

# Properties of La-silicate high-*K* dielectric films formed by oxidation of La on silicon

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In this article, we present data on the properties of La-based high-*k* dielectric films prepared by oxidation of La deposited by physical vapor deposition on silicon. Films are characterized by x-ray photoelectron spectroscopy, infrared absorption, and capacitance versus voltage analysis. We find that when we oxidize La metal sputter deposited on Si substrates, it reacts with the silicon substrate to form La silicate. La films as thick as 300 Å will react completely with Si under moderate oxidation conditions (900 °C for 10 min) suggesting a very rapid silicidation reaction between La and Si. Under some processing conditions the as-deposited films contain a small La<sub>2</sub>O<sub>3</sub> component that reduces to La silicate upon anneal at high temperatures. La-silicate films do not phase separate into La<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> upon annealing at 1050 °C, and their resistance to H<sub>2</sub>O incorporation depends critically on the oxidation temperature. Electrical measurements show a high concentration of positive fixed charge. © 2003 American Institute of Physics. [DOI: 10.1063/1.1531818]

## I. INTRODUCTION

Continuing miniaturization of the complimentary metal oxide semiconductor (CMOS) devices has resulted in the need for a new higher dielectric constant material to replace SiO<sub>2</sub> as the gate dielectric.<sup>1</sup> Several such high-*k* materials, mainly oxides and silicates of group III and IV metals, are currently under investigation.<sup>2,3</sup> Most of the attention has focused on materials that are reported to be stable in contact with silicon.<sup>4</sup> These thermodynamic calculations apply strictly to the metal oxide and silicon in contact at equilibrium conditions. In reality, physical and chemical deposition processes are inherently nonequilibrium and involve many potential reactions that are not taken into account by purely thermodynamic considerations. Interaction between deposition precursors, reaction intermediates, and/or the substrate can lead to the formation of interfacial layers, which may be SiO<sub>2</sub>, a silicate, or both. For dielectrics derived from Y, a group III metal, it has been found that a rapid silicidation reaction competes with the oxidation process and leads to the formation of multiple layer stacks consisting of SiO<sub>2</sub>/YSiO/Y<sub>2</sub>O<sub>3</sub> in both physical vapor deposition (PVD)<sup>5</sup> and chemical-vapor deposition<sup>6</sup> dielectrics. The oxide of La, another group III metal, is predicted to be stable in contact with Si. However, several recent studies report preferential formation of La-silicate materials over the oxide due to a very efficient mechanism for Si diffusion in La metal and/or La oxide.<sup>7,8</sup> In this article, we report the composition, stability, and electrical properties of La-based high-*k* materials prepared by oxidation of thin La films sputter deposited on Si surfaces. We study the effect of substrate pretreatment on La and Si reactivity and, additionally, we investigate the role of the oxidation temperature on the film's propensity to absorb H<sub>2</sub>O from the ambient.

## II. EXPERIMENT

We have prepared La-based high-*k* films by plasma assisted dc sputtering of La metal on H-terminated Si (100) substrates and *ex situ* furnace oxidation in the presence of N<sub>2</sub>O as described by Chambers and Parsons and Chambers *et al.*<sup>5,9</sup> The H-terminated Si (100) substrates were prepared by a J T Baker 100 Clean dip for 5 min, deionized water rinse for 5 min, and buffered oxide etch dip for 1 min. They were subsequently blown dry with dry nitrogen and placed in the loadlock of the deposition system. Nitrided Si substrates were prepared by *in situ* exposure of the H-terminated Si to N<sub>2</sub> plasma at 300 °C and 50 mTorr for 20 min. This procedure results in ~10 Å of nitride.

The La metal target was purchased from ESPI metals (Ashland, Oregon) and was 99.9% pure. The films described in Sec. III C were deposited in a different PVD system equipped with magnetron sputtering and a La target from Target Materials (Columbus, Ohio) with a purity of 99.9%; oxidation was performed in dry air in a rapid thermal annealing (RTA) furnace.

Metal film thickness was calculated from a calibration curve obtained by *ex situ* step height measurements performed with a Tencor S profilometer. Steps were prepared by partially covering Si substrates with a glass slide during deposition. This calibration should be regarded as an upper limit to the metal film thickness since La undergoes oxidation when exposed to moisture and oxygen. Films exposed to air for over a day gained significant (at least 50%) thickness indicating that they were only partially oxidized during the initial step height measurements.

Characterization of the film composition was performed by x-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (IR). A Riber LAS3000 instrument equipped with a single-pass, cylindrical mirror (MAC2) analyzer and a Mg K $\alpha$  ( $h\nu = 1253.6$  eV), nonmonochromatic x-ray source

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was used at a  $75^\circ$  takeoff angle with 0.1 eV step size to obtain the XP spectra. Charge compensation was performed by setting the adventitious C 1s peak to a binding energy of 286.0 eV. Fourier-transform infrared (FTIR) transmission spectra were obtained using a Magna-IR System 750 from Thermo Nicolet (Madison, Wisconsin). All spectra were corrected by subtracting the FTIR spectrum of a plain Si substrate. High-resistivity, double-polished Si substrates were used for that part of the study.

Metal-insulator-semiconductor (MIS) capacitors were fabricated via shadow mask deposition of evaporated Al (2000 Å). The electrical properties of the films were investigated by capacitance versus voltage ( $C$ - $V$ ) measurements using an HP4284 LCR. All  $C$ - $V$  measurements, unless otherwise stated, were performed at a frequency of 1 MHz and scanned from depletion to accumulation. A Nikon Eclipse Optical Microscope equipped with a digital camera was used to photograph selected capacitors. The digital images were then processed using ImageJ<sup>10</sup> to obtain the capacitor area, which was typically  $3.5 \times 10^{-4}$  cm<sup>2</sup>. Capacitors with small areas were selected for the measurements so as to avoid instrumental errors associated with measuring large capacitances. The capacitance versus voltage ( $C$ - $V$ ) data were analyzed using the NCSU  $C$ - $V$  program<sup>11</sup> to obtain the equivalent oxide thickness (EOT), and flatband voltage.

### III. RESULTS AND DISCUSSION

#### A. Composition of La containing dielectrics formed on clean H-terminated Si (100)

La-metal films with thicknesses from 15 to 330 Å were deposited on H terminated Si (100) substrates and oxidized *ex situ* at 900 °C in N<sub>2</sub>O (5 slpm) at atmospheric pressure for times ranging from 30 s to 10 min and equal to the duration of the deposition. X-ray photoelectron spectroscopy was then used to analyze the surface composition (top ~50 Å) of the films, and the spectral regions containing the Si2p/La4d, O1s, and La3d peaks are displayed on Fig. 1. The thicknesses given correspond to the original thickness of the metal deposited. The resulting dielectric film thickness is approximately twice the original metal thickness. For the thinner films, we were able to probe the Si-dielectric interface and detect the substrate Si<sup>0</sup> peak<sup>12</sup> at 99.3 eV in the Si2p spectra. The absence of silicide peaks is consistent with the selected oxidation conditions. The spectral region around the Si2p peaks [Fig. 1(a)] also contains contributions from the La4d peaks<sup>13</sup> at 101.9 and 105.5 eV that overlap with the SiO<sub>2</sub> peak expected at 103.3 eV.<sup>12</sup> No attempts were made to deconvolve the peaks.

For the O1s spectra in Fig. 1(b) we can observe a clear transition from a double to a single peak as the film thickness increases. The shoulder at ~533.0 eV is clearly visible for the thinnest (15 Å of La metal) film and indicates the presence of a SiO<sub>2</sub> interfacial layer.<sup>12</sup> As the film thickness increases and we lose the ability to probe the interface, the O1s spectra exhibit a single peak at ~531.8 eV. This peak lies between the SiO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> peaks at 533.3 and 529.9 eV<sup>13</sup> respectively, consistent with the formation of La-O-Si silicate bonding units. For the thinnest film, the peak position is

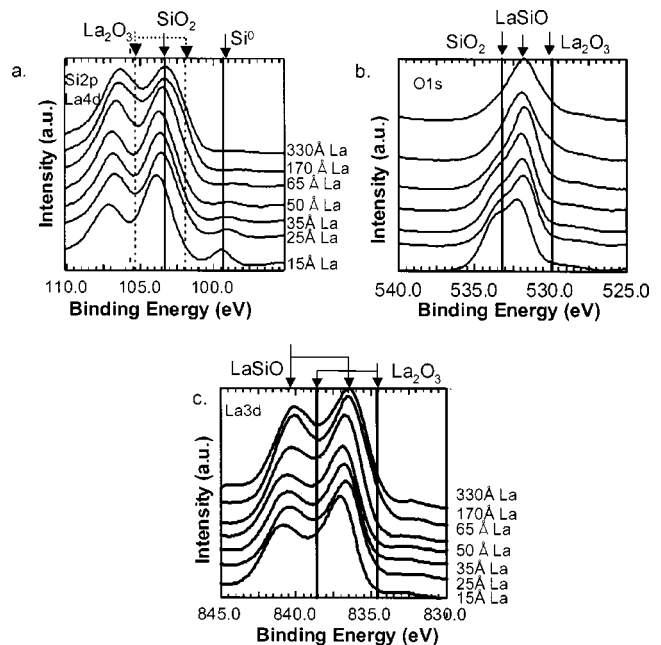


FIG. 1. Si2p/La4d, O1s, and La3d spectra for a series of La metal films with thickness ranging from 15 to 330 Å, oxidized at 900 °C in N<sub>2</sub>O. Interfacial SiO<sub>2</sub> was detected for the thinnest films. Based on the position of the O1s and the La3d peaks, we conclude that the material is La silicate for all thicknesses studied.

marginally shifted to a higher-binding energy indicating the presence of a more Si-rich silicate layer close to the interface. The La4d and La3d spectra in Figs. 1(a) and 1(c) are also consistent with the silicate composition for all thicknesses studied. The La3d and La4d features shift slightly to a lower-binding energy as the film thickness increases suggesting a higher-La fraction in the thicker films. However, this shift is very slight with the largest changes occurring between 15 and 25 Å.

The O1s and La3d peak positions remain practically unchanged with film thickness implying that the diffusion of Si atoms into the La metal film proceeds very rapidly at the temperatures studied and the silicidation reaction may proceed at a faster rate than the oxidation. Mixing of La with Si probably occurs even during the metal film deposition at high temperature increases the La and Si mobility. These results are consistent with a mechanism in which La silicide is formed, and subsequently as oxidants diffuse through the film it oxidizes to form La silicate, and interfacial SiO<sub>2</sub>. Such a mechanism is consistent with previous studies<sup>14,15</sup> that report a fairly rapid intermixing of Si and La layers even at temperatures as low as 150 °C. However, we acknowledge that our results could also be explained by rapid Si diffusion in La<sub>2</sub>O<sub>3</sub> films as observed recently both for metal-organic chemical-vapor deposition<sup>7</sup> and *e*-beam evaporated oxide films.<sup>8</sup>

These findings share some common features with previous observations regarding Y-based films formed in similar manner. Chambers and Parsons<sup>5</sup> found that competition between two reactions, silicidation at the bottom of the deposited metal and oxidation at the top, resulted in two regimes

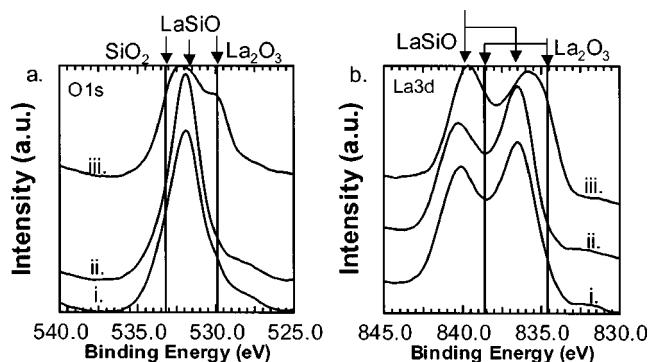


FIG. 2. O1s and La3d XPS spectra for three identical films (170 Å La metal, 5 min, 900 °C, N<sub>2</sub>O oxidation) deposited on (i) H-terminated Si (100), (ii) plasma nitrated Si (100), and (iii) 1000 Å of thermal SiO<sub>2</sub>. Films (i) and (ii) have practically identical composition as measured by XPS, while film (iii) is also a silicate but has a small La<sub>2</sub>O<sub>3</sub> content as evidenced by the shoulder of the O1s peak at ~530 eV and the shift of the La3d peak towards lower-binding energies.

for growth. For thin Y films, the Si/Y mixing was sufficiently fast to form a single layer having silicate composition as observed in our lanthanum studies. However, a second regime was identified for relatively thicker films (>80 Å) in which competition between silicidation and oxidation resulted in the formation of a SiO<sub>2</sub>/YSiO/Y<sub>2</sub>O<sub>3</sub> layered structure. This second regime was never identified in our work, and the difference is quite interesting since both Y and La are group III metals and may be expected to have similar chemical properties. An IR study of the interfacial reactions between rare-earth-metal oxides and Si substrates by Ono and Katsumata<sup>16</sup> found that the fraction of silicate bonding increases with the ionic radius of the rare-earth element. Larger atoms, in general, leave more free space for Si diffusion. The extent of silicate formation for PVD Y- and La- based dielectrics corroborates the conclusion that enhanced Si diffusivity in the lanthanum system is a key factor that controls whether the oxide or silicate of the metal is preferentially formed.

## B. Effect of substrate on the film composition

We analyzed the composition of thick films (170 Å metal) deposited on various substrates, and results are shown in Fig. 2. Figures 2(a) and 2(b) show O1s and La3d XPS spectra, respectively, for the following three films: 170 Å of La metal oxidized at 900 °C for 5 min in N<sub>2</sub>O deposited on (i) H-terminated Si (100); (ii) *in situ* plasma nitrated Si (100); and (iii) 1000 Å of thermal SiO<sub>2</sub>. The O1s spectra for samples (i) and (ii) are practically identical and are consistent with La-silicate formation. Sample (iii), formed on 1000 Å thermal SiO<sub>2</sub>, shows a primary feature at ~531.5 eV and a significantly smaller one at 529.9 eV, indicating that LaO–Si with a small fraction of La<sub>2</sub>O<sub>3</sub> bonding are present in the film. The La3d spectrum for sample (iii) is shifted towards the low-binding energies compared to those for samples (i) and (ii), consistent with the presence of La<sub>2</sub>O<sub>3</sub> in sample (iii), and with our interpretation of the O1s spectra for this film. The peak broadening may be due to a graded composition in sample (iii).

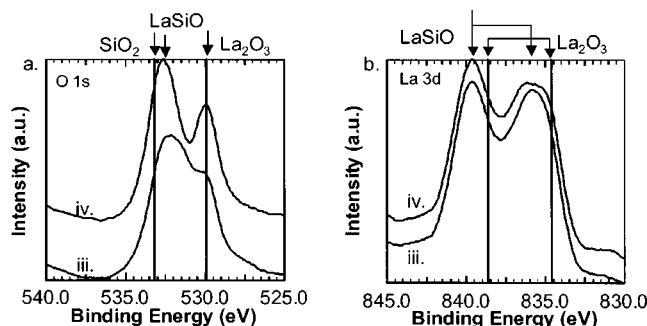


FIG. 3. O1s and La3d XPS spectra for 170 Å (iii) and 1000 Å (iv) La metal deposited on 1000 Å of thermal SiO<sub>2</sub> and oxidized at 900 °C in N<sub>2</sub>O for 5 min. Both films have primarily silicate composition with a small fraction of La<sub>2</sub>O<sub>3</sub>. The thicker film exhibits a higher La<sub>2</sub>O<sub>3</sub> content.

To gain further insight into the reactions of La metal on thick SiO<sub>2</sub>, a very thick La film (1000 Å) was deposited on SiO<sub>2</sub> for comparison with sample (iii). Figure 3 shows XPS data for samples formed by depositing 170 Å of La on 1000 Å SiO<sub>2</sub> (sample iii), and 1000 Å La on 1000 Å SiO<sub>2</sub> (sample iv). Film stacks were oxidized at 900 °C for 5 min. The O1s XPS spectra [Fig. 3 (a)] for both films exhibit a primary peak at ~531.5 eV, and a secondary peak at ~530 eV consistent with the presence of some La<sub>2</sub>O<sub>3</sub> in a mainly silicate film. The thicker La layer results in a more pronounced and narrower La<sub>2</sub>O<sub>3</sub> feature. The broadening of the La3d peaks [Fig. 3(b)] for samples (iii) and (iv) towards the low-binding energies compared with films (i) and (ii) is also consistent with the existence of La<sub>2</sub>O<sub>3</sub> in films (iii) and (iv).

We now discuss differences in reactions on plasma nitrated and thermally oxidized substrates. Comparing data from samples (i) and (ii), the presence of an ultra-thin layer of nitrated Si in sample (ii) does not impede significantly the diffusion of Si atoms into the La-metal film. This result is in contrast to that obtained from studies of Y on nitrated Si<sup>17</sup> where the presence of ~10 Å of nitrated Si did impede reaction of Y and Si. The larger ionic radius of the La atom compared to that of Y may account for this difference. It is also conceivable that in both cases, metal nitride layers (La–N or Y–N) are formed at the interface. The lattice constants for La–N is expected to be ~5.33 Å (Ref. 18) which is significantly larger than the 4.88 Å (Ref. 18) expected for Y–N, thus facilitating the diffusion of the Si atoms through the La–N layer.

The XPS detection of Si near the top of films (iii) and (iv), which were deposited on 1000 Å of thermal SiO<sub>2</sub>, shows the remarkable ability of La metal to reduce SiO<sub>2</sub> during thermal treatment likely by breaking Si–O bonds. It was shown above that Si atoms are highly mobile in La and La oxide and diffuse through >1000 Å of deposited metal to form La–O–Si units at the sample surface. In the case of La–SiO<sub>2</sub> reactivity, the silicidation reaction requires additionally the breaking of fairly strong (4.85 eV) Si–O bonds. As a result, one expects thicker metal films would be more likely to have La<sub>2</sub>O<sub>3</sub> at the surface. The data in Fig. 3 supports this idea. The intensity of the La<sub>2</sub>O<sub>3</sub> peak in the La3d spectrum is significantly larger for the film prepared from the thicker (1000 Å) original La metal. The O1s peak for sample

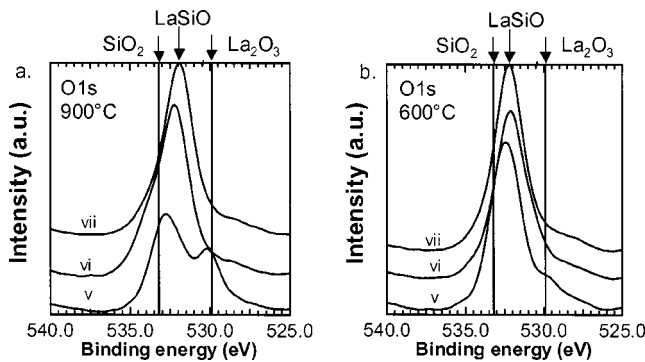


FIG. 4. O1s XP spectra for a 150 Å metal film oxidized for 5 min at 900 or 600 °C in dry air. Sample (v) is as deposited. Sample (vi) was annealed at 1050 °C in Ar for 10 s, and sample (vii) was annealed at 1050 °C in Ar for 30 s. The La silicate can withstand 30 s inert anneal at 1050 °C without phase separation. The small amount of  $\text{La}_2\text{O}_3$  present in the as-deposited films is reduced to silicate upon anneal.

(iv) in Fig. 3(a) is narrower than that of sample (iv) consistent with a more homogeneous composition for sample (iv). Neither sample spectra show evidence for a  $\text{SiO}_2$  O1s feature at 533.3 eV consistent with a La-rich top layer.

The broadening of the O1s spectra for sample (iii) towards high-binding energies may be ascribed to the presence of more  $\text{SiO}_2$  in the film as compared to samples (i), (ii), and (iv). This result is consistent with a large amount of  $\text{SiO}_2$  initially under the deposited metal. As discussed below in Sec. III C, we do not see evidence for phase separation of La silicate into  $\text{La}_2\text{O}_3/\text{SiO}_2$  even after annealing for 30 s at 1050 °C. Thus, we believe that the presence of  $\text{La}_2\text{O}_3$  in films (iii) and (iv) is likely due to a slower reaction between La and  $\text{SiO}_2$ , compared to the reaction between La metal and H-terminated Si or nitrated Si substrates in samples (i) and (ii).

The conclusions of this work regarding the ability of La metal to reduce thick layers of  $\text{SiO}_2$  during thermal treatment corroborate previous observations by Copel *et al.*<sup>8</sup> who demonstrated that reoxidation of a 23 Å  $\text{LaO}_x/20$  Å thermal  $\text{SiO}_2$  structure at 850 °C resulted in the complete reduction of the  $\text{SiO}_2$  and the formation of La–O–Si. Stemmer *et al.*<sup>19</sup> also reports some silicate formation for  $\text{La}_2\text{O}_3/\text{SiO}_2/\text{Si}$  structures, annealed at 800 °C.

### C. Thermal stability of La-silicate films

The propensity of the La-silicate films to phase separate into the  $\text{La}_2\text{O}_3$  and  $\text{SiO}_2$  components was investigated by subjecting the films to extended thermal treatment at 1050 °C in a rapid thermal anneal (RTA) instrument in Ar atmosphere. For this purpose, La metal (150 Å) was deposited via magnetron sputtering on H-terminated Si and RTA oxidized *ex situ* at either 600 or 900 °C in dry air for 5 min. Each dielectric film was cleaved into three pieces and subjected to a different thermal treatment. Sample (v) received no further annealing beyond the oxidation step. Sample (vi) was annealed in Ar at 1050 °C for 10 s, and sample (vii) was annealed at the same temperature for 30 s. Figure 4 shows the O1s XP spectra for samples (v) through (vii) for films oxi-

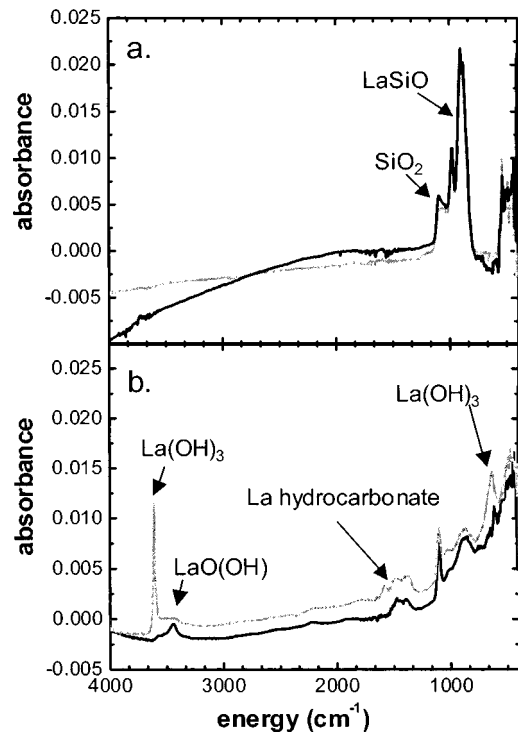


FIG. 5. FTIR spectra for two dielectric films taken about 10 min after oxidation (solid black line) and after 10 days of air exposure (solid gray line). The films were formed by oxidizing 330 Å La-metal films at either 900 °C (a) or 600 °C (b) for 10 min in  $\text{N}_2\text{O}$ . The film oxidized at 900 °C exhibits features consistent with the presence of  $\text{SiO}_2$  and La–O–Si. No significant reaction with  $\text{H}_2\text{O}$  or  $\text{CO}_2$  is detected even after a 10-day exposure to ambient air. The film oxidized at 600 °C is chemically unstable in contact with air, and its spectrum exhibits features consistent with the formation of a La hydrocarbonate. Air exposure intensifies those features.

dized at 900 and 600 °C. With longer annealing time, the O1s peak position shifts marginally towards lower-binding energies, but phase separation is not observed.

Additionally, both 900 and 600 °C as-deposited films exhibit a small  $\text{La}_2\text{O}_3$  content as evidenced by the low-binding energy shoulders in the O1s and  $\text{La}3d$  (not shown) peaks. This oxide is not present in the  $\text{N}_2\text{O}$  oxidized films and is probably due to the different oxidation environment or the faster temperature ramp in the RTA instrument than in the conventional furnace used for samples discussed in previous sections. The oxide is reduced to silicate upon thermal anneal, and this silicate exhibits remarkable thermal stability even upon a 30 s thermal excursion at 1050 °C which exceeds the thermal budget currently experienced by the CMOS gate dielectric during dopant activation.

### D. Atmospheric $\text{H}_2\text{O}$ absorption of La-silicate films

The hygroscopic nature of the silicate films was investigated by FTIR. Thick La films (330 Å metal) were deposited on high resistivity Si substrates and oxidized for 10 min at either 600 or 900 °C. The IR spectrum of each sample was recorded within 10 min of the oxidation. The films were left in ambient air, and the IR spectrum between 4000 and 400  $\text{cm}^{-1}$  was recorded periodically.

Figure 5 shows spectra recorded immediately (within 10 min after oxidation) and after 10 days of ambient exposure

for films oxidized at 900 [Fig. 5(a)] or 600 °C [Fig. 5(b)]. The 900 °C film oxidized exhibits an absorption feature at 1100  $\text{cm}^{-1}$  corresponding to the Si–O–Si asymmetric stretch in  $\text{SiO}_2$ .<sup>20</sup> The peak due to the Si–O–Si bending mode located at 810  $\text{cm}^{-1}$  is superimposed onto a broader set of peaks located between 780–1020  $\text{cm}^{-1}$  and indicative of La-silicate structure.<sup>16</sup> The  $\text{La}_2\text{O}_3$  feature<sup>21</sup> at 450  $\text{cm}^{-1}$ <sup>22</sup> could not be investigated due to instrument limitations. The IR spectrum of the film oxidized at 900 °C remains practically unchanged after ten days of air exposure.

The film oxidized at 600 °C exhibits a far richer absorption spectrum. Following oxidation, interfacial  $\text{SiO}_2$  formation is revealed by the Si–O–Si asymmetric stretching mode at 1100  $\text{cm}^{-1}$ . The intensity of the silicate peaks between 780–1020  $\text{cm}^{-1}$  is significantly reduced while several other peaks appear in the spectrum. Significant reaction with moisture is revealed by the hydroxyl group stretching mode peaks at 3440  $\text{cm}^{-1}$  for OH in  $\text{LaO}(\text{OH})$  and the small shoulder near 3600  $\text{cm}^{-1}$  caused by OH in  $\text{La}(\text{OH})_3$ . The broad feature between 1500 and 1300  $\text{cm}^{-1}$  suggests the presence of hydrocarbonate phases,  $\text{La}_2(\text{OH})_{6-3x}(\text{CO}_3)_x$ , possibly from reaction with atmospheric  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Infrared spectroscopy has been used previously to observe reactions between atmospheric  $\text{CO}_2$ , moisture, and  $\text{La}_2\text{O}_3$  powders,<sup>22–24</sup> and films.<sup>25</sup> After ten days of ambient exposure, the peaks become more intense, and three peaks at 3610, 1580, and 640  $\text{cm}^{-1}$  appear in the spectrum. The very strong features at 3610 and 640  $\text{cm}^{-1}$  are assigned to the O–H stretching and La–OH bending modes of  $\text{La}(\text{OH})_3$ .<sup>22,23</sup> The peak at 1580  $\text{cm}^{-1}$  is probably due to the formation of another La hydrocarbonate.<sup>23,24,26</sup>

The oxidation temperature appears to affect significantly the film's reactivity with atmospheric components such as moisture and  $\text{CO}_2$ . Rare-earth oxides and  $\text{La}_2\text{O}_3$  powders<sup>23</sup> are known to react with atmospheric components. Rosynek and Magnuson<sup>22</sup> demonstrated that prolonged (~40 h) annealing of La hydrocarbonate in vacuum leads to a first stage dehydration at 200 °C and complete dehydration at around 400 °C. The carbonate decomposes between 400 and 800 °C. XPS analysis of films oxidized at 600 and 900 °C and kept in the controlled atmosphere of a dessicator reveals that both materials have similar silicate compositions. Thus, we believe that oxidation at either 600 or 900 °C is sufficient to desorb all the impurities that form within the 1–2 min air exposure prior to oxidation. The oxidation temperature was the only step in the preparation of these samples that was varied. It is likely that oxidation at 900 °C results in a more densely packed film structure than oxidation at 600 °C. A higher porosity would facilitate the diffusion of atmospheric elements in the 600 °C silicate film and allow hydrocarbonate formation within minutes of air exposure.

Nieminen *et al.*<sup>25</sup> have reported IR results for  $\text{La}_2\text{O}_3$  films grown on Si. The as-deposited films exhibit  $\text{LaO}(\text{OH})$  and carbonate features that disappear following a 30 min  $\text{N}_2$  anneal at 800 °C. However, these reappear and strong  $\text{La}(\text{OH})_3$  features develop after subsequent exposure to air. The chemical stability exhibited by the 900 °C La silicate in this study is quite remarkable and noteworthy.

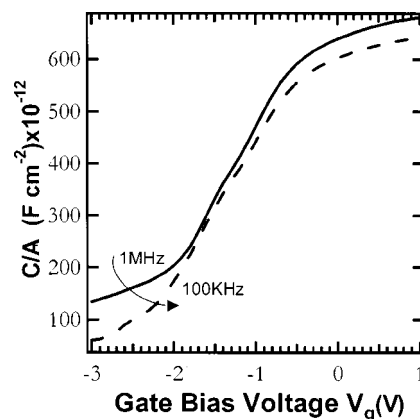


FIG. 6. Representative  $C$ - $V$  data for a dielectric film prepared by oxidizing 10 Å La metal in a 900 °C,  $\text{N}_2\text{O}$  atmosphere for 5 s. The low-frequency (100 kHz) curve tracks quite well the high-frequency (1 MHz) one. The stretch out of the curve along the  $V_g$  axis is indicative of a significant concentration of interface traps distributed throughout the band gap. Analysis of the 1 MHz curve yields an EOT=15.3 Å. The flatband voltage ( $-1.08$  eV) is shifted by approximately  $-1.1$  eV revealing the presence of a positive fixed charge. No attempt was made to distinguish the oxide trapped and interface trapped charge. The gate material is Al and the area of the capacitor is  $3.53 \times 10^{-4} \text{ cm}^2$ .

### E. Electrical measurements on La-silicate films

The electrical properties of the La-silicate films were evaluated by  $C$ - $V$  measurements on MIS capacitors with Al gates. No forming gas anneal was performed. Figure 6 shows a representative curve taken at 1 MHz and 100 KHz for 10 Å La metal oxidized at 900 °C for 5 s in  $\text{N}_2\text{O}$ . The area of the capacitor was measured at  $3.53 \times 10^{-4} \text{ cm}^2$  optically. The transition from depletion to accumulation appears to stretch over 1 V. This voltage stretchout is characteristic of the interface trap charge that is uniformly distributed throughout the band gap. Analysis of the 1 MHz curve with the NCSU  $C$ - $V$  program<sup>11</sup> that corrects for quantum-mechanical effects yields an equivalent oxide thickness (EOT) of 15.3 Å. The flatband voltage was  $-1.08$  V, shifted by about  $-1.1$  V from its expected position, in agreement with previous findings by Guha *et al.*<sup>27</sup> and Copel *et al.*<sup>8</sup> The direction and magnitude of the flatband voltage shift indicates the presence of a positive fixed charge with a density of about  $1 \times 10^{13} \text{ cm}^{-2}$ , which is unacceptably high for CMOS technology. The origin of the charge is not yet understood, and no attempt was made to distinguish oxide trapped and interface trapped charge in this work. However, Copel *et al.*<sup>8</sup> report that the charge appears to be an intrinsic material feature rather than being due to oxygen deficiency of the film. Physically thinner films exhibited unacceptably high-leakage currents. The frequency dispersion of the  $C$ - $V$  curve is relatively small. Overall, the electrical results are reasonable and consistent with previous reports. It is not clear whether forming gas anneal would reduce the number of interface traps. Figure 7 presents hysteresis of the same film on the first and fifth cycle. The insert graph shows a magnified portion of the curves around the flatband voltage. The hysteresis is about 25 mV, corresponding to a mobile charge density of about  $2 \times 10^{11} \text{ cm}^{-2}$ . The  $C$ - $V$  curve shifts marginally towards more positive voltages as the voltage is scanned from deple-

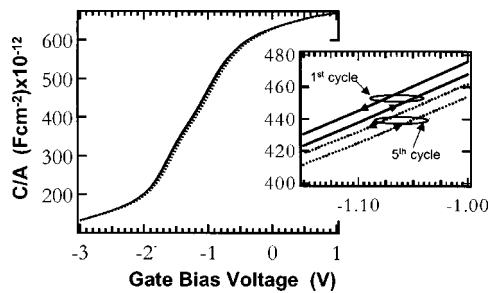


FIG. 7. Hysteresis curves for the capacitor in Fig. 6. The inset shows a magnification of the flatband voltage area. The magnitude is  $\sim 25$  mV without post-metallization anneal.

tion to accumulation and vice versa several times. The displacement of the flatband voltage is  $\sim 20$  mV after the first cycle and reduces to  $\sim 7$  mV for each of the subsequent three cycles. This shift in the  $C$ - $V$  curves under stress indicates another instability in the films, and can be explained by the generation of negative charge in the gate dielectric.<sup>28</sup> Similar observations have been documented for other high- $k$  materials such as ultrathin  $ZrO_2$ <sup>29</sup> and  $SiO_2/ZrO_2$ <sup>30</sup> films. The magnitude of the hysteresis remains practically unchanged from the first to the fifth cycle, however the observed shift in the flatband voltage under stress is fairly undesirable as it implies a threshold voltage instability when applied to field-effect transistors.

#### IV. CONCLUSIONS

Thin dielectric films were created by La metal PVD and *ex situ* furnace oxidation in  $N_2O$ . XPS analysis revealed that regardless of the initial metal thickness the films were a La-silicate material with fairly constant composition. Oxidation at 600 and 900 °C yielded materials of fairly similar silicate composition that did not phase separate into  $La_2O_3$  and  $SiO_2$  even when subjected to inert atmosphere anneals at 1050 °C for 30 s, conditions that exceed the current gate dielectric thermal stability requirements. The oxidation temperature, however, had a severe effect on the chemical stability of the films to air exposure. La-silicate films oxidized at 600 °C were susceptible to La hydrocarbonate and  $LaO(OH)$  formation within minutes of air exposure. Prolonged ambient exposure resulted in the formation of  $La(OH)_3$ . Films oxidized at 900 °C, on the other hand, showed no sign of reaction with moisture or  $CO_2$  that were within the detection limits of the FTIR instrument. Despite the good properties of these silicate films, large concentrations of a positive fixed charge have been observed. Unless it can be neutralized or somehow reduced, this charge limits the usefulness of La silicate as a replacement for  $SiO_2$  in CMOS technology

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