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 SiF₂ 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 10⁶ for AM-1 of 100 mW/cm², and that the spin density is 1.5x10¹⁶ cm⁻² or less for the film deposited at 320 °C with a rate of several cm/sec.

1. Introduction

a-Si films have been mainly produced by the glow discharge decomposition of material gases such as SiH₄ or SiF₄ and H₂ 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. 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 SiF₂ and thermally decomposed hydrogen are used as the material sources instead of using the conventional SiH₄. SiF₂ is almost only one intermediate species which has a life time long enough to be transported, and hydrogen H₂ is decomposed by the catalytic reaction between H₂ 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 °C by a furnace in the figure. SiF₂ is produced from both SiF₄ gas and silicon pieces, by following the chemical reaction; SiF₄ + Si → 2 SiF₂. The conversion rate from SiF₄ to SiF₂ increases as the furnace temperature TF increases, and it is believed that about 60 % of SiF₄ is converted to SiF₂ at TF=1150 °C³.

SiF₂ is immediately introduced into a deposition quartz tube. H₂ gas is also introduced into the deposition tube and decomposed into atomic hydrogen by the catalytic chemical reaction between H₂ gas and a heated tungsten filament-heater. The filament is placed in the flow of H₂ 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 °C 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
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 P$_g$ 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 $T_s$. In this case, the current of tungsten filament heater $I_w$ 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 $\sigma_d$. Although the deposition rate is likely to increase as the substrate temperature increases, the photo-sensitivity decreases remarkably over $T_s$=300 °C. Thus, here, $T_s$ was mainly fixed at 320 °C.

3. Properties of Deposited a-Si Films

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

Figure 3 shows the infrared absorption spectra for the samples deposited at both $I_w$=6 A and $I_w$=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 $I_w$. For instance, the hydrogen content is about a few atomic % for the sample of $I_w$=6 A but increases to several atomic % for $I_w$=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 $I_w$. In the figure, it is demonstrated that the photo-sensitivity exceeds over $10^6$ for the sample of $I_w$.
Fig. 3 Infrared absorption spectra of thermal CVD a-Si films deposited at heater-current $I_w=6\,\text{A}$ and $I_w=8\,\text{A}$.

less than 8 A, and that it is likely to decrease as $I_w$ 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 $I_w=8\,\text{A}$ is less than 9 ppm which is a detectable limit of our measurements, however, it increases up to 200 ppm for the film of $I_w=13\,\text{A}$. 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 $I_w=8\,\text{A}$ was estimated as $1.5 \times 10^{16}$ 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.

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 $\mu$/sec.

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[References]