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# High-rate, Low-temperature Deposition of Multifunctional Nano-crystalline Silicon Nitride Films

**Jae-Dam Hwang[a], Kyoung-Min Lee**[b], Ki-Su Keum[a], Youn-Jin Lee**[a] and Wan-Shick Hong*[a,b]**

## Abstract

The solid phase compositions and dielectric properties of silicon nitride ($SiN_x$) films prepared using the plasma enhanced chemical vapor deposition (PECVD) technique at a low temperature (200°C) were studied. Controlling the source gas mixing ratio, R = $[N_2]/[SiH_4]$, and the plasma power successfully produced both silicon-rich and nitrogen-rich compositions in the final films. The composition parameter, X, varied from 0.83 to 1.62. Depending on the film composition, the dielectric properties of the $SiN_x$ films also varied substantially. Silicon-rich silicon nitride (SRSN) films were obtained at a low plasma power and a low R. The photoluminescence (PL) spectra of these films revealed the existence of nano-sized silicon particles even in the absence of a post-annealing process. Nitrogen-rich silicon nitride (NRSN) films were obtained at a high plasma power and a high R. These films showed a fairly high dielectric constant ($\kappa = 7.1$) and a suppressed hysteresis window in their capacitance-voltage (C-V) characteristics.

**Keywords**: PECVD, $SiN_x$, nanocrystalline-Si, low-temperature deposition

## 1. Introduction

Silicon nitride ($SiN_x$) thin films have been used extensively in the display industry, e.g., as gate dielectric and passivation layers [1, 2]. Also, SRSN films that contain nc-Si particles have been studied actively for luminescence, optical sensing, and data-retention applications [3, 4]. As flexible electronics gain attention in the field of next-generation display devices, the deposition of good dielectric films at sufficiently low temperatures becomes crucial in the development of reliable devices. $SiN_x$ layers grown using the PECVD method usually have a slightly silicon-rich composition. For a dielectric layer of thin film transistors (TFTs), a nitrogen-rich composition, or a composition that is close to stoichiometric (x = 1.33), is desired. The low-temperature dielectric film may also be applied to other types of devices such as flexible electropwetting displays [5]. Low-temperature deposition of silicon nitride films often leads to an increased dangling bond density and a reduced specific gravity. The resulting materials exhibit not only poor performance, but also lack of process control. Therefore, it is very important to find process parameters that could provide a control for the composition of the low-temperature films that would be suitable for specific applications. In this study, an attempt was made to fabricate $SiN_x$ films with a wide range of compositions at a process temperature of 200°C. We used a source gas mixing ratio, R = $[N_2]/[SiH_4]$, and a plasma power as control variables.

## 2. Experimental details

$SiN_x$ films were deposited in a capacitively-coupled radio frequency (R.F.) PECVD system using helium-balanced 5 % silane ($SiH_4$) and pure nitrogen ($N_2$) as the source gases. The substrate temperature was 200°C and the process pressure was 0.5 torr. The base pressure was set lower than $5.0\times10^{-6}$ torr. The total gas flow rate was maintained at 40 sccm, and the mixing ratio, R = $[N_2]/[SiH_4]$, was varied from 1 to 40. The plasma power was varied from 10 to 100 W. The composition of the $SiN_x$ films was analyzed via FTIR spectroscopy in the middle-infrared range of 400-4,000 $cm^{-1}$, with a resolution of 4.0 $cm^{-1}$. The photoluminescence characteristics were analyzed using a He-Cd laser with a wavelength of 325 nm as a pumping source. The electrical properties of the $SiN_x$ films were measured by constructing a metal-insulator-semiconductor

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*Member, KIDS; ** Student Member, KIDS
Corresponding author: Wan-Shick Hong
[a] Department of Nano Science and Technology, University of Seoul, Seoul 130-743, Korea
[b] Department of Nano Engineering, University of Seoul, Seoul 130-743, Korea
**E-mail**: wshong@uos.ac.kr **Tel:** +82-2-2210-5718 **Fax:** +82-2-2248-5380

(MIS) structure. The top electrodes were defined using the SF-100 XPRESS Maskless Lithography System. High-frequency (1 MHz) C-V measurements were performed using an HP4280A LCR meter. The bias voltage was varied at a sweep rate of 0.1 V/s, starting from accumulation to strong inversion, and then to complete reversal.

## 3. Result and Discussion

An attempt was made to find a process window in which a wide spectrum of compositions and microstructures can be attained for a low-temperature deposition. A full-factorial design of the experiment was performed using the gas mixing ratio, R = [$N_2$]/[$SiH_4$], and the plasma power (10–100 W) as the two main variables. The changes in the deposition rate with the process parameters are presented in Figure 1.

As expected from numerous other studies, a high-value plasma power and a low-value R led to a high deposition rate. The deposition rate was influenced more by the plasma power than by the gas mixing ratio. Considering the error bars, it can be ascertained that the data were highly reproducible. This result indicates that the control of the film composition can be manifested without significantly sacrificing the deposition rate. Also, the plasma power is readily available as a compensation scheme for an insufficient deposition rate, if there would be any need to boost the film thickness.

The deposition rates obtained at the plasma power of 100W were higher than those of the low-temperature $SiN_x$ films deposited from $SiH_4$ and $NH_3$ [6]. A higher power would more readily produce energetic radicals, which would accelerate the network formation on the growing surface. However, too high a [$N_2$]/[$SiH_4$] ratio, especially at a low power, may have overpopulated the growing surface with less-reactive nitrogen radicals and resulted in a low deposition rate.

Figure 2 shows FTIR spectra of the samples presented in Figure 1. The Si-N stretching vibration mode is observed near 840 $cm^{-1}$, the N-H stretching vibration mode near 3350 $cm^{-1}$, the Si-$H_n$ stretching vibration mode near 2,100–2,200 $cm^{-1}$, the N-H bending vibration mode around 1180 $cm^{-1}$, and the Si-H bending vibration mode near 640$cm^{-1}$. Increasing the gas ratio R and the plasma power results in an increase of N-H bonds (near 3350 $cm^{-1}$), and a decrease of Si-H bonds (near 2100 ~ 2200 $cm^{-1}$). Assuming that the relative peak intensities of Si-H and N-H bonds are representative of the compositional change in the $SiN_x$ network, we suggest that the combination of R and the plasma power can control the composition over a wide range.

The composition parameter, $x$ = [N]/[Si], in the solid film was calculated using the integrated areas of the characteristic peaks, as follows [7]:

$$[Si] = \frac{1}{4}\,[I_{Si\text{-}N}+I_{Si\text{-}H}] + \frac{1}{2}\,I_{Si\text{-}Si} \quad \text{and} \qquad (1)$$

$$[N] = \frac{1}{3}\,[I_{N\text{-}H} + I_{Si\text{-}N}] \qquad (2)$$

wherein $I_{Si\text{-}N}$, $I_{Si\text{-}H}$, $I_{Si\text{-}Si}$, $I_{N\text{-}H}$, and $I_{Si\text{-}N}$ are the integrated

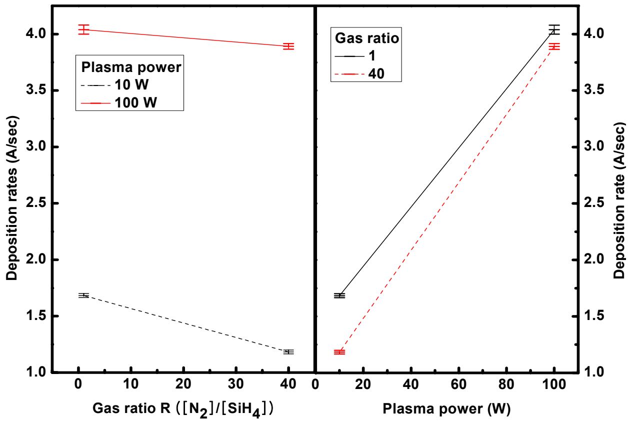


**Fig. 1.** Change in Deposition rates with the gas mixing ratio and the plasma power.

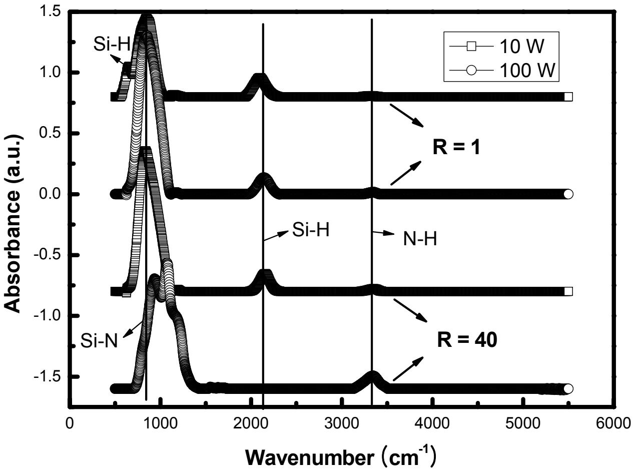


**Fig. 2.** FTIR spectra of $SiN_x$ films presented in Fig. 1.

intensities of the bonding types indicated in the subscript, respectively.

Figure 3 shows the change in composition parameter, *x*, with the plasma power and the gas mixing ratio. The combination of the plasma power and the gas mixing ratio may yield a wide range of film composition from $x = 0.83$ to $x = 1.62$. When the plasma power was high, the resulting film exhibited a higher *x* than the low-power film deposited from the same R. A high plasma power would enhance dissociation of the nitrogen gas, and incorporation of atomic nitrogen into the growing network could be increased accordingly. This observation indicates that the composition of low-temperature $SiN_x$ films can be controlled from silicon-rich to nitrogen-rich in accordance with specific applications, by controlling the plasma power and the gas mixing ratio.

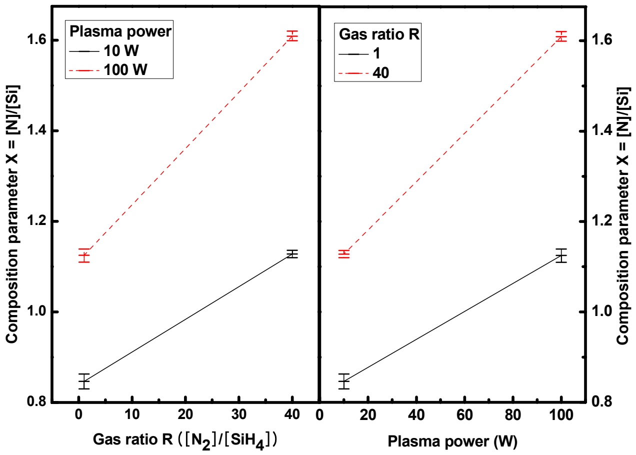


**Fig. 3.** Change in the composition parameter with the plasma power and the gas mixing ratio R.

Figure 4 shows PL spectra of $SiN_x$ films presented in Figures 2 and 3. The NRSN film ($x = 1.62$) showed characteristic peaks at 400 and 500 nm. These peaks were identified to be dangling bonds of N and Si, respectively. On the other hand, SRSN films ($x = 1.11$ and 1.12) have a peak at 690 nm. This peak corresponded to a band-to-band transition in nano-size silicon particles [8]. The extremely silicon-rich film ($x = 0.83$) had several peaks in the range of 800 ~ 900 nm, in addition to N and Si dangling bond peaks. The PL peaks in the long-wavelength range corresponded to band-to-band transition inside silicon particles either of amorphous phase or of nano-crystalline clusters.

The substantial difference in the film microstructures, as suggested by the PL spectra, implies that these films may exhibit various electrical characteristics. It also implies that, by controlling the process parameters, the dielectric properties of the $SiN_x$ films can be designed.

Figure 5 shows the PL spectra of the SRSN films prepared at various values of R. When R was increased from 5 to 20, the total flow rate, process pressure, substrate temperature and plasma power were fixed at 40 sccm, 0.5 torr, 200°C and 30 W, respectively. As the gas mixing ratio R increased, the wavelength that corresponded to the center of the silicon peak decreased from 700 to 610 nm. Due to the quantum confinement effect, the optical band gap of the nc-Si depended on the size of the nc-Si [9]. An increase in $N_2$ in the source gas could have decreased the size of the

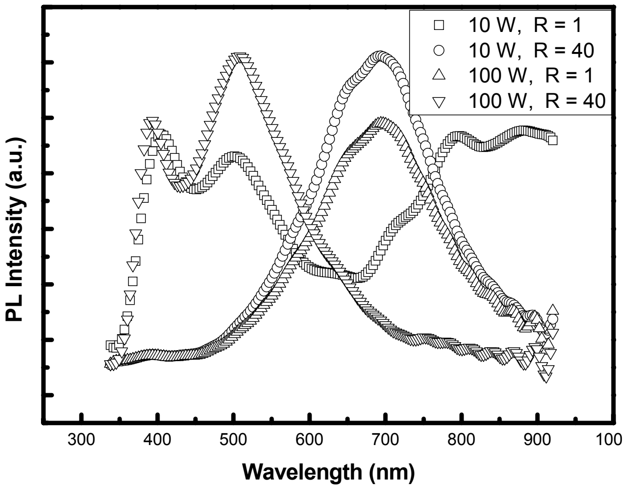


**Fig. 4.** The PL spectra of $SiN_x$ films deposited at various conditions.

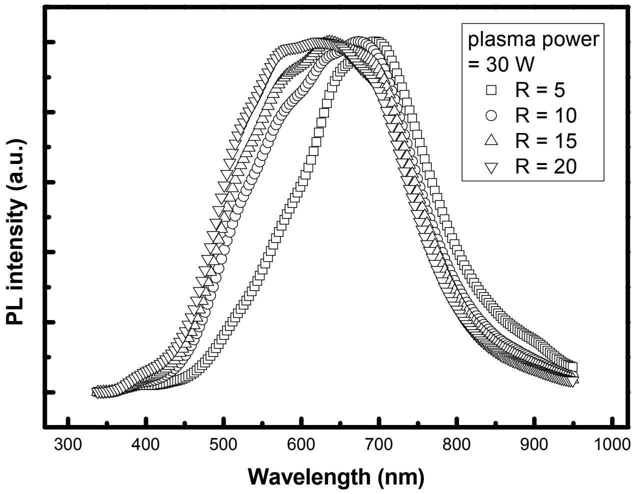
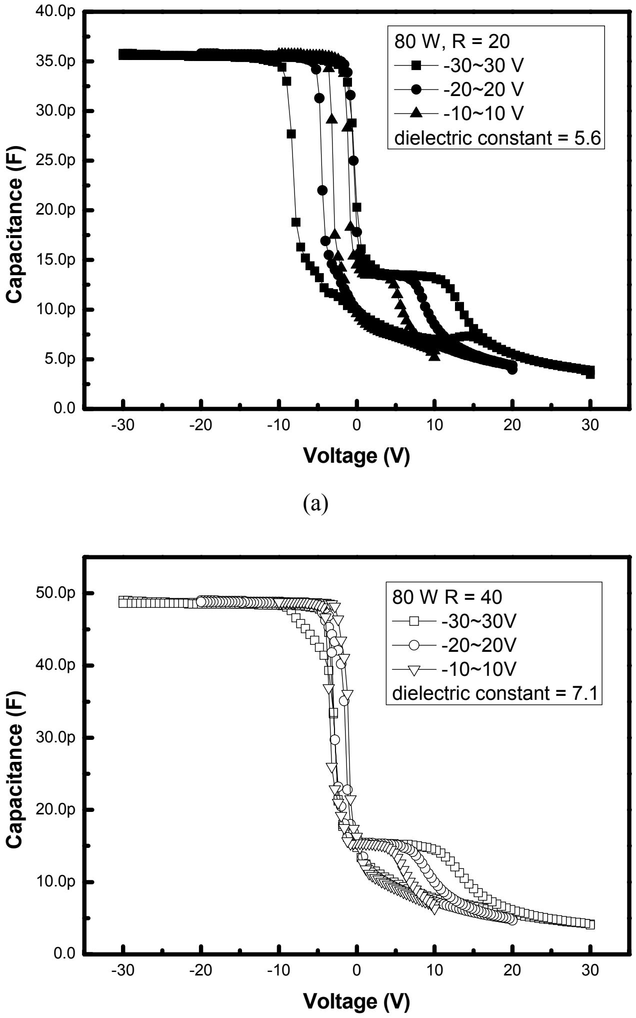


**Fig. 5.** The PL spectra of Si-rich $SiN_x$ films deposited at various R values.

nc-Si particles inside the SRSN film. Therefore, this result suggests that the size of the nc-Si inside the SRSN film can be controlled by changing the gas mixing ratio R. If this material is applied to electro-luminescence, control of the color of the emitted light would be possible by changing R.

Figure 6 shows the C-V measurement results of the NRSN films produced at two different values of R, 20 and 40. When R = 20, the C-V characteristic curve showed a significant hysteresis behavior, which was asymmetric at about V = 0. The shift in the accumulation-depletion transition increased as the sweep voltage range increased from ±10V to ±30V. When R increased to 40, however, the hysteresis window was reduced. The dielectric constant also increased from 5.6 to 7.1 as R increased. This result implies that increasing R may produce a film that is low in dangling bond and high in atomic packing density.



(a)

(b)

**Fig. 6.** Capacitance-voltage characteristics of the nitrogen-rich $SiN_x$ films at (a) R = 20 and (b) R = 40.

## 4. Summary

The composition of the low-temperature $SiN_x$ films could be controlled over a wide range by varying the source gas mixing ratio R and the plasma power. In the silicon-rich $SiN_x$ films, the composition parameter $x$ decreased to 0.83 as R and the plasma power decreased. The PL spectra of these films showed a characteristic peak in the silicon band-to-band transition, which suggests the existence of nano-sized silicon particles inside the silicon nitride matrix. The increase in R shifted the center of this peak to a shorter wavelength, which indicates the average size of the nano particles. The nitrogen-rich $SiN_x$ films were deposited at a high plasma power and a high R. As R increased from 20 to 40, the dielectric constant increased from 5.6 to 7.1 and the hysteresis in the C-V characteristics was reduced significantly.

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