Impacts of the Oxygen Precursor on the Interfacial Properties of La\(_x\)Al\(_y\)O Films Grown by Atomic Layer Deposition on Ge

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Abstract: Amorphous La\(_x\)Al\(_y\)O films were grown on n-type Ge substrate by atomic layer deposition using O\(_3\) and H\(_2\)O as oxidant, respectively. A comparison of the XPS results indicated that a thicker interfacial layer with the component of LaGeO\(_x\) and GeO\(_x\) was formed at O\(_3\)-based La\(_x\)Al\(_y\)O/Ge interface, causing lower band gap value as well as the conduction band offset (CBO) value relative to Ge substrate for O\(_3\)-based La\(_x\)Al\(_y\)O film, with a concomitant degeneration in the interfacial properties. In contrast, for the H\(_2\)O-based film, the leakage current of more than one order of magnitude less than that of O\(_3\)-based La\(_x\)Al\(_y\)O film was obtained. All the results indicated that H\(_2\)O is a more appropriate oxidant for improving the interfacial properties in the atomic-layer-deposited La\(_x\)Al\(_y\)O dielectric on Ge.

Keywords: atomic layer deposition; interfacial properties; La\(_x\)Al\(_y\)O; band alignments

1. Introduction

With Si-based complementary-metal-oxide-semiconductor (CMOS) devices approaching their fundamental limits, high dielectric constant (high-k) materials grown on germanium and other high mobility semiconductors have been investigated to increase the drain current in the channel region [1,2]. Unfortunately, one primary challenge for Ge used in MOSFET devices is generally the poor electrical performance of native Ge oxide, resulting in poor interfacial properties at the insulator/Ge interface for most high-k dielectrics deposited on Ge substrate without any surface passivation process [3,4]. In order to improve the interface quality, appropriate passivation should be carried out. Attention had been focused on the formation of thermally grown GeO\(_2\) prior to the high-k dielectrics deposition process [5,6]. However, GeO\(_2\) becomes unstable at high temperature when deposited on Ge because it would react with Ge atoms to form substoichiometric oxide or volatile GeO [7,8], deteriorating the electrical performance of Ge-based MOS devices. Recently, rare earth oxides have been considered as a promising passivation interlayer for high-k dielectric grown on Ge [9]. Furthermore, La-based dielectric materials have been shown to form a good passivation layer due to the formation of a stable La germanate compound on Ge substrate which could prevent the formation of volatile GeO [10,11]. Among various deposition methods for growing high-k dielectric films, atomic layer deposition (ALD) has been considered as one of the most promising technique to produce high-k dielectric films in high quality due to the outstanding characteristics for precise thickness and composition control, excellent uniformity and process compatibility to conventional CMOS process [12,13]. O\(_3\) and H\(_2\)O are two kinds of oxygen source precursors commonly used in the ALD process. It has been reported that the difference of oxidants would have an impact on the ALD reaction mechanism and surface chemistry of the deposited film [14], with a further influence on the relative electrical properties.
In this paper, the effect of H$_2$O and O$_3$ on the interfacial properties of La$_x$Al$_y$O films grown by atomic layer deposition on Ge was systematically investigated. X-ray photoelectron spectroscopy (XPS) analysis of the LaAlO$_3$ films was used to provide direct observation on the band alignments of La$_x$Al$_y$O films relative to Ge substrate. Attention was focused on the electrical performance of La$_x$Al$_y$O/Ge structures to analyze the influence of different oxygen precursors on the interfacial properties.

2. Experiment

La$_x$Al$_y$O gate dielectric films were deposited on n-type Ge (100) wafers with resistivity of 0.1–1 Ω·cm by ALD technique using La($^\infty$ PrCp)$_3$ and TMA as La and Al precursor, while two kinds of oxygen source precursors (O$_3$ and H$_2$O) were used as oxidant, respectively. Prior to the deposition, Ge substrates were treated with acetone and hydrous alcohol, and then dipped into 2%-HF solution for 30 s to remove the native GeO$_x$ layer, followed by a 60 s rinse in de-ionized water. The precursors were alternately introduced to the reactor chamber using high purity N$_2$ (>99.999%) as the carrier gas. A typical ALD growth cycle for La$_2$O$_3$ with O$_3$ used as the oxygen precursor was 0.1 s La($^\infty$ PrCp)$_3$ pulse/4 s N$_2$ purge/0.3 s O$_3$ pulse/10 s N$_2$ purge, whereas for Al$_2$O$_3$ with O$_3$ used as the oxygen precursor, it was 0.1 s TMA pulse/3 s N$_2$ purge/0.5 s O$_3$ pulse/4 s N$_2$ purge. Moreover, when H$_2$O was used as the oxygen precursor, a typical ALD growth cycle for La$_2$O$_3$ was set as 0.3 s La($^\infty$ PrCp)$_3$ pulse/4 s N$_2$ purge/0.3 s H$_2$O pulse/9 s N$_2$ purge, while for Al$_2$O$_3$, it was 0.1 s TMA pulse/3 s N$_2$ purge/0.1 s H$_2$O pulse/4 s N$_2$ purge. Using these parameter values, for La$_2$O$_3$, a linear relation with a growth rate of approximately 0.85 Å/cycle was obtained, and the steady-state growth rate of Al$_2$O$_3$ films was approximately 0.93 Å/cycle with O$_3$ as the oxygen precursor. Besides, when H$_2$O was used as the oxidant, the growth thickness per ALD cycle for La$_2$O$_3$ was ~0.75 Å, while the growth rate of Al$_2$O$_3$ was approximately 0.92 Å/cycle. At the deposition temperature of 300 °C, the film thickness was tuned to fix at ~10 nm and ~5 nm by varying the number of ALD cycles while setting the La/Al pulse ratio as 1:1.

Post-deposition rapid thermal annealing was carried out at 600 °C for 90 s in N$_2$ ambient. The crystallization characteristics of the La$_x$Al$_y$O films were checked by grazing incidence X-ray Diffraction (GIXRD) at the angle of incidence $\omega =$ 0.5°. None of the films reveal any diffraction peaks, indicating in the thermal stability of the films. The physical thickness of the deposited films was optically measured using Woollam M2000U (Woollam Co., Inc., Lincoln, NE, USA) spectroscopic ellipsometry (SE) by fitting the ellipsometry data using a Gen-Osc mode consisting of Gaussian and Tauc-Lorentz oscillators and considering the native GeO$_x$. The composition and band structure of the deposited La$_x$Al$_y$O films was examined by XPS measurements. All the wafers were etched by Ar$^+$ ion beam bombardment for 10 s (~0.26 nm/s) to remove the influence of the impurities on the surface. C 1s peak from adventitious carbon at 284.6 eV was used as an internal energy reference during the XPS analysis. In this experiment, the ~10 nm La$_x$Al$_y$O film was used to obtain the XPS spectra for thick amorphous La$_x$Al$_y$O, and the ~5 nm La$_x$Al$_y$O/Ge structure was thin enough to obtain XPS spectra from both the La$_x$Al$_y$O film and the underlying germanium substrate. The electrical properties of the 5 nm films were measured using a metal-insulator-semiconductor (MIS) capacitor structure. A metal gate with a diameter of 300 µm was fabricated by depositing 150 nm Al using the electron-beam evaporation through a shadow mask, followed by annealing in forming gas ambient (97% N$_2$/3% H$_2$) at 400 °C for 20 min. The capacitance-voltage (C-V) and leakage current density-voltage (J-V) measurements were carried out using Agilent B1500A analyzer.

3. Results and Discussion

As shown in Figure 1, the variations in O 1s XPS spectra for the 5 nm O$_3$-based and H$_2$O-based La$_x$Al$_y$O films annealed at 600 °C were analyzed to investigate the chemical bonding states near the La$_x$Al$_y$O film and Ge substrate interfaces. The O 1s spectra were fitted with five Gaussian–Lorentzian line-shaped peaks, which are at 529.0, 529.7, 530.4, 531.3 and 531.9 eV. These peaks correspond to the chemical bonds of La-O-La, La-O-Ge, La-O-Al, Al-O-Al and Ge-O-Ge, respectively [15-17].
For La-O-La, La-O-Al and Al-O-Al chemical bonds; the intensity of the peaks varies slightly, indicating the difference of oxidant has negligible influence on the chemical bond structures of the upper deposited La xAlyO layers. However, compared with the La xAlyO film using H2O as oxidant, an obvious increment in the intensity of La-O-Ge and Ge-O-Ge peaks could be observed for the O3-based La xAlyO film, which illustrates that more interfacial oxide layer (mainly consisting of LaGeOx and GeOx) was formed at the O3-based La xAlyO/Ge interface during the deposition and post-deposition annealing process [18], which may be caused by the higher oxidability of O3 [19].

![Figure 1](image1.png)

**Figure 1.** Shallow core-level spectra of O 1s for the 5 nm (a) O3-based and (b) H2O-based La xAlyO films.

In order to study the chemical bonding states near the La xAlyO film and Ge substrate interfaces more clearly, further investigation was applied to the variations in Ge 3d XPS spectra for the 5 nm O3-based and H2O-based La xAlyO films, as shown in Figure 2. The Ge oxide (GeOx) spectra, which are located at a higher binding energy with respect to the Ge0 peak originating from the Ge substrate, can be deconvoluted into four GeOx peaks (Ge1+, Ge2+, Ge3+, Ge4+) with energy shift of 0.8, 1.8, 2.6, and 3.4 eV, respectively. These GeOx species were likely present due to the formation of an interfacial layer between the La xAlyO film and Ge substrate. Here, the Ge4+ peak originates from GeO2, and other Ge3+, Ge2+ and Ge1+ peaks originate from Ge sub-oxides [20]. A comparison of Figure 2a,b revealed the same variation trend of the formation of interfacial oxide layer as analysed in the O 1s XPS spectra; that is, larger amounts of LaGeOx and GeOx, including GeO2 and Ge sub-oxides, were formed at La xAlyO/Ge interface in the O3-based case. The variation of these interfacial oxides would have an influence on the interfacial characteristics of La xAlyO film/Ge structure and then affect its electrical properties, and this aspect will be discussed in detail later in this paper.

![Figure 2](image2.png)

**Figure 2.** Shallow core-level spectra of Ge 3d for the 5 nm (a) O3-based and (b) H2O-based La xAlyO films.
The band offsets of LaₓAlᵧO films relative to the Ge substrate were determined by a core level photoemission-based method similar to that of Kraut et al. [21,22], as illustrated in Figure 3a. Accordingly, the valence band offset (VBO, ΔEᵥ) is given by Equation (1):

$$ΔEᵥ = (E_{3d}^{Ge} - E_{V}^{Ge}) - (E_{2p}^{Al} - E_{V}^{Thick LaₓAlᵧO}) - (E_{3d}^{LaₓAlᵧO/Ge} - E_{2p}^{Al})$$  

(1)

where $E_{3d}^{Ge} - E_{V}^{Ge}$ is the energy difference between Ge 3d and valence band maximum (VBM) in the bulk clean Ge substrate, as shown in Figure 3b; $(E_{2p}^{Al} - E_{V}^{Thick LaₓAlᵧO})$ is the energy difference between Al 2p and VBM in the 10 nm LaₓAlᵧO film, as shown in Figure 3c; and $(E_{3d}^{Ge} - E_{2p}^{Al}) - E_{V}^{Al}$ is the energy difference between Ge 3d and Al 2p core levels in the 5 nm LaₓAlᵧO on n-Ge(100), as shown in Figure 3d. Then, according to Equation (1), the VBOs for the films with O$_3$ and H$_2$O as oxidant can be figured out as 3.34 and 3.11 eV, respectively.

![Figure 3](image_url)

Figure 3. (a) schematic of band energy alignment diagram for a LaₓAlᵧO/Ge structure; XPS core level spectra of (b) Ge 3d and valence band for bulk clean n-Ge(100); (c) Al 2p and valence band for 10 nm LaₓAlᵧO films; and (d) Al 2p and Ge 3d for 5 nm LaₓAlᵧO films on n-Ge(100).

The corresponding conduction band offset (CBO, ΔEₖ) between LaₓAlᵧO and Ge can be obtained by Equation (2):

$$ΔEₖ = E_{G(LaₓAlᵧO)} - ΔEᵥ - E_{G(Ge)}$$  

(2)

It is generally known that the band gap of germanium is 0.67 eV at room temperature. In order to obtain the CBOs of LaₓAlᵧO films relative to germanium, the band gap of amorphous LaₓAlᵧO on Ge substrate needs to be determined.

The band gaps of LaₓAlᵧO films were measured by examining the energy loss of the O 1s core levels for the 10 nm samples by XPS measurements. After being etched for ~2 nm, the XPS spectra signals can be considered as coming from the pure deposited films. In principle, the photoexcited electrons passing through dielectric films can suffer inelastic losses due to plasmon (collective
oscillation) and single particle excitation (band-to-band transition excitation) [23]. It is proved that
the band gap equals the energy distance between the photoemission peak centroid and the onset
of the features due to single particle excitations, and it is usually obtained from the inelastic energy
loss features observed on the high binding energy side of the core level photoemission peaks [24].
Besides, the onset of the O 1s loss spectrum can be determined by linearly extrapolating the segment
of maximum negative slope to the background level [25,26]. Using this method, as shown in Figure 4,
the band gaps of the O3-based and H2O-based La$_x$Al$_y$O films were determined to be 5.98 and 6.06 eV,
respectively. Accordingly, the CBOs of O3-based and H2O-based La$_x$Al$_y$O films relative to Ge were
figured out as 1.97 and 2.28 eV, respectively.

![Figure 4. O 1s energy-loss spectra for the 10 nm (a) O3-based and (b) H2O-based La$_x$Al$_y$O films.](image)

Results of the calculated band gaps and band offsets are shown in the schematic diagram in
Figure 5. It is worth noting that the band gap values of the deposited La$_x$Al$_y$O films are smaller than
those of pure amorphous La$_x$Al$_y$O film of ~6.2 eV [27], which implies that the composition of the
deposited film is not pure La$_x$Al$_y$O. As is known; to some extent, the influence of the XPS signals
from the possible interfacial oxide layer (GeO$_2$, $E_g$ ~5.8 eV) would diminish the band gap values of
the deposited La$_x$Al$_y$O films [28]. Thus, the variation of the band gaps would reflect the degree of the
formation of interfacial oxide layer between the deposited La$_x$Al$_y$O film and Ge substrate. That is, a
thicker interfacial oxide layer should exist at the O3-based La$_x$Al$_y$O/Ge interface, as the band gap of
O3-based La$_x$Al$_y$O film is slightly smaller than that of the H2O-based sample. This result is in good
agreement with the interfacial chemical bonds information extracted from the O 1s and Ge 3d spectra
as mentioned above. In addition, the CBO of GeO$_2$ relative to Ge (~0.54 eV) is much smaller than that
of La$_x$Al$_y$O on Ge (~2.2 eV) [28,29]. Consequently, due to the existence of a thinner interfacial layer, a
bigger value of CBO is obtained when H2O was used as oxidant.
Figure 5. Results of the calculated band offsets for the La$_x$Al$_y$O/Ge structures with O$_3$ and H$_2$O as oxidant.

Figure 6 shows the C-V characteristics of the fabricated MIS capacitors using 5 nm O$_3$-based and H$_2$O-based La$_x$Al$_y$O films as insulators. For simplicity, the MIS capacitor structures using O$_3$-based and H$_2$O-based La$_x$Al$_y$O films as insulators were assigned as MIS capacitor S1 and MIS capacitor S2, respectively. The C-V curves were obtained by sweeping forward (bias from negative to positive) and backward (bias from positive to negative) at a frequency of 100 kHz. The flat band voltages ($V_{FB}$) of the C-V curves were extracted from the simulation software Hauser NCSU CVC program, taking into account quantum mechanical effects [30]. Compared with MIS capacitor S2, a positive $V_{FB}$ shift could be observed in the C-V curves for MIS capacitor S1, which is an indication of the presence of more effective negative oxide charges in the bulk of the O$_3$-based gate dielectric. Ruling out the influence of generally positive charged fixed oxide charges ($Q_f$) and mobile ionic charges ($Q_m$), the oxide trapped charges ($Q_{ot}$), negative charged were suspected to be responsible for the positive shift of $V_{FB}$ [31]. The charge trapping behavior of the fabricated capacitors was investigated through the C-V hysteresis characteristics. The hysteresis width ($\Delta V_{FB}$) extracted from the dual-swept C-V curves for MIS capacitors S1 and S2 are 154 and 95 mV, respectively. For the O$_3$-based sample, a larger $\Delta V_{FB}$ of the dual-swept C-V curves illustrates the existence of more oxide trapped charges in the O$_3$-based gate dielectric, which is in consistent with the shift tendency of $V_{FB}$. Additionally, it is worth noting that, compared with what is shown in Figure 6b, the C-V curves for MIS capacitor S1 (Figure 6a) slope gently and exhibit a more obvious anomalous hump phenomenon in the weak inversion region, indicating the formation of more interface traps at the O$_3$-based La$_x$Al$_y$O film/Ge interface.

![C-V characteristics of MIS capacitors using 5 nm (a) O$_3$-based and (b) H$_2$O-based La$_x$Al$_y$O films as insulators.](image-url)
From the XPS results as mentioned above, we can conclude that a thicker interfacial layer consisting of LaGeO$_x$ and GeO$_x$ exists between O$_3$-based La$_x$Al$_y$O film and Ge substrate. Such an interfacial layer, as reported, has a much lower dielectric constant (5~6) than that of La$_x$Al$_y$O [32,33], resulting in a smaller accumulation capacitance value for MIS capacitor S1. Being a thermally stable germanate compound on the surface of Ge substrate, LaGeO$_x$ was reported to be of help in suppressing Ge out-diffusion and improving interface quality. However, among the germanium oxides, GeO is volatile and sublimes leaving behind a defective interface contained lots of defects and dangling bonds, which makes it known to have an adverse influence on the interfacial properties [11]. Additionally, it has been reported that at temperatures of up to 430 °C, GeO$_2$ becomes unstable, and will react with substrate Ge atoms generating volatile GeO, following the reaction of GeO$_2$ + Ge → 2GeO [7]. Therefore, compared with the H$_2$O-based La$_x$Al$_y$O, the increase in oxide-trapped charges and interface traps in O$_3$-based La$_x$Al$_y$O film/Ge structures should be attributed to the extra formation of volatile GeO.

Figure 7 shows the leakage current density as a function of the applied electrical field for the fabricated Al/5 nm La$_x$Al$_y$O/n-type Ge capacitor structure. As we know, the polarity of gate leakage current through gate dielectrics depends on the gate bias polarity and substrate doping type. For the n-type Ge substrate used in this work, electron injection from the conduction band is the dominant tunneling current component under positive gate bias [34]. At the applied electrical field of 3 MV/cm, the leakage current density of the O$_3$-based and H$_2$O-based film was measured to be $2.29 \times 10^{-5}$ and $1.68 \times 10^{-4}$ A/cm$^2$, separately. Compared with the O$_3$-based La$_x$Al$_y$O film, a decrease of more than one order of magnitude in the leakage current density was found for the H$_2$O-based film. Such a decrease is suspected of benefitting from the larger conduction band offset mentioned above. The larger conduction band offset means the existence of higher potential barriers between the La$_x$Al$_y$O film and n-Ge substrate, which would weaken the tunneling effect of electrons in the MIS capacitors, resulting in lower gate leakage current. In addition, less structural defects and dangling bonds in the H$_2$O-based La$_x$Al$_y$O film/Ge structure mean a smaller possibility to create a conduction path by forming a continuous chain connecting the gate to the semiconductor, which may also provide an explanation for the significant decrease of gate leakage current in MIS capacitors S2.

![Figure 7](image)

**Figure 7.** $I$-$V$ characteristics of MIS capacitors using 5 nm O$_3$-based and H$_2$O-based La$_x$Al$_y$O films as insulators.

4. Conclusions

In this paper, amorphous La$_x$Al$_y$O films were deposited on Ge substrate by ALD using O$_3$ and H$_2$O as oxygen precursor, respectively. Due to the higher oxidability of O$_3$, the formation of interfacial layer (mainly consisting of LaGeO$_x$ and GeO$_x$) was enhanced at O$_3$-based La$_x$Al$_y$O/Ge interface, leading to a slight decrease of the band gap for O$_3$-based La$_x$Al$_y$O film, as well as the CBO value.
relative to Ge substrate compared with that of the H$_2$O-based sample. Additionally, the extra formation of volatile GeO causes the increase of oxide trapped charges and interface traps in O$_x$-based La$_x$Al$_y$O$_z$ film/Ge structure. As a result, a much lower gate leakage current was obtained when the H$_2$O-based La$_x$Al$_y$O$_z$ film was used as MIS gate insulator, indicating that H$_2$O is a more appropriate oxidant applied for the deposition of La$_x$Al$_y$O$_z$ dielectric on Ge substrate to achieve suitable band alignments and favorable interfacial properties.

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