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Investigations of GaN metal-oxide-semiconductor capacitors with sputtered HfO_2 gate dielectrics

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ABSTRACT

This work elucidates the properties of Al/HfO_2/GaN metal-oxide-semiconductor capacitors using reactively sputtered HfO_2 as a gate dielectric. The influence of GaN surface treatments and the post-annealing of HfO_2 films on the leakage current, flat-band voltage, interface trap densities, dielectric constants, and effective oxide charges of the GaN MOS capacitors are presented. The Ga oxynitride on the surface of GaN was effectively removed by chemical solutions that also slightly reduced the dielectric constant, slightly increased the flat-band voltage, eliminated the hysteresis of the capacitance–voltage measurement, and yielded a similar leakage to that without surface treatment. A highest dielectric constant of HfO_2 (17) was obtained when the sample was annealed at 600 °C for 20 min, while the lowest interface trap density (5.3×10^{11} cm^{-2}) was obtained when the sample was annealed at 800 °C for 40 min. The leakage mechanism was well fitted by the Schottky emission and Frenkel–Poole emission models at a lower and higher electric field.

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III-Nitride semiconductors have been demonstrated to have potential applications in high-power, high-speed, and high-temperature devices because of their attractive fundamental properties such as high direct band-gap, chemical stability and high electron saturation velocity. Recently, GaN-based transistors such as metal-semiconductor field-effect-transistors (MES-FETs), hetero-junction FETs (HFETs), and high-electron-mobility transistors (HEMTs) have been reported [1–4]. All such devices suffer from the gate leakage problem. A large leakage current flows at the metal and GaN interface, making a good Schottky contact difficult to achieve. Metal-oxide-semiconductor FETs (MOS-FETs) and MOS-HFETs with an oxide interlayer between the metal and the semiconductor have much smaller leakage currents. Therefore, GaN-based MOS-FETs and MOS-HFETs have been important topics of research [5–8].

GaN-based MOS-FETs provide a number of advantages over Si-based devices. MOS capacitors are good forerunners of MOS-FETs or MOS-HFETs that can be employed to study the properties of the semiconductor–insulator interface. Previously, numerous gate dielectrics, such as Ga_2O_3, SiO_2, Si_3N_4, Al_2O_3, HfO_2, MgO, SiN_xO_y, Ta_2O_5, and ZrO_2 [9–16] have been studied using MOS structures. Among these, HfO_2 has attracted the most attention by far due to its good thermal stability and high dielectric constant. Optimizing the GaN MOS structure involves two major challenges—lowering the interface traps and improving the oxide quality. Many effective techniques are available for depositing insulators on GaN. They include plasma-enhanced chemical vapor deposition (PE-CVD), e-beam evaporation, low-pressure CVD, photo-CVD, sputtering and atomic layer deposition [10–12,14,15]. Among these techniques, sputtering offers the advantages of simplicity process, low cost and high throughput. Besides, various chemical solutions such as H_3PO_4, $H_2SO_4 + H_2O_2$, H_3PO_4, HF, and HCl have been applied to clean the GaN surface prior to the oxide deposition [9–13]. The performance of the MOS capacitors depends sensitively on the surface chemistry of as-grown GaN. However, the relationship between surface treatments of GaN and corresponding MOS properties has not been elucidated. Moreover, no research into GaN MOS capacitors with a sputtered HfO_2 as an oxide layer has been conducted.

This work systematically studies the Al/HfO_2/GaN MOS capacitor using reactively sputtered HfO_2 as an insulator. The effect of GaN surface treatments and the annealing conditions of HfO_2 films on the leakage current, flat-band voltage, interface traps densities, dielectric constants and effective oxide charges of the GaN MOS capacitors are presented. The dominant leakage mechanism is also described.

1. Experimental

N-type GaN films were grown on (0 0 0 1) sapphire substrate by metal-organic chemical vapor deposition (Aixtron rf-200/4). A low-temperature GaN nucleation

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layer, 25 nm thick, was first deposited at 520 °C. This was followed by a 1.5 μm GaN grown at 1050 °C. Although the threading dislocations of GaN could be reduced by increasing the thickness, the thickness of GaN was well chosen to yield a favorable surface flatness, which is key to a metal–semiconductor interface, with help of the *in situ* reflectmetry using an 500 nm monochromatic light. The precursors were trimethylgallium (TMG) for Ga, ammonia for nitrogen and silane for n-type doping, with hydrogen carrier gas. The Si doping concentration was around 2×10^{18} cm^{-3}. Before the oxide layers were deposited, the GaN samples were prepared by sequentially rinsing in de-ionized (DI) water, hot acetone, IPA, DI water, chemical solution (5 min), and finally repeating DI water/hot acetone/IPA/DI water rinsing. The chemical solutions adopted herein included diluted hydrochloric acid (HCl, H_2O:HCl = 1:1), buffer oxide etchant (H_2O:HF = 50:1) and potassium hydroxide (KOH, 1 M). HfO_2 thin films were deposited by reactive sputtering (dc, 200 W) using Hf metal as a target, in an Ar/O_2 ambient (Ar:O_2 = 10:5 sccm). The background and working pressure during sputtering were 1×10^{-6} and 5×10^{-3} Torr, respectively. The as-deposited HfO_2 was thermally annealed at temperatures from 500 to 800 °C, for 5, 20, 40, and 60 min. The circular 250 nm-thick Al gate electrode was formed by e-beam evaporation. The optimized post-annealing condition of the metal electrodes (10 min in nitrogen ambient at 400 °C) was used throughout. Binding energies was obtained by high-resolution X-ray photoemission spectroscopy (HRXPS, Ulvac/PHI Quantera SXM). The grazing-incident X-ray diffraction (GIXRD, Rigaku D/MAX2500) was used to characterize the phase of HfO_2 films. The electrical properties of the fabricated MOS capacitors were characterized by measuring high-frequency capacitance–voltage (*C*–*V*) and current density–voltage (*J*–*V*) curves with an Agilent 4294A precision impedance analyzer and an Agilent semiconductor parameter analyzer (E5270B mainframe with module E5287A), respectively.

2. Results and discussion

Quantitative analysis of the as-grown HfO_2 thin films by HR-XPS indicated that the compositional ratio of O/Hf approached 2 (not shown), even without thermal annealing, indicating a good stoichiometry manipulation of the sputtering. HR-XPS was also conducted to examine the HfO_2/GaN interface. The GaN surfaces of the samples studied herein were treated with different aqueous solutions but all the HfO_2 thin films were deposited under identical conditions. *In situ* Ar^+ ion sputtering was used to remove slowly the HfO_2 until the underlying Ga 2p signals appeared during HR-XPS measurement. Fig. 1(a) and (b) plots corresponding data for O 1s and Ga 2p, respectively. The bottom profile is constructed from signals from the as-grown GaN for comparison. Both the O 1s and Ga 2p signals were shifted to a binding energy that was approximately 2 eV lower than that of untreated GaN. These shifts were independent of the chemical solutions selected. All of the broad Ga $2p_{1/2}$ peaks in the vicinity of 1115 eV for the chemical treated samples could be deconvoluted into two peaks, exhibiting a chemical shift of ~2 eV, indicating a Ga oxynitride interfacial layer was presented. The origin of the interlayer is ascribed to the initial stages of sputtering because no such signal form the as-cleaned GaN surfaces could be resolved.

The effects of surface treatments on the electrical properties of GaN MOS diodes were studied by comparing the KOH, HCl, and BOE treated samples. An untreated sample was used for reference. The leakage currents for all of the treated and non-treated MOS samples were as small as $\sim 2 \times 10^{-9}$ A/cm^2 (Fig. 2(a)). Surface treatments caused small deviations of the leakages. Regardless of treatment methods, the leakage current of MOS capacitor declined as the HfO_2 thickness increased (Fig. 2(b)), indicating that the main leakage current comes from the oxide layers not the interfaces. Fig. 2(c) plots well-behaved *C*–*V* curves that were measured at 1 MHz. No frequency dispersion was observed (100 kHz to 1 MHz), suggesting that the films have promising dielectric properties. Electrical hysteresis of the *C*–*V* curves due to the trapped charges within the oxide layers of the non-treated samples was observed, but decreased to a negligible level upon treatment with aqueous solution. Since the HfO_2 films were deposited under the same conditions, the hysteresis behavior was attributed to the native Ga oxynitride over the as-grown GaN surface. Moreover, the surface-treated samples had a lower accumulation capacitance than the non-treated one. From

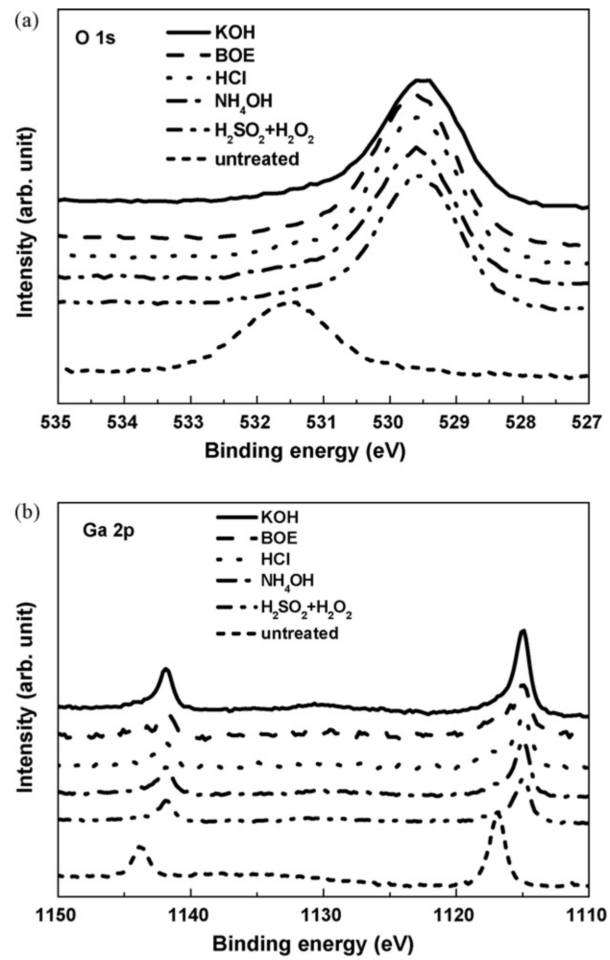

Fig. 1. HR-XPS profiles of the GaN/HfO_2 interfaces: (a) O 1s and (b) Ga 2p.

Table 1
ε_{GaN}, *EOT*, V_{FB}, N_{eff} and D_{it} values for Al/HfO_2/GaN MOS capacitors with different annealing temperatures and times.

Temperature (°C)	Time (min)	ε_{GaN}	*EOT* (nm)	V_{FB} (V)	N_{eff} ($\times 10^{12}$ cm^{-2})	D_{it} ($\times 10^{11}$ cm^{-2})
600	20	17	8.1	0.77	2.1	8.1
	40	14	10.1	0.75	1.6	6.8
	60	14	9.9	0.67	1.5	6.6
700	20	13		0.85	1.7	10.4
	40	11	12.6	0.86	1.4	9.5
	60	10	13.8	0.79	1.3	7.4
800	20	14	10.2	0.73	2.0	6.4
	40	12	11.2	0.72	1.5	5.3

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