

# **Bonding structure and hydrogen content in silicon nitride thin films deposited by the electron cyclotron resonance plasma method**

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## **Abstract**

The bonding structure and hydrogen content of amorphous hydrogenated silicon nitride ( $a\text{-SiN}_x\text{:H}$ ) thin films have been investigated by infrared spectroscopy and ion beam techniques. Electron cyclotron resonance plasma enhanced chemical vapor deposition was used to produce these films under different values of gas flow ratio, deposition temperature, and microwave power.

The amount of bonded hydrogen was calculated from the N-H and Si-H infrared absorption bands. An increase of the  $\text{SiH}_4$  partial pressure during deposition was found to have the same effect on the H content as an increase of the substrate temperature: both cause a decrease of the N-H bond density and an increase in the number of Si-H bonds. This is explained by a competitive process in the formation of N-H and Si-H bonds during the growth of the film, whereby Si-H bonds are favored at the expense of N-H bonds when either the  $\text{SiH}_4$  flow or the substrate temperature are increased. Such tendency to chemical order is compared with previous results in which the same behavior was induced by thermal annealing or ion beam bombardment.

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## 1. Introduction.

The need for high- $k$  dielectrics in the microelectronics industry has led to intensive research in a number of materials with potential applications as gate dielectrics in complementary metal-oxide-semiconductor (CMOS) transistors [1]. This is motivated by the continuous downscaling of the channel length into the 100 nm range, which requires a reduction of gate oxide thickness to 1.5-2.0 nm in order to maintain the transconductance of the device. In this ultrathin range Boron penetration from the  $p^+$ -polysilicon gate and hot-electron effects degrade the lifetime of the device. Many ultrathin (<3 nm) silicon dioxide films are now nitrated in order to reduce those effects and prolong the lifetime of the device.

However, as the thickness of the nitrated silicon dioxide is further decreased, gate leakage (direct and Fowler-Nordheim tunneling currents) through the dielectric layer becomes a major concern. Higher-permittivity dielectric films, which could be made thicker with capacitances equivalent to those of the ultrathin oxides, are being sought to reduce the leakage currents.

Silicon nitride and/or oxynitride alloys are the preferred candidates to reach the equivalent oxide thickness between 1 and 1.5 nm that will be needed for 70 nm channel lengths, while scaling down to the 50 nm node will require alternative dielectrics of even higher values of  $k$ , such as  $Ta_2O_5$  or  $TiO_2$ .

But the applications of silicon nitride are not limited to CMOS gate dielectrics. Silicon nitride has been widely used as passivation and protection layer due to its low permeation to alkali and small ions [2]. In solar cells and photodiodes those properties are combined with the choice of refractive index and thickness to form an antireflection coating. And in thin film transistors (TFTs) silicon nitride is the dielectric of choice for the gate structure of these devices due to its better interface properties with amorphous or polycrystalline silicon [3, 4].

The aim of this paper is to contribute to the understanding of the structural properties of silicon nitride and the role played by the hydrogen atoms which are incorporated during the growth of the film. The amount of hydrogen depends on the method of deposition and the precursor gases, and because of this hydrogen the chemical composition of silicon nitride is better described as  $SiN_x:H$ . In the present work we will study the evolution of the hydrogen content with deposition conditions and compare it with the evolution resulting from thermal treatments and ion beam bombardment. From this analysis we will be able to propose a network bond reaction driven by the tendency to maximum bonding energy.

## 2.- Experimental procedure.

The  $\text{SiN}_x\text{:H}$  films which are the subject of this study were obtained using an electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD) system (Plasma Technology AMR) equipped with a load-locked vacuum chamber and pumped by a Leybold turbomolecular pump capable of reaching base pressures of  $10^{-7}$  Torr [5]. Electronic grade nitrogen and silane were used as precursor gases. Nitrogen was introduced into the ECR chamber as the plasma gas, while silane entered into the deposition chamber through a gas dispersal ring.

The substrates were p-type silicon wafers suitable for infrared spectroscopy. They were subjected to standard RCA cleaning steps ending with a diluted  $\text{HF:H}_2\text{O}$  (1:10) solution to remove superficial oxide. After a final deionized water rinse and drying with nitrogen they were introduced into the deposition chamber. Different sample series were deposited with a constant  $\text{N}_2$  gas flow of 50 sccm and  $\text{SiH}_4$  flows ranging between 2 and 5 sccm, so that the  $\text{N}_2/\text{SiH}_4$  gas flow ratio (referred as  $R$  in the following) had values between 10 and 25. We concentrate our study on three deposition temperatures ( $T_d$ ): 230 °C, 310 °C and 470 °C. Microwave power ( $P$ ) was 200 W for these three series, but an additional set of samples varying  $P$  between 300 W and 500 W was also prepared. In this latter case  $R$  was kept constant at 12.5 ( $\text{SiH}_4$  flow of 4 sccm) and  $T_d$  was 470 °C.

All samples were analyzed by Fourier transform infrared spectroscopy (FTIR) with a Nicolet Magna-IR 750 spectrometer. The spectra were taken in transmission mode at normal incidence. After subtracting the spectrum of the silicon substrate, the three well known absorption bands of  $\text{SiN}_x\text{:H}$  at  $3340\text{ cm}^{-1}$  (N-H stretching),  $2155\text{ cm}^{-1}$  (Si-H stretching) and  $830\text{-}890\text{ cm}^{-1}$  (Si-N stretching) were studied. From the Si-H and N-H stretching bands the concentrations of bonded hydrogen ( [Si-H] and [N-H] ) were determined using the well-known calibration factors originally obtained by Lanford and Rand [6] and confirmed by some of us in a recent work using a different calibration technique [7].

The samples were also subjected to composition measurements with ion beam techniques. By Rutherford back-scattering spectroscopy (RBS) we determined the nitrogen to silicon ratio, while the total hydrogen content could be measured separately by elastic recoil detection analysis (ERDA). In both cases we used 1.5 MeV  $\text{He}^+$  ions: in RBS at a scattering angle of  $160^\circ$  and in the case of ERDA at  $26^\circ$  [8].

### 3. Results.

Figure 1 shows the density of bonded hydrogen calculated from the infrared absorption bands of the Si-H and N-H bonds. We plot in this graph the results corresponding to the series deposited at the substrate temperatures of 230 °C and 470 °C. The trends are clear and indicate that the density of N-H bonds increases as the N<sub>2</sub> to SiH<sub>4</sub> gas flow ratio is increased (i.e. as the SiH<sub>4</sub> flow decreases), while the density of Si-H bonds follows the opposite trend. Higher values of deposition temperature have the same effect as increasing the SiH<sub>4</sub> flow: they produce a decrease in the number of N-H bonds and an increase in [Si-H].

As to the Si-N absorption band, its peak position (wavenumber at maximum absorption) is related to the N-H concentration due to the higher electronegativity of hydrogen with respect to silicon. The vibration frequency of a chemical bond is directly related to the electronegativity of the nearest neighbors due to the attraction that they exercise on the electronic cloud of the bond. This produces a shortening of the bond length, which in its turn causes an increase in the oscillation frequency. In figure 2 we have done a plot of the Si-N wavenumber as a function of gas flow ratio for the three different temperatures. There is a clear correlation with the N-H bond concentration of figure 1.

In order to emphasize the relation between the Si-N wavenumber and the N-H bond concentration we have compiled in figure 3 all the data corresponding to the different series that have been studied. Three of these series have the N<sub>2</sub> to SiH<sub>4</sub> flow ratio as deposition variable and correspond to three different substrate temperatures: 230 °C, 310 °C, and 470 °C, while the fourth series has the microwave power as the variable and correspond to a deposition temperature of 470 °C. The effect of increasing the microwave power on [N-H] and [Si-H] is analogous to increasing the N<sub>2</sub> to SiH<sub>4</sub> gas flow ratio, because higher values of  $P$  mean a higher proportion of nitrogen species activated by the plasma (this has been corroborated by Langmuir probe measurements [8]).

### 4. Discussion.

The opposite trends followed by the N-H and Si-H bond densities have been observed in previous works by some of us as a function of annealing temperature [9] and ion beam bombardment [7]. In those works the infrared absorption bands were studied for different sample series subjected to rapid thermal annealing (RTA) treatments at temperatures ranging between 300 °C and 1050 °C and irradiated with heavy ions at fluences between 10<sup>11</sup> and 10<sup>14</sup> cm<sup>-2</sup>. Those results were explained by network bond reactions taking place at different temperature ranges or activated by the ion irradiation. Such chemical reactions are driven by

the tendency for maximum bonding energy (stronger bonds are favored at the expense of weaker bonds). Therefore the energy balance of those reactions is exothermic, although they need an activation energy that was provided by the thermal annealing process or by the ion beam.

In the present study we observe that a similar behavior takes place during the growth process as a function of two different variables:  $R$  (precursor gas flow ratio) and  $T_d$  (substrate temperature). Increasing the  $\text{SiH}_4$  flow during the deposition (i.e. decreasing  $R$ ) has the same effect as increasing the substrate temperature: both favor Si-H bonds at the expense of N-H bonds. It seems as if the  $\text{SiH}_4$  flow and the temperature were acting as limiting factors for the formation of Si-H bonds. Once any of these variables is increased, the Si-H concentration increases at the expense of the number of N-H bonds.

The chemical reaction that explains this behavior is illustrated in figure 4 and it is given by the following equation:



This is a well-known [10] network bond process favored by the tendency to chemical order, whereby the formation of Si-H and Si-N bonds is favored at the expense of Si-Si and N-H bonds. Taking into account nominal bond energies [11, 12] this process is exothermic, with a favorable energy balance of 0.25 eV.

The bond scheme drawn in figure 4 might illustrate how reaction (1) proceeds in a near stoichiometric environment such as that of the samples being analyzed here. An interesting point of discussion is the nitrogen atom electronic orbital hybridization. In the initial situation it is bonded to two silicon atoms and one hydrogen atom, and the most stable configuration is the  $sp^3$  tetrahedral hybridization [13, 14]. In the final situation the nitrogen will be bonded to three silicon atoms as a consequence of the bond interchange reaction. In this case, the interaction between the doubly occupied  $p_z$  nonbonding orbital perpendicular to the bond plane and the internal  $d$  orbitals of the three silicon atoms makes the  $sp^2$  planar hybridization of the nitrogen atom highly stable [13, 15]. Such interaction receives the name of  $p_\pi-d_\pi$  and it is known to occur only in the N-Si<sub>3</sub> and N-Ge<sub>3</sub> bonding, giving them a characteristic planar geometry in contrast with the more usual tetrahedral hybridization of nitrogen.

The chemical reaction given by equation (1) does not produce any change in composition, only in chemical configuration. Nevertheless, the results of the measurements of atomic concentration by RBS-ERDA indicate a slight decrease of the N/Si ratio (denoted as  $x$  in the chemical formula) and of the H atomic percent (at%) when increasing the  $\text{SiH}_4$  flow

(i.e. when decreasing  $R$ ). For the series deposited at 310 °C,  $x$  decreases from 1.6 to 1.2 as the  $\text{SiH}_4$  flow increases from 2 sccm to 5 sccm, while the atomic percent of hydrogen decreases from 24.7 to 18.4 at% in that same interval. For the other two series the trends are similar [8]. This is mainly due to an increase in the number of Si atoms, being the number of N atoms roughly constant, and it is consistent with a decrease of the N-H bond concentration that is more significant than the corresponding increase of the Si-H bond density (figure 1).

## 5. Conclusions.

The formation of Si-H and N-H bonds appear as a competitive process during the growth of  $\text{SiN}_x\text{:H}$  films. When the  $\text{SiH}_4$  flow or the substrate temperature are increased Si-H bonds are favored at the expense of N-H bonds. The behavior of the N-H bond density is corroborated by changes in the Si-N infrared band peak wavenumber, which shifts to lower values when the N-H concentration decreases.

The substitution of N-H bonds with Si-H bonds is driven by the tendency for chemical order or maximum bonding energy, whereby stronger bonds are favored at the expense of weaker bonds according to a well known network bond reaction originally proposed by Yin and Smith [10]. The same behavior has been observed in previous experiments where  $\text{SiN}_x\text{:H}$  samples were irradiated with high energy beams of heavy ions [7] or subjected to rapid thermal annealing treatments [9].

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## REFERENCES

- <sup>1</sup> D. A. Buchanan, IBM Journal of Research and Development **43** (1999) 245.
- <sup>2</sup> I. A. Ross, Proceedings of the IEEE **86** (1998) 7.
- <sup>3</sup> T. P. Ma, IEEE Trans. Electron Devices **45** (1998) 680.
- <sup>4</sup> S. S. He, M. J. Williams, D. J. Stephens, G. Lucovsky, J. Non-Cryst. Solids **164-166** (1993) 731.
- <sup>5</sup> S. Summers, H. S. Reehal, G. H. Shirkooshi, J. Phys. D **34** (2001) 2782.
- <sup>6</sup> W. A. Lanford, M. J. Rand, J. Appl. Phys. **49** (1978) 2473.

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- <sup>7</sup> W. Bohne, W. Fuhs, J. Röhrich, B. Selle, G. González-Díaz, I. Mártil, F. L. Martínez, A. del Prado, *Surf. Interface Anal.* **30** (2000) 534.
- <sup>8</sup> L. Wang, H. S. Reehal, F. L. Martínez, E. San Andrés, A. del Prado, *Semicond. Sci. Technol.* **18** (2003) 633.
- <sup>9</sup> F. L. Martínez, A. del Prado, I. Mártil, G. González-Díaz, W. Bohne, W. Fuhs, J. Röhrich, B. Selle, I. Sieber, *Phys. Rev. B* **63** (2001) 245320.
- <sup>10</sup> Z. Yin, F. W. Smith, *Phys. Rev. B* **43** (1991) 4507.
- <sup>11</sup> I. N. Levine, *Physical Chemistry*, McGraw-Hill, New York, 1988.
- <sup>12</sup> F. W. Smith, Z. Yin, *J. Non-Cryst. Solids* **137-138** (1991) 871.
- <sup>13</sup> G. Lucovsky, Z. Zing, D. R. Lee, *J. Vac. Sci. Technol. B* **14** (1996) 2832.
- <sup>14</sup> Z. Jing, G. Lucovsky, J. L. Whitten, *J. Vac. Sci. Technol. B* **13** (1995) 1613.
- <sup>15</sup> N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984.

## Figure Captions

**Figure 1.** N-H and Si-H bond densities versus precursor gases flow ratio. Closed symbols correspond to N-H bond densities, while open symbols refer to Si-H concentrations. Two different sample series are considered corresponding to deposition temperatures of 230 °C (squares) and 470 °C (triangles). Lines are guides for the eye. Error bars are an estimate of 10 % uncertainty in the calculation of FTIR band areas.

**Figure 2.** Wavenumber at absorption peak of the Si-N stretching band versus precursor gases flow ratio. The data correspond to three sample series deposited with three different substrate temperatures: 230 °C, 310 °C and 470 °C. Lines are a guide for the eye.

**Figure 3.** Correlation between the Si-N peak wavenumber and the N-H bond density. This graph compiles the data from the three series deposited at different substrate temperatures and an additional series in which the microwave power used to ignite the plasma was varied.

**Figure 4.** Schematic illustration of the trend for chemical order, whereby the Si-H and Si-N bonds are favored at the expense of Si-Si and N-H ones as predicted by the free-energy model of Yin and Smith. In the present work this behavior is observed as the SiH<sub>4</sub> gas flow or the substrate temperature are increased.



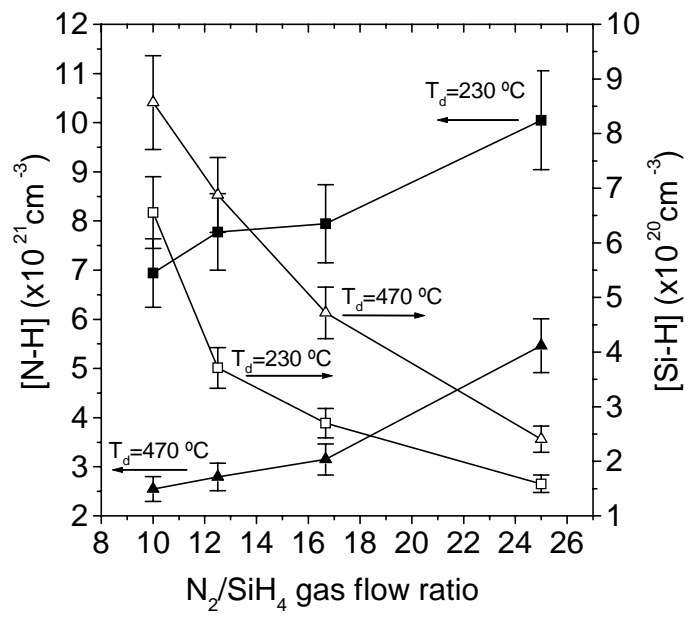


Figure 1

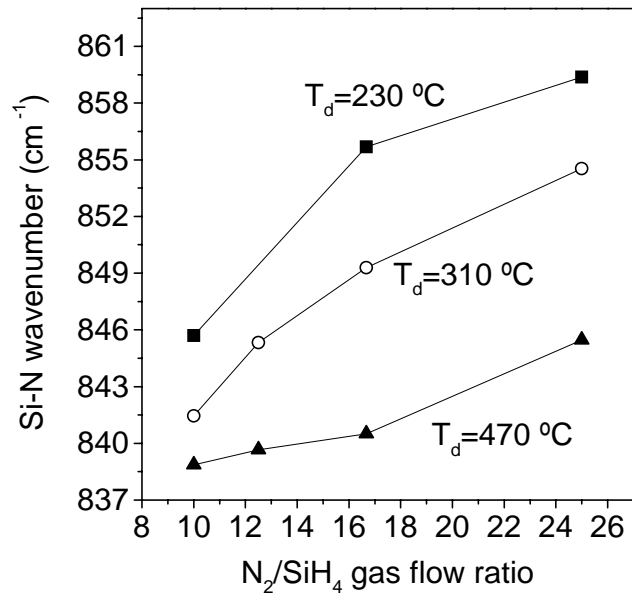


Figure 2

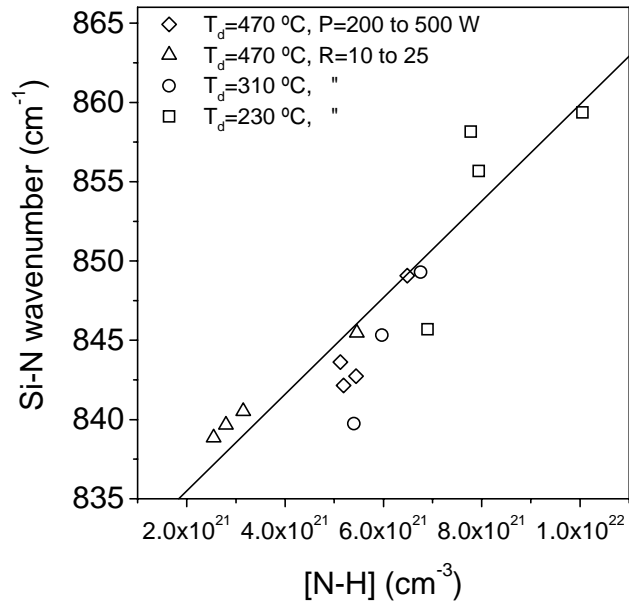


Figure 3

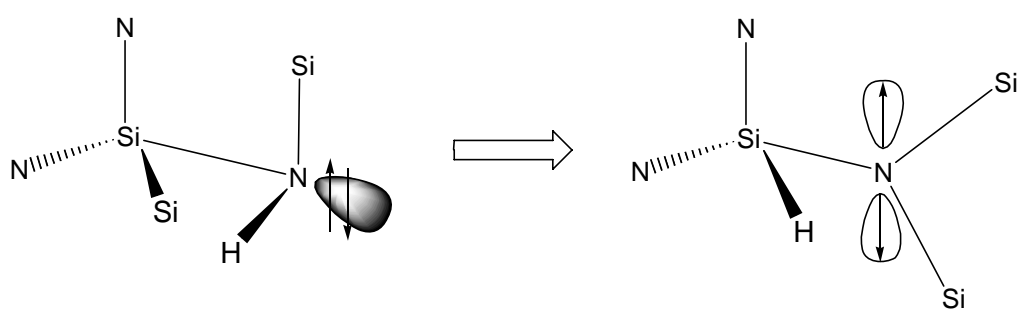


Figure 4