

between the elements. At low temperatures and short diffusion distances, this region may contain added structure due to the formation of particularly stable amorphous alloy compositions. In iron-silicon, this region develops in a smooth manner without any significant added structure. In titanium-silicon, a significant plateau of a particular composition of amorphous alloy is found to develop.

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## Structure and Chemistry of Silicon Nitride and Silicon Carbonitride Thin Films Deposited from Ethylsilazane in Ammonia or Hydrogen

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Amorphous silicon nitride or silicon carbonitride thin films were deposited on (100) silicon substrates by the pyrolysis of ethylsilazane,  $[\text{CH}_2\text{CH}_3\text{SiH}_n\text{NH}]_n$ , in ammonia or hydrogen in the temperature range 873–1073 K at 0.1 MPa. Studies by means of Auger electron spectroscopy, Rutherford backscattering spectroscopy, and nuclear reaction analysis indicated the removal of carbon species present in the precursor to yield silicon nitride when the deposition was carried out in ammonia. Carbon-related bonds were, however, partially ruptured in the precursor when hydrogen was used, resulting in the formation of silicon carbonitride. The hydrogen content was determined by elastic recoil detection to decrease from 18 to  $10 \pm 1\%$  in silicon nitride and from  $21$  to  $8 \pm 1\%$  in silicon carbonitride with increasing deposition temperature. Fourier transform infrared spectroscopy analysis showed only Si-H<sub>n</sub> bonds ( $n = 1, 2, 3$ ) in silicon carbonitride and only N-H<sub>n</sub> bonds ( $n = 1, 2$ ) in silicon nitride. The refractive index increased with the deposition temperature from 1.86 to 2.10 for silicon nitride and from 1.81 to 2.09 for silicon carbonitride. The average deposition rate measured by ellipsometry increased with temperature from 1.9 to 49 nm/min. The apparent activation energies calculated from the slopes of the Arrhenius plot were equal to 19 and 43 kJ/mol in the mass transport regime and to 181 and 197 kJ/mol in the kinetic regime for silicon carbonitride and silicon nitride, respectively.

### Introduction

As a consequence of their superior physical, chemical, and thermal properties, silicon nitride and silicon carbonitride thin films have been the subject of extensive research during the past two decades for both structural and microelectronic device applications. Chemical vapor deposition (CVD) is commonly used to produce thin films of these materials.<sup>1</sup> Many different chemical species have been used to form silicon nitride, but most involve reactions between silane<sup>2-4</sup> or a silicon halide<sup>1,5</sup> and either ammonia or nitrogen in the temperature range 1000–1400 K. Silicon carbonitride has been deposited by adding propane as a carbon source to the gas mixture of silicon halide, ammonia, and hydrogen at temperatures above 1400 K.<sup>6</sup>

Even though CVD provides a unique way to produce both silicon nitride and silicon carbonitride films of high density and purity, irrespective of the substrate geometry,<sup>1</sup> high deposition temperatures have remained a major limitation of this process. High deposition temperatures may lead to interlayer atomic diffusion and thus substrate degradation, to peeling of the film because of mismatch in thermal expansion coefficients, and to temperature-induced changes in the shape or the crystallinity of the substrate.<sup>7</sup> These problems can be minimized, however,

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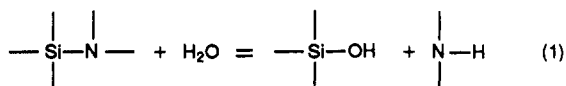
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through the use of organosilicon compound precursors which already contain the bond structures of the silicon-based ceramics and thus lead to lower deposition temperatures.<sup>8</sup>

Since Yajima<sup>9</sup> developed the first useful organosilicon compound, a poly(carbosilane) precursor of silicon carbide, there has been vigorous research on the synthesis of polymeric precursors to yield silicon-based ceramic materials upon pyrolysis. Most of the work has been focused on the synthesis of precursors to silicon carbide, and few polymeric compounds have been developed for the production of silicon nitride.<sup>10,11</sup> This is probably due to the lability of the Si-N bond in the precursor with respect to reaction with moisture (eq 1).<sup>10</sup> Moisture sensitivity is



responsible for oxygen incorporation in the polymer, which in turn leads to significant oxygen contamination of the products of pyrolysis. The strong competitive formation of silicon carbide in the final product upon pyrolysis of C-Si-N backbone polymer brings about another difficulty for the synthesis of silicon nitride.<sup>11</sup>

Seyferth et al.<sup>12</sup> reported that the reaction of methyl-dichlorosilane with anhydrous ammonia in diethyl ether leads to the formation of a cyclic compound of methylsilazane, which can be used as a precursor to silicon nitride. Further cross-linking through Si<sub>2</sub>N<sub>2</sub> bridges with the aid of a strong catalytic base has been explored to increase molecular weight and to produce high-yield ceramic materials upon pyrolysis.<sup>13</sup> While these studies emphasize the synthetic routes from polymer to ceramic, it was demonstrated recently that the cyclic methyl monomer can be used as a gaseous precursor for the deposition of silicon-based ceramic films by metalloorganic chemical vapor deposition.<sup>14-18</sup> These films were susceptible to oxygen contamination,<sup>14-17</sup> and complete removal of carbon was not possible upon deposition in the presence of ammonia.<sup>14</sup>

In the present work, an ethylsilazane compound was synthesized and used as a precursor to deposit silicon nitride and silicon carbonitride thin films at moderate temperatures. Their compositions, optical constants, and deposition kinetics were analyzed by means of several

techniques. The hydrogen content and its bonding configuration, which is known to have a great influence on the physical, chemical, and electrical properties of the materials,<sup>19</sup> were also studied and correlated with the molecular structure of the precursor.

### Experimental Procedures

The liquid ethylsilazane monomer, [CH<sub>2</sub>CH<sub>3</sub>SiHNNH]<sub>n</sub>, was synthesized by a method similar to that of Seyferth et al.<sup>12</sup> The preparation involved the reaction of ethyldichlorosilane with anhydrous ammonia in diethyl ether. In brief, a 1-L three-neck round-bottom flask equipped with a dry-ice acetone condenser, an overhead paddle stirrer, and a no-air rubber septum was flame dried under nitrogen. Diethyl ether (400 mL) and ethyldichlorosilane (50 mL) were cannulated into the flask cooled to 273 K in an ice bath. An excess of anhydrous ammonia was bubbled into the flask with vigorous stirring until the solution was strongly basic. A large amount of white precipitate formed. The reaction mixture was stirred for another 2 h and then filtered under argon. The solvent was removed via trap-to-trap distillation under vacuum leaving an oily residue. The precursor was analyzed in an infrared spectrophotometer (Perkin-Elmer 983) equipped with NaCl windows in the wavenumber range 400-4000 cm<sup>-1</sup> to reveal the absorption peaks associated with individual bonds present in the precursor.

The chemical vapor deposition of silicon nitride and silicon carbonitride was carried out by reacting gaseous ethylsilazane with ammonia or hydrogen in a horizontal cold-wall reactor at 0.1 MPa in the temperature range 873-1073 K. The CVD reactor was described previously.<sup>17</sup> To minimize contamination, especially by water and oxygen molecules, the reactor was evacuated to 10<sup>-4</sup> Pa by a diffusion pump and purged several times with ultrahigh-purity (99.999% minimum) argon and hydrogen (Matheson) which were further purified by passing them through copper- and titanium-getter furnaces, respectively. The substrates were cleaved from p-type (100) single-crystal silicon wafers (Monsanto). They were cleaned in a 10% hydrofluoric acid solution for 1 min and rinsed in deionized water. The liquid ethylsilazane was injected into a stainless steel cylinder maintained at 373 K by a motorized syringe assembly. 200 std cm<sup>3</sup>/min of electronic-grade ammonia (99.9995% minimum, Matheson) or the gettered ultrahigh-purity hydrogen (99.999% minimum), passed through the container, carried the vaporized precursor into the reactor tube. An additional 300 std cm<sup>3</sup>/min of ammonia or hydrogen was also separately fed into the system to dilute the vaporized precursor further. The vapor pressure of the liquid ethylsilazane precursor was around 2.4 kPa at 373 K. The molar concentration of ethylsilazane in the input gas was kept at 2.5%.

The elemental composition of the deposits was determined by Auger electron spectroscopy (AES, Perkin-Elmer PHI 560) with a primary electron beam at 3 keV. During analyses, the films were sputtered by a 2-keV Ar<sup>+</sup> beam with a raster area of 2 × 2 mm<sup>2</sup>. The composition was also studied by Rutherford backscattering spectroscopy (RBS).<sup>20</sup> The carbon and oxygen contents of the films were determined by nuclear reaction analysis (NRA).<sup>21</sup>

The structure of the films and the hydrogen bonding configuration were studied by Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer 1760) in the transmittance mode with a resolution of 0.5 cm<sup>-1</sup>. The spectral contribution of the silicon substrates (610 cm<sup>-1</sup>)<sup>22</sup> was subtracted from the experimental data by a computer method to obtain spectra of the deposits. The hydrogen content of each film was determined by elastic recoil detection (ERD) of forwardscattered hydrogen atoms caused by 2.8-MeV He<sup>+</sup> ions impinging on the sample at a glancing angle of 15°. A silicon surface barrier detector was used to detect the hydrogen particles. A 10-μm-thick Mylar foil was used in front of the detector to filter all but the lightest particles (i.e., H).

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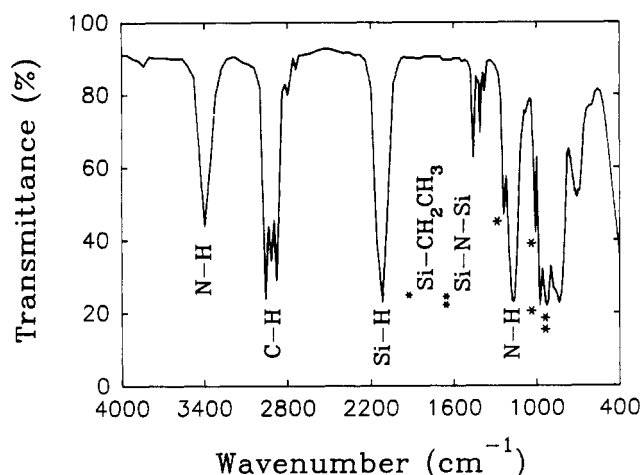


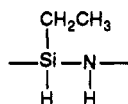
Figure 1. IR transmittance spectrum of the ethylsilazane precursor.

Details of this technique are described elsewhere.<sup>23,24</sup> ERD, unlike RBS, is not a standardless technique. A 350-nm-thick polystyrene film on silicon was used for calibration of the hydrogen content.

The average thickness and the refractive index of the deposits were determined by taking five measurements across each film with a He-Ne laser ellipsometer (Rudolph Research AutoEL-II) operating at a wavelength of 632.8 nm and a polarizer-analyzer angle of 70°.

### Results and Discussion

An understanding of the molecular structure of the precursor, such as its Si/N ratio and environments, is essential in order to obtain deposits of desired structure and composition.<sup>10</sup> As shown in Figure 1, the infrared absorption peaks at 3384 and 1172  $\text{cm}^{-1}$  arising from N-H stretching and bending modes together with the band at 929  $\text{cm}^{-1}$  (Si-N-Si asymmetric stretching) indicated the presence of Si-NH-Si structures in the precursor.<sup>25</sup> The Si-CH<sub>2</sub>CH<sub>3</sub> group was recognized by the characteristic vibrational frequencies appearing at 969, 1012, and 1233  $\text{cm}^{-1}$ .<sup>25</sup> Multiple peaks appearing at 2875, 2912, and 2955  $\text{cm}^{-1}$  were due to the C-H stretching vibrations of C-CH<sub>3</sub> and Si-CH<sub>2</sub>- groups.<sup>25</sup> The symmetric and asymmetric -CH<sub>3</sub> deformations yielded lines at 1378 and 1456  $\text{cm}^{-1}$ , respectively, whereas Si-CH<sub>2</sub>- groups showed a deformation mode at 1412  $\text{cm}^{-1}$ .<sup>25</sup> The Si-H bond gave rise to a stretching mode at 2111  $\text{cm}^{-1}$ .<sup>25</sup> The early elemental analysis and spectroscopic investigation of polysilazane suggested that it possesses a cyclic structure, in which [CH<sub>2</sub>CH<sub>2</sub>SiHNH]<sub>n</sub> rings are not linked together via Si<sub>2</sub>N<sub>2</sub> bridges.<sup>26</sup> The repeating structural unit in the ethylsilazane precursor is<sup>12</sup>



Typical AES spectra of the films deposited at 1073 K are shown in Figure 2. The Ar peak (KLL, 215 eV) which appears in both spectra is due to sputtering. For the films deposited in the presence of ammonia (b), several peaks

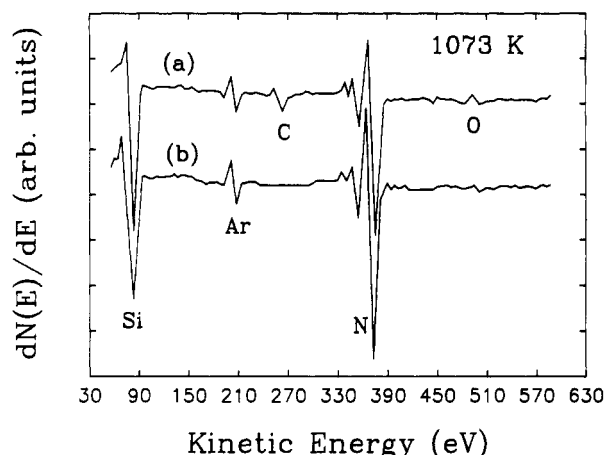


Figure 2. AES spectra of the films deposited at 1073 K in the presence of hydrogen (a) and ammonia (b).

corresponding to Si (LMM, 89 eV), N (KLL, 383 eV), and O (KLL, 511 eV) were detected in the kinetic energy range 30–600 eV. Carbon which has a KLL line at around 272 eV was undetectable by this technique, its content was found to be below the detection limit of 0.1% by NRA. Even though carbon removal in the presence of ammonia is not well understood, the transition of ethylsilazane to silicon nitride most probably takes place via a nucleophilic cleavage of CH<sub>2</sub>CH<sub>3</sub> groups from silicon in the precursor.<sup>13</sup> In the present work, essentially all carbon species were removed leaving pure silicon nitride. The approximate atomic compositions determined from AES peak-to-peak heights were Si 35, N 64, and O less than 1% for silicon nitride, and Si 43, N 48, C 7, and O 2% for silicon carbonitride with an uncertainty of  $\pm 1\%$ , deduced from the noise-to-signal ratio of the instrument. The oxygen contents of the films were shown by NRA to be negligible (less than 0.1%) in silicon nitride and equal to 1.8% in silicon carbonitride. The high values of the oxygen contents determined by AES are probably due to oxygen contamination during sputtering when the base pressure of the spectrometer was of the order of  $10^{-5}$  Pa.

It is clear that, when the deposition was conducted in hydrogen, a fraction of Si-C bonds in the precursor was incorporated in the deposit to form silicon carbonitride. Since the ethylsilazane compound has a Si:C ratio of 1:2, the observed low carbon content (films deposited at 873 K showed the highest carbon atomic concentration of  $11 \pm 1\%$ ) indicates the possible thermal dissociation of Si-CH<sub>2</sub>- bonds in the precursor upon pyrolysis. Reactions involving free radicals usually take place during the pyrolytic decomposition of organosilicon compounds with the H radical being the first product from the cleavage of the labile Si-H bond, which catalyzes further decomposition of the precursor and thereby causes recombination of radicals.<sup>10</sup> This complex rearrangement process induces the formation of Si-C units in the film structure and the evolution of volatile hydrocarbons which are responsible for the depletion in carbon of the deposits.

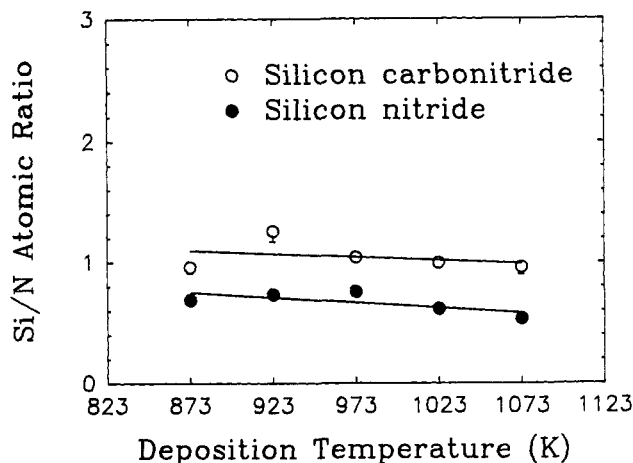
While the films grown in the presence of hydrogen exhibited carbon contents of  $7\text{--}11 \pm 1\%$ , their Si/N ratios appeared also to be consistently higher than those of silicon nitride deposited at the same temperatures as shown in Figure 3. Since the Si/N ratio in the precursor is unity, the higher nitrogen concentration in silicon nitride as compared to silicon carbonitride (its ratios were scattered between 0.55 and 0.75, irrespective of the deposition temperature) may be interpreted in the following manner. The pyrolysis of organosilicon compounds is often considered

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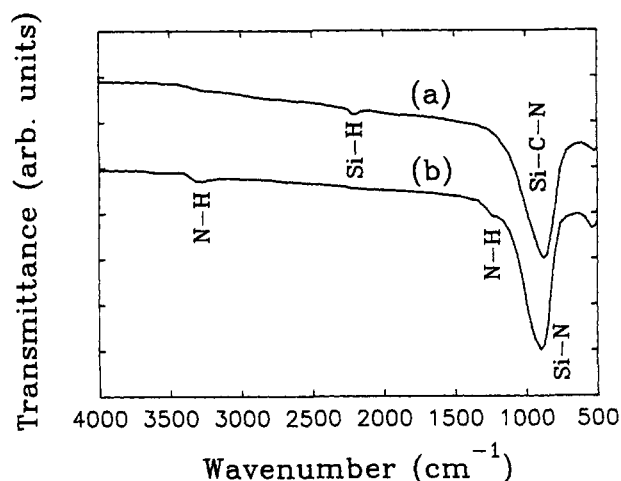
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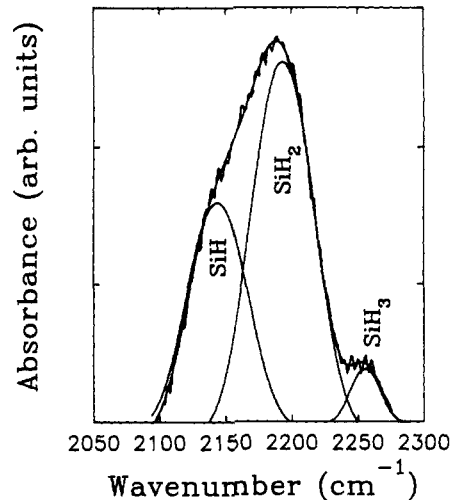
**Figure 3.** Atomic ratios of Si/N in silicon nitride and silicon carbonitride films as a function of deposition temperatures. The error bar indicates the standard deviation of the atomic ratio Si/N.



**Figure 4.** IR transmittance spectra of the films deposited at 1073 K in the presence of hydrogen (a) and ammonia (b).

to occur by selective bond breaking at high temperatures.<sup>27</sup> The thermal dissociation of ethyl and hydrogen groups from silicon and the formation of additional Si-N residue in the presence of ammonia radicals (presumably,  $\text{NH}_2$ ) should lead to an increase in the nitrogen contents of the deposit. In the films grown in the presence of hydrogen, on the other hand, the Si/N ratio appeared to be close to that of cyclic ethylsilazane (Figure 3). To validate and confirm the results determined by AES, selected silicon nitride (973 K) and silicon carbonitride (1023 K) films were further studied by RBS. Their Si/N ratios were found to be 0.73 and 1.0 for silicon nitride and silicon carbonitride, respectively, in good agreement with the AES results (0.75 and 0.99, Figure 3). These studies indicate that the relative atomic concentrations of Si, N, and C are primarily influenced by the types of carrier gases, while deposition temperature merely affects the atomic composition of the films. AES depth profiling of each sample indicated that the atomic composition of these elements remained quite uniform ( $\pm 2\%$ ) throughout the film thickness.

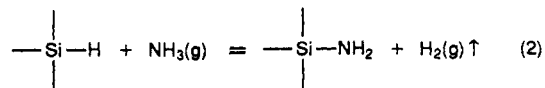
Figure 4 shows infrared transmittance spectra of the films deposited at 1073 K in the presence of hydrogen (a) and ammonia (b). The strong line centered at  $847\text{ cm}^{-1}$  in spectrum b is assigned to Si-N modes. It is indicative of the formation of amorphous silicon nitride since crys-



**Figure 5.** Curve-fitting of Si-H band centered at  $2184\text{ cm}^{-1}$  in silicon carbonitride deposited at 1073 K. Three bands corresponding to the Si-H ( $2143\text{ cm}^{-1}$ ), Si-H<sub>2</sub> ( $2192\text{ cm}^{-1}$ ), and Si-H<sub>3</sub> ( $2260\text{ cm}^{-1}$ ) exist with an approximate band ratio of 6:13:1.

talline silicon nitride ( $\alpha$ - or  $\beta$ - $\text{Si}_3\text{N}_4$ ) is characterized by multiple peaks appearing in the wavenumber range  $400\text{--}800\text{ cm}^{-1}$ .<sup>22</sup> The Si-N band centered at  $847\text{ cm}^{-1}$  appeared to be broadened near the baseline around  $1173\text{ cm}^{-1}$ . This feature can be assigned to the N-H bending mode at  $1170\text{ cm}^{-1}$ . The broad and asymmetric peak ( $3212\text{--}3454\text{ cm}^{-1}$ ), centered at  $3340\text{ cm}^{-1}$ , can be attributed to a N-H stretching band ( $3320\text{ cm}^{-1}$ ) together with N-H<sub>2</sub> symmetric ( $3280\text{ cm}^{-1}$ ) and asymmetric ( $3345\text{ cm}^{-1}$ ) stretching modes,<sup>28</sup> indicating the formation of Si-NH<sub>2</sub> structures as well as Si-NH-Si structures in the films. All the films deposited in the presence of ammonia displayed similar spectra which were unaffected by the deposition temperature.

There was no indication of the presence of Si-H bonds ( $2100\text{--}2300\text{ cm}^{-1}$ )<sup>25</sup> in silicon nitride. The absence of Si-H bonds in the film indicates that they are thermally dissociated upon pyrolysis of the precursor. This may promote the decomposition of ammonia and the recombination of the product radicals giving rise to the formation of amine structures through the reaction

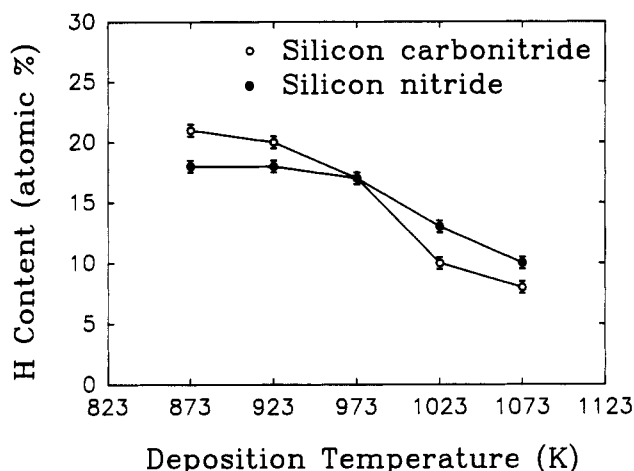


In addition to the strong line at  $830\text{ cm}^{-1}$  which may result from the fundamental stretching mode of silicon carbonitride,<sup>27</sup> the main difference between spectra (a) and (b) is the presence of a broad asymmetric band in the range of Si-H vibrational modes, which is observed to be more intense in the films deposited below 1073 K. Curve fitting<sup>29</sup> of the experimental spectrum showed that the absorption envelope centered at  $2184\text{ cm}^{-1}$  consists of three peaks centered at 2143, 2192, and  $2260\text{ cm}^{-1}$  with an approximate band ratio of 6:13:1 as shown in Figure 5. Since silicon atoms bonded to a single hydrogen (Si-H bond) should give rise to only one stretching vibration, it is an indication of the existence of multiple hydrogen-to-silicon bonds. It is known that the splitting of the triple bond group to symmetric and asymmetric stretching component is only around  $10\text{ cm}^{-1}$  in  $(\text{SiH}_3)_2$ <sup>30</sup> and the one for the

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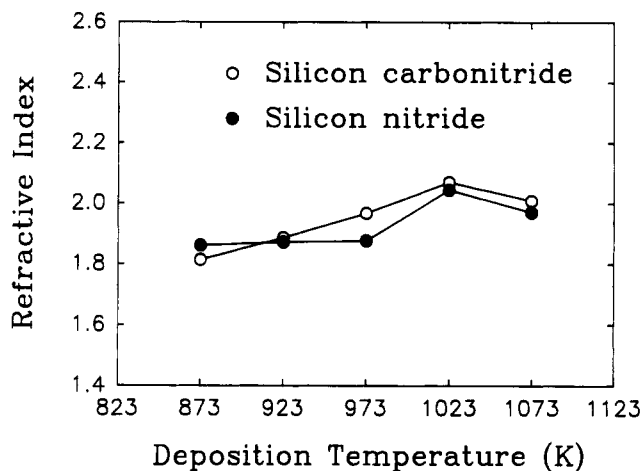
**Figure 6.** Hydrogen content of silicon nitride and silicon carbonitride, as a function of deposition temperature. The error bar indicates a typical instrumental error of  $\pm 1\%$ .

double bond group is expected to be even smaller than for the triple bond.<sup>31</sup> It is, thus, reasonable to attribute the observed features in the  $2184\text{-cm}^{-1}$  region to the stretching modes of three different Si-H groups. Since an increasing number of hydrogen atoms bonded to a specific Si atom has an additive effect on the Si-H vibrational frequency,<sup>32</sup> they may be assigned to Si-H, Si-H<sub>2</sub>, and/or (Si-H<sub>2</sub>)<sub>n</sub> chains and Si-H<sub>3</sub> groups dispersed throughout the interconnected Si network. Si-H bands at three frequencies in the range  $2000\text{--}2150\text{ cm}^{-1}$  have been also found in amorphous silicon.<sup>31</sup> The observed peak position of the Si-H band ( $2143\text{--}2260\text{ cm}^{-1}$ ) appeared to be moved to higher wavenumbers, than those reported for amorphous silicon ( $2000\text{--}2150\text{ cm}^{-1}$ ). This effect may be attributed to the inductive effect induced by attached nitrogen atoms whose electronegativity is greater than that of silicon atoms.<sup>33</sup>

The infrared bending modes of multiple hydrogen bonds are expected to be observed in the range from  $800$  to  $900\text{ cm}^{-1}$ .<sup>31</sup> In the present study, however, lines corresponding to these vibrations were not seen because of the strong absorption arising from the Si-N lattice vibration.

None of the films exhibited the C-H band around  $2900\text{ cm}^{-1}$ , which is present in the IR spectrum of the precursor (Figure 1). This observation implies that C-H bonds in the precursor can be effectively cleaved upon pyrolysis and that the dissociated carbon is incorporated into volatile hydrocarbons.<sup>13</sup>

IR spectra are often used to detect the presence of oxygen in amorphous silicon nitride films.<sup>2,22,34,35</sup> In none of the samples, were peaks detected, corresponding to Si-O, Si-O<sub>2</sub>, and Si-O-N<sub>x</sub> bond structures which are known to have strong absorption in the  $800\text{--}1150\text{-cm}^{-1}$  region.<sup>22</sup> The transmittance minima of both silicon nitride and silicon carbonitride showed a mere shift from  $847$  to  $854\text{ cm}^{-1}$  for silicon nitride and from  $830$  to  $833\text{ cm}^{-1}$  for silicon carbonitride, likely an indication of the compositional uniformity of the films,<sup>22</sup> independent of the de-



**Figure 7.** Refractive index of silicon nitride and silicon carbonitride as a function of deposition temperature.

position temperature and in agreement with the AES studies.

The atomic concentration of hydrogen in the films, determined by ERD, was found to decrease from 18% at 873 K to 10% at 1073 K for silicon nitride and similarly, from 21 to 8% for silicon carbonitride as shown in Figure 6. The hydrogen content in silicon carbonitride showed a steeper dependence on deposition temperature. The curves indicate an apparent transition temperature of 973 K at a hydrogen content of  $17 \pm 1\%$  for both silicon nitride and silicon carbonitride. Below this temperature, the hydrogen concentration has a weak dependence on temperature varying from 18 to 17% and 21 to 17% for silicon nitride and silicon carbonitride, respectively. On the other hand, the hydrogen content rapidly decreased from 17 to 10% and 17 to 8% as the deposition temperature was increased from 973 to 1073 K. Even though the apparent temperature dependence of the hydrogen content observed in this system is not fully understood at present, both the dissociation of hydrides taking place near the substrate and the out-diffusion of hydrogen atoms from the films are thermally enhanced, and both mechanisms may be responsible for this observation. It will be shown below that these two regions correspond to the mass transport and the kinetic regimes.

The variations of the refractive index of silicon nitride and silicon carbonitride thin films with temperature are shown in Figure 7. The refractive index of amorphous Si<sub>3</sub>N<sub>4</sub> is generally reported to be between 1.8 and 2.1.<sup>2</sup> The measured refractive indexes increased with deposition temperature from 1.86 to 2.10 for silicon nitride and from 1.81 to 2.09 for silicon carbonitride. It is well established that impurities such as hydrogen and oxygen may dramatically reduce the refractive index of silicon nitride.<sup>19</sup> The oxygen contents measured in the present work were found to be negligible for silicon nitride (undetectable, by NRA) and of the order of 1.8% for silicon carbonitride, irrespective of the deposition temperatures. The apparent temperature dependence of the refractive index can, however, be correlated with the hydrogen content of the films which varies strongly with temperature (Figure 6). In addition to the chemical effect, it has been proposed that hydrogen lowers the film density and thus decreases the refractive index.<sup>19</sup>

The temperature dependence of the deposition rate of silicon nitride and silicon carbonitride follows an Arrhenius relationship as shown in Figure 8. The deposition rate is found to vary from 1.9 to 49 nm/min depending on the temperature and the type of carrier gas. Two distinct

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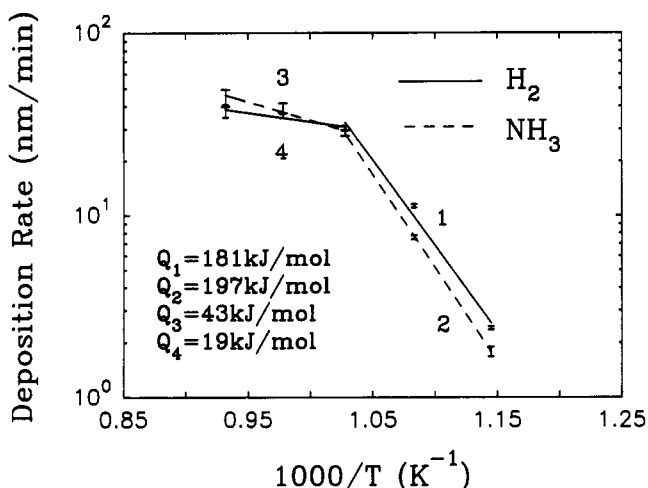
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**Figure 8.** Arrhenius plot of deposition rate as a function of reciprocal temperature. The error bar indicates the standard deviation of the deposition rates estimated from five thickness measurements.

regions are apparent in the curves with a transition around 973 K indicating changes in the nature of the rate-controlling step with deposition temperature. In the lower temperature range, a relatively steep temperature dependence is observed and the deposition rate is limited by the kinetics of a surface reaction. The average activation energies of 181 kJ/mol for silicon carbonitride and 197 kJ/mol for silicon nitride, calculated from the slope of the Arrhenius plot, fall into the range 80–400 kJ/mol usually reported for the kinetic-limited regime in CVD processes.<sup>36</sup>

The apparent activation energies are lower than the thermal dissociation energies of individual bonds in the precursor (above 340 kJ/mol).<sup>37</sup> This observation suggests that the formation of silicon nitride and silicon carbonitride from ethylsilazane takes place via selective bond breaking at the surface which may be activated by reactive gas molecules such as ammonia and hydrogen. Because of the complex processes involving decomposition, reaction, and polymerization of products taking place during the deposition, it is difficult to determine the rate-limiting reaction step for the formation of both silicon nitride and silicon carbonitride. However, as shown in Figure 8, the first-order line regressions over the standard deviation of deposition rates indicate a difference of 16 kJ/mol in the

activation energies between hydrogen and ammonia in the kinetic regime. The rate-limiting reaction path is different. The decomposition of ammonia and the removal of carbon could be possible rate-determining steps for the formation of silicon nitride.

As shown in Figure 8, above 973 K the slope of the Arrhenius curve abruptly changed and yielded average activation energies of 19 kJ/mol for silicon carbonitride and 43 kJ/mol for silicon nitride. These values are typical of those measured in the mass transport regime. It is well known that the temperature dependence of gas-phase diffusion coefficients is mild, varying as  $T^{1.5-2.0}$ .<sup>36</sup> As a consequence, the curves exhibit a smaller slope in the mass transport regime. In this regime, the deposition process is controlled mainly by the diffusion of either reactants or byproducts, presumably volatile hydrocarbons and hydrogen, through the boundary layer present between the gas phase and the deposit.

### Summary

A liquid ethylsilazane compound was synthesized from the reaction of ethyldichlorosilane with ammonia in diethyl ether and used as a precursor for the deposition of silicon nitride and silicon carbonitride thin films at moderate temperatures.

The conversion of ethylsilazane to silicon nitride involves both the thermal dissociation of Si–C, Si–H, and C–H bonds and the formation of Si–N bonds which appeared to occur via the catalytic effect of  $\text{NH}_2$  radicals decomposed from ammonia. In contrast, only C–H and N–H bonds in the precursor were ruptured in hydrogen which led to the formation of silicon carbonitride.

While the Si/N and Si/(N + C) ratios of the films determined by both AES and RBS do not appear to be dependent on the deposition temperature, the hydrogen content was decreased as the temperature of the substrates was increased for both silicon nitride and silicon carbonitride.

The hydrogen bonding configurations in the films were found to be greatly influenced by the type of carrier gas. Only N–H bonds were observed in silicon nitride and only Si–H bonds in silicon carbonitride.

It has been shown that the use of organosilicon precursors can provide novel strategies for the preparation of high-quality silicon nitride and silicon carbonitride thin films at deposition temperatures as low as 873 K.

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