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メタデータ	言語: eng
	出版者:
	公開日: 2017-10-03
	キーワード (Ja):
	キーワード (En):
	作成者:
	メールアドレス:
	所属:
URL	https://doi.org/10.24517/00009724

Doping effect of oxygen or nitrogen impurity in hydrogenated amorphous silicon films

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O, N, or C impurity was separately incorporated into a-Si:H films by hot-wall glow discharge decomposition. The effect of the impurity incorporation was investigated by electrical and electron spin resonance measurements. Both O and N impurities were found to increase the dark conductivity by decreasing its activation energy in a-Si:H films. Furthermore, it was found that O and N impurities delay the photoresponse. C impurity, however, has no appreciable effect on them. These findings suggest that O and N impurities shift the Fermi level upward and form a trapping state for photoexcited electrons, supporting our O_3^+ and N_4^+ model.

For the application of hydrogenated amorphous silicon (a-Si:H), it is inevitable to control the dark conductivity and photoresponse. Especially, the dark conductivity is well known to be very sensitive to the preparation condition. For example, the contents of unintentionally incorporated impurities, such as O, N, and C, appear to affect the dark conductivity. Furthermore, we have already reported that a large number of charged dangling bonds exist in a-Si:H.[1] The origin of the charged dangling bond is probably ascribed to the charged O or N impurity-defect pair as we proposed.[1] For establishing the model, however, more reliable and direct evidence is necessary. Thus, it is important to clarify the effect of the impurity incorporation on the properties of a-Si:H.

For the investigation of the impurity effect, we employed the hot-wall glow discharge decomposition (HWGD) system for reducing the impurity content. The system was found to be effective for eliminating the impurity content.[2] Comparing the result of the HWGD, the conventional glow discharge decomposition and the ultrahigh vacuum systems, we had found that the dark conductivity σ_d, the activation energy E_a, and the density of charged dangling bonds are closely correlated with the N and/or O impurity content.[2] However, in the previous work, O, N, and C, contents were not controlled separately, resulting in an ambiguity on the effect of each impurity,

In the present study, a-Si:H films were prepared by the HWGD system with various O, N, or C contents. Each impurity was separately incorporated to a-Si:H films by exactly controlling the mole fraction of N_2, O_2, or CH_4 gas in the source gas.

The HWGD system equipped with a turbo molecular pump and an oil rotary pump was employed. The deposition space is surrounded by a silicon tube reactor and an IR radiation source with a gold mirror. rf power is supplied via capacitively coupled electrodes. Detailed setup was described in the previous paper.[2] "Pure" a-Si:H film was prepared by decomposition of pure silane gas. Gases for the incorporation of impurities were diluted with He gas. The effect of He gas on the properties of a-Si:H is negligibly small because there is no change in the proper-

ties of a-Si:H films prepared with pure silane and with silane diluted by He. All films were prepared by an rf power of 50 W and at a substrate temperature of 300 °C. Prior to the deposition, the silica tube reactor was baked at a temperature above 400 °C. The film thickness was kept around 3 μm.

Because of a small amount of impurity in a-Si:H secondary ion mass spectrometry (SIMS) measurements were performed for evaluating their content. The impurity content was determined through the mole fraction of the impurity gas by a combination of SIMS, electron probe microanalysis (EPMA), and infrared (IR) absorption measurements. For characterization of the films, optical absorption, electron spin resonance (ESR), and conductivity measurements were carried out. Measuring the photoconductivity, films were illuminated by a white light of the Xe lamp through an IR-cut filter (60 mW/cm^2), corresponding to the AM1 light source. For evaluating the photoresponse, a decay of the photocurrent from the steady state was measured at room temperature with an He-Ne laser switched off by an acousto-optical device. Details for the measurement was described in the previous paper.[3]

First of all, we will describe the result of SIMS measurements. The SIMS depth profile for a few samples of the present a-Si:H films revealed that an intentional and separate incorporation of O, N, or C impurity was excellently performed as we expected. For "pure" films, the O, N, and C impurity contents are reduced down to 2×10^{18} cm^{-3}, 8×10^{17} cm^{-3}, and 8×10^{16} cm^{-3}, respectively, as shown in the previous paper.[2] For impurity-incorporated films, the content of the intentionally added impurity is found to have a desired value, while the contents of other impurities have corresponding values for "pure" films.

Figure 1 shows the impurity content in the film Y(film) against the gas-phase impurity mole fraction Y(gas). Here, Y(gas) is defined by Y(gas) $= [X_2]/\{[X_2] + [SiH_4]\}$. In addition to the result of the SIMS measurements, those of EPMA measurements combined with IR absorption measurements were also used to determine the impurity content in the films. As seen in the figure, both the O and N contents are found to be roughly proportional to the mole fraction of the impu-
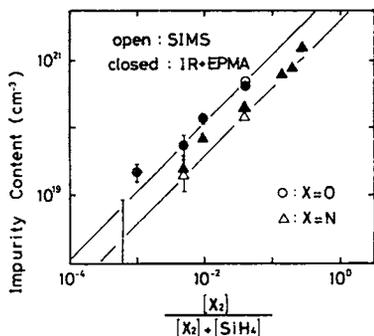
FIG. 1. Calibration line for the impurity content in the film derived from various means against the gas-phase impurity mole fraction in source gas.

rity gas. The incorporation probability A, defined by $Y(\text{film}) = A \times Y(\text{gas})$, is determined to be about 0.3 for O impurity, and about 0.1 for N impurity, assuming that the Si content is 4×10^{22} cm^{-3} in a-Si:H. This implies that the O impurity is easily incorporated into a-Si:H films, compared with the N impurity. These A values are smaller than those for As and P using AsH$_3$ and PH$_3$ gases, respectively.[4] Most of the impurity content for the present films were determined by Y(gas) through the calibration line in Fig. 1. The linear relation between Y(film) and Y(gas) has been reported for P-doping in a-Si:H by Stutzmann et al.[5] Based on their model, the linear relation is attributed to the PVD (physical vapor deposition) condition.

Optical absorption and ESR measurements were performed for determination of the optical gap E_g and the neutral dangling bond density N_S, respectively. Within the present content range of impurities, below about 10^{21} cm^{-3} for all impurities, there is no appreciable change both in E_g and N_S with the impurity incorporation. The average E_g is about 1.66 eV and the deviation from the average value is within ± 0.01 eV. N_S is roughly 1×10^{16} cm^{-3}, including the bulk and surface defects.[6]
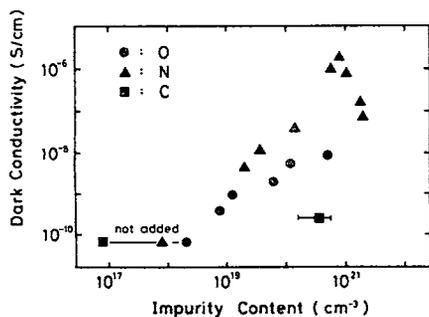
FIG. 2. Dark conductivity σ_d as a function of O, N, and C contents.
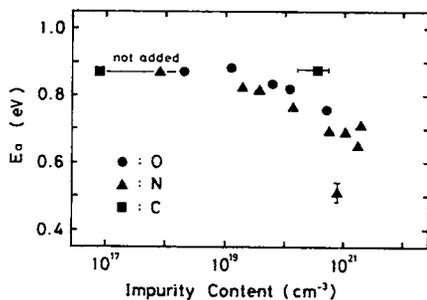
FIG. 3. Activation energy E_a for the dark conductivity σ_d as a function of O,N, and C contents.

Figure 2 shows the dark conductivity σ_d as a function of O, N, and C contents. Three solid symbols (square, triangle, and circle) combined by the horizontal bar represent σ_a with respective impurity contents for "pure" a-Si:H film. The horizontal error bar on the solid square represents the experimental error for the measurement of the C content. σ_d increases with an increase in the O and N contents up to 1×10^{21} cm^{-3}, while it does not appreciably change with the C content. σ_d, however, appears to decrease with an increase in the N content above 1×10^{21} cm^{-3}.

In order to clarify the origin of the increase in σ_d, the activation energy E_a of σ_d was derived from the temperature dependence of σ_d. Figure 3 shows the activation energy E_a as a function of the impurity content for respective impurities. A vertical error bar on the solid triangle in the figure represents the experimental error of E_a. Two horizontal bars have the same meanings as those in Fig. 2. It is revealed that E_a decreases from around 0.9 to around 0.5 with an increase in the impurity content, corresponding to the change in σ_d. This finding suggests that the Fermi level E_F shifts toward the conduction band with increasing the O and N contents, and it does not appreciably change with the addition of C. The amount of the shift is larger for the N incorporation than for O incorporation. Since there is no appreciable change in E_g due to the impurity incorporation, we ignored the effect of E_g on E_a. For N incorporated films, E_a appears to increase with the N content above 1×10^{21} cm^{-3}. It is possible that the fact results from the change in the incorporation scheme of N or a widening of the mobility gap with the constant optical gap E_g.

Similar behaviors of σ_a and E_a due to the N incorporation have already been reported by previous papers.[7,8] Here, it should be noted that even if the impurity is only O, atom σ_d increases with the O content. Hishikawa et al. have already reported that σ_d of a-Si:H films prepared by the UHV chamber increases with increasing the amount of air leakage.[9] So far, however, there is no report on an increase in σ_d and E_F caused by the O incorporation alone.

The photoconductivity σ_P also increases with an increase in the O and N contents, while it does not change appreciably with the C incorporation. The increase is
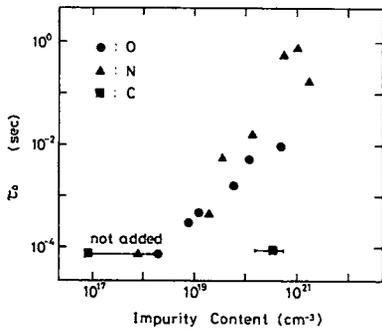
FIG. 4. Decay time τ_0 as a function of O, N. and C contents.

thought to result from the upward shift of E_F.[10] For the N incorporation, σ_F increases with the N content from 10^{-5} to 10^{-3} S/cm, while σ_d from 10^{-10} to 10^{-6} S/cm. For the O incorporation, σ_d increases with the O content from 10^{-10} to 10^{-4} S/cm, while σ_d increases from 10^{-10} to 10^{-8} S/cm. Therefore, the photosensitivity σ_P/σ_d decreases from 10^5 to 10^3 for the N incorporation, and from 10^5 to 10^4 for the O incorporation.

The results of light-induced ESR measurements at 77 K also show that the density of charged dangling bonds increases with an increase in the O and N contents, whereas the density of neutral dangling bonds remains unchanged. The results of the measurement of optical absorption due to defects using the constant photocurrent method (CPM) also suggest the increase in the density of charged dangling bonds.

Finally, the photocurrent decay from the steady state after the switching-off of the steady illumination was investigated. We define a decay time τ_0 as a time when the photoconductivity $\sigma_P(t)$ decays to $1/e$, where the steady state σ_P is fixed to be 1×10^{-6} S/cm by changing the illumination intensity.[3] Figure 4 shows the decay time τ_0 as a function of the impurity content. It is revealed that the N incorporation dramatically increases τ_0 by 4 orders, and the O incorporation by 2 orders. Such a degradation in the photoresponse should be suppressed for the application to a-Si:H optical sensor devices which need a rapid response. The degradation of the photoresponse shows a formation of a new trap state below the conduction band by the N or O incorporation.

The present results mentioned above are reasonably explained in terms of the following model.[1] Some of the N and O atoms incorporated in a-Si:H become fourfold-coordinated N_4^+ and threefold-coordinated O_3^+, respectively, acting as a donor. According to our model,[1] a photoexcited electron is captured at N_4^+ or O_3^+, resulting in the bond breaking. Then N_4^+ or O_3^+ changes to N_3^0 or O_2^0, respectively, creating neutral Si dangling bonds Si_3^0 at the neighboring site.[3] This appears to be the origin of the light-induced ESR signals. The increase in τ_0 due to the N or O incorporation shown in Fig. 4 is attributed to a trapping of photoexcited electrons by N_4^+ or O_3^+.[3] Figures 2 and 3 indicate that the N incorporation increases both σ_d and τ_0 more prominently than the O incorporation. However, the increase in σ_d by the N incorporation is far smaller than that by the P or As incorporation.[5] Through the present study it is found that C atoms do not have a prominent effect in moving the Fermi level.

In summary, both O and N impurities were found to increase the dark conductivity by decreasing its activation energy in a-Si:H films. Furthermore, it was found that both of them delay the photoresponse. C impurity, however, has no appreciable effect on them. These findings suggest that O and N impurities shift the Fermi level upward and form a trapping state for photoexcited electrons, supporting our O_3^+ and N_4^+ model.[1]

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