Intrinsic deep-defect-related recombination process in hydrogenated amorphous silicon

Jong-Hwan Yoon

Department of Physics, College of Natural Science, Kangwon National University, Chunchon, Kangwon-Do 200-701, Korea

(Received 30 August 1993; revised manuscript received 16 November 1993)

Intrinsic deep-defect-related recombination process has been investigated in a series of undoped hydrogenated amorphous silicon (*a*-Si:H) films grown under different deposition conditions. Steady-state photoconductivity (σ_{ph}) was measured as a function of deep-defect density N_d, Urbach energy E_u, and dark Fermi energy E_F. It was found that σ_{ph} strongly depends on these parameters while E_F stays at the energy levels lower than 0.82 eV below E_c, but it is nearly independent of those if E_F stays above 0.82 eV. A possible distribution of deep-defect-related recombination centers and recombination process has been suggested.

I. INTRODUCTION

Several works have shown that spin-active dangling-bond defects with $g=2.005$ are the most likely recombination centers. Street[1] and Voget-Grote *et al.*[2] have studied the spin-density dependence of σ_{ph} in *a*-Si:H films with a wide range of spin density N_s, which is induced by varying the deposition conditions and the electron irradiation of different doses, respectively. They observed that for the high-defect samples above $N_s=1\times10^{17}$ cm^{-3}, σ_{ph} is proportional to $1/N_s$, suggesting that spin-active defects are the dominant recombination centers. Dersch, Schweitzer, and Stuke[3] have suggested the recombination process controlled by spin-dependent tunneling and diffusion of localized band-tail electrons and holes in the samples with a high- and low-defect density, respectively. They have suggested that recombination is through a well-defined peak in the gap states caused by the spin-active dangling bonds. On the other hand, there is much experimental and theoretical evidence that spin-active defects are not the unique recombination centers in determining the recombination process. Previously referred works[1,2] have also shown that σ_{ph} appears to be nearly independent of N_s in the range below $N_s=1\times10^{17}$ cm^{-3}. For the samples with a wide range of defect density induced by the same treatment, e.g., light soaking, there are two distinct N_s dependences of σ_{ph}. This fact indicates that there must be either a second type of recombination center, nonparamagnetic in nature, or the effect of spin-active defects on σ_{ph} may be indirect. Guha and Hack[4] have suggested that recombination at a continuous distribution of states located between the trap–quasi-Fermi levels, caused by other defects together with spin-active dangling bonds, can give a better explanation of much of the experimental data. Qiu *et al.*[5] have suggested that light-induced degradation of $\mu\tau$ product arises from the creation of new recombination centers near the dark Fermi level with a larger capture cross section than that of neutral dangling bonds. Therefore, the nature of the recombination centers and the recombination process in *a*-Si:H are still a matter of considerable uncertainty. In particular, there are few experimental results on intrinsic deep-defect-related recombination process. In this work, the recombination process has been studied in a series of undoped *a*-Si:H films grown under different deposition conditions. Photoconductivity has been investigated as a function of total deep-defect density, Urbach energy, and dark Fermi energy. A possible model for recombination process has been suggested.

II. EXPERIMENTS

The *a*-Si:H films used in this study were deposited onto Corning 7059 glass substrates in a dc glow-discharge reactor, which has never been exposed to doping gases. Two groups of samples were prepared under different deposition conditions. The first group of samples was grown at a base pressure of about 10^{-7} torr [high-voltage (HV) samples], and the second group of samples was grown at a base pressure of about 10^{-5} torr [low-voltage (LV) samples]. For both groups of samples, we varied only the substrate temperature from 100 °C to 300 °C, keeping other deposition conditions unchanged. The deposition was carried out in 10-cubic centimeter per minute at STP SiH_4 flow at 650 mtorr pressure and 0.12 W/cm^2 power density. σ_{ph} was generated by uniformly absorbed light ($\lambda=650\pm20$ nm) at intensity with a generation rate of $G=4\times10^{17}$ cm^{-3} s^{-1}. Total deep-defect density N_d was determined by the conversion of the integrated excess subgap absorption to the N_d using the formula $N_d(\text{cm}^{-3})=1.9\times10^{16}\int\Delta\alpha_{CPM}(\text{cm}^{-1})dE$ (eV).[6] The subband-gap absorption spectrum was measured using the constant-photocurrent method (CPM). Urbach energy E_u was also taken from the CPM absorption spectrum. Dark Fermi energy was determined from the Arrhenius plot of dark conductivity. The coplanar electrode configuration was used for CPM and conductivity measurements.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show the dependence of photoconductivity σ_{ph} on total deep-defect-density N_d in the HV and LV samples, respectively. In both cases, σ_{ph} increases

0163-1829/94/49(12)/8000(5)/$06.00

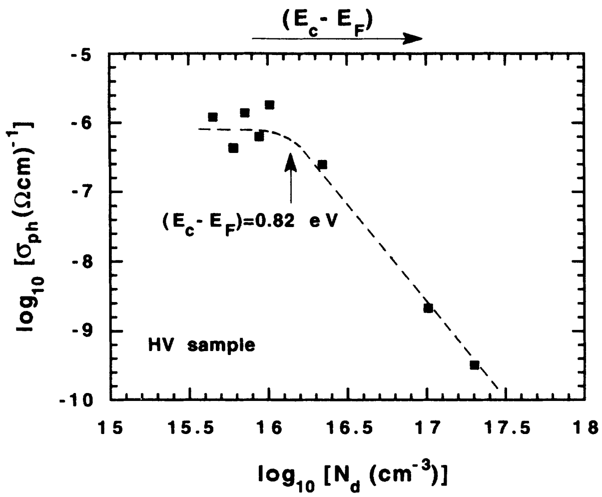

FIG. 1. Photoconductivity σ_{ph} vs total intrinsic deep-defect density N_d for samples prepared at a base pressure of about 10^{-7} torr (HV sample). Top abscissa denotes the (E_c-E_F). The arrow in the figure denotes the σ_{ph} at N_d corresponding to $(E_c-E_F)=0.82$ eV.

with decreasing N_d, followed by saturation. This behavior is similar to the result on the electron-spin-resonance spin density dependence of σ_{ph}, reported earlier by Voget-Grote *et al.*[2] They observed that the abrupt change in the σ_{ph}, as a beginning point of saturation, occurs near $N_s=1\times10^{17}$ cm^{-3}. They observed that for the samples with spin-active-defect density $N_s>1\times10^{17}$ cm^{-3}, σ_{ph} is approximately proportional to N_s^{-1}, giving evidence that spin-active defects are the predominant recombination center. Figures 1 and 2, however, show that σ_{ph} is approximately proportional to N_d^{-3}. Moreover, Figs. 1 and 2 show that the values of N_d corresponding to the abrupt change in the σ_{ph} are not in

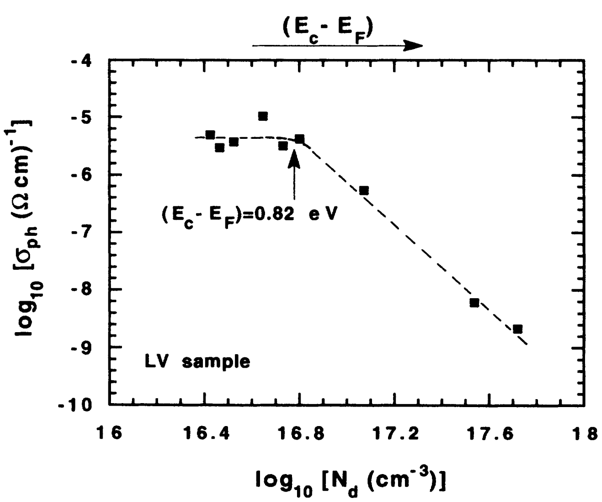

FIG. 2. Photoconductivity σ_{ph} vs total intrinsic deep-defect density N_d for samples prepared at a base pressure of about 10^{-5} torr (LV sample). Top abscissa denotes the (E_c-E_F). The arrow in the figure denotes the σ_{ph} at N_d corresponding to $(E_c-E_F)=0.82$ eV.

agreement in both groups of samples. For the HV samples, the abrupt change in the σ_{ph} occurs about $N_d=1.1\times10^{16}$ cm^{-3}, whereas for the LV samples, it occurs about $N_d=6\times10^{16}$ cm^{-3}. Figures 1 and 2 also show that σ_{ph} in the LV samples is higher than that in the HV samples with similar N_d. These results are not to be expected if the effect of N_d on σ_{ph} dominates. From these results we can argue that recombination process is indirectly affected by total subband-gap defect density N_d itself. On the other hand, in order to understand the abrupt change in the σ_{ph} shown in Figs. 1 and 2, a correlation between the abrupt change in the σ_{ph} and dark Fermi energy E_F was explored. Fermi energy was determined from the dark-conductivity activation energy (E_c-E_F) in as-grown state. The dark-conductivity activation energy was plotted as a function of the N_d for each group of samples. The value of (E_c-E_F) at the N_d corresponding to the abrupt change in the σ_{ph} was then determined. The arrow in Figs. 1 and 2 indicates the (E_c-E_F) at the N_d corresponding to the abrupt change in the σ_{ph}. We find that for the two groups of samples, the abrupt change in the σ_{ph} occurs approximately at the same position of (E_c-E_F). This is a very surprising and interesting result. In the samples used in this work, the abrupt change in the σ_{ph} occurs $(E_c-E_F)=0.82$ eV as shown in Figs. 1 and 2. For both groups of samples, as shown in Figs. 1 and 2, we find that σ_{ph} strongly depends on N_d while E_F stays at energy levels lower than 0.82 eV below E_c, which is also consistent with the result that dark Fermi position is the dominant factor in determining the recombination process in *a*-Si:H film, but it is nearly independent of that if E_F stays above 0.82 eV. As a result, it can be argued that the concentration of subband-gap defects effectively affects the σ_{ph} if the dark Fermi level locates at an energy level lower than 0.82 eV below E_c.

It is also well known that recombination arises from recombining between electrons and holes trapped temporally in localized band-tail states through recombination centers located at midgap. Therefore, σ_{ph} may be affected by both band-tail widths. In this work, we have also studied the dependence of σ_{ph} on E_u, which is the characteristic energy of the valence-band tail width (Urbach energy), in the HV and LV samples. Figures 3 and 4 show the σ_{ph} plotted as a function of Urbach energy E_u in the HV and LV samples, respectively. The E_u was taken from the CPM absorption spectrum. Figures 3 and 4 show that σ_{ph} increases exponentially with decreasing E_u, followed by saturation within substantial scatter, and that the abrupt change in the increase of σ_{ph} also occurs in both groups of samples. However, Figs. 3 and 4 show not only that the values of E_u (indicated by arrows) corresponding to the abrupt change in the σ_{ph} are not identical in both groups of samples, but also that σ_{ph} in the LV samples is higher than that in the HV samples with similar E_u. In order to understand these results, in the same manner as shown in Figs. 1 and 2, a correlation between the abrupt change in the σ_{ph} and dark Fermi energy E_F was explored. The dark-conductivity activation energy (E_c-E_F) was plotted as a function of E_u for each group

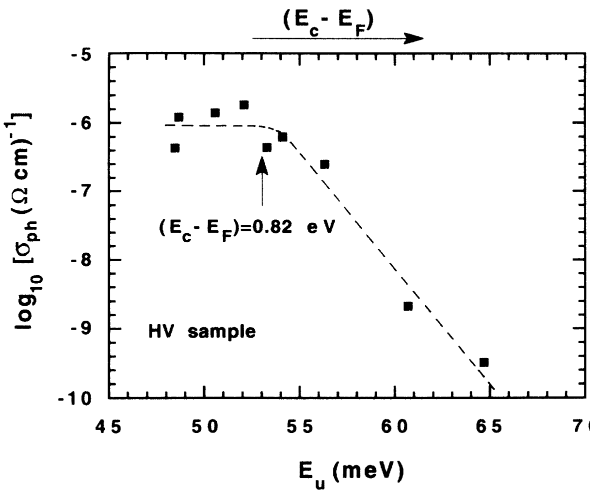

FIG. 3. Photoconductivity σ_{ph} vs Urbach energy E_u for samples prepared at a base pressure of about 10^{-7} torr (HV sample). Top abscissa denotes the (E_c-E_F). The arrow in the figure denotes the σ_{ph} at E_u corresponding to $(E_c-E_F)=0.82$ eV.

of samples. The values of (E_c-E_F) at E_u corresponding to the abrupt change in the σ_{ph} were then determined. The arrow in Figs. 3 and 4 indicates the (E_c-E_F) at the E_u corresponding to the abrupt change in the σ_{ph}. Figures 3 and 4 show that for both groups of samples, the abrupt change in the σ_{ph} occurs nearly at the same value of $(E_c-E_F)=0.82$ eV. This behavior is very similar to that observed in the dependence of σ_{ph} on N_d, as shown in Figs. 1 and 2. We also observed that the (E_c-E_F) decreases with decreasing E_u in the HV and LV samples. In the range of $(E_c-E_F)>0.82$ eV, σ_{ph} increases exponentially with decreasing E_u. This observation also indicates that σ_{ph} is affected by E_u if E_F stays at an energy level lower than $E=0.82$ eV below E_c.

As shown above, the key feature of the presented results is that if dark Fermi level locates in the range of $(E_c-E_F)>0.82$ eV, σ_{ph} is strongly affected by N_d and E_u. This observation means that the position of E_F is the very important factor in determining the recombination process. We have, therefore, studied the correlation between σ_{ph} and dark Fermi energy E_F. Figure 5 shows the dark Fermi-energy dependence of σ_{ph} in the HV and LV samples. The dark Fermi energy was determined from the dark-conductivity activation energy. Figure 5 shows the σ_{ph} plotted as a function of (E_c-E_F). σ_{ph} increases exponentially with decreasing the (E_c-E_F), followed by saturation, as observed in the presented results. In the range of $(E_c-E_F)>0.82$ eV, the σ_{ph} increases with decreasing (E_c-E_F), but in the range of $(E_c-E_F)<0.82$ eV, the σ_{ph} is nearly independent of the (E_c-E_F). This behavior is the same in both groups of samples, grown under different deposition conditions. This result also suggests that σ_{ph} is affected by the position of E_F if E_F stays at energy levels lower than 0.82 eV. This behavior is also similar to the results on the dependence of σ_{ph} on N_d and E_u. However, Fig. 5 shows that for the entire range of (E_c-E_F), the values of σ_{ph} in the HV and LV samples with the same value of (E_c-E_F) are identical. That is possible if the deep-defect states enveloped by two energy levels, $E=0.82$ eV and dark Fermi level E_F, are the dominant recombination centers. A possible explanation is the following.

Photoconductivity σ_{ph} can be written by $\sigma_{ph}\sim 1/N_rK$, where N_r is the density of recombination centers and K is the rate coefficient for recombination at a recombination center. Bhattacharya *et al.*[7] have shown that the recombination-rate coefficient is closely correlated with the valence-band tail width (Urbach energy E_u), and increases exponentially with E_u. They have suggested that the change in σ_{ph} mainly arises from the change of the recombination-rate coefficient K rather than subgap defect density N_d. However, our results in Figs. 1–4 show that σ_{ph} is closely correlated with both N_d and E_u when

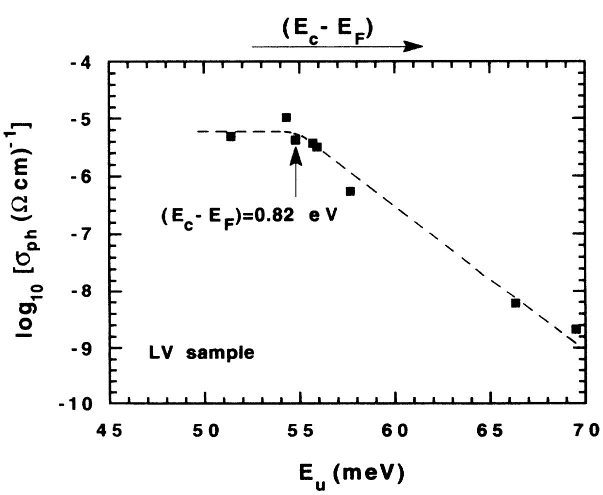

FIG. 4. Photoconductivity σ_{ph} vs Urbach energy E_u for samples prepared at a base pressure of about 10^{-5} torr (LV sample). Top abscissa denotes the (E_c-E_F). The arrow in the figure denotes the σ_{ph} at E_u corresponding to $(E_c-E_F)=0.82$ eV.

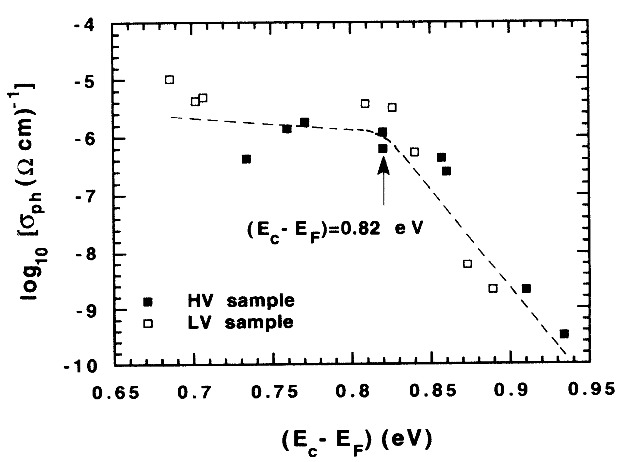

FIG. 5. Photoconductivity σ_{ph} vs dark-conductivity activation energy (E_c-E_F) for samples prepared at a base pressure of about 10^{-7} torr (HV sample) and about 10^{-5} torr (LV sample). The arrow denotes the σ_{ph} at $(E_c-E_F)=0.82$ eV.

E_F locates in the range of $(E_c - E_F) > 0.82$ eV. In turn, because there is also a close correlation between N_d and E_u, it is difficult to distinguish between the effects of these two parameters. While if E_F stays at the energy levels higher than 0.82 eV below E_c, then σ_{ph} is nearly independent of N_d and E_u, inconsistent with the suggestion of Bhattacharya *et al.* That is probably the case that the density of the effective recombination center N_r remains unchanged despite the change of N_d and E_u.

On the other hand, Fermi-level dependence of photoconductivity shown in Fig. 5 differs from results reported earlier,[8-10] which show a continuous change in a photoconductivity as the Fermi level is changed. However, most of the reported results have been obtained from not only undoped samples but also lightly phosphorus-doped ones, which have the additional gap states above midgap. The samples used in this study were undoped ones, grown in a reactor which has never been exposed to doping gases. Fermi level was changed by only varying a substrate temperature. The decreases of substrate temperature results in mainly the increase of gap states below midgap and valence-band tail width, while the density of gap states above midgap remains nearly unchanged.[11] No or little change of gap states above midgap may lead to no change in photoconductivity despite the change of Fermi level in the range of $(E_c - E_F) < 0.82$ eV.

In order to understand our results on the basis of the above discussion, we suggest that the deep-defect states enclosed by two energy levels, $E = 0.82$ eV and E_F, are the dominant recombination centers. Figure 6 shows the simplified distribution of midgap states. For the interpretation of presented results, the minimum position in the distribution of the midgap states was located at 0.82 eV below E_c. A and B states are the donorlike and acceptorlike states, respectively. They would be positive and neutral, respectively, when they are empty. If the dark Fermi level E_F locates below $E = 0.82$ eV, almost the entire B states are neutral, but A states with the energy higher than Fermi level E_F would be positive, while those lower than Fermi level E_F are neutral. The positively charged A states (shaded area in Fig. 6) have, therefore, the relatively higher capture probability for electrons in the conduction-band tail states. The electrons captured into these states will subsequently recombine with the holes in the valence-band tail. Following this suggestion, the shift of E_F toward $E = 0.82$ eV due to the sample preparation conditions results in the decrease in the density of recombination centers, accompanying the increase in the σ_{ph} and subsequent saturation, as shown in Figs. 1–4. On the other hand, dark Fermi level is determined by the total deep-defect density N_d, in particularly by the A-state density. Though the values of N_d are the same in the HV and LV samples, the difference between Fermi levels in

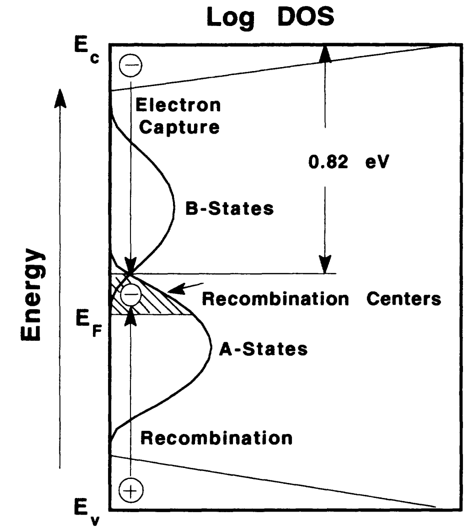

FIG. 6. The simplified distribution of intrinsic deep-defect-related midgap states and recombination centers. A and B states are the donorlike and acceptorlike states, respectively. The shaded area is the suggested recombination centers.

the HV and LV samples may be caused because the N_d is the sum of A- and B-state densities. The difference of σ_{ph} in the HV and LV samples with similar N_d and E_u may arise from the disagreement of E_F due to the different deposition conditions. This can be also supported by the result shown in Fig. 5. The agreement of Fermi levels in the HV and LV samples results in the same amount of recombination centers, enclosed by two energy levels, $E = 0.82$ eV and E_F.

IV. SUMMARY

Intrinsic deep-defect-related recombination process has been studied in a series of undoped a-Si:H samples grown under different deposition conditions. Photoconductivity σ_{ph} was measured as a function of deep-defect density N_d, Urbach energy E_u, and dark Fermi energy E_F. It was found that σ_{ph} strongly depends on these parameters while E_F stays at the energy levels deeper than 0.82 eV below E_c, but it remains nearly unchanged within substantial scatter if E_F stays above 0.82 eV. From these results, we suggest that the deep-defect-related subgap states enclosed by two energy levels, $E = 0.82$ eV and E_F, are the dominant recombination centers.

ACKNOWLEDGMENT

This work was supported by the NONDIRECTED RESEARCH FUND, Korea Research Foundation.

[1]R. A. Street, Philos. Mag. B **46**, 273 (1982).
[2]U. Voget-Grote, W. Kummerle, R. R. Fischer, and J. Stuke, Philos. Mag. B **41**, 127 (1980).
[3]H. Dersch, L. Schweitzer, and J. Stuke, Phys. Rev. B **28**, 4678 (1983).
[4]S. Guha and M. Hack, J. Appl. Phys. **58**, 1683 (1985).
[5]C. Qiu, W. Li, D. Han, and J. Pankove, J. Appl. Phys. **62**, 713 (1988).
[6]Z. E. Smith, V. Chu, K. Shepard, S. Aljishi, D. Slobodin, J. Kolodzey, S. Wagner, and T. L. Chu, Appl. Phys. Lett. **50**,

1521 (1987).

[7]E. Bhattacharya, A. H. Mahan, R. S. Crandall, and J. I. Pankove, Appl. Phys. Lett. **54**, 1247 (1989).

[8]D. A. Anderson and W. E. Spear, Philos. Mag. **36**, 695 (1977).

[9]W. Beyer and B. Hoheisel, Solid State Commun. **47**, 573 (1983).

[10]M. Hack, S. Guha, and M. Shur, Phys. Rev. B **30**, 6991 (1984).

[11]H. Kida, H. Yamagishi, T. Kamada, H. Okamoto, and Y. Hamakawa, in *First International Photovoltaic Science and Engineering Conference,* edited by M. Konagai (The Japan Times, Tokyo, 1984), p. 417.