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Effect of an *in situ* hydrogen plasma pre-treatment on the reduction of GaSb native oxides prior to atomic layer deposition

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ABSTRACT

The influence of an *in situ* hydrogen plasma pre-treatment on the modification of native oxides of GaSb surfaces prior to atomic layer deposition (ALD) is presented. The effects of varying rf-plasma power, exposure time, and substrate temperature have been characterized by atomic force microscopy (AFM), *ex situ* X-ray photoelectron spectroscopy (XPS), as well as capacitance–voltage (C–V) measurements on fabricated devices. Results indicate that a completely oxide free surface may not be necessary to produce a good electrical interface with a subsequent ALD Al_2O_3 dielectric; the most effective hydrogen plasma treatments resulted in the absence of Sb-oxides, a reduction in elemental Sb, and an increase in the Ga_2O_3 content at the interface. The use of an *in situ* hydrogen plasma pre-treatment eliminates the need for wet chemical etches and may also be relevant to the deposition of other high-k dielectrics, making it a promising technique for realizing high performance Sb-based MOS-devices.

1. Introduction

III–V compound semiconductors are attracting widespread attention as an alternative material to Si in advanced complementary metal–oxide–semiconductor (CMOS) applications; their high electron and hole mobilities, as well as relatively narrow bandgaps make them increasingly attractive for high-speed, low power applications [1–4]. A significant amount of work already exists on n-channel III–V metal–oxide–semiconductor field-effect transistors (MOSFETs) demonstrating excellent electron mobility and high drive currents [4–7]. However, hole mobility in III–V p-channel MOSFETs typically lags in comparison to Si [6]. Among the III–V semiconductors, GaSb is a promising material for both n- and p-channel devices due to its high electron and hole mobilities (bulk mobility ~6000 cm^2/Vs and 850 cm^2/Vs, respectively), which are found to be amongst the highest of the III–V semiconductor materials [6]. However, the poor quality of the gate oxide/GaSb interface has limited the use of GaSb in microelectronics. Unlike the silicon-silicon dioxide interface pair, the native oxide found on GaSb is complex in structure and composition, forming heavily defected interfaces that pin the semiconductor Fermi-level near midgap and limit the device's ability to modulate charge.

The increasing need to integrate high-k dielectric thin films into CMOS structures has led researchers to turn to atomic layer deposition (ALD) for insulator growth. ALD is a gas phase deposition technique that utilizes self-limiting chemistries in order to produce thin solid films with excellent atomic-level thickness control [8]. ALD is widely accepted as a means to produce high quality films over large surface areas with excellent uniformity and conformality [8,9]. These key attributes are inherent to the self-limiting nature of the ALD surface reactions: alternating reactant exposures of two gaseous precursors create a saturated chemisorbed surface which leads to film growth one sub-monolayer at a time [8]. The sequential behavior of the precursor exposures helps avoid the formation of gas-phase particles and creates thin, continuous, pin-hole-free films that are critical to the operation of CMOS devices. Therefore, particular attention should be focused on the development of techniques to form low-defect interfaces between III–V surfaces and high-k films deposited by ALD.

GaSb is known to have a highly reactive surface [10–12]. On exposure to air it will form a complex native oxide composed of not only Sb-oxides and Ga-oxides, but elemental Sb as well [12,13]. Therefore, a significant effort has been focused on surface preparations prior to ALD that remove native oxides and passivate GaSb atoms in order to ensure the best possible interface [14]. Current approaches for oxide removal primarily consist of wet etches, such as HCl [6,7,10,12,15], HF [15], $(NH_4)_2S$ [13,16], and NH_4OH [15,16]; however, due to the rapid re-oxidation of the GaSb after oxide removal and a general lack of reproducibility, a better means of interface cleaning is desirable. Recent progress in the field of ALD on III–Vs has led researchers to a proposed "self-cleaning" mechanism through the use of the ALD precursor trimethylaluminum

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(TMA), in which the native oxides are consumed during the initial TMA half-cycle [6,12,16–19]. While effective, this process has not been proven to be standalone for oxide removal, as it is typically preceded by a wet chemical etch that removes the bulk of the native oxide. Alternatively, hydrogen (H_2) plasma cleaning has been considered a potential candidate for efficient low temperature oxide removal from III–V semiconductors during molecular beam epitaxy (MBE) regrowth processes [20–23]. Under appropriate conditions, it has been shown that H_2-plasma treatments in ultra-high vacuum can result in high quality, defect-, impurity-, and oxide-free GaSb surfaces [19,20]. These observations suggest the usefulness of a H_2 plasma process for surface preparation prior to ALD, as well; however, to fully utilize this potential requires a full understanding of the oxide removal process and its effect on surface composition and roughness of the remaining surface.

In this work, we first evaluate the effectiveness of TMA as a standalone process by investigating the removal of native oxides on GaSb surfaces that have undergone no additional wet chemical treatment. Subsequently, we examine the use of an *in situ* H_2 plasma pre-treatment as a means to obtain a suitable electrical interface prior to the deposition of high-*k* Al_2O_3 films on GaSb substrates *via* plasma-enhanced ALD (PEALD). *Ex situ* X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), as well as capacitance–voltage (*C*–*V*) measurements, were performed to establish the effect of the rf-plasma power, substrate temperature, and plasma exposure time on the growth interface. Results indicate that a completely oxide-free surface may not be necessary to produce a good electrical interface.

2. Experimental

Epitaxial layers of GaSb (*p*-type, Be-doped 2×10^{17} cm^{-3}) were grown *via* molecular beam epitaxy (MBE) on bulk GaSb (100) wafers (unintentionally doped p-type). The substrate temperature was 460 °C, and the growth rate was 0.5 monolayers/s. Growth interrupts were used to ensure a smooth surface. The recipe was 55 repeats of 60 s GaSb/20 s Sb_2 interrupt, yielding 500 nm of GaSb.

Samples were allowed to oxidize in air at room temperature for one day and then cleaved into 3 mm × 5 mm pieces. Samples were loaded into a Beneq TFS-200 ALD viscous flow-type reactor equipped with a UHV load-lock chamber and setup in a remote plasma configuration. Plasmas were generated by capacitive coupling using a 13.56 MHz rf-power source. The distance between the sample and the grid, which acts as the bottom electrode, was 4 cm and ensured that samples were not in direct contact with the plasma. The H_2 plasma pre-treatment was typically performed using a rf plasma power of 50 W at a substrate temperature of 150 °C for 10 min, with the exception of when a plasma parameter was being investigated. Hydrogen gas (99.999%) was mixed with argon (99.999%) to ensure plasma ignition. The hydrogen and argon gases had flow rates of 20 sccm and 140 sccm, respectively. During plasma processing, the pressure within the reaction chamber was 1.5 Torr. After plasma exposure, samples were coated with 6 μ-pulses of the ALD precursor, trimethylaluminum (TMA). All TMA exposures were done at 150 °C and each μ-pulse was 150 ms followed by a 1 s argon purge to remove potentially reactive species from the reaction chamber.

Samples were unloaded from the ALD reactor and analyzed using an *ex situ* monochromatic X-ray photospectroscopy (XPS) with an Al Kα source in order to assess the subsequent surface chemistry. XPS spectra were fit with Thermo Avantage software using a Shirely baseline and corrections were made for charge shifting when the C 1s peak was not found to be at 285 eV. Investigations of the resulting surface morphology were performed using an *ex situ* Digital Instruments Atomic Force Microscope (AFM) (MultiMode^{TM} NanoScope® IV) in tapping mode with Si tips. AFM scans were taken over areas of 1 μm × 1 μm, 4 μm × 4 μm, and 10 μm × 10 μm.

To assess the electrical quality of the oxide/semiconductor interface, p-type GaSb (1 0 0) MOS capacitors were fabricated with high-*k* Al_2O_3 deposited *via* PEALD from TMA and oxygen plasma. Al_2O_3 films were deposited at a substrate temperature of 150 °C on H_2 plasma treated GaSb epilayer surfaces for 100 cycles, resulting in film thicknesses of ~16 nm. Film thicknesses were verified using *in situ* ellipsometry on concurrent silicon wafers. After the dielectric deposition, samples were annealed in a forming gas mixture of 9:1 N_2/H_2 at 350 °C for 30 min. MOS capacitors were fabricated and consisted of a Ti/Au (100/1000 Å) e-beam evaporated top gate, an oxide mesa defined using aqueous 10:1 buffered oxide etch, and a Pd/Pt/Au (120/100/1000 Å) e-beam evaporated top-side ohmic substrate contact. Frequency-resolved capacitance–voltage (*C*–*V*) measurements were acquired using a semiconductor characterization system at room temperature.

3. Results

3.1. TMA vs H_2 plasma

TMA half-cycle exposure has often been cited as a means for “self-cleaning” III–V surfaces prior to Al_2O_3 ALD [16,18]. However, its effectiveness as a standalone process, without prior use of wet chemical etches, has yet to be demonstrated. Furthermore, since all samples in this study were exposed to a TMA-passivation following the H_2 plasma treatment, it is important to understand the role of the TMA precursor in the oxide removal. Therefore, we compared the use of TMA without a wet chemical treatment, a H_2 plasma without TMA, and the combination of a H_2 plasma followed by exposure to TMA.

Fig. 1 displays XPS Sb 3d and Ga 3d core level spectra associated with the as-grown GaSb epilayer covered with a native oxide layer consisting of Sb-oxides and Ga-oxides as indicated by a shift to higher binding energies with respect to the “bulk” substrate features at 528 eV for Sb $3d_{5/2}$ and 19.1 eV for Ga 3d [11,16]. Detailed non-linear curve fitting for both the Sb 3d and the Ga 3d core levels (Fig. 1) indicates that Sb-oxide appears in the +4 (Sb_2O_4) valence form, which is a mixture of both Sb_2O_5 and Sb_2O_3 [11], and Ga-oxide is comprised of both the +1 state (Ga_2O) and the +3 state (Ga_2O_3), with peak positions found at 530.5 eV (Sb_2O_4), 20.1 eV (Ga_2O), and 20.7 eV (Ga_2O_3) [11,18]. The AFM image of Fig. 3a demonstrates the amorphous quality of the native oxide of the untreated GaSb surface, with an RMS roughness of 0.67 nm.

TMA-only samples were exposed to 6 μ-pulses of the TMA precursor (less than 1 s total exposure time) in order to ensure complete surface saturation. XPS spectra from this sample are plotted in Fig. 2b, with the as-grown epilayer data repeated in Fig. 2a for comparison. As evident by both the Sb 3d and the Ga 3d spectra, a considerable amount of oxide is left on the surface after TMA exposure. While oxide clearly remains, it is believed that overall, the native oxide was reduced by the TMA as indicated by the observation of an Al—O peak in the Al 2*p* spectra (not shown here), as well as the appearance of atomic terraces seen in the AFM image of Fig. 3b. The underlying principle of ALD is that it is a self-limiting process: once the surface is saturated with TMA, no more precursor can be adsorbed. Since there was no oxidizer half-cycle, the oxygen in the Al—O bonds had to come from a ligand exchange between the GaSb native oxide and the TMA precursor. Once the initial layer of Al_2O_3 was formed, no further reduction of the native oxide could take place by additional exposure to TMA, limiting the “clean up” effect of the TMA to only the first few monolayers. This is especially critical in the GaSb system, since the native oxide is on the order of 3–5 nm [10,11] thick, which is considerably greater than that found on Si.