Structural and electrical characteristics of atomic layer deposited high κ HfO_2 on GaN

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High κ HfO_2 was deposited on *n*-type GaN (0001) using atomic layer deposition with $Hf(NCH_3C_2H_5)_4$ and H_2O as the precursors. Excellent electrical properties of $TiN/HfO_2/GaN$ metal-oxide-semiconductor diode with the oxide thickness of 8.8 nm were obtained, in terms of low electrical leakage current density ($\sim 10^{-6}$ A/cm^2 at $V_{FB}+1$ V), well behaved capacitance-voltage (*C-V*) curves having a low interfacial density of states of 2×10^{11} cm^{-2} eV^{-1} at the midgap, and a high dielectric constant of 16.5. *C-V* curves with clear accumulation and depletion behaviors were shown, along with negligible frequency dispersion and hysteresis with sweeping biasing voltages. The structural properties studied by high-resolution transmission electron microscopy and x-ray reflectivity show an atomically smooth oxide/GaN interface, with an interfacial layer of GaON $\sim$1.8 nm thick, as probed using x-ray photoelectron spectroscopy. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2746057]

GaN and its related compound semiconductors, besides being used in blue light emitting diodes and lasers, have been studied for applications in high-temperature and high-power electronics because of their wide energy band gaps, high breakdown fields, and high saturation velocities in high fields. Excellent device performances have been demonstrated in the GaN-based high electron mobility transistors (HEMTs), in which the Schottky-barrier gates, however, have caused a large gate leakage. There has been a great interest in the development of GaN-based metal-oxide-semiconductor field-effect-transistors (MOSFETs) due to their relatively low leakage currents and capability of greater voltage swings, compared with HEMTs. In addition, the gate oxide used in surface passivation may minimize or eliminate the current collapse that occurs in unpassivated devices due to the traps existed in the regions between gate and drain.

The research on high κ gate dielectrics on Si as well as GaAs during the past few years has shown remarkable results in achieving atomically smooth oxide/semiconductor interfaces, dielectric thickness in a nanometer range, low gate leakages, and low interfacial density of states (D_{it}). However, efforts of high κ oxides on GaN, in general, have not reached the level of material and electrical quality mentioned above. Several high κ gate oxides have been studied for GaN-based MOS diodes and MOSFETs, such as $Ga_2O_3(Gd_2O_3)$,[1–3] MgO,[4] Sc_2O_3,[5,6] and Gd_2O_3.[3,7,8]

HfO_2 and its alloys are now the backbone for the high κ and metal gate technology in the recent Intel's announcement of the 45 nm node microprocessor.[9] Atomic layer deposition (ALD) is a chemical vapor deposition technique based on alternative surface reactions that saturate the surface in each reaction cycle, and is now being widely used in high κ dielectrics deposition.

In this work, effective surface passivation of GaN has been demonstrated using ALD-HfO_2. An ALD-HfO_2/GaN heterostructure, with oxide thickness of 8.8 nm (including an interfacial layer of $\sim$1.8 nm), has shown an atomically smooth oxide/GaN interface, as demonstrated using high-resolution transmission electron microscopy (HRTEM) and x-ray reflectivity (XRR). The interfacial layer has a composition of GaON, as probed using an x-ray photoelectron spectroscopy (XPS). Roughness of the oxide surface, the oxide/interfacial layer interface, and the oxide/GaN interface has been studied using XRR and determined to be 0.29, 0.5, and 0.3 nm, respectively. A low electrical leakage current density of $<10^{-8}$ A/cm^2 at 1 MV/cm (10^{-6} A/cm^2 at $V_{FB}+1$ V, where V_{FB} is the flatband voltage), capacitance-voltage curves with very small frequency dispersion and hysteresis in biasing voltage sweeping, and a small interfacial density of states (D_{it}) of $\sim 10^{11}$ cm^{-2} eV^{-1} (determined using the Terman Method) have also been achieved. The small D_{it} demonstrated here is perhaps one of the lowest ever measured in high κ dielectrics on GaN.

GaN (0001) samples (with an *n*-type doping of 5×10^{17} cm^{-3}) were metal organic chemical vapor deposition grown on *c*-plane sapphire substrates. No surface cleaning of GaN was performed prior to the ALD deposition. It is inevitable that some contaminants will reside on top of the GaN due to air exposure. HfO_2 films were grown on the GaN with a wafer temperature of 200 °C and a chamber pressure of 1 Torr using alternating pulses of tetrakis(ethylmethylamino-)hafnium (TEMAH) and H_2O as the precursors. High-purity Ar (99.999%) was used as diluted and purged gas. To take the process within a self-limited region, the pulse period was maintained at 2–3–2–3 s/cycle (i.e., 2 s each for TEMAH

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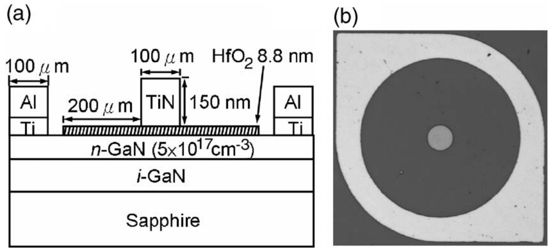

FIG. 1. (a) Schematic cross-sectional view of the fabricated $TiN/HfO_2/GaN$ MOS diode, with the top view shown in (b).

and H_2O and 3 s for Ar) with 0.1 Torr for a partial pressure of the precursors.

Studies of electrical leakage currents and D_{it}'s were performed on $TiN/HfO_2/GaN$ MOS diodes. Current density versus biasing field (*J-E*) and capacitance versus voltage (*C-V*) were measured using Agilent 4156C and 4284, respectively, where J is the leakage current divided by the measured area and E is the biasing voltage divided by the film thickness. HRTEM specimens were prepared with mechanical polishing, dimpling, and ion milling using a Gatan PIPS system operated at 4 keV. The analytical work of TEM sample was performed using a Philips JEOL 2100F type TEM. XRR measurements were performed using Cu K_α radiation in a standard Huber four-circle x-ray diffractometer operated at 50 kV and 200 mA. The incident light was monochromatized by a flat Ge(111) crystal. Two sets of slits were used to eliminate Cu K_{α_2} contamination and to obtain a wave-vector resolution in the scattering plane of the order $0.015\ nm^{-1}$. The specular reflectivity was measured with a series of θ–2θ scans. XRR technique serves to characterize the film thickness, the interfacial roughness, and the electron density.[10,11]

Fabrication of the MOS diodes is discussed in the following. TiN 150 nm thick was deposited on the ALD-HfO_2 using rf sputtering, with the pattern of the metal gate defined by photolithography. The Ohmic contact with the doped GaN layer was achieved by etching HfO_2 using dilute hydrofluoric acid ($HF:H_2O=1:100$). Subsequently, the exposed GaN surface contaminants were removed using dilute hydrochloric acid, followed by an e-beam evaporated metal Ti/Al (30/60 nm) on GaN. The schematic cross-sectional view of the fabricated $TiN/HfO_2/GaN$ MOS diode is shown in Fig. 1(a), with the top view of the diode shown in Fig. 1(b).

Figure 2 shows a cross-sectional HRTEM image of an amorphous ALD-HfO_2 film on GaN. The oxide consists of two layers with an overall thickness measured by TEM to be 8.8 nm. The top layer is $HfO_2 \sim 7.0$ nm thick, and the bottom interfacial layer is ~ 1.8 nm thick, with a composition of GaON. The different contrasts are due to a heavier mass of Hf in comparing with that of Ga. The composition of the interfacial layer between HfO_2 and GaN was analyzed using XPS with an Al $K\alpha$ source (photon energy 1486.6 eV), as shown in the inset (I) of Fig. 2. The broad Ga $2p$ peak could be deconvoluted to the peak (1116.8 eV) of bulk GaN substrate and the Ga oxynitride peak (1118.55 eV). There is a chemical shift of 1.75 eV between the two peaks.

An XRR fringe pattern is shown in the inset (II). From the period of oscillations, the oxide film thickness, and the values of the roughness of the oxide surface and the interface between the oxide and GaN have been calculated using the theoretical fitting model. An interfacial roughness of a range of 0.3 nm has been obtained in the HfO_2/GaN interface. It is interesting to observe that the roughness on top of HfO_2 and the oxide/GaN interface is similar of ~ 0.3 nm, indicating the existence of a correlation between the oxide surface and the interface. The atomic-scale correlation was also observed earlier in Au/GaAs, a metal/semiconductor heterostructure.[10] A rougher interface (~ 0.5 nm) between HfO_2 and the interfacial layer may indicate chemical reactions among TEMAH, H_2O, and GaN native oxides during the ALD process.

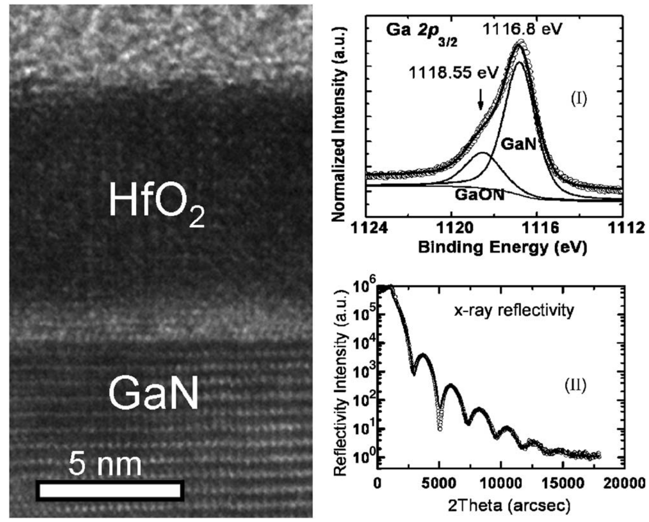

FIG. 2. Cross-sectional high-resolution TEM image of HfO_2 8.8 nm thick on GaN. Inset (I): the XPS spectrum of Ga $2p_{3/2}$ core level shows the existence of an interfacial layer of GaON. (II): low angle x-ray reflectivity of HfO_2 on GaN, with experimental data (dots) and a theoretical fit (line).

In a separate experiment, nanometer thick HfO_2 films were deposited on GaN with electron beam evaporation underultra high vacuum (UHV).[12] The interface is atomically sharp, without any interfacial layer between GaN and the UHV-deposited HfO_2, as studied using HRTEM, and the XRR measurements whose fitting involves no interfacial layer. The XPS investigation also confirms this. Comparing the results of ALD- and UHV-deposited HfO_2 on GaN, the interfacial layer of GaON occurring in the former case has been formed during the initial stage of the ALD process, similar to the formation of silicate in ALD-HfO_2 on Si.

The $TiN/HfO_2/GaN$ MOS diode after 375 C annealing in forming gas for 20 min shows well behaved *C-V* characteristics of varying frequency from 1 to 500 kHz with accumulation, depletion, and a dielectric constant of 11.6, as exhibited in Fig. 3(a). Note that very little dispersion in the accumulation regime was observed along with the very small hysteresis with sweeping biasing voltages, as shown in the inset of Fig. 3(a). Annealing at 600 °C for 10 min in a pure argon gas flow did increase the dielectric constant from 11.6 to 16.5, and the EOT is correspondingly decreased from 2.96 to 2.08 nm, where EOT is the equivalent oxide thickness, defined as κ_{SiO_2} (thickness of high κ dielectrics)/ ($\kappa_{high\kappa}$). A slight increase in dispersion and hysteresis was observed, as shown in Fig. 3(b) and its inset. Furthermore, from the *C-V* curves a very low D_{it}, roughly $2\times10^{11}\ cm^{-2}\ eV^{-1}$ at midgap was obtained using the Terman method, with a detailed calculation discussed in Ref. 13. The low D_{it} value is similar to what was obtained in the UHV-$Ga_2O_3(Gd_2O_3)/GaN$.[14,15]

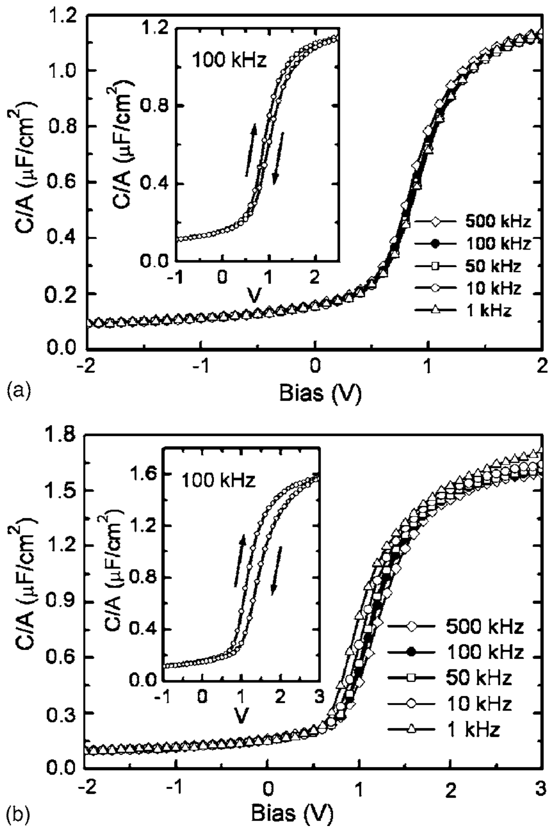

FIG. 3. *C-V* curves of $TiN/HfO_2/GaN$ MOS diode under various frequencies from 1 to 500 kHz, with (a) annealing at 375 and (b) 600 °C.

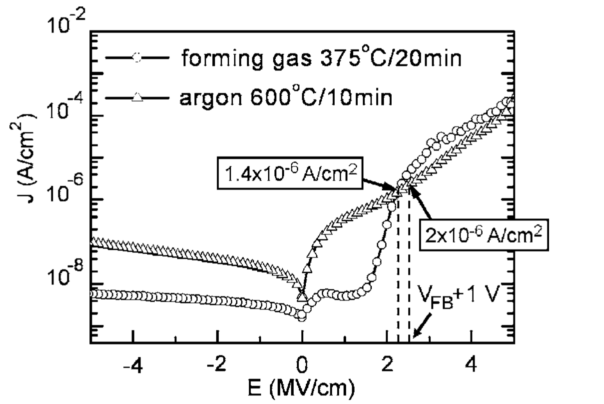

FIG. 4. Leakage current density J (A/cm^2) vs E (MV(cm) for $TiN/HfO_2/GaN$ MOS diode in different thermal processes.

Figure 4 shows the *J-E* curves of MOS diodes after annealing at 375 °C in forming gas and at 600 °C in pure argon. The leakage current density at $V_{FB}+1$ V is 1.4×10^{-6} and 2×10^{-6} A/cm^2 for sample annealed at 375 and 600 °C, respectively. The corresponding electrical fields for $V_{FB}+1$ V are 2.22 and 2.45 MV/cm for sample annealed at 375 and 600 °C, respectively, as labeled in Fig. 4. The leakage current density increased after 600 °C annealing may have been caused by the formation of polycrystalline HfO_2 from amorphous films.

Asymmetrical characteristics of *J-E* curves under the forward and reverse biases were obtained, which were also observed previously in thicker dielectric films.[6,15,16] The leakage current densities in the reverse bias remain very low even at high electrical fields, most likely due to extremely low minority carriers available, as explained with the very low intrinsic carrier concentration ($\sim10^{-10}$ cm^{-3}) in GaN. However, the higher leakage current densities at the forward bias are resulted from the transport of the majority carriers.

In conclusion, the electrical and structural properties achieved in this work in employing ALD-HfO_2 on GaN have approached the level of high κ dielectrics on Si and GaAs, namely, a low D_{it} of $\sim2\times10^{11}$ cm^{-2} eV^{-1}, a low leakage current density of 10^{-7}–10^{-8} A/cm^2 at 1 MV/cm for an 8.8 nm thick oxide (an EOT of 2.08 nm), the thermodynamic stability of the heterostructure (with 600°C annealing), high κ value, and negligible frequency dispersion in the *C-V* measurements.

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