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A. Morimoto, H. Yokomichi, T. Atoji, et al.

LIGHT-INDUCED CREATION OF DEFECTS AND RELATED PHENOMENA IN SILICON-BASED AMORPHOUS SEMICONDUCTORS

A. Morimoto, H. Yokomichi, T. Atoji,
M. Kumeda, I. Watanabe and T. Shimizu
Dept. of Electronics, Kanazawa University, Kanazawa 920, Japan

ABSTRACT

Light-induced creation of defects and their annealing process were studied by ESR, photoconductivity and photoluminescence measurements for $a\text{-}Si_{1-x}N_x$:H and $a\text{-}Si_{1-x}C_x$:H films besides a-Si:H films with various spin densities and H contents. The results show that the degradation of the photoconductivity and the photoluminescence is mainly attributed to creation of dangling bonds due to bond breaking.

INTRODUCTION

A number of studies on the Staebler-Wronski (S-W) effect in hydrogenated amorphous Si (a-Si:H) have been carried out. Various models have been proposed for the degradation due to a strong illumination , i.e., the decrease in the photoconductivity , the fatigue of the photoluminescence, and the increase in the ESR spin density. The origin of the S-W effect, however, is still controversial. The S-W effect for $a\text{-}Si_{1-x}N_x$:H or $a\text{-}Si_{1-x}C_x$:H films is scarcely investigated until now. In this paper, we present the results of our investigation on the changes of the ESR spin density, the photoluminescence and the photoconductivity due to white light illumination at room temperature for $a\text{-}Si_{1-x}N_x$:H and $a\text{-}Si_{1-x}C_x$:H films. The relation among these changes is investigated.

EXPERIMENTAL

a-Si:H films with various H contents and $a\text{-}Si_{1-x}N_x$:H films were prepared both by glow discharge decomposition (GD) and reactive sputtering (SP). $a\text{-}Si_{1-x}C_x$:H and $a\text{-}Si_{1-x}Ge_x$:H films were prepared only by GD. ESR and photoconductivity measurements were carried out both at liquid N_2 temperature (LNT) and room temperature (RT). Photoluminescence measurement was carried out only at LNT within a few minutes. He-Ne laser light (632.8 nm) and monochromatic light derived from a Xe lamp through interference filters with 0.1 mW/cm^2 were used for excitation of photocurrent. The He-Ne laser light and Ar^+ laser light (488 and 514.5 nm) with a few hundred mW/cm^2 were used for excitation of the photoluminescence. Strong illumination was carried out for more than 1 h with more than 120 mW/cm^2 by using white light from the Xe lamp through an IR cut filter.

RESULTS

I. $a\text{-}Si_{1-x}N_x$:H films

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In order to clarify the nature of defects in a-$Si_{1-x}N_x$:H films, we carried out the light-induced ESR at LNT. Figure 1 shows how the spin density N_s changes with white light illumination at LNT for SP a-$Si_{0.68}N_{0.32}$:H film[1]. I_0 in the figure is about 0.1 mW/cm^2. The g-value and the linewidth do not change with illumination. Illumination at LNT shows a remarkable increase in the light-induced ESR signal intensity. After cessation of illumination, a considerable part of the increased N_s remains at LNT, but disappears at RT. In the case of strong illumination, a part of N_s increased at LNT remains even at RT. Similar results are obtained for a-$Si_{1-x}N_x$:H films with various x.

All the present results can be explained as follows. A large number of Si dangling bonds with negative electron correlation energy U (D_n) exist in a-$Si_{1-x}N_x$:H films ($x \neq 0$) besides Si dangling bonds with positive U (D_p), and the sign of U is changed into a positive one due to illumination at LNT for some of D_n. The light-induced ESR signal arises both from D_p^0 centers created by the change of the sign of U and from D_n^0 centers created by trapping photo-excited electrons and holes. D_n^0 centers return to the ESR inactive $D_n^+ + D_n^-$ centers rapidly at LNT after cessation of illumination, whereas D_p^0 centers created by the former mechanism remain at LNT and return to $D_n^+ + D_n^-$ centers with raising the temperature to RT. In a-Si:H films, such phenomena do not appear, because no defects with negative U exist.

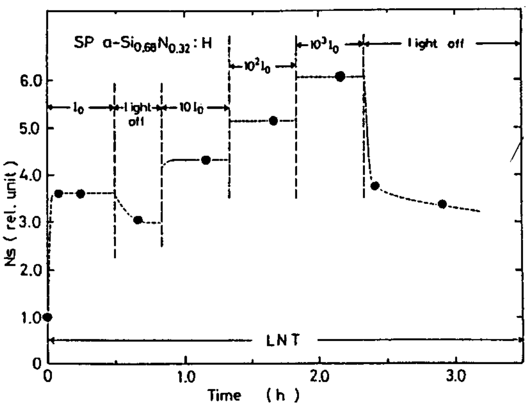

Fig. 1 Spin density N_s derived from light-induced ESR signal at LNT with various illumination intensities and N_s derived from ESR at LNT after cessation of illumination for SP a-$Si_{0.68}N_{0.32}$:H film.

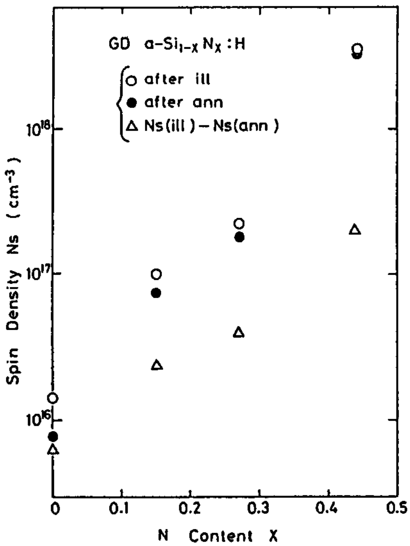

Fig. 2 Spin density N_s for annealed and strongly illuminated GD a-$Si_{1-x}N_x$:H films and the difference between them as a function of x.

In a-Si:H films, it is known that a prolonged and strong illumination creates ESR centers originating from dangling bonds[2-4]. In a-$Si_{1-x}N_x$:H films, the photo-created ESR centers remain at RT as described above. Figure 2 shows N_S in the dark for a-$Si_{1-x}N_x$:H films annealed at 200 ° C and strongly illuminated at RT as a function of N content x. The density of photo-created ESR centers ΔN_S stable at RT increases with an increase in x, whereas $\Delta N_S/N_S$ decreases with x because of a large increase in N_S before illumination with x as shown in Fig. 2.

The relation between the increase in N_S in the dark and the decrease in $\eta\mu\tau$ due to strong illumination is shown in Fig. 3. Data for various a-$Si_{1-x}N_x$:H films without illumination are also shown together. Changes due to the illumination are indicated by the arrows. The relation between $\eta\mu\tau$ and N_S for unilluminated films is represented by a formula $\eta\mu\tau \propto N_S^{-\gamma}$ with $\gamma \fallingdotseq 2$. Changes due to strong illumination are also represented by a formula $\eta\mu\tau(\mathrm{ill})/\eta\mu\tau(\mathrm{ann}) = \{N_S(\mathrm{ill})/N_S(\mathrm{ann})\}^{-\gamma}$ with $\gamma \fallingdotseq 2$. Since the reciprocal lifetime $1/\tau$ is expected to be proportional to N_S, $\gamma \fallingdotseq 2$ suggests that the decrease in the mobility μ with an increase in N_S. In a-$Si_{1-x}N_x$:H films without strong illumination, the decrease in $\eta\mu\tau$ with an increase in x can be attributed to the increase in the density of dangling bonds[5] and in the density of tail states. The similarity of γ value between those with and without strong illumination suggests that the decrease in $\eta\mu\tau$ with strong illumination can be attributed to the increase in the density of dangling bonds accompanied by the increase in the density of tail states.

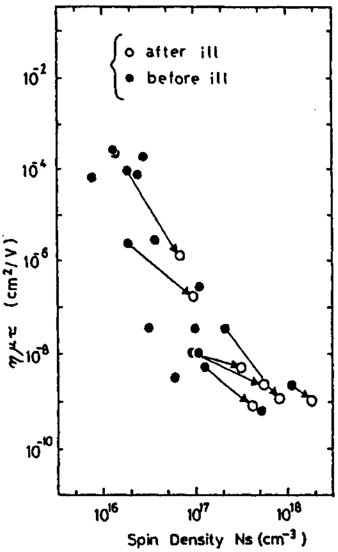

Fig. 3 Relation between spin density N_S and $\eta\mu\tau$ for a-$Si_{1-x}N_x$:H films before illumination and after strong illumination at RT.

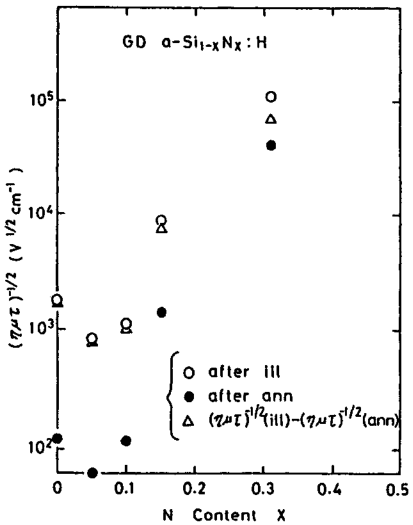

Fig. 4 Degradation of $\eta\mu\tau$ due to strong illumination for GD a-$Si_{1-x}N_x$:H films. $(\eta\mu\tau)^{-1/2}$ is expected to be approximately proportional to N_S from Fig. 3.

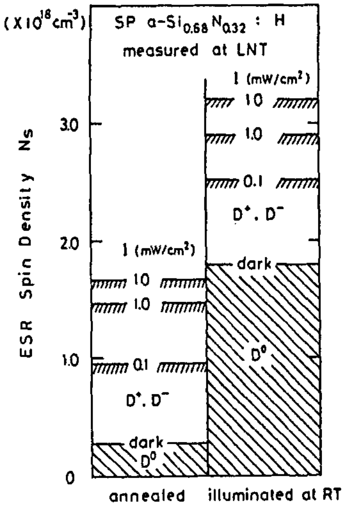

Fig. 5 Spin density derived from ESR and light-induced ESR measured at LNT both for SP a-$Si_{0.68}N_{0.32}$:H films annealed and strongly illuminated at RT.

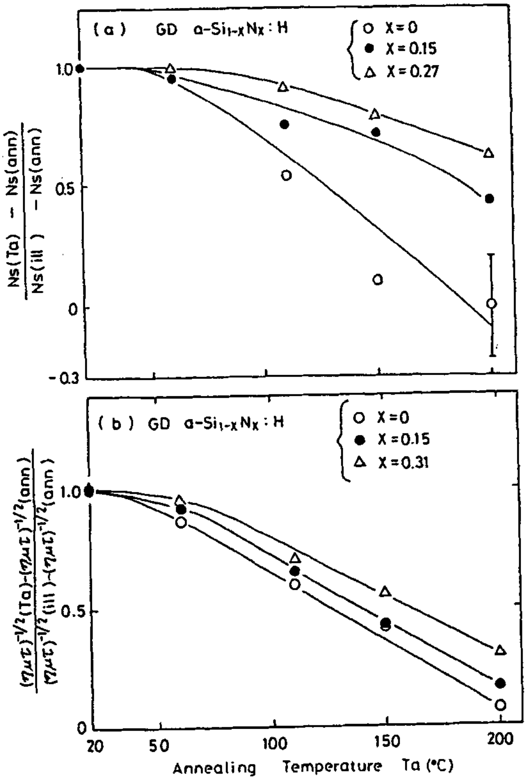

Fig. 6 Recovery of N_s (a) and $\eta\mu\tau$ (b) due to annealing for 10 min for GD a-$Si_{1-x}N_x$:H films.

The result of the degradation of the photoconductivity due to strong illumination is shown in Fig. 4. Here, $(\eta\mu\tau)^{-1/2}$ is plotted against x in order to compare with Fig. 2, because $(\eta\mu\tau)^{-1/2}$ is approximately proportional to N_s. $\Delta(\eta\mu\tau)^{-1/2} = (\eta\mu\tau)^{-1/2}(\text{ill}) - (\eta\mu\tau)^{-1/2}(\text{ann})$ corresponding to the increase in the defect density increases with an increase in x. A good correlation between ΔN_s and $\Delta(\eta\mu\tau)^{-1/2}$ suggests that the decrease in $\eta\mu\tau$ due to strong illumination is mainly attributed to the increase in the density of dangling bonds.

In contrast, the comparison of the transient photoconductivity at LNT to the transient light-induced ESR at LNT shows no good correlation between them. The reason is not clear at present, but it is possible that the low temperature photoconductivity is not largely affected by the density of recombination centers[6].

In order to clarify what kind of dangling bonds are created by strong illumination, we carried out light-induced ESR both for the films annealed and strongly illuminated at RT. The result is shown in Fig. 5. For SP a-$Si_{0.68}N_{0.32}$:H film annealed at 200 °C for 1 h, the density of D_p^0 is 2.7×10^{17} cm^{-3} and that of D_n^+ and D_n^- is 1.4×10^{18} cm^{-3}. Strong illumination causes a remarkable increase only in D_p density, though it does not cause any increase in D_n density.

An experiment of the photoluminescence fatigue was also carried out. The relative decrement of the photoluminescence intensity due to strong illumination, $\Delta I_{PL}/I_{PL} = \{I_{PL}(ann)-I_{PL}(ill)\}/I_{PL}(ann)$, increases with x. It might appear that the increase in $\Delta I_{PL}/I_{PL}$ with an increase in x is inconsistent with the decrease in $\Delta N_s/N_s$ with an increase in x. However, we can show that the changes of $\Delta I_{PL}/I_{PL}$ and $\Delta N_s/N_s$ with x are qualitatively consistent on the basis of the relation between I_{PL} and N_s, $I_{PL} = I \exp(-4\pi R_c^3 N_s/3)$, proposed by Street et al.[7], because N_s increases largely with x. Here, R_c is the critical distance between defects and photo-excited carriers at which radiative and non-radiative recombination rates are equal. The transition from $D^+ + D^-$ to $2D^0$ is expected to occur during the photoluminescence measurement. It is, however, not clear at present how such a transition affects I_{PL}.

It is important to investigate a recovery process as well as the degradation process of $\eta\mu\tau$ and N_s in order to clarify the origin of the degradation. Figure 6 shows the recovery processes of N_s (a) and

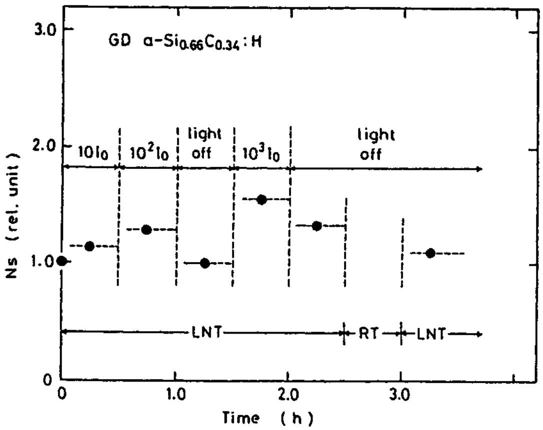

Fig. 7 Spin density N_s derived from light-induced ESR signal at LNT with various illumination intensities and N_s derived from ESR at LNT after cessation of illumination for SP a-$Si_{0.66}C_{0.34}$:H film.

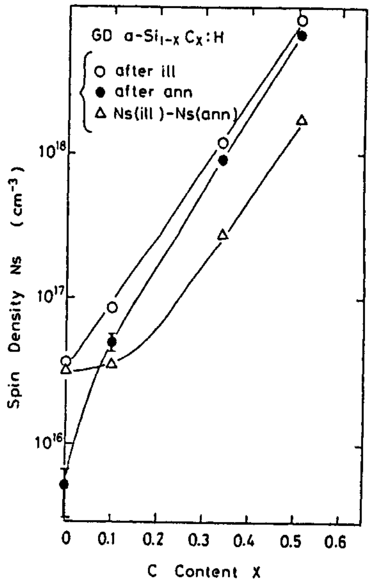

Fig. 8 Spin density N_s for annealed and strongly illuminated GD a-$Si_{1-x}C_x$:H films and the difference between them as a function of x.

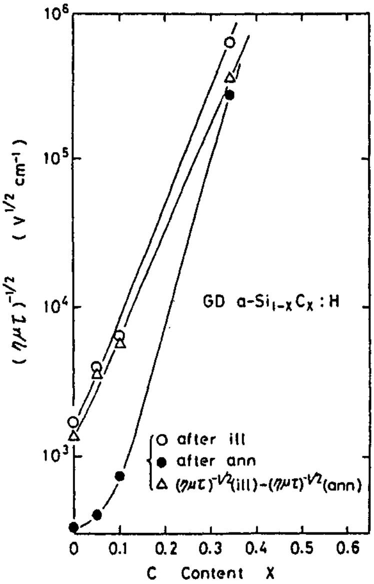

Fig. 9 Degradation of $\eta\mu\tau$ due to strong illumination for GD $a\text{-}Si_{1-x}C_x{:}H$ films. $(\eta\mu\tau)^{-1/2}$ is expected to be approximately proportional to N_s.

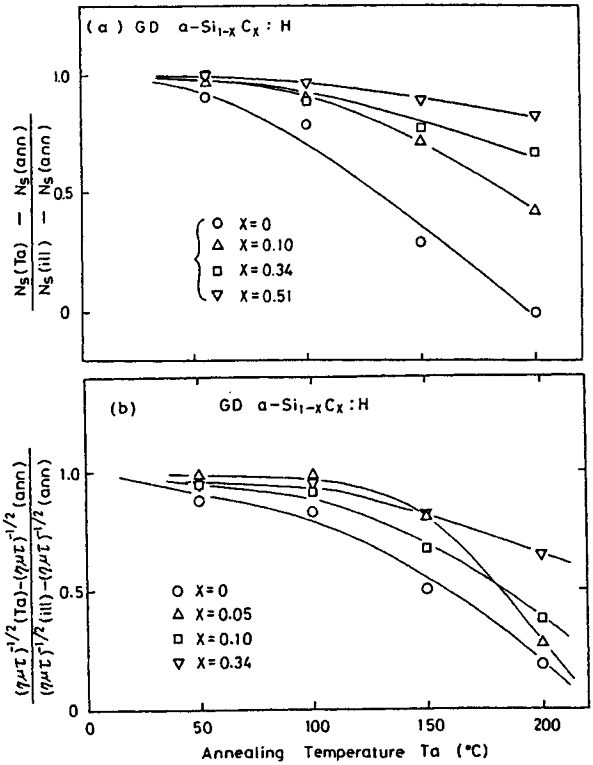

Fig. 10 Recovery of N_s (a) and $\eta\mu\tau$ (b) due to annealing for 10 min for GD $a\text{-}Si_{1-x}C_x{:}H$ films.

$\eta\mu\tau$ (b) by isochronal annealing for 10 min at each annealing temperature T_a. $\{N_s(T_a)-N_s(ann)\}/\{N_s(ill)-N_s(ann)\}$ represents the ratio of the remaining N_s after annealing at T_a to the increased N_s. $(\eta\mu\tau)^{-1/2}$ is used in Fig. 6(b) because of the same reason as in Fig.3. $\eta\mu\tau$ for GD $a\text{-}Si_{1-x}N_x{:}H$ films shows a recovery process similar to N_s. These results also support that the degradation of $\eta\mu\tau$ is mainly attributed to the increase in N_s. The incorporation of N atoms is found to prevent the recovery of the films from the degradation state.

II. $a\text{-}Si_{1-x}C_x{:}H$ films

Also in $a\text{-}Si_{1-x}C_x{:}H$ films, the light-induced ESR measurement was carried out at LNT. Figure 7 shows how the spin density changes with a white light illumination for GD $a\text{-}Si_{0.66}C_{0.34}{:}H$ film. I_0 in the figure is about 0.1 mW/cm^2. Though the g-value and the linewidth do not largely change with illumination, a slight asymmetry appears with strong illumination. This shows that the light-induced ESR signal possibly contains the band tail ESR signals as well as the ESR signal of D_n^0 and D_p^0 centers. Therefore the density of total

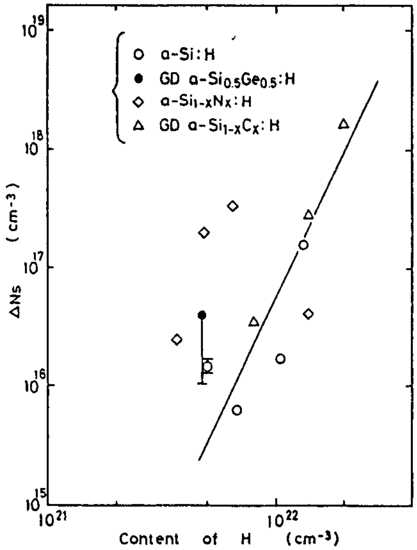

Fig. 11 Increment of spin density ΔN_S as a function of H content N_H for various films.

dangling bonds, D_p and D_n, may be less than the N_s values shown in this figure.

Figure 8 shows N_S in the dark for annealed and strongly illuminated $a\text{-}Si_{1-x}C_x$:H films as a function of x. ΔN_S increases with x, whereas $\Delta N_S/N_S$ decreases with x, as in the case of $a\text{-}Si_{1-x}N_x$:H films.

The result of the degradation of the photoconductivity due to strong illumination is shown in Fig. 9. Here, $(\eta\mu\tau)^{-1/2}$ is plotted as in the case of $a\text{-}Si_{1-x}N_x$:H films. $\Delta(\eta\mu\tau)^{-1/2} = (\eta\mu\tau)^{-1/2}(ill) - (\eta\mu\tau)^{-1/2}(ann)$ corresponding to the increment of the defect density increases with an increase in x. The result of the photoluminescence measurement also shows a close relation between I_{PL} and N_S as in the case of $a\text{-}Si_{1-x}N_x$:H films. The good correlations between ΔN_S and $\Delta(\eta\mu\tau)^{-1/2}$ and between ΔN_S and I_{PL} suggest that the degradation due to strong illumination is mainly attributed to the increase in the density of dangling bonds.

The results of the experiment on the recovery process from the degradation state are shown in Figs. 10(a) and 10(b). The results are similar to those shown in Fig. 6 for $a\text{-}Si_{1-x}N_x$:H films.

III. EFFECT OF HYDROGEN

In order to reveal what causes the creation of dangling bonds, we investigated a relation between ΔN_S due to strong illumination at RT and the H content of the films N_H. The result is shown in Fig. 11. ΔN_S and N_H for a-Si:H films, $a\text{-}Si_{1-x}Ge_x$:H and $a\text{-}Si_{1-x}C_x$:H films have a good correlation, indicating that H atoms in the films play an important role in the degradation due to strong illumination. In the case of $a\text{-}Si_{1-x}N_x$:H films, N atoms , in addition to H atoms, play an important role in the degradation. This is probably attributed to the low coordination number of N atoms.

DISCUSSION AND CONCLUSION

The results of the light-induced ESR at LNT in a-$Si_{1-x}N_x$:H and a-$Si_{1-x}C_x$:H films without strong illumination suggest the following idea. The binary alloy films with N or C atoms have both D_p and D_n. Without illumination, only D_p^0 are ESR active, whereas with illumination at LNT, both D_p^0 and D_n^0 become ESR active. The ratio of the density of D_n to the density of D_p for a-$Si_{1-x}N_x$:H film is much larger than that for a-$Si_{1-x}C_x$:H film as can be seen from Figs. 1 and 7. The presence of D_n in a-$Si_{1-x}N_x$:H films is presumably attributed to 3-fold coordination of N atoms with lone pair electrons. An origin of the presence of D_n in a-$Si_{1-x}C_x$:H films is not clear, though it might be due to a large N_H in these films.

The investigation of the strong illumination effect on $\eta\mu\tau$ and I_{PL} for a-$Si_{1-x}N_x$:H and a-$Si_{1-x}C_x$:H films shows that the degradation of $\eta\mu\tau$ and I_{PL} due to strong illumination can mainly be attributed to the creation of dangling bonds due to bond breaking. The increase of N or C content x increases the density of dangling bonds created by bond breaking due to strong illumination and prevents the recovery from the degradation state. This suppression of the recovery has a good correspondence with the result that the incorporation of N or C atoms makes the film heat-resistent[8,9].

In conclusion, ESR with various illumination intesities at LNT in the present work can reasonably be explained by both the change of $D^+ + D^-$ centers into $2D^0$ centers and bond breaking. The degradation of the photoconductivity at RT and the photoluminescence can mainly be attributed to the creation of dangling bonds due to bond breaking in contrast with the Adler's proposal[10] that the S-W effect is brought about by the change of D^+ and D^- into $2D^0$.

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