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Transmission of oxygen radicals through free-standing single-layer and multilayer silicon-nitride and silicon-dioxide films

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Free radicals from processing plasmas are known to cause damage to dielectric films used in semiconductor devices. Many radicals are highly reactive and can readily interact with the material exposed to the plasma. This can modify the chemical structure of the material causing deterioration of electrical and mechanical properties of the films. This work detects the transmission of oxygen radicals through single- and double-layer silicon-nitride and silicon-dioxide freestanding films. The films were exposed to oxygen plasma. A fluorophore dye was used to detect the oxygen radicals traversing through the films. By measuring the fluorescence of the dye before and after multiple timed-plasma exposures, the transmission properties of oxygen radicals through the material were found. The results indicate that the absorption length of oxygen radicals increases with increasing plasma exposure times for Si_3N_4 films because the oxygen plasma oxidizes the top layer of the film and forms a *less dense* silicon oxynitride layer. For SiO_2 films, the absorption length was found to *decrease* as a function of plasma exposure time because of oxidation of the SiO_2 surface which leads to the formation of a *denser* oxide layer on the surface of the sample. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.5000135]

I. INTRODUCTION

Most processing plasmas contain free radicals and other active species that interact with the material to be processed. The radicals are often highly reactive so they can often modify the chemical structure of the material. They can also penetrate deep into or pass entirely through thin films.[1–3] In this work, the transmission properties of oxygen radicals through thin freestanding dielectric films are measured. This information can be used to investigate the effects of radicals, ions, and other active species on various types of thin films, which can be especially useful in semiconductor manufacturing. During semiconductor processing, thin films that are incorporated into semiconductor devices are often exposed to processing plasmas. These are commonly used for deposition, etching, ashing, sputtering, and cleaning.[4,5] For some processing steps, such as etching, radicals are desirable as they are often required for the chemical reaction that is needed for etching to take place. However, radicals can also cause damage to the films.[6–10] Deep penetration of radicals into the bulk of the film can compromise the quality and reliability of a device.[11–14] Thus, it is important to measure the transmission properties of various radicals through materials that are typically used in semiconductors. One way to measure the radical penetration depth is by looking at the depth of radical-induced damage in the film. However, it is possible that radicals can continue through the film beyond the region of measurable damage. For example, if the required activation energy for reaction with the film is not available, some radicals can pass through the film without interaction. Moreover, by measuring the number of transmitted radicals through films of various thicknesses, the absorption lengths of the radicals can be determined.

II. REACTIVE-OXYGEN SPECIES (ROS) DETECTION

Alexa 488, which is a fluorescent dye (a fluorophore) that selectively reacts with oxygen radicals, was used as the radical detector for this work. These dyes are commonly used to label bioactive reagents (antibodies, peptides, and nucleic acids) and other organic compounds. This fluorophore emits a bright-green fluorescence (515 nm) when excited at a wavelength of 490 nm when unreacted.[15] Oxygen radicals react with the dye, degrading it and rendering it unable to fluoresce. This process is called quenching. This is similar to the mechanism by which high-intensity light photobleaches dyes.[16] The number of reactions can be determined by the amount of quenching of the dye. The quenching can be used to infer the relative concentrations of the oxygen radicals present. Alexa 488 is also thermally stable and the fluorescence lifetime of the dye is temperature independent over the range of temperatures used here.

It was previously demonstrated that Alexa 488 fluorophore dyes can be used to detect and measure the number of oxygen radicals from an air plasma that are incident on the surface of a wafer chuck in an electron-cyclotron resonance (ECR) plasma.[6] Alexa dyes have several major advantages over other commonly used free-radical detection systems such as laser-induced fluorescence (LIF) and vacuum-ultraviolet absorption spectroscopy (VUVAS).[17,18] They are inexpensive and can be "painted" on the surface of any solid object in order to measure the radical flux which is incident

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on the surface. The fluorophore technique can also measure the number of radicals in the bulk of the plasma instead of the radical fluence at the location of the sample.

LIF, VUVAS, and other commonly used radical-measurement techniques are expensive, complex and often require significant modifications to the plasma reactor. Therefore, fluorescent dyes can be an optimal radical detector because they are much more suitable for the types of measurements that are reported here.

III. TRANSMISSION OF OXYGEN RADICALS THROUGH FREESTANDING FILMS

A. Silicon-nitride films

In this section, we measure the transmission properties of oxygen radicals produced by a plasma through silicon-nitride (Si_3N_4) thin films. Silicon-nitride dielectric *freestanding* films of thicknesses 50 and 100 nm were used for this work. These films were manufactured by SIMpore Inc., part numbers SN100-A50Q05 (50 nm Si_3N_4) and SN100-A100Q05 (100 nm Si_3N_4). A schematic of the Si_3N_4 freestanding films used is shown in Fig. 1.

To proceed, in a 96-well microtitre plate, multiple sets of 150-μM, 200 μl Alexa solutions were prepared. The freestanding films were placed over the wells of the microtitre plate containing the Alexa fluorophore as shown in Fig. 2. As mentioned earlier, the fluorophore detects oxygen radicals that react with the fluorophore.[6] This configuration was exposed to plasma in an electron-cyclotron resonance (ECR) reactor. By optimizing the plasma parameters, it can be made to produce significant amounts of free radicals. The number of radicals produced in the ECR reactor for various plasma parameter settings has been previously reported.[6] Oxygen was chosen as the feedgas in order to maximize the number of reactive-oxygen radicals. Using the fluorometer, the fluorescence of the dye can be measured before and after plasma exposure.[6] Thus, the amount by which the dye is quenched after plasma exposure is related to the number of oxygen radicals that have passed through the freestanding dielectric film.

In order to determine that the configuration used in this experiment worked properly, it was first necessary to undertake several control experiments. For the first control set, the well containing Alexa dye was fully covered using a piece of silicon wafer and exposed to the oxygen plasma in order to ensure that the radicals do not pass through the silicon substrate. The plasma exposures were done in the electron-cyclotron resonance (ECR) reactor for three separate times: 15, 30, and 40 min. The thickness of the silicon wafer is 500 μm which is the same thickness as that for the silicon substrate of the silicon-nitride windows used here. The reactor pressure was held constant at 50 mtorr and the microwave power was fixed at 800 W for each exposure. After plasma exposure, the quenching of the Alexa dye was measured using the fluorometer and compared with the fluorescence of the dye that was not exposed to the plasma. No significant change in fluorescence was observed between these two conditions, which confirms that the radicals did not penetrate through the silicon substrate.

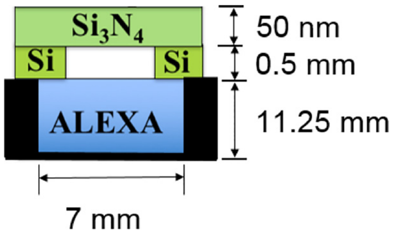


FIG. 2. Schematic of the freestanding film (not to scale) covering a well of a microtiter plate containing Alexa dye. The well containing Alexa is 7 mm in diameter and 11.25 mm deep. The silicon frame around the window is 500 μm thick. Fifty and 100 nm-thick Si_3N_4 windows were used. The wells are completely sealed with Kapton tape to ensure that only the radicals transmitted through the freestanding film can interact with the dye.

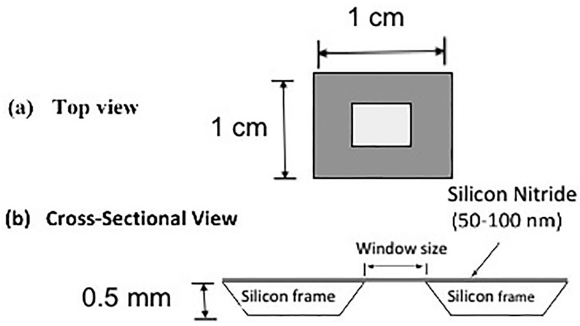


FIG. 1. Schematic of the freestanding silicon-nitride films. (a) Top view of the 2.5 × 2.5 mm freestanding silicon-nitride window on a silicon frame. (b) Cross-sectional view of the window. The silicon frame is 500-μm thick and the dimension of the whole TEM grid (including the window and the frame) is 5 × 5 mm. Fifty and 100-nm thick silicon-nitride windows were used.

In the second control experiment, the setup shown in Fig. 2 was exposed to an argon plasma to ensure that the dye was not affected by an inert-gas plasma. The dye was covered with a 50-nm thick silicon-nitride window and exposed to argon plasma for 20 min. The fluorescence of the dye was measured before and after the plasma exposure. Under these conditions, only a very small amount of quenching of Alexa was observed. The result is shown in Fig. 3. This effect is believed to be produced from the residual moisture and air in the vacuum chamber.

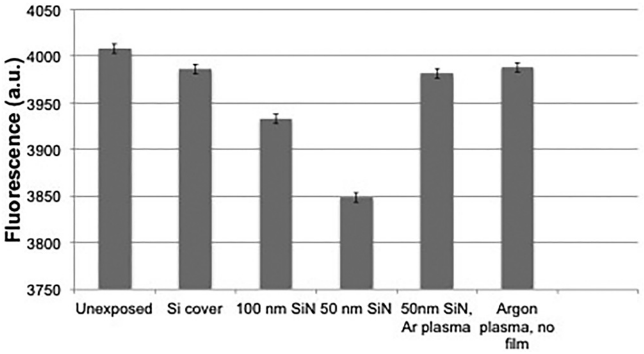


FIG. 3. Fluorescence of Alexa after various plasma exposures. Oxygen plasma was used for these experiments unless otherwise indicated in the figure. The errors in measurements (shown by the error bars) are due to small variations in the concentration of Alexa between experiments and errors introduced by the fluorometer during the measurements.

After the control experiments, the transmission properties of the oxygen radicals through the single-layer silicon-nitride freestanding films were measured. Again, both 50 and 100 nm films were used. Using the fluorometric data, the number of radicals that penetrated through the Si_3N_4 membrane is shown in Fig. 4 as a function of the thickness of the freestanding film. The data were plotted using a semi-log scale with a linear fit which allows information to be extracted easily about the absorption length of the oxygen radicals through the Si_3N_4 film.

The absorption of radicals in the film can be described by the following Beer-Lambert law expression:

$$\frac{I(x)}{I_0} = e^{-\alpha x}, \tag{1}$$

where I(x) is the number of radicals transmitted through a film with a thickness of x nm, I_0 is the number of radicals incident on the surface of the film, α is the absorption coefficient in nm^{-1}, and x is the film thickness in nm. The absorption length, λ, is given by the following expression:

$$\lambda = \frac{1}{\alpha}. \tag{2}$$

Figure 4 shows the absorption length of oxygen radicals for 15, 30, and 40 min plasma-exposure times. The results indicate that the absorption length of oxygen radicals increases slightly with plasma-exposure times. Specifically, the absorption length for the 15-min plasma exposure was found to be 33 nm. After the 30 and 40 min exposures, the absorption lengths increased to 37 and 40 nm, respectively.

It has previously been reported that silicon-nitride films are oxidized when they are exposed to oxygen plasma.[19–24] Thus, it can be hypothesized that as the oxygen radicals interact with the Si_3N_4 film, they oxidize the top layer of the film. The oxidation is likely to be due to interaction of oxygen with silicon dangling bonds present in the dielectric. The Si-N bond in the film can also be broken due to interaction with the plasma that can lead to a flux of nitrogen from the film into the plasma and subsequent oxidation of the dielectric.[22,23] Losses in the Si-N bond concentration were not observed when the film was exposed to argon plasma. The oxidized layer has a lower density than the original Si_3N_4 film,[24] and thus, it is easier for radicals to penetrate through this layer.

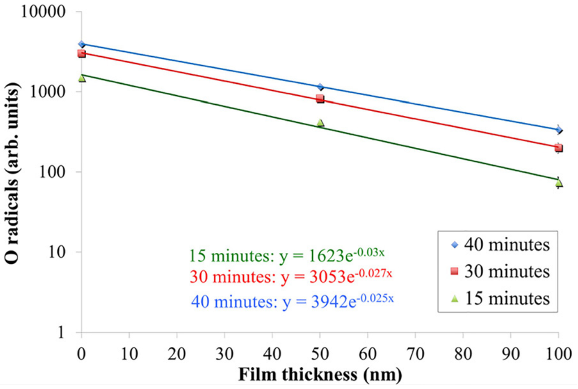


FIG. 4. Transmission of oxygen radicals through silicon-nitride freestanding films. The y-axis (in logarithmic scale) denotes the relative number of O radicals traversing through the silicon-nitride membrane and interacting with the dye. The data points at zero film thickness are the fluorescence measurements where the dye was exposed to plasma without any silicon-nitride membrane used as a cover.

1. Film density as a function of depth as measured using x-ray reflectivity

In order to analyze changes to the film density, grazing-angle x-ray reflectivity (XRR) measurements[24] were made on the pristine and plasma-exposed Si_3N_4 films. A schematic of the configuration is shown in Fig. 5. From the XRR measurements, the density of each film as a function of depth was obtained by curve fitting.[25] The density *vs.* depth profiles of the films are shown in Fig. 6. The XRR measurements indicate that the oxygen-plasma exposure decreases the density of the top layer of the Si_3N_4 sample and the depth of the top layer increases as a function of plasma-exposure time. The density of the top layer corresponds to the mass density of the SiO_xN_y film as reported elsewhere.[20–22,24] It is important to note that the thickness of the Si_3N_4 freestanding films was measured before and after the plasma treatment using XRR and reflectometry and no significant change in thickness was found. Similar XRR measurements for SiO_2 will be presented in Sec. III B.

2. Chemical analysis

In order to analyze the chemical-bond concentrations in the silicon-nitride film after exposure to oxygen plasma, Fourier transform infrared (FTIR) measurements were performed on both pristine and plasma-exposed 50 nm silicon-nitride films. By comparing the FTIR spectra of the pristine and plasma-exposed films, the effect of radicals on the chemical bonds of silicon nitride can be determined.

The FTIR measurements were made using the transmission mode with a resolution better than 4 cm^{-1}. An average of 64 spectra within the 400–4000 cm^{-1} range was made. In transmission mode, the infrared light penetrates through the entire film and the absorption of the film can be measured.[26,27] However, the silicon substrate surrounding the freestanding film does not absorb infrared light because the Si-Si bond is non-polarized.[26] Therefore, the FTIR spectrum of the entire TEM window is the same as the FTIR spectrum of the silicon-nitride freestanding film. Figure 7 is the FTIR absorption spectrum of a pristine silicon-nitride freestanding film with major peaks labeled.

From the literature, for silicon-nitride films, the Si–N stretch mode should be at ~860 cm^{-1}, the Si–H stretch mode should be at ~2000 cm^{-1}, and the N–H stretch mode should

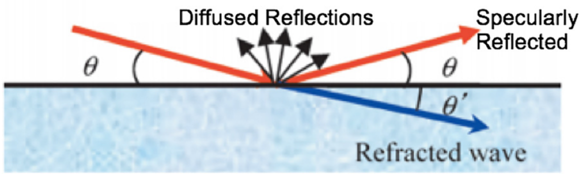


FIG. 5. Schematic of the setup for XRR measurements.

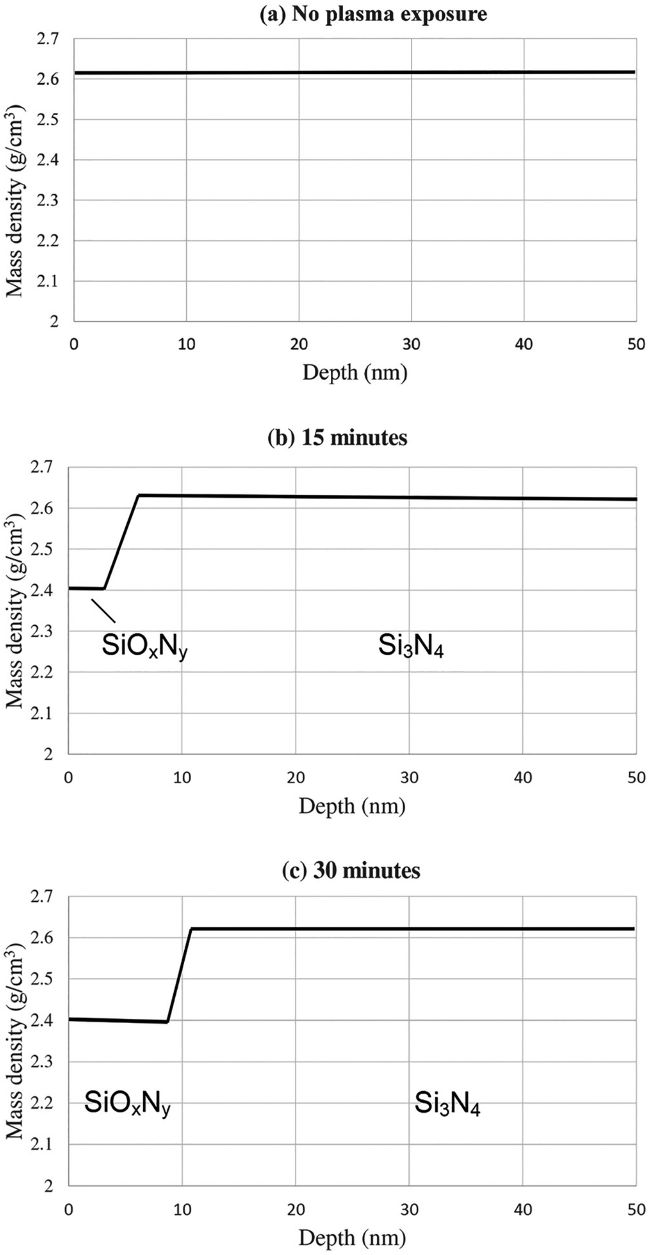


FIG. 6. Density vs. depth profile of silicon-nitride films with and without plasma treatments (a) No plasma treatment. (b) 15-min plasma exposure. (c) 30-min plasma exposure.

be at 3350 cm^{-1}.[28,29] However, in our measurements, the Si–H stretch mode is at a higher wave number ~2100 cm^{-1}. This can be attributed to the difference in electronegativity of the Si–H bond in silicon nitrides and in Si-rich silicon nitrides, which was suggested by Lucovsky.[31] We can also monitor the Si–O–Si stretch mode at 1100 cm^{-1} which would indicate any oxidation of the film. The spectrum in Fig. 7 shows no observable peak in that region.

Figure 8 shows a differential spectrum of the oxygen-plasma-exposed silicon-nitride sample in the 500–1500 cm^{-1} range which corresponds to both Si-N and Si-O-Si stretch regions.[28,29] The differential spectrum was obtained by subtracting the spectrum of the pristine film from that of the plasma-exposed film. This spectrum indicates a loss in the Si-N bond concentration and a corresponding peak in the Si-O-Si stretch region. No other changes were observed. This validates the hypothesis that exposure to the oxygen plasma oxidizes the silicon-nitride film. It also shows that the oxidation is due to a loss of Si-N bonds at the surface of the dielectric, as mentioned previously.[19,22,23,30]

Based on the FTIR measurements, we now know that part of the silicon-nitride film is oxidized by the oxygen plasma. The oxidized silicon layer is less dense than the silicon nitride itself,[19,22–24] so we hypothesize that the increase in the absorption length that we observe after longer plasma exposures is due to the less-dense oxidized layer on the surface of the silicon-nitride film. The grazing angle x-ray reflectivity (XRR) measurements[32] presented earlier concur with these results.

B. Double-layer silicon-dioxide and silicon-nitride films

In this section, transmission measurements were made using a double-layer freestanding film. It consists of silicon-dioxide films of various thicknesses deposited on the silicon-nitride window. The silicon-dioxide films were deposited, using a plasma-enhanced chemical-vapor deposition (PECVD) process, on the 50-nm silicon-nitride freestanding films previously used, thus forming a double-layer freestanding film. The deposition was done at the Wisconsin Center for Applied Microelectronics (WCAM) at the University of

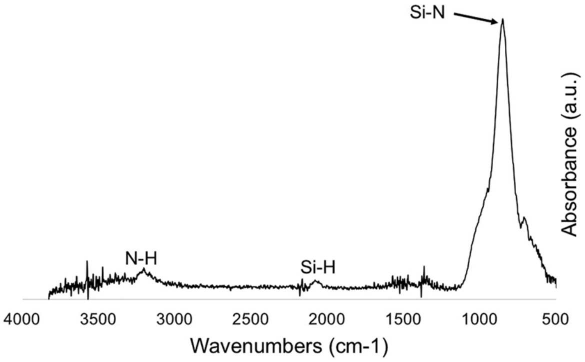


FIG. 7. FTIR spectrum of silicon nitride. The spectrum shows a large Si-N peak and small Si-H and N-H peaks, as expected. Other measurements reported in the literature show the same peaks for silicon-nitride films.[24,25,28,30]

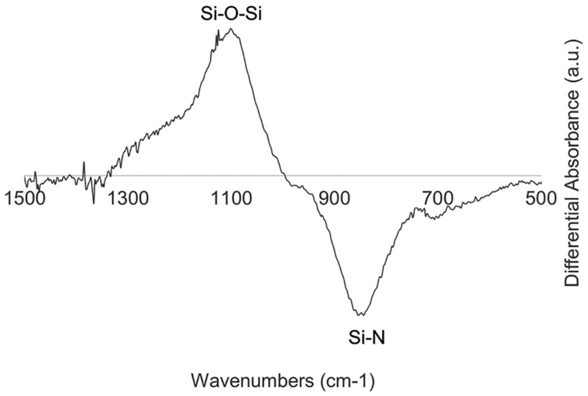


FIG. 8. Differential FTIR spectrum of the plasma-exposed silicon-nitride film. The plasma parameters were 50 mtorr, 800 W with 30 minutes of exposure. Oxygen was used as a feedgas.

TABLE I. PECVD recipe.

		Gas flow (sscm)					
Deposit material	Deposition pressure (mT)	N_2	N_2O	2% silane	5% NH_3	RF power (W)	Deposition rate (nm/min)
SiO_2	900	0	810	440	0	36	~5 to 6

Wisconsin – Madison. The tool used for the PECVD process was a PlasmaTherm PT70 reactor. The PECVD recipe used to deposit SiO_2 is listed in Table I.

1. Transmission of oxygen radicals through silicon-nitride and silicon-dioxide double-layer films

Similar to the single layer Si_3N_4 films, the double-layer films (SiO_2 on Si_3N_4) were placed over the wells of a microtiter plate containing Alexa and exposed to oxygen plasma in the ECR reactor. A schematic of the configuration is shown in Fig. 9. The same plasma conditions were used as in the case of the freestanding single-layer silicon-nitride films as described earlier. The plasma exposures were made with three orientations of the films. They are: (1) Si_3N_4 film only, (2) SiO_2 on Si_3N_4 with the SiO_2 facing the plasma, and (3) SiO_2 on Si_3N_4 with the Si_3N_4 facing the plasma. Figure 10 shows the relative number of oxygen radicals that are transmitted through the freestanding films after 15 and 30 min of plasma exposure. As expected, the results show that fewer radicals are transmitted through the double-layer SiO_2-Si_3N_4 film compared with the single-layer Si_3N_4 film. However, for the double-layer freestanding films, more radicals are transmitted through the double-layer film when the SiO_2 layer was facing away from the plasma compared with the case where the SiO_2 layer faced the plasma. The results suggest that the plasma exposure modifies the SiO_2 and Si_3N_4 films differently.

2. Film density

In order to investigate the effects of oxygen-plasma exposure on the densities of the SiO_2 films, XRR measurements were made on the plasma-exposed and pristine samples and the results were compared. Figure 11 shows the orientation of the double-layer freestanding films for the XRR measurements where the double-layer film was exposed with the SiO_2 side facing the plasma. When the films were exposed with the Si_3N_4 side facing the plasma, the Si_3N_4 side of the film placed was on top during the XRR measurements. The density *vs.* depth curves obtained from the XRR data are shown in Fig. 12. For the pristine samples, the densities of both the SiO_2 layer and the Si_3N_4 layer are uniform throughout the film except for the presence of a ~3 nm native-oxide layer on the surface of the SiO_2 film. The 3-nm layer on the surface of the SiO_2 film can be seen in the density *vs.* depth profile shown in Fig. 12. It is identified as a native-oxide layer, because its density matches that of the density of native silicon oxide reported elsewhere.[33–35] After the films were exposed to oxygen plasma for 30 minutes with the SiO_2 side facing the plasma, the top ~17 nm of the SiO_2 layer was modified as shown by the increase in density seen in the density *vs.* depth profile. When the sample was exposed to the plasma with the Si_3N_4 side facing the plasma (Fig. 12), no observable change in the density of the SiO_2 layer was found. However, the top ~10 nm of the Si_3N_4 layer was modified to an SiO_xN_y-like layer. A similar change in density of the Si_3N_4 layer was seen when the Si_3N_4-only freestanding film was exposed to plasma (see Fig. 6).

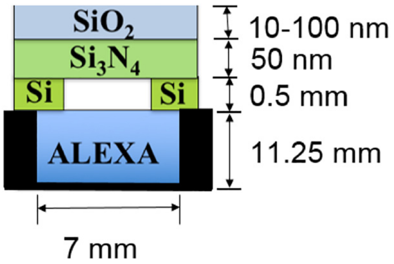


FIG. 9. Schematic of the freestanding films covering a well of a microtiter plate containing Alexa dye. The wells are completely sealed to ensure that only the radicals transmitted through the freestanding films can interact with the dye. The well containing Alexa is 7 mm in diameter and 11.25 mm deep. The silicon frame around the window is 500 μm thick. The Si_3N_4 layer is 50 nm thick and the SiO_2 film thickness ranges from 10 and 100 nm.

In order to investigate the effect of the oxygen radical dose on the modification of the double-layer films, thinner (10-nm) SiO_2 films were deposited on 50-nm Si_3N_4 freestanding films and exposed to oxygen plasma for 15 and 30 min. The same plasma conditions were used as before, i.e., 50-mtorr pressure and 800-W microwave power with oxygen as the feedgas. The films were exposed with the SiO_2 side facing the plasma. The density of each layer of the freestanding film was determined using x-ray reflectivity measurements before and after plasma exposure.

Figure 13 shows a schematic of the pristine double-layer film and Figs. 14 and 15 show the modification to the film

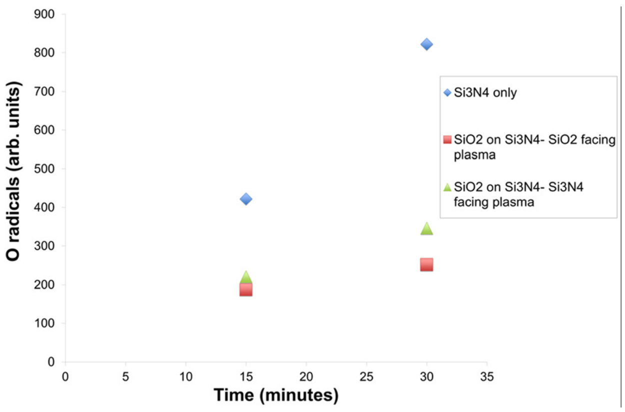


FIG. 10. Oxygen radical transmission through double-layer silicon dioxide on silicon nitride freestanding films.

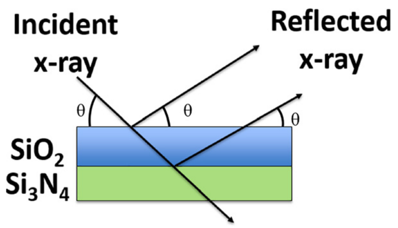
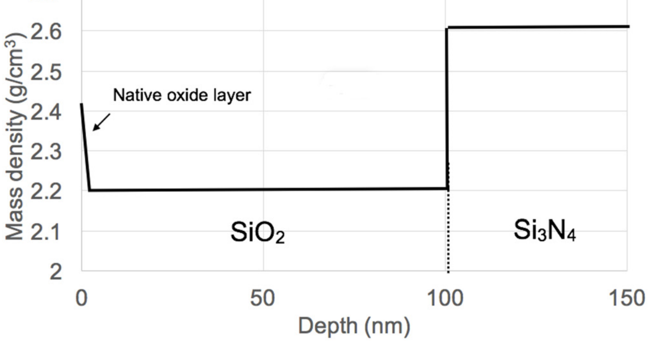


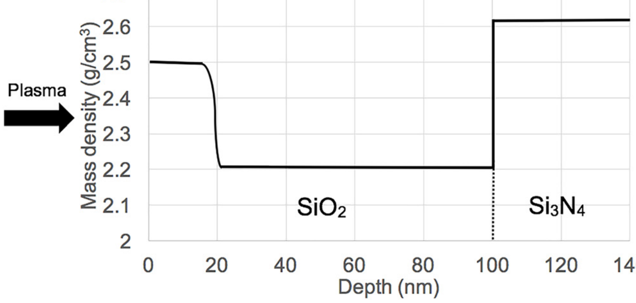
FIG. 11. Schematic of the setup for x-ray reflectivity measurements for the double-layer freestanding films. The thickness of the silicon-nitride film is 50 nm and the thickness of the silicon-dioxide film varies between 10 and 100 nm.

after 30 and 60 min of oxygen-plasma exposure. After the 30-min exposure, the entire silicon-dioxide film as well as the top 3 nm of the silicon-nitride film was modified. When the plasma exposure time was doubled, the depth of the modification layer of the silicon nitride film increased to 5 nm. It is important to note that these measurements are accurate to about 1 nm. After repeating this measurement several times, it can be concluded that the depth of the modified layer in silicon nitride varies between 5 and 6 nm and is roughly proportional to the exposure time.

(a) No plasma exposure



(b) SiO_2 facing plasma



(c) SiO_2 facing away from plasma

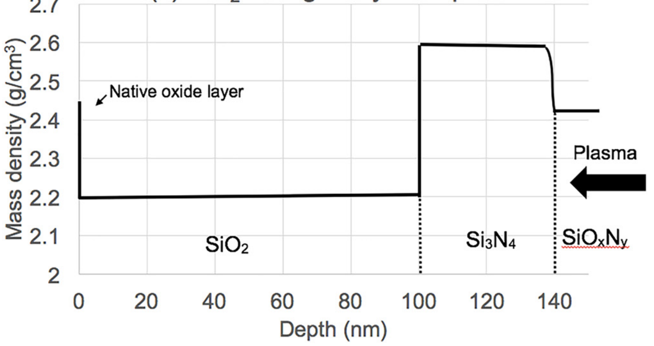


FIG. 12. Density vs. depth profiles of SiO_2 on Si_3N_4. The plasma parameters were: 50 mtorr pressure and 800 W microwave power with oxygen as the feedgas. The plasma-exposure time was 30 min.

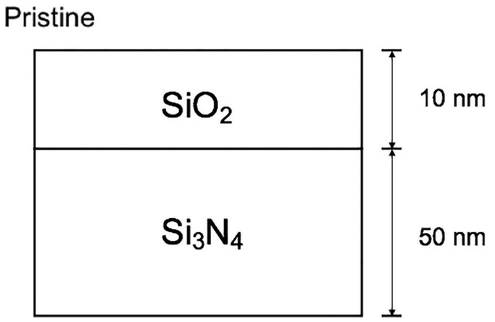


FIG. 13. Schematic of the double layer freestanding film (no plasma exposure).

These results indicate that the dose of the oxygen radicals affects both the SiO_2 and Si_3N_4 films. It was previously shown here that the modification depth of the Si_3N_4 films increased with plasma-exposure times. These results show that the plasma also modifies the SiO_2 film. Thus, with longer plasma-exposure times, it is possible to modify *both* the SiO_2 and Si_3N_4 layers composing the double-layer freestanding film. Using XRR measurements (and FTIR measurements that are presented in the following section), it can be seen that the oxygen radicals tend to further oxidize the surface of the SiO_2 layer, thus increasing the density of the film. Conversely, the density of the Si_3N_4 layer decreases due to the formation of a less dense $SiOxN_{1-x}$ layer which is due to the interactions with oxygen radicals.

3. Chemical-bond concentrations

In order to characterize the change in density of the SiO_2 film, Fourier Transform Infra-Red (FTIR) measurements were performed on these samples to analyze the changes in their chemical-bond concentrations. As before, the FTIR measurements were made in transmission mode with a resolution better than 4 cm^{-1}. Sixty-four spectra were averaged over a range of 400–4000 cm^{-1}. For FTIR measurements in transmission mode, both orientations of the films (SiO_2 layer facing or away from the plasma) produce the

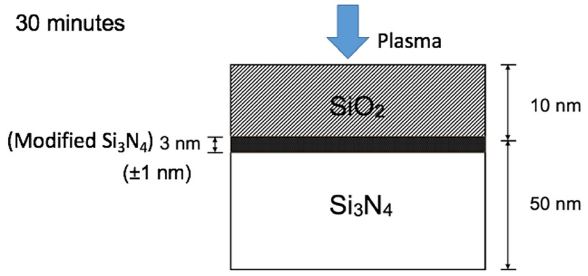


FIG. 14. Schematic of the double-layer film after 30 min of oxygen-plasma exposure. The shaded region is the modified layer of the film. After 30 min of plasma exposure, the entire SiO_2 layer and top 3 nm of the Si_3N_4 layer were modified.

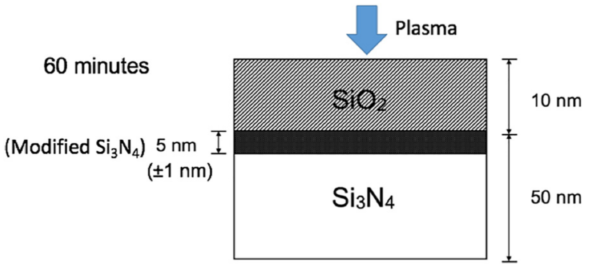


FIG. 15. Schematic of the double-layer film after 60 minutes of oxygen-plasma exposure. The shaded region is the modified layer of the film. After 60 min of plasma exposure, the entire SiO_2 layer and top 5 nm of the Si_3N_4 layer were modified.

same FTIR spectra. Figure 16 shows the Si-O-Si peaks obtained from the FTIR spectra. The FTIR results show that there is an increase in the Si-O-Si bond concentration after the oxygen-plasma exposure with the SiO_2 side facing the plasma. It is hypothesized that oxygen penetrates into the dielectric film and binds with the Si dangling bonds that are present in the SiO_2 layer which in turn increases the Si-O-Si bond concentration as well as the density of the material.

C. Transmission properties of oxygen radicals through silicon dioxide films

In order to measure the absorption lengths of the silicon-dioxide part of the double-layer film, 10–100 nm thick layers of SiO_2 were deposited on the 50 nm Si_3N_4 films and the number of radicals transmitted through the freestanding films was measured as a function of SiO_2 film thickness. For these experiments, the silicon-dioxide film was facing the plasma and the plasma parameters were chosen such that the underlying silicon-nitride layer was *not* modified by the plasma exposure. Thus, any changes in the number of transmitted radicals can be attributed only to modification of the SiO_2 layer.

The absorption of radicals in the double layer film can be described by the following expression:

$$\frac{I(x)}{I_0} = (e^{-\alpha_1 x_1}) \times (e^{-\alpha_2 x_2}), \tag{3}$$

where I(x) is the number of radicals transmitted through the double-layer film. The total thickness of the Si_3N_4 film is x_1 and the total thickness of the SiO_2 films is x_2. Thus, we can state that the double layer film thickness is $x = (x_1+x_2)$ nm. I_0 is the number of radicals incident on the surface of the film, α_1 is the absorption coefficient of the Si_3N_4 film, and α_2 is the absorption coefficient of the SiO_2 film.

As mentioned earlier, the thickness of the Si_3N_4 film (x_1) is kept constant at 50 nm for all experiments in this section. Generally, we would expect the absorption coefficient of the Si_3N_4 film, α_1, to change with plasma exposure. However, in this case, the thickness of the SiO_2 film and the plasma parameters were chosen such that the underlying Si_3N_4 layer was not modified by the plasma under this configuration, i.e., when the SiO_2 side faces the plasma. Thus, we can assume that the absorption length in the Si_3N_4 film does not change with plasma exposure. Hence, Eq. (3) can be expressed as

$$\frac{I(x)}{I_0} = C\,(e^{-\alpha_2 x_2}), \tag{4}$$

where C is a constant. Thus, the absorption length of the radicals in SiO_2, λ (in nm) is given by the following expression:

$$\lambda = \frac{1}{\alpha_2}. \tag{5}$$

Figure 17 shows the relative number of oxygen radicals transmitted through the double-layer freestanding film as a function of SiO_2 film thickness. As stated previously, the double-layer film was exposed to the plasma with the silicon-dioxide side facing the plasma. From the plot in Fig. 17, the absorption coefficient α_2 can be determined for different plasma exposure times. By using Eq. (5), the absorption lengths of the oxygen radicals in SiO_2 can be determined from the values of α_2 at different plasma exposure times.

The plot indicates that the absorption length for SiO_2 decreases as a function of plasma-exposure time. As described earlier, exposure to oxygen plasma causes further oxidation of the SiO_2 films that leads to surface densification.

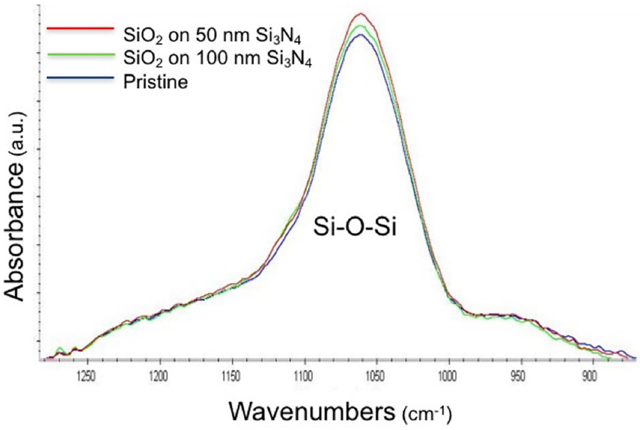


FIG. 16. FTIR spectra of SiO_2 films before and after plasma exposure. The Si-O-Si region is shown here.

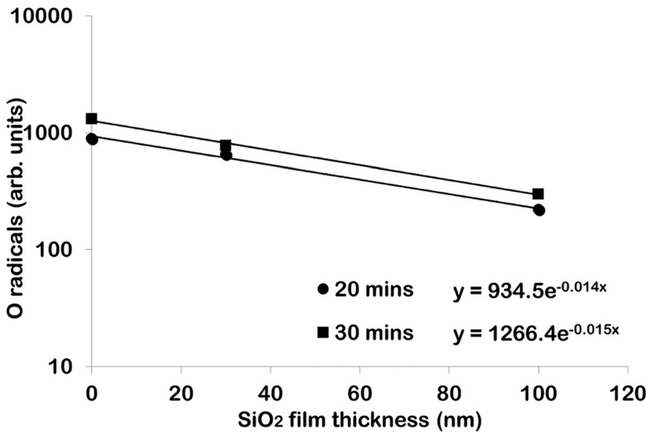


FIG. 17. Oxygen radical transmission through SiO_2 as a function of film thickness. The y axis is in log scale.

Thus, the decrease in absorption length due to longer plasma exposures is attributed to surface densification of SiO_2. The thicknesses of the films were measured using XRR before and after plasma exposure, and no significant difference in the thickness of either the SiO_2 or the Si_3N_4 films was found.

D. Radical energies

One of the important issues that needs to be investigated is the minimum energy of the radicals that is needed for them to react in the dielectric film causing observable changes. This will allow us to determine if the modification of the film caused by the radicals depends on the energy of these species as they travel through the film. In order to do so, the standard enthalpies of the chemical reactions of oxygen radicals with silicon nitride and silicon-dioxide films were calculated in order to determine how the energy of the radicals affects the extent of modification of the dielectric films and whether additional energy is required for the reactions to take place. The symbol ΔH_f^0 is used to represent the enthalpy and it is typically measured in the units of energy per amount of substance, usually expressed in kJ mol^{-1}. The standard enthalpy change of the reactions is calculated by subtracting the sum of the standard enthalpies of formation of the reactants (each being multiplied by its respective stoichiometric coefficient, v_1, v_2, etc.) from the sum of the standard enthalpies of formation of the products (each also multiplied by their respective stoichiometric coefficients), as shown in the equation below.[36]

$$\Delta H^{0} = \Sigma(\nu_1 \Delta H^{0}{}_{f})\,(\text{products}) - \Sigma(\nu_2 \Delta H^{0}{}_{f})\,(\text{reactants}) \qquad \text{(III)}$$

Table II shows the standard enthalpies of the elements and compounds that are present in the chemical reactions involving oxygen radicals, silicon-nitride, and silicon-dioxide films. The enthalpy values were collected from the NIST database.[37] By applying Hess's law[38,39] and using the enthalpy values listed in Table II, the standard enthalpy of reaction of all the possible chemical reactions between oxygen radicals and SiO_2 and Si_3N_4 films can be calculated. The possible reactions and their calculated enthalpies of reactions are presented in Tables III and IV. The calculated enthalpy values show that all the chemical reactions listed in the tables below are exothermic. Hence, the reactions can take place spontaneously provided there is sufficient activation energy present in the reactants.

TABLE II. Table of standard enthalpies. The data are taken from the NIST Chemistry WebBook. (http://webbook.nist.gov/chemistry/).

	ΔH_f^0 (kJ mol^{-1})
Si (s)	0
O (g)	249
SiO_2 (s)	−911
Si_3N_4 (s)	−744.75
N_2 (g)	0
N_2O (g)	82.05
NO_2 (g)	33.2
NO (g)	91.3

TABLE III. Enthalpy of formation of SiO_2.

Chemical reaction	ΔH^{0} (kJ mol^{-1})
$Si_{(s)} + 2\,O^*_{(g)} \rightarrow SiO_{2(s)}$	−911

As mentioned above, reactants must have enough energy to overcome the required activation energy, E_{act} for the reaction to take place. The activation energies for the reactions listed in the tables above range from 0.9 to 2 eV. The thermal energy of particles at room temperature is 0.025 eV, which is not enough to overcome the activation energy for the reactions to take place. However, the plasma emits a significant number of photons in the visible, UV, and VUV range with energies ranging from about 2 to 10 eV.[40] These photons may provide the initial energy required for the reactions to take place.[40] Depending on their wavelengths, some of the photons in the UV and VUV range can penetrate into the dielectric film and enhance the chemical reactions.[19,41,42] Once the reaction starts, the energy released from the exothermic reactions may also provide energy for more reactions to take place.[23] Furthermore, it has been reported by Takeda *et al.* that bombardment of O_2^+ ions can lead to surface activation of the Si film and increase the rate of oxidation.[43]

IV. SUMMARY

We hypothesized that oxygen radicals from a plasma can penetrate into the bulk of dielectric films and modify the material. The extent of this modification is related to the radical dose and energy present for the reactions to take place. Alexa fluorophore will be used to measure the number of oxygen radicals transmitted through freestanding dielectric films and the absorption lengths of the radicals can be determined from these measurements.

Freestanding single-layer Si_3N_4 films and double-layer freestanding SiO_2-Si_3N_4 films of various thicknesses were exposed to an ECR plasma for a range of time intervals. The Alexa dye was used to measure the number of oxygen radicals that were transmitted through the freestanding films.

It was found that exposure to oxygen plasma oxidizes the Si_3N_4 film and forms a silicon oxynitride-like layer on top. The thickness of this layer increases with plasma-exposure time. Using XRR measurements, it was found that the thickness of the modified top layer of the silicon-nitride film increased from ∼4 to ∼9 nm when the plasma-exposure time increased from 15 to 30 minutes. This layer was found to have a lower mass density, which accounts for the increase in radical absorption length. The absorption length

TABLE IV. Chemical reactions between silicon nitride and atomic-oxygen radicals and their corresponding enthalpies.

Chemical reaction	ΔH^{0} (kJ mol^{-1})
$Si_3N_4\,{}_{(s)} + 6\,O^*_{(g)} \rightarrow 3\,SiO_2\,{}_{(s)} + 2\,N_2\,{}_{(g)}$	−3482
$Si_3N_4\,{}_{(s)} + 8\,O^*_{(g)} \rightarrow 3\,SiO_2\,{}_{(s)} + 2\,N_2O_{(g)}$	−3816
$Si_3N_4\,{}_{(s)} + 14\,O^*_{(g)} \rightarrow 3\,SiO_2\,{}_{(s)} + 4\,NO_2\,{}_{(g)}$	−5341
$Si_3N_4\,{}_{(s)} + 10\,O^*_{(g)} \rightarrow 3\,SiO_2\,{}_{(s)} + 4\,NO_{(g)}$	−4113

for a 15-min plasma exposure was found to be 33 nm. After the 30 and 40 min exposures, the absorption lengths increased to 37 and 40 nm, respectively.

For the double-layer film with the SiO_2 layer facing the plasma, the oxygen plasma oxidized the top layer of the SiO_2 film and formed a *denser* oxide layer on top that reduced the absorption length of the radicals. The formation of the denser oxide layer was confirmed by both XRR and FTIR measurements. The absorption length was found to be 70 nm for a 20-minute plasma exposure. After 30 min of plasma exposure, the absorption length was reduced to 66 nm. With thinner (10 nm) SiO_2 on Si_3N_4 films, it was shown that the plasma can modify both the top SiO_2 film and a portion of the bottom Si_3N_4 layer. After 30 minutes of plasma exposure with the 10 nm SiO_2 side facing the plasma, the entire SiO_2 layer and the top 3 nm of the underlying Si_3N_4 film were modified. When the plasma exposure time was doubled, the modification depth of the Si_3N_4 film increased to 5 nm. The most probable chemical reactions between oxygen radicals and silicon nitride and silicon dioxide films were considered and their corresponding enthalpies are calculated in order to determine the energy requirements for these reactions to take place. It was found that all of these reactions are exothermic suggesting that the reactions release energy and they can happen spontaneously given sufficient activation energy in the reactants. The initial activation energy for the reactions to take place may be provided by photons or other species emitted from the plasma and further reactions may be catalyzed by the energy released from the exothermic process.

This technique can be used with various types of free-standing films which will allow measurements of the transmission properties of radicals through different materials and multilayer thin films. Other commercially available fluorescent dyes are available that can selectively react with other types of free radicals. This is a simple and effective way to measure the transmission properties of reactive species through thin films.

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