## CHAPTER VI CHANGES OF MIDGAP STATES

Since there are only a few data concerned with the peak energy location of $D^0$ in a-$Si_{1-x}Ge_x$:H and there is no data concerned with that in a-$Si_{1-x}C_x$:H, a lot of researches determining their energy location should be performed by means of different techniques.

### 6-3. Thermal Recovery Process of Midgap-state Profile of Light-soaked Undoped a-Si:H

Undoped a-Si:H films (about 1.2 $\mu$m thickness) were deposited by the rf glow-discharge decomposition of pure $SiH_4$. In order to measure dark conductivity ($\sigma_2$), photoconductivity ($\Delta\sigma_{ph}$), and the activation energy ($\delta_2 = E_C - E_F$) of dark conductivity in a-Si:H films, samples with coplanar electrodes were fabricated by depositing a-Si:H onto Corning 7059 glass substrates heated to 250 ℃ for sample 21099 and heated to 310 ℃ for sample AK362, and subsequently by evaporating Al at room temperature. Thus-determined properties are shown in Table 6-1. Oxygen, carbon, and nitrogen concentrations estimated using secondary-ion mass spectrometry (SIMS) were $7x10^{19}$, $1x10^{19}$, and $3x10^{18}$ $cm^{-3}$ in sample 21099, respectively, and they were $5x10^{19}$, $2x10^{19}$, and $8x10^{17}$ $cm^{-3}$ in sample AK362, respectively.

The heterojunctions were fabricated by depositing the films onto p c-Si substrates heated to 250 ℃ for sample 21099 and heated to 310 ℃ for sample AK362. The acceptor density ($N_A$) of p c-Si was $1.0x10^{16}$ $cm^{-3}$. Since Mg has been known to form a good Ohmic contact with undoped a-Si:H, Mg was then evaporated on an area (0.785 $mm^2$) of as-deposited a-Si:H films at room temperature. For other heterojunctions, Mg was evaporated after a-Si:H films were exposed to the AM1 light with 100 $mW/cm^2$ at room temperature. As soon as the sample 21099 heated to 150 ℃ in a vacuum, the transient HMC was measured using the Sanwa MI-415 capacitance meter (2 MHz). It was also measured 30-min later, 1-h later, and 2-h later. However, the transient HMC of sample AK362 could not be measured at 150 ℃ because of low resistivity of its a-Si:H film. Therefore, after the sample was

**TABLE 6-1.** Film properties of samples 21099 and AK362.

| Sample | As-deposited | Light exposure | Anneal[c] | Anneal[d] |
|---|---|---|---|---|
| 21099[a] | | | | |
| $\sigma_2$ ($\times 10^{-8}$ S/cm) | 0.1 | 0.01 | 0.09 | 0.2 |
| $\Delta\sigma_{ph}$ ($\times 10^{-4}$ S/cm) | 2 | 0.2 | 1 | 2 |
| $E_C$-$E_F$ (eV) | 0.71 | 0.78 | 0.76 | 0.69 |
| AK362[b] | | | | |
| $\sigma_2$ ($\times 10^{-8}$ S/cm) | 1 | 0.02 | 0.6 | 2 |
| $\Delta\sigma_{ph}$ ($\times 10^{-4}$ S/cm) | 3 | 0.2 | 2 | 3 |
| $E_C$-$E_F$ (eV) | 0.63 | 0.70 | 0.66 | 0.62 |

[a] AM1, 100 mW/cm$^2$ for 3.3 h.
[b] AM1, 100 mW/cm$^2$ for 4 h.
[c] 150 ℃ for 3 h.
[d] 200 ℃ for 1.5 h.

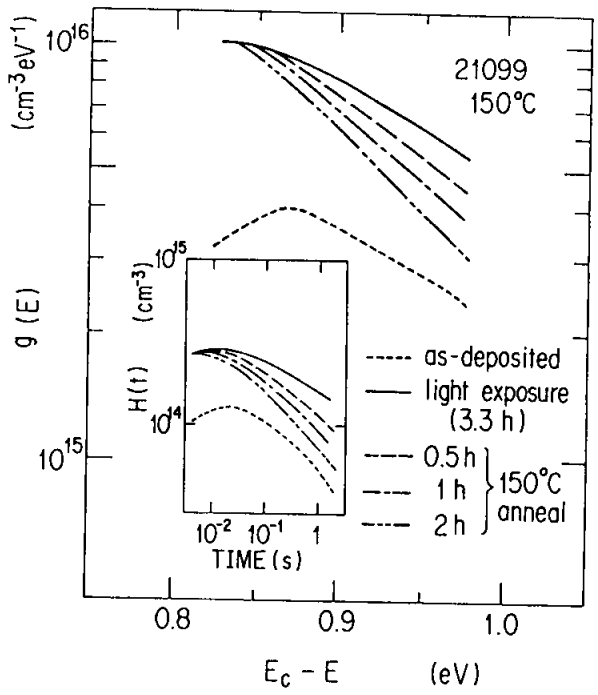


**Fig.6.6.** Changes of g(E) at measuring temperature of 150 °C. The signal H(t) of transient HMC, from which the g(E) was calculated, is inserted.

annealed at 150 ℃ for 3 h, the sample was cooled down, and then the transient HMC was measured at 80, 100, and 120 ℃. After this, the sample was annealed at 200 ℃ for 1.5 h, and then the transient HMC was measured at 80, 100, 120 ℃. The signal H(t) of transient HMC for as-deposited films did not change before and after the heterojunctions were annealed even at 200 ℃ for 1.5 h in a vacuum. Figure 6.6 shows the time-resolved g(E) and the corresponding signals H(t) of the transient HMC in the inset. These g(E) were calculated from these H(t) using the attempt-to-escape frequency for electrons ( $\nu_n$) of $10^{12}$ $s^{-1}$. The signal of H(t) for the as-deposited film did not change at all during the thermal annealing process at 150 ℃, indicating that contact properties were not affected by this thermal treatment. Therefore, changes of H(t) in the light-soaked film should be ascribed to the changes of the bulk g(E) in a-Si:H.

Two sorts of models have been proposed for explaining the thermal annealing kinetics;

(1) monomolecular kinetics,[4)]

(2) bimolecular kinetics.[5)]

Lee et al.[5)] have proposed a bimolecular annealing process with constant $E_a$;

$$d[\Delta N_s(t)]/dt = -\gamma_a \exp(-E_a/kT)\Delta N_s(t)^2 \quad , \qquad (6\text{-}1)$$

while Stutzmann et al.[4)] have proposed a monomolecular annealing process with a distribution of $E_a$;

$$d[\Delta N_s(E_a,t)]/dt = -\nu_a \exp(-E_a/kT)\Delta N_s(E_a,t) \quad . \qquad (6\text{-}2)$$

Though they discussed the change ( $\Delta N_s$) of the total density estimated from ESR, the transient HMC method enables us to investigate the annealing behavior of midgap states at each energy position ($E_C$-E). Let us consider the bimolecular annealing process at each energy position;

$$d[\Delta g(E,t)]/dt = -\gamma_a \exp(-E_a/kT)\Delta g(E,t)^2 \qquad (6\text{-}3)$$

and

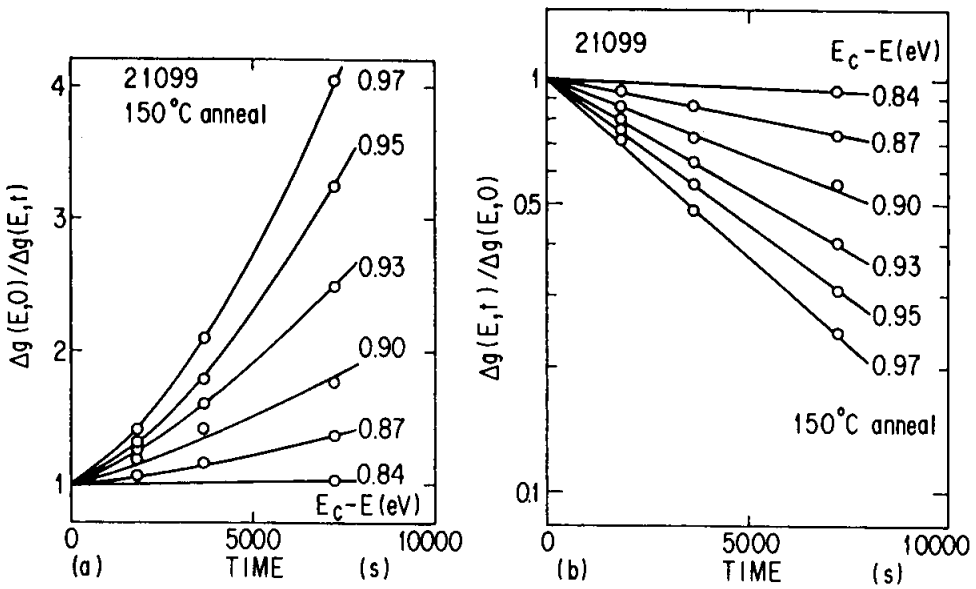


**Fig.6.7.** Annealing behavior of light-induced midgap states plotted assuming (a) bimolecular kinetics and (b) monomolecular kinetics.

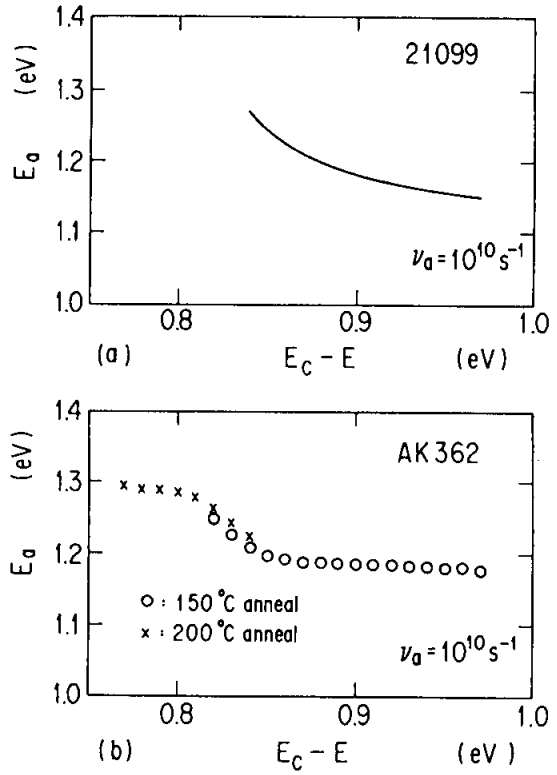


**Fig.6.8.** Activation energy for thermal annealing; (a)obtained from slopes in Fig.6.7(b), and (b)estimated from films annealed at 150 and 200 ℃.

$$\Delta g(E,t) = g(E,t) - g_0(E) \quad , \qquad (6\text{-}4)$$

where $g(E,0)$ and $g_0(E)$ are the midgap-state profiles for the light-soaked film and the as-deposited film, respectively, t is the annealing time, and $\gamma_a$ is the pre-exponential factor of the bimolecular decay rate. The integral of Eq. (6-3) implies that

$$\Delta g(E,0)/\Delta g(E,t) = 1 + \gamma_a \exp(-E_a/kT)\Delta g(E,0)t. \qquad (6\text{-}5)$$

Although this equation predicts a linear relation between $\Delta g(E,0)/\Delta g(E,t)$ and t, the experimental data did not produce the straight lines, as shown in Fig. 6.7(a).

The monomolecular annealing process is given by

$$d[\Delta g(E,t)]/dt = -\nu_a \exp(-E_a/kT)\Delta g(E,t) \quad , \qquad (6\text{-}6)$$

and the integral of this equation implies that

$$\ln[\Delta g(E,t)/\Delta g(E,0)] = -\nu_a \exp(-E_a/kT)t \quad , \qquad (6\text{-}7)$$

where $\nu_a$ is the pre-exponential factor of the monomolecular decay rate. As is shown in Fig. 6.7(b), the data produce a straight line for each value of $(E_C\text{-}E)$, indicating that the experimental results can be predicted by Eq. (6-7). Values of $E_a$ obtained from the slope of the curves of Fig. 6.7(b) are plotted as a function of $(E_C\text{-}E)$ in Fig. 6.8(a). Here, the value of $\nu_a$ is tentatively assumed to be $10^{10}$ $s^{-1}$, which Stutzmann et al.[4] reported. The value of $E_a$ decreases monotonously with an increase in $(E_C\text{-}E)$.

From the above results, at least phenomenologically, the monomolecular annealing kinetics with a distribution of $E_a$ are more suitable for explaining these experimental data.

The behavior of $E_a$ for states closer to the conduction band has been investigated. Although the real-time measurement of g(E) in sample AK362 could not be carried out at 150 ℃ due to its low resistivity, $E_a$ could roughly be estimated using Eq. (6-7) from low-temperature (80-120 ℃) measurements in the films

annealed at 150 and 200 ℃. The g(E) after light exposure increased by a factor of about 1.7 compared with the g(E) for the as-deposited film, but the energy position of the peak of midgap states did not change by light exposure. After annealing at 150 ℃ for 3 h, the g(E) for ($E_C$-E) in the range higher than 0.8 eV decreased. In the film annealed at 200 ℃ for 1.5 h, the g(E) for ($E_C$-E) in the range higher than 0.85 eV approached to the g(E) for the as-deposited film, while for ($E_C$-E) in the range lower than 0.85 eV it was still larger than the g(E) for the as-deposited film. The value of $E_a$ which was roughly estimated from this experiment is shown in Fig. 6.8(b), and $E_a$ seems to get saturated in lower ($E_C$-E).

This is the first report which elucidates the relation between $E_a$ and ($E_C$-E). Although Stutzmann et al.[4] and Smith et al.[6] predicted that midgap states should have a distribution of $E_a$, they did not discuss the relation between $E_a$ and ($E_C$-E). The values of $E_a$ are similar to those reported by Qiu et al.,[8] while they are rather larger than those reported by Stutzmann et al..[4] Shepard et al.[13] have predicted from photoconductivity measurements that the g(E) above the Fermi level (maybe doubly-occupied dangling bonds, $D^-$) closest to the midgap is annealing first, with which the present results coincide if the correlation energies between $D^0$ and $D^-$ are kept constant.

## 6-4. Optically and Thermally Induced Reversible Changes of Midgap States in Undoped a-Si:H

Undoped a-Si:H/p c-Si heterojunctions were fabricated as follows. Undoped a-Si:H films (1.2-1.5 $\mu$m thickness) were deposited by the rf glow-discharge decomposition of pure $SiH_4$ gas onto p c-Si substrates heated to $T_s$=200-300 ℃. After turning off the plasma, the substrate temperature was kept as it was for 10 min. Then the specimen was cooling down slowly. The acceptor density ($N_A$) in p c-Si was $1.0\times10^{16}$ $cm^{-3}$. Since Mg is known to form a good Ohmic contact with undoped a-Si:H, Mg was evaporated on an area (0.785 $mm^2$) of as-deposited films at room temperature