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OPTICALLY AND THERMALLY INDUCED REVERSIBLE CHANGES OF MIDGAP STATES IN UNDOPED a-Si:H

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Midgap-state profiles in undoped hydrogenated amorphous silicon (a-Si:H) have been measured after light soaking, rapid cooling, and annealing using the heterojunction-monitored capacitance (HMC) method. After a short-time (≤ 4 h) light soaking under AM1 with 100 mW/cm2 at room temperature, the increase in midgap states which were assigned to be singly occupied dangling bonds (D^0) in as-deposited films was observed. The attempt-to-escape frequency (ν_n) for electrons of those states was about 7×10^{11} s^{-1}. Successive long-time (≤ 75 h) light soaking, however, produced another midgap states with ν_n of 2×10^{13} s^{-1}. Both light-induced metastable states with two kinds of ν_n were located at around 0.85 eV below the conduction band edge. After annealing those samples up to 200 °C for 2 h, both states were completely recovered, but the recovering behavior was quite different from one with a small ν_n to the other with a large ν_n. On the other hand, the states produced by rapid cooling from 300 °C were similar to those induced by the short-time light soaking in their ν_n as well as recovering behavior by the annealing.

1. INTRODUCTION

The existence of the light-induced reversible changes in hydrogenated amorphous silicon (a-Si:H) has attracted considerable attention, mostly because of the degradation of the efficiency of amorphous solar cells. This effect, which is known as the Staebler-Wronski effect,[1] arises from the creation of metastable defects by light soaking, and it is recovered by the annealing at 150-200 °C. Han and Fritzsche,[2] and Qiu et al.[3] reported that two kinds of light-induced states were produced by the light soaking; one was detected by photoconductivity ($\Delta\sigma_{ph}$) measurements, and the other was observed by constant photocurrent measurements (CPM). Kumeda et al.[4] pointed out from the results of electron-spin-resonance (ESR) that singly occupied dangling bonds (D^0) created by the short-time (3 h) light soaking were easily annealed out, while D^0 created by the long-time (53 h) light soaking was resistant to the annealing. In this paper, changes of midgap-state profiles are investigated before and after the light soaking, the rapid cooling, and the annealing by means of the heterojunction-monitored-capacitance (HMC) method[5] which is applicable to the undoped a-Si:H.

2. EXPERIMENT

Undoped a-Si:H / p-type crystalline silicon (p c-Si) heterojunctions were fabricated as follows. Undoped a-Si:H films (1.2-1.5 μm thickness) were deposited by 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 cooled down slowly. The acceptor density (N_A) of the p c-Si was 1×10^{16} cm^{-3}. Since magnesium (Mg) is known to form an ohmic contact with undoped a-Si:H,[6] 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 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 were 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-state density (N_I) of undoped a-Si:H was estimated from the high-frequency (1 MHz) capacitance-voltage characteristics at room temperature using the steady-states HMC method.[5] The HMC signal H(t), which is obtained from transient capacitance of the heterojunction measured at 2 MHz, approximately corresponds to the density-of-states distribution [g(E)] through $g(E) \propto H(t)/kT$, and the energy location below the conduction band edge (E_C) is expressed by $E_C - E = kT\,ln(\nu_n t)$, where k is the Boltzmann's constant, T is the absolute measuring 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 of the time (t_p) at the peak of H(t).[5]

3. RESULTS AND DISCUSSION

3.1. Light soaking

The value of N_I increased with between one-second and one-third powers of the illumination time (t_{IL}), whose behavior was quite similar to the results obtained from the ESR measurement. The value of the activation energy (ΔE_{ac}) of dark conductivity of the film was independent of t_{IL} when t_{IL} was longer than 3 h, although ΔE_{ac} of light-soaked films was larger than that of as-deposited films. The H(t) signals did not change after the as-deposited film was annealed at 200 °C for 2 h in a vacuum, and the H(t) signals for as-deposited films were quite similar to those for the films annealed at 200 °C for 2 h after the light soaking. After the short-time (≤ 4 h) light soaking, the magnitude of H(t) increased without any shift of t_p, while after the long-time (≥ 75 h) light soaking t_p was shifted toward shorter time and kept

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constant, as is clearly shown in Fig. 1. From the temperature dependence of t_p, v_n and the energy position (E_p) corresponding to the peak of H(t) were estimated as follows; v_{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 v_{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 can, 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,[7] 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 be originated from the change of v_n. Figure 2 schematically summarized the above results.

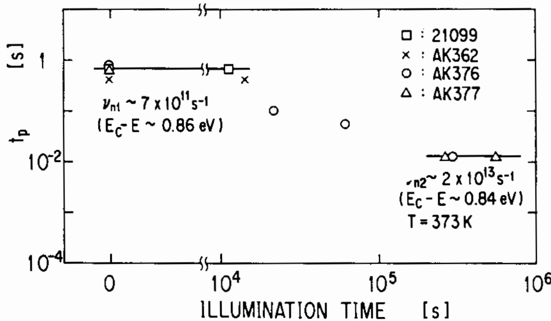

FIGURE 1
The dependence of the time (t_p) at the peak of H(t) on illumination time. The solid lines are guides to eye.

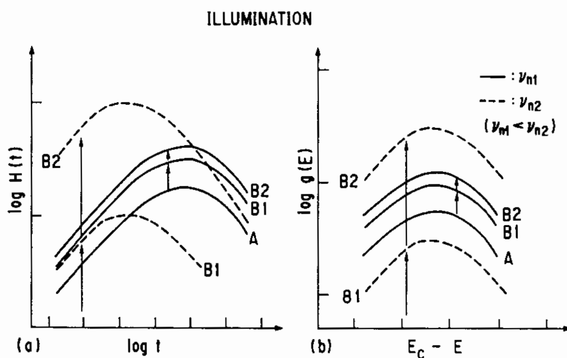

FIGURE 2
Schematic changes of midgap states by light soaking. The solid and dashed lines represent the states with small and large v_n respectively. A, B1, and B2 correspond to the as-deposited (completely annealed), the short-time light-soaked, and the long-time light-soaked films, respectively. (b) was estimated from (a) using the relations of g(E)≈H(t)/kT and E_C-E≈kT *ln* (v_nt).

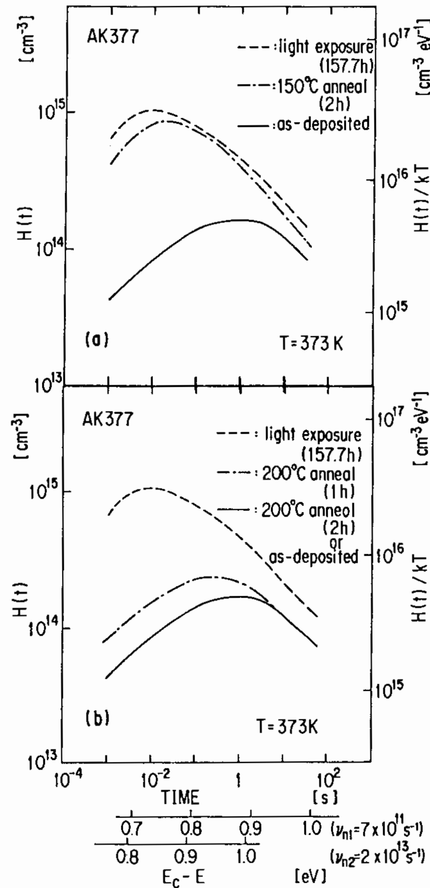

FIGURE 3
Changes of H(t) by annealing for the long-time light-soaked film.

3.2. Annealing of light-soaked films

Figure 3(a) shows the changes of H(t) for the long-time light-soaked films by a 150 °C annealing for 2 h, and Fig. 3(b) shows those by a 200 °C annealing. Since the H(t) signals include information on two kinds of midgap states, two sorts of energy scales corresponding to v_{n1} and v_{n2} are shown in the abscissa below the time scale. We previously studied the annealing kinetics using the short-time light-soaked films,[8] from which monomolecular annealing kinetics were found to be suitable for explaining the results. In Fig. 3(a), the change in H(t) at t>10 s must be originated from the change of the states having v_{n1} because the activation energy for annealing (E_{AN}) estimated from the figure has the same behavior as E_{AN} obtained from the short-time light-soaked film,[8] while the change in H(t) at t<10^{-1} s is thought to arise from the change of the states having v_{n2} because those states are dominant in the region. Since the energy dependence of E_{AN} for the short-time light-soaked films is known,[8] changes in E_{AN} and H(t) for the annealing process in

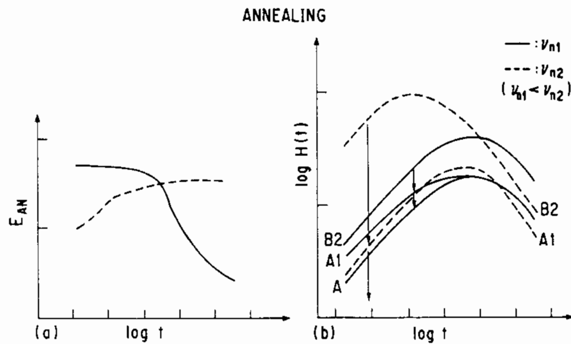

FIGURE 4
Activation energies for the annealing and schematic changes of midgap states by the annealing. The solid and dashed lines represent the states with small and large ν_n, respectively. B2, A1, and A correspond to the long-time light-soaked, the short-time annealed, and the completely annealed films, respectively.

the long-time light-soaked films can be schematically described as shown in Fig. 4.

3.3. Rapid cooling

In the film deposited at 200 °C, N_l in the rapidly-cooled film for T_{RC} = 200 °C was equal to that (about 10^{16} cm^{-3}) in the as-deposited film, N_l for T_{RC} = 250 °C decreased as low as N_l (about $5x10^{15}$ cm^{-3}) in a good quality film, and then N_l increased with an increase of T_{RC}. In the good quality films deposited at 250 and 300 °C, on the other hand, N_l did not change in the range of $T_{RC} \leq 250$ °C, and then N_l increased with a further increase of T_{RC}. From the transient HMC method, the states increased by rapid cooling from 300 °C were the states having ν_{n1}.

3.4. Correspondence with other results

Both states produced by the light soaking, which are distinguished by the difference in ν_n, must be originated from spin centers because the behavior of N_l by the light soaking is quite similar to that obtained from ESR. From the study of as-deposited films,[5] the states with ν_{n1} were found to be D^0, 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} are noted as $D_L{}^0$, since the states can be created only by the light soaking.

Han and Fritzsche,[2] and Qiu et al.[3] 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 CPM. The second states had a large capture-cross section (σ_{n2}) for electrons, and were detected by $\Delta\sigma_{ph}$ 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 $\Delta\sigma_{ph}$ decreased by the short-time (3-4 h) light soaking at 100 K, while an absorption coefficient (α_{sub}) at 1.0 eV obtained by CPM did not change. By the same light soaking at 300 K, however, $\Delta\sigma_{ph}$ decreased and α_{sub} increased. These indicate that the density of the first states (N_1) increases only at high temperature while the density of the second states (N_2) increases at any temperature because $\Delta\sigma_{ph}$ and α_{sub} are expressed as $\Delta\sigma_{ph} \propto 1/(\sigma_{n1}N_1+\sigma_{n2}N_2)$ and $\alpha_{sub} \propto N_1+N_2$, respectively and $\sigma_{n1}<\sigma_{n2}$. 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. The origin of $D_L{}^0$ is still an open question, although Okushi et al.[9] have insisted the model in which the dangling-bond-like centers are produced by a spatially intimated coupling of pairs between dangling bonds and positively ionized impurities.

5. CONCLUSION

The midgap states having a small ν_n were optically as well as thermally created, while the midgap states having a large ν_n were created only by light soaking. Both states were located around 0.85 eV below the conduction band edge.

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