# Moisture resistance of insulating films for compound semiconductor devices

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## 1. Introduction

Silicon nitride ($Si_3N_4$) films are widely used to protect the surface of semiconductor devices since they are stronger than silicon dioxide ($SiO_2$) films in humidity tests. However, since silicon nitride (SiNx) films for compound semiconductor devices are deposited at a low temperature by plasma enhanced chemical vapor deposition (PE-CVD), the large density of Si-H and N-H bonds exist in the films. It is thought that the moisture resistance of the SiNx films with defects is poorer than that of $Si_3N_4$ films deposited at the high temperature. Moreover, the application of compound semiconductor devices to operation at microwave frequencies demands a low parasitic capacitance. Accordingly, we need a method of designing the films which minimizes the film thickness and dielectric constant while keeping the moisture resistance. We have been engaged in manufacturing microwave devices with a various insulator film [1]. On the other hand, we have studied the evaluation method of the moisture resistance by a contrast of Fourier-transform infrared (FTIR) absorption spectra before and after a pressure cooker test (PCT) [2]. In this paper, we demonstrate for the first time that the difference in the moisture resistance can be explained by the oxidation of films and the change in defect densities evaluated by the FTIR spectra.

## 2. Experiments

Table I Insulator films for humidity test.

| Film | Deposition | Refractive Index | Permittivity |
|---|---|---|---|
| SiO | PE-CVD | 1.5 | 4 |
| SiON | PE-CVD | 1.7 | 5 |
| SiNx | PE-CVD | 1.7 – 2.0 | 6 - 7 |
| $Si_3N_4$ | Cat-CVD | 2.1 | 7 |

The silicon oxide (SiO), silicon oxynitride (SiON), SiNx and $Si_3N_4$ films were deposited on the GaAs wafer at the temperature around 300 ºC by a various type of PE-CVD and catalytic chemical vapor deposition (Cat-CVD) as shown in Table I. The film thickness is about 50 nm on both surface of the wafers. Moisture-resistivity for insulator films was examined by a PCT in $H_2O$ vapor at 2 atm and 121 ºC for 96 h. The oxidation ratio of the films is estimated by the Si-O and Si-N peak area measured by FTIR spectra. The densities of Si-H and N-H bonds in insulator films were estimated by FTIR absorption spectra [1]. The densities of X-Y bonds are abbreviated by the [X-Y] in this paper.

## 3. Results and discussion

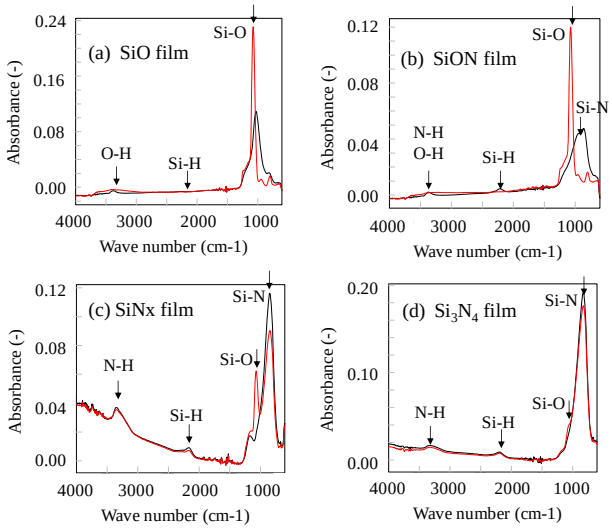


Fig. 1 FTIR absorption spectra for (a) SiO films, (b) SiON films, (c) $SiN_x$ films prepared by PECVD and (d) $Si_3N_4$ films deposited by Cat-CVD before (black spectra) and after PCT (red spectra)

Figure 1 shows the examples of FTIR absorption spectra for insulator films prepared by PE-CVD and Cat-CVD before and after the PCT. As shown in Fig. 1(a) and Fig. 1 (b), the FTIR signal due to Si-O bonds for PECVD SiON and SiO films sharpens at the wave number at 1076 $cm^{-1}$ after PCT with an extinction in the intensity of the signal due to Si-N bonds at the wave number around 800$cm^{-1}$. Little change is observed in the FTIR signal for Si-H bonds in SiON and SiO films after the PCT. It is carefully noticed that the absorbance peaks of O-H and/or N-H bonds broaden after PCT. As shown in Fig. 1(c), the FTIR signal due to Si-O bonds appears at the wave number around 1100 $cm^{-1}$ for PECVD $SiN_x$ films after the PCT with a decrease in the intensity of the signal due to Si-N bonds at the wave number around 800$cm^{-1}$. These changes originate from the oxidation by moisture penetration into $SiN_x$ films. On the other hand, little changes in the FTIR signal at the wave number around 1100 $cm^{-1}$, 3500 $cm^{-1}$for

N-H, Si-H bonds are observed for $SiN_x$ films after the PCT. As shown in Fig. 1(d), little changes in FTIR signal for N-H, Si-H, Si-O and Si-N bonds are observed for a Cat-CVD $Si_3N_4$ films after the PCT.

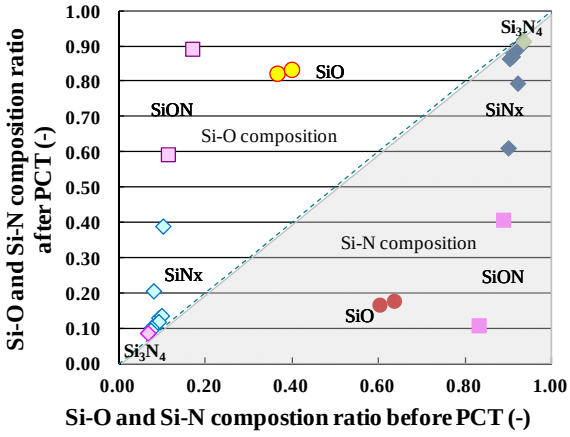


Fig. 2 The Si-O and Si-N composition ratio before/after PCT

Figure 2 shows the relationship between the Si-O and Si-N composition ratio before and after PCT, which are calculated from the peak area of FTIR. The Si-O and Si-N composition ratios are defined by [Si-O] / ([Si-N] + [Si-O]) and [Si-N] / ([Si-N] + [Si-O]). The Si-O and Si-N composition ratios for SiNx and $Si_3N_4$ films are not drastically changed after PCT. On the other hand, the ratios for SiON and SiO films are remarkably changed after PCT. Since the change in the ratio is the index for oxidation and de-nitrification, the result shows that the SiNx and $Si_3N_4$ films deposited under well conditions have a strong resistance for humidity in contrast to that of SiON and SiO films. As a result, the most moisture-resistive insulator film is the Cat-CVD $Si_3N_4$ film.

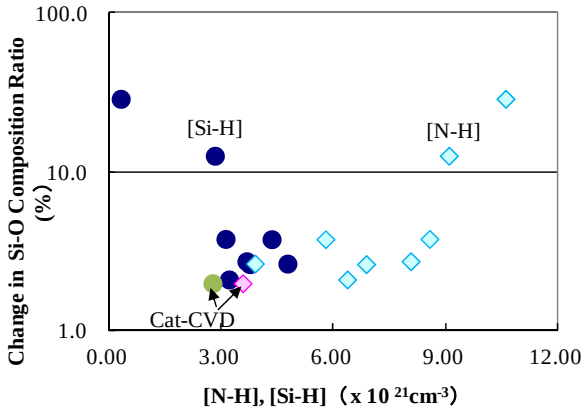


Fig. 3 The oxidation of the silicon nitride films by PCT

To analyze the characteristics of the moisture-resistive film, we show the dependence of the change in Si-O composition ratio by the PCT on [Si-H] and [N-H] as shown in Fig. 3. The change in Si-O composition ratio is obtained by calculating the difference of [Si-O] / ([Si-N] + [Si-O]) between before and after PCT. The oxidation decreases with a decrease in [N-H] as shown in Fig. 3. However, the dependence of the oxidation on [Si-H] is not observed.

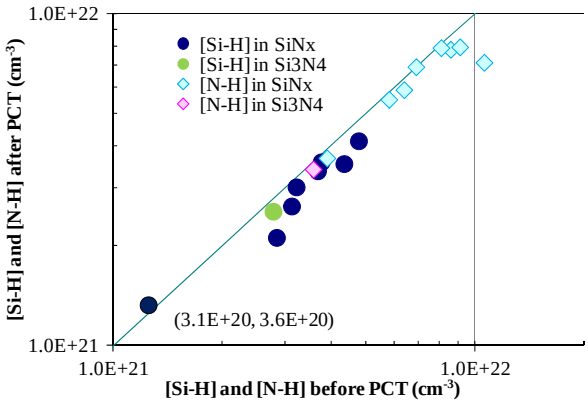


Fig. 4 The densities of Si-H and N-H bonds in the silicon nitride films before and after PCT

To analyze the role of the Si-H and N-H bonds on the oxidation, we show [Si-H] and [N-H] in SiNx and $Si_3N_4$ film before and after PCT as shown in Fig. 4. We have realized that the [Si-H] and [N-H] remains unchanged after PCT. We can understand the cause since a wet oxidation reaction does not create the additional O-H and Si-H bonds as follows: $Si_3N_4 + 6\ H_2O = 3\ SiO_2 + 4\ NH_3$. The reaction explains that the Cat-CVD $Si_3N_4$ film with a minimum [N-H] has the highest moisture-resistivity since the N-H bonds promote to create the $NH_3$ molecules. However, the characteristics of the SiO film created under the PCT is considered to be poor as the temperature of the PCT is low compared to that of the silicon oxidation process around 1000 ºC [3]. To understand the role of defects in the film created at low temperature, we should study the reaction and diffusion of water molecules in insulator films with defects.

## 4. Conclusions

We have demonstrated for the first time that the difference in the moisture resistance can be explained by the oxidation of films and the change in defect densities evaluated by the FTIR spectra. The most moisture resistive insulator film is a Cat-CVD $Si_3N_4$ film of a refractive index of 2.1, which has a minimum density of N-H bonds.

## References


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