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Low-Temperature Hydrolysis (Oxidation) of Plasma-Deposited Silicon Nitride Films

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Plasma-deposited silicon nitride films formed under different temperature and gas composition conditions were hydrolyzed in a saturated water vapor environment at 85 °C. The extent of hydrolysis was measured by monitoring the change in the Si–O–Si absorbance area at $\sim$1070 cm^{-1} with a Fourier transform infrared spectrometer. Films deposited at electrode temperatures below 250 °C and films formed at high NH_3:SiH_4 flow ratios had significant hydrolysis rates. The hydrolysis of the films was linear with time and occurred at the oxide/nitride interface. N–H bond concentration and film density were the primary factors affecting the hydrolysis rate.

Introduction

Plasma-deposited (PD) silicon nitride has been widely used in the semiconductor industry as both a passivation layer and as a metal-isolation layer. Particularly when applied as a passivation layer, such films must display excellent resistance to water diffusion and oxidation (or hydrolysis).[1,2] At elevated temperatures (>900 °C), chemically vapor deposited (CVD) and even hot pressed silicon nitride converts to silicon dioxide under an O_2 or H_2O ambient condition, albeit slowly.[3-11] The proposed reaction mechanisms involve the substitution of oxygen for nitrogen:[11]

$$Si_3N_4 + 6H_2O \rightarrow 3SiO_2 + 4NH_3 \qquad (1)$$

$$Si_3N_4 + 3O_2 \rightarrow 3SiO_2 + 2N_2 \qquad (2)$$

Since the PD silicon nitride is of lower quality than CVD silicon nitride, due to lower density, nonstoichiometric composition, and high hydrogen concentration, it is expected that PD silicon nitride films will hydrolyze at a greater rate than CVD silicon nitrides. Indeed, the hydrolysis rate for PD silicon nitride has been reported to be 3.5 nm/h in steam at 1200 °C.[12] While this rate is equivalent to that of CVD silicon nitride, it must be remembered that at 1200 °C, the PD nitride film anneals, thus increasing the density and decreasing the film hydrogen content (i.e., film quality approaches that of a CVD nitride). No mention was made of the exact deposition conditions in ref 12, although it appears that the deposition temperature was 300 °C and a mixture of $NH_3/N_2/SiH_4$ was used. It is likely that the hydrolysis rate for these films would be much higher if film properties did not change during hydrolysis.

Surface hydrolysis of both PD and CVD silicon nitrides has also been observed.[11,13-15] An oxide $\sim$1.0 nm thick formed on the surface of a PD nitride exposed to ambient conditions.[15] Furthermore, oxide thicknesses up to 0.9 nm were observed on CVD silicon nitride films exposed to air for 1 month.[11]

Plasma nitrides are known to contain large quantities of hydrogen bonded to both silicon and nitrogen.[15-26] Annealing studies have shown that the hydrogen is unstable and leaves the film upon heating.[22-25] It is possible that these low-stability sites might also be attacked by hydrolysis. Indeed, in a study on the high-temperature hydrolysis of CVD silicon nitride, the hydrolysis rate depended on the N–H concentration.[3] In a separate study, remote PD silicon nitride films with high concentrations of N–H bonds hydrolyzed rapidly.[26]

When hydrolyzed, nitride film integrity is affected since hydrolysis converts silicon nitride into a silicon oxynitride or a silicon oxide. The ability of the nitride to protect underlying device structures from water and alkali-metal ion contaminants is thus compromised.

In the present study, we report the effects of low-temperature hydrolysis on PD silicon nitride films. Hydrolysis at low temperature was chosen to minimize film property changes. Both nitride deposition temperature and gas-phase composition were varied to study chemically different plasma silicon nitride layers and to determine primary factors affecting the hydrolysis rate. Fourier transform infrared spectroscopy (FTIR) was used to measure the hydrolysis rate and to determine hydrogen concentration within the film.

Experimental Procedure

Silicon nitride films were deposited in a stainless steel, parallel-plate reactor with 3-in.-diameter electrodes. The upper electrode was powered, and the lower electrode, upon which the

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(1) van De ven, E. P. G. T. *Solid State Technol.* **1981**, *24* (4), 167.
(2) Sinha, A. K.; Levinstein, H. J.; Smith, T. E.; Quintana, G.; Haszko, S. E. *J. Electrochem. Soc.* **1978**, *125*, 601.
(3) Chramova, L. V.; Smirnova, T. P.; Ayupov, B. M.; Belyi, V. I. *Thin Solid Films* **1981**, *78*, 3030.
(4) Singhal, S. C. *J. Am. Ceram. Soc.* **1976**, *59*, 81.
(5) Hench, L. L.; Freiman, S. W. *J. Mater. Sci.* **1981**, *16*, 2767.
(6) Lieb, S.; MacCrone, R. K.; Theimer, J.; Maby, E. W. *J. Mater. Res.* **1986**, *1*, 792.
(7) Harai, T.; Niihara, K.; Goto, T. *J. Am. Ceram. Soc.* **1980**, *63*, 419.
(8) Horton, R. *J. Am. Ceram. Soc.* **1969**, *52*, 121.
(9) Enomoto, T.; Ando, R.; Morita, H.; Nakayam, H. *Jpn. J. Appl. Phys.* **1978**, *17*, 1049.
(10) Singhal, S. C. *J. Mater. Sci.* **1976**, *11*, 500.
(11) Raider, S. I.; Flitsch, R.; Aboaf, J. A.; Pliskin, W. A. *J. Electrochem. Soc.* **1976**, *123* (4), 560.
(12) Kern, W.; Rosler, R. S. *J. Vac. Sci. Technol.* **1977**, *14*, 1082.
(13) Madden, H. H. *J. Electrochem. Soc.* **1981**, *128* (3), 625.
(14) Maguire, H. G.; Augustus, P. D. *J. Electrochem. Soc.* **1972**, *116* (6), 791.
(15) Claassen, W. A. P.; Valkenburg, W. G. J. N.; Habraken, F. H. P. M.; Tamminga, Y. *J. Electrochem. Soc.* **1983**, *130*, 2419.
(16) Claassen, W. A. P.; Valkenburg, W. G. J. N.; Willemsen, M. F. C.; Wijgert, W. M. v. d. *J. Electrochem. Soc.* **1985**, *132*, 893.
(17) Lanford, W. A.; Rand, M. J. *J. Appl. Phys.* **1978**, *49*, 2473.
(18) Chow, R.; Lanford, W. A.; Ke-Ming, W.; Rossler, R. S. *J. Appl. Phys.* **1983**, *53*, 5630.
(19) Mar, K. M.; Samuelson, G. M. *Solid State Technol.* **1980**, *23* (4), 137.
(20) Adams, A. C. *Solid State Technol.* **1983**, *26* (4), 135.
(21) Nguyen, V. S.; Lanford, W. A.; Reiger, A. L. *J. Electrochem. Soc.* **1986**, *133*, 970.
(22) Reinberg, A. R. *J. Electron. Mater.* **1979**, *8*, 345.
(23) Stein, H. J.; Wells, V. A.; Hampy, R. E. *J. Electrochem. Soc.* **1979**, *126*, 1750.
(24) Maeda, M.; Nakamura, H. *J. Appl. Phys.* **1985**, *58* (1), 484.
(25) Budhani, R. C.; Binshah, R. F.; Flinn, P. A. *Appl. Phys. Lett.* **1988**, *52*, 284.

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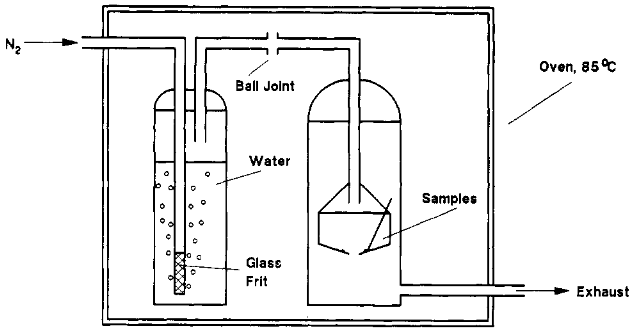

Figure 1. Schematic of the hydrolysis apparatus.

samples were placed, was resistance heated. An electrode separation of 3.8 cm was used. All films were deposited at a pressure of 300 mTorr, 10 W of radio frequency power at 13.5 MHz, and a total flow rate of 60 sccm by using mixtures of ammonia (NH_3) and 10% silane (SiH_4) in helium. Substrate temperatures from 200 to 350 °C were used. Gas composition was varied from 50:1:9 to 5:5.5:49.5 NH_3:SiH_4:He. Deposition temperatures were measured with a thermocouple inserted into a thermowell in the lower electrode.

The PD silicon nitride films were deposited onto p-type (100) silicon wafers. Film thicknesses used in the hydrolysis study were approximately 100–140 nm. Density measurements were performed by depositing "thick" nitride films of 1–2 μm, determining the thickness with an ellipsometer and an interferometer, and measuring the weight change by using a Mettler microbalance. The density measurements were consistent with previously reported results.[2] Films ~300–350 nm thick were used for hydrogen concentration measurements.

X-ray photoelectron spectroscopy (XPS) was invoked to ascertain the ratio of nitrogen to silicon in the films by integration of the Si 2p and N 1s peak areas. The plasma reactor was connected through a series of load locks to a Kratos XSAM 800 surface (XPS) analysis system. Compositional analyses were performed on films deposited in the plasma reactor and then transferred under vacuum to the analysis system. This transfer apparatus will be described in a future publication. Due to the vacuum transfer process, ion milling (to clean the surface) was not needed prior to sample analysis. Al Kα X-rays were used for excitation in the XPS analysis. The sample surface was angled at 15° from the normal with respect to the analyzer, and the chamber pressure was $<10^{-9}$ Torr during the analysis. X-ray sensitivity factors were obtained from ref 27.

XPS sputter depth profiling was performed on some of the hydrolyzed films. A Kratos macrobeam, with 4-keV Ar^+ ions at a chamber pressure of 5×10^{-6} Torr, was used to sputter the samples. The sputter depth was estimated by ellipsometry, and a constant sputter rate of ~0.8 nm/min was assumed.

Figure 1 shows the hydrolysis apparatus employed in this study. The hydrolysis chamber consisted of a glass water bubbler and a glass vessel into which the silicon nitride films were loaded. A saturated water stream, created by bubbling gaseous nitrogen through a glass frit immersed in water, was brought into contact with the silicon nitride samples. Both the bubbler and the samples were placed inside a constant-temperature oven maintained at 85 °C. Typical hydrolysis times of 100–200 h were used.

FTIR spectra of the films were obtained with a Mattson Instruments Cygnus 25 at 8-cm^{-1} resolution. FTIR data were analyzed by using IR spectra of the unhydrolyzed silicon nitride films as the background spectra.[28] In this manner, difference spectra were obtained from which the Si–O absorbance at 1070 cm^{-1} was measured. Difference spectra were necessary since the Si–O stretch overlaps the N–H absorbance at 1170 cm^{-1}. The spectra were subsequently base-line corrected, and the Si–O absorption area was integrated over the range 1250–970 cm^{-1}. The most serious difficulty with this method of measuring Si–O absorbance area relates to the overlap between the Si–O absorbance and the N–H absorbance and to a much lesser extent to the overlap between the Si–O absorbance and the Si–N (850 cm^{-1}) absorbance. If the N–H peak decreases in size while the Si–O peak increases, the difference Si–O peak area will be smaller than the true Si–O peak area by the change in N–H peak area. Fortunately, the change in N–H absorbance area was small compared to the change in Si–O absorbance. Thus, although the integrated Si–O absorbance area is not precise, the increase in Si–O area provides a qualitative measurement of the extent of film hydrolysis.

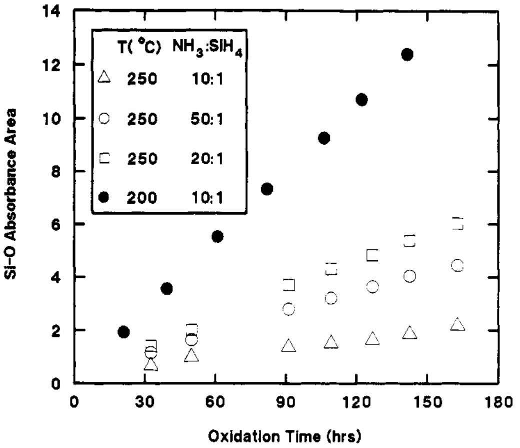

Figure 2. Si–O absorbance area vs hydrolysis time. Deposition conditions: NH_3:SiH_4 flow ratio 10:1; pressure 300 mTorr; ratio frequency 13.5 MHz; power 10 W.

N–H and Si–H absorbance areas were determined from the N–H stretch at 3450–3100 cm^{-1} and the Si–H bend at 2300–2100 cm^{-1}. Absorbance areas were then corrected for film thickness, and the absorbance cross sections from ref 17 were used to estimate hydrogen concentration. It should be noted that multiple absorptions occur within each of the peak areas mentioned above due to various silicon and nitrogen bonding configurations with hydrogen.[24,26]

Hydrolysis rates were determined by dividing the Si–O absorbance area by the hydrolysis time (the hydrolysis rate was linear with time, Figure 2, for all films used in the study). Some hydrolysis rates are also quoted in nitride film thickness loss per unit time. Due to the variation of silicon concentration in the films, a direct conversion of Si–O absorbance area to nitride hydrolysis rate was not possible. If the silicon density is high, then a greater Si–O absorbance area may be required for an equivalent nitride film thickness loss when compared to a less dense sample. Additionally, the sample may not convert completely into SiO_2; oxygen may simply replace nitrogen without forming an SiO_2 matrix.

To determine representative hydrolysis rates, a few films were completely hydrolyzed such that no Si–N absorption was observed in the FTIR spectrum. The oxide area of the partially hydrolyzed film was then divided by the oxide area for the fully hydrolyzed film. This fraction was used to determine the total nitride thickness consumed at time *t*, with the original nitride thickness prior to hydrolysis measured by ellipsometry. We were unable to use this technique for films that hydrolyzed at very slow rates (<0.1 nm/h) due to the extended periods required for complete hydrolysis. For these films, XPS sputter depth profiling was used to estimate remaining nitride thickness in order to determine hydrolysis rates. This estimation was somewhat complicated by the fact that the interface was not sharp but had an oxygen diffusion tail extending into the nitride. Thus, when hydrolysis rates were estimated by XPS profiling, the total oxygen sputter profile area was integrated and an equivalent oxide thickness computed from the integrated area.

Hydrolysis of the backside of the wafers was minimal (0.0012 × absorbance cm^{-1}/h). Clearly, the additional oxide from the substrate changed absolute Si–O areas, but the qualitative trends were still valid.

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(26) Tsu, D. V.; Luckovsky, G.; Mantini, M. J. *Phys. Rev. B* **1986**, *33*, 7069.

(27) Wagner, C. D.; Davis, L. E.; Zeller, M. V.; Taylor, J. A.; Raymond, R. H.; Gale, L. H. *SIA, Surf. Interface Anal.* **1981**, *3*, 211.

(28) Films were transferred under air; thus an initial oxide layer was formed on the sample before analysis. While this oxide layer would clearly affect the initial hydrolysis rate, it was found to have little effect on the bulk rate.

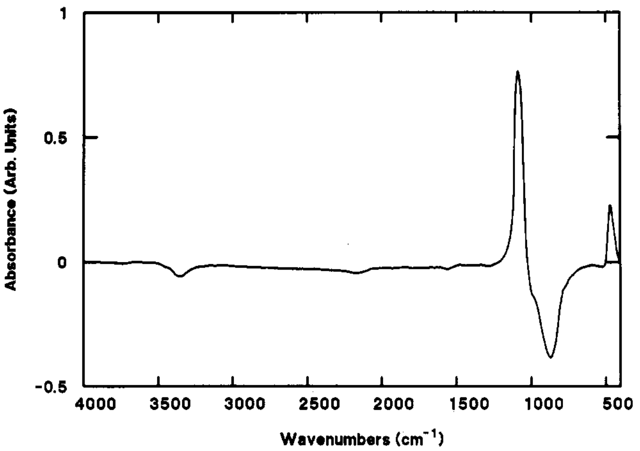

Figure 3. FTIR difference spectrum of a film deposited at 200 °C, hydrolyzed for 210 h at 85 °C under saturated water conditions.

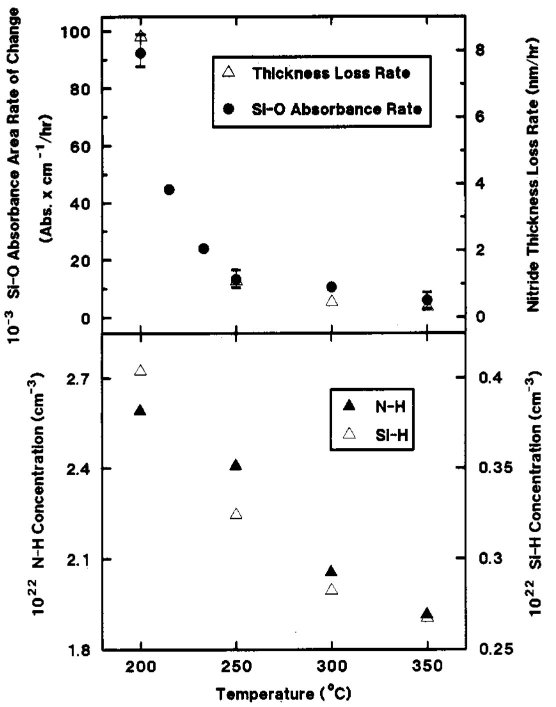

Figure 4. Hydrolysis rate (top) and N–H and Si–H concentration (bottom) for films deposited at temperatures ranging from 200 to 350 °C; NH_3:SiH_4 flow rate of 10:1; pressure 300 mTorr; ratio frequency 13.5 MHz; power 10 W. Error bars indicate highest and lowest hydrolysis rate measured by using Si–O absorbance area.

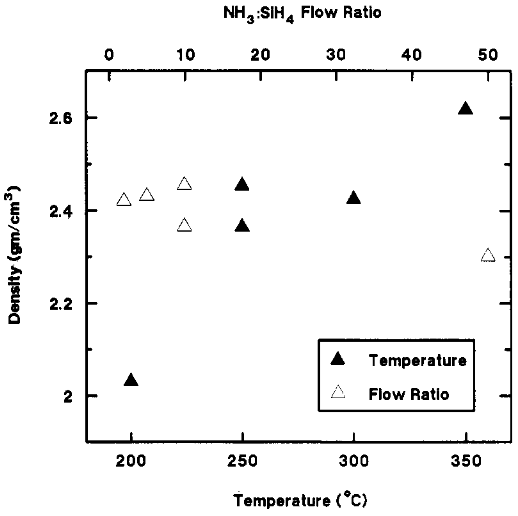

Figure 5. Film density as a function of deposition temperature and gas composition; pressure 300 mTorr; radio frequency 13.5 MHz; power 10 W. The temperature was 250 °C for gas composition series; a gas flow ratio of 10:1 NH_3:SiH_4 was used for temperature series.

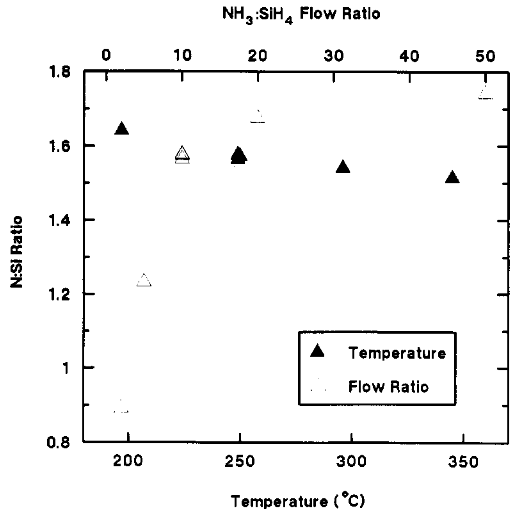

Figure 6. Silicon-to-nitrogen atomic ratio as a function of deposition temperature and gas composition. Deposition conditions are the same as in Figure 5.

Results

The difference spectrum of a hydrolyzed silicon nitride film can be used to visualize the changes due to hydrolysis. Figure 3 shows such a spectrum for a sample deposited at 200 °C with a gas flow ratio of 10:1 NH_3:SiH_4, hydrolyzed for 210 h. The negative absorbance peaks correspond to bonds that have been eliminated; the positive peaks correspond to bonds that have been formed during film hydrolysis. Specifically, Si–H (2200 cm^{-1}), N–H, N–H_2 (3500–3300 cm^{-1}), N–H_2 (1540 cm^{-1}), and Si–N (850 cm^{-1}) peaks decrease in intensity, while Si–O peaks (1070 and 450 cm^{-1}) increase.

Substrate temperature effects are shown in Figure 4, top, where the gas flow ratio used for film deposition was 10:1 NH_3:SiH_4. The hydrolysis rate decreases slightly for films deposited at temperatures above 250 °C but increases rather dramatically at lower substrate temperatures. In fact, 100-nm-thick PD silicon nitride films deposited at room temperature convert almost completely into oxides after 1 day of exposure to ambient conditions. Furthermore, the highest hydrolysis rate observed in this study is for films deposited at 200 °C. This observation correlates with the increase in N–H, and Si–H absorbance areas in the as-deposited films (Figure 4, bottom), as well as the decrease in film density as the deposition temperature decreases (Figure 5).

To further investigate factors influencing the hydrolysis rate, a second set of experiments was performed. Here, the flow rate was varied while deposition temperature was maintained at 250 °C. Under these conditions, the Si–H and N–H absorbance areas changed significantly for the silicon nitride films. Films formed under high NH_3:SiH_4 ratios contained large quantities of N–H but barely detectable Si–H absorptions (Figure 7, bottom); the converse was true for high SiH_4:NH_3 ratios. These observations are consistent with previous studies.[15,16] One should note that the Si:N ratio also changed dramatically with reactant flow ratios (Figure 6). Film density remained fairly constant (Figure 5) with a slight decrease at NH_3:SiH_4 flow ratios of 50:1. At a deposition temperature of 250 °C, films

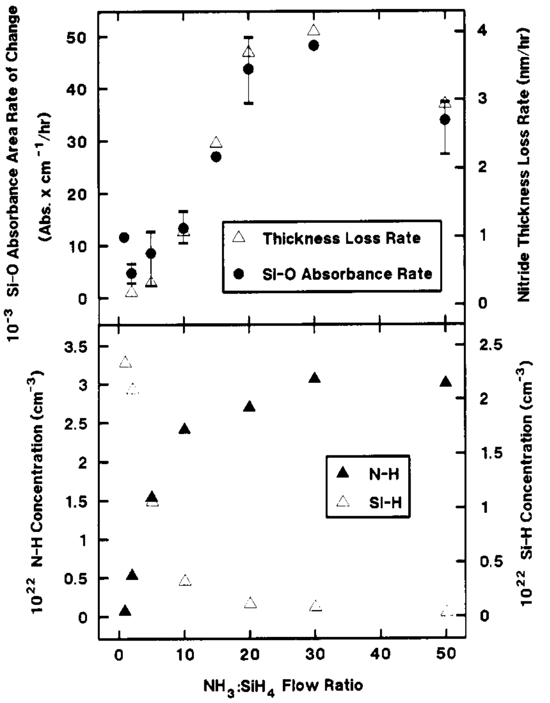

Figure 7. Hydrolysis rate (top) and N-H and Si-H concentration (bottom) for films deposited at gas flow ratios ranging from 1:1.1 to 50:1 NH_3:SiH_4; temperature 250 °C; pressure 300 mT; radio frequency 13.5 MHz; power 10 W. Error bars indicate highest and lowest hydrolysis rate measured by using Si–O absorbance area.

deposited at high SiH_4 flows did not hydrolyze significantly, while films deposited at high NH_3 flows hydrolyzed at increased rates (Figure 7, top). An interesting feature of the flow-rate study is the reduction in hydrolysis rate as the NH_3:SiH_4 flow ratio increases to 50:1. Finally, a slight but reproducible hydrolysis rate increase is observed at the highest SiH_4:NH_3 flow ratio (5.5:5).

The XPS depth profile spectra in Figure 8 show the different oxide thickness of two PD silicon nitride films, deposited at 250 (top) and 300 °C (bottom) and hydrolyzed for 138 h. Clearly, the film deposited at 250 °C has the thicker oxide, but in both films, a broad interface is observable. While the oxygen tail appears to penetrate more deeply into the 300 °C film, oxygen knock-on effects and mixing occur during the sputter process. Therefore, it is difficult to draw any inferences about varying oxygen diffusion into the film. However, we can conclude that an intermediate oxynitride layer is formed in the tail due to the broadness of the Si 2p peak.

Discussion

Data from the gas composition series exhibit a strong positive correlation between the N-H bond concentration and the hydrolysis rate for PD silicon nitride films. This is consistent with the observation in ref 26 that remote plasma CVD silicon diimide films, which had large N-H bond concentrations, converted to oxide very rapidly and with the assertion in ref 3 that oxide formation from CVD silicon nitride in dry O_2 is dependent on N-H concentration. As noted in ref 26, the N-H structure is isoelectronic with atomic oxygen. Thus, only a substitution of O for N-H is required to convert these imide groups to oxide.

The difference spectrum in Figure 3 indicates that Si-H bonds are also eliminated during hydrolysis. These bonds are obviously reactive in the hydrolysis process; however, because a negative correlation is observed between the Si-H concentration and hydrolysis rate (Figure 7), it is unlikely that these bonds provide the primary hydrolysis sites.

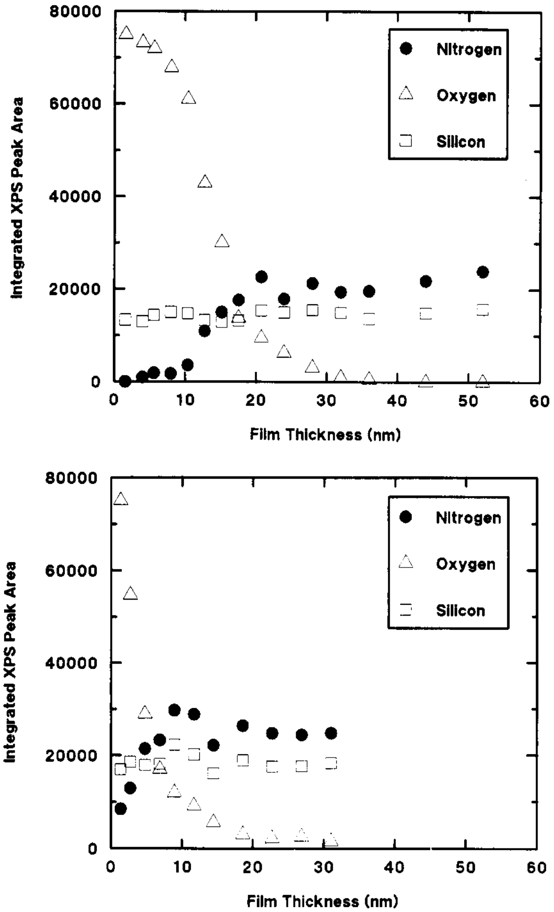

Figure 8. XPS sputter depth profile of hydrolyzed PD silicon nitride films hydrolyzed for 138 h. Deposition conditions are the same as in Figure 4. Film deposited at 250 °C (top); film deposited at 300 °C (bottom).

Although only small changes in the N-H bond concentration are observed for films deposited at different temperatures (relative to the large changes in N-H bond concentration for the flow series films, Figures 4, bottom, and 7, bottom), a pronounced change in hydrolysis rate is noted. The large increase in hydrolysis rate for the low-deposition-temperature films ($T < 250$ °C) appears to be due to a density decrease.

The hydrolysis rate decrease at very high NH_3:SiH_4 ratios (Figure 7, top) is somewhat puzzling. Both the N:Si ratio and the N-H concentration increase slightly for NH_3:SiH_4 flow ratios above 20:1. One possibility is that an increase in film N-H_2 concentration occurs with increasing NH_3:SiH_4 reactant ratio. This is consistent with the argument that N-H_x species, which are the closest electronic analogues to oxygen, will also be the easiest to replace. Indeed, in ref 24, N-H structures annealed more rapidly than N-H_2 structures. Furthermore, previous data suggest that both the N-H_2/N and the N-H/N ratios increase as silicon nitride films become increasingly nitrogen rich.[29] Unfortunately, our attempts to measure the concentration of N-H_2 in the films by measuring the absorbance at 1540 cm^{-1} were inconclusive due to weak absorbance peaks.

The increase in hydrolysis rate for films deposited under high silane flow ratios is also surprising but may be due

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[29] Bustarret, E.; Bensouda, M.; Habrard, M. C.; Bruyere, J. C., to be published in *Phys. Rev. B*.

to decreasing film density with increasing film silicon content (Figure 5). Another explanation for this phenomenon may be the morphological characteristics of the films produced. Columnar growth has been observed in amorphous silicon (a-Si) films formed in low-concentration, high-power silane discharges;[30] these conditions are analogous to the deposition conditions of our high SiH_4 flow ratio films. Thus, the silicon-rich nitride films may be morphologically similar to a-Si films. Consistent with the hydrolysis rates observed for silicon-rich nitride films (Figure 7, top), columnar a-Si films hydrolyze rapidly due to enhanced diffusion of oxygen along grain boundaries.[31]

At 85 °C in a saturated water vapor environment, the PD silicon nitride hydrolysis rate was linear (Figure 2). Water diffusion through the growing oxide is not the rate-limiting process over the oxide thicknesses (5–100 nm) formed in this study; otherwise, a parabolic rate would be observed (however, diffusion-limited growth may occur with thicker oxides). Thus, it is likely that reaction of water or water fragments with Si–(NH) bonds is the rate-limiting step, where Si–N bond breaking dictates the reaction rate. Obviously, this is analogous to the rate-limiting step in the thermal oxidation of silicon.[32]

The broad oxide/nitride interface observed during hydrolysis (Figure 8), suggests that the nitride provides a barrier against water penetration. However, depth profiling also revealed an oxygen tail in the films (Figures 8). Thus, diffusion of water into the nitride must be more rapid than the hydrolysis reaction. This statement is substantiated by the decrease in hydrolysis rate as the film approaches complete conversion to oxide (for films of varying thicknesses). If hydrolysis is occurring only at the interface (diffusion rate $\ll$ reaction rate), then the rate should be linear during the entire hydrolysis period. Such data provide additional proof that the reaction of silicon with water is the rate-limiting step in the hydrolysis of PD silicon nitride under these conditions.

Due to the diffusion of oxygen beyond the oxide/nitride interface, it must be pointed out that the nitride thickness loss data presented in Figures 4, top, and 7, top, are somewhat optimistic. Film integrity may be compromised because of water penetration before the oxide/nitride interface reaches the substrate.

Oxide formation was also attempted by using dry oxygen at 85 °C. No appreciable change in the PD silicon nitride FTIR spectrum was observed for a reaction time of 120 h. Again, this effect is similar to oxide formation from silicon and CVD silicon nitrides, where reaction with steam yields higher rates of oxide formation than reaction with dry O_2.[4,32] In the case of silicon, it is assumed that water is more effective in producing an oxide due to the higher equilibrium surface concentration in the oxide and the subsequent increase in bulk concentration within the oxide.[32] For the PD silicon nitride films, this effect is probably also important. In addition, the hydrogen from water may facilitate the production of NH_3 at N–H sites, which then diffuses out of the film, leaving an oxygen in its place (eq 1). This proposal was verified by collecting and analyzing the effluent from silicon nitride hydrolysis. The nitride films used for this experiment were deposited at room temperature to maximize the hydrolysis rate and the concentration of reaction products in the gas-phase effluent. Indeed, a preliminary mass spectroscopic analysis revealed NH_3 in the effluent.

Summary and Conclusions

Plasma-deposited silicon nitride films have been hydrolyzed by using saturated water vapor at 85 °C. Films deposited at low temperatures and high NH_3:SiH_4 flow ratios exhibited the highest hydrolysis rates. The highest hydrolysis rate measured was $\sim$0.8 nm/h for a film deposited at 200 °C, the lowest temperature studied. Films deposited at high temperatures or those that were stoichiometrically silicon rich showed low hydrolysis rates (<0.1 nm/h).

Both film density and N–H concentration affected the hydrolysis rate. The hydrolysis rate was linear over the oxide thicknesses grown, suggesting that diffusion of the oxygen-containing species through the oxide was not rate limiting. In addition, an oxygen diffusion tail was observed in the nitride, and the hydrolysis rate decreased as the film neared complete hydrolysis. This implied that diffusion through the nitride was slow but not rate limiting. Thus, it is likely that the reaction of water with Si–N bonds is the rate-limiting step.

Dry O_2 was ineffective as an oxidizing agent at 85 °C. When a saturated water vapor ambient condition is used, NH_3 appeared in the effluent.

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Registry No. Silicon nitride, 12033-89-5.

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(30) Knights, J. C.; Lujan, R. A. *Appl. Phys. Lett.* **1979**, *35*, 244.
(31) Street, R. A.; Knights, J. C. *Philos. Mag. B* **1981**, *43*, 1091.
(32) Deal, B. E.; Grove, A. S. *J. Appl. Phys.* **1965**, *36*, 3770.