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*Original Scientific Article*

# Low Temperature Deposition of $SiN_x$ Thin Films by the LPCVD Method†

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*Abstract.* Thin silicon rich nitride ($SiN_x$) films were deposited using the LPCVD (Low Pressure Chemical Vapor Deposition) method. Silane diluted in argon and ammonia were used as the reactant gasses, and the low temperature deposition at 570 °C was used. The films were deposited on silicon (111) substrates. Films with the different values of the nitrogen content were deposited by varying the ratio of the flows of ammonia and silane in the horizontal tube reactor. The films were characterized in terms on the surface quality (by scanning electron microscopy), in terms of the nitrogen content $x$ by time of flight elastic recoil detection analysis and by Raman and FTIR spectroscopy. The thickness and dielectric constant were measured by ellipsometry. The films were found to have a very smooth, homogeneous surface with nitrogen content that vary from $x = 0$ to $x = 1$ in dependence on the deposition parameters. The intensity of the Si–N stretching peak has shown strong correlation with the film thickness measured by ellipsometry. The films showed a smooth surface layer and the value of dielectric constant easily controllable by the ratio of the flow of the gases in the reactor. (doi: 10.5562/cca1970)

*Keywords:* silicon nitride, thin film, LPCVD method, Raman, FTIR

## INTRODUCTION

Silicon nitrides are materials which have a very promising perspective for applications in microelectronics and optoelectronics. While having very good mechanical (Young modulus 300 GPa) and thermal properties (heat resistant up to 1850 °C) they can also be used to produce very low loss waveguides for the optoelectronic industry[1] because of its high index of refraction ($n = 2$). In addition to stoichiometric silicon-nitride(Si3N4), silicon rich nitride ($SiN_x$, $0 < x < 4/3$) is also an interesting material for the optoelectronic industry because of its photoluminescence properties.[2] One of the methods to produce silicon nitride and silicon-rich nitride is the process of Low Pressure Chemical Vapor Deposition (LPCVD) by the reaction of silane ($SiH_4$) and ammonia ($NH_3$). Actually when depositing silicon-rich nitride two processes are taking place at the same time:

a) the thermal decomposition of silane

$$SiH_4(g) \rightarrow Si(s) + 2H_2(g) \quad (1)$$

b) the deposition of silicon nitride

$$3SiH_4(g) + 4NH_3(g) \rightarrow Si_3N_4(s) + 12H_2(g) \quad (2)$$

Depending on the temperature of the deposition the deposited amorphous silicon thin film is either amorphous ($T < 600$ °C), polycrystalline (600 °C $< T <$ 900 °C) or monocrystalline ($T > 900$ °C). Depending on the partial pressure of the gasses entering the reactor either stoichiometric silicon nitride ($Si_3N_4$) or non-stoichiometric silicon rich nitride ($SiN_x$, $0 < x < 4/3$) can be deposited.

## EXPERIMENT

The silicon-rich nitride thin films were deposited using the LPCVD method on silicon substrates. Ammonia and silane diluted in argon (26 % $SiH_4$, 74 % Ar) were used

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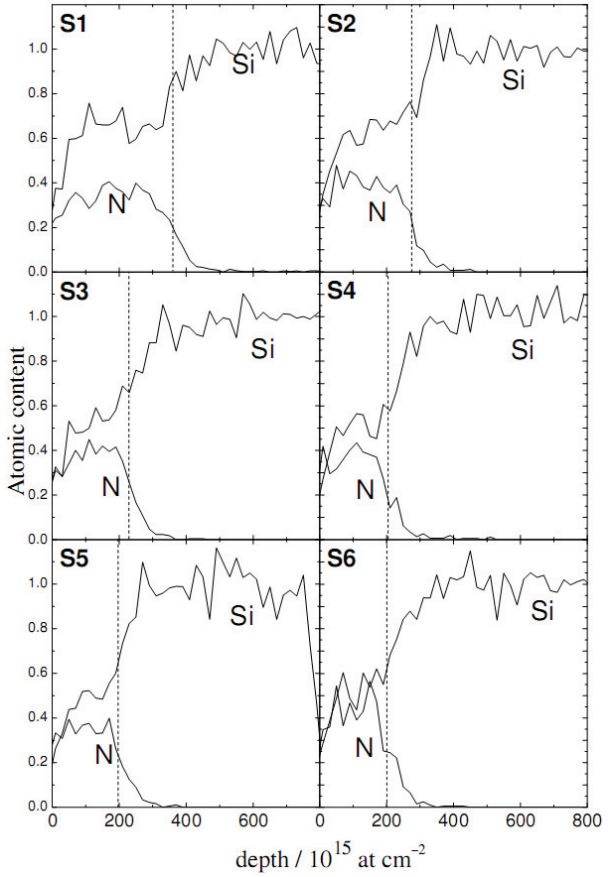


**Figure 1.** The TOF-ERDA depth profiles of nitrogen and silicon in samples **S1**–**S6**. The dashed line indicates the border between the $SiN_x$ film and the silicon substrate.

as reactant gasses. The depositions were made at the temperature of 570 °C and the time of each deposition was 30 minutes. The partial pressure of the diluted silane was kept constant at the gas flow of 310 cm$^3$ min$^{-1}$ while the flow of ammonia was varied to obtain films with different nitrogen content *x*. The details of the LPCVD reactor used are given elsewhere.[3] Six samples were produced labeled **S1**–**S6** representing ammonia flows of 16, 25, 34, 43, 52 and 61 cm$^3$ min$^{-1}$ respectively. The Raman spectra were recorded using Horiba Jobin Yvon T6400 Raman spectrometer. The 514.5 nm

**Table 1.** The thickness *d* and the nitrogen content *x* of the samples **S1**–**S6**

| Sample | *d* / nm | *x* |
|---|---|---|
| **S1** | 57 ± 5 | 0.55 ± 0.05 |
| **S2** | 41 ± 4 | 0.64 ± 0.07 |
| **S3** | 34 ± 3 | 0.75 ± 0.08 |
| **S4** | 31 ± 3 | 0.74 ± 0.08 |
| **S5** | 29 ± 3 | 0.73 ± 0.08 |
| **S6** | 29 ± 2 | 0.86 ± 0.08 |

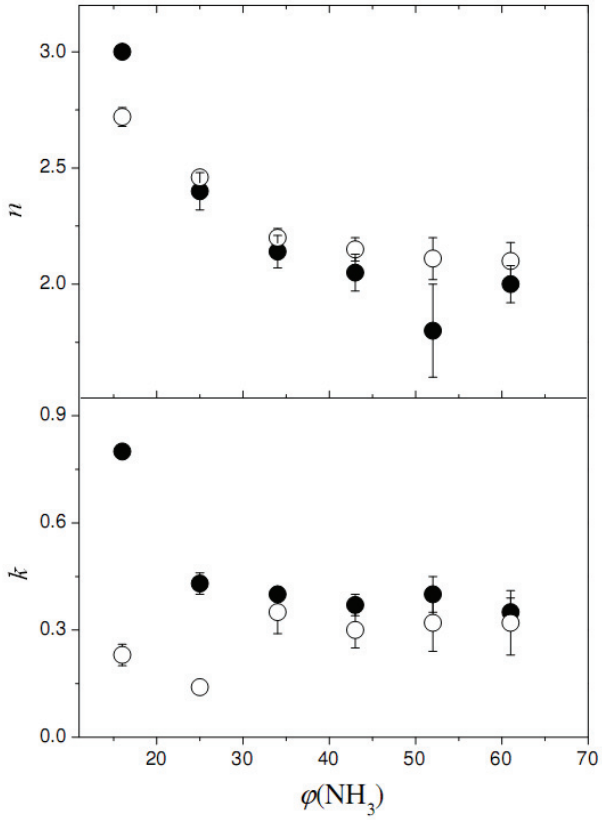


**Figure 2.** The real *n* and imaginary *k* part of the refractive index of the deposited samples as determined by ellipsometry; full circles at 405 nm and open circles at 632.8 nm.

line of the Coherent argon ion laser was used for the excitation of the samples. The infrared absorption spectra were made using the Perkin Elmer, Spectrum GX Fourier Transform Infrared (FTIR) spectrometer. The TOF-ERDA measurements were made using a 20 MeV beam of $^{81}Br^{5+}$ ions with the angle of incidence of 10° in relation to the surface of the samples. The SEM images were taken with a FE-SEM JEOL 7000F scanning electron microscope. The AUTO EL IV ellipsometer at the wavelengths of 405 and 632.8 nm was used for the measurements of both – the thicknesses and the refractive indices of deposited thin films.

## RESULTS

The TOF-ERDA measurements are presented in Figure 1. From the TOF-ERDA spectra the mean nitrogen content *x* in the samples and the mean thickness of the layer were calculated and are reported in Table 1. An increase of the nitrogen content and an decrease of the film thickness with the increase of the flow of ammonia are clearly visible. The decrease of the thickness is probably due to the fast reaction of silane and ammonia taking place at the beginning of the reactor tube because of

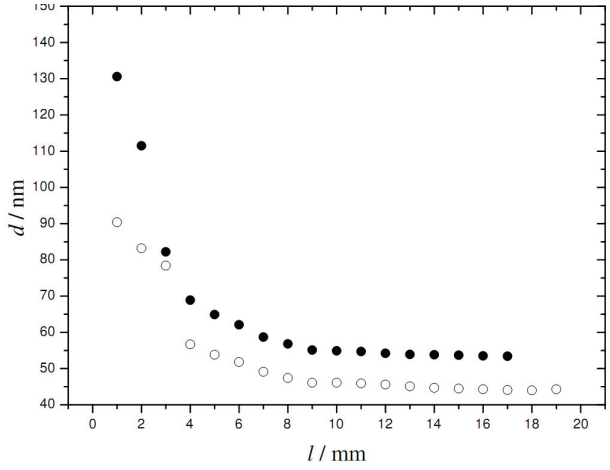


**Figure 3.** The thickness $d$ in dependence on the distance $l$ of the measure point to the edge of the sample **S2**. Full circles at 632.8 nm and open circles at 405 nm.

which less reactant gasses reach the substrates that are placed in the middle of the reactor tube. Ellipsometry was used to determine the thicknesses and the refractive indices of the deposited thin films at the wavelengths of 405 nm and 632.8 nm and are reported in Figure 2. A clear decrease of both the real and imaginary part of the refractive index with the increase of the ammonia flow is observed. This is to be expected since the higher the nitrogen content the closer the refractive index gets to the index of refraction of stoichiometric $Si_3N_4$ which is $n = 2$, $k = 0$. For the sample **S1** the real part and for samples **S1** and **S2** also the imaginary parts of the refractive index are clearly higher at 405 nm than at 632.8 nm. This is to be expected since the refractive index of amorphous silicon is much higher at 405nm than at 632.8 nm while the refractive index of $Si_3N_4$ is almost constant in the visible range. If we approximate the

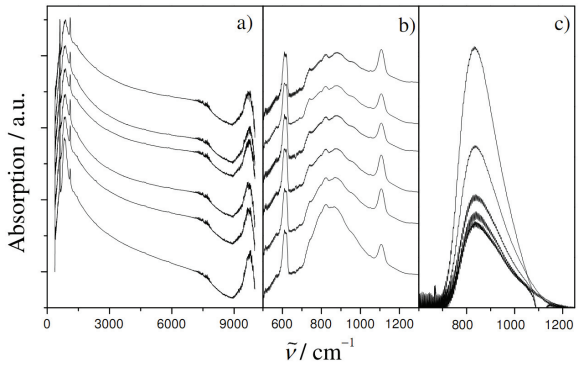


**Figure 4.** IR spectra of the samples: a) whole IR spectra from 0 to 10000 cm$^{-1}$; b) an expanded area of the spectra from 500 to 1300 cm$^{-1}$; c), Si–N stretching mode after subtraction of the background. In all three subfigures the spectra are of the samples **S1**–**S6** from below to above.

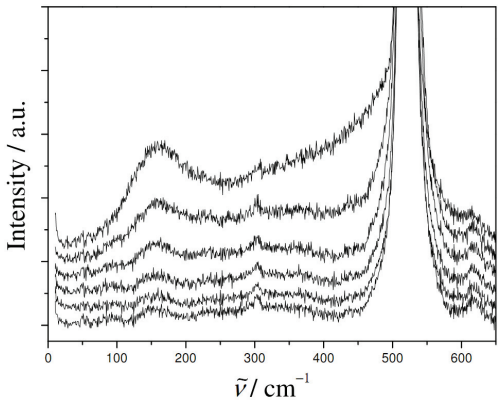


**Figure 5.** The Raman spectra of the samples **S1**–**S6**, from above to bellow respectively.

silicon-rich nitrides as a mixture of amorphous silicon and silicon-nitride[4] it follows that the lower the nitrogen content, the higher the content of the amorphous silicon phase in the samples and therefore the higher the difference between the measured refractive indices at 405 and 632.8 nm. This effect is also visible in Figure 2. Note that the values of the refractive indices shown in Figure 2 are the values measured in the centre of the samples (samples were deposited on circular silicon wafers). The thickness and the refractive index of the films were found to vary in dependence on the distance of the measured point from the edge of the substrate. The thickness variation in dependence on the position on the sample for the samples **S2** is shown in Figure 3. The thickness of the films clearly decreases from the edge of the samples towards the center, becoming almost constant in the centre. This is because the reactant gasses reach the centre of the samples by diffusion which insures a homogenous thickness, while near the edge of the samples part of the direct flow of the gasses reaches the substrates causing the deposited film to be much thicker than in the centre of the samples. The thicknesses in the centre were found to be in good agreement with the values obtained by the TOF-ERDA method. The infrared spectra are reported in Figure 4. Two sharp peaks around 610 cm$^{-1}$ and around 1100 cm$^{-1}$ which belong to the absorption of the silicon substrate with thin oxide layer on the top on which the $SiN_x$ layers were deposited are observed as well as a broader peak at around 840 cm$^{-1}$ which corresponds to the absorption of the Si–N stretching mode. In Figure 4c) the spectrum of the bare silicon substrate was subtracted from the measured spectra so that a pure spectrum of the deposited film can be seen. A decrease of the intensity of the Si–N stretching peak intensity with the increase of the nitrogen content in the samples can be observed. This is in agreement with the already mentioned decrease of the samples thickness with the increase of the nitrogen content observed by both TOF-ERDA and ellipsometry.

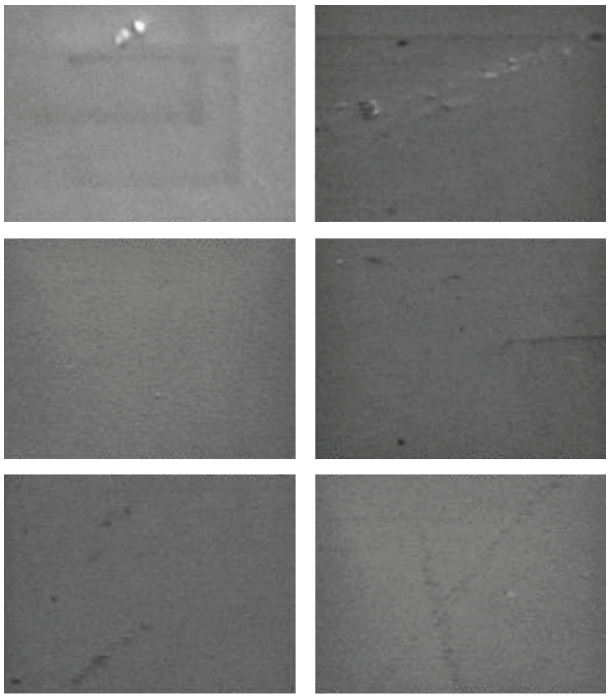

**Figure 6.** The SEM images of samples **S1** (top left), **S2** (top right), **S3** (middle left), **S4** (middle right), **S5** (bottom left) and **S6** (bottom right).

The Raman spectra are reported in Figure 5. A broad band corresponding to the TA vibration band is present around 160 $cm^{-1}$, and the LO vibration band can be seen around 410 $cm^{-1}$, although it is greatly overshadowed by the much more intense optical phonon peak of the crystalline silicon substrate on which the samples were deposited. Because the thickness of the deposited films is much less then the penetration depth of light in the samples (for the values of the imaginary part of the refractive index given in Figure 2 the penetration depth in the visible is from 100 to 400 nm depending on the sample) and because the Raman scattering cross section is much higher for crystalline than for amorphous silicon, the dominant feature in the measured Raman spectra is the Raman spectra of the substrate. However the presence of the broad TA vibration peaks leads to the conclusion that the deposited samples are mainly amorphous, although it is impossible to be absolutely certain that no silicon nano-crystals are present in the samples since their Raman spectra would overlap with the one from the substrate. To ascertain these depositions on different types of substrates (for example silica) need to be made. The SEM images are shown in Figure 6. All images show a very smooth surface with no sign of microscopic substructures. The spots on the images are actually small particles of dust which were deliberately brought into field of view and were used to focus the image. The absence of any microscopic substructure suggests very low surface roughness of the samples which is an important characteristic for use in microelectronics and optoelectonics.

## CONCLUSION

Silicon-rich nitride thin films were deposited on silicon wafers. They were found to have very good surface quality (no microscopes structure was noticed on the SEM images) and their nitrogen content was found to vary from 0.55 to 0.86. A wider range of the values of the flow of ammonia are planned to be used in future depositions to produce silicon-rich nitrides in the full range of values of the nitrogen content ($0 < x < 1.33$).

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