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 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 ℃. 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 1.0×10^{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 (as-deposited films). For other heterojunctions, Mg was evaporated at room temperature after the a-Si:H films were exposed to AM1 light with 100 mW/cm^2 at room temperature (light-soaked films), or after those films, which had been kept at a given high temperature (T_{RC}) in H_2 atmosphere for 10 min, were immediately dropped into liquid nitrogen (rapidly-cooled films).

The midgap-states density (N_I) of undoped a-Si:H was estimated from the high-frequency (1-MHz) capacitance-voltage (C-V) characteristics at room temperature using the steady-state HMC method, as mentioned in Chapter III. The HMC signals of H(t), which are obtained from the transient capacitances of their heterojunctions measured at 2 MHz, approximately correspond to their density-of-states distributions [g(E)] through (See Chapter IV)

$$g(E) = H(t)/kT \quad , \tag{6-8}$$

and the energy location below the conduction band edge (E_C) is expressed by

$$E_C - E = kT\ln(\nu_n t) \quad , \tag{6-9}$$

where k is the Boltzmann's constant, T is the measuring absolute temperature, t is the time after the reverse bias is applied to the junction, ν_n is the attempt-to-escape frequency for electrons which can be estimated from the temperature dependence (353-393 K) of the time (t_p) at the peak of H(t).

First, the illumination-time dependence is considered. The value of N_I increased with about one-third powers of the illumination time (t_{IL}), whose behavior was quite similar to the results obtained from the ESR measurements, as described in Section 6-1. The value of the activation energy (δ_2) of dark conductivity of the film was independent of t_{IL} as long as t_{IL} was longer than 3 h. The value of δ_2 of light-soaked films, however, was larger than that of as-deposited films, as is similar to the data in Table 6-1. The H(t) signals did not change before and after the as-deposited film was annealed at 200

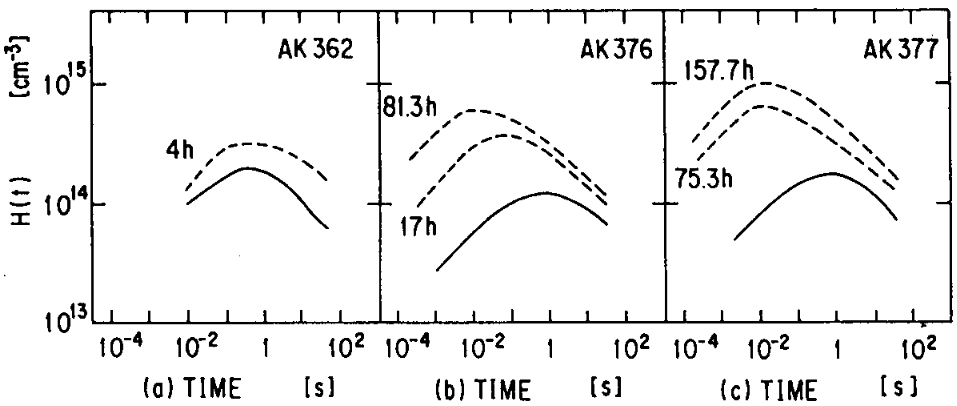

Fig.6.9. Dependence of H(t) signals on illumination time: (a) 4-h illumination on sample Ak362; (b) 17 h and 81.3 h on AK376; and (c) 75.3 h and 157.7 h on AK377. The solid curves represent H(t) for as-deposited films.

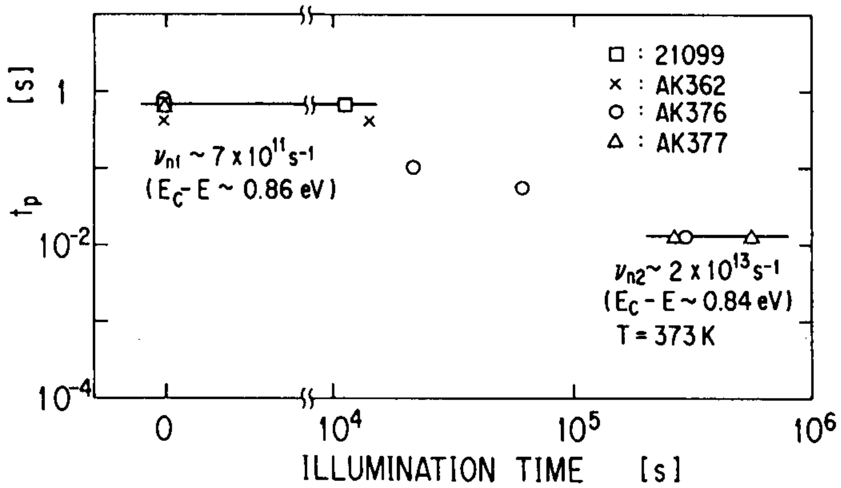

Fig.6.10. Dependence of time(t_p) on illumination time(t_{IL}). The solid lines are guides to eye.

℃ for 2 h in a vacuum, and the H(t) signals for the films annealed at 200 ℃ for 2 h after the light soaking were quite similar to those for as-deposited films.

Figure 6.9 shows the dependence of H(t) signals on t_{IL}. After short-time (≦ 4-h) light soaking, the magnitude of H(t) increased without any shift of t_p, while after long-time (≧ 75-h) light soaking t_p was shifted toward shorter time and kept constant, as is clearly shown in Fig. 6.10. From the temperature dependence of t_p, ν_n and the energy position (E_C-E_p) corresponding to the peak of H(t) were estimated; ν_{n1} and (E_C-E_{p1}) for the as-deposited and the short-time light-soaked films were about 7×10^{11} s^{-1} and 0.86 eV, respectively, and ν_{n2} and (E_C-E_{p2}) for the long-time light-soaked films were about 2×10^{13} s^{-1} and 0.84 eV, respectively. Although the change of t_p could, as one possibility, be thought to arise from the change of the free electron concentration in the depletion region of a-Si:H which leads to the change in the reverse current of the heterojunction,[14] the reverse current for the long-time light-soaked film was the same as that for the as-deposited film, indicating that the change of t_p must originate from the change of ν_n. Figure 6.11 schematically summarizes the above results. The solid curve A represents the g(E) in the as-deposited film. After the short-time light-soaking, both midgap states increased. However, the midgap states with ν_{n2} (the dashed curve B1) are still hidden by those with ν_{n1} (the solid curve B1). Subsequent light-soaking makes the midgap states with ν_{n2} (the dashed curve B2) larger than those with ν_{n1} (the solid curve B2). Therefore, the rate of increase of midgap states with ν_{n2} must be larger than that with ν_{n1}.

Second, the change of light-soaked films by thermal annealing is discussed. Figure 6.12(a) shows the changes of H(t) for the long-time light-soaked films by a 150-℃ annealing for 2 h, and Fig. 6.12(b) shows those by a 200-℃ annealing. Since the H(t) signals include information on two kinds of midgap states, two sorts of energy scales corresponding to ν_{n1} and ν_{n2} are shown in the abscissa below the time scale. Section 6-3 has studied the thermal annealing kinetics using the short-time

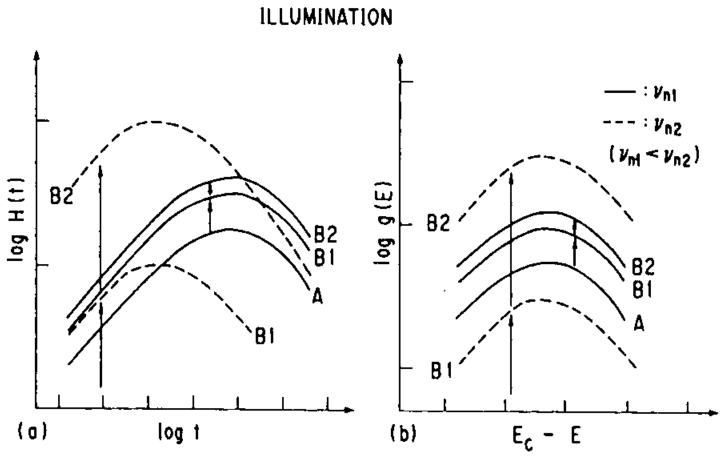

Fig.6.11. Schematic changes of midgap states by light soaking. The solid and dashed lines represent the states with small and large ν_n, respectively. A, B1, and B2 correspond to the as-deposited (or completely annealed), the short-time light-soaked, and the long-time light-soaked films, respectively. (b) is estimated from (a) using the relations of $g(E)=H(t)/kT$ and $E_C-E=kT\ln(\nu_n t)$.

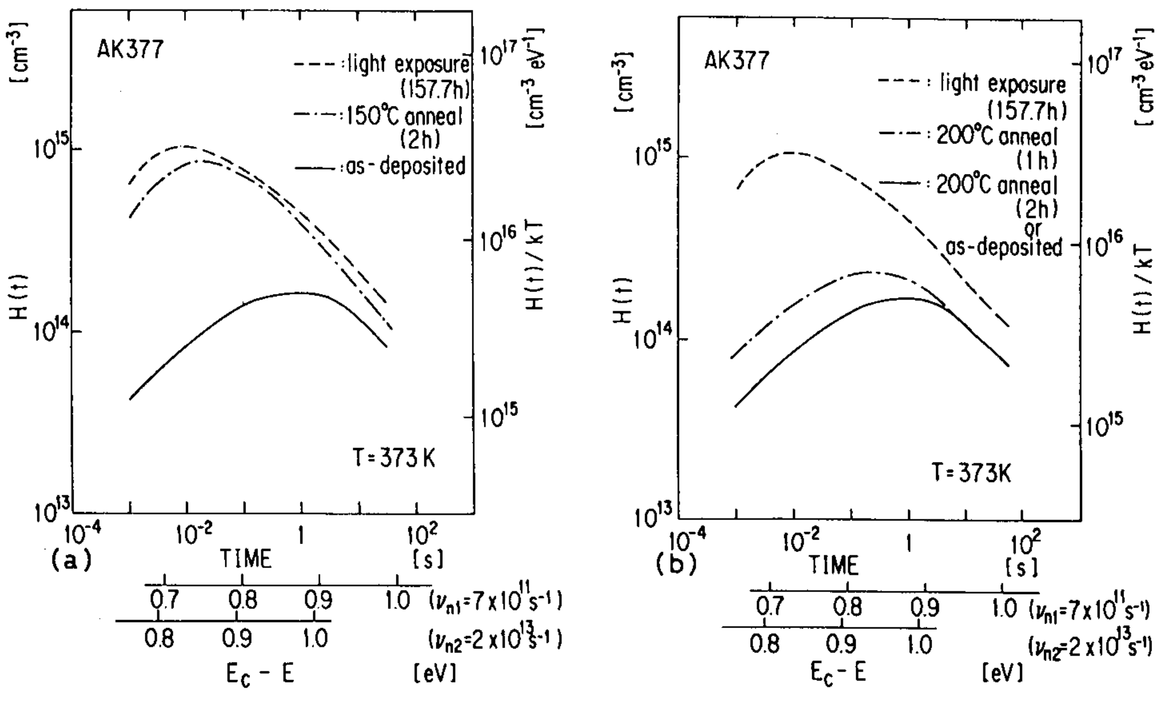

Fig.6.12. Changes of measured H(t) by (a) 150-℃ annealing and (b) 200-℃ annealing for long-time light-soaked film.

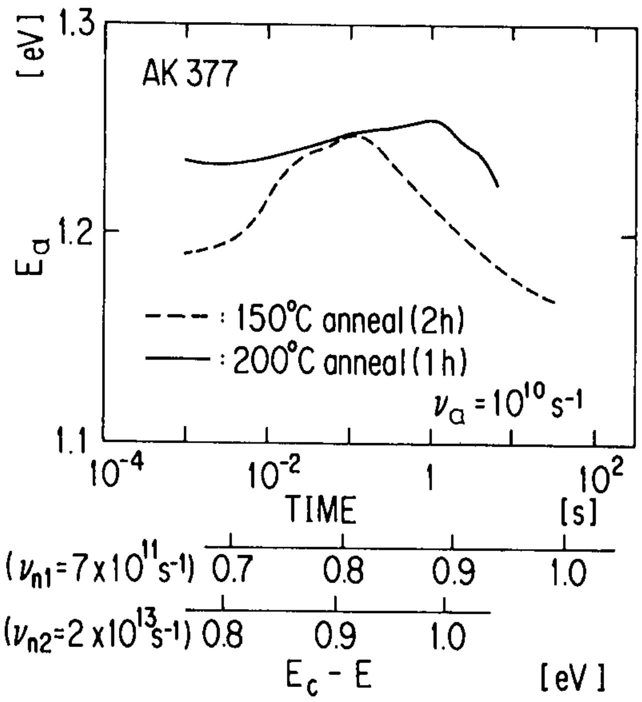

Fig.6.13. Activation energies estimated from studies of annealing at 150 ℃ for 2 h and subsequent annealing at 200 ℃ for 1 h.

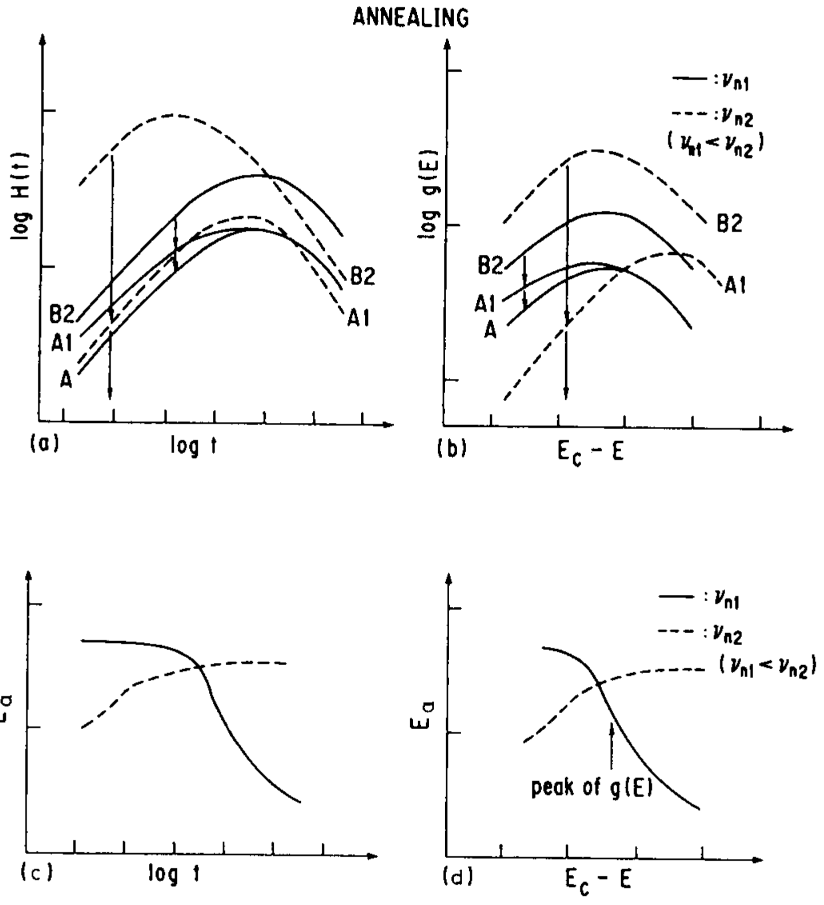

Fig.6.14. Schematic changes [(a) and (b)] of midgap states by thermal annealing and activation energies [(c) and (d)] for thermal annealing. The relation between (E_C-E) and t is given by $E_C\text{-}E=kT\ln(\nu_n t)$. The relation between H(t) and g(E) is expressed as g(E)=H(t)/kT. The solid and dashed lines represent the states with small and large ν_n, respectively. B2, A1, and A correspond to the long-time light-soaked, the short-time annealed, and the completely annealed films, respectively.

light-soaked films, from which the monomolecular annealing kinetics are found to be suitable for explaining those results. Figure 6.13 shows the activation energies for the 150-℃ annealing (2 h) and the 200-℃ annealing (1 h) from Fig. 6.12, assuming a monomolecular annealing process. In Fig. 6.13, the dashed curve at $t>10^{-1}$ s and the solid curve at $t<10^{-1}$ s are quite similar to the curve shown in Fig. 6.8, and those curves represent the activation energies for midgap states with ν_{n1}. So, the dashed curve at $t<10^{-1}$ s and the solid curve at $t>10^{-1}$ s must be affected by the activation energies for the midgap states with ν_{n2}. Since the energy dependence of E_a for the short-time light-soaked films is already known as shown in Fig. 6.8, changes in E_a and $H(t)$ for the annealing process in the long-time light-soaked films can be schematically described as shown in Fig. 6.14. After the long-time light-soaking, there are the midgap states with ν_{n1} (the solid curve B2) and those with ν_{n2} (the dashed curve B2). The annealing at 150 ℃ for 1 h makes the midgap states decrease a little. Those decreases of midgap states correspond to that of the midgap states with ν_{n2} at $t<10^{-1}$ s and that of those with ν_{n1} at $t>10^{-1}$ s. Midgap states with ν_{n2} still dominate at $t<10^{-1}$ s and those states with ν_{n1} are still dominant at $t>10^{-1}$ s. The annealing at 200 ℃ for 1 h makes the midgap states decrease to the curve of A1. The value of E_a at $t<10^{-1}$ s is close to that with ν_{n1}, and E_a at 10^{-1} s<t<1 s must be close to that with ν_{n2} . In final, the subsequent 200-℃ annealing for more 1 h gets the midgap states with ν_{n2} hidden by those with ν_{n1} (the solid curve A).

Third, the effect of rapid cooling is mentioned using Fig. 6.15. Smith and Wagner[6)] have combined the creation process with the annealing process, where both have been proposed by Stutzmann et al.[3,4)];

$$dN_s/dt = c_{sw}np - \nu_a \exp(-E_a/kT)N_s \tag{6-10}$$

and the product of n and p in the dark is expressed by

$$np = N_C N_V \exp(-E_{g2}/kT) \quad , \tag{6-11}$$

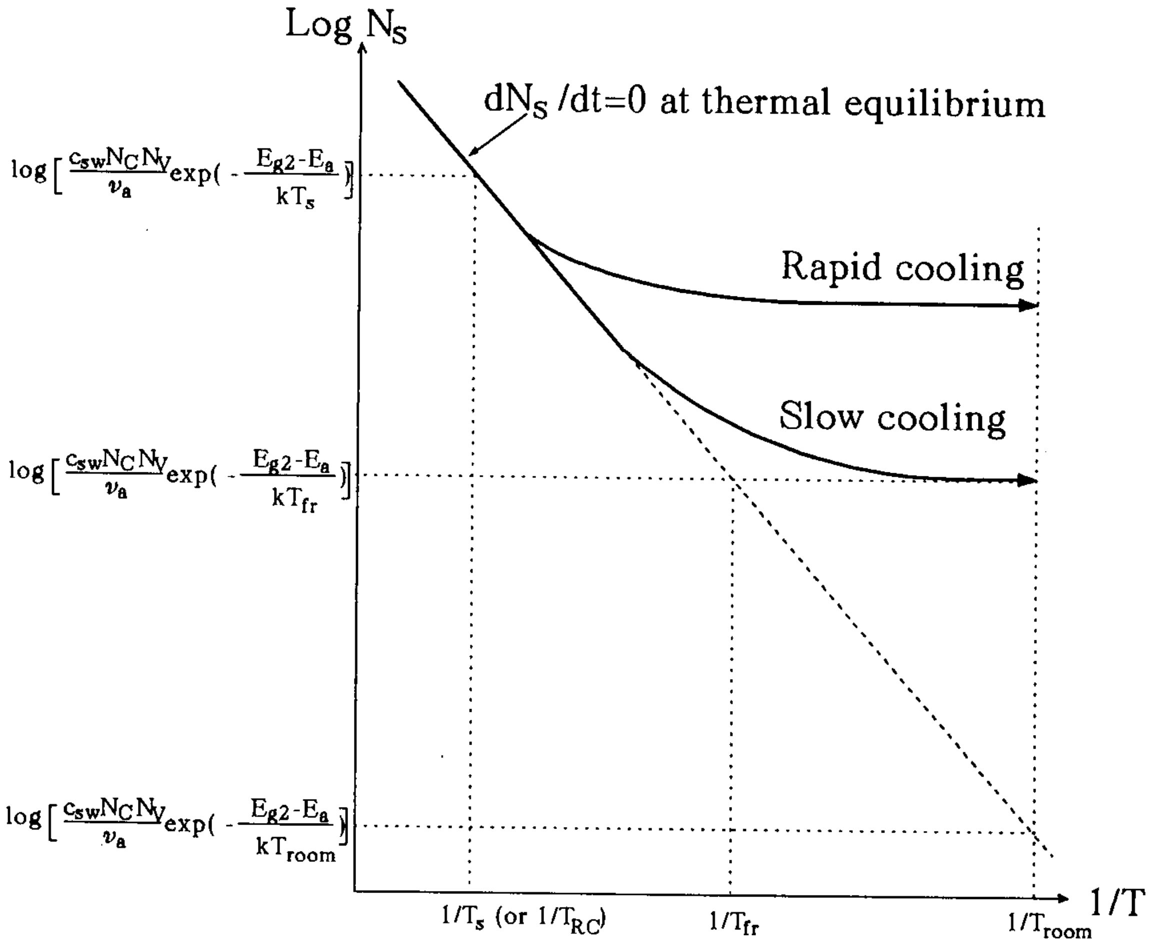

Fig.6.15. Schematic sketch of temperature-dependent midgap-state density.

where N_s is the total density of midgap states and c_{sw} is the constant related with the Staebler-Wronski effect, n and p are the free carrier densities in the conduction band and the valence band, respectively, and N_C and N_V are the effective densities of states in the conduction band and the valence band, respectively. During the deposition at a substrate temperature (T_s) or keeping the film at a given temperature (T_{RC}), the equilibrium condition ($dN_s/dt=0$) is assumed to be held. In this case, the total density of midgap states is expressed as

$$N_s = (c_{sw}N_CN_V/\nu_a)\exp[-(E_{g2} - E_a)/kT] \quad , \qquad (6\text{-}12)$$

where T represents T_s or T_{RC}. If the substrate was cooled very slowly from the high temperature to room temperature (T_{room}), the total density observed from ESR would be expressed as

$$N_s = (c_{sw}N_CN_V/\nu_a)\exp[-(E_{g2} - E_a)/kT_{room}] \quad , \qquad (6\text{-}13)$$

which means that N_s should be lower than 10^{15} cm^{-3}. However, it is impossible to cool down so slowly. Therefore, N_s is frozen in at some temperature (T_{fr}) which strongly depends on the cooling rate and it is expressed as Eq. (6-13) where T_{fr} replaces T_{room}. The actual cooling rate causes the value of N_s to become of the order of 10^{15} cm^{-3}.

In the case of the film deposited at 200 ℃, N_I in the rapidly-cooled film for T_{RC}=200 ℃ was equal to that (about 10^{16} cm^{-3}) in the as-deposited film. The value of N_I for T_{RC}=250 ℃ decreased as low as N_I (about 5×10^{15} cm^{-3}) in a good quality film. And then N_I increased with an increase of T_{RC}. In the case of the good quality films deposited at 250 ℃ and 300 ℃, on the other hand, N_I (about 5×10^{15} cm^{-3}) did not change in the range of $T_{RC} \leq 250$ ℃, and then N_I increased with a further increase of T_{RC}. The midgap states may equilibrate during the deposition at 250-300 ℃, and the midgap states are frozen in at the temperature lower than 250 ℃ during the real slow cooling because the value of N_I at T_s=300 ℃ was close to that at T_s=250 ℃. From the result of rapid cooling from T_{RC}=250 ℃, the value

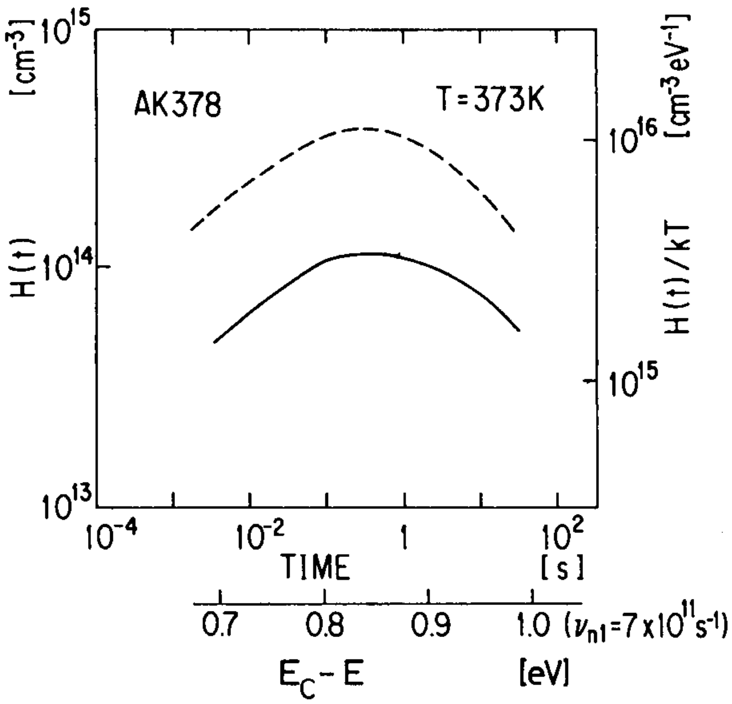

Fig.6.16. Change of measured H(t) by rapid cooling from 300 ℃. The solid and broken curves represent H(t) of as-deposited and rapidly-cooled films, respectively.

of 5×10^{15} cm^{-3} is considered to correspond to N_S at equilibrium near 250 ℃. Then, when the films are heated up to 300 ℃, the midgap states equilibrate at 300 ℃, which means that N_S at equilibrium becomes larger than 5×10^{15} cm^{-3}. By the rapid cooling, N_S becomes close to N_S at equilibrium near 300 ℃, resulting in the increase of N_S. The deposition condition of T_S=200 ℃, which is considered not to obey Eq. (6-12), is not good. So, this film has a lot of midgap states even if the substrate is cooled down slowly. When this film is heated to 250 ℃, the midgap states equilibrate at 250 ℃ according to Eq. (6-12). The rapid cooling makes the value of N_S keep at the condition near 250 ℃.

From the transient HMC method, the states increased by rapid cooling from 300 ℃ were the states having ν_{n1}, since t_p in the rapid cooling film was the same as t_p in the as-deposited film, as shown in Fig. 6.16. Therefore, the metastable states induced by rapid cooling are assigned to the midgap states in as-deposited films.

Finally, these results obtained by the HMC methods are discussed and compared with other results. Both states produced by the light soaking, which are distinguished by the difference in ν_n, must originate from electron-spin centers because the behavior of N_I by light soaking is quite similar to that obtained from ESR. From the study of as-deposited films, the states with ν_{n1} are found to be D^0 of Si, and those states could also be thermally created because they exist in the as-deposited and the rapidly-cooled films. On the other hand, the other states with ν_{n2}, which will be noted as D^0_L, can be created only by light soaking.

Han and Fritzsche,[7] and Qiu et al.[8] reported that two kinds of metastable states could be produced by light soaking. The first light-induced reversible states had a small capture-cross section (σ_{n1}) for electrons, and were detected by a constant photocurrent measurement (CPM). The second states had a large capture-cross section (σ_{n2}) for electrons, and were detected by an increment ($\Delta\sigma_p$) of conductivity using a small incident light flux with a 2-eV photon energy. The value of σ_{n1}

was smaller by about one order of magnitude than σ_{n2}, and both states were located in the midgap. The value of $\Delta\sigma_p$ decreased by the short-time (3-4 h) light soaking at 100 K, while an absorption coefficient (α_1) at 1.0 eV obtained from CPM did not change. By the same light soaking at 300 K, however, $\Delta\sigma_p$ decreased and α_1 increased. The values of $\Delta\sigma_p$ and α_1 are expressed as

$$\Delta\sigma_p = B_2/(\sigma_{n1}N_1 + \sigma_{n2}N_2) \tag{6-14}$$

and

$$\alpha_1 = B_3(N_1 + N_2) \quad , \tag{6-15}$$

respectively, and

$$\sigma_{n2} \fallingdotseq 10\sigma_{n1} \quad , \tag{6-16}$$

where B_2 and B_3 are constants, N_1 is the density of the first states, and N_2 is the density of the second states. If the value of N_2 were smaller by the order of 10 than the value of N_1, the increment of N_2 could hardly be detected by the increment of α_1 according to Eq. (6-15), but it could easily be detected by the change of $\Delta\sigma_p$ according to Eq. (6-14) because of Eq. (6-16). Therefore, these indicate that the density of the first states increases only at high temperature, while the density of the second states increases at any temperature and that the value of N_2 is still smaller than that of N_1 in the short-time light-soaking. In the light of our results, the first states correspond to D^0 just as they concluded, and the second states should correspond to D_L^0 because ν_n is proportional to σ_n. Indeed, in the case of deuterated amorphous silicon (a-Si:D), only the midgap states with ν_{n1} were reported to increase by light-soaking.[15] That is why the rate of conductivity decrease in a-Si:D is reported to be smaller than that in a-Si:H. The origin of D_L^0 is still an open question, although Okushi et al.[16] have insisted a model in which the dangling-bond-like centers are produced by a spatially intimated coupling of pairs between dangling bonds and positively ionized impurities.

6-5. Summary

(1) The steady-state and transient HMC methods have been applied to determining densities and profiles of midgap states in undoped a-$Si_{1-x}Ge_x$:H, undoped a-Si:H and undoped a-$Si_{1-x}C_x$:H. The midgap states are correlated with D^0; the density in a-$Si_{1-x}Ge_x$:H ($E_0 \leqq 1.63$ eV) represents the D^0 density of Ge, and in a-Si:H and a-$Si_{1-x}C_x$:H ($E_0 \leqq 1.88$ eV) it represents the D^0 density of Si. The density of midgap states increases slowly with the Ge content in the film, while it increases rapidly with the C content. The peak of the midgap-state profile appears clearly in a-Si:H and a-$Si_{1-x}Ge_x$:H, but it does not appear clearly in a-$Si_{1-x}C_x$:H.

(2) Thermal annealing kinetics of metastable gap states in short-time light-soaked a-Si:H have been investigated. Monomolecular kinetics are suitable for explaining the experimental data. The thermal activation energy (E_a) for annealing decreases monotonously with an increase in (E_C-E). This is the first report which elucidates the relation between E_a and (E_C-E).

(3) The midgap states having a small ν_n are created both optically and thermally, while the midgap states having a large ν_n are created only by light soaking. Both states are located around 0.85 eV below the conduction band edge.