

Postdeposition reactivity of sputter-deposited high-dielectric-constant films with ambient H₂O and carbon-containing species

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(Received 12 May 2003; accepted 4 November 2003)

The room temperature reactivity of group III and IV based high-dielectric-constant films during long-term (>1 year) exposure to ambient atmosphere (H₂O- and C-containing species such as CO₂) has been studied in order to assess the stability of the materials. We prepare the films by physical vapor deposition of metal on Si (100) surfaces which is followed by oxidation in N₂O (1 atm), and monitor the formation of carbonate/alkoxylate and hydroxide species using Fourier transform infrared spectroscopy. For La-based films we find that the oxidation temperature has a strong effect on the reactivity with the ambient. For Hf- and Zr-based films, formation of various carbonate or alkoxylate species is confirmed within minutes of exposure, while substantial reaction with H₂O is not detected. Hf-based films, in general exhibit superior stability upon long-term exposure.

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I. INTRODUCTION

The search for an alternative material to the SiO₂ gate dielectric in complimentary metal-oxide-semiconductor (CMOS) devices has led to the investigation of the properties of several candidate materials.¹ Postdeposition stability to ambient exposure is one of the key issues that need to be examined as reactions with ambient gases like H₂O, CO₂, and vapors of organic solvents present in the laboratory atmosphere may lead to significant degradation of the electrical properties of the film as well as initiation of undesirable interface reactions at either the dielectric/semiconductor or dielectric/gate metal interface. In this case, *in situ* capping techniques will have to be utilized to prevent the undesired reactions, adding significant challenges to successful integration. In a previous publication, we demonstrated that the reaction of H₂O with La-based films, as detected by the presence of OH groups, leads to oxidation of a 25 Å layer of *a*-Si during a 10 s inert anneal at 1050 °C.² Such an occurrence may result in significant degradation of the capacitance of the gate stack. In this article we investigate and compare the stability of Hf-, Zr-, and La-based films during extended exposure to ambient.

Infrared spectroscopy is a powerful technique for the identification of bulk material reactions with atmospheric H₂O- and C-containing species such as atmospheric CO₂ and solvent vapors. Hydration of a thin film is evidenced by the appearance of a broad absorption band at 3600–3000 cm⁻¹ due to the O–H stretching modes of both undissociated H₂O molecules and surface H-bonded OH species.³ The O–H stretch mode of bulk hydroxide gives rise to a sharp peak at ~3600 cm⁻¹.⁴ Additional features due to the OH bending mode for the undissociated H₂O molecules is located at ~1630 cm⁻¹, respectively.³ Free surface OH groups are detected by sharp features at ~3775 cm⁻¹ for terminal or

monobridged OH groups, and at ~3670 cm⁻¹ for tribridged OH groups.^{3,5}

Carbon dioxide can interact in a variety of configurations with metal oxide systems.⁶ Formation of linearly coordinated (“end-on”) CO₂ complexes results in the appearance of strong IR absorption bands in the 2400–2200 cm⁻¹ range.⁷ The “side-on” coordination of CO₂ on pairs of coordinately unsaturated O²⁻–Mⁿ⁺ ions leads to the formation of carbonate-like components, such as free surface carbonate ions, and coordinated (chemisorbed) including unidentate, bidentate, and bridged species that produce IR active features in the 2000–1000 cm⁻¹ spectral range.^{6,7} An estimate of the relative population for each species is difficult because of the natural breadth of lines, the large variety of species, and the presence for each carbonate species of band pairs corresponding to the symmetric and antisymmetric stretching of the O–C–O groups and the stretch mode of the C–O group. For simplicity, we will refer to all these modes as CO. Formation of bicarbonate species (hydrocarbonate) from the reaction of CO₂ with surface OH groups contributes to the spectral variety. However, since the formation of these species is accompanied by the appearance of the bulk OH stretching mode at ~3610 cm⁻¹ and the bending mode at ~1230 cm⁻¹ it is easier to distinguish their existence.^{3,7–9}

In this work we only report on the carbonate product from the reaction of the high-*k* film with atmospheric CO₂. The spectra for the end-on range coordination of the CO₂ (2400–2200 cm⁻¹) were complicated by difficulties in background subtraction of the gas phase CO₂ contribution, so we did not make a detailed analysis of the spectra in that range.

Other C-containing organic molecules such as methanol, hexanes, formic acid, etc. whose vapor is usually present in the laboratory ambient are also known to react with metal oxides and also produce IR active features in the 1100–1700 cm⁻¹ range.^{9–12} Discrimination between the IR features due to reactions with CO₂ and those due to the other organic

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species is very difficult. However, we stress that during the course of this work the films were not exposed deliberately to organic species. Additionally, the concentration of the atmospheric CO_2 is substantially higher than the traces of these contaminants present in the air, so even though we cannot rule out that some of the observed CO features are due to reactions of the films with organic species, we believe that the bulk of the CO features are carbonates formed by reaction of the films with the atmospheric CO_2 .

II. EXPERIMENT

We prepare the dielectric films using the methods described in earlier publications.^{13,14} Briefly, we deposit thin metal films on high-resistivity H-terminated Si (100) surfaces using dc sputtering and oxidize *ex situ* in a tube furnace in N_2O (1 atm) at either 600° or 900°C. The metal film thickness estimate is based on step-height measurements performed with a Tencor profilometer. Since the metal films may react when exposed to air the metal film thickness reported here should be regarded as an upper limit to the true metal film thickness deposited. Following oxidation, the Fourier transform infrared spectroscopy (FTIR) absorption spectrum is recorded using a Thermo-Nicolet bench equipped with a Deuterated Tri-Glycine Sulfate detector (KBr beamsplitter) at 256 scans with a 4 or 8 cm^{-1} resolution. The spectrum of a corresponding clean Si substrate is also recorded for use as a background spectrum for the computation of the absorption spectrum of the film. This “background” piece originates from the same 4 in. wafer as the deposited sample and this same background sample is maintained throughout the collection of each IR versus time set. We find that maintaining the same background sample is critical for reliable data analysis. After the initial FTIR spectrum is taken the sample is exposed to the laboratory ambient, and the spectrum of both the sample and the background is recorded periodically.

The control software supplied by the bench manufacturer is used for the computation of the absorption spectra, baseline correction, smoothing (using a Savitsky–Golay 5 point, $\sim 10 \text{ cm}^{-1}$ algorithm) and integration of the peaks. Smoothing is performed only on spectra exhibiting significant substrate interference oscillations and results in small degradation in the resolution. All the FTIR spectra presented in this article are plotted in the same absorption units so that a direct comparison of the peak intensity and area is feasible. The reported peak areas were obtained by integration of the peaks in the fully processed spectra, corrected for baseline and smoothed to remove interference oscillations. However, we also performed the integration separately on the raw, and baseline corrected absorption spectra, and all three results are within 10% variation ensuring that processing of the spectra does not result in the introduction of artifacts.

III. RESULTS

A. La-based films

Figures 1 and 2 show the 4000–2500 cm^{-1} [Figs. 1(a) and 2(a)] and 2000–1100 cm^{-1} [Figs. 1(b) and 2(b)] sections of the FTIR spectra for 300 Å of La metal on Si oxidized at

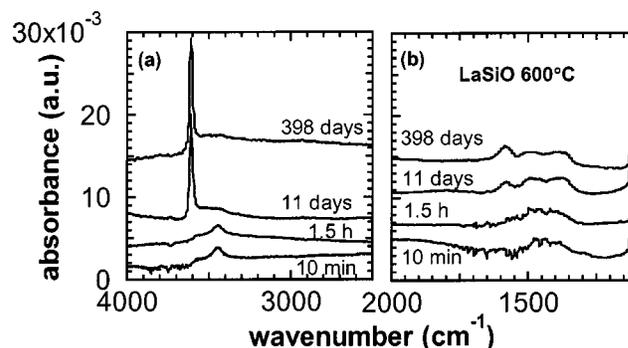


FIG. 1. (a) 4000–2500 and (b) 2000–1100 cm^{-1} range of the FTIR spectra at various exposure times for a thick (300 Å La metal) LaSiO sample oxidized for 10 min in N_2O at 600°C. The broad peak at 3600–3000 cm^{-1} is due to H-bonded OH. The peaks at 3450 and 3610 cm^{-1} are attributed to the OH stretching mode of $\text{LaO(OH)/LaCO}_3\text{OH}$ and La(OH)_3 , respectively. The peaks in the 1650–1250 cm^{-1} range are assigned to the CO stretching mode in several carbonate species. Both the OH and CO peaks grow with exposure time.

600 and 900°C, respectively. For the film oxidized at 600°C we observe that the spectrum taken 10 min after removal from the furnace already exhibits a broad peak between 3600 and 3200 cm^{-1} with a strong component at $\sim 3450 \text{ cm}^{-1}$ and a shoulder at $\sim 3570 \text{ cm}^{-1}$ due to the OH stretching mode. Exposure to air for 1.5 h increases the intensity of the feature without changing its qualitative characteristics. Long-term exposure for 11 days, however, leads to the appearance of a strong feature at $\sim 3610 \text{ cm}^{-1}$ while the intensity of the broad peak appears marginally reduced. Exposure for 400 days does not result in any further significant spectral variations. For the same sample the 2000–1100 cm^{-1} region of the spectrum exhibits a small peak between 1550 and 1250 cm^{-1} characteristic of the CO stretching mode immediately following oxidation.⁶ Further exposure intensifies the feature and on the eleventh day, two distinct broad peaks centered at ~ 1480 and 1380 cm^{-1} are resolved. Additionally, a new well-resolved peak at $\sim 1570 \text{ cm}^{-1}$ appears in the spectrum. Exposure of the sample in air for over a year intensifies the 1570 cm^{-1} peak.

The film oxidized at 900°C exhibits much simpler IR spectra even for yearly exposure to air. In the spectrum taken after oxidation we see that there is a small peak at ~ 3700

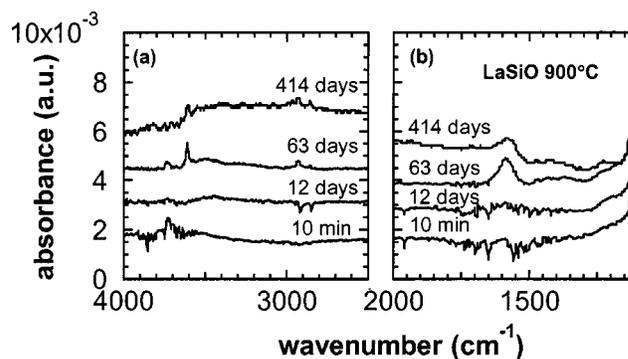


FIG. 2. (a) 4000–2500 and (b) 2000–1100 cm^{-1} range of the FTIR spectra at various exposure times for a thick (300 Å La metal) LaSiO sample oxidized for 10 min in N_2O at 900°C. For exposure up to 12 days the spectra do not show any appreciable reaction of the film with H_2O and CO_2 . For longer exposure time the formation of hydroxide and carbonate is confirmed.

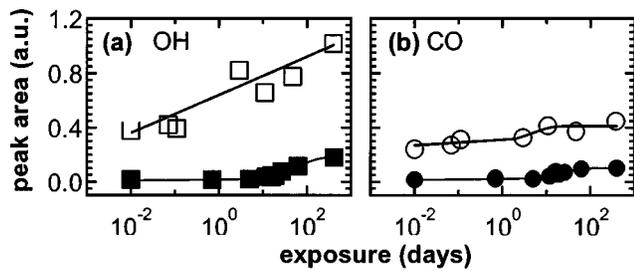


FIG. 3. OH (squares) and CO (circles) peak areas as a function of exposure for LaSiO films oxidized at 600 °C (open symbols) and 900 °C (closed symbols). The film prepared at 900 °C exhibits superior stability to air exposure.

cm^{-1} indicative of free surface OH and a very small broad feature centered at 3500 cm^{-1} . The peak at 3500 cm^{-1} is better resolved on the twelfth day and intensifies on the 63rd day. Additionally, a sharp feature at $\sim 3610 \text{ cm}^{-1}$ similar to that observed for the 600 °C film appears. Exposure for over a year intensifies the broad OH peak at $3600\text{--}3000 \text{ cm}^{-1}$. The $2000\text{--}1100 \text{ cm}^{-1}$ portions of the IR spectrum taken within 10 min from removal from the oxidation furnace is practically flat and remains unaffected on the twelfth day mark. On the 63rd day we observe the appearance of a sharp feature at 1570 cm^{-1} along with a broad and less intense feature between 1550 and 1250 cm^{-1} . Exposure for over a year does not affect significantly the intensity of these peaks.

Figure 3 presents the evolution of the peak area with exposure time for the OH stretching region ($3670\text{--}3000 \text{ cm}^{-1}$) [Fig. 3(a)] and the CO stretching region ($1670\text{--}1250 \text{ cm}^{-1}$) [Fig. 3(b)]. Integration of each peak component was not feasible due to peak overlap because of the limited resolution of the measurement, the natural width of the lines and the large variety of formed species. The squares represent the total OH stretching mode peak area and the circles the total CO stretching mode peak area. Open symbols refer to the film oxidized at 600 °C and solid symbols to the film oxidized at 900 °C. The lines are used only as guides to the eye and do not represent any attempt to model the reactions.

Confirming the observation based on the spectra the film oxidized at 600 °C exhibits significantly larger reactivity, as the peak area is proportional to the concentration of the species. Both the OH and the CO areas increase with exposure time and double within a year. The 900 °C film initially exhibits resistance to reactions with H_2O and C-containing species as evidenced by the minute OH and CO peak areas. Prolonged exposure in excess of ten days begins to degrade the material and sizable amounts of OH and CO are then detected. However, for 900 °C the amount of OH and CO detected within a year is only $\sim 20\%$ and $\sim 30\%$, respectively, that for the 600 °C film at the same time period.

B. Hf-based films

Figures 4(a) and 5(a) present the OH stretching mode region and in Figs. 4(b) and 5(b) the CO stretching mode region of the FTIR spectra for 300 Å of Hf metal films oxidized for 10 min in N_2O at 600 °C (Fig. 4) and 900 °C (Fig. 5), respectively. The spectra for both films share qualitative

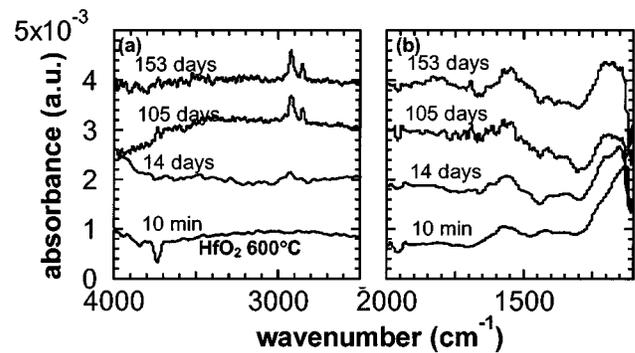


FIG. 4. (a) $4000\text{--}2500$ and (b) $2000\text{--}1100 \text{ cm}^{-1}$ range of the FTIR spectra at various exposure times for a thick (300 Å Hf metal) $\text{HfO}_2/\text{HfSiO}$ sample oxidized for 10 min in N_2O at 600 °C. The film does not react significantly with H_2O but it reacts with CO_2 to form various carbonate species during and after oxidation. For longer exposure times we begin to observe CH bonding in the film.

similarities and are significantly less complicated than that for the 600 °C La-based films. For both the 600 and 900 °C Hf-based films the region between 3650 and 3000 cm^{-1} is fairly flat; for long air exposure (>100 days) we may be starting to detect an OH signal. We can also see the formation of carbonate species as evidenced by the well defined peak at $\sim 1570 \text{ cm}^{-1}$ and the broader peak between 1450 and 1250 cm^{-1} for both Hf-based samples immediately following removal from the oxidation furnace. There is a clear increase in the peak intensity from the spectrum obtained at 10 min and the 14 or 21 day mark. Longer ambient exposure does not appear to affect the peak intensity significantly. However, after approximately two weeks of exposure a new feature between 3000 and 2800 cm^{-1} appears in the spectra for both samples. This feature is compatible with the CH stretching mode in both CH_2 and CH_3 . The intensity of this feature is comparable for both samples and increases with exposure time.

In Fig. 6 we present the integrated intensities for the CO [Fig. 6(a)] and CH region [Fig. 6(b)] for the Hf films oxidized at 600 °C (open symbols) and 900 °C (solid symbols). The lines are intended as a guide for the eye. The peak area

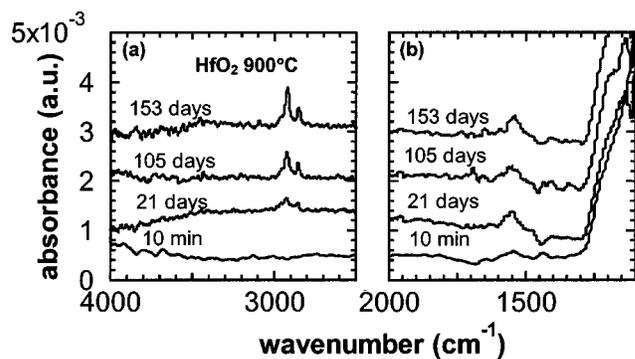


FIG. 5. (a) $4000\text{--}2500$ and (b) $2000\text{--}1100 \text{ cm}^{-1}$ range of the FTIR spectra at various exposure times for a thick (300 Å Hf metal) $\text{HfO}_2/\text{HfSiO}$ sample oxidized for 10 min in N_2O at 900 °C. The film does not react significantly with H_2O but it reacts with CO_2 to form various carbonate species during and after oxidation. For longer exposure times we begin to observe CH bonding in the film.

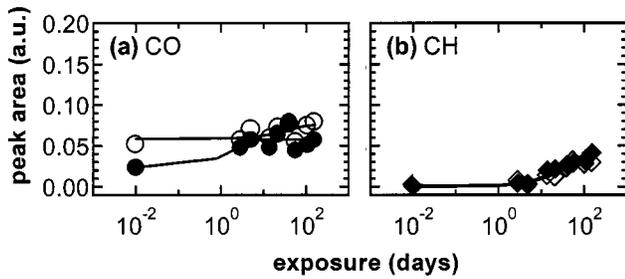


FIG. 6. CO (circles) and CH (diamonds) peak areas as a function of exposure for $\text{HfO}_2/\text{HfSiO}$ films oxidized at 600 °C (open symbols) and 900 °C (closed symbols). The concentration of the carbonates is higher for the film prepared at 600 °C while the CH concentration is similar for both samples.

units are the same as for Fig. 3. These plots confirm the qualitative remarks made above. It appears that there is a small but distinguishable change in the CO peak area after exposure to the ambient for a day. Further exposure leaves the signal practically unaffected and the amount of carbonate is larger for the film oxidized at 600 °C. The CH peak appears after ten day air exposure, its area is comparable for both samples and increases with exposure time.

C. Zr-based films

Figures 7 and 8 present the long-term air exposure effects on the composition of Zr-based films produced by oxidation of 450 Å of Zr metal in N_2O (1 atm) for 20 min at 600 °C (Fig. 7) and 900 °C (Fig. 8), respectively. In Figs. 7(a) and 8(a) we present the OH stretching mode region and in Figs. 7(b) and 8(b) the CO stretching mode region. Apart from the detection of some isolated surface OH at 3740 cm^{-1} for both samples the 3600–3000 cm^{-1} spectral region is fairly simple and does not indicate any reaction of the films with air moisture. The 1800–1100 cm^{-1} region features a number of well-resolved peaks at ~ 1720 , 1550, 1440, and 1300 cm^{-1} and shoulders at ~ 1495 and 1370 cm^{-1} . For the film prepared at 600 °C the two spectra taken at 53 and 158 days of exposure appear very similar and only the broad feature at ~ 1550 cm^{-1} appears to increase in intensity and width with time. For the film prepared at 900 °C the major spectral feature is located at ~ 1440 cm^{-1} and appears stable

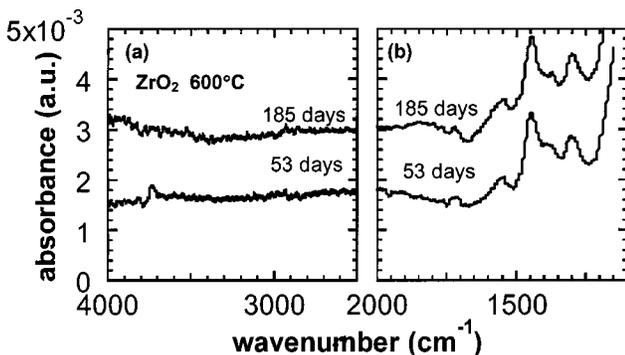


FIG. 7. (a) 4000–2500 and (b) 2000–1100 cm^{-1} range of the long-term exposure FTIR spectra for a thick (450 Å Zr metal) $\text{ZrO}_2/\text{ZrSiO}$ sample oxidized for 20 min in N_2O at 600 °C. The film does not react significantly with H_2O but it reacts with CO_2 to form various carbonate species during and after oxidation.

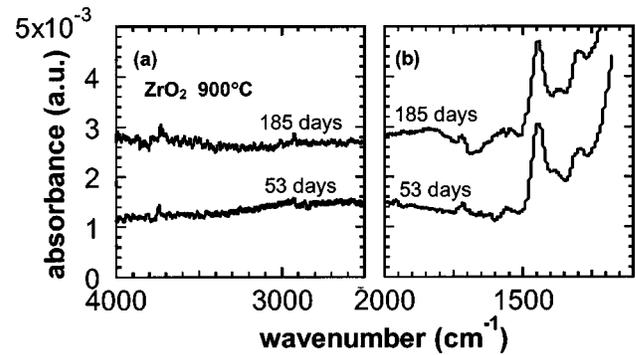


FIG. 8. (a) 4000–2500 and (b) 2000–1100 cm^{-1} range of the long-term exposure FTIR spectra for a thick (450 Å Zr metal) $\text{ZrO}_2/\text{ZrSiO}$ sample oxidized for 20 min in N_2O at 900 °C. Film does not react significantly with H_2O but it reacts with CO_2 to form various carbonate species during and after oxidation.

in time. The area of this peak is larger than the corresponding area for the 600 °C film. By contrast the peak at ~ 1300 cm^{-1} appears more intense in the 600 °C film spectrum. On the 53rd day the peak at ~ 1550 cm^{-1} is barely resolved. Extended exposure leads to growth of this feature.

Figure 9 presents the total peak area in the CO stretching region as a function of exposure time. Six measurements were performed within the span of ~ 130 days. The peak area for the 600 °C film appears to increase with exposure and is $\sim 50\%$ larger than that for the 900 °C film that remains practically unchanged during the study period.

IV. DISCUSSION

A. La-based films

The oxidation temperature appears to have a significant effect on the stability of these films. Films oxidized at 600 °C exhibit very rich IR spectra, and the time evolution of the features provides some interesting information regarding the hydration mechanisms. For short exposure times the presence of OH in the film is evidenced by the broad peak between 3600 and 3000 cm^{-1} , indicative of adsorbed undissolved

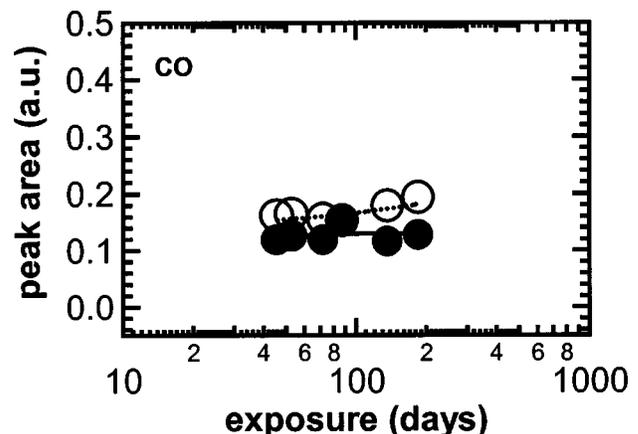
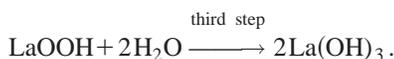
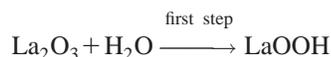
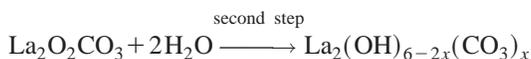
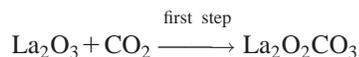


FIG. 9. CO (circles) peak areas as a function of exposure for $\text{ZrO}_2/\text{ZrSiO}$ films oxidized at 600 °C (open symbols) and 900 °C (closed symbols). The concentration of the carbonates is higher for the film prepared at 600 °C similar to observations for the Hf-based films.

ciated H₂O- and H-bonded surface OH. The peak at 3450 cm⁻¹ and shoulder at 3570 cm⁻¹ can be assigned to hydroxyl groups in LaCO₃OH and LaO(OH).¹⁵ Longer exposure leads to some loss of intensity from this broad feature and the appearance of the sharp peak at ~3610 cm⁻¹ that can be assigned to the OH stretching in La(OH)₃.^{4,16}

Further evidence for the formation of the carbonate phase is provided by the IR peaks detected at the 1600–1250 cm⁻¹ range. The peaks at ~1480 and ~1370 cm⁻¹ can be traced to the formation of the unidentate CO₃²⁻ entity, while the feature at the ~1570 cm⁻¹ is representative of the bidentate CO₃²⁻ species.⁴ Alternatively, this peak can be assigned to bidentate formate species COO–H.⁹

This peak assignment is only a partial identification of the species that may be responsible for the spectral variety. There are many different types of lanthanum hydroxycarbonates [La₂(OH)_{6-2x}(CO₃)_x] and more detailed analysis is beyond the scope of this article. However, these species are characterized in detail in studies that involved La₂O₃ powders exposure to CO₂, and H₂O in well-controlled environments.^{4,15,16} Bernal *et al.*¹⁶ exposed three different samples of La₂O₃ in air for several months to years and found that air exposure transformed them to partially carbonated lanthanum hydroxide. The thermal decomposition of the air stabilized samples was studied using thermogravimetric analysis, temperature programmed desorption, IR spectroscopy and x-ray diffraction (XRD) and a schematic reaction mechanism for the thermal decomposition of the lanthanum hydroxycarbonate was proposed. By reversing the steps of this mechanism we can describe the reaction of La₂O₃ films with H₂O and CO₂ through the scheme:



This mechanism strictly refers to reactions of La₂O₃. XPS analysis of thick (>300 Å) La films oxidized at both 600 and 900 °C reveals that the composition is compatible with La-silicate bonding.¹⁴ The existence of significant bulk Si concentration adds to the number of possible species formed.

There is a difference in the intensity distribution of the carbonate peaks for the films oxidized at 600 and 900 °C. For the 900 °C film the area of peak at ~1570 cm⁻¹ assigned to bidentate CO₃²⁻ is significantly larger than that of the broad peak at 1500–1250 cm⁻¹ which mainly contains contributions due to the unidentate CO₃²⁻.

The overall difference in the reactivity between the 600 and 900 °C films is quite remarkable. Both films have silicate composition, which are known to retain their amorphous state even at high temperature anneals.¹⁷ It is possible that oxidation at 900 °C leads to a more dense film, reducing significantly the voids through which diffusion of atmo-

spheric species occurs. As a result, the extent of the bulk reaction is significantly reduced. Reactions of La₂O₃ powders with CO₂ and H₂O have also been characterized as bulk processes.¹⁶

Our results are consistent with observation made on atomic layer epitaxy La₂O₃ films.¹⁸ Formation of LaO(OH) and carbonates was detected by FTIR and XRD for stored films. Inert anneals at 800 °C resulted in desorption of both the OH and carbonate containing entities but subsequent exposure to air led to regeneration of the contaminants. Compared with this result, the stability exhibited by the 900 °C film is quite noteworthy.

B. Hf-based films

Carbon dioxide is known to interact with the surface of metal oxides to form carbonate species that resist desorption even upon high temperature anneals.¹⁹ For the Hf-based films we observe formation of carbonates immediately following oxidation, their concentration almost doubles within the first day and remains practically stable thereafter. There is a difference in the amount of carbonate formed between the 600 and 900 °C films; the higher temperature results in lower carbonate concentration. We will explain this difference as due to surface reactions of HfO₂ crystallites with CO₂.

Spectroscopic ellipsometry measurements on both the 600 and the 900 °C films indicated high surface roughness, suggesting that both films are crystalline in bulk. XPS analysis showed that both films have a graded composition of HfO₂/HfSiO/SiO₂ with the bulk of the film being HfO₂. XRD and FTIR studies performed by Neumayer and Cartier¹⁷ concluded that HfO₂ crystallizes at temperatures as low as 500 °C. Based on these findings we believe that the bulk of both the 600 and the 900 °C films are crystalline.

HfO₂ crystallites are known to react with CO₂ on available surface sites to form carbonates.⁸ It is expected that the higher temperature anneal will result in larger size crystallites. For two films equal in thickness, the available surface area is larger for the film with the smaller grains (lower oxidation temperature). Based on that, we expect that the film prepared at 900 °C, will exhibit lower concentration of carbonate species in agreement with the experimental observations. It is worth noting that the dominant carbonate bonding appears to be that of bidentate for both the 600 and the 900 °C film as the peak area representing this feature centered at 1570 cm⁻¹ is larger than the broad peak between 1500 and 1250 cm⁻¹ ascribed to unidentate species.⁸ (The peak at ~1570 cm⁻¹ can also be assigned to bidentate formate species.⁹) We must note the similar trend for the 900 °C La-based film that exhibited high stability during air exposure.

For both films OH is barely detectable even after 100 days of exposure. The absence of the sharp OH feature at 3610 cm⁻¹ indicates that the formation of bicarbonate species is not favored. FTIR spectra of HfO₂ films prepared with chemical solution deposition¹⁷ show appreciable amounts of H-bonded OH and adsorbed H₂O in the as-deposited films that is removed during anneals. Morterra *et al.*⁸ also ob-

served significant amount of H bonded as well as free surface OH on HfO₂ crystallites. In our case we believe that the adsorbed H₂O and OH on the metal film are removed during the oxidation step. Reaction of the surface sites with CO₂ during oxidation then stabilizes the surface with the formation of carbonate species.

While no significant amount of OH is detected in the films we observe that for long exposures both films show signs of CH bonding. This observation is particularly peculiar since the CH signal is comparable for both films and the growth of the signal is not accompanied by a reduction in the carbonate species or the appearance of OH in the film. Contamination cannot be ruled out as a possible source but it appears improbable as all the samples were kept in the same container and the CH peaks appears only in the IR spectra of the Hf-based films.

C. Zr-based films

The observations for the Zr-based films share similarities with those for the Hf-based films. We can observe only traces mainly of free surface OH (at $\sim 3700\text{ cm}^{-1}$) for long exposure times. The intensity of the peaks assigned to unidentate carbonates appears unchanged with exposure while the peak area of the bidentate species grows with time. (The peak at $\sim 1570\text{ cm}^{-1}$ identified as bidentate carbonate can also be assigned to bidentate formate species.⁹) The peak at $\sim 1750\text{ cm}^{-1}$ for both films can be assigned to the formation of bridged or "organic" carbonate species.⁷ The amount of carbonate bonding is higher for the film prepared at 600 °C in agreement with the observations for the Hf films. XPS analysis of the samples confirms that the bulk of the film is ZrO₂ with some ZrSiO and SiO₂ at the interface. Spectroscopic ellipsometry measurements show high surface roughness for both films and XRD performed on samples prepared at 900 °C confirms that the film was crystalline mixture of the monoclinic and tetragonal phases of ZrO₂. ZrO₂ is known to crystallize above 400 °C (Ref. 17) and it is expected that both films are crystalline. The film prepared at 600 °C has a higher surface area and as a result the amount of carbonate formed by the reaction of available surface sites with CO₂ is expected to be larger than for the 900 °C film. The amount of carbonate for both Zr films is significantly higher than for the Hf-based films. At the IR spectra taken at the 185th day of exposure we may be starting to observe traces of CH bonding similar to that observed for the Hf-based films but with significantly lower intensity.

V. CONCLUSIONS

We have studied the air exposure stability of high-*k* dielectric films prepared by oxidation of La, Hf, and Zr metal on H-terminated Si. For LaSiO we find that films prepared at 600 °C show significant reactions with C-containing species and H₂O to form lanthanum-hydroxycarbonates within minutes of air exposure. Similar films prepared at 900 °C show very high stability for the first ten days of exposure; subse-

quently they also show formation of hydroxycarbonate but at a much lower concentration. We attribute this difference in reactivity to densification of the 900 °C film that inhibits diffusion of atmospheric components through the bulk of the film.

For the HfO₂ films we observe minimal reaction with H₂O while the reaction with C-containing species results in the formation of both unidentate and bidentate carbonates and possibly alkoxyates. Additionally, for long exposures we observe significant CH bonding a rather puzzling observation. We explain the larger concentration of carbonates observed for the 600 °C films in terms of surface area available for reaction in predominantly crystalline films. Our observations for the long-term effects of air exposure on the ZrO₂ films mirror those for the HfO₂ films. In addition to the usual carbonate species in those films we also observe the formation of bridged carbonates but we do not observe any significant amount of CH bonding.

From the three materials examined in the course of this work the Hf based materials exhibit the best long-term stability to air exposure; minimal reactions with H₂O and the smaller concentration of C-containing species. The LaSiO films prepared at 900 °C show short-term air stability comparable to that of the Hf films, a finding rather surprising for a material that is generally classified as hygroscopic. This demonstrates that processing conditions can alter the inherent stability properties of the materials significantly.

ACKNOWLEDGMENTS

Financial support from SRC and NSF (Grant No. CTS-0072784) is gratefully acknowledged.

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