

concentrations of these traps are large enough to affect the carrier generation lifetime.

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Kinetics and Compositional Dependence on the Microwave Power and SiH₄/N₂ Flow Ratio of Silicon Nitride Deposited by Electron Cyclotron Resonance Plasmas

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ABSTRACT

Silicon nitride layers have been deposited at a low temperature, 150°C, in an electron cyclotron plasma from nitrogen and silane as gas precursors. Deposition conditions have been varied in a wide range. Nitrogen flows from 25 to 400 sccm and silane flows from 2.5 to 35 sccm have been used in our experiments. The microwave power was varied from 100 to 1500 W. The result of the nitride growth kinetics show strong dependence on the silane to nitrogen flow ratio and on the microwave power. For large flow ratios and small powers the kinetics exhibits a nearly linear behavior whereas for low flow ratios and high powers a saturated regime was observed. Ellipsometry, infrared spectroscopy, and etch rate studies showed that the best material quality, 95% Si₃N₄, is obtained in the saturated regime for the lowest flow ratios and the highest powers used.

Silicon nitride is a material widely used in microelectronics as interlevel isolation dielectrics, capping layers, and also for gate dielectrics in metal-nitride-oxide-silicon (MNOS) devices, thin film transistors (TFT), and storage capacitors for dynamic random access memories (DRAMs). Ultralarge scale integration (ULSI) fabrication is a continuously demanding processes with a decreasing thermal budgets. The trend toward low deposition temperatures and high deposition rates has prompted previous efforts in developing new plasma enhanced chemical-vapor-deposition (PECVD) processes.

Radio frequency (RF)¹⁻³ and microwave (MW) plasmas^{1,4,5} have been used to deposit silicon nitride at low temperatures from SiH₄ and N₂¹⁻⁴ or NH₃.^{1,3} Most of the processes are based on SiH₄/NH₃ mixtures since it was found that SiH₄/N₂ process is less controllable.⁶ However, the use of silane and ammonia gives rise to a large hydrogen incorporation in the grown layers. In order to reduce the N-H bond concentration, monoethylamine, NH₂CH₃, has been proposed as an alternative precursor to NH₃.⁵ Even with SiH₄/N₂ RF plasmas N-H bonds were observed in the layers,^{1,2} although in concentrations lower than with SiH₄/NH₃ mixtures.¹ Up to present, only very low deposition rates of silicon nitride from SiH₄/N₂ MW plasmas have been reported.³

Electron cyclotron resonance (ECR) plasma is a very attractive method for producing high quality dielectrics at low temperatures. Using SiH₄ and N₂ as precursors, this method has been applied to deposit silicon nitride layers with very small N-H bonds concentrations. The Si₃N₄ de-

posited by this method exhibited high density, good etch resistance, and low hydrogen content.⁷⁻¹²

In this paper we report studies on growth kinetics of ECR deposited Si₃N₄ in a wide variety of deposition conditions and the properties of the deposited films in relation to the kinetics and deposition conditions.

Experimental

The silicon nitride layers were deposited in a "low profile" ECR plasma reactor from Plasma Quest (Model 357) with a background pressure in the reaction chamber below 10⁻⁷ Torr. The main difference between this system and the standard "mirror" configuration consists in that one of the electromagnets has been moved to the neighborhood of the sample holder in order to collimate the plasma column.^{10,14} In this way, better ion current uniformity and thickness homogeneity may be obtained.¹⁰

One of the precursor gases, N₂, was introduced directly into the resonance zone and forms the plasma. A second gas entrance enables the introduction of the reactive gas, 5% argon-diluted SiH₄, just above the sample. The reaction chamber was evacuated to the background pressure prior to sample loading and the working pressure was maintained constant and in the range from 1 to 10 mTorr during deposition in all the experiments. In this pressure range and with this gas inlet configuration, the reaction between gas precursors and nucleation inside the plasma are prevented and, thus, highly compact layers may be obtained.

The nitrogen flow was changed in wide margins, from 400 sccm in the upper range to the lowest values, about

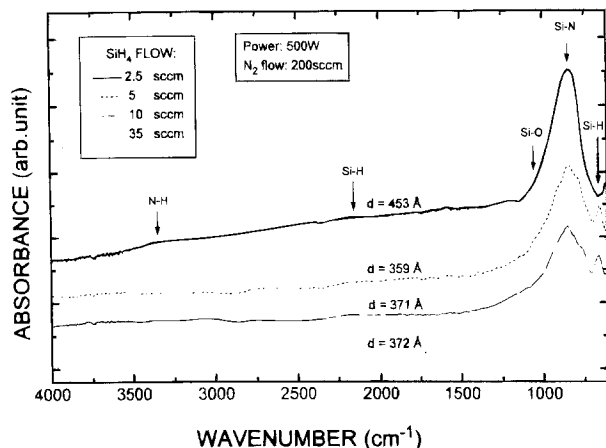


Fig. 1. Reflection mode FTIR spectra of nitride layers realized with 500 W of microwave powers, 200 sccm N_2 flow, and silane flows from 2.5 to 35 sccm.

25 sccm that enabled the maintenance of a stable plasma. The silane flow, indicated as pure gas through all the text, was varied between 2.5 to 35 sccm. The effect of varying microwave power from 100 to 1500 W on the growth rate and layers composition was also studied. During the deposition the sample holder was maintained at a temperature below 150°C by means of an externally controlled circulating bath.

The silicon nitride layers were deposited on (100) p-type 3 in. silicon slices. Just before loading in the vacuum chamber, the substrates were degreased and the native oxide removed with a buffer etch.

The as grown layers were characterized by means of reflection Fourier transform infrared (FTIR) spectroscopy to identify the vibrational modes of the different bonds present in the material.

The dielectric constants of the samples were measured by spectroscopic ellipsometry over an energy range of 1.5 to 4.5 eV. An air-film-substrate structure with varying composition and thickness of the layers was used to simulate the experimental spectra. The optical data of the different layers were taken from the literature.¹³ The thicknesses of the best fits to the experimental spectra were taken as measures. The dielectric constants of the silicon nitride layers in the 1.5 to 3.2 eV range were obtained using the numerical procedure previously described.¹⁴ In this energy range experimental errors in the ellipsometric angles are very low and enable a good numerical inversion of the ellipsometric equations. The thicknesses obtained in this way were checked in some of the sample series with etched step heights measured by means of a profilometer. A good agreement between direct measurements and the thicknesses of the simulated structures was obtained in all the checked samples. Thickness homogeneity of some films was also tested with a profilometer, and it resulted in better than 4% in 3 in. wafers in all the checked samples.

A freshly prepared H_3PO_4 (85%) solution at 160°C was used to measure the etch rate of the layers deposited under different conditions. Simultaneously, Si_3N_4 films grown by standard high temperature chemical vapor deposition (HTCVD) process were etched to give a comparison. These HTCVD silicon nitride layers were deposited at 820°C from $NH_3:SiH_2Cl_2$ (2.5:1) mixtures.

Results

Infrared characterization.—In order to have a qualitative idea of possible contamination and the presence of unwanted bonds in the layers, FTIR measurements have been performed in one of the sample series. In this series, we have maintained fixed a microwave power of 500 W and 200 sccm of nitrogen flow, while the SiH_4 was varied between 2.5 and 35 sccm. Figure 1 shows four of these spectra obtained in samples deposited with different SiH_4 flows. A freshly prepared Si substrate was used as a reference mir-

ror to get the system response. For ease of discussion later in this paper, the thicknesses of the layers obtained from ellipsometry are also included in the figure. In all of these spectra, the band associated with the stretching mode, 850 to 890 cm^{-1} , of the Si-N bond is clearly seen.¹⁵ This band and the thickness of the layer increase as the SiH_4 flow used in deposition decreases. In the high energy side of the band, a shoulder at around 1050 cm^{-1} related with the Si-O band¹⁵ may be observed. This shoulder is specially evident in the sample deposited with the largest SiH_4 flow. This band might be associated with the unavoidable presence of a native oxide layer at nitride-silicon interface. However, because a native oxide layer typically has a thickness of only a few tens of angstroms and because the thicknesses of all the layers are similar, this argument may not support the strong difference between the samples deposited with the largest and the lowest silane flows. Chamber wall degassing during deposition may give rise to oxygen contamination and be responsible for the presence of the Si-O band. A small shift of the Si-N band toward higher energies, specially clear in the sample deposited with the largest SiH_4 flow, may be observed. This shift may be due not only to the geometrical effects of the increasing Si-O shoulder but also to partial substitution of N atoms by oxygens. These are more electronegative than nitrogen, and thus may give rise to bond shortening and small increases of the vibration frequency.¹⁶

Only small traces, of N-H and Si-H stretching vibrations at around 3350 and 2160 cm^{-1} frequencies, respectively,¹⁷ may be detected in some of the spectra. The peak at around 650 cm^{-1} present in samples grown under silane-rich conditions may be due to rocking and waving modes of the Si-H band.^{18,19} Spencer *et al.*¹⁰ have performed transmission mode IR measurements in layers thicker than ours, and they observed that, in changing the SiH_4/N_2 ratio from 0.035 to 0.015, the stretching Si-H to N-H band ratio was inverted and changed from 5:1 to 1:5 while the total hydrogen band content remains unchanged and approximately equal to 5%. In our experiments, the flow ratio was varied from 0.175 to 0.015, however, we do not observe any appreciable change in the stretching Si-H to N-H band ratio. It is important to note that although our experiments cover the flow ratio range used by Spencer *et al.*,¹⁰ silane flows are larger in our case.

Ellipsometry.—Ellipsometric measurements allowed us to check the quality of the ECR Si_3N_4 layers. We simulate the layers with a mixed composition of pure Si_3N_4 , amorphous silicon, and some voids to check how compact the layers are. The dielectric constants of Si_3N_4 and amorphous silicon have been taken from the literature.²⁰ We have not included oxide in the layer composition because only in the worst cases does it seem to be important and because its effect in this energy range is rather similar to void inclusion and the fittings are not sensitive to the relative percentage of both components. Using an air/ Si_3N_4 /Si structure we got the thicknesses and composition of several sample series deposited under different conditions. Figure 2 shows the film quality, percent of Si_3N_4 , vs. pure SiH_4 flow with the microwave power as a parameter. The layer composition became 95% pure Si_3N_4 increasing the microwave power and decreasing the SiH_4 flow. A wide range of powers get acceptable compositions of the film. The films exhibited richness up to 75% of Si_3N_4 for most of powers when the SiH_4 flow was under 20 sccm. Only for the worst conditions of both low power and large silane flow ellipsometric fits detected the presence of amorphous silicon. In these cases the amorphous silicon content is indicated in the figure. The remaining layers are exclusively composed by Si_3N_4 and voids. This seems to suggest that most of our experiments have been realized under defect of silane.

Because of the presence of voids, we have tried to improve the compactness of the layers with a thermal treatment at 900°C for 1 h. After this annealing no differences in thickness could be detected. Therefore, this low temperature ECR plasma process gets highly dense silicon nitride films.

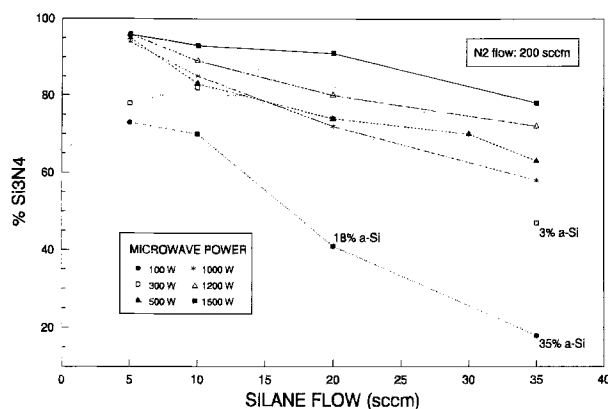


Fig. 2. Si_3N_4 content as a function of the SiH_4 flow of different samples series realized with 200 sccm of N_2 and microwave powers from 100 to 1500 W. Amorphous silicon content is indicated only for the samples in which it is appreciable.

In order to know under which conditions the N_2 flow is a critical parameter of the process, six new series of samples were made. The nitrogen flow was varied from 200 sccm to the minimum value at which it is possible to maintain a stable plasma, 25 sccm. In these series the silane flows were 5 or 35 sccm and the microwave powers 500, 1000, and 1500 W. In the four sample series deposited with 1000 and 1500 W no appreciable changes in the quality of the layer nor in the growth rate were observed for all the N_2 flow range explored. Figure 3 shows the percentage of Si_3N_4 in the two series deposited with a microwave power of 500 W. As can be seen, in the samples deposited with 5 sccm of SiH_4 , the change of the nitrogen flow does not significantly affect the quality of the nitride film. On the contrary, with 35 sccm of SiH_4 , layers deposited with N_2 flows below 500 sccm became poor in Si_3N_4 whereas the amorphous silicon and void contents increased. These results suggest that for large microwave power, it does not matter how large the nitrogen flow is, however, for small power and large SiH_4 flows a minimum nitrogen flow is required to consume all the silane arriving at the sample surface and thus to obtain better stoichiometric nitride films. Regarding the deposition rate, even for the samples deposited with 500 W and 35 sccm of SiH_4 , no significant differences were observed by changing the nitrogen flow, and, in any case, they were below 4%.

In the sample series used for IR measurements, we have numerically inverted the ellipsometric equations to get the refractive index of the isolated nitride layer.¹⁴ Figure 4 shows the refractive index in the 1.5 to 3.2 eV range of the different films. The refractive index of a HTCVD silicon nitride layer, also included in Fig. 4 for reference, fits well with the standard values of 100% pure Si_3N_4 .²⁰ A good

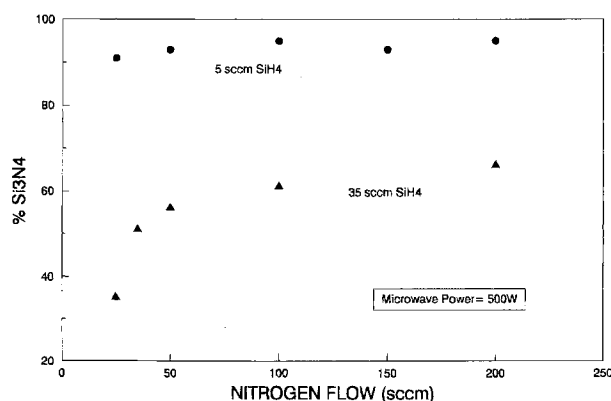


Fig. 3. Si_3N_4 content vs. N_2 flow of two sample series realized with 5 and 35 sccm of SiH_4 .

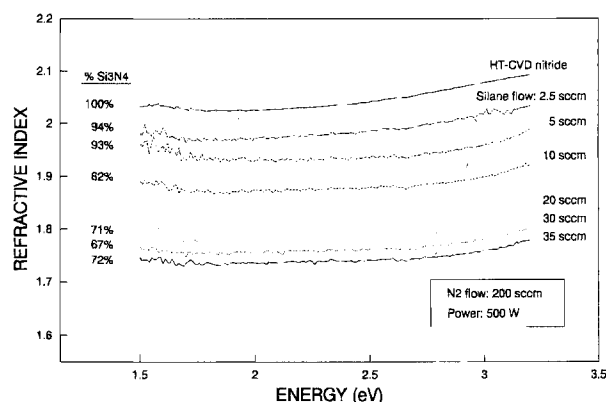


Fig. 4. Energy dependence of the refractive index of nitride layers deposited with 500 W, 200 sccm of N_2 , and SiH_4 flows from 2.5 to 35 sccm. Refractive index of a HTCVD nitride layer is included. Percentages of Si_3N_4 estimated from ellipsometry of each layer are indicated in the left margin.

correlation between the quality of the layers and the obtained refractive index may be seen.

Taking as a reference the refractive index at the He-Ne wavelength (6328 Å) a best value of $n = 1.97$ is obtained for the 94% Si_3N_4 layer as compared with $n = 2.03$ obtained at the same energy in the HTCVD layer. For this energy, the refractive indexes of ECR silicon nitride layers referenced in the literature^{4,7,9-11} lie between 1.8 to 2.5 depending on the particular deposition conditions. All of these authors observe that the refractive index depends critically on the SiH_4/N_2 flow ratio. In generation, an increase of this ratio results in an increase of the refractive index, reaching values above two when the silane flow exceeds a certain value, giving rise to a strong increase in the amorphous silicon incorporated to the layer.⁹ As can be seen in Fig. 4, in no case we have got refractive indexes over 2.0. Moreover, the refractive index decreased when the silane flow is increased. This behavior is coincident with the Si_3N_4 richness of the layers with the only exception of the 35 sccm SiH_4 flow in which this trend is inverted.

Growth kinetics.—With the thicknesses obtained from ellipsometric measurement the deposition rates in a wide range of experimental conditions may be obtained. The Si_3N_4 growth rates varied from 150 Å/min up to 3500 Å/min depending on the experimental conditions. Series with a fixed nitrogen flow of 200 sccm and varying silane flows, from 2.5 to 35 sccm are chosen to draw the dependence of the deposition rate with the microwave power as shown in Fig. 5. To add to the following discussion, an additional series using 400 sccm N_2 flow has also been included in this figure. As can be seen the deposition rate increases for

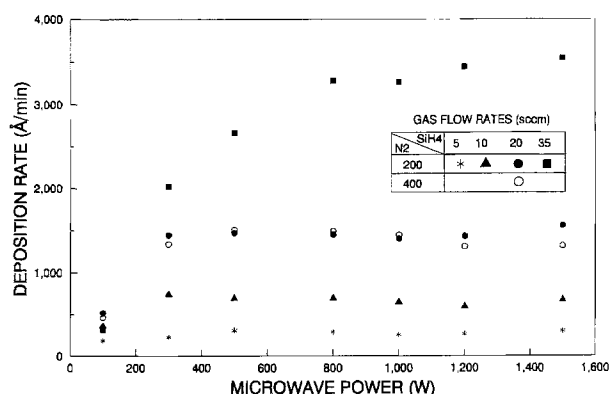


Fig. 5. Deposition rate vs. microwave power with the SiH_4 as a parameter. Two series with 20 sccm of SiH_4 and different N_2 flows, 200 and 400 sccm, are included.

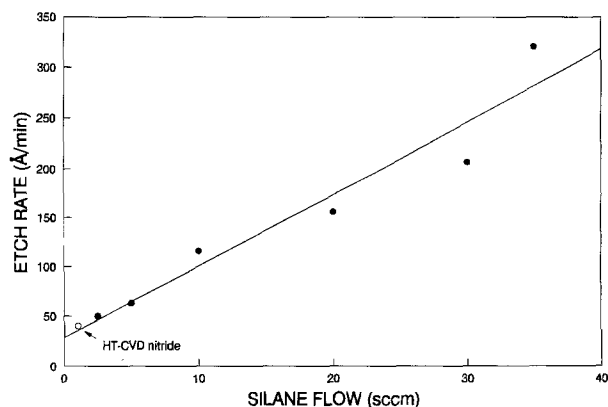


Fig. 6. Etch rate vs. silane flow of a sample series deposited with 200 sccm of N_2 and 500 W.

small increasing microwave powers and come to a saturation value for large power values. This saturation is not clearly seen for the largest value of the silane flow. A similar behavior, an initial rise of the deposition rate and a trend to saturation with increasing powers, has been observed by some authors,^{7,10} while another author⁹ only observed a linear increase of the microwave power. The deposition rate for which the kinetics curves become saturated does not depend on the nitrogen flow. This is supported by the fact that the sample series deposited with 400 sccm of N_2 is practically indistinguishable from that deposited with 200 sccm N_2 flow and the same silane flow, 20 sccm. The power value for which the kinetic curve becomes saturated is different for every SiH_4 flow. However, if we divide the SiH_4/N_2 flow ratio by the minimum value of the microwave at which the curve becomes nearly saturated, roughly the same value, $\geq 10^{-4} W^{-1}$ is obtained for any curve. This seems to suggest that once enough ions or activated nitrogen atoms are supplied to consume the silane molecules arriving at the surface, an additional increase of the microwave power or the nitrogen flow do not result in an increase of the deposition rate.

Etch rate.—Another standard test of the layer quality is to compare the etch rates with those of a well-known material, for example, HTCVD silicon nitride. An H_3PO_4 solution (85%) at $T = 160^\circ C$ was used for nitride etching. Samples for etch rate measurement were deposited under the same experimental conditions, 500 W and 200 sccm of N_2 , as those for refractive index measurements. The only difference was that these samples were considerably thicker than those used for ellipsometry in order to enable an accurate determination of the etch rate. As it can be seen in Fig. 6 the lowest etch rates, close to the HTCVD nitride values, were obtained for the smallest silane flows used. This quality trend is completely analogous to that observed with the refractive index (see Fig. 4).

Discussion

In any plasma reactor an important parameter is the ratio between the pressure and the RF or MW power which gives a measure of the plasma activation capability. Here the pressure is an indirect measure of the arrival rate of reactive species to a surface. At low pressure, as in our case, where precursors collisions inside the plasma are rather unlikely, an alternative measure of the arrival rate may be the flows of the different precursors. Further, in our case the reactive gas was introduced downstream and thus, probably, most of the growth occurs via surface reactions. The fact that the deposition rate tends to zero when the density of activated N_2 species decreases seems to support this argument. Thus, we have chosen the SiH_4/N_2 flow ratio normalized by the minimum value of the microwave power to reach the saturation regime, to give a characteristic parameter of our reactor. Although only a qualitative idea of this parameter can be extracted from Fig. 5, an estimated value of about $10^{-4} W^{-1}$ may be given.

Ellipsometric, infrared, and etch rate measurements also seem to support the above arguments. To obtain nearly stoichiometric nitride films small silane to nitrogen flow ratios are required. This has been previously suggested by Tsu *et al.*²¹ The microwave power plays also an important role because by increasing the power, the density of activated species seems to increase.

With the above arguments in mind we may propose the following simple deposition scheme: (i) silane molecules or activated silane radicals are absorbed at the silicon surface and (ii) nitrogen ions or activated nitrogen molecules impinge at the surface reacting with the absorbed silane species and causing hydrogen release.

This last step is also supported by the fact that negligible Si-H bonds were detected by IR measurements and only in the worst cases large silane flows and low microwave powers (see Fig. 2), ellipsometric measurements give account of appreciable amorphous silicon contents.

Conclusions

Silicon nitride layers close to the stoichiometric composition, 95% pure Si_3N_4 , have been obtained by ECR plasmas using N_2 and 5% argon-diluted silane. Depending on the experimental conditions, deposition rates ranging from 150 to 350 Å/min were obtained. The deposition kinetics depend critically on the SiH_4/N_2 flow ratio and the microwave power. For large flow ratios the deposition rate seems to increase more or less linearly for small increasing microwave powers and becomes saturated for large powers. This suggests that most of the growth occurs via surface reactions promoted by nitrogen ions or activated atoms.

Present result shows that nearly stoichiometric nitride films may be obtained in the saturation regime, low SiH_4/N_2 flow ratio, and high microwave powers.

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