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Local atomic structure in thin films of silicon nitride and silicon diimide produced by remote plasma-enhanced chemical-vapor deposition

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We have grown thin films of silicon nitride by remote plasma-enhanced chemical-vapor deposition and have studied the chemical bonding by infrared absorption, x-ray photoelectron spectroscopy, Rutherford backscattering, and Auger-electron spectroscopy. Films were grown using two different gases as the source of nitrogen, N_2 and NH_3. We have found that films grown from N_2 and deposited at substrate temperatures in excess of 350 °C have a composition corresponding to stoichiometric Si_3N_4, whereas films deposited from NH_3 require substrate temperatures in excess of about 500 °C to eliminate bonded H and yield the same stoichiometric composition. In contrast films grown from NH_3 at temperatures in the range of 50 to 100 °C have a chemical composition corresponding to silicon diimide, $Si(NH)_2$. Films grown from NH_3 at intermediate substrate temperatures are solid solutions of Si_3N_4 and $Si(NH)_2$.

I. INTRODUCTION

There is considerable interest in thin-film dielectrics that can be deposited at low substrate temperatures (T_s) in the range from 150 to 500 °C. Applications include gate insulators and passivation layers for elemental and compound-semiconductor device structures, and insulating layers for thin-film devices based on amorphous Si. There are two approaches that have been used to produce films at low T_s: plasma-enhanced chemical-vapor deposition (PECVD) (Ref. 1) and photoenhanced chemical-vapor deposition (PCVD) (Ref. 2). The conventional approach to PECVD employs a capacitive coupling of rf power into a glow discharge that contains the gas mixture appropriate for the growth of a particular insulating film. For example, silicon nitride films have been produced using gas mixtures of SiH_4 and either N_2 or NH_3, and silicon dioxide films from mixtures of SiH_4 and O_2, N_2O, CO_2, or $Si(C_2H_5O)_4$. Dielectric films produced in this way contain relatively high concentrations of bonded hydrogen, about 5 at. % in the oxides to as much as 30 at. % in the nitrides.[1] The hydrogen is incorporated in the form of SiH and NH groups in the nitrides and SiH and OH groups in the oxides.[1] In general, these films have not performed well as gate insulators in metal-insulator-semiconductor (MIS) or metal-oxide-semiconductor (MOS) device structures, but have found other applications in microelectronics technology. We have performed calculations that indicate that SiH, SiOH, and SiNH bonding groups can produce localized states in the energy gaps of both SiO_2 and Si_3N_4.[3] In addition, there is experimental evidence that these bonding groups are associated with trapping and/or recombination sites in these insulators.[4] We have developed an alternative approach to PECVD that can generate oxide and nitride films with substantially reduced amounts of bonded hydrogen.[5–8] In this process, designated as remote plasma-enhanced CVD (RPECVD), we excite only one of the reactant gases (or a mixture of this gas with a rare-gas diluent) and remove the excited species from the plasma region. We combine the extracted species (which can include atoms, molecules, radicals, and electrons) with neutral silane outside of the plasma region and deposit a thin film on a heated substrate, also outside of the plasma glow region. We have studied the chemical composition of the films as function of the deposition variables and have identified the conditions that result in decreased amounts of bonded hydrogen. Other aspects of this deposition process, as well as device applications of these films, are discussed elsewhere.[5–8] The process we have used is qualitatively similar to one that has been previously described in the literature and designated as indirect plasma-assisted CVD.[9,10]

Section II of this paper outlines the steps in the deposition process and Sec. III addresses the spectroscopic studies that we have used to characterize the chemical composition and local atomic structure of the deposited thin films. Section IV is a discussion of the local atomic bonding in the nitride films. Section V contains a short discussion of some aspects of the reaction chemistry, and Sec. VI summarizes the results of this study.

II. DEPOSITION PROCESS

The RPECVD deposition process consists of the following steps: (a) rf excitation of a gas or gas mixture that contains nitrogen atoms (in our studies these are NH_3 and an N_2- and He-gas mixture); (b) transport of the excited species out of the plasma region; (c) mixing of the transported species with neutral silane or disilane; and (d) a CVD reaction at a heated substrate to generate a thin dielectric film.[5–8] The process that we have used is similar to techniques previously discussed by Streetman and co-workers[9] and Meiners.[10] We have implemented this process in the deposition chamber shown in Fig. 1. The important attributes of this chamber are: (a) a capability for supplying gases from two different feed lines, one at

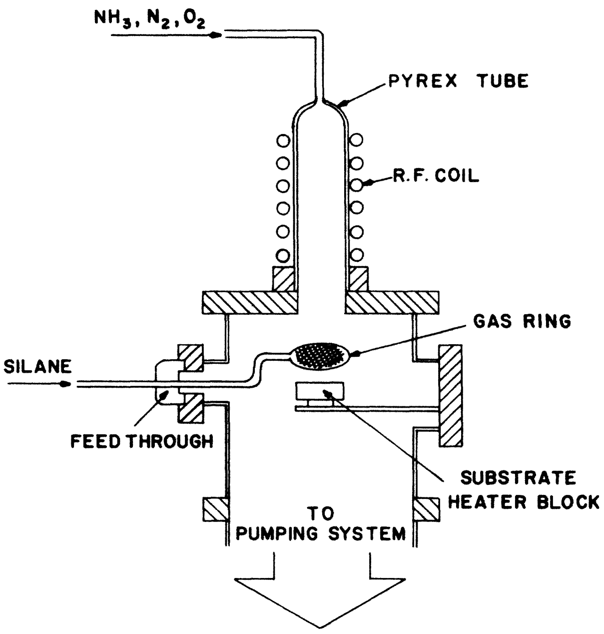

FIG. 1. Schematic representation of RPECVD deposition chamber.

the top of the chamber and one coupled to the dispersal ring at the center of the chamber; (b) a provision for rf inductively exciting the gas delivered at the top of the chamber; and (c) a capability for heating the substrate. The chamber is brought to a base pressure of about 3×10^{-8} Torr using a 500-(l/s) turbomolecular pump and a thermal bakeout. If the chamber has been up to "air" for a substantial period of time, we also use a "preburn" of N_2 or NH_3 at a pressure of about 10^{-3} Torr. During the deposition process, which is carried out at a pressure of about 300 mTorr, a roots blower-rotary piston process pumping system is used.

We have used two different sets of reactant gases to produce nitride films.[6,7] The equations describing the overall chemical reactions for these different reactants are given below and the deposition conditions are tabulated in Table I:

(I) $(NH_3)^* + SiH_4 \rightarrow Si(NH)_2(100\,^\circ C)$ to $Si_3N_4(>500\,^\circ C)$

and

(II) $(N_2,He)^* + SiH_4 \rightarrow Si_3N_4(200\text{—}400\,^\circ C)$.

We have also substituted ND_3 for NH_3 in the first reaction, (I). For completeness and for comparisons we make later on, Table I includes deposition parameters for the process by which we have generated SiO_2 films.[5-8]

Consider the first process [reaction (I)] involving a reaction between NH_3 and SiH_4. NH_3 is rf-excited and brought in through the gas feed line at the top of the chamber. Excited molecular,[11,12] atomic, and/or radical species and electrons are transported out of the plasma region and mixed with the neutral SiH_4, which is delivered through the gas-dispersal ring. The fraction of ions (and hence electrons as well) in the mixture is small, approximately 10^{-6} to 10^{-4}.[13] The gas-flow rates, combined with a rf power of 25 W into the top gas delivery tube are such that the plasma glow is confined to the gas-delivery tube, which is outside of the deposition chamber. Moreover, the transport conditions are such that backstreaming of SiH_4 gas into the gas delivery tube is unlikely. The combination of gas-flow rates and pressures is such that the mean free path for bimolecular collisions is in the range of 0.05—0.1 mm, and the distances between the top of the chamber and the dispersal ring, and between the dispersal ring and the substrate, are each 5.0 cm. This means any chemical interactions between the species extracted from the plasma region and the neutral SiH_4 which involve a small number of molecular collisions will take place in the immediate vicinity of the dispersal ring. By analogy with studies done on plasma-excited mixtures of SiH_4 and PH_3 and AsH_3 (Ref. 11) and NH_3,[12] we believe that reactions between NH and NH_2 groups [derived from the plasma excitation of the NH_3 (Ref. 12)] and SiH_4 result in the generation of $(SiH_3)_2$-NH and SiH_3-NH_2,[11] which serve as precursor species for the CVD process. The generation of these precursor species is consistent with our observations regarding the bonding of hydrogen in these films. We find evidence via ir spectroscopy for NH and NH_2 groups in the deposited films, and depositions using ND_3 instead of NH_3 have established that the source of the H in the NH and NH_2 groups is the NH_3 and not the SiH_4. We are currently studying the gas-phase and surface reactions in this process to determine the validity of this assumption regarding precursor formation and its role in the CVD process. We cannot rule out other active species in film formation such as radicals produced via (a) plasma excitation of the NH_3, or (b) through reactions of the plasma-generated species (including electrons) with the SiH_4. Qualitatively similar considerations apply to the depositions in which we excite a N_2- and He-gas mixture rather than NH_3. Films grown from the N_2- and He-gas mixture do not display ir-detectable NH or NH_2 groups (detection limit about 0.5

TABLE I. Deposition parameters for the RPECVD process. Base pressure, $<5\times10^{-8}$ Torr; operating pressure, 300 mTorr. Gas mixtures: 10 vol % silane in Ar, 20 vol % O_2 in He; and 20 vol % N_2 in He.

Excited gas	Atomic ratio [O or N]/[Si]	Gas-flow rate Excited gas (sccm)	silane	Substrate temperature (°C)	Deposition rate (Å/s)
O_2(He)	44	132	12	250—500	1.75
N_2(He)	42	125	12	200—400	0.10
NH_3	167	100	6.0	50—500	0.50

TABLE II. Variation of deposition rate with dilution.

Substrate temperature T_s (°C)	Gas-flow ratio $[N_2]/([N_2]+[He])$	Thin-film growth rate (Å/min)
400	0.42	3.8
400	0.20	5.7
400	0.11	6.7
400	0.03	8.6

at. %), and this leads us to believe that if there is precursor formation involving a reaction between the transported nitrogen species and SiH_4 that the precursor species are qualitatively different than those produced through the reaction of the NH_3 products and SiH_4. Films deposited at low T_s from the N_2- and He-gas mixture display weak ir absorption corresponding the SiH bonding groups.

We have varied the $[N_2]/[He]$ ratio and found that the deposition rate is a function of this ratio. For example, changing the gas mixture from [cubic centimeters per minute at standard temperature and pressure (sccm)] 75 sccm N_2/100 sccm He to 25 sccm N_2/100 sccm He increases the growth rate by 50%. Additional dilution with He serves to increase the deposition rate still further. Table II indicates the variation of the deposition rate with He dilution defined as $[N_2]/([N_2]+[He])$, where $[N_2]$ and [He] are the flow rates and, at constant pressure, also the effective concentrations of N_2 and He, respectively. We also note that films produced at different levels of He dilution display the same bonding of Si and N as evidenced by identical ir spectra. We have also observed changes in the bonding of H in films produced by diluting NH_3 with either Ar or He.[7] Differences in the film composition have enabled us to conclude that the rare-gas species play two distinct roles; first, as simple diluents (for example, reducing N-atom deexcitation collision rates), and second, as active participants in the deposition chemistry through Penning-type energy-transfer collision reactions.[13]

III. SPECTROSCOPIC ANALYSIS OF THE DEPOSITED FILMS

We have studied the chemical bonding in the deposited thin films by ir, x-ray photoemission spectroscopy (XPS), Rutherford backscattering spectroscopy (RBS), and Auger-electron spectroscopy (AES). We discuss the ir results in considerable detail since they provide the most direct information relative to bonding of the constituent atoms. The XPS, RBS, and AES studies have also yielded important information relative to the local bonding of Si and N, primarily the ratio of silicon to nitrogen atoms. Figures 2(a)–2(c) give the ir-absorption spectra of films grown from reaction (I) involving excited NH_3 and neutral silane, and deposited at different substrate temperatures. There is a relatively large amount of literature dealing with the frequencies of the various SiH, NH, and SiN vibrations.[14–16] We summarize these data in Table III, and give the displacement vectors associated with the various SiN vibrations in Fig. 3. The displacement vectors for the SiH and NH modes have also been discussed in the literature,[14–16] but are not emphasized in this paper. They are simply either high-frequency bond-stretching vibrations wherein the H atom moves along the direction of the SiH or NH bond, or lower-frequency, doubly degenerate bending vibrations wherein the H-atom motion is perpendicular to the bond direction.[15]

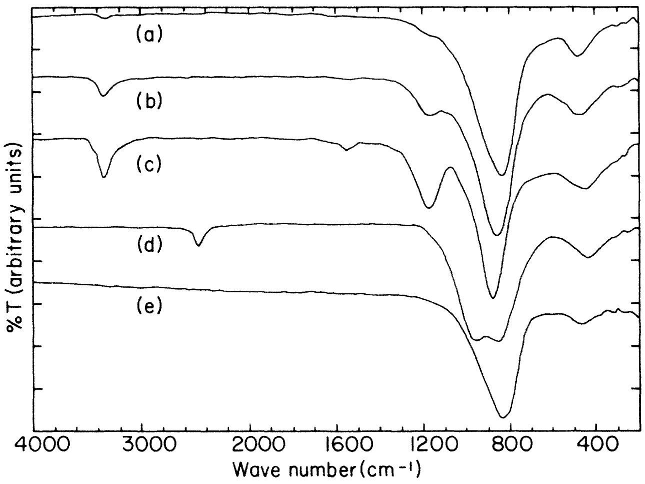

FIG. 2. ir absorption spectra for films grown from excited NH_3 at various T_s: (a) 500 °C, (b) 250 °C, and (c) 100 °C; (d) for a film grown from excited ND_3 at a T_s of 250°C, and (e) for a film grown at $T_s = 400$ °C from an excited N_2- and He-gas mixture.

There are a number of ir-absorption bands that are common to all of the spectra shown in Figs. 2(a)–2(c); these are (a) a NH stretching vibration centered at about 3335 cm^{-1}, (b) a NH bending vibration at 1175 cm^{-1}, (c) a SiN stretching vibration whose frequency varies between 885 and 835 cm^{-1} depending on T_s, and (d) a Si breathing vibration whose frequency varies between 430 and 490 cm^{-1} also as a function of T_s. In addition, films grown at the lowest T_s, 100 °C, display a shoulder on the high-frequency side of the 3335-cm^{-1} band and an additional weak feature at 1545 cm^{-1}. We interpret these additional features as a NH_2 stretching vibration and a NH_2 scissors bending vibration, respectively. There is no evidence for any absorption associated with SiH vibrations, which would occur between 2100 and 2200 cm^{-1}. The limit of ir detection of SiH bands is about 0.5 at. % H. Figure 2(d) shows the ir absorption for a film grown with deuterated ammonia, ND_3, instead of NH_3. This film displays ND stretching and bending vibrations at frequencies of 2475 and 970 cm^{-1}, respectively, but shows no evidence for absorption associated with NH or SiH groups. This means that the source of the bonded H (or D) in the films shown in Figs. 2(a)–2(d) is the NH_3 (or ND_3) and not the SiH_4.

Consider next films produced by reaction (II) involving the excited mixture of N_2 and He. The deposition rate for these films is less than 0.1 Å/sec for the gas ratio of 75 sccm N_2/100 sccm He, and increases by about 50% when the N_2 flow rate is reduced to 25 sccm. The maximum deposition rate achieved to date with higher levels of He dilution (see Table II) approaches 0.15 Å/sec and is comparable to minimum deposition rates we have found for process (I) in which we excite NH_3 instead of the N_2- and

TABLE III. Vibrational frequencies.

Bonding group	Motion	Frequency (cm^{-1})	ir activity	Reference
SiN	stretch	830—890	strong	14,16
SiH(Si_3N_4)	stretch	2100—2200	medium	15,16
(SiO_2)		2250	medium	19
NH	stretch	3335	medium	14
	bend	1175	strong	14
SiSi	"breathing"	430—490	weak	19
SiO	stretch	1050—1080	strong	25
	bend	800	weak	25
	rock	465	medium	25
OH	stretch	3650	medium	25
ND	stretch	2480	medium	14
	bend	970	strong	14

He-gas mixtures. Using the most concentrated N_2- and He-gas mixtures, we have found polysilane powder deposits in the pumping manifold of the deposition system, indicating incomplete consumption of the SiH_4 gas.[17] This is consistent with the relatively short lifetime of excited N atoms. Increased dilution of the N_2 with He increases the deposition rate by inhibiting recombination and/or deexcitation reactions involving collisions between N atoms and nitrogen molecules.[18]

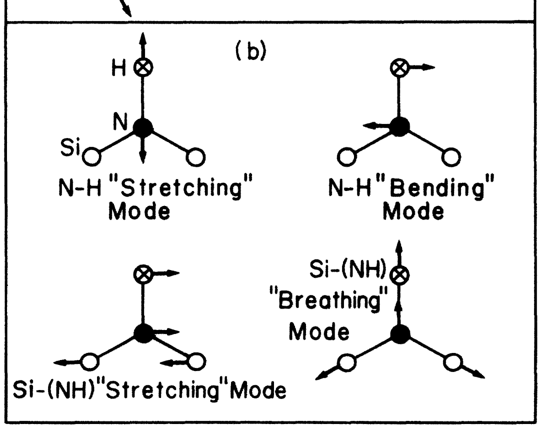

FIG. 3. Atomic displacements in ir-active vibrations involving Si, N, and H atoms: (a) the Si breathing and Si—N stretching vibrations in Si_3N_4, and (b) the N—H stretching and bending vibrations, and the Si—(NH) stretching and breathing modes in $Si(NH)_2$.

Figure 2(e) indicates the ir spectra of a film grown from the excited N_2- and He-gas mixture. These films are qualitatively different than films produced using NH_3 or ND_3. The films are characterized by the following absorption bands: (a) a SiH stretching vibration at about 2180 cm^{-1} (this band is not evident on the trace shown in the diagram for $T_s = 400\,°C$, but does show up in films grown at lower T_s, $< 350\,°C$), (b) a SiN vibration at 835 cm^{-1}, and (c) a silicon breathing vibration at about 470 cm^{-1}. In addition, there is no ir evidence for NH vibrations of any sort. In the next section we quantify the ir results, and use these as the basis for a model of the local atomic structure. At this point we note that films produced from NH_3 (ND_3) have hydrogen incorporated in NH (ND) or NH_2 (ND_2) bonding groups, while films produced from N_2- and He-gas mixtures show no NH bonds, but do contain SiH bonds at lower T_s conditions. In the first instance we have shown that the source of the bonded hydrogen is the NH_3 (ND_3), whereas in the second case it is clearly the silane.

IV. LOCAL ATOMIC STRUCTURE IN DEPOSITED FILMS

We focus initially on the hydrogen concentrations, and use the following empirical relationships to estimate the number of SiH and NH bonds:

$$[H]_i = K_i \int a(\omega)d\omega = K_i a_m \Delta\omega ,$$

where $[H]_i$ is the bonded-hydrogen concentration (the subscript i is used to distinguish between SiH and NH bonding), $a(\omega)$ is the absorption constant at the energy ω, a_m the maximum value of the $a(\omega)$, and $\Delta\omega$ the half width of the absorption band. Langford and Rand[19] have used a resonant nuclear-reaction technique to obtain values of K_i for SiH and NH vibrations. They find that $K_{SiH} = 7.1\times10^{16}$ cm^{-1} and $K_{NH} = 8.2\times10^{16}$ cm^{-1}. Applying these results to our absorption data, we find that [H] ranges from about 0.5 to 4.4×10^{22} cm^{-3} for films produced from the excited NH_3. This decrease in the bonded-hydrogen concentration comes about as T_s is increased from 100 to 500 °C (see Fig. 2). In this instance the bonded H is in the form of NH groups. For the films produced using the excited N_2- and He-gas mixture, [H] ranges from 1.0×10^{22} cm^{-3} for $T_s=200$ °C to a value below the detection limit of about 10^{21} cm^{-3} for $T_s>350$ °C. In this instance the bonded H is in SiH groups only (see Fig. 2).

Figure 4(a) gives the variation of the SiN stretching-mode frequency as a function of T_s for films produced using the ammonia source. Note that the SiN frequency decreases monotonically as T_s is increased, and that the frequency of this mode approaches a value of about 835 cm^{-1} in films deposited at the highest T_s we have explored. This limiting value of the SiN stretching frequency is very close to the frequency of 835 cm^{-1} that is found in Si_3N_4 films produced by the process [reaction (II)] in which the source of nitrogen is the N_2- and He-gas mixture. The frequency of the SiN vibration in the film grown from ND_3 is slightly lower, by about 10 cm^{-1}, than what we find in a film grown from NH_3 at the same T_s. This is a manifestation of the fact that for $T_s=250$ °C there is still a significant fraction of either NH or ND bonds present and that the density of these bonds contributes to the shift of the SiN frequency shown in the figure. The motion involved in the SiN stretch is such that if NH or ND bonds are present the H or D atoms are, to a very good approximation, rigidly displaced along with the nitrogen atom.[13,14] This means that the effective-mode mass is larger in the deuterated film, 16 as compared to 15 amu, and this in turn accounts for the reduced frequency. Figure 4(b) gives a similar plot for the frequency of the Si breathing mode. The frequency of this mode also shows a systematic shift with T_s; however, in this case the high-T_s limit does not coincide with the frequency of the Si breathing mode in Si_3N_4 produced using the N_2 reaction. We believe that the difference derives from differences in the way hydrogen is bonded in the films produced from NH_3 and N_2- and He-gas mixtures; in NH bonds in the first case and SiH bonds in the second. The results for the deuterated film, in which this vibration is shifted from 460 to 430 cm^{-1} when compared with a hydrogen containing film grown at the same T_s, support this explanation. It should be noted that amorphous Si films containing a variety of different alloy atoms including H, F, N, O, and C also show absorption bands between 450 and 500 cm^{-1},[20] and it has proven very difficult to isolate the atomic displacement vectors associated with all of these bands. Our results on the silicon-atom breathing mode in various types of nitride films have yielded a similar situation with regard to a precise description of atomic displacements.

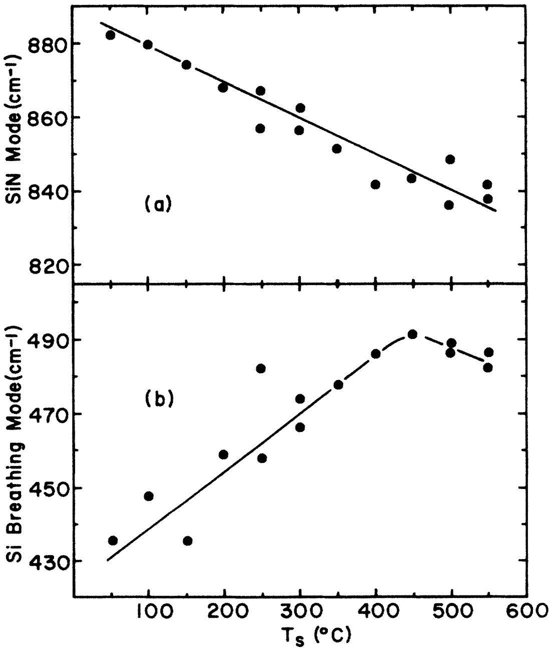

FIG. 4. Temperature dependence of (a) the Si—N stretching-mode frequency and (b) the Si breathing-mode frequency in films deposited from excited NH_3.

Figure 5 includes schematic representations of the local atomic structure at the nitrogen-atom sites in the two different types of "silicon nitride" films. Figure 5(a) gives the structure for films grown by process (I) at high temperature and by process (II) at all temperatures, and Fig. 5(b) does so for films grown by process (I) at low temperature. Consider first the films produced by process (II) using the excited N_2- and He-gas mixtures. The properties of these films produced at T_s in excess of about 350 °C are essentially the same as those of Si_3N_4 films produced by high-temperature (> 700 °C) CVD reactions. The properties we have explored include the frequency of the SiN vibration, the index of refraction, and the etch rate in phosphoric acid. This bonding model is supported by estimates of [Si]/[N] ratios that are obtained from XPS, RBS, and AES studies. At low T_s these films also contain a significant concentration of SiH bonds, approximately 9%. This concentration decreases as T_s increases. However, we find little variation in the SiN and Si breathing-mode vibrational frequencies. This leads us to conclude that the local atomic structure at the Si and N sites is the same over the entire concentration range, ex-

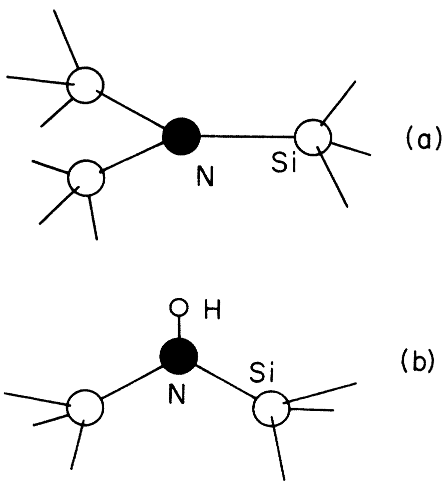

FIG. 5. Local bonding arrangements at the nitrogen atom sites in (a) Si_3N_4 and (b) $Si(NH)_2$.

cept for the decrease in the number of SiH bonds. The local bonding at the Si and N sites is (1) each Si atom has a tetrahedral arrangement of four nitrogen neighbors, and (2) each N atom has three Si neighbors and these are in a planar geometry with the nitrogen atom at the center of an equilateral triangle defined by its three Si neighbors.[21]

The ir spectra indicate that the local atomic structure at the nitrogen atoms sites of the high-T_s films grown from the NH_3 reaction [process (I)] is the same as that in the films grown from process (II). In addition, the index of refraction and the etch properties of these films are also essentially the same as those produced from the N_2-He reaction. The only differences between the process-(II) and high-T_s process-(I) films are (1) the presence of a small concentration of SiH bonds in the films produced from the N_2-He reaction and no detectable SiH bonds in the films grown from excited NH_3, and (2) a small concentration of NH bonds in the films grown from NH_3 and none in the films grown from N_2-He. As stated above, we believe that these differences in hydrogen bonding determine, in part, the differences in the frequencies of Si breathing modes.

Figure 5(b) indicates the model for the local atomic structure in the low-T_s films produced from NH_3. The concentration of NH bonds, determined from the ir measurements, and the [Si]/[N] ratio, estimated from XPS and RBS studies, all combine to yield a chemical composition very close to $Si(NH)_2$, silicon diimide, or polysilazane. This material has been synthesized in powder form,[22] but to the best of our knowledge it has never been discussed in the context of a deposited thin film. Our depositions then represent the first time a report has been made relative to production of silicon diimide in a polymerized solid-state form. The structure shown in Fig. 5(b), and inferred from the ir results, consists of NH groups inserted between pairs of Si atoms with the NH bond in the plane defined by the Si—N—Si linkage. The local bonding geometry of the Si—N—Si linkage and the orientation of the NH group in the same bonding plane is the same as that in the molecule silazane.[22] The local bonding in the solid-state polymerized diimide is then in effect the SiO_2 local atomic structure with the NH group substituted for the oxygen atom. The NH group is isolectronic with oxygen, so that a structure of this sort is not surprising. There is additional evidence in molecular chemistry for this similarity in bonding and associated properties between silane derivatives having O and HN groups, as, for example, in the structure and properties of disiloxane, $(H_3Si)_2$—O, and silazane, $(H_3Si)_2$—NH.[22] Moreover, the properties of the polymerized silicon diimide, in particular, its index of refraction and etching properties, suggest that it is more like SiO_2 than Si_3N_4. We have also observed that the diimide films are not stable in a wet ambient and easily convert to SiO_2. This is consistent with the behavior of NH groups in other silane derivative materials.[23]

The ir studies show that as T_s is increased there is a continuous and smooth transition between the silicon diimide structure and the silicon nitride structure. This shift is accompanied by a loss of hydrogen, and is emphasized in Fig. 6 where we plot the variation of the SiN frequency as a function of the hydrogen concentration. The difference in the SiN stretching-mode frequencies in the silicon diimide and silicon nitride films has two possible origins: (1) from changes in the bond angle at the nitrogen atom site from 120° in Si_3N_4 to approximately 128° in the diimide,[24] and (2) from increases in the Si-N force constant between the nitride and diimide. An increase in force constant relative to the nitride is anticipated from the differences in the Si—N bond lengths in trisilylamine (1.738 Å) and silazane (1.725 Å). A model calculation based on Bethe-lattice structures suggests that the force-constant changes are more important. In addition, the ir results imply that in films formed using NH_3 and deposited at intermediate temperatures there are two different local bonding arrangements at the nitrogen atom sites, one in which there are three silicon neighbors, and a second in which there are two silicon neighbors and one hydrogen neighbor. These are incorporated in random fashion, so that the intermediate-T_s films are in effect solid solutions of Si_3N_4 and $Si(NH)_2$, an analog of silicon oxynitride materials.

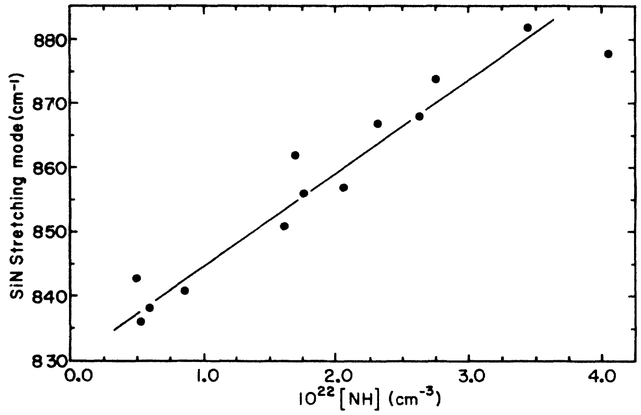

FIG. 6. Variation of the Si—N stretching-mode frequency as a function of the hydrogen-atom concentration (NH bonds) in films grown from excited NH_3.

There are two other points relative to local chemical bonding that we have made relative to films grown from NH_3. First, at very low T_s, 50 and 100 °C, we have noted the presence of a small concentration of NH_2 groups. This is deduced from the ir absorption. Second, in films grown from ND_3 we find ir evidence for ND rather than NH motions.

V. DEPOSITION CHEMISTRY

We have developed an empirical model to describe the RPECVD process, and have discussed this model briefly earlier in this paper. At this point, we restate the steps in the process; first in general terms, and then in terms of reactions which we believe are representative of those that occur in the deposition process. The RPECVD process can be viewed as a four-stage process in which the constituent steps are (a) the excitation of one of the gas reactants, or a mixture of gases containing the active reactant, (b) the transport of the excited species out of the plasma region, (c) the (complete or partial) reaction of the transported species in a plasma-free region with the second-gas reactant, and (d) the deposition of a film by a CVD process on a heated substrate. In our studies, we have used three different first-step reactants, NH_3, ND_3, and a N_2- and He-gas mixture. The second reactant has been SiH_4 diluted with Ar. We have also performed a set of experiments using diluted disilane, Si_2H_6, in place of SiH_4 and have found that this substitution does not change the bonding character in the deposited films, but does increase the deposition rate by a small factor. In each instance the first step of the process creates a chemically active nitrogen species: We believe that these are NH and NH_2, HD and ND_2, and N, respectively. These species may be either neutral or excited, but the majority of these are not charged.[13] The atomic or molecular species, along with electrons (in some instances rare-gas atoms), are transported out of the plasma region and mix with the neutral silane. Back-diffusion of gases into the plasma region from the deposition chamber is unlikely due to the high flow rate (of the order of 100 sccm) and the pressure. Since the mean free path for bimolecular collisions is very small (<0.1 mm) compared to the distance between the dispersal ring and the heated substrate (5 cm), the mixing of the transported species and silane can result in gas-phase reactions that produce precursor species. The evidence for precursor formation is twofold: (a) by analogy with chemically similar gas-phase reactions that have been studied elsewhere,[11] and (b) by the nature of the bonding groups we have found in the deposited films. (We are currently building a second system which will have provisions for studying the gas-phase constituents by mass spectrometry and optical spectroscopy.) Consider first the process in which NH_3 is plasma-excited. Sequida[12] has found that the dominant species in a NH_3 discharge is NH with smaller amounts of NH_2. Other studies have shown that plasma-excited mixtures of PH_3 and AsH_3, with SiH_4 yield $(SiH_3)_2$—PH and SiH_3—PH_2, and $(SiH_3)_2$—AsH and SiH_3—AsH_2, respectively.[11] Based on these observations regarding gas-phase chemistry, and on the presence of NH and NH_2 bonding groups in the films, we believe that the gas-phase precursor species generated by reactions between NH and NH_2 and SiH_4 include bonded NH and NH_2 groups as in $(SiH_3)_2$—NH and SiH_3—NH_2, respectively. In each instance the source of the NH or NH_2 groups is the NH_3. This last point is supported by the experiments we have discussed in which ND_3 has been substituted for NH_3.

In the case of the excitation of the N_2- and He-gas mixture and the subsequent mixing of the extracted species with SiH_4, we believe that if precursor species are formed they do not contain NH or NH_2 groups. This is inferred from the absence of these bonding groups in the deposited films. One possible precursor species is trisilylamine $(SiH_3)_3$—N. The generation of this species involves at least three collisions and cannot be eliminated by the rate of gas-phase binary collisions. So far we have only mentioned precursor molecules; it is also likely that precursor radicals are formed. However, without direct spectroscopic evidence we will not speculate on the specific nature of these.

The final step in the deposition process involves a CVD reaction at the heated substrate. For depositions involving NH_3 and ND_3, there is no ir evidence for SiH bonds in the deposited films, even though some of the precursor species may contain SiH_n ($n=1$, 2, 3, or 4) groups. We believe that H is removed from SiH_n groups via a reaction in which they are replaced by NH (or NH_2) groups. Referring to Table I it should be noted that the number of NH groups available for reaction exceeds the number of SiH groups by a significant factor (in excess of 10). We find a similar behavior in the deposition process for SiO_2 films; i.e., the deposited films show no ir evidence for SiH bonding groups.[5,6,8] In this case we believe that the H atoms are replaced by O atoms in the thin-film condensation step. In the case of the SiO_2 process we believe that one of the likely precursor species is disiloxane, $(SiH_3)_2$—O. This species has been found in glow discharges involving SiH_4 and NO.[17] In depositions from N_2- and He-gas mixtures, we believe that N atoms replace H in the final condensation step, but that this reaction is not as effective as the replacement of H by NH or O, as in the depositions of $Si(NH)_2$ and SiO_2, respectively. Note that the deposition rate increases significantly as the He dilution is increased. This is consistent with there being an increased supply of N atoms available for precursor formation and the removal of SiH groups in the CVD reaction.

VI. CONCLUSION

We have described a new process for the deposition of thin silicon nitride films, and have shown that there are two compound phases that can form silicon nitride, Si_3N_4, and silicon diimide, $Si(NH)_2$. The diimide is an isoelectronic analog of SiO_2 in which each oxygen atom is replaced by a NH group. We have also been able to grow alloys of Si_3N_4 and $Si(NH)_2$. These alloys are isoelectronic analogs of the silicon oxynitrides (see note added in proof). We have also shown that the frequency of the SiN stretching vibration is a good measure of the alloy composition in the binary nitride-diimide system. We have identified the deposition conditions under which the number of SiH or NH groups can be minimized, and have thereby shown that we can generate two different types of Si_3N_4: Si_3N_4 with residual concentrations of either (1) SiH bonds, as grown from N_2- and He-gas mixtures, or (2) NH bonds, as grown from NH_3. We are currently studying trapping and recombination processes in these films to determine the electronic activity of SiH and NH centers in Si_3N_4. Recall that the tight-binding model of Lucovsky and Lin[3] predicts that the SiH center can be active as either a hole or an electron trap, but that the NH center will only be active as an electron trap.

We have designed and are currently assembling a second system which will allow for both deposition of thin films and the analysis of gas-phase species. The analysis of gas-phase species will be via mass spectrometry and optical spectroscopy. These measurements are expected to yield information relative to the details of the deposition chemistry and, in particular, resolve some of the questions raised in this paper relative to the nature of precursor species.

Note added in proof. We have recently grown thin films of amorphous SiO_xN_y by the RPECVD process discussed above. We plasma excited mixtures of NH_3 and He, and O_2 and He and by varying the ratio of O_2 to NH_3, we have grown films with different values of x and y, which we have shown lie on (or very close) to the join line between SiO_2 and Si_3N_4. These films contain no detectable SiH bonds (by ir), and only relatively small concentrations of NH bonds. There is no evidence for Si—Si bonds via AES. Our ir absorption measurements yield a single dominant feature (exclusive of the NH bending vibration absorption) in the spectral range from about 800 to 1200 cm^{-1}. This vibration is a stretching vibration involving motion of the oxygen atoms and/or the nitrogen atoms in phase opposition to a motion of their silicon neighbors; hence the high ir activity. The oxygen and nitrogen atom motions are strongly coupled in the oxynitrides, hence these films display a single feature which tracks monotonically and essentially linearly between the corresponding frequencies of the two end members. This behavior parallels what we discussed above for the nitrid-diimide alloys, and gives additional support to the analogy we have made concerning the local atomic structure of silicon diimide and its intimate relationship to that of SiO_2.

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