Moisture Resistance of Insulating Films for Compound Semiconductor Devices

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Abstract
We demonstrate that differences in moisture resistance can be explained by film oxidation and changes in defect densities evaluated by Fourier-transform infrared spectroscopy. The insulating film with the highest moisture resistance was a stoichiometric silicon nitride (Si₃N₄) film with a refractive index of 2.1 and containing the least N–H bonds. We propose that the density of N–H bonds is a more appropriate index of moisture resistance than the refractive index by considering the oxidation mechanism of silicon nitride (SiNₓ), silicon oxynitride (SiOₓNᵧ), and silicon oxide (SiOₓ) films.

INTRODUCTION
Si₃N₄ films are widely used to protect the surface of semiconductor devices because they are more resistant to humidity than silicon dioxide (SiO₂). However, depositing silicon nitride (Si₃N₄) films at low temperatures with plasma-enhanced chemical vapor deposition (PE-CVD)—a common process in compound semiconductor devices—generates a high density of Si–H and N–H bonds, which may explain the poorer moisture resistance of Si₃N₄ films versus Si₃N₄ films deposited at high temperatures. Moreover, operating compound semiconductor devices at microwave frequencies requires the device to have low parasitic capacitance. Because of these requirements, many wish to develop a fabrication method that decreases the film thickness and dielectric constant of silicon nitride films while maintaining moisture resistance. We have worked to manufacture microwave devices with various insulating films [1]. Along with this, we have studied a technique to evaluate moisture resistance by comparing Fourier-transform infrared (FTIR) absorption spectra before and after a pressure cooker test (PCT) [2]. In the present paper, we demonstrate that moisture resistance can be compared by evaluating film oxidation and the changes in defect density from FTIR spectra.

EXPERIMENTS
The Si₃N₄, SiNₓ, SiOₓNᵧ, and SiOₓ films were deposited on GaAs wafers at ~300 °C by catalytic chemical vapor deposition (Cat-CVD) and by various types of PE-CVD, as shown in Table I. The film thickness was ~50 nm on both sides of the wafers. The moisture resistance of the insulator films was examined by a PCT in water vapor at 2 atm and 121 °C for 96 h. The oxidation ratio of the films was estimated by evaluating the Si–O and Si–N peak areas from FTIR spectra (MFT-2000; JASCO Corporation). The densities of Si–H, O–H, and N–H bonds in the insulator films were also estimated from FTIR absorption spectra [2]. To convert the absorption bands to bond densities, we used the absorption cross-sections of the Si–H and N–H bonds in the SiNₓ film [3] and the Si–H and O–H bonds in the SiOₓ film [4]. We did not consider the oxidation of the GaAs substrates because the FTIR signals for the Ga–O and As–O bonds (~500 cm⁻¹) are outside of the measurement range of the instrument. We denote the densities of X–Y bonds by using [X–Y] in this paper. To analyze the wavenumber from the FTIR absorption spectra and assess the diffusion barrier for H₂O and NH₃ molecules in the insulator films, we used semi-empirical molecular orbital calculations [5]. The model clusters comprised several hundred atoms based on their crystal structures: high-cristobalite SiO₂, Si₂N₂O, and beta-Si₃N₄ belong to the space groups O₅(Fd3m), C₂ᵥ(Cmc2₁), and C₆h(P6₃/m), respectively [6]. When we assessed SiOₓ clusters with an O–H bond, we removed a silicon atom and terminated the oxygen dangling bonds with hydrogen atoms.

<table>
<thead>
<tr>
<th>Film</th>
<th>Deposition</th>
<th>Refractive Index</th>
<th>Permittivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₃N₄</td>
<td>Cat-CVD</td>
<td>2.1</td>
<td>7</td>
</tr>
<tr>
<td>SiNₓ</td>
<td>PE-CVD</td>
<td>1.7 – 2.0</td>
<td>6 – 7</td>
</tr>
<tr>
<td>SiOₓNᵧ</td>
<td>PE-CVD</td>
<td>1.7</td>
<td>5</td>
</tr>
<tr>
<td>SiOₓ</td>
<td>PE-CVD</td>
<td>1.5</td>
<td>4</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION
Figure 1 shows examples of FTIR absorption spectra for insulating films prepared by Cat-CVD and PE-CVD before and after the PCT. For the Cat-CVD Si₃N₄ films (Fig. 1(a)), the PCT led to few changes in the Si–O and Si–N bond peaks. For the PE-CVD SiNₓ films (Fig. 1(b)), the PCT caused a Si–O bond peak to appear ~1100 cm⁻¹ and
decreased the intensity of the Si–N bond peak at ~800 cm\(^{-1}\). These changes were caused by oxidation from moisture penetrating into the SiN\(_x\) films. For the PE-CVD SiO\(_x\)N\(_y\) and SiO films (Fig. 1(c) and (d)), the PCT sharpened the Si–O bond peak at ~1076 cm\(^{-1}\) and extinguished the Si–N bond peak at ~800 cm\(^{-1}\).

Figure 1 shows the Si–O and Si–N composition ratios before and after PCT, which we calculated from the peak area of the FTIR signal. The Si–O and Si–N composition ratios are defined by \([\text{Si–O}] / ([\text{Si–N}] + [\text{Si–O}])\) and \([\text{Si–N}] / ([\text{Si–N}] + [\text{Si–O}])\), respectively. The PCT did not drastically change the Si–O and Si–N composition ratios for the SiN\(_x\) and SiN\(_4\) films. In contrast, the PCT changed these ratios drastically in the SiO\(_x\)N\(_y\) and SiO films. Because the changes in these ratios are indices of oxidation and de-nitration, these results show that the properly deposited SiN\(_x\) and SiN\(_4\) films were much more resistant to humidity than the SiO\(_x\)N\(_y\) and SiO films. The SiN\(_4\) film was most resistant to oxidation and thus to moisture.

Figure 2 shows extended FTIR absorption spectra from 1500 to 4000 cm\(^{-1}\). For the SiN\(_4\) and SiN\(_x\) films (Figs. 2(a) and (b)), the PCT caused few changes in the FTIR signal for the N–H and Si–H bond peaks at ~2200 cm\(^{-1}\) and ~3350 cm\(^{-1}\), respectively. The PCT broadened the O–H or N–H bond peaks in the SiO\(_x\)N\(_y\) films (Fig. 2(c)) and the O–H bond peak in the SiO films (Fig. 2(d)). We believe the broad absorption peaks from 2200 to 3750 cm\(^{-1}\) to be composed of three different components because they have outstanding inflection points at ~3000 cm\(^{-1}\) and ~3500 cm\(^{-1}\). The PCT suppressed the Si–H bond peak in the SiO\(_x\)N\(_y\) films. In contrast, the FTIR signal from the Si–H bond peak in the SiO films was too small both before and after PCT to note any change. To analyze this small signal we considered the peak area, which we calculated by integrating the absorption in the spectra; we will discuss this calculation later in the paper.

Figure 3 shows the Si–O and Si–N composition ratios before and after PCT. Sample (a) was prepared by Cat-CVD, while samples (b–d) were prepared by PE-CVD.
To analyze the moisture resistance of the SiNₓ and Si₃N₄ films, we show in Fig. 4 how the Si–O composition ratio changed after the PCT based on [Si–H] and [N–H]. We obtained the change in Si–O composition ratio by comparing [Si–O] / ([Si–N] + [Si–O]) before and after the PCT. Less oxidation occurred at lower [N–H], but oxidation did not depend on [Si–H].

To show how the Si–H and N–H bonds influenced oxidation, in Fig. 5 we show how the PCT changed the densities of [Si–H] and [N–H] in the SiNₓ and Si₃N₄ films. Both [Si–H] and [N–H] remained unchanged after PCT. Wet oxidation does not create additional O–H and Si–H bonds based on the following reaction: Si₃N₄ + 6 H₂O → 3 SiO₂ + 4 NH₃. Breakage of Si–N bonds by H₂O molecules involves hydroxide ions attacking Si atoms and hydrogen ions attacking N atoms, as in HF etching [7]; the oxidation reaction sequence in silicon nitride can be expressed as:

≡Si–N + 3 H₂O → ≡Si–OH + ≡SiNH + 2 H₂O → (≡Si–OH)₂ + ≡SiNH₂ + H₂O → (≡Si–OH)₃ + NH₃ → . . . → ≡SiOSiOSi ≡ + H₂O + NH₃

Here, ≡Si–X denotes a Si atom terminated by X and ≡Si denotes a Si atom and three back bonds connected to either N or O atoms. This explanation why the Si₃N₄ film with the least [N–H] was most resistant to moisture: the N–H bonds help create NH₃ molecules by skipping the first step of the reaction chain. However, the SiO₂ film created by the PCT is of low quality because the PCT temperature was lower than the standard temperature for oxidizing silicon, ~1000 °C [8].

To investigate the characteristics of the poor-quality SiO₂ film, in Fig. 6 we show the [Si–H], [O–H], and [N–H] densities in the SiO₂Nx and SiO₂ films before and after the PCT. For the SiO₂Nx and SiO₂ films, the increases in [N–H] and [O–H] after the PCT contrast the large decrease in [Si–H]. If the SiO₂Nx film is composed of Si₂N₂O and defects, a wet oxidation reaction does not create additional O–H and Si–H bonds based on the following reaction: Si₂N₂O + 3 H₂O → 2 SiO₂ + 2 NH₃. Thus, we assume the SiO₂Nx film to be composed of SiNₓ, Si₂N₂O, and SiO₂, which explains the creation of bonds in the SiO₂Nx and SiO₂ films. Also, the density of N–H bonds should not increase in the presence of excess H₂O molecules. Based on these assumptions and reasonings, we will now discuss the creation of O–H bonds in the SiO₂ film.

First, we believe the increase in [O–H] to be related to the creation of O–H bonds from the following reaction between excess H₂O molecules and the SiO₂ network: H₂O + ≡Si–O–Si ≡ → ≡Si–OH + HO–Si ≡. While the broad peak from 2200 to 3750 cm⁻¹ cannot be explained by increases in ≡Si–OH (O–H bonds), we attribute the broad peak from 3000 to 3750 cm⁻¹ to the following structures: 1) molecular water that is free, hydrogen-bonded, or structurally bound; 2) O–H bonds, hydrogen-bonded to neighboring O–H bond groups; 3) H₂O molecules; 4) O–H bonds (3672 cm⁻¹) [9]. A molecular orbital calculation (Fig. 7) shows that, to explain the broad absorption from 2200 to 3000 cm⁻¹, we must assume a structure with excess oxygen.
such as a hydrogen-terminated peroxy radical (SiO–OH). However, we cannot propose the SiO–OH formation process at the present time because it does not seem to be related to water oxidation, as shown by this reaction:

\[ \text{Si} – \text{OH} + \text{H}_2\text{O} \rightarrow \text{SiO} – \text{OH} + \text{H}_2. \]

Figure 7. Modeled cluster of SiO–OH and Si–OH bonds in a SiO\textsubscript{x} film and the respective wavenumbers (\(v\)), derived from a molecular orbital calculation.

Second, we believe the decrease in [Si–H] is related to the following reaction: \(\text{Si} – \text{H} + 3\text{H}_2\text{O} \rightarrow \text{SiH(OH)}\textsubscript{3} (\text{aq}) + 3/2\) \(\text{H}_2\). This reaction etches the SiO\textsubscript{x} film because SiH(OH)\textsubscript{3} is likely soluble in water, forming a compound such as Si(OH)\textsubscript{4} [10]. Unfortunately, our FTIR spectra could not show that etching occurred because it was not sufficiently sensitive to detect small changes in atomic compositions in the film.

Finally, to discuss the penetration of H\textsubscript{2}O molecules into the films, we derived energy barriers from molecular orbital calculations. The penetration barriers for the Si\textsubscript{3}N\textsubscript{4}, Si\textsubscript{3}N\textsubscript{2}O, and Si\textsubscript{2}NO films are 2.1, 1.8, 1.6, and 0.5 eV, respectively [11]. Because the penetration barrier is the activation energy of interstitial diffusion, the unknown actual diffusion barriers are considered to be in the corresponding barrier of interstitial diffusion. If we consider the oxidized Si\textsubscript{3}N\textsubscript{4} and Si\textsubscript{N} films to be Si\textsubscript{2}NO and Si\textsubscript{2}O films, this oxidation lowers the diffusion barrier, easing the diffusion of H\textsubscript{2}O and NH\textsubscript{3} molecules into the oxide films versus the Si\textsubscript{3}N\textsubscript{4} and Si\textsubscript{N} films, although we have not yet investigated the diffusion of NH\textsubscript{3} molecules.

Figure 8 summarizes the oxidation process in the presence of moisture: the H\textsubscript{2}O molecules attack the surface of the silicon nitride; the H\textsubscript{2}O molecules diffuse into the silicon nitride; the bulk silicon nitride oxidizes from breakage of Si–N bonds and generation of Si–O and N–H bonds; NH\textsubscript{3} molecules form and diffuse out of the silicon oxide (oxynitride) to desorb from the surface of the silicon oxide. Considering the oxidation mechanism of silicon [8], the oxide thickness \(x\) after a long time can be expressed as \(x_t = Bt\), where \(t\) is the oxidation time and \(B\) is a parameter proportional to the diffusivity of the H\textsubscript{2}O molecules in the oxide layer. Silicon oxidation is universally controlled by the thermal silicon dioxide and the silicon substrate. The oxidation of the insulator film depends on the film species, the film quality, the humidity, the pressure, and the temperature. Therefore, the [N–H] in the silicon nitride and the [O–H] in the oxide layer can be sensitive indices for moisture resistance, which is inversely proportional to the growth rate of the oxide and the quality of the oxide layer.

**CONCLUSIONS**

The most moisture-resistant film was the stoichiometric silicon nitride (Si\textsubscript{3}N\textsubscript{4}) film with a refractive index of 2.1 and minimum [N–H]. We propose that [N–H] is a more appropriate index for moisture resistance than the refractive index, because the N–H bonds help create NH\textsubscript{3} molecules during oxidation of silicon nitride. We demonstrated that the moisture resistance of the SiO\textsubscript{2}N\textsubscript{y} and SiO\textsubscript{x} films rapidly decreased after PCT because their surfaces easily changed to low-quality oxide films containing excess H\textsubscript{2}O molecules and many O–H bonds.

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**ACRONYM**

Cat-CVD: Catalytic Chemical Vapor Deposition

**REFERENCES**