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Temperature dependence of the biaxial modulus, intrinsic stress and composition of plasma deposited silicon oxynitride films

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Silicon oxynitride films were deposited by plasma-enhanced chemical-vapor deposition. The elemental composition was varied between silicon nitride and silicon dioxide: $SiO_{0.3}N_{1.0}$, $SiO_{0.7}N_{1.6}$, $SiO_{0.7}N_{1.1}$, and $SiO_{1.7}N_{0.5}$. These films were annealed in air, at temperatures of 40–240 °C above the deposition temperature (260 °C), to determine the stability and behavior of each composition. The biaxial modulus, biaxial intrinsic stress, and elemental composition were measured at discrete intervals within the annealing cycle. Films deposited from primarily ammonia possessed considerable hydrogen (up to 38 at. %) and lost nitrogen and hydrogen at anneal temperatures (260–300 °C) only marginally higher than the deposition temperature. As the initial oxygen content increased a different mechanism controlled the behavior of the film: The temperature threshold for change rose to ≃350 °C and the loss of nitrogen was compensated by an equivalent rise in the oxygen content. The transformation from silicon oxynitride to silica was completed after 50 h at 400 °C. The initial biaxial modulus of all compositions was 21–30 GPa and the intrinsic stress was −30 to 85 MPa. Increasing the oxygen content raised the temperature threshold where cracking first occurred; the two film compositions with the highest initial oxygen content did not crack, even at the highest temperature (450 °C) investigated. At 450 °C the biaxial modulus increased to ≃100 GPa and the intrinsic stress was ≃200 MPa. These increases could be correlated with the observed change in the film's composition. When nitrogen was replaced by oxygen, the induced stress remained lower than the biaxial strength of the material, but, when nitrogen and hydrogen were lost, stress-relieving microcracking occurred. © *1995 American Institute of Physics.*

I. INTRODUCTION

The intrinsic stress and biaxial modulus properties are important metrics for determining the stress in components comprised of multiple thin films, and necessary for assessing the durability of multilayered structures.[1] Knowledge of these values allows the processing conditions to be optimized, and a specific composition to be selected for both its properties and intended application. Valuable insight into the parameters that affect the growth and thermal degradation of thin films can also be obtained.

The intended applications for these films are as interface coatings to raise the fracture strength and toughness of ceramic matrix composites[2] and as protective overlay coatings for polymer matrix composites.[3] These applications require the film be stable at high temperatures (significantly higher than the deposition temperature) for extended periods. The effects of deposition conditions and temperature on the film's initial biaxial modulus and intrinsic stress need to be determined to establish the film's suitability.

The objective of this study is to quantify the biaxial stress and biaxial modulus of silicon oxynitride films; as deposited and after annealing above the deposition temperature. By varying the film composition from a mostly amorphous silicon nitride composition (a-SiN:H) to a predominantly amorphous silica (a-SiO_2) composition, the mechanical and thermal stability of different oxygen/nitrogen contents can be evaluated. The effect of the oxygen content on the biaxial stress and modulus properties is determined for each film, as deposited, and throughout the annealing cycle.

In addition to the intended applications of these thin films, the mechanical properties and thermal stability of silicon oxynitride films are relevant in two areas. The first is the effect of the silicon oxynitride sublayer on the oxidation rate of silicon nitride (at 1100–1400 °C). This layer exists as an intermediate suboxide when nitrogen atoms at the surface are continuously substituted to form a silicon dioxide top layer. An interfacial region of silicon oxynitride forms between the silica surface and the silicon nitride bulk and moves progressively inward as oxidation continues and oxygen diffuses into the bulk.[4] The thickness of the sublayer, and how it affects the oxidation rate of silicon nitride, are unresolved. A second area is the use of silicon oxynitride as passivation and dielectric layers in gate stacks for field-effect transistors (FETs); either as a single-layer oxide dielectric or in multiple-layer $SiO_2/Si_3N_4/SiO_2$, ONO (oxide, nitride, oxide) dielectrics.[5] Adding oxygen to silicon nitride to form an oxynitride has been shown to reduce the charge transport in metal-nitride-oxide-semiconductor (MNOS) structures.[6] The SiO_xN_y layer can either be deposited by plasma-enhanced chemical-vapor deposition (PECVD), or formed at the Si_3N_4/SiO_2 interface (of ONO dielectrics) when oxide layers are thermally grown.

Compared to other thin-film materials such as silicon nitride, silicon, silicon dioxide, and silicon carbide, there is little information available about the properties of plasma-

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TABLE I. Experimental parameters used to deposit a-SiO_xN_y:H films.

Substrate temperature	260 °C
Pressure	650 mTorr
Power	0.12 W/cm^2
Frequency	13.56 MHz
Electrode separation	5 cm
Deposition time	1 h
Total flow rate	345–435 sccm

deposited silicon oxynitride. Processing data that correlate different source gases (used for deposition) with the film composition are available,[7–10] but mechanical and thermal stability data as reported here have not been measured.

II. EXPERIMENT

A. Film deposition

The silicon oxynitride films were deposited in a parallel-plate PECVD apparatus with a biased top electrode (13.56 MHz) and a grounded substrate (specimen holder) that contained a resistance heater. As the apparatus has been previously described,[3] only those criteria specific to this experiment are now presented (Table I). A constant pressure, 650 mTorr, and substrate temperature, 260 °C, were maintained. The silicon source gas was silane, diluted to 5% by hydrogen (99.999% pure). The flow rates of the SiH_4/H_2 mixture and nitrogen (99.999%) were held constant at 200 and 60 sccm, respectively. The flow of nitrous oxide (N_2O) and ammonia (NH_3) was varied over the range reported to deposit silicon oxynitride.[7–10] R, the relative amount of N_2O present $[=[N_2O]/([NH_3]+[N_2O])]$, ranged from 0.12 to 1 (Table II). Concurrently, the silane-to-ammonia ratio was held constant, except for one experiment that omitted ammonia. The radio-frequency (13.56 MHz) plasma power density was kept constant at 0.12 W/cm^2 for all the experiments. And the deposition time was limited to 1 h.

The elemental compositions were determined by Rutherford backscattering and a nuclear resonance technique, which used ^{15}N atoms accelerated to 6.4–7.0 MeV, to quantify the hydrogen concentration.[11] The SUNY Albany Dynamitron linear accelerator and particle recoil detection equipment were used.

Previous studies of the thermal stability of plasma deposited silicon nitride films used Fourier transform infrared spectroscopy to identify the vibrational modes present in the films.[12] Owing to the limited quantitative information we obtained in that study, we did not record the IR spectra of the films investigated in this study. Absorption bands due to N-H, Si-N, Si-O, Si-H, and possibly N-H_2 would be expected (and have been previously reported),[10] and the most useful information we would expect is to identify the bonding sites most likely to lose hydrogen when the films were annealed (i.e., nitrogen or silicon): information that is interesting but not necessary for this study.

TABLE II. Gas flows used to deposit a-SiO_xN_y:H films by PECVD.

	Gas flow (sccm)			
Experiment	SiH_4[a]	N_2O	NH_3	N_2
a	10	10	75	60
b	10	50	75	60
c	10	100	75	60
d	10	100	0	60

[a]5% in H_2, so 190 sccm H_2 was also present.

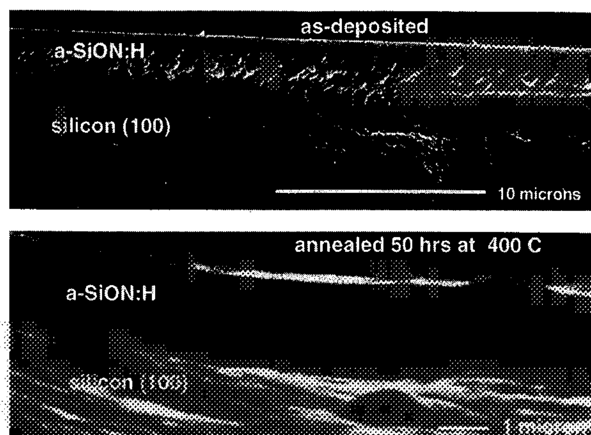

FIG. 1. Electron micrographs of the fracture edges of an a-SiO_xN_y film on a silicon (100) substrate.

SiO_xN_y film thicknesses were obtained from profilometry measurements (Dektek 3030, Veeco Instruments) and electron micrographs of fractured silicon witness wafers (Fig. 1). The uniformity of the film thickness was ±8% and the films adhered exceptionally well.

The silicon oxynitride film was simultaneously deposited on three different single-crystal materials located adjacent to each other on the grounded electrode: Si(100), sapphire (a plane), and hydrothermal quartz $(11\bar{2}1)$. All three substrates were rectangular (40×5 mm^2—silicon and sapphire, and 20×3 mm^2—quartz) with large length-to-beam dimensions required for cantilever-beam measurements.[13] The curvature (flatness) of each substrate was measured prior to deposition, and then following deposition and each annealing cycle. From the changes in curvature and knowledge of the substrate's thermal-expansion coefficients, Young's modulus and Poisson's ratio, the film's biaxial modulus and intrinsic and thermal stress were determined.[1,14–16]

B. Film annealing

All annealing was performed in a programmable air-circulating furnace at a very slow ramp rate, 0.07 °C min. Very slow heating was used to avoid cracking (from thermal shock) and to slow the evolution of gases: Films containing hydrogen evolve that hydrogen when heated above the deposition temperature.[12] Rapid heating and the presence of an appreciable hydrogen content (more than 25 at. %) can result in the evolved hydrogen coalescing to form blisters on the film;[17] the size of the blisters depend upon the temperature and duration of the anneal. These films failed prematurely at the apex of the blister when the force of the gas pressure, added to the intrinsic and thermal stresses, exceeded the tensile strength of the film.

TABLE III. Comparison of the thermal-expansion coefficients and the Young's modulus (or elastic constants) of the three substrates used to determine the biaxial modulus of SiO_xN_y.

Substrate	Thermal-expansion coefficient (10^{-6}/°C); 25–400 °C		Biaxial modulus (GPa)	Elastic constants (GPa)	
	Parallel to c axis	Parallel to a axis		Parallel to a axis	Perpendicular to a axis
Silicon (100)	3.2		180		
Sapphire (Al_2O_3)		7	486	345	
Quartz (SiO_2)		16		75	95

The anneal cycle consisted of the following temperatures and dwell times: 1 h at 300 °C; then 1 h, 24 h, and an additional 25 h at 350 °C; 1 h, 49 h, and then 100 h at 400 °C; and finally 1 h at 425 °C and another hour at 450 °C. All heat treatments were successive and accumulative, and the change in the curvature of the coated substrate was measured at each increment in the cycle. The annealing cycle was interrupted in this manner to record the change in the stress and modulus to better understand the thermal and kinetic stability (effects of temperature and time) of the modulus and intrinsic stress of films with different initial oxygen contents.

C. Stress and modulus measurements

The film's biaxial intrinsic stress was calculated from the measured change in the radius of curvature of rectangular substrates. Using the theory for a cantilever beam,[1,7] the total stress σ in the film f is calculated using Stoney's equation,[18]

$$\sigma=[E_s/6(1-\nu_s)](t_s^2/t_f)(1/\Delta\ \mathrm{Rad}),$$

where the change in curvature Δ Rad, Young's modulus E, Poisson's ratio ν, and the coefficient of thermal expansion α of the substrate s are known (Table III). The change in the radius of curvature

$$\Delta\ \mathrm{Rad}=\mathrm{Rad}_{\mathrm{final}}-\mathrm{Rad}_{\mathrm{initial}}$$

was determined (at room temperature) by measuring the distance h the beam deflected for a predefined chord length C, $\mathrm{Rad}=C^2/8h$.[13,14] Typically, 5–40 μm deflections were measured over a 40 mm substrate length.

The biaxial modulus for each SiO_xN_y composition was derived by simultaneously depositing the film on three different substrates (silicon, sapphire, and quartz). The intrinsic properties (modulus and intrinsic stress) and composition of the films (on each substrate) will be the same as the processing parameters are identical. As the films are amorphous the orientation and texture of the substrate are unlikely to affect the stress and modulus. The effect of the different substrates is to vary the thermal stress

$$\sigma_{\mathrm{thermal}}=\left(\frac{E_f}{(1-\nu_f)}\right)\int(\alpha_f-\alpha_s)dT$$

as the thermal-expansion coefficients for each single-crystal substrate are markedly different (Table III). As the measured stress value σ is the sum of the biaxial intrinsic stress $\sigma_{\mathrm{intrinsic}}$ and the thermal stress $\sigma_{\mathrm{thermal}}$, the biaxial modulus $(E_f/1-\nu_f)$ is determined by solving a simultaneous equation for two substrates:

$$E_f/(1-\nu_f)=(\sigma_{\mathrm{substrate\ A}}-\sigma_{\mathrm{substrate\ B}})(T_d-25\ °\mathrm{C})\times(\alpha_{\mathrm{substrate\ B}}-\alpha_{\mathrm{substrate\ A}}),$$

where T_d is the deposition temperature. Using three substrates allowed three modulus values to be calculated for each film composition. This provided greater confidence in the values as these calculations possess many potential sources for uncertainty (i.e., variability in the substrate thickness and dependence upon many physical constants). We estimate an uncertainty of $\pm$35 MPa for our total stress measurements, due to systematic uncertainties. The standard deviation reported for the biaxial modulus and intrinsic stress arise from the inherent variability in calculating mechanical properties of thin films.

The results are discussed in two sections: first, a study of the processing conditions and the resulting stoichiometry and stress in the film and, second, the behavior of each film composition during the annealing cycle.

III. RESULTS

Table IV lists the composition, biaxial modulus, intrinsic stress, and hydrogen content of the same film types exam-

TABLE IV. Effect of the gas composition on the stoichiometry and intrinsic stress of the SiO_xN_y films.

$R=N_2O/(N_2O+NH_3)$	Growth rate (Å/min)	SiO_xN_y composition x	y	Biaxial modulus (GPa)	Intrinsic stress (MPa)	Hydrogen content (at. %)
0.12	135± 5	0.3	1.0	⋯	−30±15	38
0.40	440±30	0.7	1.6	30±5	70±10	22
0.57	440±30	0.7	1.1	21±7	80±25	15
1.00	420±30	1.7	0.5	32±9	52±20	12

TABLE V. Comparison of the biaxial modulus and intrinsic stress of the a-SiO_xN_y films after deposition and annealing ($\pm 2\sigma$ uncertainty).

	Biaxial modulus ($E/1-\nu$) and intrinsic stress σ_i of SiO_xN_y films											
	As deposited		300 °C		350 °C		400 °C		425 °C		450 °C	
Experiment	$E/(1-\nu)$ (GPa)	σ_i (MPa)	$E/(1-\nu)$ (GPa)	σ_i (MPa)	$E/(1-\nu)$ (GPa)	σ_i (MPa)	$E/(1-\nu)$ (GPa)	σ_i (MPa)	$E/(1-\nu)$ (GPa)	σ_i (MPa)	$E/(1-\nu)$ (GPa)	σ_i (MPa)
I		−30±15		500								
II	30±5	70±10	49±8	114±7	69±8	220±20	76±8	440±50				
III	21±7	80±25	26±7	82±20	33±7	120±30	50±8	165±35	75±15	200±50	85±15	195±50
IV	30±9	52±20	28±10	48±20	39±15	83±25	53±13	110±30	90±20	205±50	92±20	190±50

ined in this study. The biaxial modulus of the "as-deposited" SiO_xN_y films was similar (21–32 GPa), irrespective of the elemental composition; approximately one-third lower than the biaxial modulus of a-SiN:H films [$E/(1-\nu)\approx 80-100$ GPa],[19] but higher than that reported for a-SiO_2 films.[16] The intrinsic stress values were obtained using the same thermal-expansion coefficient reported for a-SiN:H films, $\alpha = 1.5\times 10^{-6}/°C$.[19] Lacking a reported α value for plasma-deposited a-SiON:H films, this value provides a reasonable estimate for all film compositions. Films with a low oxygen content will possess properties similar to a-SiN:H films, and as the oxygen content increases, the films will increasingly resemble amorphous fused quartz, which has a similar expansion coefficient ($\alpha = 0.55\times 10^{-6}/°C$).[20,21] In all instances, the biaxial intrinsic stress of the as-deposited SiO_xN_y films was low (<100 MPa) and, except for the film with the least oxygen, the stress was tensile.

A. Composition of as-deposited SiO_xN_y

The nitrogen content in the film is determined primarily by the nitrous oxide and ammonia concentrations. A small quantity of nitrogen gas was incorporated in the gas flow as a ballast to reduce changes to the plasma properties when the N_2O and NH_3 content varied. It should not contribute to the growth mechanism at the SiH_4:N_2 ratios employed here (1:6); typically, ratios of 1:100 are required for stoichiometric a-SiN:H growth,[22] and then at a rate of only ≃30 Å/min. This is insignificant compared to the ≃440 Å/min growth rates achieved using N_2O and NH_3.

A comparison of the growth rates and film compositions obtained with different nitrogen precursor gas combinations R [$=[N_2O]/([N_2O]+[NH_3])$] is given in Table IV. The growth rate is controlled by the SiH_4:(N_2O+NH_3) ratio and the magnitude of R; the pressure, plasma power density, and temperature were the same for all experiments. A low value of R (≃0.12) limited the growth rate and produced a silicon-rich film. Higher R values (0.4 to 1) yielded higher growth rates and silicon-lean films. The constant Si:(O+N) content in the film suggests the growth rate is limited by the SiH_4 concentration. Comparing these film growth parameters suggests that nitrous oxide is a significantly more efficient nitrogen precursor than is ammonia. Finally, the density of the films obtained from each experiment ranged from 2.3 to 2.6 g/cm^3. The uncertainty (±0.15 g/cm^3) associated with these values precludes any correlation of the density with the elemental composition or processing conditions.

The oxygen content followed the R value: Low R values corresponded to a low oxygen content that increased as R increased. Any beneficial effect owing to a higher oxygen content, or lower hydrogen content (the hydrogen content decreased as the amount of ammonia was reduced) was not observed, and would not be apparent until the films were annealed.

B. Behavior of the biaxial modulus and intrinsic stress of annealed SiO_xN_y films

Thin films deposited at temperatures much lower than the thermodynamic equilibrium temperature possess non-equilibrium microstructures and compositions that are vulnerable to changes once the anneal temperature exceeds the deposition temperature. The additional thermal energy may break the weakest atomic bonds (i.e., Si—H and N—H bonds) and rearrange the bonding network (i.e., incorporate previously dangling Si, N, and O bonds). Hydrogen (and possibly nitrogen)[12] will be lost, the stoichiometry altered, and a volumetric contraction will increase the density. A stronger bonding structure will raise the biaxial modulus and stress. Monitoring the progression of these changes in the stress and biaxial modulus allows the causal relationship between high temperatures and changes in elemental composition and microstructure to be investigated.

The film grown using the lowest R value ($SiO_{0.3}N_{1.0}$) was the least durable. When the film was heated above the deposition temperature it cracked and no investigation of the biaxial modulus was possible. The high ammonia concentration was responsible for the high nitrogen and hydrogen content (Table IV), which affected the film's behavior, and, the behavior mimicked that of a-SiN:H films with a comparably high hydrogen content.[12]

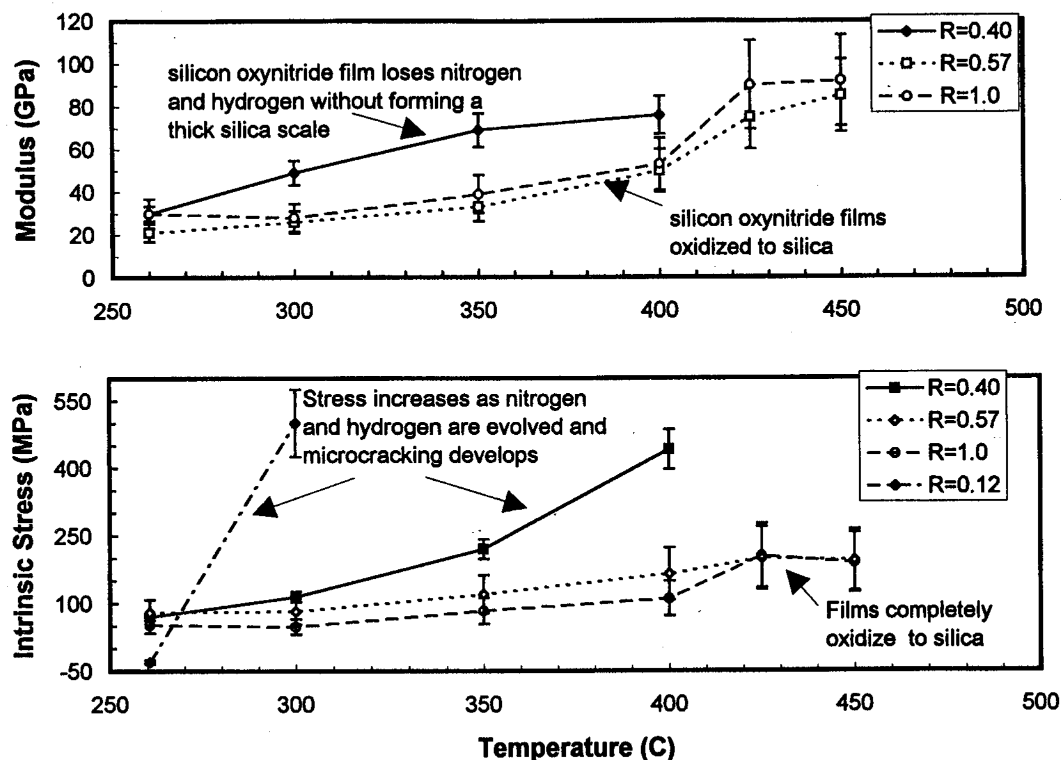

FIG. 2. Comparison of the change in the biaxial modulus and the intrinsic stress of $a\text{-SiO}_x\text{N}_y$ films after a 1 h soak at each temperature in the annealing cycle.

The film with the next highest oxygen content ($SiO_{0.7}N_{1.6}$) resisted cracking until the 400 °C anneal. The biaxial modulus increased most rapidly during the initial stage of the heating cycle (Table V): approximately 60% increase at 300 °C, 40% increase at 350 °C, and then remained constant (Fig. 2). All three biaxial moduli values for this film composition were in very close agreement. The appropriate temperature-dependent biaxial modulus was used to calculate the thermal stress, and the remainder of the total measured stress is attributed to the intrinsic stress (which includes the initial intrinsic stress and the induced stresses due to microstructural and compositional changes). Unlike the biaxial modulus, the intrinsic stress increased more rapidly at higher temperatures ($\simeq$60% then $\simeq$90% increase at 300 and 350 °C, respectively; Fig. 2). Initially, the increase in the intrinsic stress matched the increase in the biaxial modulus (at 300 °C). At higher temperatures (350 °C) the intrinsic stress increased at double the rate of the biaxial modulus, until stress-relieving microcracks developed at 400 °C. At the onset of cracking the total biaxial stress will have exceeded the material's biaxial strength. As cracking was not extensive, stress relief was limited, and the total stress present was measured to be approximately 500 MPa—a lower bound for the strength of the film. The difference between this film strength and the combined thermal and initial intrinsic stress (20 and 70 MPa, respectively) is the stress induced by the change in composition and subsequent microstructural rearrangement ($\simeq$410 MPa minimum). At no stage during the annealing cycle did the stress or the modulus stabilize, each annealing stage recorded a continuing increase in both values.

If the biaxial modulus of the as-deposited films (30 GPa) had been used in all subsequent calculations to determine the intrinsic stress (i.e., if the initial value had been assumed to be invariant with temperature) the calculated thermal stress at room temperature would be underestimated by 70%; however, as the thermal stress is only 4% of the biaxial stress, the overall effect of underestimating the intrinsic stress would be small ($\simeq$3%).

The film compositions deposited at the highest two R values behaved similarly, albeit very differently compared to the lower-oxygen-content films. The biaxial modulus of the $SiO_{0.7}N_{1.1}$ film increased slowly over the initial temperature cycle ($\simeq$25% increase at 300 and 350 °C), and then more rapidly (50% increases) at higher temperatures (400 and 425 °C). After that it appeared to stabilize (Tables V and VI; Fig. 3). The intrinsic stress did not rise until the 350 °C anneal (50% increase) and then rose more gradually through 400 °C, until stabilizing at 425 °C. The modulus and intrinsic stress were not affected by the 450 °C anneal temperature. Prolonged annealing at a constant temperature (350 and 400 °C) increased both values at a gradual rate (33%) (Table V and Fig. 2). However, there was a time limit to the changes that could be achieved at a constant temperature; after 50 h at 400 °C, the biaxial modulus and intrinsic stress had stabilized and did not change during the additional 100 h soak at 400 °C (Fig. 3), nor when annealed to 425 and 450 °C.

The $SiO_{1.7}N_{0.5}$ films displayed a similar behavior to that described for $SiO_{0.7}N_{1.1}$. The biaxial modulus and stress only increased at the 350 °C temperature threshold and remained constant when annealed for longer durations (Tables V and VI; Fig. 2). There was another increase in the modulus and

TABLE VI. Comparison of the biaxial moduli and intrinsic stress of a-SiO_xN_y films after extended annealing at a constant temperature ($\pm 2\sigma$ uncertainty).

	Annealed at 350 °C					
	1 h		25 h		50 h	
Experiment	$E/(-\nu)$ (GPa)	σ_i (MPa)	$E/(1-\nu)$ (GPa)	σ_i (MPa)	$E/(1-\nu)$ (GPa)	σ_i (MPa)
II	69±8	220±20	82±10	275±20	93±6	345±20
III	33±7	120±30	40±10	142±35	45±15	158±40
IV	39±15	83±25	53±15	116±30	37±20	90±25

	Annealed at 400 °C							
	1 h		50 h		100 h		150 h	
Experiment	$E/(1-\nu)$ (GPa)	σ_i (MPa)	$E/(1-\nu)$ (GPa)	σ_i (MPa)	$E/(1-\nu)$ (GPa)	σ_i (MPa)	$E/(1-\nu)$ (GPa)	σ_i (MPa)
II	50±8	165±35	70±30	225±40	74±40	224±35	70±35	210±35
IV	53±13	110±30	108±25	270±50	85±30	209±50	100±30	230±50

ntrinsic stress (≃30%) at 400 °C. Again, annealing for longer than 50 h at 400 °C, or at 425 and 450 °C, had no effect on either value.

C. Changes in the film composition with annealing

The elemental composition of each film was determined before the anneal, and then after 25 and 50 h at 350 °C, and then at 400 °C. The stoichiometry changed during the annealing cycle (Table VII), and these changes were accompanied by changes in the biaxial modulus and stress.

A substantial SiO_2 layer formed after only 25 h at 350 °C. The silica scale was significantly thicker in films grown using a high N_2O gas fraction (≃2 μm in $SiO_{0.7}N_{1.1}$ after 25 h at 350 °C) compared to the oxygen-lean film

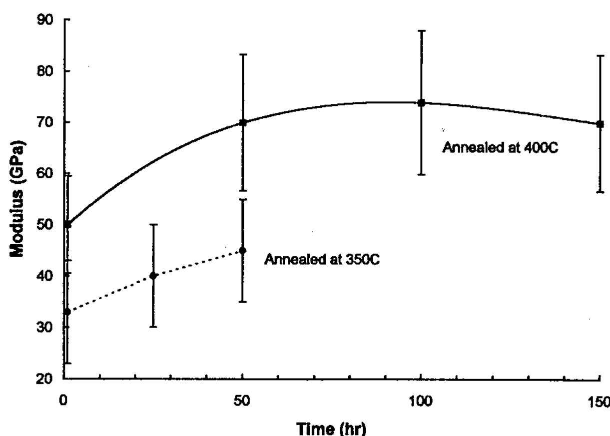

FIG. 3. Change in the biaxial modulus of the $SiO_{0.7}N_{1.1}$ film when annealed at 350 °C and then 400 °C.

($SiO_{0.7}N_{1.6}$) grown using predominantly NH_3 (≃0.2 μm after 25 h at 350 °C). As the anneal continued, the silica layers grew at disparate rates (Table VII), depending on the initial film composition. The hydrogen content in the SiO_xN_y region of the film remained comparable to the initial value (Fig. 4) and much reduced in the silica layer.

In each film the combined thickness of the SiO_2 and SiO_xN_y layers remained constant (within the accuracy of the measurement technique) through the annealing protocol. This indicated that the growth of the SiO_2 layer resulted not only from the loss of nitrogen and hydrogen (which should result in contraction), but also from the inward diffusion of atmospheric oxygen. For this to be feasible, oxygen must diffuse through the nascent silica layer to the underlying SiO_xN_y layer at a rate that permits the observed SiO_2 growth rate. Although oxygen diffusion through silica is low, extrapolation of Norton's diffusion rate[23] suggests that oxygen can diffuse through a 1 μm SiO_2 film at 350 °C in ≃28 h. This allows oxygen-diffusion as a mechanism for sustaining the growth of the silica layer; however, this does not explain the discrepancy in the thickness of the silica layers in different films, nor how a reaction that forms SiO_2 proceeds at these low temperatures (this issue is addressed in Sec. IV).

The observed change in the composition was consistent with the changes that occurred in the biaxial modulus and intrinsic stress, for each film composition studied. First, consider the high-oxygen-content films that formed an appreciable SiO_2 scale after 25 h at 350 °C ($SiO_{0.7}N_{1.1}$ and $SiO_{1.7}N_{0.5}$). The increase in the intrinsic stress and modulus of these films began at 350 °C and stabilized after 50 h at 400 °C (Figs. 2 and 3); the same temperature range where the films transformed from SiO_xN_y to SiO_2. Additional an-

TABLE VII. Changes in the elemental composition of a-SiO_xN_y films after different anneals. (The first reported thickness value corresponds to the composition of the top surface, and the composition and thickness of the lower region is the second value listed.)

Initial composition	Annealing parameters				
	1 h at 300 °C	25 h at 350 °C	50 h at 350 °C	1 h at 400 °C	50 h at 400 °C
$SiO_{0.3}N_{1.0}$	7500 Å $SiO_{0.25}N_{0.75}$; $H \simeq 38$ at. %				
$SiO_{0.7}N_{1.6}$		1800 Å SiO_2; $H \simeq 11$ at. % 24 600 Å $Si_{0.8}N_1$; $H \simeq 23$ at. %	3000 Å, SiO_2; $H \simeq 10$ at. % 23 000 Å $SiO_{0.9}N_{0.9}$; $H \simeq 21$ at. %		3500 Å SiO_2; $H \simeq 7$ at. % 20 800 Å $SiO_{0.9}N_{0.9}$; $H \simeq 20$ at. %
$SiO_{0.7}N_{1.1}$		19 500 Å SiO_2; $H \simeq 10$ at. % 7400 Å $Si_{0.8}N_1$; $H \simeq 12$ at. %	23 500 Å SiO_2; $H \simeq 8$ at. % 3500 Å $SiO_{0.8}N_1$; $H \simeq 11$ at. %	24 000 Å SiO_2; $H \simeq 8$ at.% 2500 Å $SiO_{1.4}N_{0.3}$; $H \simeq 10$ at. %	
$SiO_{1.7}N_{0.5}$		22 000 Å SiO_2; $H \simeq 8$ at. % 4000 Å $SiO_{1.2}N_{0.7}$; $H \simeq 11$ at. %	24 000 Å SiO_2; $H \simeq 8$ at. % 1000 Å $SiO_{1.2}N_{0.7}$; $H \simeq 9$ at. %	25 000 Å $SiO_{1.8}N_{0.2}$; $H \simeq 8$ at. %	

nealing at 400, 425, and 450 °C did not affect the stress or modulus, which was not surprising as the films had by then converted to SiO_2.

Films with a higher nitrogen content ($SiO_{0.7}N_{1.6}$) did not form a thick silica scale, but the composition changed (throughout the film) at a lower temperature than it did in films with a higher oxygen content (Table VII). As before, the change in composition was concurrent with the change in stress and modulus. Not only did these films lose nitrogen and hydrogen within the newly formed (thin) silica layer, they also lost nitrogen and hydrogen from the lower SiO_xN_y layer; furthermore, this occurred early in the temperature cycle where the biaxial modulus experienced the greatest change (from 1 h at 300 °C until 25 h at 350 °C).

IV. DISCUSSION

This study was established to determine the stability of thin a-SiON films, in air, at temperatures above the deposition temperature (260 °C). The two metrics used were mechanical stress (biaxial modulus and intrinsic stress) and elemental composition. These allowed the dependency between the stress and temperature to be followed to determine useful upper-temperature limits; however, the different oxidation behavior of films grown from different gas compositions was unexpected. This difference could not be deduced from the oxygen and nitrogen content; the N_2O content in the reaction gases during growth was a better predicator of the film's performance than was the oxygen content in the films. A high N_2O content resulted in films that rapidly formed a sizeable silica layer once a threshold temperature was exceeded. This threshold temperature was greater than that for similar films grown from a leaner N_2O content and higher NH_3 content. And the reactions that followed were different. These observations suggest the most important factor affecting the stability of PECVD silicon oxynitride films is the local atomic-bonding structure that determines how nitrogen and oxygen are held in the film. And this is dependent upon the reactive gas species present, and the reaction mechanism that governs how the precursors are incorporated into the film.

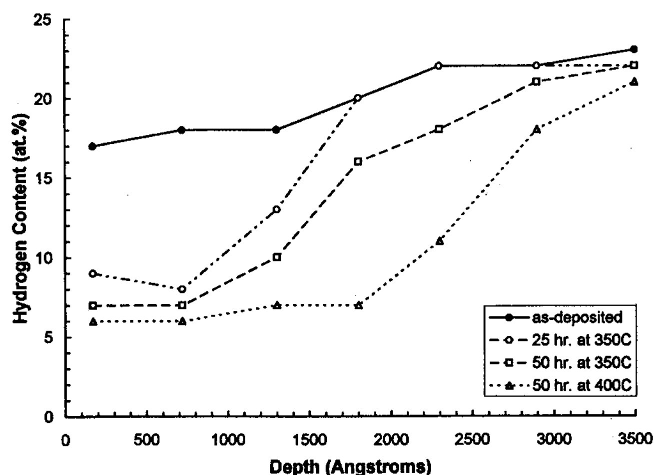

FIG. 4. A depth-resolved hydrogen profile of the a-$SiO_{0.7}N_{1.6}$:H film taken after different stages in the annealing cycle.

At annealing temperatures above the deposition temperature, nitrogen was more likely to be replaced by oxygen if it originated from N_2O rather than NH_3. The energy required to displace nitrogen will depend upon the bond strength (between the nitrogen and adjacent atoms) and the number of bonds holding nitrogen in the bonding network. A high density of dangling bonds (available nitrogen electrons not bonded to any atom) and hydrogen bonded to nitrogen will lower the total bonding energy, making it easier to break the -NH_x ($x=0-2$) bond.

When ammonia was the primary nitrogen precursor, a higher hydrogen content resulted (as N—H bonds were more prevalent) and the nitrogen in these films was lost at temperatures only 40 °C higher (maximum) than the deposition temperature (i.e., the $SiO_{0.3}N_{1.0}$ and $SiO_{0.7}N_{1.6}$ films) (Table VII). This suggests that a sizeable portion of the nitrogen was weakly bound. The loss of nitrogen and hydrogen appears to be a temperature-dependent first-order-type reaction that involves simple bond rupture followed by nitrogen and hydrogen evolution. As -NH_x species are lost and new atomic bonds form, a volumetric contraction will markedly

increase the biaxial strain. This, combined with an increased biaxial modulus, will increase the biaxial stress. Simultaneously, the formation of new atomic bonds between adjacent atoms (possibly involving dangling bonds from the loss of volatiles) may result in a stronger bonding structure requiring a higher activation energy to replace nitrogen with oxygen.

Films grown using a higher N_2O content only lost nitrogen within the newly formed silica layer. Since this involved a substitution of nitrogen by oxygen and occurred at higher temperatures ($\simeq$40–90 °C above the deposition temperature), nitrogen is assumed to be more strongly bound than if it originated from the ammonia precursor. This would involve a second (or higher) -order reaction mechanism where the supply of oxygen becomes a potentially limiting factor in the transformation to silica.

Ironically, the rapid transformation from silicon oxynitride to silica in an oxidizing atmosphere at temperatures above the deposition temperature preserved the integrity of the film as cracking was avoided, and the composition and the modulus/stress properties remain stable at higher temperatures for longer durations, whereas, films that resist oxygen replacement, by internally reorganizing and forming new bonds once volatiles are lost, cracked at comparatively low temperatures.

Finally, it is important to emphasize that these observations only apply to the films deposited under the deposition conditions enumerated above and then annealed above the deposition temperature. These films are expected to show much greater stability at temperatures below the deposition temperature where the thermal energy is lower than that experienced during deposition.

V. SUMMARY AND CONCLUSION

Using silane, nitrous oxide, and ammonia, silicon oxynitride films of variable oxygen and nitrogen content were deposited at 260 °C by PECVD. The oxygen-to-nitrogen concentration ratio ranged from O:N of 1:4 to O:N of 3:1 with a Si:(O+N) ratio of 1:1.3 to 1:2.8. The hydrogen content decreased from 38 to 12 at. % as the nitrous-oxide–to–ammonia ratio increased. The biaxial modulus of the a-SiO_xN_y:H films was initially 20–30 GPa, approximately 1/10th that of a fully sintered crystalline silicon oxynitride, and the initial intrinsic stress was below 100 MPa (tensile). Substantially higher growth rates (threefold larger) were achieved using higher nitrous oxide contents.

The behavior (change in biaxial modulus/stress and composition) and high-temperature stability (ability to limit the biaxial stress to less than the biaxial strength) of the film appeared to be affected more by the nitrous oxide content of the precursor gases, than by the O:N ratio in the film. If nitrogen was mostly derived from ammonia, then annealing above the deposition temperature (260–350 °C) induced the loss of nitrogen and a commensurate sizeable increase in the biaxial modulus (to 80 GPa) and intrinsic stress (to 500 MPa). Increasing the N_2O content decreased the amount of hydrogen and increased the thermal energy required to liberate nitrogen. At 350–400 °C (in air) these SiO_xN_y composition films were transformed into SiO_2. This transformation increased the biaxial modulus to $\simeq$100 GPa and the intrinsic stress to 200–250 MPa. More important, the film did not crack, even at temperatures up to 450 °C.

The principle advantage of a silicon oxynitride film, compared to a silicon nitride film (with a comparable hydrogen content), was the higher growth rate (tenfold higher); however, the disadvantage of these SiON films appeared when the film was annealed at use temperatures greater than the deposition temperature. The SiON films were not compositionally stable, and the mechanical properties changed as the composition changed. Unless a transformation of the film from silicon oxynitride to silica is acceptable (with the benefit of the film not cracking), these films are not suitable for use above the deposition temperature.

[1] W. D. Nix, Metall. Trans. A **20**, 2217 (1989).
[2] A. G. Evans, F. W. Zok, and J. Davis, Compos. Sci. Technol. **42**, 3 (1991).
[3] D. R. Harding, J. K. Sutter, M. Schuerman, and E. A. Crane, J. Mater. Res. **9**, 1583 (1994).
[4] L. U. J. T. Ogbuji, J. Am. Cer. Soc. **75**, 2995 (1992).
[5] G. Lucovsky, Y. Ma, T. Yasuda, C. Silvestre, and J. R. Hauser, Jpn. J. Appl. Phys. **31**, 4387 (1992).
[6] A. E. T. Kuiper, S. W. Koo, F. H. P. M. Habraken, and Y. Tamminga, J. Vac. Sci. Technol. B **1**, 62 (1983).
[7] K. Koyama, K. Takasaki, M. Maeda, and M. Takagi, in *Plasma Processing*, edited by J. Dieleman, R. G. Frieser, and G. S. Mathad (Electrochem. Soc., Pennington, NJ, 1982), p. 478.
[8] F. H. P. M. Habraken, R. H. G. Tijhaar, W. F. can der Weg, A. E. T. Kuiper, and M. F. C. Willemsen, J. Appl. Phys. **59**, 447 (1986).
[9] F. Lebland, C. Licoppe, and Y. I. Nissim, J. Appl. Phys. **72**, 2802 (1992).
[10] G. Lucovsky and D. V. Tsu, J. Vac. Sci. Technol. A **5**, 2231 (1987).
[11] R. Chow, W. A. Lanford, W. Ke-Ming, and R. S. Rosler, J. Appl. Phys. **52**, 5630 (1982).
[12] D. R. Harding, P. Herra-Ferrerio, E. Blanquet, and M. J. Freeman, (unpublished).
[13] R. E. Rottmayerm Atomic Energy Commission Technical Report No. 62, June 1994; P. Singer, Semicond. Int. **54** (October 1992).
[14] J. W. Osenbach, J. L. Zell, W. R. Knolle, and L. J. Howard, J. Appl. Phys. **67**, 6830 (1990).
[15] H. C. Liu and S. P. Murarka, J. Appl. Phys. **72**, 3458 (1992).
[16] S. Hasegawa, Y. Amano, T. Inokuma, and Y. Kurata, J. Appl. Phys. **72**, 5676 (1992).
[17] L. U. J. T. Ogubji and D. R. Harding, in *Proceedings of the Materials Society: Elevated Temperature Coatings: I, Science and Technology*, edited by N. Dahotre, J. Hampikian, and J. J. Stiglich (TMS, Warrendale, PA, 1995).
[18] G. G. Stoney, Proc. P. Soc. A **82**, 172 (1909).
[19] T. F. Retajczyk and A. K. Sinha, Thin Solid Films **70**, 241 (1980).
[20] L. M. Mack, A. Reisman, and P. K. Bhattacharya, J. Electrochem. Soc. **139**, 1735 (1992).
[21] "Engineering Property Data on Selected Ceramics," Volume III, *Single Oxides*, MCIC-HB-07, 1981 (Metals and Ceramics Information Center, Battelle, Columbus Laboratories, Columbus, OH, 1981).
[22] W. A. P. Claassen, W. G. J. N. Valkenburg, F. H. P. M. Habraken, and Y. Tamminga, J. Electrochem. Soc. **130**, 2419 (1983).
[23] F. J. Norton, in Transactions of the Eight National Vacuum Symposium combined with the Second International Congress on Vacuum Science and Technology, edited by L. E. Preuus, 1961, Vol. 8; F. J. Norton, Nature **701** (Aug. 1961).