{-1}\).
CHAPTER V TRANSIENT HMC METHOD

changes into

\[ t_p = (1/\nu n_0T^2) \exp \left( (E_C - E_p + \Delta E_{\nu})/kT \right) \],  \quad (5-24)

indicating that the energies shown in Figs. 5.8 and 5.12 are overestimated because of the assumption that \( \Delta E_{\nu} = 0 \). The situation is the same as that reported by Lang and Cohen.\(^1\) Therefore, it is important to investigate the temperature dependence of \( \nu_n \). Furthermore, Lang and Cohen\(^1\) assumed that \( \nu_n \) was independent of energy locations of gap states which were ascribed to the same origin, while Okushi\(^2\) reported that \( \nu_n \) has an energy dependence. In the above discussion, the energy-independence of \( \nu_n \) is adopted. We have tried to investigate the temperature- and energy-dependencies of \( \nu_n \) by means of the trap filling method like ICTS which investigates the dependence of \( H(t) \) on the filling time \( (\tau_F) \),\(^2\) but difficulty has been encountered owing to the long dielectric relaxation time of amorphous films. However, the energy locations of the peak of DOS for undoped materials are found to be close to those reported by Tsutsumi et al.,\(^8\) and Kocka, Vanecek and Schaver.\(^9\)

Since the values of \( \nu_n \) are reported to be between \( 10^9 \) and \( 10^{13} \) s\(^{-1}\) for Si dangling bonds,\(^1-2\) the values obtained here are considered to be reasonable. On the other hand, there is no experimental data on the values of \( \nu_p \). The value of \( \nu_p \) estimated from the fitting procedure depends strongly on the mobility gap \( (E_{g2}) \) because \( e_p(E) \) is a function of \( (E_C - E) - E_{g2} \). The \( g(E) \) estimated with \( \nu_p = 1 \times 10^{11} \) s\(^{-1}\) and \( E_{g2} = 1.91 \) eV is the same as the \( g(E) \) shown in Fig. 5.12 with \( \nu_p = 1 \times 10^{11} \) s\(^{-1}\), \( \nu_p = 1 \times 10^8 \) s\(^{-1}\), and \( E_{g2} = 1.70 \) eV because \( E_{OB} \) is the same in both cases. The value of the mobility gap poses an open question. Vanecek et al.\(^10\) concluded that the mobility gap of a-Si:H was quite close to \( E_0 \) (\( \sim 1.7 \) eV). On the other hand, Lang and co-workers\(^6\) used the values between 1.9 and 2.1 eV for the mobility gap of a-Si:H based on the assumption of \( \nu_p = 10^{13} \) s\(^{-1}\). Jackson et al.\(^11\) reported it as \( 1.93 \pm 0.2 \) eV. However, the estimated \( g(E) \) does not change at all when the best fit is obtained using the maximum of \( \nu_p/\nu_n \) which is determined by the

97
value of $E_{g2}$. Regarding the third question, it seems like tunneling does not affect the $g(E)$ in the range of the measuring temperatures from the consideration similar to the ICTS analysis of P-doped a-Si$_{1-x}$Ge$_x$:H.\textsuperscript{12)} The value of $t_p$, when the tunneling process affects $H(t)$, is not on the linear relation between $t_p$ and $1/T$ expected from the range of higher temperature. In the present study, the linear relations between them are obtained in the whole temperature range studied here for all the samples. This transient HMC method will be applied not only to determining the $g(E)$ in other undoped amorphous silicon alloys but also to investigating the changes of $g(E)$ by light-soaking, rapid cooling, and thermal annealing in the following chapter.

5-5. Summary

A novel technique for determining the magnitude as well as energy location of midgap states in highly resistive amorphous materials has been developed from the study of the transient capacitance in the highly resistive amorphous/lowly resistive crystalline semiconductor heterojunctions. This transient HMC method has been tested and applied on undoped a-Si:H and undoped a-Si$_{1-x}$Ge$_x$:H. The $g(E)$ obtained by the transient HMC method is found to be representative of a homogeneous bulk property of the amorphous material, unaffected by their interface states.