Thermal recovery process of the midgap-state profile of light-soaked undoped hydrogenated amorphous silicon

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Changes of midgap-state profiles of light-soaked undoped hydrogenated amorphous silicon are measured in the process of a 150 °C annealing by transient heterojunction-monitored capacitance measurements. Monomolecular annealing kinetics are found to be suitable for explaining the results, and the thermal activation energy for annealing is determined at each energy position of midgap states. This activation energy decreases with an increase in the energy position measured from the conduction-band edge.

Light-induced creation of metastable defects[1] has received considerable attention because it is directly associated with the degradation of the efficiency of hydrogenated amorphous silicon (*a*-Si:H) solar cells. Stutzmann *et al.*[2] proposed the following mechanism: the rate of increase in dangling bond density (N_s) determined by electron spin resonance (ESR) measurements is given by $dN_s/dt \propto np$, where n and p are the free electron and hole concentrations, respectively, under light exposure. Each concentration is proportional to G/N_s, where G is the carrier generation rate by light exposure. They concluded that $N_s(t) \propto G^{2/3}t^{1/3}$.

Once the spin density has been increased by light exposure, the kinetics of annealing can be explored. Stutzmann *et al.*[3] proposed a monomolecular annealing process with a distribution of activation energies (E_a), while Lee *et al.*[4] proposed a bimolecular annealing process with constant E_a. Smith and Wagner[5] expanded the Stutzmann's model into a more general model which can explain the reason why N_s cannot be reduced to the value below 10^{15} cm^{-3} for undoped *a*-Si:H.

We have recently developed a heterojunction-monitored capacitance (HMC) method[6] to determine midgap-state profiles $g(E)$ in undoped *a*-Si:H. Diodes used in this method consist of *a*-Si:H/crystalline Si (*c*-Si) heterojunction structures, and the capacitance (HMC) of those diodes is measured at a frequency higher than the reciprocal of the dielectric relaxation time of *a*-Si:H. The capacitance of *a*-Si:H is determined by the thickness of *a*-Si:H due to its long dielectric relaxation time, while that of *c*-Si is determined by the depletion width of *c*-Si. The latter also reflects the space charge of the depletion region in *a*-Si:H. Therefore, the density of midgap states can be determined from the voltage dependence of HMC and the $g(E)$ can be estimated from the transient HMC.

In this letter the annealing kinetics are investigated, and E_a at each energy position of midgap states (singly occupied dangling bonds, D^0) is directly determined from the transient HMC, where the $g(E)$ can be obtained in a short time, e.g., several seconds. The method enables us to carry out the real-time measurements of $g(E)$ in the process of a 150 °C annealing.

Undoped *a*-Si:H films (about 1.2 μm thickness) were deposited by glow discharge decomposition of pure SiH_4. In order to measure dark conductivity, photoconductivity, and the activation energy ($E_C - E_F$) of dark conductivity of *a*-Si:H films, samples with coplanar electrodes were fabricated by depositing *a*-Si:H onto Corning 7059 glass substrates heated to 250 °C for the sample 21099 and heated to 310 °C for the sample AK362, and subsequently by evaporating aluminum at room temperature. Thus-determined properties are shown in Table I. Oxygen, carbon, and nitrogen concentrations estimated using secondary-ion mass spectrometry (SIMS) were 7×10^{19}, 1×10^{19}, and 3×10^{18} cm^{-3} in sample 21099, respectively, and they were 5×10^{19}, 2×10^{19}, and 8×10^{17} cm^{-3} in sample AK362, respectively. The difference of dark conductivity between samples 21099 and AK362 might result from the difference of the substrate temperature between them.[7]

The heterojunctions were fabricated by depositing the films onto *p*-type *c*-Si(*pc*-Si) substrates heated to 250 °C for sample 21099 and heated to 310 °C for sample AK362. The acceptor density (N_A) of *pc*-Si was 10^{16} cm^{-3}. Since magnesium (Mg) has been known to form an ohmic contact with undoped *a*-Si:H,[8] 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 was heated to 150 °C in a vacuum, the transient HMC was measured using 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 °C because of the low resistivity of *a*-Si:H. Therefore, after the sample was 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, and 120 °C. The signal $H(t)$ of transient HMC did not change after the heterojunctions for as-deposited films were annealed even at 200 °C for 1.5 h in a vacuum.

Figure 1 shows the time-resolved gap-state profiles $g(E)$ and the corresponding signals $H(t)$ of transient HMC in the inset. These $g(E)$ were calculated from these $H(t)$ using the attempt-to-escape frequency for electrons (ν_n) of 10^{12} s^{-1}. The $H(t)$ for the as-deposited film did not change at all during the annealing process at 150 °C, indicating that contact properties were not affected by thermal treatment. Therefore, changes of $H(t)$ in the light-soaked film should be ascribed to the changes of the bulk $g(E)$ of *a*-Si:H.

Two models have been proposed for explaining anneal-

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TABLE I. Film properties of samples 21099 and AK362.

Sample 21099[a]	As-deposited	Light exposure	Anneal[c]	Anneal[d]
σ_d ($\times 10^{-8}$ 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]				
σ_d ($\times 10^{-8}$ 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 °C for 3 h.
[d] 200 °C for 1.5 h.

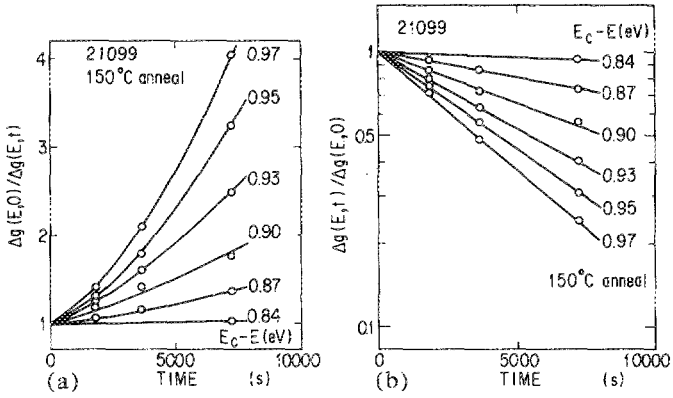

FIG. 2. Annealing behavior of light-induced midgap states plotted assuming (a) bimolecular kinetics and (b) monomolecular kinetics.

ing kinetics: (1) monomolecular kinetics[3] and (2) bimolecular kinetics.[4] Consider the bimolecular annealing process:

$$\frac{d\Delta g(E,t)}{dt} = -\gamma_a \exp\left(\frac{-E_a}{kT}\right)\Delta g(E,t)^2 \quad (1)$$

and

$$\Delta g(E,t) = g(E,t) - g_0(E), \quad (2)$$

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 γ_a is the pre-exponential factor of the bimolecular decay rate. The integral of Eq. (1) implies that

$$\Delta g(E,0)/\Delta g(E,t) = 1 + \gamma_a \exp(-E_a/kT)\Delta g(E,0)t. \quad (3)$$

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. 2(a).

The monomolecular annealing process is given by

$$\frac{d\Delta g(E,t)}{dt} = -\nu_a \exp\left(\frac{-E_a}{kT}\right)\Delta g(E,t), \quad (4)$$

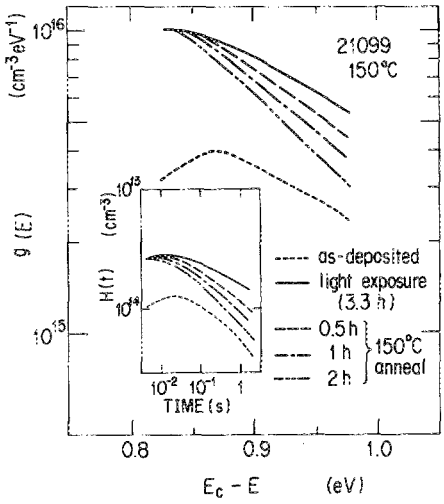

FIG. 1. Changes of $g(E)$ at the measuring temperature 150 °C.The signal $H(t)$ of transient HMC, from which $g(E)$ was calculated, is inserted.

and the integral of this equation implies that

$$\ln[\Delta g(E,t)/\Delta g(E,0)] = -\nu_a \exp(-E_a/kT)t, \quad (5)$$

where ν_a is the pre-exponential factor of the monomolecular decay rate. As is shown in Fig. 2(b), the data produce straight lines for each value of $(E_C - E)$, indicating that the experimental results can be predicted by Eq. (5). Values of E_a obtained from the slope of the curves of Fig. 2(b) are plotted as a function of $(E_C - E)$ in Fig. 3(a). We tentatively assumed $\nu_a = 10^{10}\,s^{-1}$, which Stutzmann *et al.*[3] reported. E_a decreases monotonously with an increase in $(E_C - E)$.

From the above results, at least phenomenologically, 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 low resistivity, E_a could roughly be estimated using Eq. (5) from low-temperature (80–120 °C) measurements in the films 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, and 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. The $g(E)$ for $(E_C - E)$ in the range higher than 0.85 eV in the film annealed at 200 °C for 1.5 h 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. E_a which was roughly estimated from this experiment is shown in Fig. 3(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.*[3] and Smith *et al.*[5] 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.*,[9] while they are rather larger than those reported by Stutzmann *et al.*,[3] Shepard *et al.*[10] predicted from photoconductivity measurements that the density of states above the Fermi level (maybe doubly occupied dan-

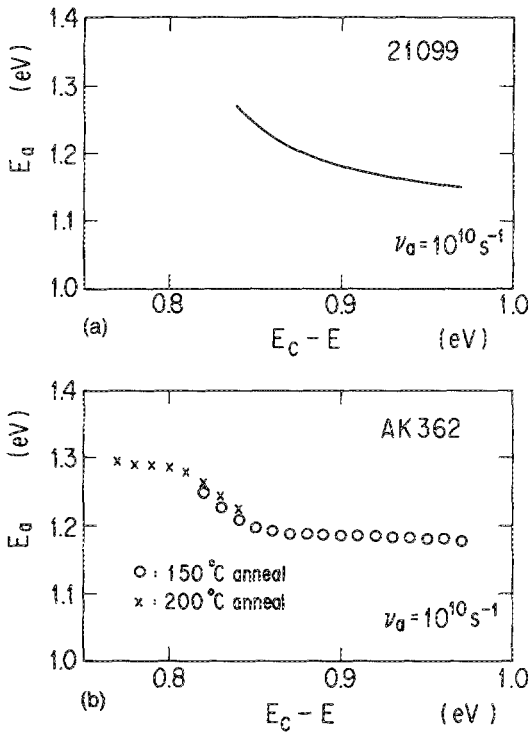

FIG. 3. Activation energy for annealing: (a) obtained from the slope in Fig. 2(b), and (b) estimated from the films annealed at 150 and 200 °C.

gling bonds, D^-) closest to the midgap is annealed first, with which the present results coincide if the correlation energies between D^0 and D^- are kept constant.

In summary, annealing kinetics of metastable defects in a-Si:H have been investigated. Monomolecular kinetics are suitable for explaining the experimental data. The thermal activation energy for annealing decreases monotonously with an increase in $(E_C - E)$. This is the first report which elucidates the relation between E_a and $(E_C - E)$.

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[1]D. L. Staebler and C. R. Wronski, Appl. Phys. Lett. **31**, 292 (1977).
[2]M. Stutzmann, W. B. Jackson, and C. C. Tsai, Appl. Phys. Lett. **45**, 1075 (1984).
[3]M. Stutzmann, W. B. Jackson, and C. C. Tsai, Phys. Rev. B **34**, 63 (1986).
[4]C. Lee, W. D. Ohlsen, P. C. Taylor, H. S. Ullal, and G. P. Ceasar, Phys. Rev. B **31**, 100 (1985).
[5]Z. E. Smith and S. Wagner, Phys. Rev. B **32**, 5510 (1985).
[6]H. Matsuura, J. Appl. Phys. **64**, 1964 (1988).
[7]A. Matsuda, Pure Appl. Chem. **60**, 733 (1988).
[8]H. Matsuura, T. Okuno, H. Okushi, S. Yamasaki, A. Matsuda, N. Hata, H. Oheda, and K. Tanaka, Jpn. J. Appl. Phys. **22**, L197 (1983).
[9]C. Qiu, W. Li, D. Han, and J. Pankove, J. Appl. Phys. **64**, 713 (1988).
[10]K. Shepard, Z E. Smith, S. Aljishi, and S. Wagner, Mater. Res. Soc. Symp. Proc., edited by A. Madan, M. J. Thompson, P. C. Taylor, P. G. LeComber, and Y. Hamakawa (Materials Research Society, Pittsburgh, 1988), Vol. 118, p. 147.