# *Impurity and Silicate Formation Dependence on $O_3$ Pulse Time and the Growth Temperature in Atomic-Layer-Deposited $La_2O_3$ Thin Films*

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**Citation:**

Park, T. J., Y. -C Byun, R. M. Wallace, and J. Kim. 2017. "Impurity and silicate formation dependence on $O_3$ pulse time and the growth temperature in atomic-layer-deposited $La_2O_3$ thin films." Journal of Chemical Physics 146(5), doi:10.1063/1.4975083

# Impurity and silicate formation dependence on $O_3$ pulse time and the growth temperature in atomic-layer-deposited $La_2O_3$ thin films

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(Received 27 September 2016; accepted 17 January 2017; published online 3 February 2017)

Atomic-layer-deposited $La_2O_3$ films were grown on Si with different $O_3$ pulse times and growth temperatures. The interfacial reactions and impurity behaviors were observed using *in situ* X-ray photoelectron spectroscopy. Longer pulse time of $O_3$ formed the solid $SiO_2$ interfacial barrier layer, which suppressed La–silicate formation. Meanwhile, the carboxyl compound acting as an impurity phase was replaced with $LaCO_3$ on increasing the $O_3$ pulse time due to further oxidation and reaction of La. Higher growth temperatures enhanced La–silicate formation by mixed diffusion of Si and $La_2O_3$, during which most of the $La_2O_3$ phase was consumed at 400 °C. C and N impurities decreased with increasing growth temperature and completely disappear at 400 °C. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4975083]

$La_2O_3$ gate dielectric has several advantages over $HfO_2$ and $ZrO_2$ such as a larger conduction band off-set with Si and a higher permittivity,[1–6] but atomic-layer-deposition (ALD) process of $La_2O_3$ film is somewhat exacting due to the hygroscopic growth behavior, diffusion of Si from the substrate into the film and a carbonate phase formation during ALD or post-deposition annealing.[1,2,5,7] Even though the hygroscopic growth behavior could be suppressed effectively using $O_3$ as an oxygen source,[7] the presence of drastic out-diffusion of Si from the substrate and impurities in the gate dielectric is still a critical problem with the implementation of $La_2O_3$ as a gate dielectric for next generation metal-oxide-semiconductor field-effect transistors. The impurities in the gate dielectric provide a leakage current path and act as a source of charge trapping sites thereby resulting in serious power consumption in the standby mode, shorter device lifetime, and threshold voltage instability.[8–12] In this work, $La_2O_3$ gate dielectric films were grown on the Si substrate using $O_3$ as an oxygen source, and the changes in the C- and N-related impurities and Si diffusion behavior in the dielectric were traced as a function of growth temperature and $O_3$ pulse time using *in situ* X-ray photoelectron spectroscopy (XPS) analysis.

ALD $La_2O_3$ thin films (30 cycles) were grown on a 4 in. RCA (Radio Corporation of America)-cleaned (100) Si substrate at 250, 350, and 400 °C in a SUNALE™ ALD reactor. Tris(N,N'-diisopropylformamidinato) lanthanum [La($^i$PrfAMD)$_3$] which was provided by Dow Chemical Company, Ltd., was used as the La precursor.[7,13] $O_3$ with a concentration of ~380 g/m$^3$ from the TMEIC OP-250H-LT $O_3$ gas generating system was used as the oxygen source. The La-pulse, purge, $O_3$ pulse, and purge times were 1, 60, 1, and 120 s, respectively. A longer "purge time" after $O_3$ pulse suppressed a hygroscopic growth behavior resulting in an undesirable La–hydroxide phase formation in the dielectric.[14] Meanwhile, to examine the influence of the $O_3$ pulse time on the film properties, the pulse time was set to 0.1, 1, and 10 s with a deposition temperature of 250 °C. Ultra-high purity $N_2$ (99.999%) was used as the purge gas, and the working pressure of the ALD reactor was ~7.6 Torr. The HF (Hydrofluoric acid)-cleaned Si substrate was baked for 10 min at 250 °C inside the ALD reactor prior to the ALD process to facilitate the thermal desorption of surface contaminants. During this step, an extremely thin $SiO_2$ layer would be grown on the Si substrate.

This ALD system is connected to an ultra-high vacuum (UHV) cluster system through a buffer vacuum chamber. The UHV cluster system is equipped with an *in situ* high-resolution XPS analytical module so that the Si wafers can be moved from the ALD reactor to the XPS system via an UHV tube at a pressure of ~$1.5 \times 10^{-10}$ Torr without exposure to air or other forms of contamination. Details of the UHV analytical system were reported elsewhere.[15] Monochromatic Al $K\alpha$ was used as an X-ray source (1486.7 eV) with a line width of ~0.25 eV and spectrometer pass energy of 15 eV. The binding energies (BEs) of the spectra were calibrated using Si–Si bonding (Si 2*s*) from the Si substrate.

Figure 1(a) shows the O 1*s* core level spectra of $La_2O_3$ films grown at 250 °C with $O_3$ pulse time of 0.1, 1, and 10 s. The peaks at the BE of ~529.1, ~530.5, and ~531.9 eV correspond to $La_2O_3$, La–silicate, and $SiO_2$ interfacial layer (IL), respectively.[2,16,17] The peaks corresponding to the three phases, i.e., $La_2O_3$, La–silicate, and $SiO_2$ are obviously observed in the case of a shorter $O_3$ pulse time of 0.1 s, but with increasing $O_3$ pulse time, the peak intensity for La–silicate decreased and those for $La_2O_3$ and $SiO_2$ increased. This suggests that at the initial growth stage, the increased $O_3$ pulse time oxidized the Si surface further to form a solid $SiO_2$ barrier

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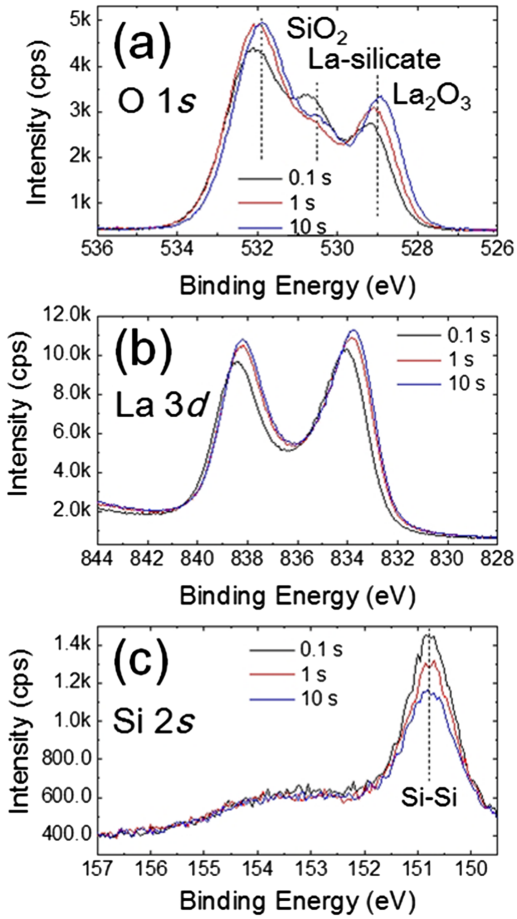


FIG. 1. (a) O 1*s*, (b) La 3*d*, and (c) Si 2*s* core level spectra of $La_2O_3$ films grown with various $O_3$ pulse times of 0.1, 1, and 10 s.

against Si out-diffusion from the substrate (the increase in $SiO_2$ peak intensity), which suppressed the silicate phase formation (the decrease in the La–silicate peak intensity).[13] Therefore, the increase in the $La_2O_3$ peak intensity with $O_3$ pulse time is attributed to the suppressed $La_2O_3$ consumption for the La–silicate phase formation. It is also possible that the residual surface impurities screening reactive sites for the precursor molecule adsorption were decreased by longer $O_3$ pulse resulting in enhanced $La_2O_3$ growth, which would increase the $La_2O_3$ peak intensity. This is supported by La $3d_{5/2}$ core level spectra in Fig. 1(b), where the peak intensity slightly increases with $O_3$ pulse time. The peak shift towards the lower BE direction is due to the suppression of the silicate phase formation as discussed above.[2,16] Since the Si 2*p* core level spectrum overlaps with the La 4*d* spectrum, the Si 2*s* core level spectra are acquired [Fig. 1(c)] to gain information on the interfacial $SiO_2$ layer. By measuring the relative peak intensity of the Si–Si bonding, the corresponding increase of interfacial $SiO_2$ layer thickness with increasing $O_3$ pulse time is confirmed.

The residual impurities present in the film were also significantly affected by the $O_3$ pulse time. Figure 2(a) shows the C 1*s* core level spectra with deconvoluted results of $La_2O_3$ films grown using different $O_3$ pulse times of 0.1, 1 and 10 s. The peak at a BE of ~286 eV indicated by blue color corresponds to the C impurity with lower oxidation states such as C–O–H, C–N, and C–O, ($C_{LO}$) originating from the partially reacted or oxidized ligand molecules in the precursor.[18–26] The peak at a BE of ~288.5 eV indicated by red color corresponds to the C impurity with higher oxidation state and carboxyl compound intermediate phases such as acetate and formate,[20–24,27,28] ($C_{HO}$) which were generated by the further oxidation of $C_{LO}$. Finally, the peak at a BE of ~290 eV corresponds to the La–$CO_3$ (carbonate) phase with the highest oxidation state. The adventitious C–C bonding was hardly observed at a BE of ~285 eV because the baking prior to ALD process eliminated the C surface contamination on the Si substrate. The changes in the peak area (intensity) of each as a function of the $O_3$ pulse time were summarized in Fig. 2(b). While the peak area for $C_{HO}$ decreases with increasing $O_3$ pulse time, that of the $LaCO_3$ phase increases and saturates over 1 s. This suggests that $C_{HO}$ was oxidized further with increasing $O_3$ pulse time to be easily consumed along with

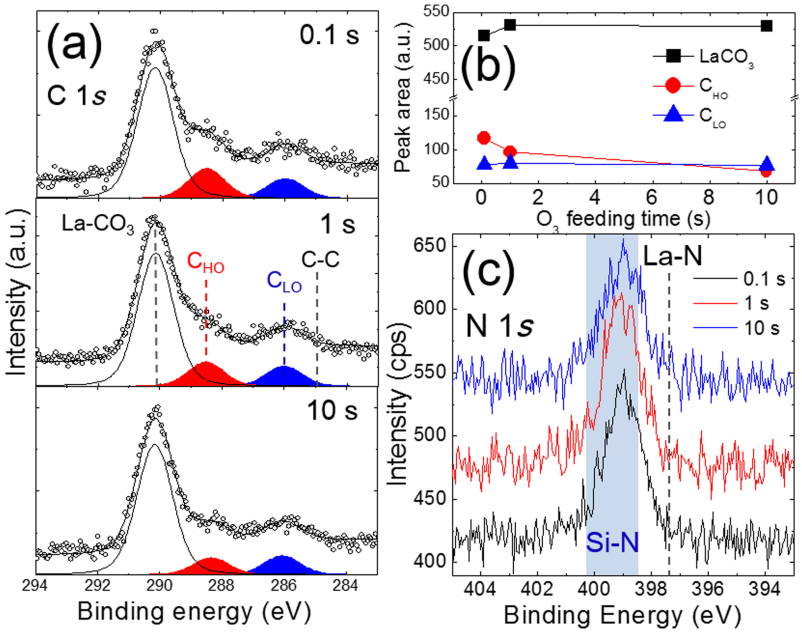


FIG. 2. (a) C 1*s* core level spectra of $La_2O_3$ films grown using the $O_3$ pulse time of 0.1, 1, and 10 s with the deconvolution result, (b) changes in the peak area of C 1*s* sub-peaks as a function of the $O_3$ pulse time, and (c) N 1*s* core level spectra.

La atoms (or ions) generating the $LaCO_3$ phase in the film, as also reported elsewhere.[27,29–35] The excess of further-oxidized $C_{HO}$ over 1 of $O_3$ pulse time can be eliminated as a form of a volatile phase; it hardly participates the $LaCO_3$ phase formation, which saturated the peak area for the La–$CO_3$ phase over 1 s. The peak area for $C_{LO}$ is constantly small in whole range of $O_3$ pulse time, which seems to be an inevitable minimum residue at the growth temperature of 250 °C. The N originating from the amidinate ligands in the La precursor formed Si–N bonding at the interface between the film and Si substrate by its reaction with the substrate during ALD, which results in the peaks at the BE of ~398.5-400.5 eV in N 1*s* core level spectra of Fig. 2(c).[27,36] The peak intensity decreased with increasing $O_3$ pulse time because the N impurity was eliminated effectively as a form of a volatile $NO_x$ phase. The La–N bonding at the BE of ~397.5 eV originating from incomplete metal-ligand bond scission was hardly observed because $O_3$ with the strong oxidation power would break the La–N bond effectively. The larger peak for La–N bonding was reported in the case of the $La_2O_3$ film grown with $H_2O$, a weaker oxidant.[37]

Meanwhile, it is known that the physico-chemical structure and interface property of the ALD film are crucially affected by growth temperature. Figure 3(a) shows O 1*s* core level spectra of $La_2O_3$ films grown at 250, 350, and 400 °C, where the peak is composed of three sub-peaks corresponding to $La_2O_3$, La–silicate, and (interfacial) $SiO_2$ at the BE of ~529, ~530.5, and ~532 eV, respectively. As the growth temperature is increased, the peak intensity for La–silicate increased with the consumption (decrease) of $SiO_2$ and $La_2O_3$. This means that a higher growth temperature enhanced the mixing of $La_2O_3$ and out-diffused Si from the substrate during ALD.[2,16] Eventually, the peak corresponding to the $La_2O_3$ phase almost disappeared at the growth temperature of 400 °C. This is higher than the temperature where the $La_2O_3$ and $SiO_2$ phases are mostly mixed in the $La_2O_3$ film grown with $H_2O$ (350 °C)[37] because the higher physical densities of the $La_2O_3$ film and interfacial $SiO_2$ grown with $O_3$ suppressed the La–silicate formation.[12] Carbon impurity related phases, such as La–$CO_3$, have a negligible effect on the O 1*s* spectra, since the measured C concentration in the films is less than ~4%. The silicate formation was also clearly observed in La $3d_{5/2}$ core level spectra of Fig. 3(b), where the peak shifted towards higher BE with increasing growth temperature. Meanwhile,

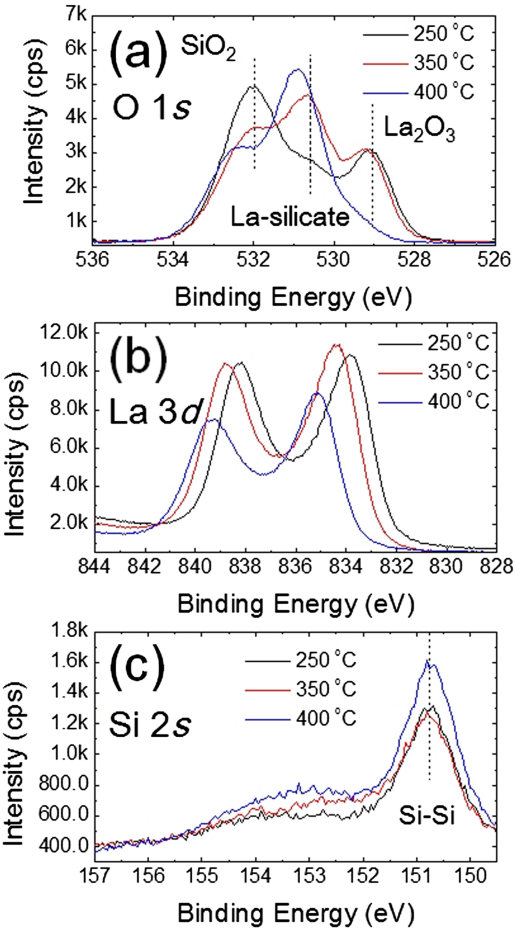


FIG. 3. (a) O 1*s*, (b) La 3*d*, and (c) Si 2*s* core level spectra of $La_2O_3$ films grown at 250, 350, and 400 °C.

the peak intensity decreased at 400 °C because the growth rate of the film was suppressed possibly by the reduction of surface chemical functional groups for the sequential film growth due to higher growth temperature. The increased La–silicate phase with growth temperature was confirmed in Si 2*s* spectra in Fig. 3(c), which is consistent with the results from the O 1*s* and La 3*d* spectra.

The amount of residual impurity in the film was significantly reduced with increasing growth temperature. Figure 4(a) shows the C 1*s* core level spectra of the $La_2O_3$ films grown at 250, 350, and 400 °C. The peak at the BE

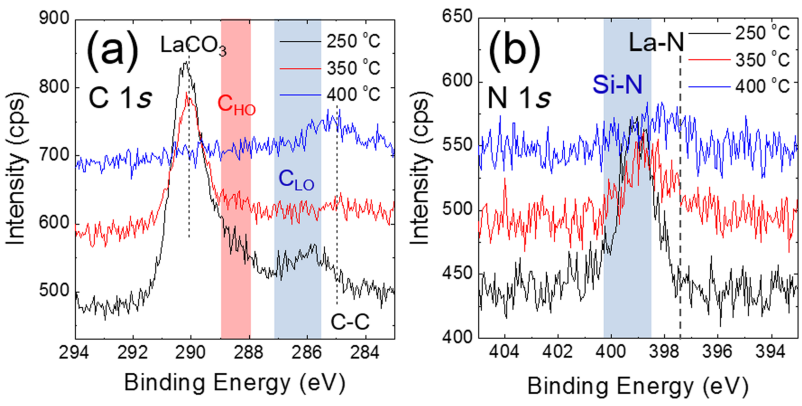


FIG. 4. (a) C 1*s* and (b) N 1*s* core level spectra of $La_2O_3$ films grown at 250, 350, and 400 °C.

of ~290, ~288.5, and ~286 eV corresponds to La–$CO_3$, $C_{HO}$,[18–26] and $C_{LO}$.[18–22,27,28] $C_{LO}$ was almost eliminated at the growth temperature of 350 °C, where the $LaCO_3$ and $C_{HO}$ were significantly reduced. Eventually, at a growth temperature of 400 °C, most of the C impurities ($LaCO_3$, $C_{HO}$, and $C_{LO}$) were eliminated. This is because a higher growth temperature might provide enough thermal energy to decompose or oxidize the C impurities to volatile phase which would be easily gassed-out. The N impurity also decreased with increasing growth temperature as observed in N 1*s* core level spectra of the $La_2O_3$ films of Fig. 4(b), where the intensity of the peak at the BE of ~398.5 to ~400 eV corresponding to Si–N bonding also decreased significantly with increasing growth temperature for the same reason as the C impurity.

The interfacial reactions and impurity behaviors in ALD $La_2O_3$ films grown with various $O_3$ pulse times and growth temperatures were observed using *in situ* XPS. With increasing $O_3$ pulse time, an interfacial La–silicate formation by mixing of diffused Si and $La_2O_3$ was suppressed by the growth of the solid $SiO_2$ interfacial barrier layer. Carboxyl compound impurity residue in the film was further oxidized with long $O_3$ pulse, which resulted in the $LaCO_3$ phase in the film. N impurity decreased with increasing $O_3$ pulse time because it was eliminated in its volatile $NO_x$ form. A higher growth temperature of ALD $La_2O_3$ film enhanced the mixing of diffused Si and $La_2O_3$ resulting in an increased La–silicate phase at the interface with the Si substrate. At 400 °C, the $La_2O_3$ phase was mostly consumed to form La–silicate. C and N impurities also decreased with increasing growth temperatures due to enough thermal energy for decomposition, which were mainly eliminated at 400 °C.

We thank Dr. M. Rousseau, Dr. D. Shenai, Dr. X. Liu, Dr. H. Yi, and Dr. J. Suydam at Dow Chemistry for La-formidinate precursor and Dr. P. Sivasubramani for his XPS work. This work was partly supported by the Future Semiconductor Device Technology Development Program (Grant No. 10045216) funded through KEIT (Korea Evaluation Institute Of Industrial Technology) by MOTIE (Ministry of Trade, Industry & Energy) and COSAR (Consortium of Semiconductor Advanced Research), and the IT R&D program of MOTIE/KEIT (Grant No. 10048933), and Basic Science Research Program through the NRF (National Research Foundation) of Korea funded by the MSIP (Ministry of Science, ICT & Future Planning) (No. 2015R1A5A1037548).

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