Secular Change of ESR and Conductivity in Amorphous Silicon Films

by

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Abstract

Annealing behaviors of the ESR signal and the electrical conductivity and the secular change of them are investigated for rf-sputtered amorphous Si films annealed in N_2 or (N_2+H_2) gas. For the samples annealed in (N_2+H_2) gas, the secular change of the conductivity and the ESR signal was observed. It is suggested that most of spins in samples annealed above 400 °C are dangling bonds around crystallites newly produced in the process of crystallization, and that the dangling bonds are easily wiped out with H_2 gas.

1. Introduction

In amorphous Si(a-Si) prepared by rf-sputtering or evaporation, the large ESR signal due to dangling bonds has been observed,[1] and the hopping conduction is known to be observed in temperature range $T \lesssim 300$ K.[2]

Recently, the influence of oxygen, by which the a-Si sample is contaminated during the deposition, on the spin density N_s and the electrical conductivity σ was investigated by P. G. Le Comber *et al.*[3] and S. K. Bahl *et al.*.[4] G. A. N. Connel *et al.*[5] have developed a method of hydrogenating sputtered a-Ge for studying variation of the electrical properties with the number of dangling bonds. However, above-mentioned measurements on σ and N_s are immediately carried out after fabrication of the sample, and there is no work on the secular change of σ and N_s for a-Si and a-Ge except for that on σ for evaporated Ge films.[6] The investigation on these secular changes is important in connection with a device application, because they furnish information on the stability of the structure of a-Si or a-Ge. Moreover the a-Si material prepared by the decomposition of silane (SiH_4) has been of considerable technological interest because of the possible application of this material to solar cell technology, so that the influence of hydrogen on N_s and σ has drawn wider attention.

In the present paper, the annealing behaviors of the ESR signal and σ, and the secular change of them are investigated for rf-sputtered a-Si films annealed in N_2 or (N_2+H_2) gas. A possible model for the incorporation of hydrogen atoms, the secular change of σ and N_s, and the process of the crystallization are proposed on the basis of the investigations.

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2. Experimental

The a-Si films used in this investigation were deposited on thermally grown SiO_2 substrates by rf-sputtering from Si targets. The Si targets were P doped Si single crystal with a resistivity of 0.025～0.035Ωcm. The SiO_2 substrates were set on the water-cooled substrate holder. The deposition rate was about 220 Å / min, and the film thickness was about 1 μm.

The annealing was carried out in an atmosphere of N_2 gas or a mixture of N_2 and H_2 gases in several months after deposition. The annealing time for each stage was 10 min. The ESR apparatus is an X-band spectrometer and the signals were observed during multi-stage isochronal annealing. The spin density N_s was obtained by comparison with the ESR intensity of DPPH whose spin density was determined beforehand by comparing it with that of Varian strong pitch. A probable error in the spin density is about ±30 % in an absolute value and about ±15 % in a relative one.

Each sample used for electrical conductivity measurements was annealed individually at various temperatures, then Au electrodes separated by 1 mm were evaporated on the samples. The sample was set in the surface gap cell configuration and steady electric field up to 100 V cm^{-1} was applied. Ohmic behavior was found in all cases.

3. Results

An ESR signal with Lorentzian lineshape and g-value of 2.0055 was observed for samples annealed at various temperatures. The g-value and linewidth ΔH are independent of measurement temperature, and the temperature dependence of the signal intensity obeys Curie law.[7,8)]

Figure 1 shows the annealing temperature dependences of N_s for samples annealed in N_2 gas and those in (N_2+H_2) gas. The annealing was carried out on the samples preserved in air at room temperature for three months after fabrication of samples, and the ESR measurements were carried out immediately after annealing. As seen in this figure, both N_s's decrease monotonously with annealing up to 300～400 ℃, and increase again above 400 ℃. It is found that N_s for samples annealed in (N_2+H_2) above 600 ℃ reduces to about 1/5 in comparison with that for samples annealed in N_2.

Figure 2 shows the annealing temperature dependences of σ at room temperature for samples annealed in N_2 and (N_2+H_2), respectively. These samples were annealed in three months after fabrication of samples, and the conductivity measurements were carried out immediately after annealing. As seen in this figure, the annealing behaviors of σ are similar to those of N_s shown in Fig. 1. Therefore, it is expected that the correlation between N_s and σ exists.

The samples annealed in (N_2+H_2) shown in Fig. 2 were preserved in air for eight months after annealing, then σ at room temperature was measured again. The results are shown by

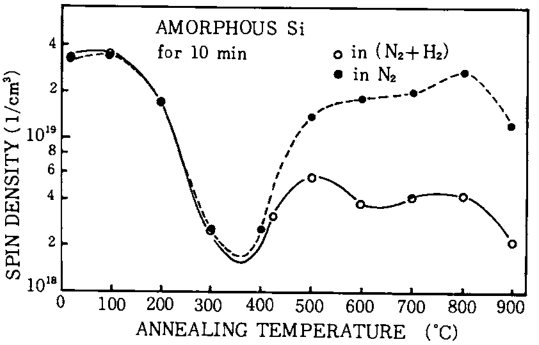

Fig. 1. Annealing temperature dependences of spin density for samples annealed in N_2 and (N_2+H_2) gas, respectively. These annealing behaviors were measured immediately after annealing.

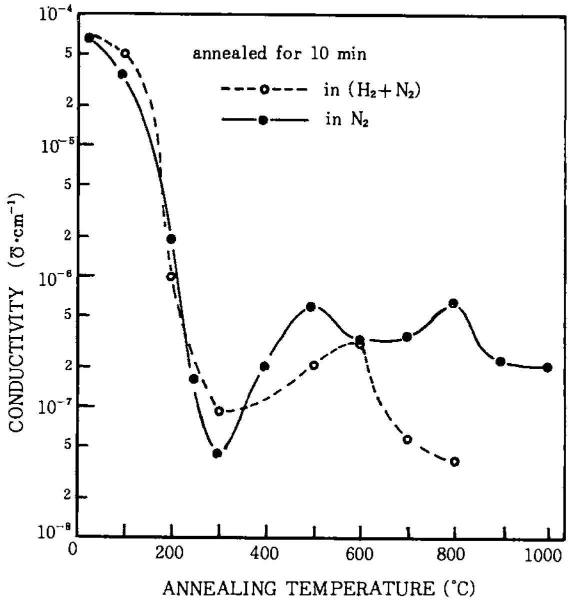

Fig. 2. Annealing temperature dependences of electrical conductivity measured at room temperature for samples annealed in N_2 and (N_2+H_2) gas, respectively. These annealing behaviors were measured immediately after annealing.

open circles in Fig. 3. In Fig. 3, the annealing temperature dependence of σ for samples annealed in (N_2+H_2) shown in Fig. 2 is shown by closed circles for comparison. As shown in Fig. 3, the difference between these two curves distinctly appears at annealing temperature above 300 °C. The origin is not clear at present. On the other hand, the secular change of σ for samples annealed in N_2 is shown in Fig. 4, and a degree of the change is slight in comparison with that for samples annealed in (N_2+H_2) as revealed from Figs. 3 and 4.

As for N_s in samples annealed in N_2, the secular change after annealing was also slight. However, for the samples preserved in air without annealing after fabrication of samples, the following secular change of N_s was observed: The increase of N_s with annealing above 400 °C seen in the samples preserved for three months could not be seen in those preserved for seven months as shown in Fig. 5. On the other hand, the secular change of N_s for samples annealed in (N_2+H_2) is not clear because of insufficient experimental data.

In measurement temperature dependence of σ for samples preserved in air for eight months after annealing at 600 °C in (N_2+H_2) shown in Fig. 3, the thermal history was observed in spite of lower measurement temperature than the annealing temperature 600 °C in the sample. The results are shown in Fig. 6. This conductivity measurement was carried out below about 430 K in flowing N_2 gas. After the third measurement shown by the sign x, the temperature dependence of σ was reversible. After the third measurement shown in Fig. 6, Au

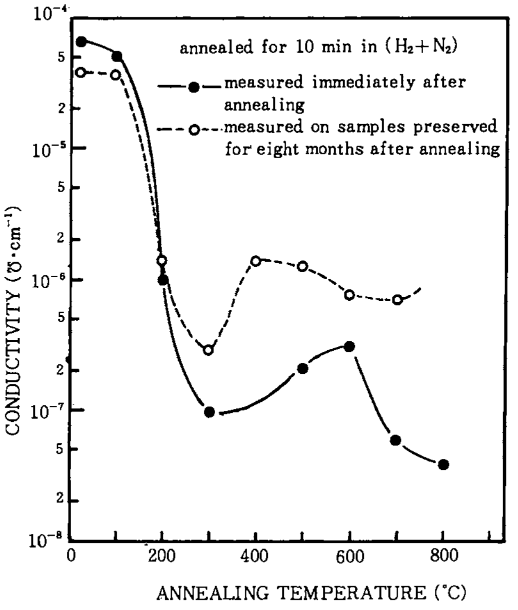

Fig. 3. Annealing temperature dependences of electrical conductivity measured at room temperature for samples preserved for eight months after annealing in (N_2+H_2) gas.

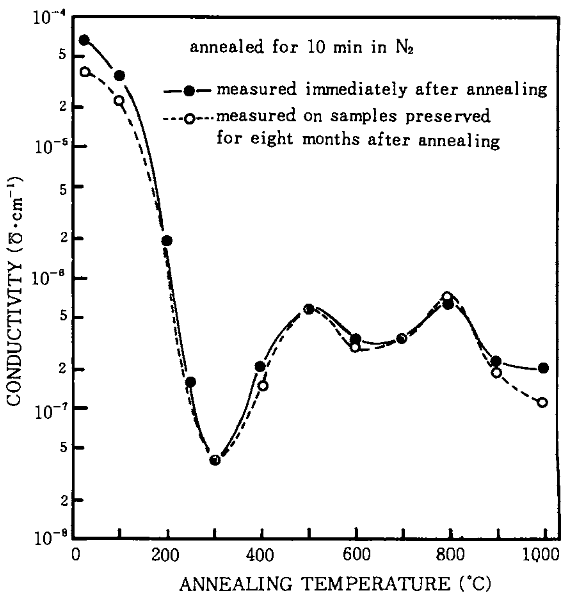

Fig. 4. Annealing temperature dependences of electrical conductivity measured at room temperature for samples preserved for eight months after annealing in N_2 gas.

electrodes were scraped off from the sample and the ESR was measured. As a result, N_s is found to be reduced to about 1/2 of the value of N_s measured immediately after annealing shown in Fig. 1. However, for the samples annealed in N_2, the thermal history as stated above was not observed.

4. Discussion and Summary

From the annealing behaviors of the dc conductivity and ESR signals, we previously proposed the following possible model for the annealing process on dangling bonds in a-Si[7]: The number of dangling bonds diminishes monotonously with annealing up to 300~400 ℃, and a continuous random network with much lower spin density should be formed by annealing at 300~400 ℃. The increase of N_s with annealing above 400 ℃ should be due to the production of dangling bonds around crystallites in the process of crystalization. The production of such a dangling bond with annealing has been also suggested from the investigation on ESR and σ for a-$Si_{57}Ge_{43}$ films.[9]

The following results obtained in the present investigation are considered to be consistent with the above-mentioned model. N_s in samples annealed in (N_2+H_2) above 400 ℃ is considerably smaller than that in samples annealed in N_2 as seen in Fig. 1. This behavior should be explained by the model that hydrogen diffuses from the surface to the inner part of the sample

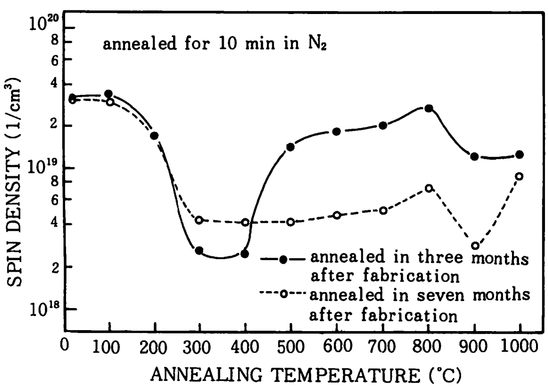

Fig. 5. Annealing temperature dependences of spin density for the sample preserved in air for seven months without annealing after fabrication of the sample (open circles). The spin density for the sample annealed in N_2 gas shown in Fig. 1 is shown by closed circles for comparison. These annealing behaviors were measured immediately after annealing.

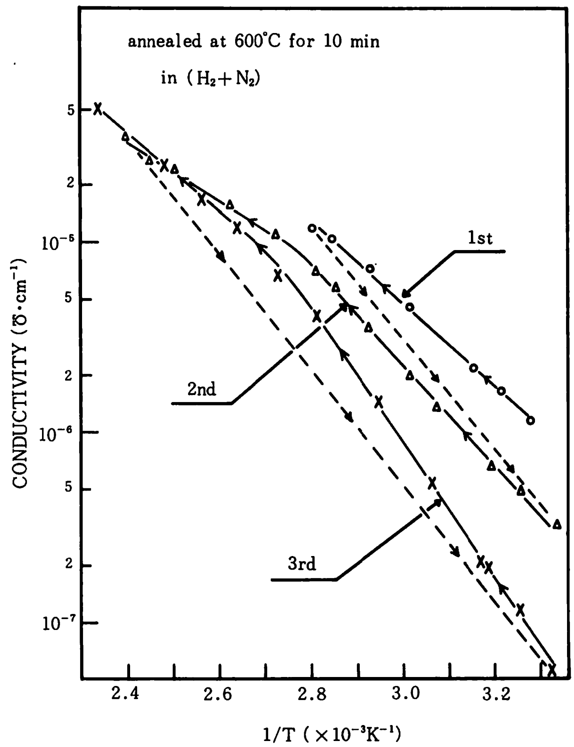

Fig. 6. Measurement temperature dependence of electrical conductivity for the sample preserved in air for eight months after annealing at 600 °C in (N_2+H_2) gas shown in Fig. 3.

during annealing, and the dangling bonds responsible for ESR around crystallites are easily wiped out. This model is also supported by the behaviors of the spin-lattice and spin-spin relaxation times obtained from saturation of the ESR signal.[10]

The similarity between both behaviors of N_s and σ as shown in Figs. 1 and 2 should suggest that dangling bonds responsible for ESR are also responsible for the electrical conduction.

When the samples preserved for eight months after annealing in (N_2+H_2) were again annealed at about 150 °C, even the samples annealed at a higher temperature than 200 °C eight months before, N_s in the samples became considerably smaller than those in the original samples (see Figs. 1 and 6). This decrease may be explained by the model that hydrogen atoms kept in the sample without combination with dangling bonds migrate to wipe out dangling bonds.

As shown in Fig. 5, the annealing behavior of N_s above 400 °C is found to depend on the time elapsed after fabrication of the sample. From this results, the following speculation is derived. When the sample was preserved for a long time after fabrication, the surface of the sample should be contaminated by impurities, *e.g.* oxygen. By annealing the sample above 400 ℃, the impurities stuck on the surface might diffuse to the inner part of the sample, and become to wipe out dangling bonds around crystallites.

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