

Carbonate formation during post-deposition ambient exposure of high-*k* dielectrics

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When thick films of group-III (La, Y)- and group-IV (Hf, Zr)-based high-*k* dielectrics are exposed to ambient for several months, Fourier transform infrared spectroscopy shows formation of carbonate species in the film bulk, likely due to reaction with atmospheric CO₂. Group-III-based films show signs of carbonate feature growth within 10 min of air exposure, especially in films processed at relatively low temperatures (<600 °C). Carbonate formation is verified also for group-IV-based films, but at a significantly reduced concentration. Post-exposure annealing can reduce the carbonate observed in the IR spectra. However, post-exposure annealing likely does not remove carbon contamination, and it results in interface silicon oxide growth. The observed reactions of high-*k* films with the ambient may impose significant constraints on the post-deposition handling of high-*k* films. © 2003 American Institute of Physics. [DOI: 10.1063/1.1623316]

Among the leading candidates to replace SiO₂ in advanced transistors¹ are oxides and silicates of Hf^{2–5} and Zr.^{6,7} La- and Y-based materials^{8–10} have also been reported to be thermodynamically stable¹¹ in contact with Si and have been given some attention. For most of these materials, little understanding has been gained regarding the effect of the processing conditions on the final material properties as well as post-deposition modifications as a result of reactions with the ambient. In this letter, we use Fourier transform infrared spectroscopy (FTIR) to study the propensity of Hf-, Zr-, Y-, and La-based high-*k* dielectrics to react with atmospheric CO₂ to form carbonates. The effect of the processing temperature (oxidation or post-deposition inert anneal) on the reactivity, as well as the effect of post-exposure anneals are also reported.

For this study, thick metal films (>300 Å, M=La, Y, Hf, and Zr) are deposited using dc sputtering on high-resistivity, H-terminated Si(100) substrates and oxidized *ex situ* at 600 or 900 °C by rapid thermal anneal in dry air, or in a tube furnace in N₂O (1 atm) as described by Chambers *et al.*¹² Thick Y₂O₃ films are deposited using plasma enhanced chemical vapor deposition (PECVD).¹³ Some Y₂O₃ films are annealed in the furnace at 900 °C in N₂. The films are permitted to react with the ambient laboratory air, and FTIR spectra are collected over regular time intervals for a period of more than one year. A ThermoNicolet IR bench equipped with a deuterated tri-glycine sulfate detector (KBr beamsplitter) is used in the transmission mode, and for a typical spectrum we collect 256 scans at 4 or 8 cm⁻¹ resolution. The instrument is purged using purified air with low concentrations of moisture and CO₂. A background spectrum is collected after each measurement using a substrate fragment that originates from the same wafer as the deposited substrate. All FTIR spectra presented are plotted at the same absorbance units to allow direct comparison of the peak intensities. Interference oscillations are removed in some of the

spectra using a smoothing subroutine. The area for the peaks of interest is calculated with the instrument control software. Metal film thickness before oxidation is calculated on the basis of step-height measurements performed with a Tencor profilometer.

Carbon dioxide is known to react with metal oxide systems,¹⁴ forming either linearly coordinated CO₂ complexes or carbonate-like components that include unidentate, bidentate, and more complicated polydentate bridged structures.¹⁵ The linear coordination of CO₂ produces strong IR absorption bands in the 2300–2400 cm⁻¹ range, while the various carbonate species produce IR active features in the 1000–1800 cm⁻¹ spectral range.^{14,15} Species identification 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 stretching mode of the C–O groups. In this letter, we focus on the formation of carbonate species, and for simplicity we will refer to all the observed modes as CO.

Figure 1 shows the 1100–2000 cm⁻¹ range of FTIR absorption spectra of PVD La- and PECVD Y-based high-*k* dielectrics after short and long exposure to ambient air. The La PVD samples are known to be of bulk silicate composition.⁹ Both PVD and PECVD Y samples are known to have a layered Y₂O₃/YSiO/SiO₂ structure.^{12,16} The spectrum of the as-deposited Y PECVD sample [spectrum (vi)] taken after 4 h exposure exhibits the larger absorption peaks in the 1200–1700 cm⁻¹ range that are assigned to several unidentately and bidentately bound carbonate species.^{14,15} When a similarly deposited sample is annealed in N₂ at 900 °C immediately after deposition and then exposed to air for 4 h, much less carbonate formation is observed [spectrum (v)] compared to the sample that was not annealed. Y-silicate films formed at 600 and 900 °C by oxidizing PVD Y on silicon show clear CO-related features after three days of air exposure (data not shown). LaSiO samples also show reactivity that depends strongly on the thermal history of the film. During the first 10 min of air exposure, the film oxi-

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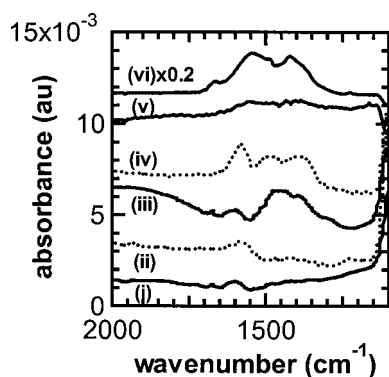


FIG. 1. FTIR spectra for ambient exposure of group-III-based high- k dielectrics (i) 300 Å of La metal oxidized in N_2O at 900 °C and exposed for 10 min in ambient. (ii) Same as (i), but exposed for 414 days. (iii) 300 Å of La metal oxidized in N_2O at 600 °C and exposed for 10 min. (iv) Same as (iii), but exposed for 398 days. (v) 300 Å of PECVD Y_2O_3 deposited at 400 °C, annealed at 900 °C in N_2 and exposed for 4 h. (vi) 300 Å of PECVD Y_2O_3 as-deposited at 400 °C and exposed for 4 h (scaled by 0.2). All samples form carbonate species as witnessed by the absorption peaks at 1200–1700 cm^{-1} .

dized at 600 °C [spectrum (iii)] exhibits significant carbonate content, while the film oxidized at 900 °C [spectrum (i)] shows only minimal concentrations of carbonates.

Figure 2 is a plot of the area of the CO peaks versus exposure showing the effect of long-term ambient exposure on the FTIR spectra for the group-III-based samples. The intensity of the carbonate peaks grows for all samples. The 900 °C PECVD Y film and the 900 °C La film show signs of extended carbonate formation after a ten day exposure.

Figure 3 shows the 1100–2000 cm^{-1} range of FTIR spectra of PVD Hf-based films oxidized at 900 and 600 °C after short (10 min) and long-term (153 days) ambient exposure. Spectra (vii) and (viii) are for films oxidized at 900 °C after short and long exposure, respectively, and spectra (ix) and (x) are for films oxidized at 600 °C. Zr-based films formed at 900 and 600 °C and exposed to air for 185 days are also shown [spectra (xi) and (xii), respectively]. Based on previous profiling experiments by x-ray photoelectron spectroscopy, both the Hf- and Zr-based films have a layered $MO_2/MSiO/SiO_2$ structure ($M=Hf$ or Zr). The spectra of the Hf film includes weak absorption peaks in the 1200–1700 cm^{-1} range, with the most prominent peak lo-

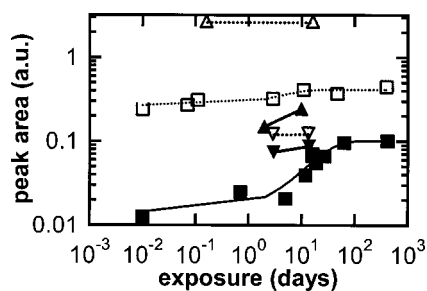


FIG. 2. Integrated carbonate peak area vs exposure for the group-III-based samples: ■ PVD La film oxidized at 900 °C, □ PVD La film oxidized at 600 °C, ▲ PECVD Y_2O_3 annealed at 900 °C in N_2 , △ as-deposited at 400 °C PECVD Y_2O_3 , ▼ PVD Y film oxidized at 900 °C, and ▽ PVD Y film oxidized at 600 °C. Exposure results in growth of the carbonate peaks for all samples, but the films subjected to thermal treatment at 900 °C are relatively more stable. The lines are intended as a guide to the eye and do not represent a modeling attempt.

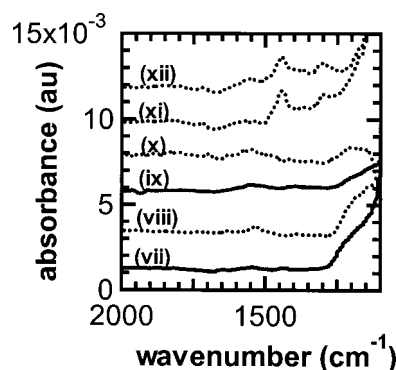


FIG. 3. FTIR spectra for group-IV-based high- k dielectrics. (vii) 300 Å of Hf metal oxidized in N_2O at 900 °C and exposed for 10 min in ambient. (viii) same as (vii), but exposed for 153 days. (ix) 300 Å of Hf metal oxidized in N_2O at 600 °C and exposed for 10 min. (x) same as (ix), but exposed for 153 days. (xi) 450 Å of Zr metal oxidized in N_2O at 900 °C and exposed for 185 days. (xii) 450 Å of Zr metal oxidized in N_2O at 600 °C and exposed for 185 days. Some carbonate formation is observed for all samples.

cated at ~ 1550 cm^{-1} , compatible with the formation of mainly bidentate and some unidentate carbonate species. For the Zr-based films, the most prominent feature is located at ~ 1440 cm^{-1} , and well-resolved peaks can be seen at ~ 1720 , 1550, and 1300 cm^{-1} . Figure 4 shows the effect of exposure on the CO peak area for the Hf and Zr samples. The carbonate peak area/intensity increases with exposure time, but the rate is significantly lower than that observed for the group-III-based films (note difference in scale of Figs. 2 and 4).

Several of the films that received extended ambient exposure were subsequently annealed in Ar at 600–900 °C, and IR spectra were collected after annealing. For example, when the LaSiO sample originally oxidized at 600 °C and exposed >400 days was annealed in Ar at 600 °C for 10 min, partial removal of the carbonate species IR signature is observed. An additional 10 min Ar anneal at 900 °C results in almost complete removal of the IR signal. However, a distinct increase in the IR absorbance is observed at ~ 1100 cm^{-1} , indicating significant growth of interfacial SiO_2 . When the Zr oxide samples formed at 600 and 900 °C are exposed to air for >185 days and annealed at 900 °C, the carbonate concentrations do not change significantly, but again the IR spectrum indicates substantial increase in the thickness of the interfacial SiO_2 layer.

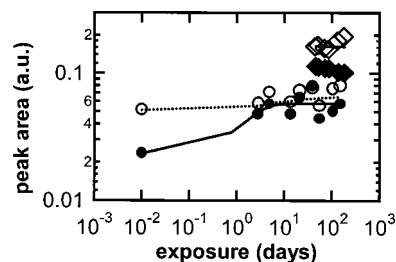


FIG. 4. Integrated carbonate peak area vs exposure for the group-IV-based samples: ● PVD Hf film oxidized at 900 °C, ○ PVD Hf film oxidized at 600 °C, ◆ PVD Zr film oxidized at 900 °C, and ◇ PVD Zr film oxidized at 600 °C. Exposure results in growth of the carbonate peaks for the Hf samples. Both Hf and Zr films oxidized at 900 °C exhibit smaller carbonate concentrations than the films oxidized at 600 °C. The lines are intended as a guide to the eye and do not represent a modeling attempt.

The stability of high- k dielectrics during air exposure may be an important issue for device integration. The net effect of the carbonate on the electrical properties of the films is not clear. However, it is well established that carbon doping of SiO₂ leads to the reduction of the dielectric constant of the film.¹⁷ For group-III-based materials post-deposition high temperature anneals (900 °C) can improve stability and remove the carbonate IR signature, but it is likely that C may remain as impurity even after the thermal treatment, affecting the insulating properties of the material. Additionally, high-temperature treatments result in the increase in the thickness of the interfacial silicon oxide layer and reduction in the overall capacitance of the gate stack. The CO absorbed from the ambient likely acts as a source of oxygen in the observed Si oxidation reactions and the very thin films (<5 nm) required for gate stack applications are expected to be particularly susceptible to interface oxidation. The reactivity of the group-IV-based films under ambient exposure is significantly lower than that of the group-III films. However, some reaction is detectable after a 10 min exposure, and post-deposition anneals do not remove the carbonate signature from the IR spectra.

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