CHAPTER VI CHANGES OF MIDGAP STATES

Since there are only a few data concerned with the peak energy location of $E_0$ 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 $^\circ$C for sample 21099 and heated to 310 $^\circ$C 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 $7 \times 10^{19}$, $1 \times 10^{19}$, and $3 \times 10^{18}$ cm$^{-3}$ in sample 21099, respectively, and they were $5 \times 10^{19}$, $2 \times 10^{19}$, and $8 \times 10^{17}$ cm$^{-3}$ in sample AK362, respectively.

The heterojunctions were fabricated by depositing the films onto p c-Si substrates heated to 250 $^\circ$C for sample 21099 and heated to 310 $^\circ$C for sample AK362. The acceptor density ($N_A$) of p c-Si was $1.0 \times 10^{16}$ 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 $^\circ$C 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 $^\circ$C 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>As-deposited</th>
<th>Light exposure</th>
<th>Anneal&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Anneal&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>21099&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.1</td>
<td>0.01</td>
<td>0.09</td>
<td>0.2</td>
</tr>
<tr>
<td>$\sigma_2$ (x10^-8 S/cm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta \sigma_{ph}$ (x10^-4 S/cm)</td>
<td>2</td>
<td>0.2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>$E_C-E_F$ (eV)</td>
<td>0.71</td>
<td>0.78</td>
<td>0.76</td>
<td>0.69</td>
</tr>
</tbody>
</table>

| AK362<sup>b</sup> | 1            | 0.02           | 0.6                 | 2                   |
| $\sigma_2$ (x10^-8 S/cm) |             |                |                     |                     |
| $\Delta \sigma_{ph}$ (x10^-4 S/cm) | 3           | 0.2            | 2                   | 3                   |
| $E_C-E_F$ (eV) | 0.63         | 0.70           | 0.66                | 0.62                |

<sup>a</sup> AM1, 100 mW/cm² for 3.3 h.

<sup>b</sup> AM1, 100 mW/cm² for 4 h.

<sup>c</sup> 150 °C for 3 h.

<sup>d</sup> 200 °C 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 °C for 3 h, the sample was cooled down, and then the transient HMC was measured at 80, 100, and 120 °C. After this, the sample was annealed at 200 °C for 1.5 h, and then the transient HMC was measured at 80, 100, 120 °C. The signal $H(t)$ of transient HMC for as-deposited films did not change before and after the heterojunctions were annealed even at 200 °C 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 °C, 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 $E_a$:

$$d[\Delta N_S(t)]/dt = -\gamma a \exp(-E_a/kT) \Delta N_S(t)^2 \quad (6-1)$$

while Stutzmann et al. \(^4\) have proposed a monomolecular annealing process with a distribution of $E_a$:

$$d[\Delta N_S(E_a,t)]/dt = -\nu a \exp(-E_a/kT) \Delta N_S(E_a,t) \quad (6-2)$$

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:

$$d[\Delta g(E,t)]/dt = -\gamma a \ exp(-E_a/kT) \Delta g(E,t)^2 \quad (6-3)$$

and
CHAPTER VI  CHANGES OF MIDGEAP STATES

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 °C.
\[ \Delta g(E,t) = g(E,t) - g_0(E), \quad (6-4) \]

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

\[ \frac{\Delta g(E,0)}{\Delta g(E,t)} = 1 + \gamma_a \exp(-E_a/kT) \Delta g(E,0)t. \quad (6-5) \]

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

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

and the integral of this equation implies that

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

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 \( (E_C-E) \), 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 \( (E_C-E) \) 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 \( (E_C-E) \).

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 °C due to its low resistivity, \( E_a \) could roughly be estimated using Eq. (6-7) from low-temperature (80-120 °C) measurements in the films.
CHAPTER VI  CHANGES OF MIDGAP STATES

annealed at 150 and 200 °C. 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 °C 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 °C 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 μm 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 °C. 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 1.0x10^{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.