# Study the Properties of Silicon Nitride Films prepared by High Density Plasma Chemical Vapor Deposition

Utpal Gangopadhyay, Do Young Kim, Igor Oskarovich. Parm, Kaustuv Chakrabarty, Chi Hyung Kim, Myung Suk Shim and Junsin Yi New materials Lab.(BK 21 Lab.)

School of Information and Computer Engineering, Sungkyunkwan University, 300 Chunchun-dong, Jangan-gu, Kyunggi-do, Suwon 440-746, Korea

Phone: +82-31-290-7174, E-mail: yi@yurim.skku.ac.kr

#### **Abstract**

The characteristics of silicon nitride films deposited in a planar coil reactor using a simple high-density inductively coupled plasma chemical vapor deposition technique have been investigated. The process gases used during silicon nitride deposition cycle were pure nitrogen and a mixture of silane and helium. It has been pointed out that the strong H-atom released from the growing SiN film and Si-N bond healing are responsible for the improved electrical and passivation properties of SiN.

#### 1. Introduction

In recent years, low temperature (less than 450°C) silicon nitride layers have a number of important applications in the flat panel display. They are used extensively for the passivation of devices, i.e., protection of completed devices from a hostile environment, and as a dielectric in thin film transistor (TFT) [1] or surface passivation and anti-reflection coating (ARC) of solar cell [2]. Excellent step coverage, good adhesion to underlying layers and a diffusion barriers to water vapor and sodium ions, make SiN:H ideal for encapsulating devices after the final metallization layer. It also gives particle and scratch protection to devices during mounting operations. Researchers at the Australian National University have recently shown that the optimum surface passivation is observed for stoichiometric SiN films (n~1.9 at 633 nm) [3]. The SiN films were produced in a parallel plate that remote-plasma SiN films and high-frequency (13.56 MHz) direct-plasma SiN films both provide an excellent. The SiN films were produced in a parallel plate reactor using a silane/nitrogen (SiH<sub>4</sub>/N<sub>2</sub>) mixture (4.5% silane, 95.5% nitrogen). In order to avoid the ion bombardment of the silicon surface during the plasma deposition a high excitation frequency (13.56 MHz) was used. These well-passivating stoichiometric SiN films are easily etchable, do not absorb UV photons with wavelengths above 320 nm and act as perfect insulators. The fundamentally different passivation behavior of the last SiN films is attributed to the addition of nitrogen to process gases. For a thin film transistor application, this article demonstrates the growth conditions and chemical structure of SiN films fabricated by high-density (HD) Inductively Coupled Plasma Chemical Vapor Deposition (ICPCVD) using pure nitrogen and a silane/helium mixture (20% silane, 80% helium).

## 2. Experimental

The SiN films were deposited in a planar coil ICP CVD reactor. In this system, the intense degree of dissociation and ionization of nitrogen is established in a region away from the substrate. Silane/helium mixture passes through a distribution ring located under the plasma region. Thus, nitrogen is directly dissociated while silane is dissociated predominately by active particles from the plasma region. The process pressure for PECVD and HD-ICP are quite different. More than 100 mTorr is common for PECVD. The pressure range of HD-ICP is 1-30 mTorr. We report on the study of 20 mTorr working pressure, from 200 °C to 400 °C substrate temperature, from 3 to 50 nitrogen-to-silane gas flow ratio, 200 W ICP power (13.56 MHz). The high-density plasma was created by inductive coupling of rf power to the plasma region through a quartz plate. The diameter of the ICP source was about 20 cm. The samples were loaded on a grounded, resistance-heated stage. The distance between planar coil and sample was 15cm. Pure nitrogen was passed through the HD-ICP region from the top of the chamber. The distribution ring for the silane/helium mixture was located under the plasma region at the distance 12 cm from the coil. We illustrate the schematics of reactors in the figure 1.

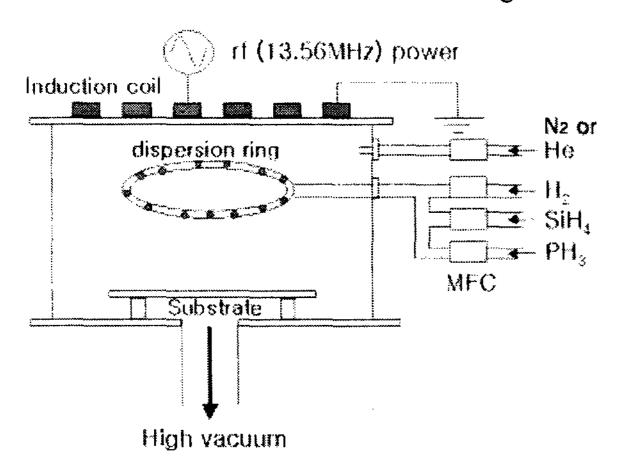


Figure 1 The schematics of reactors for SiN deposition.

## 3. Results and discussion

Figure 2 shows the dependence on temperature of refractive index and deposition rate for SiN grown in 10 sccm total gas flow, 50 nitrogen-to-silane gas flow ratio, 200 W source power and 20 mTorr discharges. The deposition rate decreases with the elevation of substrate temperature. The refractive index tends to increase slowly with the substrate temperature but it decreases from 100 °C. This may be a result of reactive Si species being strongly desorbed at this temperature before they are incorporated into the SiN film.

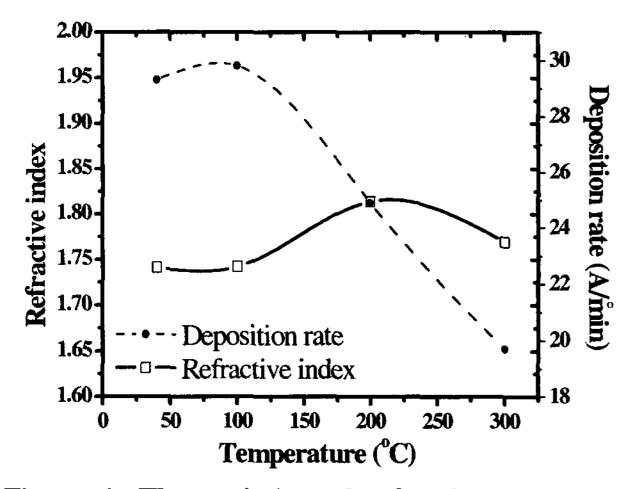


Figure 1. The variation of refractive index and deposition rate of SiN film with temperature for fixed  $N_2/SiH_4$  value 50 at 200 W source power and 20 mTorr discharges.

The parameter, which enabled us to change the refractive index of the SiN film is the nitrogen-to-silane gas flow ratio, as shown in Figure 2 for 200 °C. The refractive index possesses a strong increase for the ratio higher than 10.

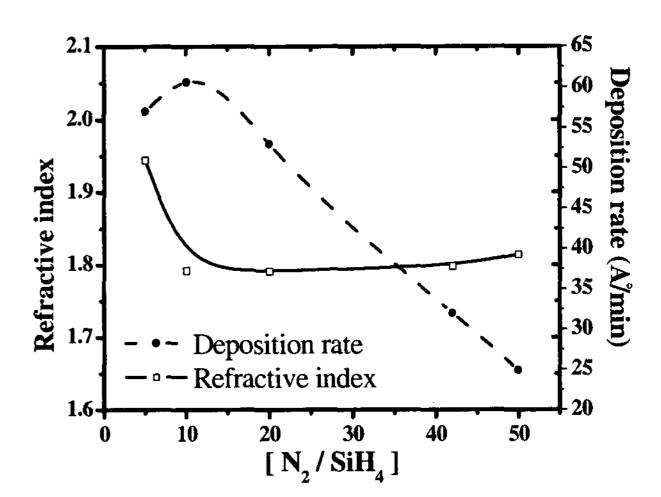


Figure 2. The variation of refractive index and deposition rate of SiN film with different  $N_2/SiH_4$  values at 200°C temperature.

The SiN films show IR spectral features at frequencies characteristic of the local bonding of the Si, N, and H atoms. The nature of the chemical bonding groups was analyzed using FTIR spectroscopy. Figure 3 displays FTIR transmission spectra from 400 to 4000 cm<sup>-1</sup> for films prepared at flow rate ratios of 5, 10, and 50 at 200 °C. Absorption peak assigned to Si-N stretching mode is observed at 880~875 cm<sup>-1</sup> for gas flow ratio more than 10. The absorption peak of the Si-N stretching mode is shifted to 840 cm<sup>-1</sup> for gas flow ratio equal to 5. Si-H and N-H bond concentrations were obtained from intensity of the absorption of Si-H and N-H stretching vibrations of about 2160 and 3330 cm<sup>-1</sup> respectively. The calculations were made for the absorbance at the absorption peak position and molecular extinction coefficients  $5.7 \times 10^{20}$  cm<sup>2</sup> for Si-H and  $3.3 \times 10^{20}$  cm<sup>2</sup> for N-H [4]. The detectable hydrogen as a whole in the SiN films was bonded to nitrogen and detected as N-H groups for the nitrogen-to-silane gas flow ratio at the 10~50 range.

The value  $2.73\times10^{22}$  cm<sup>-3</sup> was obtained at the gas ratio equal to 50. The value  $2.21\times10^{22}$  cm<sup>-3</sup> was obtained at the gas flow ratio equal to 10. Si-H groups were detected at the range  $7.67\times10^{21}$  cm<sup>-3</sup> and N-H

groups at the range  $1.31 \times 10^{22}$  cm<sup>-3</sup> for the gas flow ratio equal to 5 at 200 °C.

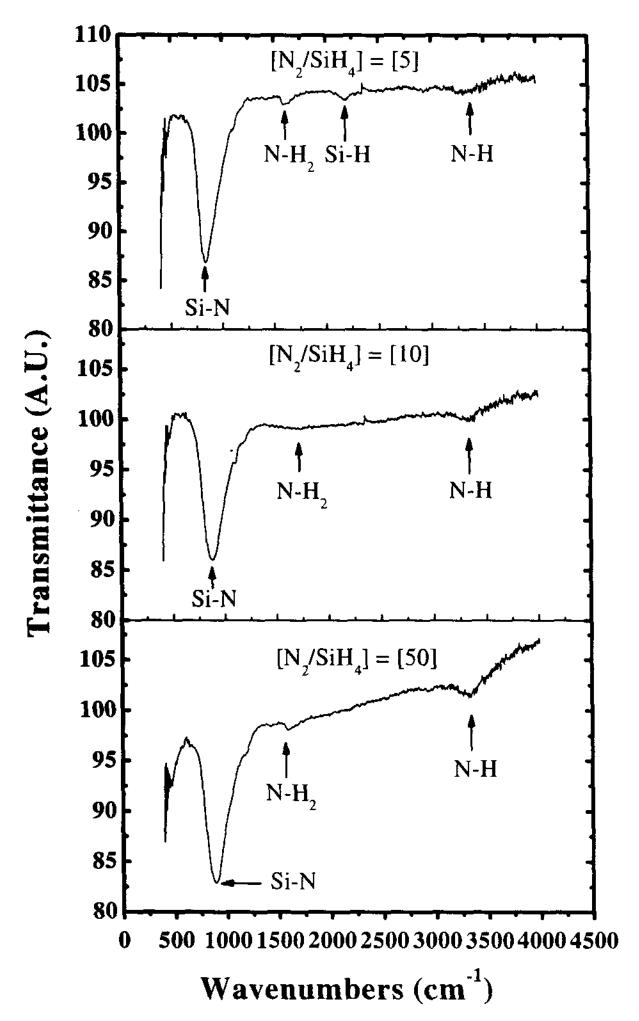


Figure 3. FTIR transmission spectra from 400 to 4000 cm<sup>-1</sup> for films prepared at flow rate ratios of 5, 10, and 50 at 200 °C.

Corresponding data for 375 °C is presented in Figure 4. Hydrogen content is about  $1.5 \times 10^{22}$  cm<sup>-3</sup> for SiN films deposited at nitrogen-to-silane gas flow ratio more than 10. Hydrogen as a whole is observed in N-H bonds. The hydrogen content is at the minimum level at the range  $4 \times 10^{21}$  cm<sup>-3</sup> for the gas flow ratio equal to 3. Our research gives us the evidence that the H-atom releases from the growing SiN that may be obtained at the temperature as low as 375 °C, by the proper choice of the nitrogen-to-silane gas flow ratio. Additional re-bonding of silicon to nitrogen is expected as hydrogen is evolved from the

film at these conditions. The reduction of bonded hydrogen and Si-N bond healing are responsible for the improved electrical and passivation properties of SiN films.

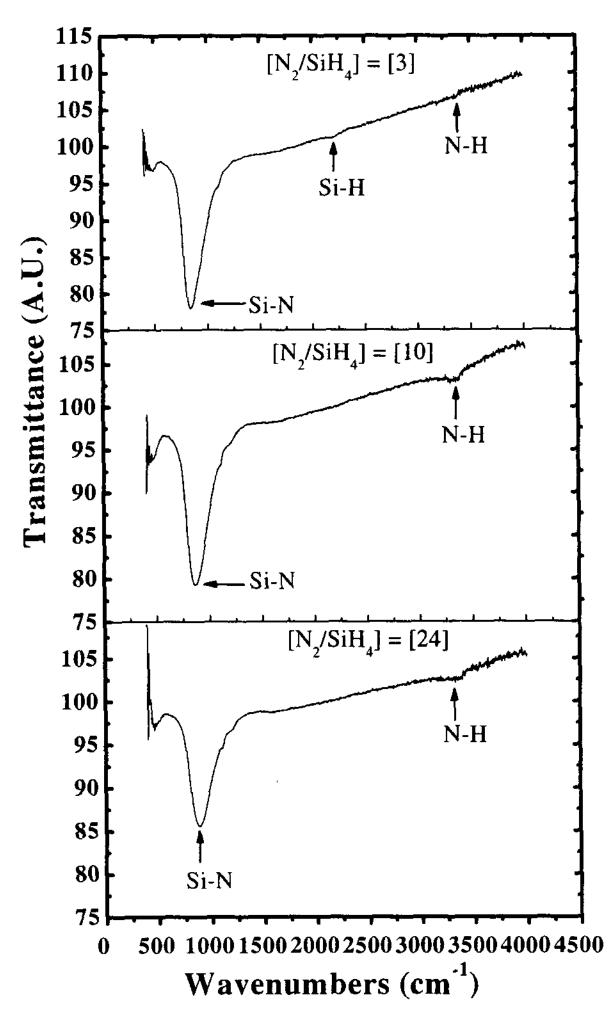


Figure 4. FTIR transmission spectra of SiN films deposited under various  $N_2/SiH_4$  gas flow ratios, using 200W source power, and 20 mTorr discharges at  $375^{\circ}C$ .

### 4. Conclusion

SiN films have been deposited using pure nitrogen and silane/helium mixture in a HD ICP CVD planar coil reactor. High quality silicon nitride is obtained with reactor conditions of 20 mTorr, 10 sccm total gas flow, nitrogen-to-silane gas flow ratio equal to 3, 200W RF power, and a substrate temperature of 375 °C. Hydrogen content predominantly in Si-H bonds at the range  $4 \times 10^{21}$  cm<sup>-3</sup> is observed in SiN films grown at these conditions. SiN films without absorption

peaks corresponding to Si-H bonds were deposited at nitrogen-to-silane gas flow ratio more than 10. High hydrogen content at the range of about  $2\times10^{22}$  cm<sup>-3</sup> is detected as N-H groups in the SiN films deposited at these gas flow ratios.

Our research gives evidence that by properly can be choosing the nitrogen-to-silane gas flow ratio, H-atom released from the grown SiN film. Additional rebonding of silicon to nitrogen is expected as hydrogen is evolved from the film at these conditions. The reduction of bonded hydrogen and Si-N bond healing responsible for the improved electrical are (particularly low leakage current) and passivation properties of SiN films. Therefore, high -density inductively coupled plasma chemical vapor deposition technique could be used for the deposition of good quality of silicon nitride film for passivation as well as gate dielectric in a TFT.

## 5. Acknowledgements

This work was supported by the advanced Materials and Process Research Center for IT at Sungkyunkwan University. (Grant No. R12-2002-057-02003-0)

#### 6. References

- [1] Hidekaza Sato, Akira Tzumi and Hideki Matsumura, Applied Physics Letter, Vol.77 (1), 2752 (2000).
- [2] Armin G. Aberle, Solar Energy Materials & Solar cells, 65, 239(2001).
- [3] Schmidt, M.Kerr, Technical Digest of the 11<sup>th</sup> Photovoltaic Science and Engineering Conference, Sapporo, 581(1999).
- [4] Belyi V. I, Vasilyeva L. L., Gritsenko V. A., Ginovker A. S., Repinsky S. M., Sinitsa S. P., Smirnova T. P., Edelman F. L., Silicon Nitride in Electronics, Nauka, Novosibirsk, p.72 (1982).