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Electrical properties of GaN-based MIS-structures with Al₂O₃ deposited by ALD using both water and ozone as the oxygen precursors

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Al₂O₃ deposited by atomic layer deposition (ALD) was focused as an insulator in metal-insulator-semiconductor (MIS) structures for GaN-based MIS-devices. As the oxygen precursors for the ALD process, water (H₂O), ozone (O₃), and both H₂O and O₃ were used. The chemical characteristics of the ALD-Al₂O₃ surfaces were investigated by an X-ray photoelectron spectroscopy (XPS). After fabrication of MIS-diodes and MIS-high-electron-mobility transistors (MIS-HEMTs) with the ALD-Al₂O₃, their electrical properties were evaluated by current-voltage (I-V) and capacitance-voltage (C-V) measurements. The threshold voltage of the C-V curves for MIS-diodes indicate that the fixed charge in the Al₂O₃ layer is decreased by using both H₂O and O₃ as the oxygen precursors. Furthermore, MIS-HEMTs with the H₂O+O₃-based Al₂O₃ showed the good DC I-V characteristics with the forward bias over 6 V, and the drain leakage current in the off-state region was suppressed by seven orders of magnitude.

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1. Introduction

AlGaN/GaN high-electron-mobility transistors (HEMTs) with the metal-insulator-semiconductor (MIS) structure are expected to be used for the next generation high-power and high-frequency switching device applications. The MIS-structure is effective for the gate leakage reduction and the large gate voltage swing. As an insulator for the MIS-structure, a lot of materials, such as Al₂O₃, HfO₂, SiO₂, AlN, and SiN, have been studied. Among such insulators, Al₂O₃ is a promising material due to its relatively large band gap and high dielectric constant, and MIS-HEMTs with Al₂O₃ have been fabricated by several deposition methods, for example, oxidation of Al layer and atomic layer deposition (ALD).

In this study, ALD was focused as the deposition method of Al₂O₃. The ALD can offer the oxide layer which is pinhole free and uniform in thickness. In the ALD process, water (H₂O) is often used as the oxygen precursor. However, it has been reported that impurities in oxides deposited by ALD on Si can be reduced by using ozone (O₃) instead of H₂O. It is considered that the hydroxyl group (-OH) as an impurity in oxides can be reduced by using O₃ instead of H₂O. In the ALD process using H₂O, the introduction of H₂O after the introduction of trimethylaluminum (TMA) causes some reactions, such as -CH₃ + H₂O → -OH + CH₄, and the surface is covered by the -OH, while the surface is covered by O in the ALD process using O₃ with the reaction, such as -6CH₃ + 2O₃ → -6O + 3C₂H₆. On the other hand, it is considered that the carbon (C) content in oxides is increased by using O₃. The high reactivity of O₃ generates many carbonates by the reaction, such as -CH₃ + O₃ → CO₂ + H₂ + -OH. Therefore, both H and C contents can be reduced by using both H₂O and O₃, namely the introduction of O₃ after the introduction of H₂O. The main effect of the O₃ pulse following the H₂O pulse is considered to cut O-H bonds and remove the -OH.

In this study, Al₂O₃ films on GaN and the GaN-based MIS-diodes and MIS-HEMTs with
Al₂O₃ were fabricated by ALD using H₂O, O₃, and both H₂O and O₃, and their chemical and electrical properties were investigated.

2. Deposition and characterization of ALD-Al₂O₃

First, to investigate the chemical characteristics of the ALD-Al₂O₃ films, 20-nm-thick Al₂O₃ layers were deposited on GaN at 250°C and 300°C by using Cambridge Nanotech ALD system. H₂O, O₃, and both H₂O and O₃ were used as the oxygen precursors, and TMA was used as the aluminum precursor, which were used as the precursors for ALD-Al₂O₃ in this study. Figure 1 shows the schematic diagram of the ALD process using both H₂O and O₃. The ALD processes using H₂O or O₃ were similar to the process shown in Fig. 1. The thicknesses of Al₂O₃ layers were confirmed by an elliprometer and transmission electron microscopy (TEM) images.

The chemical characteristics of the ALD-Al₂O₃ surfaces were investigated by an X-ray photoelectron spectroscopy (XPS; PHI Quantera SXM) equipped with a monochromated Al Kα radiation source (hν = 1486.6 eV). The electron-escape angle in this study was 45°. Figures 2(a) and (b) show Al 2p and O 1s core-level spectra obtained from the ALD-Al₂O₃ surfaces deposited at 300°C. The deposition temperature dependence of the XPS spectra was within the measurement error range. The peak position of the Al 2p level was consistent with that of the aluminum oxide regardless of the oxide precursor, while the full width at half maximum (FWHM) of the Al 2p spectrum obtained from the H₂O-based Al₂O₃ surface was wider than those obtained from the O₃-based and the H₂O+O₃-based Al₂O₃ surfaces. These results indicate that at least Al-Al metallic bonding can be reduced by using O₃ or H₂O+O₃ instead of H₂O. Kim et al. also reported similar effect in ref. 4. The band gap energy (E₅) of ALD-Al₂O₃ was estimated from the O 1s spectra shown in Fig. 2(b). The spectrum of the O 1s level was shifted to lower energy by 1.2 eV in order to check the E₅ easily, and all spectra
did not depend on the oxygen precursor within the measurement error range. The $E_g$ was approximately 6.6 eV in all cases of H$_2$O, O$_3$, and H$_2$O+O$_3$-based Al$_2$O$_3$, which is the usual value for the Al$_2$O$_3$ film deposited using the H$_2$O-based ALD.$^{11}$

The amount of impurities in the ALD-Al$_2$O$_3$ was investigated by secondary ion mass spectroscopy (SIMS). Table I shows the concentrations of H and C contents at a depth of 10 nm from the surface of ALD-Al$_2$O$_3$ deposited at 300°C. As expected, the H content was decreased, and the C content was increased by using O$_3$ instead of H$_2$O. On the other hand, by using both H$_2$O and O$_3$, both the H and C contents were decreased compared to those in the H$_2$O-based Al$_2$O$_3$, while the H content was higher than that in the O$_3$-based Al$_2$O$_3$. The amount of the H content showed the expected behavior. The possible reason why the C content in the H$_2$O+O$_3$-based Al$_2$O$_3$ was less than that in the H$_2$O-based Al$_2$O$_3$ is that the residual carbon compounds after introducing H$_2$O were released by the reaction with O$_3$. The decrease of both the H and C contents in the H$_2$O+O$_3$-based Al$_2$O$_3$ was considered to be preferable for the GaN-based MIS-devices.

### 3. Fabrication and measurement of MIS-diodes

In order to investigate the $I$-$V$ and $C$-$V$ characteristics of the MIS-diodes with ALD-Al$_2$O$_3$, the Al$_2$O$_3$/n-GaN MIS-diodes were fabricated. The epitaxial Si-doped GaN films were grown on sapphire substrates using a Taiyo Nippon Sanso SR-4000 metal organic chemical vapor deposition (MOCVD) system. The donor concentration was $1.5 \times 10^{16}$ cm$^{-3}$, which was estimated from the $C$-$V$ measurement on Schottky contacts. $20$-nm-thick Al$_2$O$_3$ layers were deposited by ALD at 250°C and 300°C with pretreatment in HCl solution. Using conventional lithography, ring-shaped ohmic contacts (Ti/Al/Ni/Au: 15/80/12/40) were fabricated onto the n-GaN surface as cathodes and annealed at 775°C for 30 s in N$_2$ atmosphere. Finally, circular-shaped metals (Pd/Ni/Au: 40/20/60 nm) were deposited as anodes inside the
ring-shaped cathodes. The anode diameter was 200 μm. The schematic cross section view of the Al₂O₃/n-GaN MIS-diode is shown in Fig. 3. For comparison, Schottky-type diodes were also fabricated in the same way as the MIS-diodes. After fabricating the diodes, I-V and C-V measurements were carried out at room temperature in the dark using an Agilent B1505A power device analyzer. The frequency of C-V measurements was 100 kHz.

Figures 4(a), (b) and (c) show the typical results of I-V measurements. The result of the Schottky-diode is also shown in Fig. 4(c). As shown in Figs. 4, the leakage current of the MIS-diodes was suppressed compared to that of the Schottky-diode, and the current through the H₂O-based Al₂O₃ was decreased with increasing the deposition temperature (T_d) from 250°C to 300°C, while the current thorough the O₃-based Al₂O₃ was increased with increasing the T_d. These results seem to suggest that impurities related to the leakage current such as -OH in the H₂O-based Al₂O₃ were decreased with increasing the T_d by the higher reaction rate between -OH and -CH₃, while such impurities in the O₃-based Al₂O₃ were increased with increasing the T_d by the increasing reaction rate between -CH₃ and O₃. The current through H₂O+O₃-based Al₂O₃ seems to show the intermediate behavior between those of the H₂O-based and the O₃-based Al₂O₃. The leakage current through Al₂O₃ deposited by ALD using O₃ was more stable for the T_d distribution than that through the H₂O-based Al₂O₃.

The typical results of C-V measurements for Al₂O₃/n-GaN MIS-diodes are shown in Fig. 5(a), (b) and (c). The dielectric constant (ε) of the H₂O-based Al₂O₃ was approximately 9.5, and that of the O₃-based and the H₂O+O₃-based Al₂O₃ was approximately 8.5, which was calculated from the expression: \( C = \varepsilon S / d \), where S is the area of the anode and d is the thickness of the Al₂O₃. These values of ε were usual values for Al₂O₃. As shown in Fig. 5(a), the threshold voltage (V_th) was defined as the point where the extrapolated line of the C-V curve crosses the horizontal axis. It was found that V_th shifted in the positive direction in all cases of oxygen precursors with increasing the T_d from 250°C to 300°C. This result suggests
that the fixed charge in the ALD-Al2O3 is decreased with increasing the \( T_d \). Table II shows the \( V_{th} \) of the \( C-V \) curve obtained from the MIS-diodes with Al2O3 deposited at 300°C. The \( V_{th} \) with Al2O3 deposited using both H2O and O3 was the closest to the ideal one whose \( C-V \) curve is shown in Fig. 5(c), which implies that the fixed charge in ALD-Al2O3 was most reduced by using both H2O and O3. Furthermore, the \( V_{th} \) of the MIS-diode with the H2O+O3-based Al2O3 was the most stable for the \( T_d \) distribution compared to those through the H2O-based and the O3-based Al2O3.

5. Fabrication and measurement of MIS-HEMTs

The AlGaN/GaN heterostructures were grown on 4-in. p-type Si (111) substrates by the MOCVD system. The grown structure consists of 25 nm Al0.26GaN layer, 1 \( \mu \)m GaN layer, and 2.5 \( \mu \)m buffer layer on 4-in. p-type Si (111) substrate.

The device process started with a mesa isolation by BCl3 plasma based reactive ion etching. Using conventional lithography, source/drain ohmic contacts (Ti/Al/Ni/Au: 15/80/12/40 nm) were made onto the devices and annealed at 850°C for 30 s while flowing nitrogen gas. 20-nm-thick Al2O3 layers were deposited by ALD at 300°C with pretreatment in HCl solution. After the gate lithography, Pd/Ni/Au (40/20/60 nm) was deposited as the gate contact. The schematic cross section view of the MIS-HEMT is shown in Fig. 6. The dimensions of the fabricated HEMTs were as follows: source-gate spacing (\( L_{sg} \)) = 4 \( \mu \)m, gate width (\( W_g \)) = 200 \( \mu \)m, gate length (\( L_{g} \)) = 2 \( \mu \)m, and gate-drain spacing (\( L_{gd} \)) = 4 \( \mu \)m. For comparison, the Schottky gate HEMTs were also fabricated in the same way as the MIS-HEMTs. In order to investigate the electrical properties, the drain current-voltage (\( I_d-V_d \)) characteristics were measured using an Agilent B1505A power device analyzer.

Figure 7(a) shows the DC \( I_d-V_d \) characteristics of the MIS-HEMT with the H2O+O3-based Al2O3. As shown in Fig. 7(a), the good pinch-off characteristics was obtained. The maximum
$I_d$ was 420 mA/mm at a gate voltage of 7 V, and the maximum $g_m$ was 80 mS/mm. Furthermore, the $V_{th}$ shift of the MIS-HEMT to the positive direction was observed. One of the reasons of the $V_{th}$ shift might be the electron trap at the gate region. As for the MIS-HEMTs with the H$_2$O-based and the O$_3$-based Al$_2$O$_3$, the typical example of the DC $I_d$-$V_d$ characteristics is shown in Fig. 7(b). As shown in Fig. 7(b), they did not show the pinch-off characteristics. This result seems to be caused by the high interface state and the trap state density due to impurities, such as -OH and carbonates introduced during the ALD process. Figure 8 shows the dependence of the $I_d$ and the gate leakage current ($I_g$) on the gate bias voltage ($V_g$). The off-state region indicates that the $I_g$ was suppressed by the MIS-structure from $10^{-2}$ mA/mm to $10^{-9}$ mA/mm, which was the measurement limit. Moreover, the forward bias over 6 V could be applied to the MIS-HEMT. In order to reduce the -OH in Al$_2$O$_3$ deposited by ALD and improve the $I$-$V$ characteristics of MIS-HEMTs, the post deposition annealing (PDA) above 700°C is effective. However, it was reported that such high temperature annealing generates microcrystallization regions in the ALD-Al$_2$O$_3$, whose grain boundaries can serve as high-leakage paths. On the other hand, by using both H$_2$O and O$_3$, the MIS-HEMT shows the good $I$-$V$ characteristics without the PDA. Therefore, the $I_g$ through the H$_2$O+O$_3$-based Al$_2$O$_3$ can be lower than the $I_g$ through the H$_2$O-based and the O$_3$-based Al$_2$O$_3$. These results obtained from the MIS-HEMTs indicate that the Al$_2$O$_3$ deposited by ALD using both H$_2$O and O$_3$ as the oxygen precursors is useful for fabricating GaN-based MIS-devices.

**6. Conclusions**

Al$_2$O$_3$ was deposited by ALD on GaN using H$_2$O, O$_3$, and both H$_2$O and O$_3$ as the oxygen precursors. XPS results indicate that Al-Al metallic bonding in the ALD-Al$_2$O$_3$ can be reduced by using O$_3$ or both H$_2$O and O$_3$ instead of H$_2$O. The leakage currents through the
O$_3$-based and the H$_2$O+O$_3$-based Al$_2$O$_3$ were more stable for the deposition temperature distribution than that through the H$_2$O-based Al$_2$O$_3$. The $C$-$V$ characteristics of MIS-diodes suggested that the fixed charge in the ALD-Al$_2$O$_3$ was most reduced by using both H$_2$O and O$_3$. From $I$-$V$ measurements on MIS-HEMTs, it was found that the MIS-HEMT with H$_2$O+O$_3$-based Al$_2$O$_3$ showed the good pinch-off characteristics with the forward bias over 6 V, and the drain leakage current was suppressed by seven orders of magnitude by the MIS-structure. These results indicate that the Al$_2$O$_3$ deposited by using both H$_2$O and O$_3$ is useful for the GaN-based MIS-devices.

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Figure captions

FIG. 1. Schematic diagram of the ALD process using H$_2$O and O$_3$.

FIG. 2. XPS (a) Al 2p and (b) O 1s spectra obtained from the ALD-Al$_2$O$_3$ surfaces.


FIG. 4. $I$-$V$ characteristics of the Schottky and MIS diodes: (a)TMA+H$_2$O (b)TMA+O$_3$ (c)TMA+H$_2$O+O$_3$.

FIG. 5. $C$-$V$ curves obtained from MIS-diodes: (a)TMA+H$_2$O (b)TMA+O$_3$ (c)TMA+H$_2$O+O$_3$.

FIG. 6. Schematic cross section view of the Al$_2$O$_3$/AlGaN/GaN MIS-HEMT.

FIG. 7. DC drain current-voltage ($I_d$-$V_d$) characteristics of the MIS-HEMTs: (a) H$_2$O+O$_3$-based Al$_2$O$_3$ (b) a typical example of the H$_2$O-based and the O$_3$-based Al$_2$O$_3$ with no pinch-off characteristics.

FIG. 8. Dependence of the drain current ($I_d$) and the gate leakage current ($I_g$) on the gate bias voltage ($V_g$).
TABLE I. Concentrations of H and C contents in the ALD-Al₂O₃ measured by SIMS.

<table>
<thead>
<tr>
<th>Oxygen precursor</th>
<th>H [×10⁻²¹ cm⁻³]</th>
<th>C [×10¹⁹ cm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>2.8</td>
<td>5.5</td>
</tr>
<tr>
<td>O₃</td>
<td>0.7</td>
<td>9.6</td>
</tr>
<tr>
<td>H₂O+O₃</td>
<td>1.2</td>
<td>3.6</td>
</tr>
</tbody>
</table>

TABLE II. Threshold voltage of the C-V curve obtained from the MIS-diodes with Al₂O₃ deposited at 300°C using H₂O, O₃, and both H₂O and O₃ as the oxygen precursors.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>H₂O</th>
<th>O₃</th>
<th>H₂O+O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vₘᵥ (V)</td>
<td>-1.15</td>
<td>-0.91</td>
<td>-0.63</td>
</tr>
</tbody>
</table>
FIG. 1. Schematic diagram of the ALD process using both H\textsubscript{2}O and O\textsubscript{3}.

FIG. 2. XPS (a) Al 2p and (b) O 1s spectra obtained from the ALD-Al\textsubscript{2}O\textsubscript{3} surfaces.
FIG. 3. Schematic cross section view of the Al₂O₃/n-GaN MIS-diode.

anode
Pd/Ti/Au
(40/20/60 nm)

200 μm

Al₂O₃: 20 nm

n-GaN : 2.3 μm

c-Sapphire Sub.

cathode
Ti/Al/Ni/Au
(15/80/12/40 nm)

FIG. 4. I-V characteristics of the Schottky and MIS diodes: (a)TMA+H₂O  (b)TMA+O₃  (c)TMA+H₂O+O₃.
FIG. 5. C-V curves obtained from MIS-diodes: (a) TMA+H$_2$O  (b) TMA+O$_3$  (c) TMA+H$_2$O+O$_3$.

FIG. 6. Schematic cross section view of the Al$_2$O$_3$/AlGaN/GaN MIS-HEMT.
FIG. 7. DC drain current-voltage ($I_d$-$V_d$) characteristics of the MIS-HEMTs: (a) H$_2$O+O$_3$-based Al$_2$O$_3$ (b) a typical example of the H$_2$O-based and the O$_3$-based Al$_2$O$_3$ with no pinch-off characteristics.

FIG. 8. Dependence of the drain current ($I_d$) and the gate leakage current ($I_g$) on the gate bias voltage ($V_g$).