Chapter 2

Preparation of Amorphous Silicon Alloys by Glow Discharge Plasma CVD Method

2.1 Introduction

The purpose of this work is to develop a visible-light thin film LED (TFLED). Therefore, the interesting amorphous silicon alloys are the materials that have wide optical energy gaps, for example, more than 2.4 eV. It has been widely reported in a large number of literatures that there are several amorphous silicon alloys that satisfy this requirement. Some of them are, for example, hydrogenated amorphous silicon nitride (a-SiN:H) [1-2], hydrogenated amorphous silicon carbide (a-SiC:H) [3-4] and hydrogenated amorphous silicon oxide (a-SiO:H) [5-6]. These materials can be prepared by several methods, such as sputtering, thermal CVD and glow discharge plasma CVD.

It is well known that the glow discharge plasma CVD is the most popular deposition method for the preparation of amorphous silicon alloys [7]. There are several advantage features in the glow discharge plasma CVD method, e.g., easy technology, low temperature process, low cost, possibility of using inexpensive substrates of almost any size or shape, providing good quality of films [8]. The film deposited by the glow discharge plasma CVD method always contain several percentages of hydrogen atoms which act as the terminators of dangling bonds.

In this work, two individual systems of the glow discharge plasma CVD were installed at the Semiconductor Device Research Laboratory (SDRL), Department of Electrical Engineering, Faculty of Engineering, Chulalongkorn University. The first one was for the fabrication of amorphous silicon solar cells [9], while the second one was for the fabrication of amorphous thin film LEDs [10-12]. The result of the fabrication of different devices by different systems is to protect the impurity contaminations. Details of the first CVD system were described in the literatures [13]. In this thesis the details of the second CVD system will be described.

In this chapter the preparation technology of amorphous silicon alloys by the glow discharge plasma CVD method is described.

2.2 Preparation of Amorphous Silicon Alloys by Glow Discharge Plasma CVD System

2.2.1 Structure of Glow Discharge Plasma CVD System

The glow discharge plasma CVD system employed in this work uses the conventional RF power. The system consists of two parts; the first part is the CVD system, and the second part is the gas controlling system. Figure 2.1 shows a schematic diagram of the glow discharge plasma CVD system. The diameter of the RF electrodes is 10 cm. The separation distance of the HV electrode and the ground electrode is approximately 2.5 cm. Table 2.1 shows some details of the glow discharge plasma CVD system. The dilutions of the reaction gases are also shown in the Table 2.1

Table 2.1 Details of the glow discharge plasma CVD system.

Chamber	Diameter 22 cm., Pyrex material
Susceptor	Diameter 10 cm.
Substrate temperature	RT-400° C
Electrode	Capacitive coupling
RF Power	13.56 MHz, maximum 150 watts
Pressure	0.01-10 Torr
Gas Dilution	$SiH_4/H_2 = 10\%$
	$NH_3/H_2 = 10\%$
	$CH_4/H_2 = 10\%$
	$C_2H_4/H_2 = 10\%$
	$CO_2/H_2 = 10\%$
	$B_2H_6/H_2 = 500$ ppm
	$PH_3/H_2 = 500$ ppm

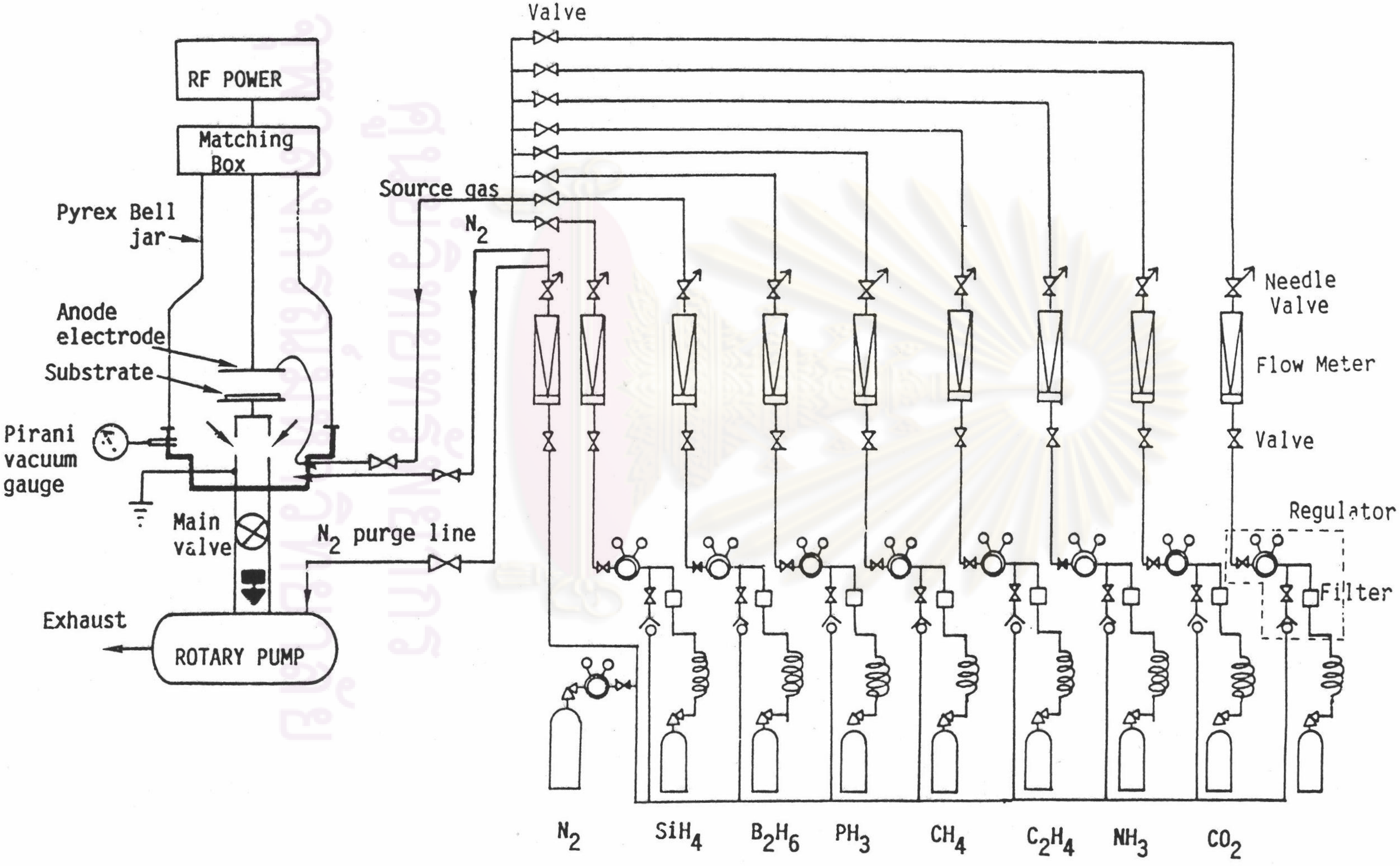

Figure 2.1 Schematic diagram of the glow discharge plasma CVD system.

2.2.2 Substrate Preparation

In this work, a series of study of the basic properties of the amorphous silicon alloys grew by the GD plasma CVD method has been done. In each deposition, various kinds of substrates were put into the CVD system. Table 2.1 summarizes the materials of the substrates and the objectives.

Table 2.1 Materials of substrates and the objectives

Substrate	Objective
Corning glass # 7059 (2 cm x 2 cm x 1 mm)	. Absorption coefficient (α) . Conductivity (σ) . ESCA
Single crystalline silicon wafer with high resistivity (mirror surface) (1 cm x 1 cm x 0.5 mm)	. Infrared absorption coefficient (IR)
Micro slide glass (2 cm x 2 cm x 0.1 mm)	. Spin density (Dangling bond density) measured by Electron spin resonance (ESR)
Glass/ITO (2 cm x 2 cm x 1 mm)	. Thin film light emitting diode

The substrates were cleaned by the process as follows:

- Trichloroethylene	Ultrasound	20 minutes
- Acetone	Ultrasound	20 minutes
- Methylalcohol	Ultrasound	20 minutes

After the cleaning process described above, the oxide layer on the single-crystalline Si wafer was etched by using hydrofluoric acid diluted in water (HF : H_2O = 1:10) about 10 minutes and rinsed with DI water.

2.2.3 Film Deposition

The process of the deposition of amorphous silicon alloy materials by the glow discharge plasma CVD method is shown in Fig. 2.2.

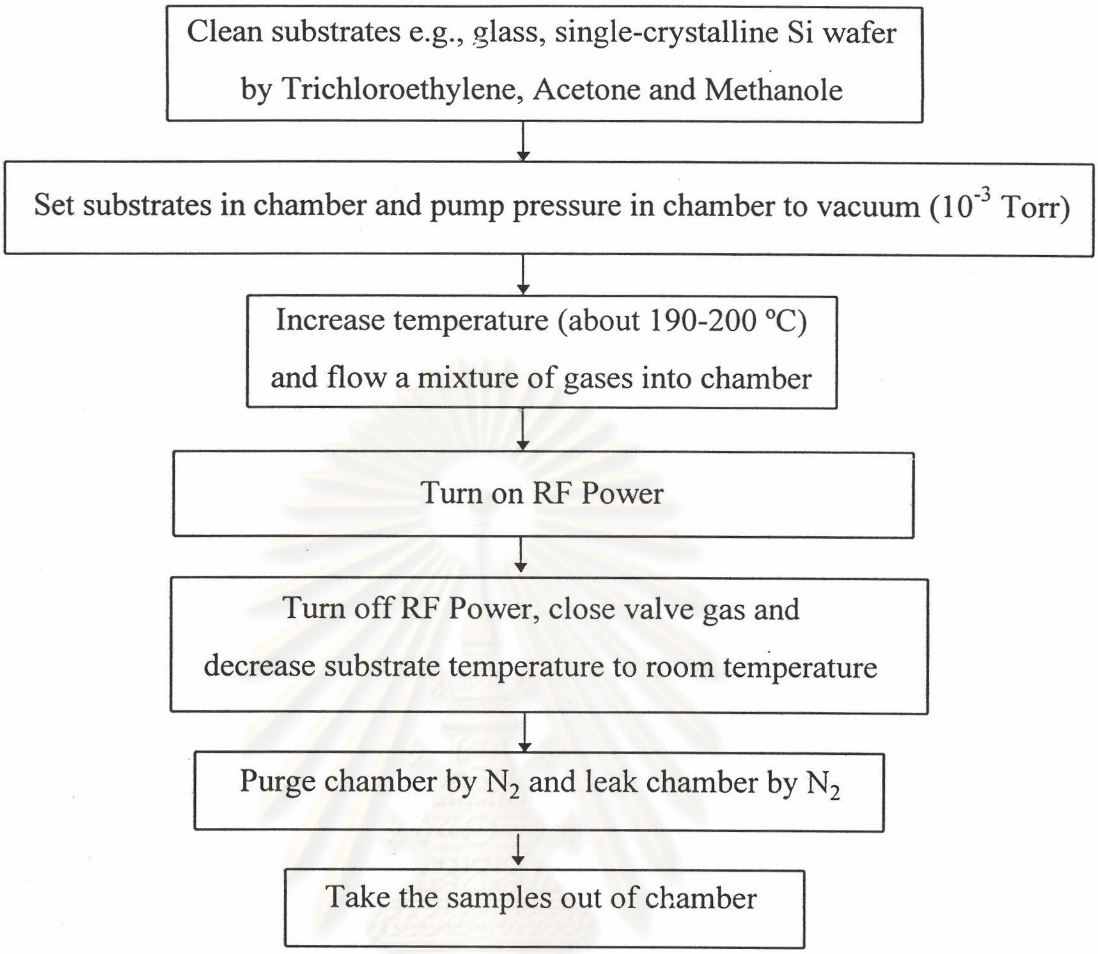

Figure 2.2 Process of the deposition of amorphous silicon alloy materials by the glow discharge plasma CVD method.

The total gas pressure during the deposition was 1 torr and controlled by the main valve. The rf power was 2 - 4 watt. The typical thickness of films for studying basic properties is about 1-2 micron. Table 2.2 summarizes the typical preparation conditions of the amorphous silicon alloys.

Table 2.2 Typical preparation conditions of the amorphous silicon alloys (a-SiN:H, a-SiC:H and a-SiO:H) by glow discharge plasma CVD method

Power Source	C-Coupling, 13.56 MHz
RF Power	2 - 4 Watt
Substrate Temperature	100 -300 °C
Total Gas Pressure	1.0 torr
Total Flow Rate	40 - 100 cc/min
Reaction Gases	
a-SiN:H	$SiH_4 + NH_3$
a-SiC:H	$SiH_4 + CH_4$ (or C_2H_4)
a-SiO:H	$SiH_4 + CO_2$

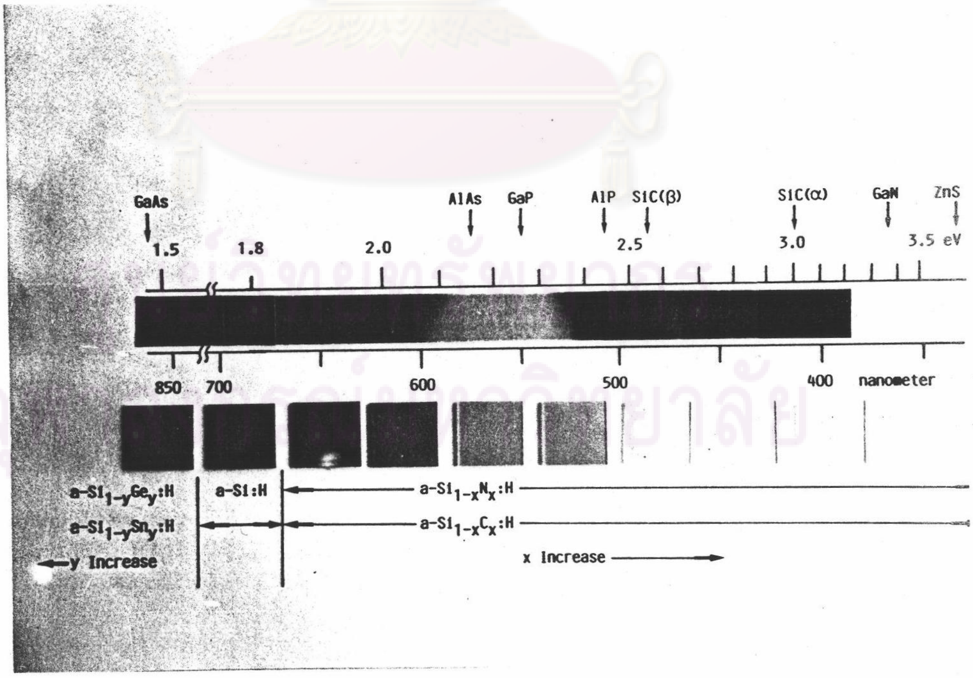

Figure 2.3 Photograph of a-SiN:H films deposited on glass substrates.

Figure 2.3 shows the photographs of some examples of the hydrogenated amorphous silicon nitride (a-SiN:H) prepared from the mixture of SiH_4 and NH_3. The substrates are corning Glass #7059. It can be seen that the color of the film changes from red to yellow, transparent due to the widening of the optical energy gaps, when the ratio of $NH_3/(SiH_4+NH_3)$ increases from left to right.

2.3 Summary

A vertical type RF glow discharge plasma CVD system was installed. The effective diameter of the area of the deposition is about 8 cm. A good uniformity of the thickness can be obtained. The installed system can be used for the deposition of the electronic grades of a-SiN:H, a-SiC:H and a-SiO:H. It will be shown in chapters 3-5 that the visible-light thin film LEDs (TFLEDs) with amorphous silicon alloy p-i-n junctions can be fabricated by the CVD system.

References

1. Jackson, W.A., Searl, T.M., and Austin, I.G. Photoluminescence excitation studies of a-SiN:H alloys. J. Non-Crystalline Solids 77&78 (1985) : 909.
2. Chuan, F.R., Zhou, S.Y., Ming, Y., and Wen-Di, J. Photoluminescence of hydrogenated a-SiN films. J. Non-Crystalline Solids 77&78 (1985) : 913.
3. Hamakawa, Y. and Tawada, Y. Valency control of glow discharge produced a-SiC:H and its aplication to heterojunction solar cell. Int. J. Solar Cells 1 (1982) : 125-144.
4. Engeman, D., Fischer, R., and Kecht, J. Photoluminescence in the amorphous system Si_xC_{1-x}. Appl. Phys. Lett. 32 (1978) : 567.
5. Street, R.A. and Knight, J.C. Luminescent in plasma-deposited Si-O alloys Phil. Mag. B 42 (1980) : 551.
6. Carious, R., Fischer, R., Holzenkampfer, E., and Stuke, J. Photoluminescence in the amorphous system SiO_x. J. Appl. Phys. 52 (1981) : 4241.
7. Anderson, D.A. and Spear, W.E. Electrical and optical properties of amorphous silicon carbide, silicon nitride and germanium carbide prepared by the glow discharge technique. Phil. Mag. 35 (January 1977) : 1-16.
8. Hamakawa, Y. (ed.). Japan annual reviews in electronics, computers and telecommunications.(JARET). Amorphous semiconductor technologies and devices pp. 1-318. Ohm-Sha and North-Holland, Tokyo, Amsterdam, 1984.
9. Kruangam, D., Siamchai, P., Boonkosum, W., and Panyakeow, S. Integrated type a-Si:H solar cells having simple configuration. The 7th International Photovoltaic Science and Engineering Conference (PVSEC-7). Nagoya, Japan. (November 22-26, 1993) : 217-219.
10. Boonkosum, W., Kruangam, D., and Panyakeow, S. Amorphous visible-light thin film light-emitting diode having a-SiN:H as a luminescent layer. Jpn. J. Appl. Physics. 32 (1993) : 1534-1538.

11. Boonkosum, W., DeLong, B., Kruangam, D., and Panyakeow, S. Novel visible amorphous silicon carbide thin film LED. The 1st International Symposium on Laser and Optoelectronics Technology and Applications (ISLOE). Singapore. (November 11-14, 1993) : 300-305.

12. Boonkosum, W., Kruangam, D., Ratvises, B., Sujaridchai, T., and Panyakeow, S. Visible amorphous SiO:H thin film light emitting diode. The 16th International Conference on Amorphous Semiconductors: Science and Technology (ICAS 16) Kobe. Japan. (September 4-8, 1995).

13. Kruangam, D. and Panyakeow, S. Study of hydrogenated amorphous silicon for optoelectronic devices. The 2nd Regional Symposium on Optoelectronics. Jakarta. Indonesia. (November 27-28. 1989) : 11-16.