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Properties of Amorphous Silicon Prepared by Using Intermediate Species SiF_2 and H_2 Gas Mixture

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A new type of amorphous silicon (a-Si) is prepared by using gas mixture of H_2 and intermediate species SiF_2, instead of using conventional SiH_4 or SiF_4 gas. It is found that the impurity-doping efficiency of this new a-Si is equal to that of the conventional hydrogenated a-Si (a-Si:H), but its optical band gap hardly changes after doping of boron while that of a-Si:H decreases, and that the Staebler-Wronski effect is only weakly observable in this new a-Si.

§1. Introduction

Among the various methods for the preparation of amorphous silicon (a-Si), the method using intermediate-state active species such as SiH_2 or SiF_2 appears attractive for efficient formation of atomic net-work of a-Si. And in these intermediate species, SiF_2 appears a only species whose life time is long enough to be transported to the area of film deposition.

Therefore, we have tried to produce a new type of hydro-fluorinated a-Si (a-Si:F:H) by the glow-discharge decomposition of H_2 and SiF_2 gas mixture. And we have already reported that, a) by using SiF_2, the deposition rate of a-Si films can be increased up to at least 20 Å/sec[1)], b) this film is heat-resistant[2)], and that, c) diffusivity of impurities in this film is much smaller than that in the conventional hydrogenated a-Si (a-Si:H)[3,4)].

However, it has been said that there is an ambiguity in the electrical properties of boron-doped a-Si:F:H when it is produced from SiF_4 and H_2 mixture[5)]. And there have been few systematic studies on the Staebler-Wronski effect for a-Si:F:H. Thus, we tried to study on further additional properties such as impurity-doping properties, optical properties after doping, and the Staebler Wronski effect for our new a-Si:F:H produced from SiF_2.

It is found that, 1) the boron- or phosphorus - doping efficiency of this new a-Si:F:H is equal to that of the conventional a-Si:H, however, that, 2) the optical band gap of this a-Si:F:H hardly changes after doping of boron while that of a-Si:H decreases. It is also found that, 3) this a-Si:F:H is stable for light soak and the Staebler-Wronski effect is only weakly observable in this new film.

§2. Fundamentals for Experiment

The apparatus for the preparation of this new type of a-Si:F:H is schematically illustrated in Fig.1. SiF_4 gas is introduced into a quartz tube through a mass flow controller (M.F.C.). The

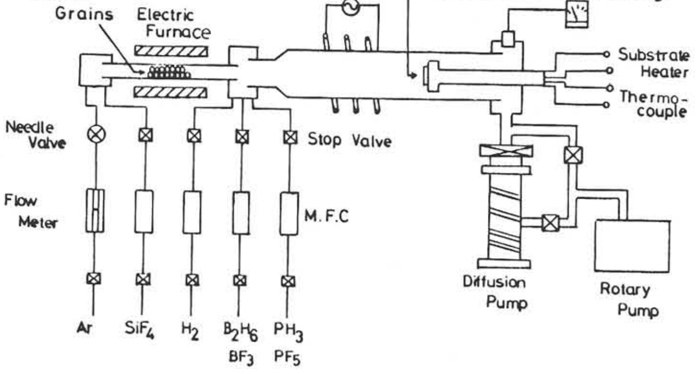

Fig.1 Schematic diagram of a-Si:F:H film deposition apparatus.

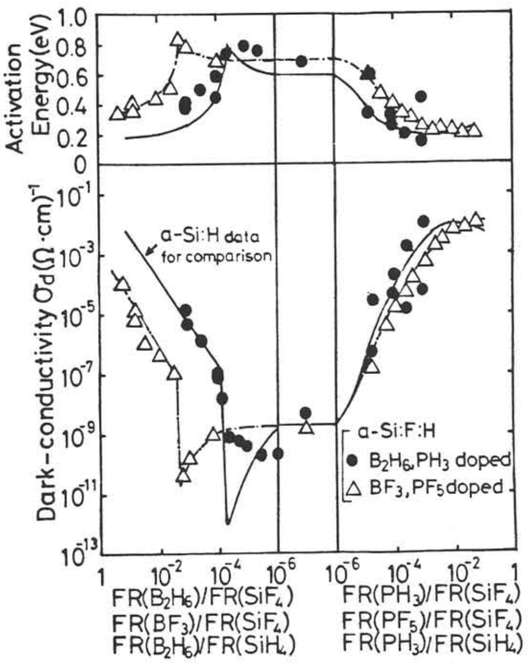

Fig.2 Dark conductivity and its activation energy for boron- or phosphorus - doped a-Si:F:H and a-Si:H.

diameter of a quartz tube is about 3.5 cm$^\phi$ and solid Si pieces of 60 g to 100 g in total weight are packed in the tube. The tube is heated at temperatures of 1150 °C to 1200 °C by an electric furnace. The SiF_4 gas is converted there to SiF_2 by following the chemical reaction; $SiF_4 + Si \longrightarrow 2\ SiF_2$ 6). The SiF_2 is mixed with H_2 and doping gases, and the mixture gas is immediately introduced into a RF-plasma deposition tube.

The temperature of substrate holder T_s was kept at 450 °C to 500 °C, the gas pressure during deposition P_g at 10 Pa to 13 Pa and the power density of RF-plasma P.D. at 0.6 W/cm^2 to 1.7 W/cm^2. FR(SiF_4) at input was kept at 50 sccm and FR(H_2) was varied from 25 sccm to 100 sccm, where the notation FR(X) refers to the flow rate of gas X.

§3.Impurity Doping Properties

B_2H_6, BF_3, PH_3 and PF_5 gases were used as doping gases of boron and phosphorus. BF_3 and PF_5 gases were particularly chosen as the gases safer than B_2H_6 and PH_3. The conductivity in dark σ_d and its activation energy were measured for the impurity doped samples.

The results are shown in Fig.2 as functions of the ratio between the flow rate of various doping gases and the flow rate of SiF_4. The similar doping properties of a-Si:H produced from SiH_4 gas are also shown by a solid curve for comparison, as functions of FR(B_2H_6)/FR(SiH_4) and FR(PH_3)/FR(SiH_4)7). It is clearly demonstrated that the efficiency of both boron- and phosphorus-doping for this new a-Si:F:H is equal to that for a-Si:H when B_2H_6 and PH_3 gases are used. Although the doping efficiency drops when BF_3 gas is used, this appears to be simply caused by larger bonding energy of B-F bonds than B-H bonds. From this figure, it is concluded that the conductivity of a-Si:F:H can be controlled even by using safer gases such as BF_3 or PF_5.

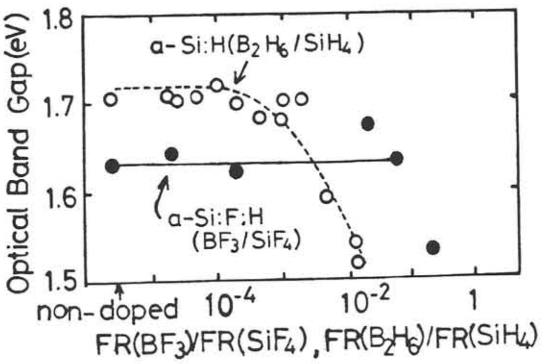

Fig.3 Optical band gap of boron-doped a-Si:F:H and a-Si:H.

It is well-known that the optical band gap of a-Si:H tends to decrease by the dope of boron8), and that this decrease of optical band gap causes to lower the efficiency of p-i-n type a-Si solar cells. Therefore, next, we checked the values of optical band gap of our a-Si:F:H films after boron doping. The results are shown in Fig.3, together with the similar results for a-Si:H8). The figure demonstrates that the optical band gap of a-Si:F:H itself is smaller than that of a-Si:H, but that, it is almost kept constant for the increase of dope of boron while that of a-Si:H tends to decrease.

One may say that our film has large amount of defects and thus the optical band gap is insensitive for the increase of boron-dope. However, the gradient of $\sqrt{\alpha h\nu}$ v.s. $h\nu$ plots is almost equal to that of a-Si:H as shown in Fig.4. Where, $h\nu$ and α refer to photon energy and absorption coefficient

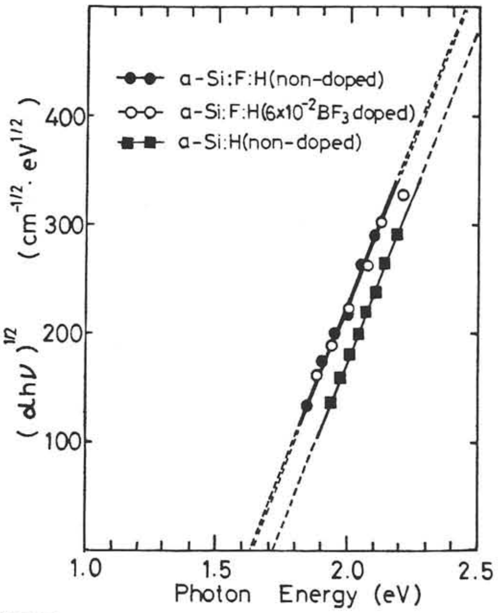

Fig.4 $\sqrt{\alpha h\nu}$ v.s. hν plots for non-doped a-Si:H, non-doped a-Si:F:H and boron-doped a-Si:F:H produced at $FR(BF_3)/FR(SiF_4)=0.06$.

of a-Si films, and the gradient of plots is believed to be related with the quality of a-Si films。Both insensitivity of optical band gap for boron doping and smaller value of optical band gap than that of a-Si:H appear to be substantial in our a-Si:F:H films.

§4.The Staebler-Wronski Effect

Finally, the Stabler-Wronski effect$^{9)}$ of our a-Si:F:H was investigated. The samples were soaked in AM-1 light of 150 mW/cm^2, and the change of conductivity by the illumination was observed. A result is shown in Fig.5 as a function of illumination times. The similar result for a-Si:H is also shown for comparison. From this figure it is clear that the change of conductivity during light soak for a-Si:F:H is smaller than that for a-Si:H although the photo-conductivity of a-Si:F:H itself is larger than that of a-Si:H. It is also found that the magnitude of the Staebler-Wronski effect, defined as σ_{dB}/σ_{dA}, is apparently much smaller for our a-Si:F:H than that for a-Si:H. Here, σ_{dA} and σ_{dB} refer to the dark conductivity before and after light soak respectively. That is, it can be said that our a-Si:F:H is much stabler than a-Si:H for illumination of light.

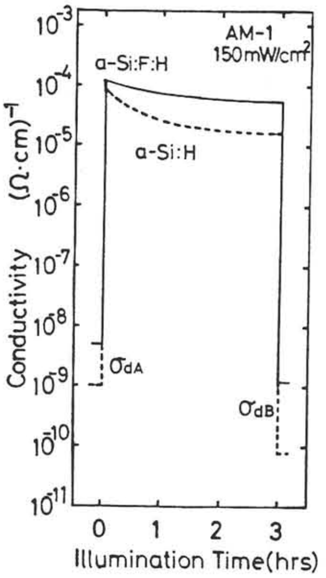

Fig.5 Change of conductivity by illumination of AM-1 light of 150 mW/cm^2, for our a-Si:F:H and a-Si:H.

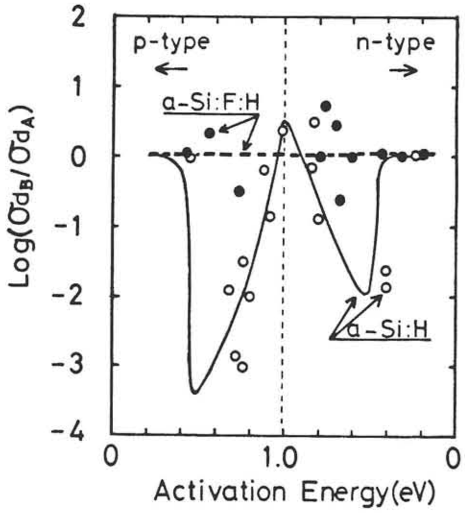

Fig.6 Magnitude of the Staebler-Wronski effect, defined as σ_{dB}/σ_{dA} in Fig.5, as a function of Fermi level position.

The reason why the Staebler-Wronski effect is observed only weakly for our a-Si:F:H is not clear. According to our recent experiment, it appears to be getting larger even for a-Si:F:H when the hydrogen content increases, even if the photo-conductivity itself is kept constant$^{10)}$. The hydrogen content can be controlled at the value as low as several atomic % by the present method. This low hydrogen content in our a-Si:F:H is a very possible reason for weak Staebler-Wronski effect.

It is known that the magnitude of the Staebler Wronski effect is related with the position of Fermi level$^{11)}$. Thus, we measured $\log(\sigma_{dB}/\sigma_{dA})$ for the various impurity-doped a-Si:F:H samples. The results are shown in Fig.6 together with the similar results summarized in Ref. (11) for a-Si:H. For a-Si:H the magnitude of the Staebler-Wronski effect varies widely by the shift of Fermi level position, but for our a-Si:F:H it is kept roughly constant. This shows that the Staebler-Wronski effect is always small in our a-Si:F:H.

§5.Conclusions

From the above experiment, the following are concluded;

1) The impurity doping efficiency of new a-Si:F:H produced from SiF_2 and H_2 mixture is almost equal to that of a-Si:H produced from SiH_4.

2) However, although the optical band gap of a-Si:H tends to decrease by doping of boron, that of this a-Si:F:H hardly changes.

3) This a-Si:F:H is much stabler for light soak than a-Si:H, and the Staebler-Wronski effect is only weakly observable in this new film.

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