Electrical properties and interfacial chemical environments of in situ atomic layer deposited Al$_2$O$_3$ on freshly molecular beam epitaxy grown GaAs


Abstract

Interfacial chemical analyses and electrical characterization of in situ atomic layer deposited (ALD) Al$_2$O$_3$ on freshly molecular beam epitaxy (MBE) grown n- and p-GaAs (001) with a (4 x 6) surface reconstruction are performed. The capacitance–voltage (C–V) characteristics of as-deposited and 550 °C annealed samples are correlated with their corresponding X-ray photoelectron spectroscopy (XPS) interfacial analyses. The chemical bonding for the as-deposited ALD-Al$_2$O$_3$/n- and p-GaAs interface is similar, consisting of Ga$_2$O (Ga$_{3+}$) and As–As bonding (As$_0$) without any detectable arsenic oxides or Ga$_2$O$_3$; the interfacial chemical environments remained unchanged after 550 °C annealing for 1 hr. Both as-deposited and annealed p-GaAs metal–oxide–semiconductor capacitors (MOSCAPs) exhibit C–V characteristics with small frequency dispersion (<5%). In comparison, n-GaAs MOSCAPs show much pronounced frequency dispersion than their p-counterparts.

Intensive research efforts have now been focused on high-k dielectrics/InGaAs due to the possible employment of InGaAs metal–oxide–semiconductor field-effect-transistor (MOSFET) in the devices beyond the 16 nm node complementary MOS (CMOS) circuits [1–4]. Reducing high interfacial state densities ($D_{it}$'s) on high k's/InGaAs, an important issue for realizing inversion-channel InGaAs MOSFETs [5], was not realized until the discovery of ultra-high-vacuum (UHV) deposited Ga$_2$O$_3$(Ga$_{3+}$) [6,7]. Moreover, thermodynamic stability at high temperatures of >850 °C [8] and capacitance–voltage (C–V) characteristics with small dispersion at accumulation in both n- and p-In$_{0.2}$Ga$_{0.8}$As MOS capacitors (MOSCAPs) [9], commonly observed in SiO$_2$/Si but not in high k's/InGaAs, has been achieved using GGO.

Atomic layer deposited (ALD) Al$_2$O$_3$ and HfO$_2$ on InGaA [10,11], due to the advantages of ALD on self-cleaning native oxides of InGaAs [12] and the precise control of film uniformity and thickness, have also received worldwide attention. C–V curves of ALD-Al$_2$O$_3$/p-GaAs with small dispersions at accumulation have been reported by several groups using various surface treatments [13–17]. However, all C–V characteristics of ALD-Al$_2$O$_3$/n-GaAs exhibit much more pronounced frequency dispersion [13–16], except the data using amorphous Si passivation [17]; the reduction of frequency dispersion was attributed to the removal of Ga$_2$O$_3$ (Ga$_{3+}$) and the presence of Ga$_2$O (Ga$_{3+}$) [17]. However, a recent report suggested that the presence of Ga$_2$O$_3$–Al$_2$O$_3$ layer above the CVD-Al$_2$O$_3$/GaAs interface reduces the frequency dispersion in C–V characteristics and lowers the $D_{it}$'s [18]. The controversy over the role of Ga$_2$O$_3$ at Al$_2$O$_3$/GaAs interfaces warrants more studies.

In this work, hetero-structures of ALD-Al$_2$O$_3$ on freshly molecular beam epitaxy (MBE) GaAs were grown in a multi-chamber MBE/ALD/analyses system, including GaAs-based solid source MBE chamber, UHV oxide deposition chamber, ALD reactor, and X-ray photoelectron spectroscopy (XPS) analysis chamber [19]. These chambers are connected with transfer modules in 10$^{-10}$ Torr. Note that no surface treatments and interfacial passivation layers were employed. This allows studies of the interfacial chemical bonding between the ALD-Al$_2$O$_3$ and pristine GaAs using XPS. Further, comparing the C–V/XPS characteristics may permit the correlation between the interfacial chemical environments with the electrical properties.

Si- and Be-doped GaAs epi-layers with a doping concentration of (1–5) × 10$^{17}$ cm$^{-3}$ were MBE-grown on 2º n- and p-type GaAs (100) wafers, respectively. With the attainment of a (4 x 6) reflective high-energy electron diffraction (RHEED) reconstruction
pattern (a Ga-stabilized surface), the samples were in situ transferred to a customized Picuson SUNALE® ALD reactor for the deposition of 1 nm ALD-Al₂O₃ at 300 °C with Trimethylaluminum (TMA)/de-ionized H₂O as precursors. The chemical analyses of ALD-Al₂O₃/GaAs interface were carried out with in situ HR-XPS using an Al Kα (1486.7 eV) monochromatic X-ray source. All XPS spectra presented in this work were measured with a pass energy of 10 eV and an energy resolution of ~0.25 eV. Additional ALD-Al₂O₃ was subsequently deposited on the samples to fabricate Al[Ni]/Al₂O₃/n(p)-GaAs/TiAu MOSCAPs for electrical measurements.

Fig. 1 (a and b) show the in situ Ga 2p₃/₂ and As 2p₃/₂ core level spectra of 1 nm ALD-Al₂O₃/n-GaAs, with 60° and 45° take-off angles, which were chosen considering the escape depth of each core level to maximize the interfacial sensitivity. In separate measurements on the freshly MBE grown GaAs surface, the full width at half maximum (FWHM) of Ga 2p₃/₂ and As 2p₃/₂ cores were obtained to be 1.08 and 1.35 eV, respectively, as shown in blue lines in Fig. 1. We hence use these as references for a fit to the corresponding spectra of Al₂O₃/n-GaAs. As can be seen in Fig. 1 (a), the asymmetric line shape of the Ga 2p₃/₂ core suggests the existence of a feature embedded in the measured spectrum. A fit reveals then its position lying about 0.63 eV below the bulk GaAs, which corresponds to the Ga³⁺ state (Ga₂O). As to the As 2p₃/₂ core, Fig. 1(b) exhibits the fitted result which shows a structure located in a higher EB of about 0.70 eV than that of the bulk GaAs. It corresponds to emission from the As–As bonding (As⁵⁺). Notice that neither arsenic oxides (the As³⁺ (As₂O₃) and As⁵⁺ (As₂O₅) states) nor gallium oxide (the Ga³⁺ (Ga₂O₃) state) were detected.

Similar measurements on a ALD-Al₂O₃/p-GaAs sample are plotted in Fig. 1 (c) (Ga 2p₃/₂) and (d) (As 2p₃/₂) in green open circles. For a point-to-point comparison with the case of n-GaAs which are drawn in red open circles, the spectra were aligned with respective to the bulk Ga 2p₃/₂ and As 2p₃/₂ states with the corresponding difference-curves plotted underneath. No major difference in interfacial chemical environments between ALD-Al₂O₃/n- and p-GaAs can be distinguished, as shown in Fig. 1 (c and d). The results indicate that the disparity between ALD-Al₂O₃/n- and p-GaAs may not be due to different interfacial chemical bonding; further, they suggest that As⁵⁺ and/or Ga³⁺ may be the reason for the disparity in C–V characteristics.

An in situ ALD-Al₂O₃(8 nm)/n-GaAs hetero-structure, the same sample for the C–V measurements, was adopted to study the chemical bonding environments of ALD-Al₂O₃/GaAs interface before and after 550 °C annealing in N₂ for 1 h. The XPS spectra of the As 3d and Ga 3d of the as-deposited and the annealed samples are shown in Fig. 2 (a–c), where the red and navy blue open circles are for as-deposited and annealed samples, respectively. To have the most interface sensitivity, As 3d and Ga 3d spectra were used since the probing depths with their high kinetic energy (KE), 1445 eV for As 3d and 1467 eV for Ga 3d, are in the range of...
8–9 nm. Therefore, most photoelectrons of As 3d and Ga 3d cores were originated from the region 8–9 nm below the surface of Al2O3, which corresponds to the position of Al2O3/GaAs interface. The As-related bonding at interface remained unchanged after Fig. 2. The comparison of XPS (a) As 3d and (b) Ga 3d and O 2s spectra of 8 nm in situ ALD-Al2O3/n-GaAs before and after 550 °C N2 annealing for 1 hr. (C) De-convoluted results of Ga 3d and O 2s spectra of as-deposited and 550 °C N2 annealed samples. Open circles are the raw data and the black lines are the fitting curves, summing up de-convoluted components.

Fig. 3. C–V characteristics of (a) as deposited (b) 550 °C N2 annealed in situ ALD-Al2O3/p-GaAs and (c) as deposited (d) 550 °C N2 annealed in situ ALD-Al2O3/n-GaAs.
the 550 °C N2 annealing, by comparing As 3d spectra between the as-deposited and the annealed samples, as shown in Fig. 2 (a). No arsenic oxide (As2O3 or As2O5) was detected after the annealing. Fig. 2 (b and c) show the comparison and the de-convoluted results of O 2s and Ga 3d spectra between the as-deposited and the annealed samples. No additional bonding other than Ga-As and Ga1+ in the annealed sample can be found, further confirming that the interfacial bonding remained unchanged after the annealing.

Fig. 3 (a–d) show the C–V characteristics (100–1000 k Hz) of the as-deposited and 550 °C N2 annealed n- and p-GaAs MOSCAPs. C–V curves with frequency dispersions (<5%) at accumulation were obtained in both p-GaAs MOSCAPs. The as-deposited n-GaAs MOSCAP gave a much pronounced frequency dispersion, which was reduced after 550 °C N2 annealing.

Note that C–V characteristics with small dispersion were attained in the as-deposited p-GaAs MOSCAPs without any post-deposition annealing, suggesting that through the in situ ALD process, the interfacial traps which cause the frequency dispersion in p-GaAs MOSCAPs may be largely averted. These are different from other ALD-Al2O3/GaAs samples with various surface treatments, which need post annealing to improve their C–V characteristics.

In conclusion, comparing the C–V characteristics and the corresponding in situ XPS analyses has given the following observations; firstly, the disparity in C–V behaviors between n- and p-GaAs MOSCAPs may not come from any surface treatment and post-deposition annealing. Secondly, the distinct C–V behavior between n- and p-GaAs MOSCAPs was observed with the presence of Ga1+, and without the existence of Ga2O3, suggesting that Ga2O3 may not cause the disparity and the presence of Ga1+ may not ensure C–V characteristics with small frequency dispersion in the n-GaAs MOSCAPs. Thirdly, although the C–V frequency dispersion of n-GaAs MOSCAP was significantly improved after 550 °C N2 annealing, a larger dispersion than that of p-GaAs MOSCAP still appeared. Since only As0 and Ga1+ were detected at the interface of as-deposited and 550 °C N2 annealed samples, either one of them or both may account for the large dispersion C–V curves (thus higher Dn’s) in the n-type samples.

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Reference