Extended Abstracts of the 17th Conference on Solid State Devices and Materials, Tokyo, 1985, pp. 99-102

C-1-1

A New Thermal CVD Method to Prepare High Quality Amorphous Silicon

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A new thermal CVD (Chemical Vapor Deposition) method to prepare high quality amorphous silicon (a-Si) is presented. In the method, intermediate state species SiF_2 and hydrogen which is decomposed thermally by the catalytic reaction are used as material gases. It is found that the photo-sensitivity of the CVD a-Si film exceeds over 10^6 for AM-1 of 100 mW/cm^2, and that the spin density is 1.5×10^{16} cm^{-3} or less for the film deposited at 320 ℃ with a rate of several Å/sec.

1. Introduction

a-Si films have been mainly produced by the glow discharge decomposition of material gases such as SiH_4 or SiF_4 and H_2 gas mixture. However, it is pointed out that the improvement of characteristics of a-Si devices appears limited by the plasma damage due to glow discharge. Therefore, there have been several trials to produce a-Si films without using plasma, and there are successful reports on photo-CVD method[1]. However, if a high quality a-Si films can be produced by a simple thermal CVD method it would be most attractive, since it does not have to worry about light sources for photo-CVD or electrodes for plasma-CVD and thus the deposition apparatus becomes simple, and additionally, since the deposition of a-Si itself will be more stabilized.

Therefore, here, we propose a new thermal CVD method to deposit a-Si, in which intermediate species SiF_2 and thermally decomposed hydrogen are used as the material sources instead of using the conventional SiH_4. SiF_2 is almost only one intermediate species which has a life time long enough to be transported, and hydrogen H_2 is decomposed by the catalytic reaction between H_2 gas and a heated tungsten filament. It is found that highly photo-sensitive a-Si films with low spin density can be obtained by this new thermal CVD method.

2. Preparation of a-Si Films

The deposition apparatus of this new thermal CVD method is schematically illustrated in Fig.1. Solid silicon pieces are packed inside a quartz tube with a diameter of about 15 mm and are heated at about 1150 ℃ by a furnace 1 in the figure. SiF_2 is produced from both SiF_4 gas and silicon pieces, by following the chemical reaction; SiF_4 + Si $\rightarrow$ 2 SiF_2 [2]. The conversion rate from SiF_4 to SiF_2 increases as the furnace temperature Tf increases, and it is believed that about 60 % of SiF_4 is converted to SiF_2 at Tf=1150 °C[3].

SiF_2 is immediately introduced into a deposition quartz tube. H_2 gas is also introduced into the deposition tube and decomposed into atomic hydrogen by the catalytic chemical reaction bewteen H_2 gas and a heated tungsten filament-heater. The filament is placed in the flow of H_2 gas and the distance between the filament and a substrate is about 5 cm. The thermo-couple, packed inside a closed quartz tube, is put just above the substrate. The elevation of temperature due to the thermal radiation from the filament is about 150 ℃ at the position of samples, when it is measured under the flow of deposition gas, a furnace 2 is at room temperature and also when the filament is heated at about 2500 °C. However, we believe that the measurement of the substrate temperature itself is quite accurate, because the a-Si films are always deposited after the temperature reaches

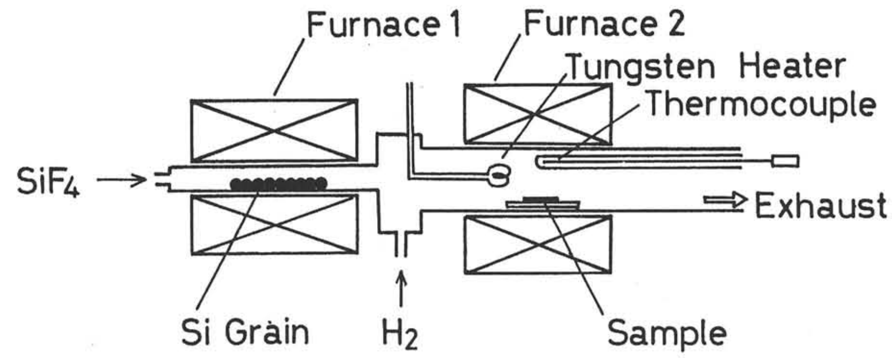

Fig.1 Schematic diagram of deposition apparatus for our thermal CVD method.

at a certain saturated value under the flow of Ar gas.

The flow rates of input SiF_4 and H_2 were fixed at 150 sccm and 50 sccm respectively and the gas pressure during deposition Pg was also fixed at about 500 Pa. Figure 2 shows the deposition rate of a-Si films, the photo-conductivity $\Delta\sigma_p$ and the photo-sensitivity $\Delta\sigma_p/\sigma_d$ as a function of the substrate temperature Ts. In this case, the current of tungsten filament heater Iw was kept at 8 A. In the present work, the photo-conductivity is defined as the difference between the conductivity under the illumination of AM-1 of 100 mW/cm^2 and the conductivity in dark σ_d. Although the deposition rate is likely to increase as the substrate temperature increases, the photo-sensitivity decreases remarkably over Ts=400 °C. Thus, here, Ts was maily fixed at 320 °C.

3.Properties of Deposited a-Si Films

As the current of heater Iw increases, the deposition rate is likely to increase monotonously. For instance, it is about a few Å/sec for Iw=6 A, but it increases up to 47 Å/sec for Iw=13 A.

Figure 3 shows the infrared absorption spectra for the samples deposited at both Iw=6 A and Iw=8 A. At first, it is confirmed that fluorine and hydrogen atoms can be incorporated in a-Si films produced by the new thermal CVD method. And it is also found that the content of fluorine or hydrogen is a function of Iw. For instance, the hydrogen content is about a few atomic % for the sample of Iw=6 A but increases to several atomic % for Iw=8 A.

The photo-conductivity, the dark-conductivity and also the photo-sensitivity of the a-Si films are shown in Fig.4 as a function of Iw. In the figure, it is demonstrated that the photo-sensitivity exceeds over 10^6 for the sample of Iw

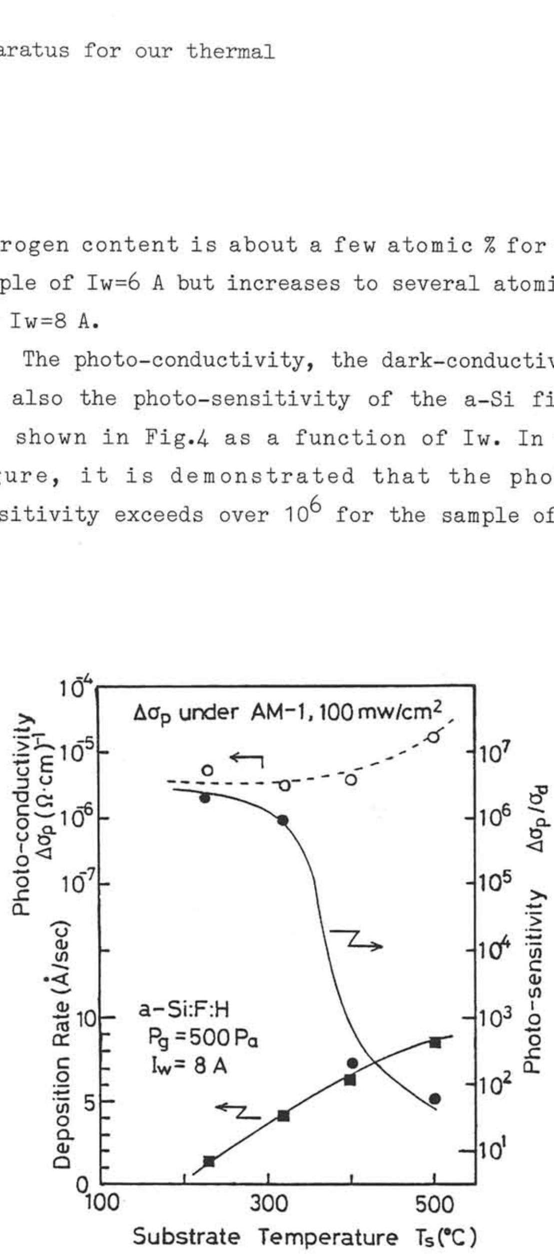

Fig.2 Deposition rate and photo-conductive properties of thermal CVD a-Si films as a function of substrate temperature.

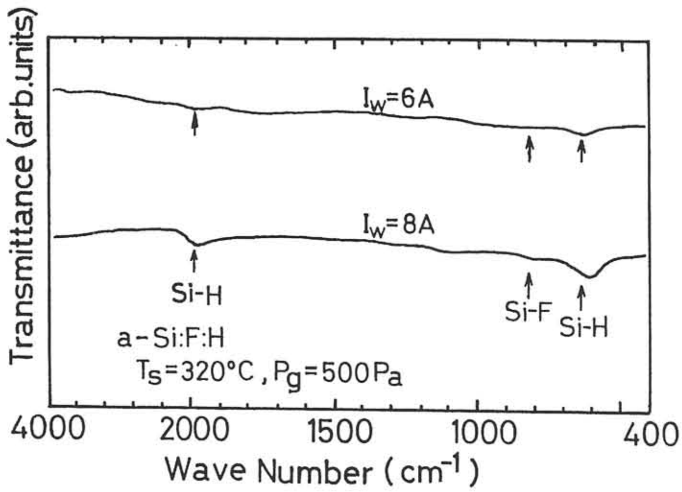

Fig.3 Infrared absorption spectra of thermal CVD a-Si films deposited at heater-current I_w=6 A and I_w=8 A.

less than 8 A, and that it is likely to decrease as Iw increases. Since the photo-sensitivity of the conventional glow discharge a-Si films is usually 10^4 to 10^5, it may be said from this figure that a highly photo-sensitive a-Si films can be produced by our CVD method.

The reason why the photo-sensitivity degrades as the heater-current increases is not clear. According to our Rutherford backscattering measurement, tungsten atoms are likely to be undesirably incorporated as the current increases. For instance, the tungsten content in the a-Si film of Iw=8 A is less than 9 ppm which is a detectable limit of our measurements, however, it increases up to 200 ppm for the film of Iw=13 A. Probably, this tungsten incorporation is the most possible reason for the degradation.

Finally, we also evaluated the spin density of our films from the experiment of the electron spin resonance (ESR). The spin density was estimated by comparing ESR signal of the calibration sample, JEOL Weak-Coal, with that of our a-Si of 1.2 mg in weight. As a result, the spin density of our a-Si deposited at Iw=8 A was estimated as 1.5×10^{16} spins/cm^3. The value is not the best one among ever reported, however, the value appears equivalent to that of the high quality glow discharge a-Si films.

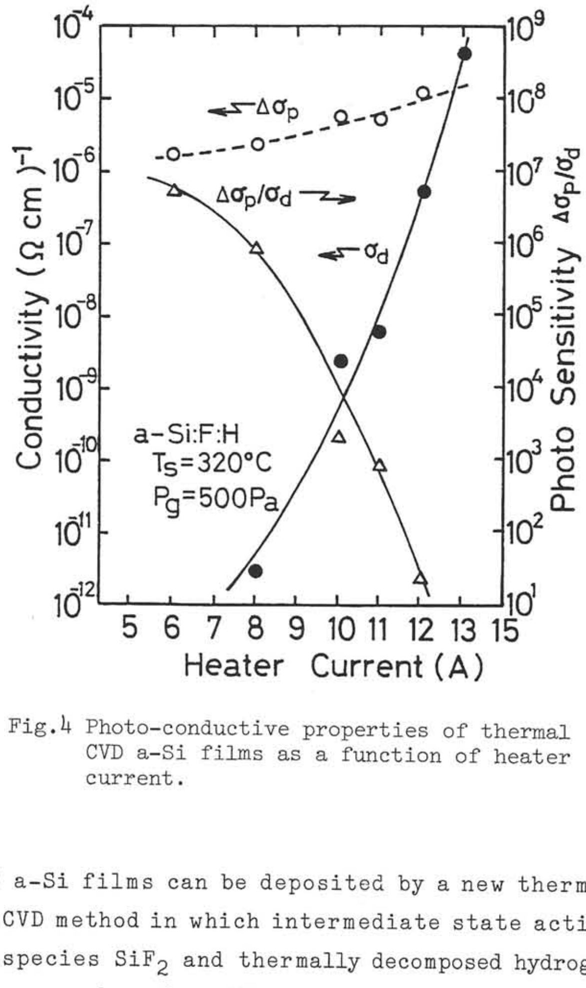

Fig.4 Photo-conductive properties of thermal CVD a-Si films as a function of heater current.

4.Conclusions

From above results, the followings are concluded;

1) a-Si films can be deposited by a new thermal CVD method in which intermediate state active species SiF_2 and thermally decomposed hydrogen are used as deposition gases.
2) This CVD a-Si film is highly photo-sensitive and also its spin density is as low as about 10^{16} cm^{-3} even for the film deposited with a rate of several Å/sec.

[Acknowledgement]

The authors are very much grateful to Prof.

K. Morigaki and Dr. I. Hirabayashi at the Institute for Solid State Physics of Tokyo University for the help of ESR measurements, to Prof. M. Hirose at Hiroshima University for the support of research. This work is supported by the 1984 NHK Hoso-Bunka Foundation and also by the 1985 Grant-in Aid for Scientific Research from the Ministry of Education of Japan.

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