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Thermal Stability of the Interface between Atomic Layer Deposited High-*k* ZrO_2 and GaN

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Abstract

The thermal stability of high-*k* ZrO_2/GaN interface related to formation/annihilation of interfacial GaOx layer between ZrO_2 and GaN is studied by X-ray photoelectron spectroscopy (XPS). It is observed that deterioration of interface quality starts at temperatures higher than 500 ºC, which is evidenced by increase in Ga-O bond to Ga-N bond ratio and the reduction of Ga-N binding energy.

1. Introduction

GaN-based heterostructure devices such as high electron mobility transistors (HEMTs) have been used extensively for high frequency, high power, and low noise applications. Metal-insulator-semiconductor HEMTs (MISHEMTs) using high-*k* dielectrics as the gate insulators has been reported to improve the device performance [1]. By virtue of its high dielectric constant along with reasonably high conductance band offset (CBO) and valance band offset (VBO) aligned to GaN substrate, ZrO_2 is a promising dielectric material candidate for GaN MISHEMTs [2]. Excellent DC and RF electrical characteristics of GaN MISHEMTs utilizing ZrO_2 as gate dielectrics are reported [3]. However, the thermal stability of the ZrO_2 dielectric layer at the interface as one of the most challenging requirements for application of ZrO_2 as a gate dielectric remains un-explored. In this work, a detailed investigation of the thermal stability of ZrO_2/GaN interface is carried out by using X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HR-TEM).

2. Experiment

ZrO_2 dielectric layers were deposited on GaN-on-sapphire substrates by using ALD method. The un-doped GaN-on-sapphire wafers were grown by Metal Organic Chemical Vapor Deposition (MOCVD) using a commercial reactor. For the investigation of ZrO_2/GaN interface, samples with 2 nm thick ZrO_2 on GaN surface were utilized for XPS measurements while ZrO_2 dielectric layers with a thickness of 10 nm were deposited for HR-TEM characterization. ZrO_2 dielectric layers were deposited by a Cambridge Nanotech Savannah ALD system at 0.6 Torr and 250 ºC. The tetrakis-(diethylamino)-zirconium and H_2O were used as the precursors. The growth rate for ZrO_2 was ~0.09 nm per ALD cycle. After dielectric layer deposition, different post-deposition anneals (PDAs) using rapid thermal annealing (RTA) in N_2 atmospheres for 30 s were performed under five different temperatures (300 ºC, 400 ºC, 500 ºC, 600 ºC and 700 ºC). The XPS measurements were carried out using a monochromatic Al Kα X-ray source of energy 1486.7 eV. The spectra are curve-fitted with a combination of Gaussian and Lorentzian line shapes using a Shirley-type background subtraction. All peaks were referenced to the C 1s peak at 284.6 eV to compensate for any variations in the peak core-level positions due to binding energy (BE) shift caused by surface charging.

3. Results and Discussion

Ga 3*d* core-level XPS spectra obtained under different post-deposition annealing temperatures are depicted in Fig. 1. It can be seen from Fig. 2 that each Ga 3*d* spectrum could be deconvolved into two components, corresponding to the Ga-N and Ga-O bonds. The existence of the Ga-O spectrum for the as-deposited sample (indicated by N.A in Fig. 1) may be attributed to the parasitic oxidation of the GaN surface after cleaning during ALD deposition process. The Ga-N bonds show an obvious increase in binding energies (BEs) with the increase of annealing temperatures when the annealing temperatures are lower than 500 ºC. Further increase in annealing temperature shows a reduction of the BEs. For clarity, the dependence of Ga-N bond binding energies and ratio of the Ga-O to Ga-N XPS peak area on annealing temperatures are plotted in Fig. 2. It can be seen that the Ga-N bond binding energies are strongly coincident with the ratio of Ga-O to Ga-N peak area. A higher defect density at ZrO_2/GaN interface could cause stronger upward band bending thus lower Ga-N bond binding energy. Therefore, the results in Fig.2 suggest a noticeable improvement of ZrO_2/GaN interface quality when the samples are annealed at temperatures below 500 ºC. However, further increase in anneal temperature results in the deterioration of the ZrO_2/GaN interface. This can be further supported by HR-TEM observation as shown in Fig.3. Compared with the as-deposited sample, an abrupt interface without any interfacial layers is observed for sample annealed under 500 ºC. This may be attributed to the "clean up" effect for ALD ZrO_2 on GaN after annealing at

500 ºC. Such “clean up” effect is widely reported on ALD deposited high-k dielectrics on III-V semiconductor interfaces such as Al_2O_3/III-As and Al_2O_3/III-N.

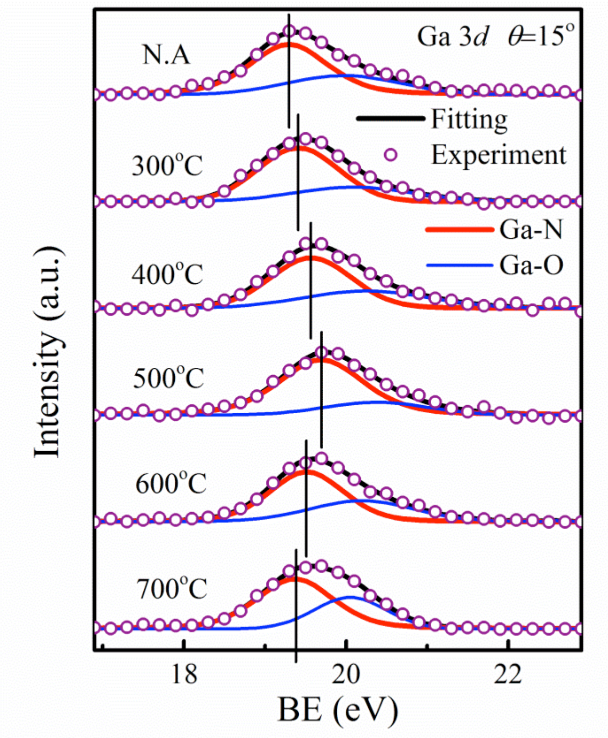

Fig. 1 The measured (open circles) and fitted (lines) XPS Ga 3*d* core-level spectra for ZrO_2 on GaN samples measured at take-off angle θ of 15º under different annealing temperatures. The as-deposited sample is indicated as N.A.

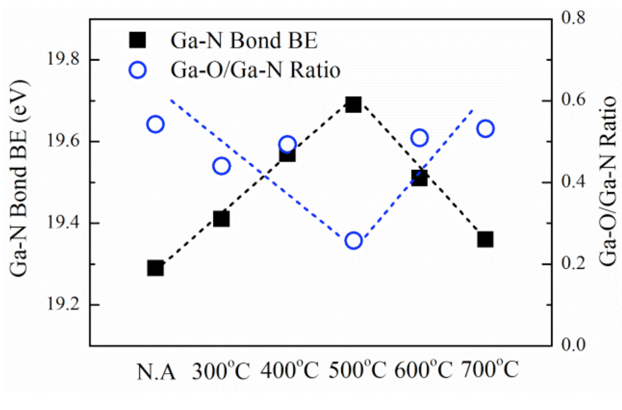

Fig. 2 Change of Ga-N bond binding energy and integrated XPS intensity ratio of Ga-O bond to Ga-N bond for ZrO_2/GaN under different temperatures. The as-deposited sample is indicated as N.A.

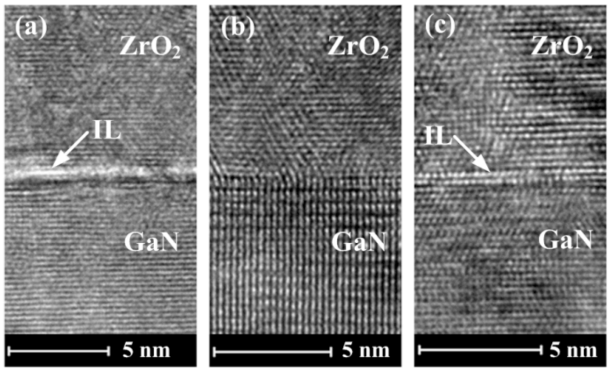

Fig. 3 Cross-sectional TEM images of high-*k* ZrO_2 dielectric layers on GaN: (a) as-deposited (N.A) and (b) with a 500 ºC annealing in N_2 for 30 s and (c) with a 700 ºC annealing in N_2 for 30 s. The interfacial layer is indicates as IL.

4. Conclusions

The thermal stability of high-*k* ZrO_2/GaN interface related to formation/annihilation of interfacial GaO_x layer between ZrO_2 and GaN is studied. Deterioration of interface quality was observed for the samples subjected to annealing at temperatures higher than 500 ºC. This is evidenced by increase in Ga-O bond to Ga-N bond ratio and the reduction of Ga-N binding energy. The results are further confirmed by HR-TEM. The findings provide important process guidelines for the use of ALD ZrO_2 for GaN MISHEMTs.

Acknowledgements

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