

# Thin Film Solar Cell based on Microcrystalline Silicon Nanostructure grown in Low Temperature Condition

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## ABSTRACT

In this meeting, we present the recent developments in thin film silicon solar cell research conducted by interdisciplinary efforts at Seoul National University. High quality microcrystalline silicon thin films for solar cell applications are grown by Hot-Wire Chemical Vapor Deposition (HWCVD) in low temperature condition. In an effort to control the crystalline fraction of silicon films, the effect of HCl addition is studied, and it is confirmed by Raman spectra that the increasing amount of HCl results in higher crystalline silicon fraction in the deposited films. Electrical and optical properties of p-type/n-type hydrogenated microcrystalline silicon ( $\mu\text{-Si:H}$ ) films are characterized with various  $\text{B}_2\text{H}_6$  and  $\text{PH}_3$  gas ratios. The best p-type/n-type layer producing operation condition and film properties are determined.

**Keywords:** solar cell, hot-wire chemical vapor deposition, dark conductivity, microcrystalline silicon.

## 1 INTRODUCTION

Microcrystalline silicon ( $\mu\text{-Si:H}$ ) has been studied extensively as a potential material for applications in solar cells, displays and large area electronics because of its advantages over amorphous silicon in the stability under illumination, mobility and optical absorption in the infrared radiation. This material has a complex microstructure and its optical properties have a marked crystalline characteristic: an optical band gap of 1.12 eV like crystalline silicon. This implies the spectral absorption of microcrystalline silicon thin films covers a much larger range than amorphous silicon which possesses an optical band gap between 1.6 and 1.9 eV. Compared to a-Si:H that absorbs light up to 800 nm,  $\mu\text{-Si:H}$  thin films absorb light of a wider spectra range, extending up to 1100 nm wavelength. It also has higher carrier mobility and better stability against light induced degradation.

Among most popular deposition techniques to get  $\mu\text{-Si:H}$  films, HWCVD has several advantages over plasma enhanced chemical vapor deposition (PECVD), such as versatility in deposition of all kinds of silicon layers (a-Si:H,  $\mu\text{-Si:H}$ , poly-Si) with less hydrogen content at low temperature, the absence of ion bombardment during

deposition, high growth rate, efficiency of gas use and suitability for scaling up in large area applications [1, 2]. In an effort to increase the crystalline fraction in the silicon films prepared by HWCVD, we studied the effect of HCl addition in silicon films deposited on a glass substrate.

The p-type microcrystalline silicon film plays an important role in achieving high conversion efficiency in silicon thin film solar cell [3]. For the high conversion efficiency, the p-layer needs to have high conductivity and wide optical band gap. Because of its high conductivity and wide optical band gap, p-type  $\mu\text{-Si:H}$  is considered to be a better alternative than p-type a-SiC:H and a-Si:H [4]. The conductivity of p-type  $\mu\text{-Si:H}$  by HWCVD is higher than that by PECVD. For example, the conductivity for p-type  $\mu\text{-Si:H}$  prepared by PECVD was  $\sim 0.01 \text{ Scm}^{-1}$  [5], whereas the conductivity of p-type  $\mu\text{-Si:H}$  by HWCVD was  $\sim 2.8 \text{ Scm}^{-1}$  [6].

## 2 EXPERIMENTS

The HWCVD system in this experiment consists of a reactor equipped with a load lock and a turbo molecular pump. The reactor wall is cooled by water. The base pressure is  $\sim 5 \times 10^{-6}$  Torr and the working pressure is 0.1 Torr. A helical-shaped filament or three straight tungsten (W) filaments in parallel connection are used as hot wires located above the substrate. The filament and the substrate temperatures ( $T_{\text{fil}}$  and  $T_{\text{sub}}$ ) are separately maintained.

First, The silicon films were deposited on a Corning 1739 glass at 320 °C under a reactor pressure of 10 Torr with the helical-shaped tungsten filament at 1600 °C with a gas mixture of  $\text{SiH}_4$  (10% $\text{SiH}_4$ -90%He) and HCl (99.999%). For deposition, the flow rate of 10% $\text{SiH}_4$ -90%He gas was fixed at 100 standard cubic centimeters per minute (sccm) whereas the flow rate of HCl gas was varied at 0, 2, 6, 12 and 20 sccm. The distance between the wire and the substrate was 2 cm. The temperatures of the hot wire and the substrate were measured by an infrared optical pyrometer and the direct contact of a thermocouple with a substrate, respectively. The crystallinity of silicon films was analyzed by Raman spectroscopy. In order to prevent thermal crystallization by an incident laser beam of Raman spectroscopy, the power of the Ar ion laser (514.532 nm) was kept below 0.05 mW. The high resolution transmission electron microscopy (HRTEM) of FEI Tecnai - F20 (200kV)

is adopted to observe the nanocrystalline silicon grains directly. The sample was prepared by FEI Nova 600 dual beam (DB) focused ion beam (FIB).

In p-type/n-type layer dark conductivity experiments, the temperatures of the hot wire and the substrate were measured by an infrared optical pyrometer and the direct contact of a thermocouple with a substrate, respectively. The p-type/n-type silicon films were deposited using 30% silane ( $\text{SiH}_4$ ) diluted in hydrogen ( $\text{H}_2$ ) as a source gas and 5% diborane ( $\text{B}_2\text{H}_6$ )/phosphine ( $\text{PH}_3$ ) diluted in hydrogen ( $\text{H}_2$ ) as a dopant gas. Electrical and optical properties and the crystalline volume fraction of the films were measured. The dark conductivity ( $\sigma_{\text{dark}}$ ) was measured by a probe station (MST-6000C) with an analyzer (Agilent-HP, 4155) with coplanar Al electrodes deposited by an electron-gun evaporator. The optical band gap of p-type films was determined from transmittance and reflectance spectra of the films by an ultraviolet-visible transmission (UV-vis) spectrometer (Varian, Cary5000).

### 3 RESULTS

Figure 1 shows Raman spectra of the silicon films deposited for 20 min. For comparison, the Raman spectra for a silicon single crystal wafer was also measured and shown as a dotted line. Raman spectra clearly showed the continuous improvement of crystallinity of deposited silicon films approaching that of a single crystalline silicon wafer as the flow rate of HCl increased. To determine the volume fraction of crystalline silicon in the films, the Raman spectra were decomposed into three peaks for monocrystalline region centered at about  $520 \text{ cm}^{-1}$ , polysilicon region around  $505 \sim 517 \text{ cm}^{-1}$  and amorphous region around  $480 \text{ cm}^{-1}$  [7]. From the decomposed peaks, the crystalline volume fraction of the films was determined to be 0.44, 0.60, 0.67, and 0.79, respectively, for the HCl flow rate of 0, 2, 6, 12 and 20 sccm by using  $I_c/(I_c+I_a)$ , where  $I_c$  and  $I_a$  represent the integrated intensity

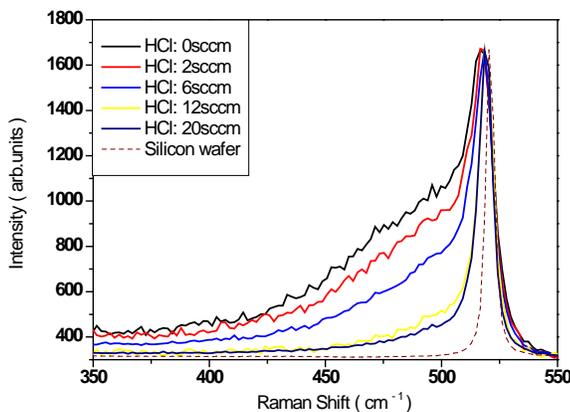


Figure 1: Si Raman spectra for various HCl gas ratios.

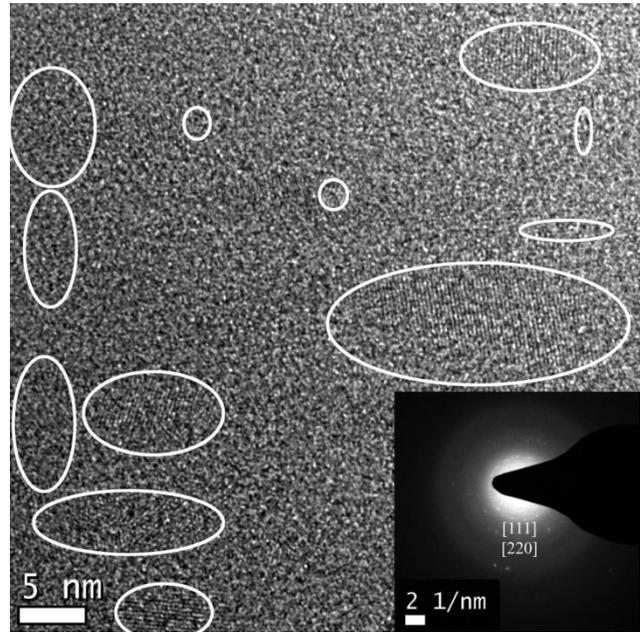


Figure 2 : The HRTEM microstructure image of  $\mu\text{c-Si:H}$  thin film – microcrystalline grains are found in white circles.

of crystalline and amorphous peaks, respectively. These quantitative data also show that the crystalline fraction of silicon increases with increasing flow rate of HCl. Crystal region of the grown film is shown in Figure 2.

For p-type/n-type layer dark conductivity experiment, the five different  $\text{B}_2\text{H}_6$  gas ratios of 1.42, 1.53, 1.81, 2 and 2.22 were used, which was determined by  $R_d = [\text{B}_2\text{H}_6] / ([\text{SiH}_4] + [\text{H}_2])$ . The five different  $\text{PH}_3$  gas ratios of 0.29, 0.55, 1.42, 2.37 and 3.32 were used, which was determined by  $R_d = [\text{PH}_3] / ([\text{SiH}_4] + [\text{H}_2])$ . The conductivity measurement results are described in Figure 3 and 4. Figure 4 also shows p-type layer optical band gap information. The dark conductivity of the films was estimated by the relation

$$\sigma_{\text{dark}} = \frac{I_g}{V_{\text{tw}}},$$

where  $V$  is the applied voltage,  $t$  is the thickness of films,  $w$  is the length of the electrode,  $I$  is the measured current and  $g$  is the distance between electrodes.

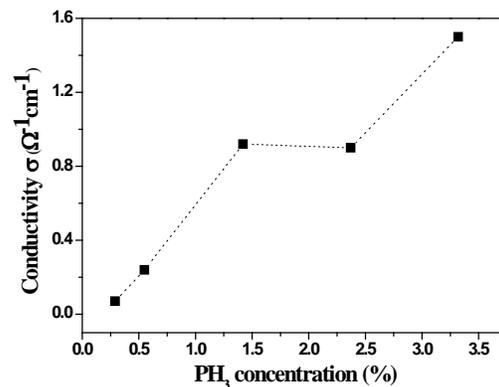


Figure 3 : n-type silicon conductivity

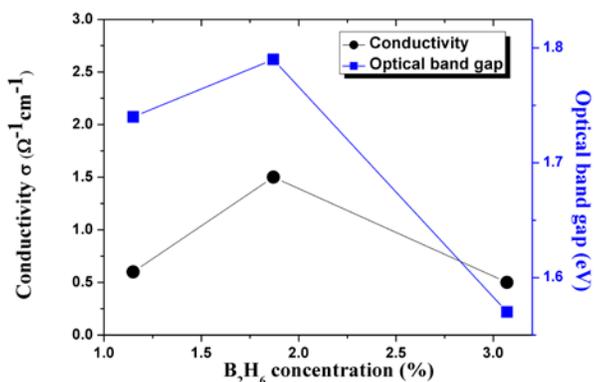


Figure 4 : p-type silicon conductivity and optical band gap

## 4 CONCLUSION

The crystalline fraction of silicon films deposited at low temperature by HWCVD was shown to increase systematically with increasing HCl flow rate, and the improvement of silicon crystallinity by HCl addition is promising in the application for displays and solar cells. The conductivity of p-type films prepared by said method is affected by mobility, carrier concentration, crystalline fraction and activation energy. The dark conductivity ( $\sigma_{\text{dark}}$ ) varied from 0.6 to 1.5  $\text{Scm}^{-1}$  and the optical bandgap varied from 1.57 to 1.79 eV as the  $\text{B}_2\text{H}_6$  gas ratio varied from 1.15 to 3.07. The dark conductivity ( $\sigma_{\text{dark}}$ ) varied from 0.07 to 1.5  $\text{Scm}^{-1}$  as the  $\text{PH}_3$  gas ratio varied from 0.29 to 3.32. The best p-type window material was obtained at the substrate temperature of 350°C, the filament temperature of 1800°C, and the  $\text{B}_2\text{H}_6$  gas ratio of 1.87 with an optical band gap of 1.79 eV and the dark conductivity of 1.5  $\text{Scm}^{-1}$ .

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## REFERENCES

- [1] M. Fonrodona, D. Soler, F. Villar, J. Escarre, J. M. Asensi, J. Bertomeu, J. Andreu, *Thin Solid Films* 501 (2006) 247-251.
- [2] H. Matsumura, *Japanese Journal of Applied Physics Part 2-Letters* 30 (1991) L1522-L1524.

- [3] S. Miyajima, M. Kim, Y. Ide, A. Yamada, M. Konagai, *Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers* 42 (2003) 3328-3332.
- [4] Z. R. Yu, I. Pereyra, M. N. P. Carreno, *Solar Energy Materials and Solar Cells* 66 (2001) 155-162.
- [5] J. K. Rath, R. E. I. Schropp, *Solar Energy Materials and Solar Cells* 53 (1998) 189-203.
- [6] S. A. Filonovich, M. Ribeiro, A. G. Rolo, P. Alpulm, Phosphorous and boron doping of nc-Si : H thin films deposited on plastic substrates at 150 degrees C by Hot-Wire Chemical Vapor Deposition, in: 2008, pp. 576-579.
- [7] L. Tay, D. J. Lockwood, J. M. Baribeau, X. Wu, G. I. Sproule, *J. Vac. Sci. Technol. A* 22 (2004) 943-947.