

Infrared spectroscopic study of SiO_x films produced by plasma enhanced chemical vapor deposition

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We have studied the local atomic structure of silicon suboxide (SiO_x , $x < 2$) thin films using infrared (IR) spectroscopy. The films were prepared by plasma enhanced chemical vapor deposition (PECVD) of silane (SiH_4) and nitrous oxide (N_2O) mixtures, which were then diluted with He. The IR spectra were found to vary significantly with the degree of He dilution. Films grown with no He showed SiN, NH, and SiH bonding groups in addition to the three characteristic vibrations of the Si-O-Si linkage. The addition of He reduced the strength of the SiN, NH, and SiH absorption bands, and resulted in systematic increases in the frequency of the Si-O-Si asymmetric stretching vibration. The frequency of this Si-O-Si stretching vibration scales linearly with the oxygen concentration from approximately 940 cm^{-1} in oxygen doped amorphous silicon to 1075 cm^{-1} in stoichiometric noncrystalline SiO_2 . A deposition temperature of 350°C and a He dilution of 50% gave a film composition close to $\text{SiO}_{1.9}$. We propose a model for the deposition process that emphasizes the role of the He dilution.

I. INTRODUCTION

There is considerable interest in the deposition of dielectric films at low substrate temperatures in the range from 100 to 300°C . These films have potential applications in device structures based on crystalline compound semiconductors, and amorphous silicon. Three different approaches have been used to produce silicon oxide films in this temperature range: plasma enhanced CVD (PECVD),^{1,2} photo-CVD,³ and remote plasma enhanced CVD (RPECVD).^{4,5} In this paper we discuss a modification to the conventional PECVD process which serves to increase the chemical purity of the deposited films, but reduces the deposition rate by about a factor of 2. Films produced by the conventional PECVD process, in which a mixture of reactant gases is introduced into a capacitively coupled system, generally contain large concentrations of chemical contaminants as reflected through features in the IR transmittance spectrum (sensitivity for detection of the order of 0.5 to 1.0 at. %). For example, films grown from mixtures of SiH_4 and N_2O display absorption bands associated with SiN, NH, SiH, and OH vibrations in addition to the three characteristic bands of the Si-O-Si bonding arrangement.^{1,6} Films produced from mixtures of SiH_4 and either O_2 or $\text{Si}(\text{C}_2\text{H}_5\text{O})_4$, display SiH and OH bonds as well as the SiO_2 bands. Growth of SiO_x films by RPECVD has been shown to yield films that display no additional IR bands; however the deposition rates for this process are of the order of $1\text{--}2\text{ \AA/s}$,^{4,5} as compared to $4\text{--}5\text{ \AA/s}$ for the conventional PECVD process.^{1,2} We have found that He dilution of SiH_4 , N_2O mixtures in conventional PECVD reactors will also eliminate unwanted bonded groups such as SiH, SiN, NH, etc.,^{6,7} again at the expense of a small reduction in the deposition rate.

Since the analysis of the silicon and oxygen bonding we have employed depends on a quantitative interpretation of IR spectra, we first present in Sec. II a discussion of the IR

vibrations in silicon oxides, and then proceed to discuss our observations relative to film growth and other properties. Section III deals with the deposition of the suboxide films and includes the IR results. The final section of this paper discusses the qualitative distinctions between the conventional PECVD and RPECVD processes, and the process we have employed in this study. This section also includes a model for the deposition process chemistry that we have employed.

II. IR PROPERTIES OF SILICON OXIDES

There has been a great deal of research directed toward explaining the features in the IR and Raman spectra of vitreous SiO_2 (hereafter SiO_2),⁸⁻¹⁰ and we summarize this in Table I. There are three vibrational bands which correspond to rocking, bending, and stretching motions of the oxygen atoms. These motions are pictured in Fig. 1, where the coordinate system is referenced to the plane of the Si-O-Si bond. In this paper we emphasize the properties of the stretching mode vibrations. These form a band that is distinct from the bending and rocking bands, which have significant overlap with each other.

Included in Fig. 1 is a schematic representation of the features in the local density of vibrational states (LDOVS) of the Si and O atoms, and of the IR response. The dominant feature in the IR absorption spectrum of SiO_2 is associated with stretching motion of the oxygen atoms. This motion is coupled with silicon atom motion, and this in turn serves to maximize the coupling between the electric field of the IR radiation and the dipole moment in the solid. This vibration has been described as a rigid sublattice mode in which the oxygen and silicon atoms move in opposite directions.⁹ This in effect means that all of the oxygen atoms around a given silicon atom of the basic $\text{SiO}_{4/2}$ building block move with the same phase and the silicon atom moves with opposite phase.

TABLE I. Vibrational properties of SiO₂.^a

Frequency (cm ⁻¹)	Activity ^b	Vibrational assignment
450	Raman (<i>P</i>)	Oxygen bending
465	IR	Oxygen rocking + Si
505	Raman (<i>P</i>)	SiO ring (8 atoms)
606	Raman (<i>P</i>)	SiO ring (6 atoms)
800	Raman (<i>D</i>)	
	IR	Oxygen bending + Si
1075	Raman (<i>D</i>)	
	IR	Oxygen stretching + Si
1150	IR	Oxygen stretching
1200	Raman (<i>D</i>)	

^a Compiled from Refs. 8–10.

^b *P* indicates a polarized Raman mode, and *D* indicates a depolarized Raman mode.

Keeping this in mind we can then characterize the band edge motions within the LDOVS of the oxygen atom stretching band as being in and out-of-phase oxygen motions.¹⁰ In order for the center of mass to remain at rest, it follows the low frequency band edge, which is accompanied by silicon motion, is the in-phase motion of the oxygen atoms. The high frequency edge, where there is very little associated silicon motion, is the out-of-phase motion. These differences in motion at the two edges in the oxygen stretching band account for the differences in the relative IR activity at the peak of the stretching band near 1075 cm⁻¹, and at broad shoulder centered at about 1150 cm⁻¹.

In previous discussions of suboxide IR properties we have made two observations regarding the character of stretching band: (a) the frequency of the peak scales monotonically with the oxygen atom concentration with values of 1075

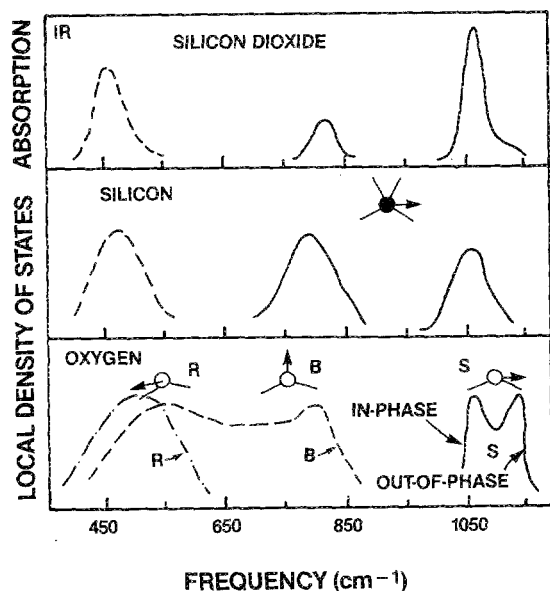


FIG. 1. (a) Calculated IR response of SiO₂; (b) Local density of vibrational states (LDOVS) for the Si atoms; and (c) LDOVS for the O atoms. R, B, and S stand for rocking, bending, and stretching motions, respectively, of the oxygen atoms. The arrows indicating in-phase and out-of-phase refer to the relative displacements of the four oxygen atoms bonded to each silicon atom in the building block unit SiO_{4/2}.

cm⁻¹ in stoichiometric SiO₂ to 940 cm⁻¹ in O doped amorphous silicon, and (b) the shoulder merges with the main band as the oxygen concentration decreases.^{6,7} The shift of the vibrational frequency with oxide composition is displayed in Fig. 2, and is a manifestation of an induction effect in which the chemical environment at each one of the silicon atoms of the Si–O–Si linkage can promote changes in the Si–O–Si vibrational frequency.¹¹ As the oxide moves off stoichiometry, $x < 2$, the silicon atoms have a higher probability of having one or more silicon atom neighbors and this shifts the Si–O–Si stretching frequency. The broadening of the band is a manifestation of a statistical distribution of different bonding arrangements at each silicon atom site. The disappearance of the shoulder is an effect that is driven by symmetry considerations. The only time that in-phase and out-of-phase oxygen atom motion has meaning is when there are four oxygen atoms bonded to each silicon atom as at the SiO₂ composition. Therefore, departures from stoichiometry into the suboxide composition range will tend to remove this distinction, and on the average reduce the sharpness of the distinction between a shoulder and main peak. This effect coupled with a broadening of the main IR feature serves to eliminate any vestige of a shoulder at compositions approaching SiO, halfway between *a*-Si and SiO₂. In discussing our results we therefore emphasize two aspects of the IR absorption that change with different deposition conditions: (a) the variation of the frequency of the IR stretching band, and (b) the nature of the high frequency shoulder.

III. EXPERIMENTAL RESULTS AND DATA ANALYSIS

We have used a conventional geometry parallel plate reactor for the growth of the SiO_x films by the PECVD process.^{1,6,7} Table II gives the geometry of the reactor chamber, and the range of deposition parameters that we have studied.

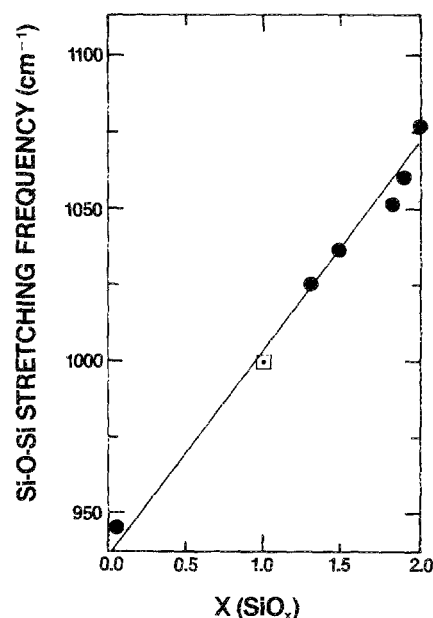


FIG. 2. Frequency of Si–O–Si stretching vibration as function of oxygen composition, x in SiO_x alloy films. The point for SiO is from Ref. 12.

TABLE II. Reactor geometry and deposition parameters.

Electrode geometry	
Diameter	27.9 cm
Anode to cathode spacing	2.5 cm
Deposition Parameters	
Substrate temperature	350 °C
rf power input	20–60 W
Total pressure	75–125 mTorr
Total gas flow rate	45–78 sccm
N ₂ O/SiH ₄ ratio	5–10
He dilution (vol %)	0–60%

In this paper we focus on the IR properties of the films as a function of the deposition variables, and in particular we emphasize the role of He dilution. Figure 3 indicates a series of IR transmission spectra for films produced in this reactor (b)–(e) and a thermally grown SiO₂ layer on crystalline Si as a reference (a). The three bands marked A₁, A₂, and A₃ in trace (a) are the characteristic IR features of SiO₂ and correspond respectively to the stretching, bending, and rocking motions discussed in the last section.^{8–10} We emphasize the stretching band which displays a minimum in the transmittance (maximum absorption) at approximately 1075 cm⁻¹. The band is relatively sharp with a full width at half maximum of about 85 cm⁻¹. Note that the high wave number shoulder extends to about 1300 cm⁻¹ and is relatively flat between 1100 and 1300 cm⁻¹. We can quantify the characteristics of this band by defining a ratio of absorption strengths between the shoulder (at 1150 cm⁻¹) and the peak absorption; this ratio is approximately 0.4 in SiO₂. We have studied the variation of the frequency of the position of maximum absorption and the ratio of the shoulder to the peak

transmittance as a function of the various deposition variables. These results are summarized in Figs. 4 and 5.

We deal with five different deposition variables: (1) the volume percent of He which is defined as

$$D = [\text{He}] / ([\text{He}] + [\text{SiH}_4] + [\text{N}_2\text{O}]),$$

where the terms in brackets are flow rates (for a fixed pressure these are equivalent to steady state concentrations), (2) the deposition pressure, (3) the total gas flow rate, and (4) the ratio of SiH₄ to N₂O. Consider first Fig. 4, where we have plotted the position of the spectral peak as function of the volume percent of He. The points in this diagram are derived from the IR transmission spectra that are shown in Fig. 3. The figure also contains an insert that gives the composition dependence of *R*, the ratio of the absorption in the high frequency shoulder (measured at a frequency of 1150 cm⁻¹) relative to that at the spectral peak. An SiO_x film grown at the lowest level of He dilution, 10%, has a large number of impurity bonding groups evident in the IR spectrum. Films grown at higher levels of He dilution do not show evidence of these groups, and therefore their concentrations can be taken to be at least below the minimum levels of IR detection (about 0.5–1 at. %). To note these differences compare traces (e) [10% He] and (b) [50% He] of Fig. 3. Trace (e) shows NH, SiH, and SiN bands in addition to the three Si–O–Si bands, while trace (b) shows only a very weak feature due to OH vibrations in addition to the Si–O–Si bands. Note further, that in the range from 10% to 50% He dilution, the increase in the Si–O–Si stretching frequency is linear with dilution, but that for higher dilutions, the rate of change of frequency is diminished. The highest vibrational frequency we obtained was 1062 cm⁻¹, which referring to Fig. 2, corresponds to a composition of approximately SiO_{1.9}.

In Fig. 5, we present the variation of the Si–O–Si stretch-

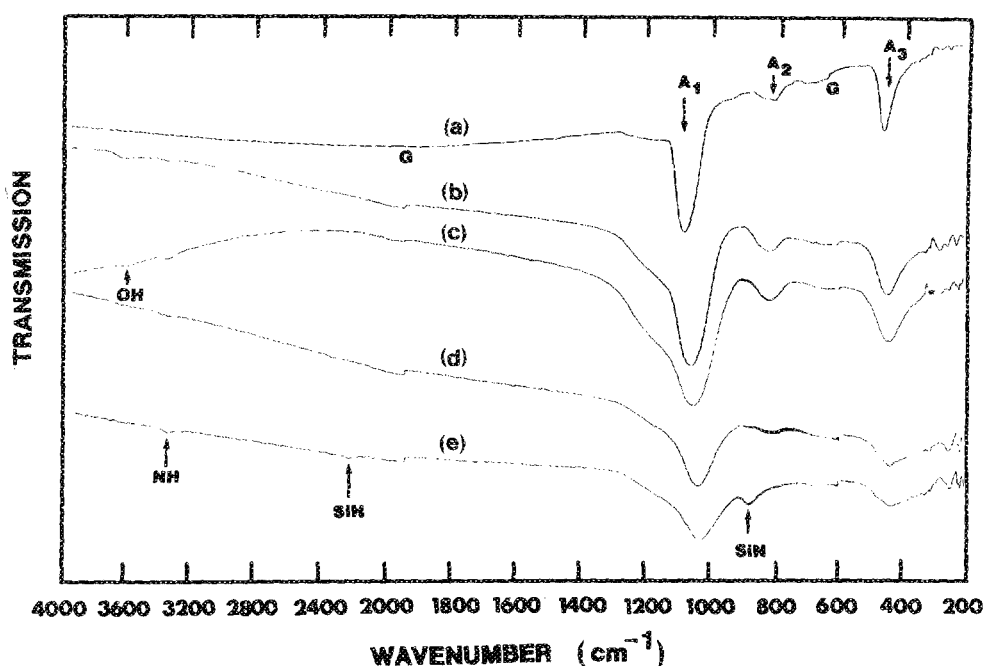


FIG. 3. IR spectra of (a) thermally grown SiO₂ film; and (b)–(e) films deposited from SiH₄/N₂O mixtures, where the He dilution is decreased from 50% in (b) to about 10% in (e). The designations A₁, A₂, and A₃ indicate the three characteristic Si–O–Si vibrations corresponding to stretching, bending, and rocking motions of the oxygen atom (see Fig. 1). We have indicated the frequencies of various impurity atom modes due to SiN, SiH, NH, and OH bonding groups.

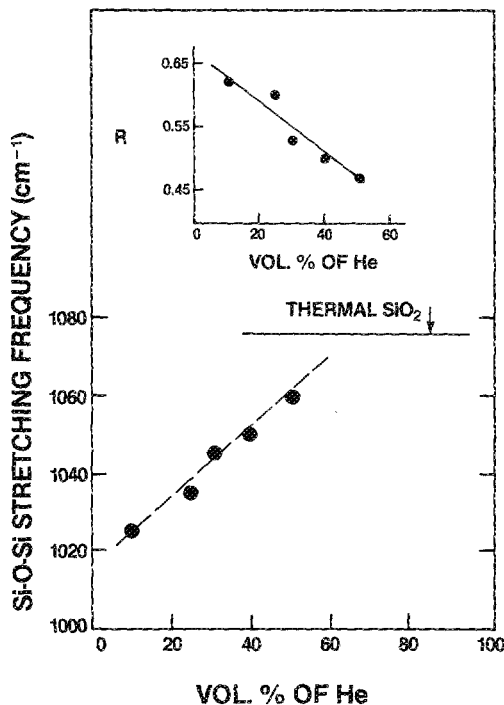


FIG. 4. Variation of the Si-O-Si vibration with He dilution for films of SiO_x deposited at a substrate temperature of 350°C , an rf power 20 W, a pressure of 100 mTorr, and a gas flow rate of 45 sccm. The insert in the diagram shows the variation of R , the ratio of absorption in the high frequency shoulder (at 1150 cm^{-1}) to that at the spectral peak, also as a function of He dilution.

ing frequency as a function of four other deposition variables. In each instance changes in the ratio R follow the same trends as shown in Fig. 4, and are not included in this figure. For a fixed $\text{SiH}_4/\text{N}_2\text{O}$ ratio of 1:5, a fixed flow rate of 62 sccm, a He volume fraction of 60%, a substrate temperature of 350°C and an input power of 50 W, the vibrational frequency increases with increasing pressure [Fig. 5(a)]. On the other hand, at a fixed substrate temperature, pressure (75 mTorr), and input power, the vibrational frequency decreases with increasing flow rate [Fig. 5(b)]. Since increasing pressure increases the residence time of gases at the deposition surface, and increasing gas flow rate decreases this residence time, these two portions of Fig. 5 demonstrate that the amount of oxygen incorporated in the film increases with increasing residence time of the constituent gases. We will provide an explanation for this in the next section of the paper. The traces in Figs. 5(c) and 5(d) demonstrate that for the ranges of the deposition variables explored that the Si-O-Si frequency does not change appreciably with changes of a factor of 3 in rf power input and a factor of 2 in N_2O to SiH_4 ratio. We believe that the small changes are, however, significant, and in particular the change in frequency with increasing N_2O is discussed in the next section of the paper.

A compilation of all the spectroscopic data we have taken indicates that the behavior we have identified relative to correlations in frequency of the Si-O-Si vibration with the ratio of absorption in the high frequency shoulder relative to the peak, and the effective FWHM for this band are internally consistent. That is, we find (a) the FWHM value increases

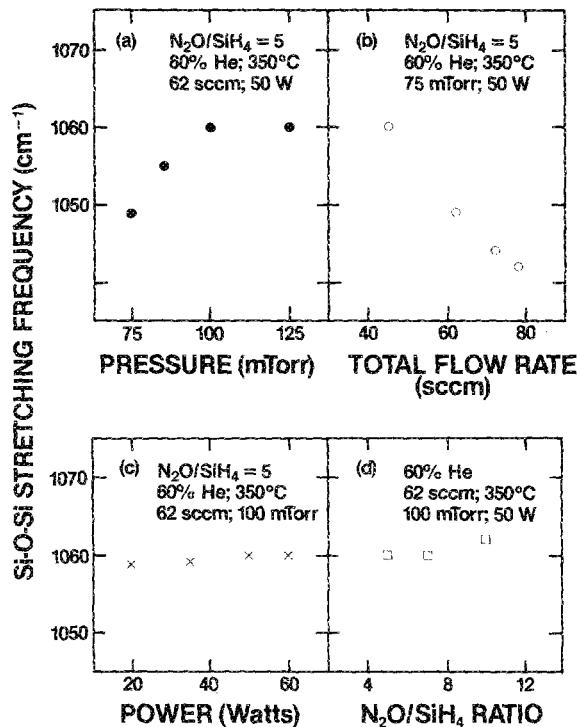


FIG. 5. The variation of the Si-O-Si frequency as a function of (a) the pressure, (b) the total gas flow rate, (c) the rf power, and (d) the ratio of N_2O to SiH_4 .

linearly from about 85 cm^{-1} in SiO_2 with a vibrational frequency of 1075 cm^{-1} to about 175 cm^{-1} in a film with a vibrational frequency of about 1025 cm^{-1} ($\text{SiO}_{1.3}$), and (b) that the ratio R increases linearly from about 0.43 in SiO_2 to 0.62 in the film with the $\text{SiO}_{1.3}$ composition. Similar variations of these spectral features have been found in suboxide films produced by the RPECVD process,⁵ and in oxide layers grown at high pressure, and substrate temperatures in the range from 550 to 800°C .¹³ Normally SiO_2 layers are grown on Si surfaces at temperatures in excess of 1000°C .

IV. DISCUSSION

A. Comparisons with conventional PECVD and RPECVD processes

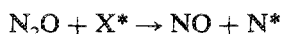
In the conventional PECVD process,^{1,2} the reactant gases are not generally diluted with a rare gas. The typical gas mixtures used are: (a) SiH_4 and N_2O , (b) SiH_4 and O_2 , and (c) SiH_4 and $\text{Si}(\text{C}_2\text{H}_5\text{O})_4$. In all instances these films are characterized by the incorporation of relative large concentrations of hydrogen, generally in the form of SiH , and SiOH bonding groups. Films grown from N_2O also display NH vibrations. In contrast, we have shown that introducing He into an $\text{SiH}_4/\text{N}_2\text{O}$ mixture serves to significantly reduce, and in some instances even substantially eliminate all of these impurity bonding groups (at least to the limit of detection by IR spectroscopy). The major question then revolves about the particular role played by the He atoms. This will be discussed shortly.

The IR spectra of films produced by the RPECVD process^{4,5} are qualitatively similar to the films grown in the con-

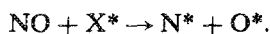
ventional PECVD reactor with He dilution. In particular the films have similar IR spectra with no detectable SiH bonding groups. The level of bonding that can be detected via IR absorption is in the range from 0.5 to 1.0 at. %. The various bonding groups discussed above may indeed be present at lower concentrations and as such they can play a significant role in the electronic properties of the films. In this regard, it has been shown that SiH and SiN bonding groups can introduce states in the energy gap of SiO₂ that lie 1–2 eV above the top of the valence band,¹⁴ and hence can be active as hole trapping centers.

B. Model for the role of He in the deposition process

From the discussions presented above, dilution of SiH₄/N₂O mixtures with He has two effects: (a) it reduces the concentrations of SiH, SiN, and NH bonding groups in the deposited films, and (b) it drives the deposited films toward an SiO₂ stoichiometric composition. The studies of Longeway *et al.*,¹⁵ and the results obtained in the RPECVD studies^{4,5} both serve to indicate the important roles of gas phase precursor formation and surface chemistry. The precursor molecule for oxide formation that has been identified in Ref. 15 is disiloxane (SiH₃)₂O. The discussions in Refs. 4 and 5 indicate that this molecule undergoes a surface reaction at the substrate in which hydrogen is replaced by O with the net effect of generating near-stoichiometric SiO₂. Knights *et al.*¹⁶ have also observed that He added to SiH₄ discharges will decrease the amount of polysilane incorporated in deposited *a*-Si:H alloy films. The role of the He dilution can be inferred on the basis of our observations regarding the SiO_x films we have grown, coupled with the other deposition studies referred to above. We can therefore assume that He dilution of SiH₄/N₂O mixtures (a) increases the rate of production of the precursor molecule disiloxane, (b) promotes a surface reaction involving replacement of SiH bonds with SiO bonds, and (c) reduces the rate at which precursor species giving rise to SiN bond groups are generated. The first two of these effects can be related to a reaction in which the N₂O is dissociated in the plasma to produce O atoms. A typical reaction sequence for this process is suggested by the results of Longeway *et al.*,¹⁵



and



X* is a species generated in the plasma, either the excited He atoms or electrons. The He atoms can also act as diluting agents which prevent the recombination, and/or the deexcitation of the excited oxygen atoms.¹⁷ The excited oxygen atoms can then (a) react with the SiH₄ to produce disiloxane, and (b) participate in the surface reaction that is necessary for the condensation of an SiO_x film.^{4,5}

The results shown in Figs. 5(a) and 5(b) indicate that the residence time of the gas mixture plays an important role in achieving stoichiometry. In our model, the important residence time is then associated with the excited oxygen atoms. This is consistent with the result shown in Fig. 5(d), where increasing the N₂O to SiH₄ ratio slightly drives the Si–O–Si

frequency up in value, pushing the film toward the SiO₂ stoichiometry.

The decrease in SiH incorporation with He dilution follows directly from the increase in oxygen incorporation. In the model discussed in Ref. 5, the surface reaction CVD step of the deposition process involves a replacement of H atoms by O atoms in the SiH bonds of the precursor molecule disiloxane. This reaction results in a polymerization of the Si–O–Si skeletal group of the disiloxane molecule. Therefore, the more excited oxygen atoms available, the more effective is the elimination of H from the deposited film. On the other hand the decrease in SiN bonds derives from a different consideration.

It has been shown that dilution of N₂ with He in the RPECVD process increases the deposition rate of Si₃N₄, and generates films which are essentially free (by IR detection) and NH and SiH bonding groups.¹⁸ This has been ascribed to the He atoms preventing the deexcitation of excited N atoms via collisions with N₂ molecules. Therefore, He dilution will result in more excited nitrogen atoms which in principle could give rise to a higher fraction of SiN bonds in the deposited films. Since this is not the case, we must assume that the rate of production of the SiN precursor species is significantly less than the rate of generation of SiO precursors so that the reactive SiH_n (*n* = 1,2,3, etc.) groups are effectively consumed by reactions with O* rather than N*. Similar considerations also apply to surface reactions. This assumption is supported by studies of oxygen and nitrogen incorporation in *a*-Si:H alloy films.^{19,20} These studies have shown that it takes only hundreds of parts per million of oxygen in the gas phase in a SiH₄ glow discharge process to generate bonded oxygen concentrations in the percent range, while to generate comparable bonded nitrogen concentrations in the same percent range, the gas phase concentration of nitrogen must be several orders of magnitude greater, i.e., in the percent range, rather than in the range of parts per million. The role of He dilution is then to drive the films toward the SiO₂ stoichiometry by reducing the incorporation of hydrogen in SiH bonding groups, and nitrogen in SiN and NH bonding groups. This effect derives primarily from the kinetics of precursor formation in the gas phase. Similar considerations may also apply to the surface reaction step of the PECVD process.

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