

Characterization of the luminescence center in photo- and electroluminescent amorphous silicon oxynitride films

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We have studied the photoluminescence (PL) mechanism of photo- and electroluminescent amorphous silicon oxynitride films grown by plasma enhanced chemical vapor deposition. The composition of the films was determined by Rutherford backscattering spectrometry and monitored by the index of refraction with single-wavelength ellipsometry. Two sets of samples were grown, each with different reactant gas residence times in the deposition chamber. For samples grown with a residence time of about 5 s, the energy of the PL peak for 2.54 eV excitation is 2.3 eV for stoichiometric films and redshifts with increasing silicon content to 1.7 eV for the most silicon-rich films. The energy of the PL peak for 3.8 eV excitation is 2.8 eV for stoichiometric films and 2.1 eV for the most silicon-rich films. For stoichiometric films, the PL intensity is independent of temperature between 80 and 300 K using 2.54 eV excitation, but the PL intensity decreases by a factor of two over the same temperature range for 3.8 eV excitation. The authors interpret these aspects of the PL as consistent with tail-state recombination. Other results imply the PL is due to a specific luminescence center related to Si-Si or Si-H bonding. A 450 °C anneal reduces the paramagnetic defect density in the films, as detected by electron paramagnetic resonance, by an order of magnitude, but does not increase the PL intensity, while a 950 °C anneal increases both the defect density and the PL intensity. In addition, films in a second set of samples, grown with a residence time of 1.8 s, display very different PL behavior than samples in the first set with the same composition. Samples near stoichiometry in the second set have a PL peak at 2.06 eV and are 20 times less intense than stoichiometric samples in the first set. Optical absorption measurements indicate both types of samples contain Si-Si bonds, with the second set containing many more Si-Si bonds than the first. Fourier-transform infrared measurements indicate the presence of a Si-H bond that is stable at temperatures of 950 °C in the first set, but not in the second set. Thus, the study as a whole suggests a complete picture of luminescence in our silicon oxynitride films must incorporate elements of both tail-state and luminescence center models. The relation of the results to other PL studies in silicon alloys and porous silicon is discussed. © 1999 American Institute of Physics. [S0021-8979(99)09317-2]

I. INTRODUCTION

Silicon dominates the electronics industry today, so it is highly desirable to develop optical components that are silicon-based and compatible with current silicon processing technology, allowing integration of electrical and optical components on a single chip. To this end, we have recently demonstrated photoluminescence (PL) and electroluminescence (EL) in amorphous silicon oxynitride films,¹⁻³ and here present efforts to identify the luminescence mechanism in this material.

One promising approach to the development of a silicon-based light emitter is porous silicon.⁴ Blue luminescence in

porous silicon, with a PL peak energy between about 2.1 and 3.0 eV, is observed only in samples containing oxygen.⁴ The origin of this band is not well understood. Because PL in silicon dioxide itself is not well understood, it is difficult to distinguish effects of the oxide from those of silicon nanoclusters, interface states, and defects, all of which have been proposed as PL centers in porous silicon.⁵⁻⁹

Another more recent area of research is the development of EL devices from amorphous silicon alloys.^{3,10-14} We have demonstrated PL and EL from silicon oxynitride films,¹⁻³ but the mechanism for the luminescence is not yet well understood. We have characterized the luminescence center in these films with the goal of using our findings to improve the efficiency of our EL devices. Because this study examines PL in near-stoichiometric silicon alloys, it will also aid in the

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interpretation of PL data in oxidized porous silicon.

Amorphous semiconductors do not have a sharply defined band structure. The statistical periodicity in the bonding does lead to extended states, which are somewhat analogous to the valence band and conduction band in a crystalline semiconductor. But, even in a chemically pure amorphous semiconductor, the long-range chemical disorder gives rise to many localized states, known as tail states, within the energy gap. In general, the density of these states decays exponentially away from the valence band and conduction band. The accepted model for luminescence in *a*-Si:H, described by Street,¹⁵ is the radiative recombination of electron-hole pairs in the tail states.

Hydrogenated amorphous silicon (*a*-Si:H) has a band gap of only about 1.6 eV. As one adds constituents such as O, N, or C to *a*-Si, two major changes occur in the electronic structure. First, the Si-Si bonding states that make up the valence band begin to be replaced by much stronger Si-O, Si-N, or Si-C bonds, increasing the energy gap to 4.6 eV in *a*-Si₃N₄ and 8.2 eV in *a*-SiO₂.¹⁶ One can obtain luminescence in the visible spectrum whose energy can be tuned by altering the composition of the material. Second, the greater chemical disorder created by the presence of the additional constituents increases the width of the tail states.¹⁷⁻¹⁹ In SiO_x, SiN_x, and SiC_x, the PL peak and width of the PL peak increase with *x*, while the temperature dependence of the PL intensity decreases with *x*. All of this behavior has been attributed to the increasing gap energy and tail state width.¹⁷⁻¹⁹

Early studies¹⁷⁻¹⁹ concentrated mainly on the PL mechanism in the alloys with a composition close to that of *a*-Si:H. The behavior of the luminescence process as a function of the alloy concentration was extensively characterized. More recently, attempts have been made to more precisely identify the microscopic origins of PL in silicon alloys, especially in compositions close to stoichiometry. However, none of the studies identify a particular defect or chemical species that results in the luminescent tail states.

We have performed a study characterizing the optical, chemical, and defect properties of luminescent silicon oxynitride films to further elucidate the nature of the luminescence center. We show herein that the center is not strictly dependent on the bulk composition of the films, but instead must be a specific chemical species. We present evidence that the radiative center is not a paramagnetic defect, and may be a diamagnetic state associated with the Si-Si bond. We also establish a correlation between bright PL and the presence of Si-H bonds after high-temperature annealing, indicating these bonds may play a role in the luminescence.

II. EXPERIMENT

Silicon oxynitride films were grown by rf plasma enhanced chemical vapor deposition (PECVD) at 13.56 MHz using 5% SiH₄ in He and 10% N₂O in He as the reagent gasses (note that our previous studies used undiluted N₂O).^{1,2} The deposition conditions were: power, 35 W; pressure, 0.1 Torr; and substrate temperature, 300 °C. The reactor volume is 24 600 cm³. Two sets of films were grown with different

deposition conditions. In one set all films were grown using 20 sccm SiH₄ in He, varying the composition by changing the N₂O flow rate between 3 and 22 sccm. The deposition rate for these films, which are designated "slow-deposition" (SD) samples, was between 5 and 7 nm/min. The other set of films was grown identically except using 55 sccm SiH₄ and 70 sccm N₂O which yielded a growth rate of 10 nm/min. These films are designated "fast-deposition" (FD) samples.

Substrates used for the PL measurements were single-side polished 2 Ω cm single-side polished silicon wafers. Substrates for the Fourier transform infrared (FTIR) studies were 20 Ω cm single-side polished Si wafers with the back-side roughened on the micron length scale. The electron paramagnetic resonance (EPR) samples were deposited on 100 Ω cm double-side polished Si that was annealed at 900 °C in nitrogen before deposition to eliminate any EPR signal from the substrate. For the transmission measurements, the substrate material was 0.090 in. fused silica made by Dupont Photomask and cut into 11/2 in. × 1/2 in. pieces. Native oxide was removed from the Si substrates with HF before deposition.

For the annealing studies, samples used for the FTIR study were deposited on a single wafer and then cut into various pieces, each of which received a different anneal treatment. EPR and quartz substrates were cut prior to deposition and placed together in the deposition system. Film uniformity was confirmed by *ex situ* ellipsometry. One piece from each sample was left as-deposited, and one each received a 30 min anneal in a quartz tube furnace in 100 sccm 10% H₂ in N₂ forming gas (FG) at 950 °C, pure N₂ at 950 °C, or pure N₂ at 450 °C. One piece from the films used for the FTIR study received a 30 min anneal at 700 °C in pure N₂.

With constant reactor volume and deposition pressure, the varying flow rates used for the different set of samples yield different reactant gas molecules residence times in the chamber. Different residence times can affect the type of radicals present in the reactor, and can thus have a dramatic effect on the microstructure of the resulting film. For samples with index of refraction 1.65, we calculate the residence time by the method given by Chapman²⁰ as 5.1 s for the SD samples, and 1.8 s for the FD samples.

The composition of all of the films was monitored via the refractive index (*n*) of the films. The thickness and refractive index of the films were measured using single wavelength ellipsometry (SWE) at 632.8 nm. The index of refraction was correlated with elemental composition in some of the films by Rutherford backscattering spectroscopy (RBS) using 1.46 or 2.0 MeV He⁺ at a detector angle of 165°. The bonding information was determined from the infrared absorption measurements over the range 400–4000 cm⁻¹ with a FTIR instrument with a resolution of 4 cm⁻¹. The reflectance–transmission (R–T) measurements were acquired using a double-beam, double monochromator, ratio recording spectrometer over a spectral range of 185 to 850 nm.

PL measurements were performed using the 488 nm (2.54 eV) line of a cw Ar⁺ laser and the 325 nm (3.8 eV) line of a cw HeCd laser. PL spectra were recorded using a 0.85 m double-grating spectrometer and a GaAs photomultiplier

TABLE I. Summary of index of refraction (n) and composition data for SD and FD samples both as-deposited (ad) and annealed in FG 950 °C as determined by SWE and RBS, respectively.

Sample	Index of refraction	% Si	% O	% N
SD1 ad	1.52	33±5	56±10	11±10
SD1 FG	1.56	34±5	57±10	9±10
SD2 ad	1.66	35±5	30±10	36±10
SD2 FG	1.67	40±4	37±7	23±7
SD3 ad	1.85	43±5	20±10	37±10
SD3 FG				
SD4 ad	1.83	42±5	21±10	37±10
SD4 FG	1.86	42±5	16±10	43±10
FD1 ad	1.66	37±5	37±10	25±10
FD1 FG	1.70	42±4	39±7	19±7
FD2 ad	1.63	35±5	40±10	25±10
FD2 FG	1.58			

tube. The spectral response for the optical system was measured and was determined to have a dip in sensitivity at 2.9 eV. A straightforward correction of the PL spectra results in misleading artifacts near 2.9 eV, so spectra will be shown as-measured and the effect of spectral response will be indicated. Because our previous studies have shown the PL to be proportional to film thickness, spectra are normalized to a constant thickness. PL temperature dependence was determined using a Joule–Thompson refrigerator at 77 and 300 K.

III. CHARACTERIZATION

The real part of the index of refraction, n , from SWE and composition of the films as determined by RBS is shown in Table I. For comparison, note that n for α -SiO₂, α -Si₃N₄, and α -Si are approximately 1.46, 1.9, and 3.8, respectively. The measurements of n can be considered exact to within the digits given. The uncertainties shown for the RBS measurements reflect the authors' estimate of the random and systematic errors that may be present, and thus represent the uncertainty in the true composition of the material. The *relative* composition of the samples is less uncertain, and should be considered accurate to 2% for Si and 6% for O and N.

Note that in stoichiometric silicon oxynitride (all Si atoms are bonded only to O and N atoms, and there are no O–O, N–N, or N–O bonds) the composition is of the form SiO _{x} N _{$(4-2x)/3$} for all values of x between 0 and 2. By this criterion, samples in this study with index of refraction between about 1.50 and 1.69 are very near stoichiometry as-deposited, with the lower index films containing more oxygen and less silicon. The samples tend to become more silicon-rich after annealing, presumably because of the evolution of O and/or N from the film.

EPR measurements were performed on stoichiometric ($n=1.65$) and silicon-rich ($n=1.85$) SD samples, and stoichiometric ($n=1.65$) FD samples. As-deposited, all samples have extremely complex EPR spectra made up of as many as five lines, with a total paramagnetic defect density of about $2 \times 10^{19} \text{ cm}^{-3}$. The complexity of these spectra make deconvolution into the separate components impossible. After a 450 °C anneal in nitrogen, the total defect density drops by about an order of magnitude for the stoichiometric

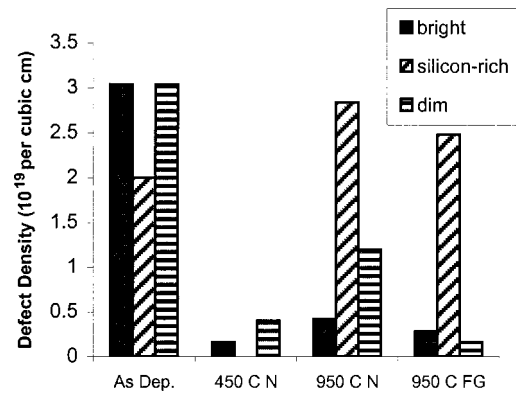


FIG. 1. Paramagnetic defect density for various annealing conditions as determined by EPR.

metric samples, and drops to undetectable levels in the silicon-rich sample. The total defect density versus the annealing condition is shown in Fig. 1 for each of the three samples. Upon annealing at 950 °C in either FG or nitrogen, a single prominent center emerges in the EPR spectra of the stoichiometric samples, with zero crossing between $g = 2.0024$ and 2.0030 . The density of this defect is about half as much in the forming gas-annealed sample as it is in the nitrogen-annealed sample. For the silicon-rich sample, the defect density increases dramatically after a 950 °C anneal in both forming gas and nitrogen.

The absorption spectrum was determined from R–T measurements for three sets of samples as deposited and after annealing at 950 °C in FG: a stoichiometric SD sample with $n = 1.65$, a silicon-rich SD sample with $n = 1.76$, and a stoichiometric FD sample with $n = 1.65$. The energy at which the absorption is 10^4 cm^{-1} (E_{04}) is shown in Table II for each sample. The absorption spectrum of the 450 °C annealed samples was indistinguishable from the as-deposited spectrum, and that of the samples annealed at 950 °C in nitrogen was indistinguishable from that of the sample annealed at 950 °C in FG in all three samples. As-deposited, the stoichiometric SD sample has an E_{04} gap of about 5.9 eV, which is approximately 1 eV higher than both the silicon-rich SD and stoichiometric FD samples. The E_{04} gap for all three samples redshifts by about 1 eV after a 950 °C anneal.

FTIR spectra were recorded for three sets of samples: a stoichiometric SD sample with $n = 1.65$ (shown in Fig. 2), a silicon-rich SD sample with $n = 1.76$, and a stoichiometric FD sample with $n = 1.65$. As-deposited, each sample has a

TABLE II. Summary of E_{04} gap for SD and FD samples both as-deposited/annealed at 450 °C in N₂, and annealed in FG or N₂ at 950 °C as determined reflectance-transmission spectroscopy.

Sample	E_{04} (eV)	
	As-deposited and 450 °C annealed	950 °C FG and nitrogen annealed
Stoichiometric SD	5.9	4.9
Silicon-rich SD	4.9	3.8
Stoichiometric FD	5.0	4.1

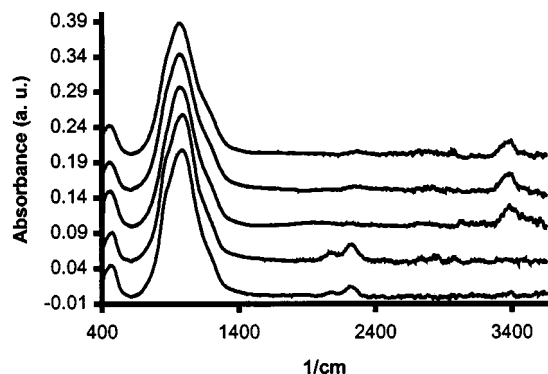


FIG. 2. FTIR spectrum for slow-deposited stoichiometric film for the annealing conditions (top to bottom): as deposited, 450 °C N₂, 700 °C N₂, 950 °C N₂, 950 °C FG.

single resonance near 463 cm⁻¹, attributed to a Si–O–Si rocking mode.²¹ The stoichiometric SD and FD samples also have a broad resonance at 980 and 994 cm⁻¹, respectively. Since these peak values lie between the Si–O stretching frequency in *a*-SiO₂ at 1060 cm⁻¹ and the Si–N stretching frequency in Si₃N₄ at 830 cm⁻¹,²¹ the resonance is likely due to a mixture of Si–O and Si–N bonds in a chemically disordered environment.²² The silicon-rich SD sample has a Si–O/Si–N stretching mode at 925 cm⁻¹, indicative of more silicon back bonds to the Si–N/Si–O bonds.²¹ Results of numerical fitting to the stretching modes in as-deposited and 950 °C forming gas-annealed samples are shown in Table III. The values of common stretching modes in *a*-SiO₂, *a*-Si₃N₄ and *a*-Si:H are provided as a reference.

After annealing at 450 °C, the only significant change that occurs in the Si–O/Si–N region is a slight increase in the height of the Si–O/Si–N stretching resonance in the stoichiometric SD sample, suggesting that the creation of new Si–N or Si–O bonds is taking place. After a 700 °C anneal in

TABLE III. Frequency of stretching modes in stoichiometric slow-deposited, silicon-rich, and stoichiometric fast-deposited samples compared to those given by Lucovsky^{a,b} for *a*-Si:H, *a*-Si₃N₄ and *a*-SiO₂.

Material	Si-O/Si-N stretch (1/cm)	Si-H stretch (1/cm)
<i>a</i> -Si:H	980/790 ^c	2000
<i>a</i> -Si ₃ N ₄	830	2150
<i>a</i> -SiO ₂	1060	2250
Stoichiometric slow		
SD1 ad	978	2263
SD1 FG	981	2221
Silicon-rich slow		
SD2 ad	925	2254
SD2 FG	927	...
Stoichiometric fast		
FD1 ad	994	2257
FD1 FG	994	...

^aG. Lucovsky, P. Santos-Filho, Z. Lu, Z. Jing, and J. L. Whitten, *J. Non-Cryst. Solids* **190**, 169 (1995).

^bG. Lucovsky, Z. Jing, S. Lu, D. R. Lee, and J. L. Whitten, *J. Non-Cryst. Solids* **182**, 90 (1995).

^cIn *a*-Si:H with O or N impurities.

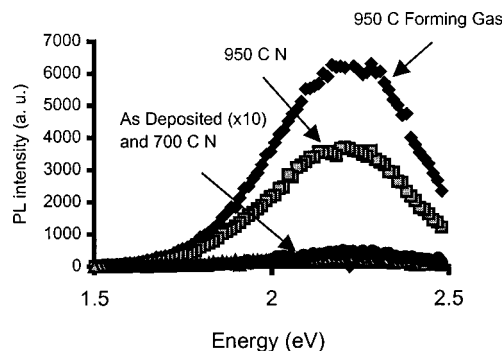


FIG. 3. PL intensity vs energy of stoichiometric slow-deposited sample for various annealing conditions.

nitrogen, the magnitude of this resonance increases in all samples. After an anneal at 950 °C in either nitrogen or FG, the magnitude of this resonance increases more than it does after a 700 °C anneal in all samples. The center of the resonance also moves to higher wave number in each sample after a 950 °C anneal.

As-deposited, a N–H stretching resonance²³ is observed in all of the samples, occurring at 3380 cm⁻¹ in the silicon-rich SD sample and the FD sample, and at 3370 cm⁻¹ in the bright SD sample. A Si–H stretching resonance²³ is also present at about 2260 cm⁻¹ in each sample. After an anneal at 450 °C in nitrogen, no statistically significant change is evident in any of the samples. After a 700 °C anneal in nitrogen, the N–H peak remains unchanged in all samples. The 2260 cm⁻¹ resonance disappears in both SD samples, but is unchanged in the FD sample. After an anneal at 950 °C in either nitrogen or FG, no Si–H or N–H is detectable in the silicon-rich SD sample or the stoichiometric FD sample. However, in the stoichiometric SD sample, the S–H resonance at 2260 cm⁻¹ actually increases in area from that in the as-deposited sample, and shifts to 2220 cm⁻¹. In addition, a second Si–H resonance appears at 2075 cm⁻¹, so that the total area of the Si–H resonance is increased by more than a factor of two after a 950 °C anneal.

IV. PL

SD films with an as-deposited index of refraction *n* less than 2.7 exhibited PL as-deposited. Films with higher *n* did not exhibit PL observable at room temperature. PL spectra for a typical SD film with *n* = 1.65 is shown in Fig. 3 for various annealing conditions. The PL peak energy using 2.54 and 3.8 eV excitation versus *n* is shown in Fig. 4 for several SD samples of various compositions as-deposited and after a 950 °C FG anneal. The energy of the PL peak for 2.54 eV is 2.21 eV for *n* = 1.6, increases to a maximum of 2.3 eV as *n* increases to 1.65, and steadily decreases to 1.71 eV as *n* continues to increase to 2.7 in the as-deposited films. The PL peak energy is not affected by a 450 °C anneal, but redshifts by about 0.05 eV after annealing at 950 °C in either FG or nitrogen for all of the samples. The energy of the PL peak for 3.8 eV is 2.8 eV for *n* = 1.65 and steadily decreases to 2.1 eV as *n* decreases to 2.1 in the as-deposited films. The PL peak redshifts by about 0.15 eV upon annealing at 950 °C. The PL from the samples with index greater than 2.1 was too weak

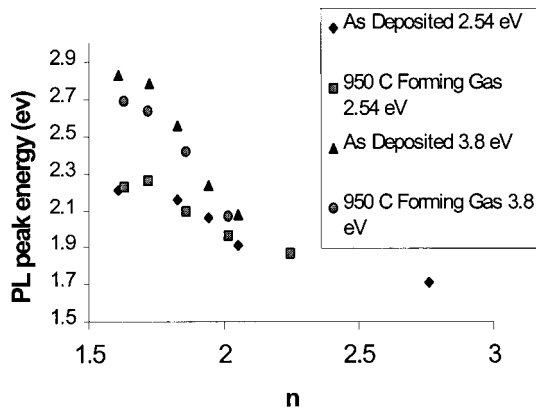


FIG. 4. PL peak energy vs index of refraction for 2.54 and 3.8 eV excitation.

to be observed using the 3.8 eV HeCd laser. Note that the PL peak energies for the two excitation energies merge at around $n = 2.1$.

The ratio of the PL intensity after annealing to the PL intensity as-deposited is shown versus the index of refraction on a log scale in Fig. 5 for all three annealing conditions. A value of this ratio above one indicates that annealing increased the PL intensity of the sample. The 450 °C nitrogen anneals have no systematic effect on the PL intensity for any of the samples, and never change the PL intensity by more than a factor of two. One SD sample with $n = 1.65$ was annealed at 700 °C, and its PL increased in intensity by a factor of ten from the as-deposited film. A 700 °C anneal on a $n = 1.76$ sample increased the PL intensity by a factor of five. The effect of a 950 °C anneal depends on the composition of the sample. For the low index films, the PL increases by almost two orders of magnitude after annealing at 950 °C in either FG or nitrogen, with the forming gas-annealed samples being about a factor of two brighter than the corresponding nitrogen-annealed sample. As n increases (the films become more silicon-rich), the improvement after 950 °C annealing lessens, until at $n = 2$, the 950 °C anneals reduce the luminescence intensity by an order of magnitude. For samples with $n > 2$, a 950 °C anneal quenches the luminescence to unobservable levels.

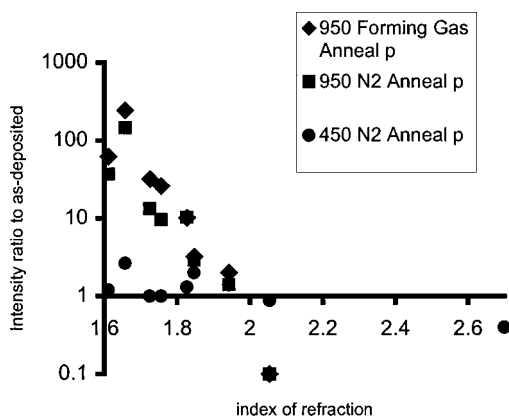


FIG. 5. Ratio of annealed PL intensity to as-deposited intensity vs index of refraction.

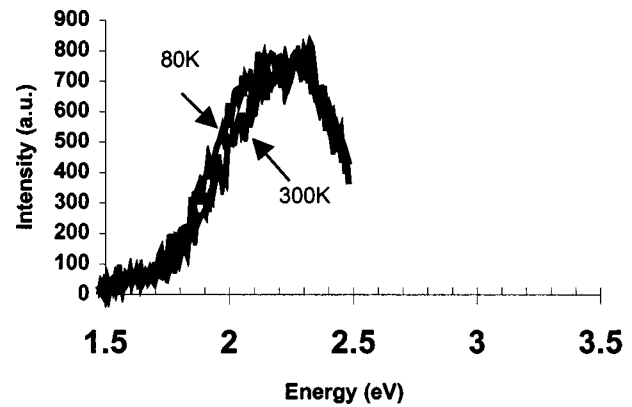


FIG. 6. 2.54 eV excited PL spectra at 80 and 300 K for stoichiometric SD sample.

We reported earlier that the effects of annealing were not dependent upon annealing ambient.¹ However, in that study, FG with 5% H₂ was used, while this study incorporates FG with 10% H₂. We speculate that the effect of the 5% FG anneal on the PL intensity and that of the pure nitrogen anneal in our previous study resulted in a difference too small to observe. The factor of two difference in the PL intensity resulting from a 10% H₂ FG and a pure nitrogen anneal has been observed for dozens of samples, and is quite reproducible for samples with index of refraction between 1.5 and 1.7.

The FD samples also exhibit PL. As-deposited, the intensity of the PL excited at 2.54 eV for a FD sample near stoichiometry is the same as it is for the SD sample of the same composition, but the PL peak is 2.06 eV, redshifted by about 0.15 eV from the SD sample. After a 950 °C anneal, the PL intensity increases by a factor of five to ten, and the peak remains unchanged. In addition, it is about a factor of 20 less intense after a 950 °C anneal than the corresponding SD sample. Several SD and FD samples near stoichiometry were examined, with varying concentrations of oxygen and nitrogen, obtaining similar results: the near stoichiometric SD films are over an order of magnitude brighter than FD films with similar composition.

We reported previously that no temperature dependence for 488 nm excitation PL was observed for samples with index of refraction near 1.65 for a temperatures as low as 80 K. We have done further temperature dependence studies, and found that the temperature dependence of our samples depends both on the PL excitation wavelength and the composition of the sample. PL spectra at 80 and 300 K for stoichiometric and silicon-rich SD samples using 488 nm (2.54 eV) excitation are shown in Figs. 6 and 7. Under 488 nm excitation, near-stoichiometric samples do not show any statistically significant difference in the PL intensity between 80 and 300 K, for both as-deposited samples and samples annealed in FG. However, more silicon-rich samples ($n = 2.05$) increase in the PL intensity by a factor of two when the temperature decreases from 80 to 300 K in both as-deposited and annealed samples.

Interestingly, upon excitation with 325 nm light, even the stoichiometric sample shows about a factor of two in-

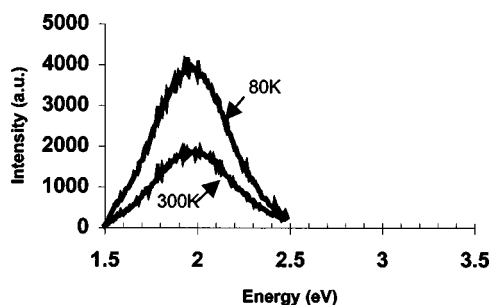


FIG. 7. 2.54 eV excited PL spectra at 80 and 300 K for silicon-rich SD sample.

crease in the PL intensity upon reduction in temperature from 300 to 80 K as shown in Fig. 8. Note that the dip in the PL intensity near 2.9 eV in this figure and in our previously published work¹ is due to the spectral response of the optical system. Thus, our previous report¹ of a PL peak at 3.15 eV is erroneous. For all samples, the temperature dependence is independent of the annealing condition.

V. DISCUSSION

A. Characterization

We first discuss the characterization results. Because the goal is to correlate them with the PL behavior, the emphasis will be on comparisons of stoichiometric SD (bright PL) and FD (dim PL) samples, and on stoichiometric SD samples before and after annealing. The two major differences between the SD and FD samples are in the Si–H bonding and the absorption measurements.

Unexpectedly, the Si–H stretching frequency in our as-deposited stoichiometric SD film of 2263 cm^{-1} does not fall between the 2150 cm^{-1} seen in $a\text{-Si}_3\text{N}_4$, and 2250 cm^{-1} seen in $a\text{-SiO}_2$.^{21,23} In fact, the stretching frequency is about 15 cm^{-1} higher than the 2250 cm^{-1} observed in $a\text{-SiO}_2$ (a difference larger than our estimated uncertainty of 6 cm^{-1}). One explanation is that the bonding is Si–H_{*n*}, with $n > 1$. However, such silicon polyhydrides are unstable at high temperatures, and it seems unlikely they would remain after a 950°C anneal. Another possibility is that the Si–H bonds are located near voids, which have been shown to increase the stretching frequency of Si–H bonds in $a\text{-Si:H}$.²⁴ In addition,

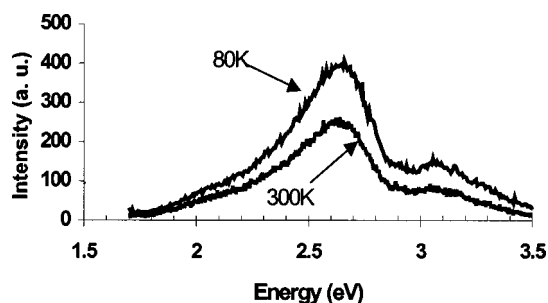


FIG. 8. 3.8 eV excited PL spectra at 80 and 300 K for stoichiometric SD sample.

several authors have reported an increase in the void concentration with increasing Si–H bonding in both $a\text{-Si:H}$ and $a\text{-Si:O:N:H}$.²⁵

The large increase in the Si–H vibration mode in the stoichiometric SD film after a 950°C anneal is puzzling. Almost all other studies on Si–H bonding in silicon oxide, nitride, and oxynitride find a dramatic decrease in the bonded Si–H content after annealing at $500\text{--}700^\circ\text{C}$.^{26–32} It is therefore unexpected that any Si–H is present in our films after 30 min at 950°C , and surprising that we observe an increase in the Si–H resonance after such a high temperature anneal. While an increase in H bonding may not be surprising after an anneal in FG, it is important to note that we observe the same increase after an anneal in ultrapure nitrogen.

Only two groups, studying $a\text{-Si:N}$, observe an increased magnitude of the Si–H stretching resonance after a high temperature anneal. Morimoto *et al.* report a decrease in the Si–H resonance in Si:N after a 800°C anneal, but then a factor of 1.5 increase in S–H after a 1000°C anneal, and attribute the increase to migration of H from N–H to Si–H.³³ Savall, Bruyere, and Stoquert report an increase in peak area of a factor of seven after an anneal of 1000°C .^{34,35} By fabricating films with silane and ammonia (NH_3) or deuterated ammonia (ND_3), they rule out the possibility that hydrogen from N–H bonds that originated in the ammonia migrates to form Si–H bonds after annealing. However, they do not rule out the possibility that N–H bonds in which the H originates from the SiH_4 precursor gas migrate to form new Si–H bonds. We point out that in our study, the nitrogen in the gas-phase deposition reaction enters in the form N_2O , so that any N–H bonds must involve H that originated in the silane.

Savall³⁵ attributes the large increase in the Si–H resonance to an increasing oscillator strength, instead of an actual increase in the number of Si–H bonds. There has been some evidence from both theoretical and experimental standpoints that oscillator strength is not constant for the Si–H stretching mode in $a\text{-Si:H}$.³⁶ Shanks³⁶ has shown that if one considers the Si–H bond to be a dipole isolated in a cavity embedded in a dielectric matrix, local field factors can lead to oscillation strength enhancement of over two orders of magnitude depending on the shape of the cavity.

The increased intensity of the Si–H stretching resonance in the stoichiometric SD films after annealing could be explained by an increase in oscillator strength of the Si–H bonds considering the evidence from FTIR that they may be located near voids. Following the calculations by Shanks detailed earlier, a slight change in the void shape with annealing could dramatically alter the oscillator strength of the nearby Si–H bonds. The increase also could be due to the H migration from N–H bonds. Note that after a 700°C anneal, the Si–H resonance is much lower than it is as-deposited, while the N–H resonance is unchanged. After a 950°C anneal, the N–H peak is gone but the Si–H peak is bigger than in the as-deposited case, consistent with H migration.

One of the major differences in the stoichiometric SD films and the stoichiometric FD and silicon-rich SD films is in the optical absorption measurements. Even though the stoichiometric SD and FD samples have approximately the same composition and index of refraction, the optical gap for

the FD sample is redshifted from the SD sample by almost 1 eV. In fact, the stoichiometric FD sample has about the same optical gap as the silicon-rich SD sample that has 5% more silicon as-deposited, indicating that more Si–Si bonding may be present in the stoichiometric FD sample than in the stoichiometric SD sample. Searle observes a discontinuous increase in the optical gap of Si:N as one approaches stoichiometric silicon nitride from the silicon-rich material, and attributes this to the percolation-like breakup of long silicon chains.³⁷ Thus, it is possible that the FD sample has only slightly more silicon than the SD sample, and still has a dramatically lower gap.

The E_{04} redshift of 1 eV seen in all of the samples after a 950 °C anneal is quite large. This, along with the increase in refractive index upon annealing reported previously,^{1,2} indicates an increase in the Si–Si bonding in these materials after high-temperature annealing. This is also consistent with the RBS data indicating an increase in the relative silicon content after annealing. Note that we previously observed evidence of Si–Si bonding from XPS, which indicates that the silicon atoms in our brightest films are bonded to between one and two other silicon atoms after an anneal.¹ However, the x-ray photoelectron spectroscopy (XPS) and FTIR results both indicate a more stoichiometric-like bonding in the films after a high-temperature anneal, which is inconsistent with the large redshift in the optical gap and the RBS results.

Wang *et al.*³⁸ resolved a similar discrepancy between FTIR and RBS in Si:O by postulating phase separation into stoichiometric and silicon-rich regions after annealing. He notes that FTIR is not sensitive to Si–Si bonds and would be unable to detect such a phase separation. XPS, though, is sensitive to Si–Si bonds and to phase separation of Si clusters. We have shown annealing leads to more stoichiometric-like bonding in our SD films, with no Si clusters present.¹ We have also shown by transmission electron microscopy that no silicon crystallites are present in the films.¹ Thus, any silicon–silicon bonds that are present must be isolated or in Si–Si chains—the presence of Si atoms bonded to four other Si atoms is ruled out by the XPS results. An alternative explanation is that the FD samples contain fewer voids than the SD samples. Since we define the energy gap as the energy for which the absorption is 10^4 cm^{-1} and a less dense material would appear to have a larger optical gap. This is because the bulk absorption measurement is scaled by the thickness of the sample to obtain the absorption per unit length, and the presence of voids gives the film a greater apparent thickness for the same amount of material.

Because of the complicated nature of the EPR spectra, especially in the as-deposited films, we are unable to conclusively identify any of the particular centers present in our films. As we noted, a 450 °C anneal reduces the paramagnetic defect density in all of the films by an order of magnitude. It is interesting that after a 450 °C anneal, there is no corresponding increase in the Si–O/Si–N stretching frequency or the bonded H in the films. Neither is any change evident in the absorption spectrum for any of the samples after a 450 °C anneal, meaning that the reduction of defect density after such an anneal is unlikely to be explained by an

increase in the Si–Si bonding. If the 450 °C anneal is healing dangling bonds by reconstruction of the network, one would expect to see an increase in some type of bonding in either the FTIR or R–T data.

The single center that appears in all of the stoichiometric films studied after a 950 °C anneal has a g value that varies from sample to sample between 2.0024 and 2.0030. Of the paramagnetic defects known to occur in silicon oxynitride, the most similar is the K center, which is a Si dangling bond backbonded to three N atoms. This center has been observed with $g=2.0032$ by Savall *et al.*³⁹ However, Cros and Krautwurm⁴⁰ have found that the g value for this defect in silicon oxynitride varies from 2.0030 for $O/(O+N)=0.04$ to 2.0044 in $O/(O+N)=0.85$. Since our films have significant amounts of oxygen, and the g value is observed to be below 2.0030 in some samples, the paramagnetic center in our films may not be the silicon dangling bond. Other common centers, the nonbridging oxygen hole center²⁶ (NBOHC), with $g=2.001$, and the nitrogen dangling bond,^{39,40} with g of about 2.0012 appearing after UV illumination, are clearly not present in our films. Thus, the identification of the paramagnetic center that appears after high-temperature annealing remains uncertain.

Finally, we point out that it is not surprising that the SD and FD samples have such different characteristics. While as-deposited they have similar compositions, they were deposited with very different residence times. Studies of the growth of silicon nitride using SiH_4 and NH_3 have shown that keeping the SiH_4/NH_3 ratio and other growth parameters constant, films grown using a residence time of 0.6 s have considerable Si–H bonding, while those grown with a residence time of 4.5 s have no Si–H bonding.⁴¹ The authors correlate the difference in Si–H bonding to an increased presence of SiH_n radicals in the plasma at a low residence time as monitored by the plasma emission spectrum.

B. PL

SD samples exhibit behavior very indicative of tail-state luminescence. The PL peak energy increases as one moves away from a -Si in composition, as is observed in a -Si alloys with O, N, and C.^{17–19} In the near stoichiometric samples, which have band gaps well above 2.54 eV, we see an increase in the PL peak energy with increasing excitation energy. In our more silicon-rich films, which have lower optical gap, the dependence on excitation energy of the PL peak is reduced. In amorphous silicon alloys, the PL peak energy E_{pl} has been shown to be independent of the excitation energy E_x if E_x is above the gap energy E_g . If E_x is below E_g , the PL peak redshifts with decreasing excitation energy.¹⁷ This is considered strong evidence that tail states play a role in the PL.

The temperature dependence of the PL efficiency in our films also increases with increasing silicon content, as observed in silicon oxide and silicon nitride,^{17,19} providing further evidence of tail-state luminescence. Temperature dependence in a -Si alloys occurs because at low temperatures, electron-hole pairs do not have enough thermal energy to hop into spatially nearby states. At higher temperatures, the

thermal energy is large enough to allow the electron to hop into nearby states and diffuse away from the hole, making radiative recombination less likely. In *a*-Si:H, the temperature at which carrier diffusion begins to become significant is about 50 K. In *a*-Si alloys, the deepest band tail states are much further into the gap and more localized than in *a*-Si. Thus, carriers trapped in states at the end of the band tails will require a larger thermal activation energy to escape. Consequently, the temperatures required for significant carrier diffusion increase with increasing alloy content, and PL efficiency in the alloys is much less temperature-dependent.¹⁷

While none of the aforementioned authors report a changing temperature dependence with different excitation energies, as we observe for our near-stoichiometric films, this too is consistent with tail-state luminescence. High excitation energies will excite carriers into shallow tail states, where the density of states is such that there will be other spatially nearby states into which the carriers can diffuse. By lowering the temperature, one decreases the thermal energy available to help the carriers diffuse. Thus, it is more likely that the electron and hole will stay near one another long enough to radiatively recombine, and the luminescence efficiency is increased. If an excitation energy well below the gap is used, the excited carriers will be in very deep states, where the density of states is low. Therefore, there will be very few nearby states into which the carriers can hop, regardless of the temperature.

Finally, we have shown the PL in our near-stoichiometric films has a characteristic lifetime of about 10 ns.¹ While the recombination lifetime in *a*-Si:H is considerably longer,¹⁵ Street and Knights report a decreasing lifetime as one decreases the silicon content in *a*-Si:O because of the more highly localized nature of the tail states in the alloys.¹⁹

Collectively, the earlier results provide strong evidence that tail states are involved in the PL mechanism in all of our materials. For our most silicon-rich materials, the PL does not differ significantly from the results of the Austin, Street, and Carius groups. On the other hand, our SD films near stoichiometry, which are in a region of composition not extensively studied, demonstrate behavior that is more indicative of luminescence from a specific center. Most convincing is the fact that after a 450 °C anneal, the paramagnetic defect density decreases by an order of magnitude, but the PL intensity remains unchanged. In a pure tail-state model, such a large reduction of defects should dramatically increase the luminescence.¹⁵ Instead, the PL intensity increases by two orders of magnitude after a 950 °C anneal, which increases the defect density slightly from the 450 °C anneal value. In addition, if the primary function of annealing is to reduce nonradiative pathways, one might expect annealed samples to have less temperature dependence than more defect-rich as-deposited samples. Lowering the temperature is known to reduce the nonradiative recombination in the silicon alloys, but we observe the same temperature dependence in all of our samples regardless of annealing treatment. The widely varying PL efficiency for samples of the same bulk composition also suggests a sufficient explanation of the PL mechanism will involve a specific center that may or may not be

related to the tail states. Thus, it seems that the effect of the 950 °C anneal is to create some luminescence center. The task then becomes to identify that center.

One difference between the stoichiometric SD and FD samples is the higher Si–O/Si–N stretching frequency in the FD sample. However, RBS confirms that this sample has slightly more oxygen than the SD sample, and this fact alone explains the increased stretching frequency. We also emphasize that we have observed bright PL in many near-stoichiometric SD samples with widely different oxygen/nitrogen ratios. Because RBS and our previous XPS results¹ show no correlation between relative concentrations of oxygen and nitrogen and PL intensity, this fact alone cannot account for the widely different PL behavior between stoichiometric SD and FD samples. That the bulk composition is not highly correlated with the PL intensity provides further evidence that a specific defect is responsible for the PL.

Many proposals have been made regarding the origin of PL in silicon-based materials. These include centers involving nanocrystals,^{5–8,42} paramagnetic defects such as the silicon dangling bond,⁴³ and NBOHC,²⁶ diamagnetic defects such as a charged N dangling bond³⁹ or Si–Si bond,^{44–46} and various molecular species⁴⁷ or unspecified defects.^{7,9,48} We will discuss each of these proposals and their relevance to our materials.

First, as is established earlier, we observe no paramagnetic centers in our films which correlate with the PL. The single prominent paramagnetic center is observed in all of our films after annealing, whether or not they exhibit bright PL. Samples annealed in FG contain smaller amounts of this center than the corresponding samples annealed in nitrogen, but the former samples have brighter PL. This eliminates from further consideration the Si dangling bond and NBOHC as suggested by Deshpande *et al.*⁴³ in Si:N and Kenyon *et al.*²⁶ in Si:O, respectively.

Savall *et al.* examined PECVD silicon nitride films near stoichiometry, obtaining results very similar to those in the present work.^{34,35,39,49} They observe 2.6 eV PL in silicon nitride with an optical gap of 5.05 eV, with an increased PL intensity for annealing temperatures between 550 and 750 °C, but a decrease at higher anneal temperatures. In a slightly more silicon-rich film (optical gap 4.75 eV), they found very weak PL that was not enhanced with annealing. After annealing at temperatures between 650 and 1000 °C and illumination by uv light, a nitrogen dangling bond is detectable by EPR in the higher-gap material, but not in the lower-gap material. They also observe an increase in the Si–H stretching resonance in the high-gap film, and a disappearance of this resonance in the low-gap film. They attribute the PL to the diamagnetic N center. However, the number of N dangling bonds continues to increase above 800 °C, while the PL intensity decreases above this temperature. In addition, theoretical and experimental studies^{50,51} have shown that the paramagnetic state of the N dangling bond is barely above the valence band and is at a higher energy level than the diamagnetic state of this defect. The diamagnetic N dangling bond is therefore unlikely to be the origin of 2.6 eV luminescence or the bright PL in our films.

Aydmlı, Serpenguzel, and Vardar⁴² examined Si:N near stoichiometry and also obtained results qualitatively similar to those in the present work. They observe the PL with a peak energy of about 2.5 eV, and an intensity that increases by more than an order of magnitude after an 800 °C anneal. More silicon-rich samples had much weaker, redshifted PL. They attribute the PL in both types of samples to quantum confinement of electron-hole pairs in silicon clusters, the presence of which was confirmed by XPS. In the samples with a bright PL, they detect a Si-H resonance at 2140 cm⁻¹ that is present after an 800 °C anneal. Though the PL behavior of these samples is similar to the films in this work, we have shown that no silicon clusters are present in our bright films.¹

As discussed earlier, however, we do have evidence for the presence of individual Si-Si bonds, which are diamagnetic and therefore undetectable by EPR. The Si-Si bond has been determined by various theoretical calculations to lie in the middle of the gap⁵² or just above the valence band edge in Si:N⁵¹ and Si:O.⁵³ This defect has been proposed as the origin of the 2.8 eV PL band in oxygen-poor bulk silica glass,^{45,46} and in PECVD-grown SiO₂ films.⁴⁴ If the bright PL in the near-stoichiometric SD sample is due to Si-Si bonding, we speculate that the dramatically redshifted and less efficient PL in the FD sample results from the fact that in the FD sample, the slightly more silicon-rich composition results in longer Si-Si chains. This lowers the gap as observed in the R-T measurements and redshifts the PL peak energy. The longer Si-Si chains form less-localized states than individual Si-Si bonds, and result in less efficient PL.

Finally, we discuss the possibility that the PL in our films is due to some novel structure or molecular species. The presence of Si-H bonding seems to be of primary importance in the luminescence behavior. Bright PL is only observed in stoichiometric SD samples and these are the only samples that contain Si-H bonds after a high-temperature anneal. The Savall and Aydmlı groups^{35,42} observe very similar behavior in their samples, with the bright PL at 2.5 eV or higher occurring after high-temperature annealing and accompanied by an unusually heat-resistant Si-H bonding resonance. These two groups also report much weaker, redshifted PL in slightly more silicon-rich materials. Aydmlı does not present Si-H bonding information for annealed silicon-rich films, but Savall reports the Si-H resonance disappears after high-temperature annealing in that group's slightly silicon-rich films.³⁵

Perhaps the Si-H resonance is unrelated to the PL, or it simply serves to passivate dangling bond nonradiative centers. On the other hand, it is possible that the Si-H is responsible for the bright, blue PL seen by all three groups. We have suggested the Si-H in our bright films may be located near voids. The Savall group has made a similar suggestion, and speculates the Si-H may be related to the bright PL in their films.³⁴ If indeed the Si-H is near voids, this may indicate a surface state near the voids is responsible for the efficient PL. We note that bright blue PL has been observed by many groups in oxidized porous silicon, which is composed of many voids.

VI. CONCLUSION

We have characterized the luminescence properties of amorphous silicon oxynitride films. The PL demonstrates several characteristics of tail-state luminescence models which adequately describe the PL in silicon-rich amorphous silicon alloys. However, a pure tail-state model does not explain the continued improvement of the PL efficiency after high-temperature annealing, or the widely varying PL behavior between films of similar bulk composition. Such phenomena indicate a specific center is responsible for the PL, as has been observed in bulk SiO₂. These results show that a complete picture of the PL in near-stoichiometric silicon alloys must incorporate elements of both tail-state and defect models. We suggest that the specific center responsible for the bright PL in our near-stoichiometric films is the Si-Si bond or a center related to Si-H bonds residing near voids.

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