Interfacial self-cleaning in atomic layer deposition of HfO$_2$ gate dielectric on In$_{0.15}$Ga$_{0.85}$As

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An interfacial self-cleaning phenomenon was found in the atomic layer deposition of HfO$_2$ on In$_{0.15}$Ga$_{0.85}$As/GaAs substrate using Hf(NCH$_3$C$_2$H$_5$)$_4$, i.e., TEMAH, and H$_2$O as the precursors. The native oxides of InGaAs were all satisfactorily removed from the interface through ligand exchange (substitution) reactions with the TEMAH precursor. It relieves the Fermi-level pinning in the HfO$_2$/InGaAs heterostructure, as verified by the clear transition from accumulation to depletion in high-frequency capacitance-voltage relations and inversion in quasistatic measurement. A very low leakage current was also found from the metal-oxide-semiconductor capacitors of Au/Ti/HfO$_2$/InGaAs.

The fabrication of metal-oxide-semiconductor field-effect transistors (MOSFETs) of GaAs-based compounds has attracted much attention for their advantages over their Si-based counterparts in high electron mobility. However, efforts in searching for appropriate gate dielectrics with satisfactory dielectric property and low density of interface traps ($D_{it}$) have never ended over the past decades due to the lack of stable passivating native oxides on the GaAs-based compounds. Recently, Ga$_2$O$_3$, Ga$_2$O$_5$(Ga$_2$O$_3$) on GaAs by in situ molecular beam epitaxy (MBE), and Al$_2$O$_3$ on GaAs as well as on InGaAs by ex situ atomic layer deposition (ALD) have attracted great interest owing to their Fermi-level unpinning for enhancement-mode MOSFETs. The ALD of high-dielectric-constant (high-$k$) oxides, such as Al$_2$O$_3$ and HfO$_2$, is particularly important because of its ability to grow ultrathin films very uniformly over large-area substrates based on sequences of self-limiting surface reaction and becomes the essential technique for fabrication of the alternative gate dielectric to replace SiO$_2$ for next generation nanoscale Si-based MOSFETs.

Self-cleaning of interfacial As$_2$O$_3$ in ALD-Al$_2$O$_3$ films on GaAs and InGaAs was found in previous studies, using Al(CH$_3$)$_3$ as the metal precursor. It provides an effective passivation of these GaAs-based substrates by Al$_2$O$_3$. However, such a self-cleaning phenomenon was not found in ALD-HfO$_2$ using HfCl$_4$ as the metal precursor, i.e., the native oxides remain intact. Although the exact mechanism of the interfacial self-cleaning effect found in the ALD of Al$_2$O$_3$ on GaAs-based semiconductors is not known yet, we believe that it may involve the interfacial reactions between the trimethylaluminum and the native As$_2$O$_3$, providing a pathway for the interfacial cleaning by forming Al$_2$O$_3$ and volatile trimethylarsine. These reactions have been understood in alkylating As$_2$O$_3$ with aluminum alkyls to form trialkylarsines. However, in the ALD of HfO$_2$ with HfCl$_4$ as the metal precursor, due to the highly ionic character of the Hf–Cl polar covalent bond (0.59 in fraction), it may be relatively too strong to break to trigger such a ligand exchange reaction with the native oxides. The metal amide derivatives, such as As[N(CH$_3$)$_2$]$_3$ and Sb[N(CH$_3$)$_2$]$_3$, have been used as precursors for III-V homo- and heteroepitaxial films prepared by chemical beam epitaxy and atomic layer epitaxy, because these precursors can provide chemical reactions for in situ cleaning and etching of native oxide and substrates as well as interfacial hydrocarbon layers of GaAs and other III-V compounds. The tetakis(ethylmethylamido)hafnium, Hf(NCH$_3$C$_2$H$_5$)$_4$, i.e., TEMAH, is one of the important metal amide precursors used for the ALD of HfO$_2$ and may provide the desired self-cleaning reactions in ALD of HfO$_2$ on the InGaAs interface. It is investigated in this work.

In$_{0.15}$Ga$_{0.85}$As/GaAs strained epilayers were used as substrates with a Si doping of 5×10$^{17}$ cm$^{-3}$ grown on Si-doped GaAs by MBE. The HfO$_2$ films having a thickness of ~7.4 nm were then grown on native-oxide-covered InGaAs in an ALD reactor at 200 °C and a pressure of 1 torr using alternating pulse of TEMAH/Ar/H$_2$O/Ar in period at 2/3/2/3 s for each self-limiting cycle. A HfO$_2$ deposition rate of 0.082 nm/cycle was measured by spectroscopic ellipsometer and high-resolution transmission electron microscopy (HRTEM). A 2-nm-thick Ti was evaporated on HfO$_2$ as gate electrode and then capped by 100 nm thick Au giving a capacitor area of 6.3×10$^{-5}$ cm$^2$ for electrical measurements. Figure 1(a) shows the cross-sectional HRTEM image of the native oxide on InGaAs. It has a saturated thickness of around 2.4 nm, consistent with the result of the native oxide on GaAs(100) after exposing under atmosphere. Figure 1(b) displays that of HfO$_2$ deposited on the native oxide/InGaAs substrate by ALD with TEMAH. It is exciting that a HfO$_2$ film free of interfacial oxide layer was obtained, i.e., not only the As oxide but also the In and Ga oxides were removed from the interface in the ALD process.

X-ray photoelectron spectroscopy (XPS) was also performed to examine the chemistry of interface in the HfO$_2$/InGaAs structure. As shown in Fig. 2, the spectra from (i) to (iii) were taken as a function of depth approaching the interface by sputtering out the top portion of the ALD-
HfO$_2$ with Ar$^+$ ions. The spectra of (iv) InGaAs substrate, (v) its native oxides, and (vi) 47 nm ALD-HfO$_2$ on Si were measured for reference. The As $3p$ difference spectra are also included in Fig. 2(c) to eliminate the influence of the HfO$_2$ background. In Figs. 2(a) and 2(b), the In $3d_{5/2}$ and Ga $2p_{3/2}$ peaks are absent from (i) the surface to (ii) the middle depth of HfO$_2$ on InGaAs. At the depth close to the HfO$_2$/InGaAs interface, in spectrum (iii), the peaks appear but have almost the same full width at half maximum and position of peaks as those of the bulk InGaAs, i.e., Ga and In oxides are unresolved and the peaks are mostly contributed from the InGaAs substrate. The result indicates that the native oxides of In and Ga are well cleaned out from the HfO$_2$/InGaAs structure. In contrast, in Fig. 2(c), the As $3p$ on the surface of HfO$_2$ film with splitting energy of around 5 eV and its difference spectra of (i)–(vi) display very weak but profound peaks of arsenic oxide (As$_2$O$_x$). The As-related signal is absent in the difference spectra of (ii)–(vi) at the middle depth of HfO$_2$ on InGaAs, and the As$_2$O$_x$ peaks are also unobserved near the interface. In the As $2p_{3/2}$ core level spectra, as shown in Fig. 2(d), we notice that the binding energy of the surface As$_2$O$_x$ peak in spectrum (i) is slightly higher (~0.6 eV) than that of native As$_2$O$_3$ [1326.3 eV (Ref. 14)] in spectrum (iv). This observation demonstrates that the As$_2$O$_x$ on the HfO$_2$ surface are As$_2$O$_3$ mixed with As$_2$O$_5$. The results from Figs. 2(c) and 2(d) clearly reveal that the As oxides are also cleaned out from the bulk and interface of the HfO$_2$/InGaAs structure. However, a very small residual amount of As$_2$O$_5$ retains on top of the HfO$_2$ film. Note that the Hf (N$_3$N$_6$N$_7$) Auger electrons of HfO$_2$ can be observed in Fig. 2(d).

The complete removal of interfacial native oxides strongly suggests the occurrence of ligand exchange reactions between TEMAH and the native oxides of InGaAs in the deposition of HfO$_2$ associated with the formation of volatile compounds, such as $M$(NCH$_3$C$_2$H$_5$)$_3$ ($M$ denotes the elements In, Ga, or As), which could be subsequently purged out from the surface of HfO$_2$ in the ALD process. Although the exact reactions are not known yet, the following two reactions are given as possible examples:

\[
3\text{Hf(NCH}_3\text{C}_2\text{H}_5\text{)}_4 + 2\text{M}_2\text{O}_3 \rightarrow 3\text{HfO}_2 + 4\text{M(NCH}_3\text{C}_2\text{H}_5\text{)}_3.
\]  

(1)

\[
\text{Hf(NCH}_3\text{C}_2\text{H}_5\text{)}_4} + \text{MO(OH)} \rightarrow \text{HfO}_2 + \text{M(NCH}_3\text{C}_2\text{H}_5\text{)}_3 + \text{HNCH}_3\text{C}_2\text{H}_5.
\]

(2)

The ligand exchange reactions may continuously proceed by chemically inducing the rearrangement or outdiffusion of In, Ga, and As cations to the surface to react with the TEMAH until the native oxides at the interface were all consumed. After that, the normal ALD on the hydroxylated surface of HfO$_2$ would be followed, giving the final thickness of HfO$_2$. Moreover, the presence of residual arsenic oxide on top of the HfO$_2$ film indicates that the reaction kinetics for As may be not as fast as that for the other two cations and some As(III) may be oxidized to As(V) in H$_2$O pulse. However, the above speculation needs further investigation.

In Fig. 3(a), the observation of the clear transition from accumulation to depletion for high-frequency capacitance-voltage (C-V) measurements; (b) plot of current density ($J_g$) against gate voltage.
voltage (HFCV) at frequency from 1 K to 1 MHz and inversion for quasistatic CV (QSCV) measurements indicate that the removal of native oxides from the interface between HfO2/InGaAs heterostructure relieves the Fermi-level pinning phenomenon. However, reduced values of HfO2 capacitance (extracted dielectric constants of 6.9 at 1 MHz and 11.3 at 1 KHz measurements), a frequency dispersion in accumulation of the HFCV curves, and a large offset between QSCV and HFCV can also be observed from Fig. 3(a). This CV degradation may be related to the following factors: (1) a low resistivity or a lossy dielectric layer in the stack of the gate dielectric, e.g., a top As2O3;16,17 (2) a high density of interface states causing the frequency dispersion near the conduction band;16,17 i.e., the calculated values of the interfacial density of state \( (D_i) \) from the 1 MHz CV curve using the Terman method are around \( 3 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1} \) near the midgap and \( 1 \times 10^{13} \text{ cm}^{-2} \text{ eV}^{-1} \) near the conduction band; and (3) other extrinsic parasitic effects inducing series resistance, capacitance, and inductance.2,18 Figure 3(b) shows the leakage current density as a function of gate voltage \( (J-V) \) in the as-deposited HfO2/InGaAs heterostructures. A very low leakage current of \( \sim 10^{-8} \text{ A/cm}^2 \) at the bias of 2 V was observed. It demonstrates the highly insulative characteristic of the ALD-HfO2 film obtained in this work.

In conclusion, an interfacial self-cleaning phenomenon was found in the atomic-layer-deposited HfO2 on InGaAs substrates by using the TEMAHE as the metal precursor. Both HRTEM and XPS show satisfactory result in removal of all the native oxides from the interface between HfO2 and InGaAs, but a slight amount of residual As oxides remains on the surface of HfO2. This self-cleaning effect relieves the Fermi-level pinning in the heterostructure of HfO2/InGaAs, as verified by the clear transition from accumulation to depletion in HFCV and the inversion in QSCV relations. However, a frequency dispersion and reduced value of capacitance in accumulation at HFCV can also be observed. Meanwhile, a very low leakage current was also found from the MOS capacitors made with the ALD-HfO2 on InGaAs.

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