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| journal or publication title | Materials Research Society Symposium Proceedings |
| volume | 258 |
| page range | 455-460 |
| year | 1992-01-01 |
| URL | http://hdl.handle.net/2297/24537 |

RELATION BETWEEN DEFECT DENSITY AND CONDUCTIVITY CHANGES WITH LIGHT-SOAKING AND ANNEALING IN a-Si:H

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ABSTRACT

It is found in a-Si:H and N-doped a-Si:H that the ESR spin density N_s increases and saturates with light-soaking slower than the dark- and photoconductivities (σ_d and σ_p) do. In the recovery process by annealing, the change in N_s also occurs slower than σ_d and σ_p . From the measurement of the activation energy for σ_d the change in σ_d is found to originate mainly from the movement of the Fermi level E_F . In order to elucidate the origin of different behaviors between N_s and σ_d or σ_p , the light-induced ESR and the constant photocurrent method measurements have been carried out.

INTRODUCTION

Photodegradation effects in a-Si:H have been extensively studied since Staebler and Wronski discovered the decrease in both the dark conductivity σ_d and the photoconductivity σ_p by an intense illumination in 1977[1]. The mechanism of the degradation, however, is still not clear. We already reported that the ESR spin density N_s increases with light-soaking (the carrier generation rate of $1.6 \times 10^{22} \text{cm}^{-3} \text{s}^{-1}$) and saturates after $10^5 \sim 10^6$ sec at $1.3 \times 10^{17} \text{cm}^{-3}$ for both undoped a-Si:H and a-Si:H with a small amount ($\sim 5 \times 10^{20} \text{cm}^{-3}$) of N or O[2].

In this paper, the behavior of the spin density increase in undoped and N-doped a-Si:H will be compared with that of the conductivity change both in the processes of light-soaking and annealing. Results of the change in the activation energy for σ_d , the light-induced ESR (LESR) and the constant photocurrent method (CPM) will be presented.

EXPERIMENTAL

Sample films were prepared with a hot wall glow discharge system which can largely reduce unintentional incorporation of impurities[3]. Undoped and N-doped a-Si:H films were prepared by decomposing SiH_4 and $\text{SiH}_4 + \text{N}_2 + \text{He}$, respectively, with an rf power of 50 W onto fused quartz substrate at 300 °C. The film thickness is around 3 μm . N content in the N-doped sample is $5.6 \times 10^{20} \text{cm}^{-3}$. Aluminum coplanar electrodes were evaporated onto the sample film with a gap of 1 mm for the electrical measurements.

The photoconductivity was measured with white light of a Xe lamp through an IR-cut filter (6 mW/cm²).

The LESR was measured also with white light of a Xe lamp through an IR-cut filter at 77 K[4] while the dark ESR was measured at room temperature. All the spin densities shown below are those obtained by subtracting the surface defect density[5].

The CPM measurements were performed using a halogen-tungsten lamp and a Xe lamp coupled with a monochromator and interference filters[4].

The light-soaking was done using a Xe lamp through an IR-cut filter (3.8 W/cm²) which corresponds to a carrier generation rate of $1.6 \times 10^{22} \text{cm}^{-3} \text{s}^{-1}$. The temperature during light-soaking was 20 ~ 30 °C.

The annealing was done for the light-soaked samples in nitrogen gas flow.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows N_s against the illumination time for undoped and N-doped a-Si:H films. Both data for two kinds of the film agree fairly well, which demonstrates no

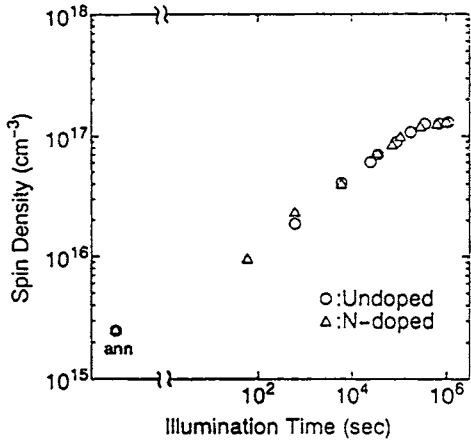


Fig. 1. Spin density as a function of illumination time for undoped and N-doped a-Si:H. "ann" means the annealed states.

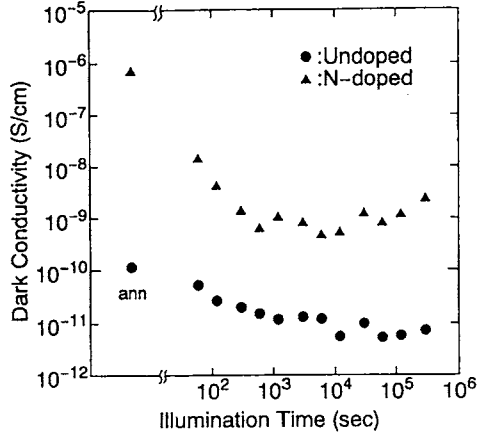


Fig. 2. Dark conductivity as a function of illumination time for undoped and N-doped a-Si:H. "ann" means the annealed states.

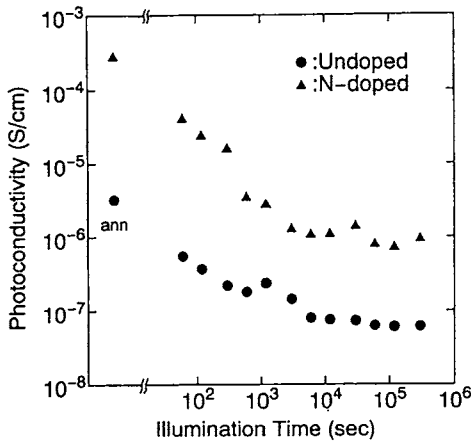


Fig. 3. Photoconductivity as a function of illumination time for undoped and N-doped a-Si:H. "ann" means the annealed states.

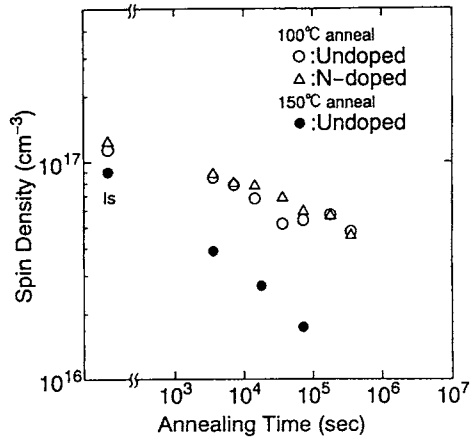


Fig. 4. Recovery of the spin density as a function of annealing time for light-soaked undoped and N-doped a-Si:H. "Is" means the light-soaked states.

appreciable change in the light-induced spin density by the addition of N of the amount of $5 \times 10^{20} \text{cm}^{-3}$.

On the other hand, both σ_d and σ_p exhibit different behaviors for these two films as shown in Figs. 2 and 3. Both σ_d and σ_p for the N-doped film are larger than those for the undoped film because the addition of N shifts the Fermi level E_F upwards. Furthermore the decreases in both σ_d and σ_p by light-soaking occurs more rapidly for the N-doped film than for the undoped film. The results can be explained by a larger downward shift of E_F by light-soaking for the N-doped film than for the undoped film caused by the same amount of the increment in N_s . It is also found from Figs. 1, 2 and 3 that N_s increases more gradually than σ_d and σ_p and saturates after a longer illumination time than σ_d and σ_p .

Figure 4 shows the decrease in N_s by annealing for light-soaked films. Figures 5 and 6 shows the recoveries of σ_d and σ_p by annealing for light-soaked films. The results shown in Figs. 4, 5 and 6 shows the recoveries of σ_d and σ_p also occurs faster than the recovery of N_s as in the case of light-soaking process. The results are summarized in Figs. 7 and 8 which respectively show σ_d and σ_p against N_s for both the light-soaking and annealing processes for the undoped and N-doped films. It is apparent that both σ_d and σ_p are not uniquely determined by N_s . A similar behavior between σ_p and N_s (derived from CPM) has already been reported by the Princeton group[6].

In order to elucidate the mechanism, the change in the activation energy E_a for σ_d was derived in the light-soaking and annealing processes by measuring the temperature dependence of σ_d . σ_d was measured only up to 60 °C for avoiding the annealing effect. The results are summarized in Fig. 9. The hysteresis of σ_d against N_s shown in Fig. 7 appears to be brought about by the hysteresis of E_a against N_s shown in Fig. 9, although enough data are not available.

There are several possibilities for different behaviors between the conductivity change and the spin density change:

- (1) Defects which can not be detected by ESR, e.g. charged defects, are responsible for the movement of E_F .
- (2) Samples are inhomogeneous and the region where current flows is different from the region where most spins exist.
- (3) The energy of dangling bonds has a distribution, and deeper dangling bonds which are more effective for carrier recombination are rapidly created by light-soaking and rapidly annihilated by annealing. This possibility was suggested by the Princeton group[6].

In order to discriminate between these possibilities, LESR and CPM measurements have been carried out. The results of LESR are summarized in Table 1 together with

Table 1. Density of the ESR centers with $g = 2.0055$ observed by dark ESR (DESR) and LESR for undoped and N-doped a-Si:H in the light-soaked and annealed states. The density of the ESR centers with $g = 2.004$ (N_e) and 2.01 (N_h) are also shown. Illumination time is shown in parenthesis.

| | | <u>Undoped</u> | | <u>N-doped</u> | |
|------|--|----------------------|------------------------|----------------------|------------------------|
| | | annealed | light-soaked (146h) | annealed | light-soaked (316h) |
| DESR | D^0 (cm^{-3}) | 2.5×10^{15} | 9.6×10^{16} | 2.5×10^{15} | 1.3×10^{17} |
| | $D^+ + D^- + D^0$ (cm^{-3}) | 2.0×10^{16} | 9.6×10^{16} | 4.0×10^{16} | 1.6×10^{17} |
| LESR | N_e (cm^{-3}) | 1.8×10^{16} | 1.6×10^{16} | 1.8×10^{16} | 5.3×10^{15} |
| | N_h (cm^{-3}) | 4.4×10^{16} | 1.4×10^{17} | 4.8×10^{16} | 7.9×10^{16} |
| | $D^+ + D^-$ (cm^{-3}) | 1.7×10^{16} | $< 2.0 \times 10^{16}$ | 3.8×10^{16} | 3.0×10^{16} |

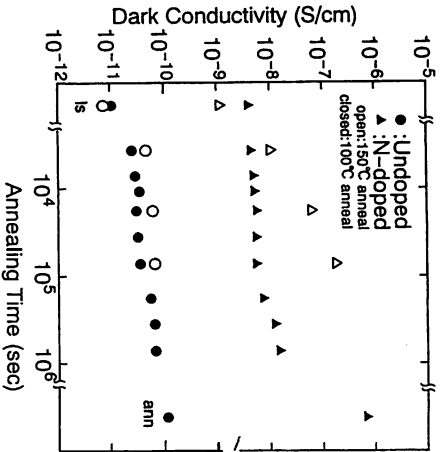


Fig. 5. Recovery of the dark conductivity as a function of annealing time for light-soaked undoped and N-doped a-Si:H. "ls" and "ann" mean the light-soaked and annealed states, respectively.

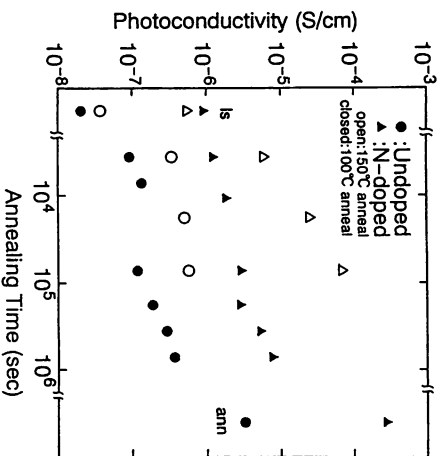


Fig. 6. Recovery of the photoconductivity as a function of annealing time for light-soaked undoped and N-doped a-Si:H. "ls" and "ann" mean the light-soaked and annealed states, respectively.

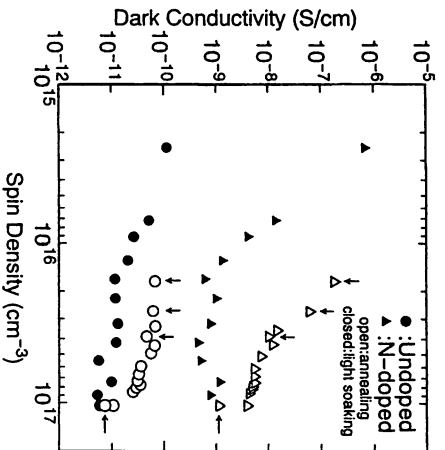


Fig. 7. Dark conductivity as a function of the spin density for undoped and N-doped a-Si:H in the processes of light-soaking and annealing. Annealing temperature is 100 °C except for the data indicated by arrows for which annealing is performed at 150 °C.

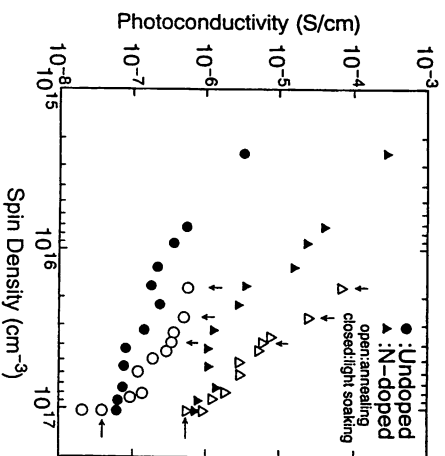


Fig. 8. Photoconductivity as a function of the spin density for undoped and N-doped a-Si:H in the processes of light-soaking and annealing. Annealing temperature is 100 °C except for the data indicated by arrows for which annealing is performed at 150 °C.

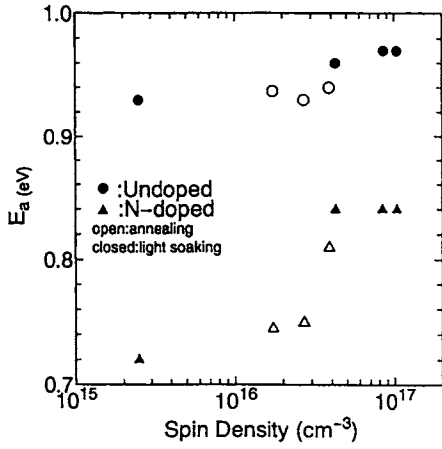


Fig.9. Activation energy for the dark conductivity as a function of the spin density for undoped and N-doped a-Si:H in the processes of light-soaking and annealing.

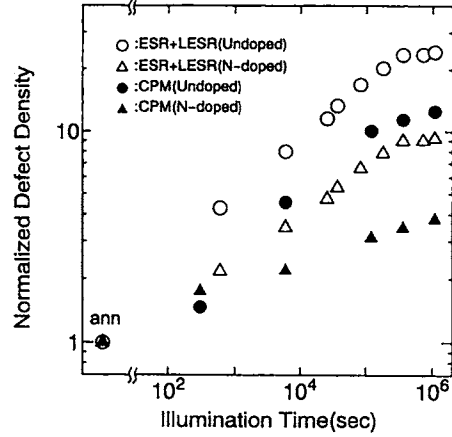


Fig.10. Normalized defect density derived from ESR and LESR and that derived from CPM as a function of illumination time for undoped and N-doped a-Si:H.

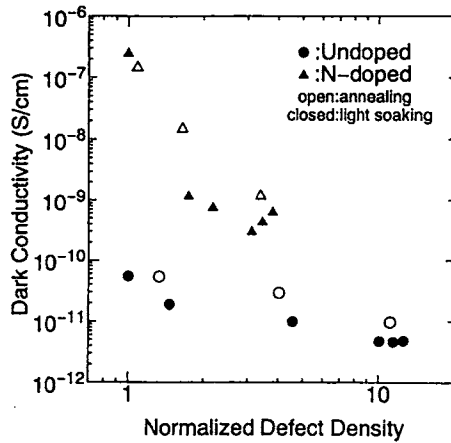


Fig.11. Dark conductivity as a function of the defect density derived from CPM for undoped and N-doped a-Si:H in the processes of light-soaking and annealing.

dark ESR. The LESR signals are decomposed into three components; $g = 2.0055$, $g = 2.004$ and $g = 2.01$ lines. LESR measurements were carried out with the light intensity of 3 mW/cm^2 and 36 mW/cm^2 for the annealed and the light-soaked samples, respectively. The larger intensity was used for the light-soaked sample because the spin density for the $g = 2.0055$ component does not saturate with a small intensity. For both the $g = 2.004$ and the $g = 2.01$ components, the spin densities are unable to be saturated even if a large intensity is used. Therefore, it should be noted that the spin densities for the $g = 2.004$ and the $g = 2.01$ centers depend on the light intensity. The difference between the spin densities for the $g=2.0055$ component in dark ESR and LESR should be the density of charged dangling bonds (D^+ and D^-). Then it is found from Table 1 that the density of charged dangling bonds does not appreciably change with light-soaking. However, it is found that the density of $g=2.01$ centers increases with light-soaking while the density of $g=2.004$ centers does not increase. The origin of these two centers is still controversial[7,8,9]. The normalized defect density derived from CPM is shown in Fig. 10 against illumination time. The behavior is closer to that of ESR shown in Fig. 1 than those of σ_d and σ_p shown in Figs. 2 and 3. The defect density derived by CPM is that of $D^0 + D^-$ [4], and the procedure to deduce the defect density by CPM has been reported in Ref. 4. In Fig. 10, the normalized density of $D^0 + D^-$ deduced from dark ESR and LESR is also shown for comparison by assuming $D^- = D^+$. The recovery by annealing was also studied by CPM. Corresponding to the relation between σ_d and N , both for light-soaking and annealing processes shown in Fig. 7, a similar plot for σ_d versus the normalized defect density obtained from CPM is shown in Fig. 11. The result clearly shows that σ_d again is not uniquely determined by the defect density deduced from CPM. The defect density derived from CPM should be the defect density in the region where current flows. Therefore the possibility (2) is unlikely. The possibility (1) also appears to be unlikely because LESR measurements show that the density of charged dangling bonds does not appreciably change with light-soaking. Therefore, the possibility (3) appears to be the most plausible among the three possibilities.

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