Digest of Tech. Papers The 14th Conf. (1982 International) on Solid State Devices, Tokyo

C — 5 — 2 Photo-Conductive, Low Impurity-Diffusive, Heat-Resisting a-Si Formed by Glow-Discharged Decomposition of SiF_2 and H_2 Mixture

Hideki MATSUMURA and Seijiro FURUKAWA

Dept. of Applied Electronics, Tokyo Institute of Technology,
Nagatsuda, Midori-ku, Yokohama 227, Japan

A new type of hydro-fluorinated a-Si (a-Si:F:H) is formed by glow-discharged decomposition of SiF_2 and H_2 gas mixture. SiF_2 is intermediate active gas, and is produced from SiF_4 gas and solid Si by the reaction; $SiF_4+Si \rightarrow 2SiF_2$. This paper is to show that this new a-Si:F:H is photo-conductive as highly as the conventional hydrogenated a-Si (a-Si:H) even for the sample formed at relatively high deposition rate and it is heat-resistant up to the temperature more than at least 500 °C for annealing in vacuum. This is also to show that impurity-diffusion constant in this film is smaller than that in a-Si:H by several orders of magnitude.

The film deposition system is schematically shown in Fig.1. SiF_4 gas is flowed through solid Si pieces heated at 1150 °C, and 50 to 90 % of SiF_4 gas is chemically converted to SiF_2. The SiF_2 gas is immediately mixed with H_2 and introduced into a glass tube for plasma deposition. The flow-rate of SiF_4 was kept at 10 sccm, that is, the net flow-rate of SiF_2 was 10 sccm or more. The flow-rate of H_2 was variated from 0 to 150 sccm. The gas pressure P_g during deposition was 0.1 Torr and the rf power 25 to 30 W. The substrate temperature T_s was variated from 250 to 550 °C, but mainly kept at 500 °C.

One of advantages to use SiF_2 gas as a F source is that the a-Si:F:H can be grown under any plasma conditions, although the condition for deposition by SiF_4 and H_2 mixture appears limited. The film growth rate was monotonically increased with increase of H_2 flow-rate and reached to the values from 5 to 10 Å/sec for H_2 flow-rate more than 100 sccm. The photo-conductivity $\Delta\sigma_p$ was also increased with increase of H_2 flow-rate and reached to 10^{-6} or 10^{-5} $(\Omega\,cm)^{-1}$ for the exposure of 1 mW/cm^2 He-Ne laser, as shown in Fig.2. The photo-sensitivity, a ratio of $\Delta\sigma_p$ to dark-conductivity σ_d, approached to 10^4 under the same light. This means that the a-Si:F:H is photo-conductive as highly as the conventional a-Si:H in spite of relatively high deposition rate.

According to nuclear reaction and Rutherford backscattering experiment, F content was almost constant and about 5 atomic % but H content was increased with increase of H_2 flow-rate. For instance, it was about 7 atomic % for the sample deposited at T_s=500 °C and at H_2 flow-rate of 120 sccm. The H content is not so low. However, as shown in Fig.3, no degradation of $\Delta\sigma_p$ and photo-sensitivity was observed even after annealing in vacuum at the temperature over 500 °C for the sample of T_s=500 °C.

Finally, the diffusivity of Sb in our film was studied from the change of Sb profile due to annealing, because the impurity diffusion was considered to be one of key factors to decide the life time of a-Si devices. The Sb profile was observed by the Rutherford backscattering method. Figure 4 shows the Sb profiles in both a-Si:H and our a-Si:F:H, and also shows their change after annealing at 400 °C for 5 hours in dry N_2. It is apparently found that the diffusivity of Sb in our film is lower than that in a-Si:H. The diffusion constant of Sb in the a-Si:F:H was estimated smaller than that in a-Si:H by several orders of magnitude.

In conclusion, so far, the following are obtained; 1) a-Si:F:H produced from SiF_2 and H_2 gas mixture is photo-conductive as highly as a-Si:H, in spite of relatively high deposition rate, 2) it is heat-resistant up to the temperature more than 500 °C at least for annealing in vacuum and for the sample deposited at T_s=500 °C, and 3) impurity-diffusion constant in this a-Si:F:H appears to be smaller than that in a-Si:H by several orders of magnitude.

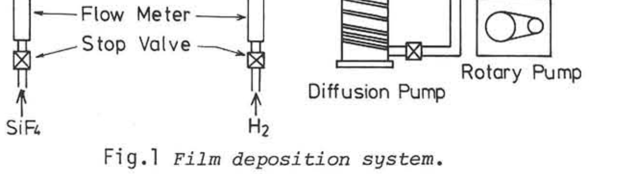

Fig.1 *Film deposition system.*

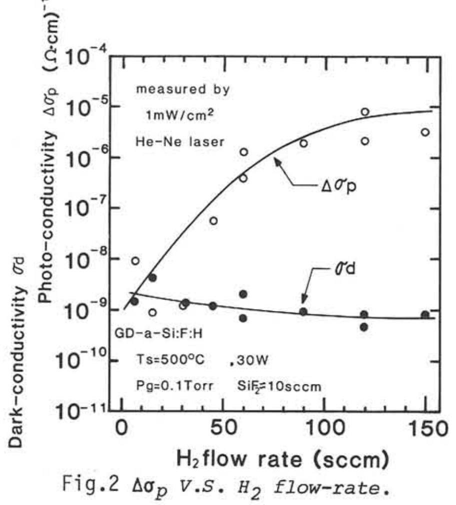

Fig.2 $\Delta\sigma_p$ *V.S.* H_2 *flow-rate.*

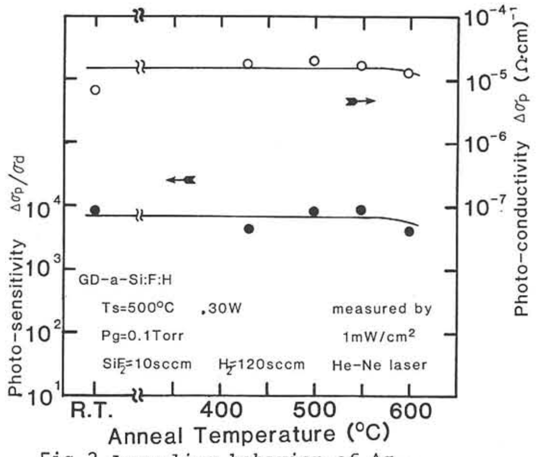

Fig.3 *Annealing behavior of* $\Delta\sigma_p$.

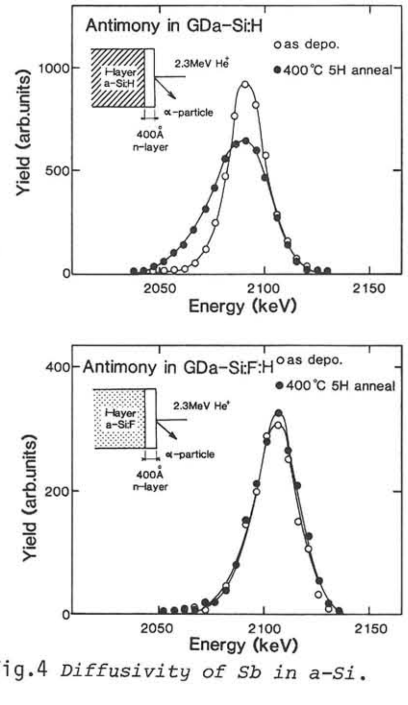

Fig.4 *Diffusivity of Sb in a-Si.*