Properties of Amorphous Silicon Prepared by Using Intermediate Species SiF$_2$ and H$_2$ Gas Mixture

Hideki Matsumura, Takashi Uesugi and Hisanori Ibara

Department of Physical Electronics, Hiroshima University, Saijo, Hiroshima 724, Japan

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$_4$ or SiF$_4$ appears attractive for efficient formation of atomic network of a-Si. And in these intermediate species, SiF$_2$ appears as only species whose lifetime 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 A/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...
diameter of a quartz tube is about 3.5 cm 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 SiF₄ gas is converted there to SiF₂ by following the chemical reaction; SiF₄ + Si → 2 SiF₂. The SiF₂ is mixed with H₂ and doping gases, and the mixture gas is introduced into a RF-plasma deposition tube.

The temperature of substrate holder T₃ was kept at 450 °C to 500 °C, the gas pressure during deposition P₆ at 10 Pa to 13 Pa and the power density of RF-plasma P.D. at 0.6 W/cm² to 1.7 W/cm². FR(SiF₄) at input was kept at 50 sccm and FR(H₂) 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

B₂H₆, BF₃, PH₃ and PF₅ gases were used as doping gases of boron and phosphorus. BF₃ and PF₅ gases were particularly chosen as the gases safer than B₂H₆ and PH₃. The conductivity in dark σd 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 SiF₄. The

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

similar doping properties of a-Si:H produced from SiH₄ gas are also shown by a solid curve for comparison, as functions of FR(B₂H₆)/FR(SiF₄) and FR(PH₃)/FR(SiF₄)¹. 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 B₂H₆ and PH₃ gases are used. Although the doping efficiency drops when BF₃ 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 BF₃ or PF₅.

It is well-known that the optical band gap of a-Si:H tends to decrease by the dope of boron², and 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:H. 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 √αhv v.s. hv plots is almost equal to that of a-Si:H as shown in Fig.4. Where, hv and α refer to photon energy and absorption coefficient.
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.

### The Staebler-Wronski Effect

Finally, the Staebler-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 \(\sigma_{DB}/\sigma_{DA}\), is apparently much smaller for our a-Si:F:H than that for a-Si:H. Here, \(\sigma_{DA}\) and \(\sigma_{DB}\) 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.

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

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**Fig.4** \(\sqrt{ahv}\) v.s. hv plots for non-doped a-Si:H, non-doped a-Si:F:H and boron-doped a-Si:F:H produced at \(P_n(SiF)_{15}/P_n(SiF_2)_{20}=0.06\).

**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 \(\sigma_{DB}/\sigma_{DA}\) in Fig.5, as a function of Fermi level position.
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 SiF₂ and H₂ mixture is almost equal to that of a-Si:H produced from SiH₄.
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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