

EFFECT OF FLUORINE CHEMISTRY IN THE REMOTE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION OF SILICON FILMS FROM Si_2H_6 - SiF_4 - H_2

Dong-Hwan Kim, Il-Jeong Lee*, Shi-Woo Rhee[†] and Sang Heup Moon**

Laboratory for Advanced Materials Processing, Dep't of Chemical Engineering,
Pohang University of Science and Technology, Pohang 790-784, Korea

**Dep't of Chemical Engineering, Seoul National University, Seoul 151-742, Korea

(Received 9 May 1995 • accepted 21 July 1995)

Abstract— SiF_4 was added into Si_2H_6 - H_2 to deposit polycrystalline silicon films at low temperatures around 400°C in a remote plasma enhanced chemical vapor deposition reactor. It was found out that the fluorine chemistry obtained from SiF_4 addition had an influence on the chemical composition, crystallinity, and silicon dangling bond density of the film. The fluorine chemistry reduced the amount of hydrogen and oxygen incorporated into the film and also suppressed the formation of powders in the gas phase, which helped the crystallization at low temperatures. Effect of SiF_4 concentration as well as the deposition temperature was also significant.

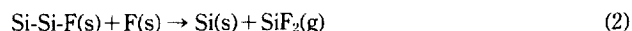
Key words: Chemical Vapor Deposition, Silicon Films, Plasma Deposition, Fluorine Chemistry, Polysilicon Films

INTRODUCTION

Silicon films have been grown mainly from silicon hydrides such as silane (SiH_4) or disilane (Si_2H_6) and sometimes from chlorosilanes such as SiH_2Cl_2 or SiCl_4 . In such cases, Si-H chemistry or Si-H-Cl chemistry plays an important role in the deposition process, *i.e.*, kinetics and crystal growth on the substrate surface. Chemical vapor deposition (CVD) of amorphous silicon films (a-Si) from silicon hydrides has been widely used for solar cells and thin film transistors and the role of hydrogen on deposition kinetics and material properties has been widely studied [Nakayama et al., 1984; Johnson et al., 1988; Toyoshima et al., 1990; Toyoshima et al., 1990; Kim et al., 1991; Langford et al., 1992]. There is presently much interest in growing epitaxial or polycrystalline silicon films at low temperatures. Deposition of epitaxial Si films at low temperatures from CVD with fluorine chemistry has been studied by many researchers [Nishida et al., 1986; Nagamine et al., 1986; Hanna et al., 1989; Yamada et al., 1989]. Also the thermodynamic equilibrium composition, along with boundaries of deposition and etching, at various temperatures and initial compositions in Si-H-F system was also studied [Lee et al., 1992]. Polycrystalline films have been used in many applications such as thin film transistor (TFT), image sensor and LSI (large scale integration) applications. In particular, in the field of active matrix liquid crystal display, the use of polysilicon as an active layer instead of amorphous silicon has drawn much attention because the electron mobility in poly-Si is much faster than a-Si and better performance can be achieved with poly-Si TFT's. In this case, low temperature processing below 600°C is desirable to utilize low cost glass substrates and one of the approaches is the annealing of low temperature deposited a-Si for solid phase crystallization. Another approach is to deposit directly with CVD by utilizing fluorine chemistry from F_2 or SiF_4 mixed with silicon hydrides

and hydrogen [Nagahara et al., 1992]. At low temperatures, it is relatively difficult to grow crystalline films because adatom mobility is low and incorporation of impurity is more likely to happen.

With fluorine chemistry, it is expected that oxygen incorporation can be suppressed from *in-situ* chemical cleaning effect of fluorine [Nagahara et al., 1992]. At the same time, following reactions from fluorine chemistry, in addition to the reaction of silicon nuclei formation, were believed to occur on the deposition surface and the microstructure of silicon tissues formed on the surface would depend on the surface reaction.



The H and F coverage of the growing surface is likely to be small from the formation and desorption of HF (reaction 1), which can enhance the surface adatom mobility. Also through the formation and desorption of SiF_2 , the preferential etching of weak amorphous tissue can be achieved (reaction 2) [Okada et al., 1989].

In this research, the effect of fluorine chemistry on the film composition and crystallinity of silicon films was studied. Also the effect of deposition temperature and the amount of SiF_4 added into Si_2H_6 - H_2 mixture in a remote plasma reactor was elucidated.

EXPERIMENT

In the remote plasma enhanced CVD reactor shown in Fig. 1, hydrogen (99.9999%) is introduced into an alumina tube on the top of the reactor and excited by inductively coupled 13.56 MHz plasma. Hydrogen flow rate was fixed at 100 sccm and plasma power was 60 watts. Activated hydrogen radical was formed by plasma chemical reaction and flowed into the deposition zone. Disilane (99.99%) and tetrafluorosilane (99.99%) were introduced into the region 10 cm down stream of the plasma and mixed with excited hydrogen and flowed toward the substrate 20 cm

[†]To whom all correspondences should be addressed.

*now at LG Electronics, Frontec Inc., Sendai, Japan

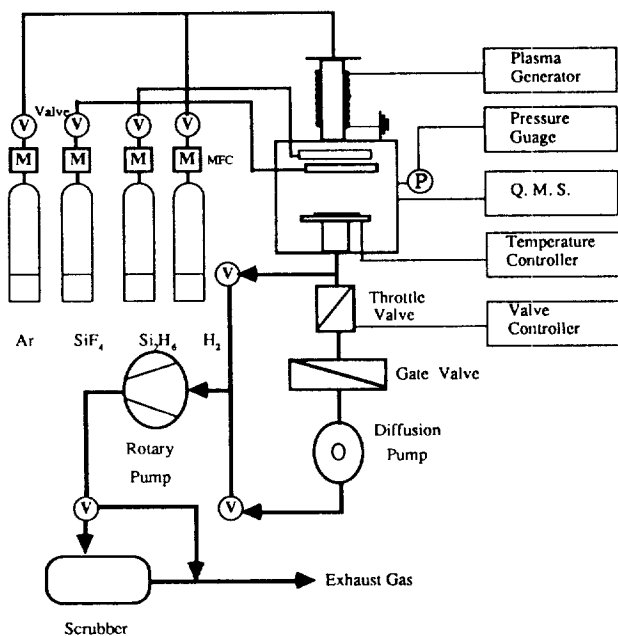


Fig. 1. Schematic diagram of the remote plasma enhanced chemical vapor deposition system.

down stream of the plasma. In the gas phase above the substrate, activated hydrogen and silane molecules will collide to produce activated silicon hydrides and fluorides which will participate in the surface chemical reactions to form silicon films.

Thermally oxidized 4 inch silicon wafer with oxide thickness of 1000 Å was used as a substrate because in liquid crystal display applications, active layers are grown on glass substrates. Reactor pressure was 400 mtorr and deposition temperatures were 300–450°C. Deposited films were characterized by Fourier transform infrared spectroscope (FT-IR) for chemical composition, Raman for crystallinity, and electron spin resonance (ESR) for the amount of silicon dangling bonds. The deposition rate was in the range of 30–100 Å/min. Near the reactor outlet, a TEM grid was inserted to collect powders if there was any homogeneous nucleation and the number of particles collected per unit area was obtained from TEM micrograph.

DISCUSSION

Fig. 2 shows FT-IR spectra representing the effect of deposition temperature on the chemical composition of the silicon films. The amount of Si_2H_6 and SiF_4 was 1 and 30 sccm, respectively. Si-H stretching vibration mode usually appears in the range of 2230–1970 cm^{-1} . A couple of bands can be seen at around 2230 cm^{-1} and 2120 cm^{-1} in the film deposited at 350°C which is close to that of the SiH_2 stretching vibration reported for a-Si:H films (2100 cm^{-1}) [Zanzucchi, 1984]. It is well known that the introduction of an electronegative component results in the peak shift of Si-H vibration to higher frequencies [Bellamy, 1975]. The bands at 2230 and 2120 cm^{-1} are probably ascribable to the Si-H stretching vibrations in the $-\text{SiHF}_2$ [Thompson, 1960] and the $-\text{SiH}_2-\text{SiF}_n$ -groups [Wadayama et al., 1990], respectively. These two peaks are not significant in the films deposited at temperatures higher than 350°C.

It was reported that bands corresponding to a deformation

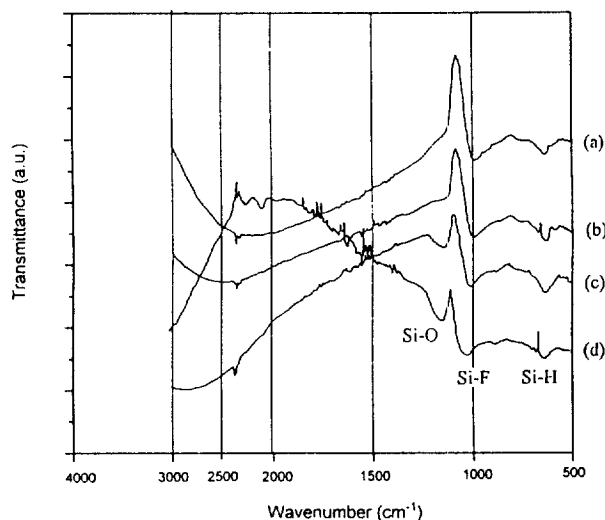


Fig. 2. IR spectra of Si films deposited at various substrate temperatures, (a) 450, (b) 415, (c) 400 and (d) 350°C with $\text{Si}_2\text{H}_6/\text{SiF}_4/\text{H}_2 = 1/30/100$ sccm, pressure at 400 mtorr and plasma power at 60 watts (H_2 plasma).

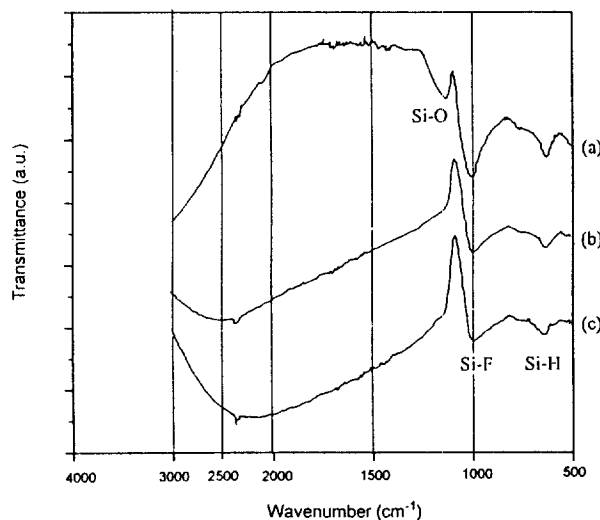


Fig. 3. IR spectra of Si films deposited with various amount of SiF_4 , (a) 10 sccm, (b) 20 sccm, (c) 30 sccm with substrate temperature at 450°C, pressure at 400 mtorr, plasma power at 60 watts (H_2 plasma) and $\text{Si}_2\text{H}_6/\text{H}_2 = 1/100$ sccm.

mode of the SiH_2 group bonded to fluorinated silicon appeared near 960, 900 and 850 cm^{-1} [Wadayama et al., 1990]. Also the band near 640 cm^{-1} corresponds to a wagging mode of Si-H [Langford et al., 1992]. The Si-F stretching region is in the range of 1050–800 cm^{-1} . The peak near 1000 cm^{-1} may be due to Si-F_4 stretching as reported by Fang et al. [Fang et al., 1980]. Shimada et al. [Shimada et al., 1980] reported that $-\text{SiF}_3$ appeared at 1015 cm^{-1} . In Fig. 2, Si-F peak appeared between 1020 and 990 cm^{-1} depending on the deposition temperature.

It has been shown that Si-O stretching modes are located at 1150–1200 cm^{-1} in the plasma-CVD a-Si:H film [Wadayama et al., 1990]. It can be seen that at low substrate temperatures, more oxygen and hydrogen are incorporated into the film. Films depo-

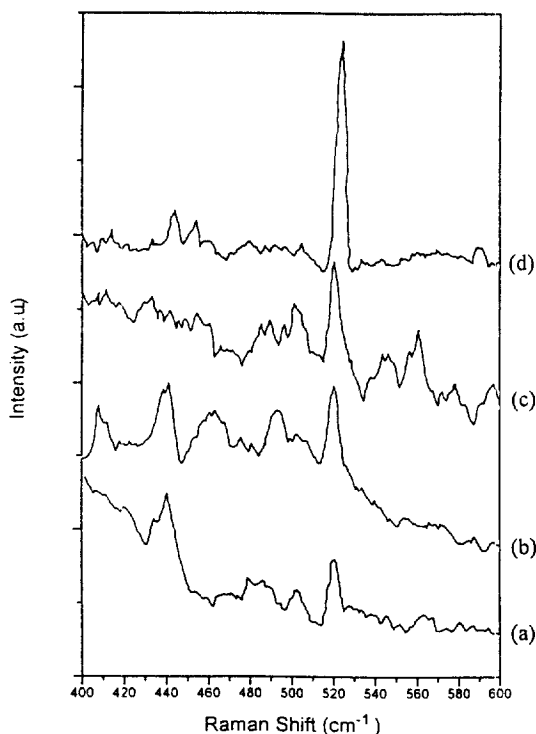


Fig. 4. Raman spectra of Si films deposited with various amount of SiF_4 , (a) 0, (b) 10 sccm, (c) 20 sccm, (d) 30 sccm with substrate temperature at 450°C , pressure at 400 mtorr, plasma power at 60 watts (H_2 plasma) and $\text{Si}_2\text{H}_6/\text{H}_2 = 1/100$ sccm.

sited at 350 and 400°C show noticeable amount of oxygen near 1150 cm^{-1} . Oxygen is due to the surface contamination from the residual gas in the chamber. Oxygen contamination is more serious at low temperatures and is a major obstacle disturbing the growth of a high quality Si film.

Fig. 3 shows the effect of SiF_4 addition on the amount of impurities incorporated into the Si film. The deposition temperature is 450°C and the amount of Si_2H_6 added is 1 sccm. With 20 and 30 sccm of SiF_4 introduced, the amount of oxygen and hydrogen incorporated into the film becomes smaller compared with 10 sccm addition. It can be seen clearly that appropriate amount of SiF_4 addition can reduce the contamination due to the *in-situ* cleaning effect of fluorine chemistry.

Fig. 4 shows the Raman spectrum of films deposited with various amount of SiF_4 addition. For amorphous Si films, broad band peak appears around 480 cm^{-1} and for crystalline Si, a sharp peak appears around 520 cm^{-1} with narrower full width at half maximum (FWHM) as the crystallinity increases [Johnson et al., 1988]. Bulk crystalline Si shows FWHM of about 3.5 cm^{-1} . With 20 and 30 sccm of SiF_4 addition, FWHM was about 4.5 and with 10 sccm, it was about 5. Without SiF_4 addition, the film was amorphous. This clearly shows that *in-situ* cleaning effect enhanced the crystallization of Si films.

Fig. 5 shows ESR peak of Si films deposited at various substrate temperatures with 20 and 30 sccm of SiF_4 . The peak at $g=2.0055$ corresponds to the Si dangling bond. As the deposition temperature increases, the amount of Si dangling bonds also increases and with 30 sccm of SiF_4 , it is slightly higher than with 20 sccm. It was believed that the Si dangling bonds were formed by the

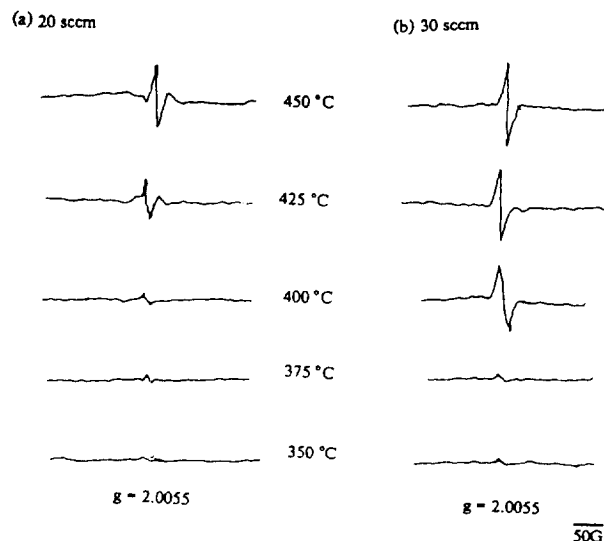


Fig. 5. ESR spectra of Si films deposited at various deposition temperatures and different SiF_4 amounts with pressure at 400 mtorr, plasma power at 60 watts (H_2 plasma) and $\text{Si}_2\text{H}_6/\text{H}_2 = 1/100$ sccm.

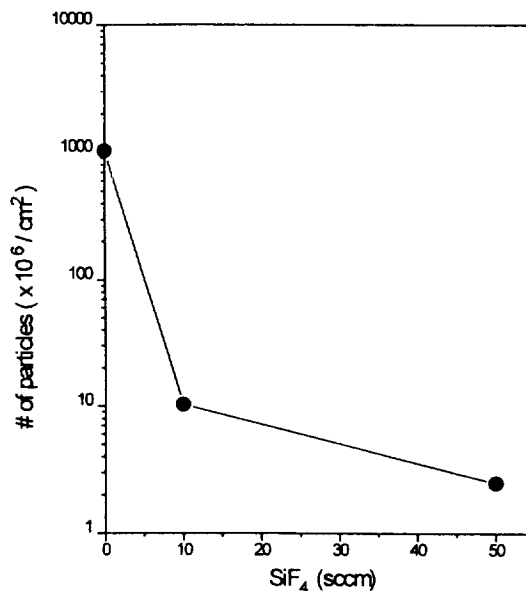


Fig. 6. The number of powders formed in the gas phase at different SiF_4 flow rate with deposition temperature at 430°C , pressure at 400 mtorr, plasma power at 60 watts (H_2 plasma) and $\text{Si}_2\text{H}_6/\text{H}_2 = 5/100$ sccm.

desorption of hydrogen and at high temperatures, hydrogen desorption is more significant. Also the fluorine chemistry enhances the hydrogen desorption through the formation of HF which favored the crystallization but also decreases the effect of hydrogen passivation of Si dangling bonds.

Fig. 6 shows the number of powders formed in the gas phase at different SiF_4 flow rates. Particles were counted from TEM micrograph and the number was expressed in terms of unit square centimeter. Up to this point, the role of SiF_4 in the gas phase has not been studied in any depth but this result clearly shows that the homogeneous nucleation during the deposition

of Si films can be suppressed by adding SiF_4 . This means that fluorine chemistry also plays a role in the gas phase. Incorporation of powders from the gas phase into the film makes it harder for the crystalline phase to grow in the film and also increases surface roughness. Usually in the chemical vapor deposition of thin films, the formation of powders in the gas phase causes serious problems on the film property and device reliability. For this reason, powder formation should be suppressed as much as possible in a CVD thin film process.

CONCLUSION

It was shown that the fluorine chemistry obtained by adding SiF_4 into $\text{Si}_2\text{H}_6\text{-H}_2$ reaction system suppressed the incorporation of oxygen and hydrogen, which enabled us to get crystalline Si films at relatively lower temperatures than Si-H system. Also the fluorine chemistry utilizing SiF_4 reduced the powder formation in the gas phase, which also helped the crystallization of Si films. Appropriate amount of SiF_4 should be added into the reactant mixture to utilize fluorine chemistry and also the deposition temperature plays an important role in the fluorine chemistry.

ACKNOWLEDGEMENT

This research was supported by LG Electronics Co. and support of Korea Research Foundation is also acknowledged.

REFERENCES

- Bellamy, L. J., *The Infrared Spectra of Complex Molecules* (Chapman and Hall, London, 1975), Vol. 1, 3rd ed., p. 380.
- Fang, C. J., Ley, L., Shanks, H. R., Gruntz, K. J. and Cardona, M., "Bonding of Fluorine in Amorphous Hydrogenated Silicon", *Phys. Rev.*, **B22**, 6140 (1980).
- Hanna, J., Kamo, A., Komiya, T., Shimizu, I. and Kokado, H., "Preparation of Si Thin Films by Spontaneous Chemical Deposition", *J. Non-cryst. Solids*, **114**, 172 (1989).
- Johnson, N. M., Ready, S. E., Boyce, J. B., Donald, C. D., Wolff, S. H. and Walker, "Hydrogen Incorporation in Undoped Microcrystalline Silicon", *J. Appl. Phys. Lett.*, **53**(17), 1626 (1988).
- Kim, S. C., Jung, M. H. and Jang, "Growth of Microcrystal Silicon by Remote Plasma Chemical Vapor Deposition", *J. Appl. Phys. Lett.*, **58**(3), 281 (1991).
- Langford, A. A., Fleet, M. L., Nelson, B. P., Lanford, W. A. and Maley, N., "Infrared Absorption Strength and Hydrogen Content of Hydrogenated Amorphous Silicon", *Phys. Rev.*, **B45**, 13 367 (1992).
- Lee, K. Y., Chung, C.-W., Han, J. H., Rhee, S. and Moon, S. H., "Thermodynamic Evaluation of Equilibrium Compositions in the Si-H-F System", *J. Electrochem. Soc.*, **139**, 3539 (1992).
- Nagamine, K., Yamada, A., Konagai, M. and Takahashi, M., "Epitaxial Growth of Silicon by Plasma Chemical Vapor Deposition at a Very Low Temperature of 250°C", *Jpn. J. Appl. Phys.*, **26**, L951 (1986).
- Nagahara, T., Fujimoto, K., Kohno, N., Kashiwagi, Y. and Kakinoki, H., "In situ Chemically Cleaning Poly-Si Growth at Low Temperature", *Jpn. J. Appl. Phys.*, **31**, 4555 (1992).
- Nakayama, Y., Takuma, Y., Akiyama, K., Otsuchi, T. and Kawamura, T., "Deposition Mechanism of a-Si:H Film in Disilane-Hydrogen Plasma", *Jpn. J. Appl. Phys.*, **23**(7), L470 (1984).
- Nishida, S., Shiimoto, T., Yamada, A., Karasawa, S., Konagai, M. and Takahashi, K., "Epitaxial Growth of Silicon by Photochemical Vapor Deposition at a very Low Temperature of 200°C", *Appl. Phys. Lett.*, **49**, 79 (1986).
- Okada, Y., Chen, J., Campbell, I. H., Fauchet, P. M. and Wagner, S., "Mechanism of Microcrystalline Silicon Growth from Silicon Tetrafluoride and Hydrogen", *J. Non-Cryst. Solids*, **114**, 816 (1989).
- Shimada, T., Katayama, Y. and Horigome, S., "Infrared Spectra of Amorphous Silicon-Fluorine Alloys Prepared by Sputtering in Fluorosilane-Argon Gas Mixture", *Jpn. J. Appl. Phys.*, **19**, L265 (1980).
- Thompson, H. W., "Si-H Vibration Frequency and Inductive Effects", *Spectrochim. Acta*, **16**, 238 (1960).
- Toyoshima, Y., Arai, K., Matsuda, A. and Tanaka, K., "Real Time *in situ* Observation of the Film Growth of Hydrogenated Amorphous Silicon by Infrared Reflection Absorption Spectroscopy", *Appl. Phys. Lett.*, **56**(16), 1540 (1990).
- Toyoshima, Y., Arai, K., Matsuda, A. and Tanaka, K., "Real Time Detection of Higher Hydrides on the Growing Surface of Hydrogenated Amorphous Silicon by Infrared Reflection Absorption Spectroscopy", *Appl. Phys. Lett.*, **57**(10), 1028 (1990).
- Wadayama, T., Kayama, H., Hatta, A., Suetaka, W. and Hanna, "In situ IR Spectroscopic Observation of a-Si:H(F) Films Growing under Spontaneous Chemical Deposition Method", *J. Jpn. J. Appl. Phys.*, **29**, 1884 (1990).
- Yamada, A., Jia, Y., Konagai, M. and Takahashi, K., "Heavily P-doped ($>10^{-21} \text{ cm}^{-3}$) Silicon Films Grown by Photochemical Vapor Deposition at a very Low Temperature of 250°C", *Jpn. J. Appl. Phys.*, **28**, L2284 (1989).
- Zanzucchi, P. J., *Semiconductors and Semimetals*, ed., Pankove, J. (Academic Press, New York), Vol. 21B, p. 113 (1984).