## Interface of atomic layer deposited HfO<sub>2</sub> films on GaAs (100) surfaces

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 $HfO_2$  films have been deposited by using a tetrakis(dimethylamino)hafnium/H<sub>2</sub>O atomic layer deposition (ALD) process on GaAs. X-ray photoelectron spectroscopy measurements show that the HF and NH<sub>4</sub>OH predeposition surface treatment results in efficient removal of the Ga and As native oxides. No interface oxidation is detected after 15 cycles of HfO<sub>2</sub> ALD implying effective passivation of the GaAs surface. Spectroscopic ellipsometry confirms linear growth at 1.0 Å/cycle on both starting surfaces, while Rutherford backscattering spectrometry indicates steady-state coverage after about 10 ALD cycles. For films grown on native oxide GaAs, complete removal of the As oxide is observed after 20 ALD cycles. © 2008 American Institute of Physics. [DOI: 10.1063/1.2908223]

Utilizing III-V semiconductor materials such as GaAs for metal-oxide-semiconductor field-effect transistor applications offers a number of advantages over Si-based technology, stemming from increased carrier mobility and device flexibility.<sup>1</sup> However, realizing this potential has proven very difficult, partly due to the highly reactive GaAs surface. The complex native oxides of GaAs are quite unstable; they may dissolve and change state with exposure to light, moisture, or moderate heat treatment,<sup>2</sup> which presents a surface that is neither easily characterized nor passivated. New advances in Si-based integrated circuit technology have introduced a variety of materials for use as insulating gate oxides,<sup>3</sup> some of which have been found suitable for GaAs devices.<sup>1,4</sup> Recent results have also introduced promising methods of GaAs surface passivation such as thermal nitridation,<sup>5</sup> sulfur termination,<sup>6</sup> OH termination using NH<sub>4</sub>OH treatments,<sup>7</sup> and thin interlayers of metal oxides such as  $Gd_2O_3$ .<sup>4</sup> In this letter, we present a study of the effects of two different GaAs surface pretreatments involving HF and NH<sub>4</sub>OH and the subsequent early atomic layer deposition (ALD) HfO<sub>2</sub> growth on these surfaces as well as on native oxide surfaces.

Depositions were performed on lightly doped *n*-type GaAs(100) substrates treated by three different methods: (1) the native oxide surface was washed with acetone, then methanol, followed by a de-ionized (DI) water rinse and high-purity N2 blow dry; (2) etched in HF, the surface was first cleaned for 5 min with J.T. Baker-100 (JTB-100) solution and rinsed for 5 min with DI water, followed by a 20 s etch in 6:1 buffered oxide etch solution, DI water rinse, and  $N_2$  blow dry; (3) etched in NH<sub>4</sub>OH, the surface received the same initial JTB-100 clean and DI water rinse, followed by a 3 min dip in a 30%  $NH_4OH$  solution, DI water rinse, and  $N_2$ blow dry. All chemical treatments were carried out at room temperature. For x-ray photoelectron spectroscopy (XPS) measurements of the treated GaAs surfaces, samples were immediately loaded into a darkened ultrahigh-vacuum XPS chamber following the chemical treatment to minimize contamination from the atmosphere or degradation of the surface from light. Substrates being used for HfO<sub>2</sub> deposition were immediately loaded into a homemade hotwall flow tube ALD reactor. Deposition on substrates being used for further XPS analysis was simultaneously performed on both sample types to eliminate run-to-run variations. The ALD reactor as well as the Rutherford backscattering spectrometry (RBS) and spectroscopic ellipsometry (SE) measurement techniques have been described elsewhere.<sup>8</sup> Most of the compositional analysis of the samples was performed ex situ by a Kratos Ultra XPS spectrometer (monochromatic Al source, hv = 1486.6 eV) at 0° takeoff angle (normal emission) with a 0.1 eV step size for high-resolution scans. Sample charging effects were partially compensated for by using the system's electron flood gun neutralizer, as well as calibrating the energy scale with the As 3d substrate peak assigned to a binding energy of 41.1 eV.<sup>9</sup> For the samples in Figs. 3(a)and 3(b), XPS analysis was performed with an achromatic Al source. The XPS spectra were background corrected and then deconvolved by using mixed Gaussian/Lorentzian functions of  $\sim 2.3 \text{ eV}$  full width at half maximum for the As  $2p_{3/2}$  peak, ~1.0 eV for the As 3d doublet, and ~1.3 eV for the Ga  $2p_{3/2}$  peak. For the As 3*d* doublet, a ratio of 3:2 was assumed with a separation of 0.7 eV. The  $HfO_2$ depositions were performed at 275 °C by using tetrakis(dimethylamino)hafnium (TDMAH) and H<sub>2</sub>O and a 1-20-1-20 s TDMAH-purge-H<sub>2</sub>O-purge pulse sequence.

The results of the different GaAs surface preparations are summarized in the high-resolution XPS scans of the As  $2p_{3/2}$ , As 3*d*, and Ga  $2p_{3/2}$  photoelectron peaks shown in Fig. 1. Figure 1(a) displays a large amount of both As and Ga native oxides on the GaAs surface prior to any chemical treatment. From the binding energy offsets to the As and Ga substrate peaks, we assign these peaks to As<sub>2</sub>O<sub>3</sub>, As<sub>2</sub>O<sub>5</sub>, and Ga<sub>2</sub>O.<sup>9,10</sup> The initial surface treatment with JTB-100 completely removes the As<sub>2</sub>O<sub>5</sub> phase and a large amount of the other native oxides, as shown in Fig. 1(b). Both the NH<sub>4</sub>OH and HF etch remove most of the remaining surface oxides, as shown in Figs. 1(c) and 1(d), respectively. NH<sub>4</sub>OH appears to leave behind a thin layer of As suboxide, as evidenced by the secondary peak at 1325 eV in the As  $2p_{3/2}$  spectrum, in addition to a trace amount of As<sub>2</sub>O<sub>3</sub> and Ga<sub>2</sub>O shown in all three spectra in Fig. 1(c). The HF treatment slightly im-

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FIG. 1. XPS spectra of the As  $2p_{3/2}$ , As 3d, and Ga  $2p_{3/2}$  peaks for the GaAs substrate surface (a) as received, (b) after JTB-100 treatment, (c) after NH<sub>4</sub>OH treatment, and (d) after HF treatment.

proves over NH<sub>4</sub>OH, removing more of both native oxides. As expected, due to the low kinetic energy of the photoelectrons, the As  $2p_{3/2}$  peak is substantially more sensitive to the presence of the surface oxides than the As 3*d*. In the As  $2p_{3/2}$  region, we observe that a clear As oxide shoulder is present at a binding energy of about 1326 eV after both chemical treatments. The oxide peak in the As 3*d* region is barely detectable after the NH<sub>4</sub>OH dip and below detection limits following the HF treatment.

SE measurements indicate a linear  $HfO_2$  growth per cycle (GPC) of 1.0 Å/cycle on both the HF and  $NH_4OH$  treated starting surfaces (data not shown). RBS measurements of hafnium coverage on HF-last samples ranging from 1 to 300 ALD cycles show that steady-state growth is attained after about 10 ALD cycles, reaching a GPC of 2.6  $\times 10^{14}$  Hf/cm<sup>2</sup> (Fig. 2). The steady-state GPC is similar to that obtained for HfO<sub>2</sub> deposition on Si(100) substrates using the same ALD chemistry. Unlike Si–H surfaces, there is also no noticeable HfO<sub>2</sub> growth barrier during the first few ALD cycles.<sup>8</sup>

By examining the initial  $HfO_2$  growth on both GaAs starting surfaces, we observe no substantial As oxide intensity in the As 3*d* region for a 15 cycle sample [Figs. 3(a) and 3(b)]. This implies that both the HF and NH<sub>4</sub>OH surface treatments effectively passivate the GaAs surface and discourage regrowth of As oxide during the HfO<sub>2</sub> film growth.



FIG. 2. RBS Hf coverage on the HF-treated surface. Steady-state GPC is reached after  ${\sim}10$  cycles.

Shown in Figs. 3(c) and 3(d) are the As 3*d* and  $2p_{3/2}$  XPS spectra for 15 and 20 ALD cycle films grown on native oxide GaAs. Comparing the spectra from Figs. 1(a) and 3(c), we observe a significant reduction in the As oxide intensity after the first 15 ALD cycles, which is further reduced after 20 ALD cycles. A 100 cycle sample deposited on the native oxide was sputtered with a low-current Ar<sup>+</sup> ion beam inside the XPS chamber to remove enough HfO<sub>2</sub> in order to make the underlying GaAs substrate signal visible; again, no As oxide is detected in the As 3*d* or As  $2p_{3/2}$  region [Fig. 3(e)]. A similar effect is observed with the Ga<sub>2</sub>O peak in the Ga



FIG. 3. XPS As 3*d* spectra for 15-cycle HfO<sub>2</sub> films on (a) HF-GaAs and (b) NH<sub>4</sub>OH-GaAs; As  $2p_{3/2}$  and As 3*d* spectra of HfO<sub>2</sub> films deposited on native oxide GaAs after (c) 15 ALD cycles, (d) 20 cycles, and (e) 100 cycles after sputtering.

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 $2p_{3/2}$  region (data not shown). The Ga oxide signal decreases in intensity as we proceed from 15 to 100 cycle HfO<sub>2</sub> films (including the Ar<sup>+</sup> sputtered sample), which indicates a thinning of the Ga oxide layer. The effect, however, is not as pronounced as the As oxide removal. There have been previous reports of As oxide consumption during an ALD process when using metal organic precursors, such as trimethylaluminum (TMA) and tetrakis(ethylmethylamino)hafnium (TEMAH).<sup>11–13</sup> A recent letter by Shahrjerdi *et al.* describing HfO<sub>2</sub> deposition on GaAs from TDMAH and H<sub>2</sub>O does not report As oxide consumption after ALD on a native oxide surface;<sup>14</sup> however, the exact mechanism behind this phenomenon is unknown, so it is quite possible that differences in experimental procedure may account for this conflict in results. It has been proposed that the oxide consumption operates through ligand exchange reactions at the HfO<sub>2</sub> surface with organic-amide precursors.<sup>15</sup> Ga and As species diffuse through the thin HfO<sub>2</sub> layer and undergo a substitution reaction with the Hf precursors, which in turn volatilizes the Ga or As species. This reaction mechanism implies that the oxide removal should be related to precursor exposure; 1 ML of adsorbed Hf precursor would ideally result in a monolayer of As oxide consumption. Our ALD process requires more than 15 cycles to consume the native As oxide. Native oxide thickness on untreated GaAs(100) wafers has been determined to be  $\sim 16$  Å,<sup>2</sup> which roughly agrees with our ellipsometry measurements.

In conclusion, predeposition treatment of GaAs(100) surfaces with HF and  $NH_4OH$  results in the efficient removal of the native oxides leaving behind trace amounts of  $As_2O_3$  and  $Ga_2O$ ; XPS indicates that the treated GaAs surface is also passivated against As oxide regrowth during HfO<sub>2</sub> ALD from TDMAH and H<sub>2</sub>O. Steady-state Hf coverage rates are quickly achieved on the HF-treated surface, with a growth rate of 1.0 Å/cycle. Native As oxide consumption is observed after 15 ALD cycles, corroborating earlier observa-

tions for an interfacial "self-cleaning" mechanism during ALD processes that utilize TMA and TEMAH precursors.

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