Atomic Layer Deposition of Metal Oxide Films on GaAs (100) surfaces

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ABSTRACT

Atomic Layer Deposition is used to deposit HfO_2 and TiO_2 films on GaAs (100) native oxides and etched surfaces. For the deposition of HfO_2 films two different but similar ALD chemistries are used: i) tetrakis dimethyl amido hafnium (TDMAHf) and H_2O at 275°C and ii) tetrakis ethylmethyl amido hafnium (TEMAHf) and H_2O at 250°C. TiO_2 films are deposited from tetrakis dimethyl amido titanium (TDMATi) and H_2O at 200°C. Rutherford Back Scattering shows linear film growth for all processes. The film/substrate interface is examined using x-ray photoelectron spectroscopy and confirms the presence of an "interfacial cleaning" mechanism.

INTRODUCTION

The deposition of high dielectric constant (high-k) films on Si surfaces has been studied extensively as a means to extend the lifetime of Si-based microelectronics. One of the major issues in the integration of high-k materials with Si is the inadvertent formation of SiO_2 interfacial layers even for oxides that are predicted to be thermodynamically stable on Si surfaces.[1-2] High mobility substrates such as GaAs and InGaAs have better electrical properties than Si but their use in the semiconductor industry has been hindered by the poor electrical quality of their native oxides.[3] However, high-k dielectrics can be deposited on any semiconductor surface and there are several recent reports of good quality devices using high-ks on GaAs surfaces.[4] Most interestingly, there are several reports of an interface etching reaction taking placing during the ALD of HfO_2 and Al_2O_3 on native oxide covered GaAs surfaces that results in a very thin interfacial layer between the high-k film and the GaAs substrate.[5-12]The common thread of all these observations is the use of metal organic precursors as the metal source. In this article we examine the evolution of the high-k/GaAs interface for three ALD processes that use metal organic precursors of the amide family.

EXPERIMENT

Film depositions were performed in a hot-wall reactor described elsewhere.[13] HfO_2 films were deposited using two different metal organic amide precursors. i) tetrakis dimethyl amido hafnium (TDMAHf) and H_2O at 275°C and ii) tetrakis ethylmethyl amido hafnium (TEMAHf) and H_2O at 250°C. For the deposition of TiO_2 films tetrakis dimethyl amido titanium (TDMATi) and H_2O were used at 200°C. Three different starting surfaces are examined. Surfaces termed "native oxide" were prepared by cleaning pieces of GaAs (100) wafers in acetone, methanol, rinsing in deionized (DI) water and blown dry in a N_2 stream. This preparation has been shown to preserve the surface native oxides.[11] Surfaces with very little oxide coverage can be prepared by: 5 min soak in JT Baker 100 (JTB) solution, 5 min rinse in DI

water, and then by either etching for 30 s in Buffered Oxide Etch (BOE) and quick DI and N_2 blow dry ("HF" surfaces) or etching for 3 min in 30 % aqueous NH_4OH solution ("NH_4OH" surfaces). Si control samples were prepared by soaking pieces of native oxide covered Si (100) wafers in JTB for 5 min, followed by 5 min DI rinse and N_2 blow dry.

Ex-situ x-ray photoelectron spectroscopy (XPS) was used to examine the composition of the interface and performed with a Kratos AXIS 165 (Al x-ray source, 1486.6 eV), equipped with a hemispherical analyzer (165 mm radius). The high resolution spectra were baseline corrected using Shirley backgrounds and deconvolved using Gaussian-Lorentzian functions. The substrate As $3d_{5/2}$ and $_{3/2}$ doublet was deconvolved by assuming functions of equal Full width at Half Maximum (FWHM), a spin-orbit separation of 0.7 eV and intensity ratio of 3:2. Sample charging effects were corrected by placing the substrate As $3d_{5/2}$ peak (As-Ga) at a binding energy (BE) of 41.1 eV and shifting the rest of the regions accordingly.[14] For the contribution of the various arsenic oxides (As_2O_3, As_2O_5, AsO_x) in the 3d region a single function was found sufficient due to the well resolved substrate and oxide peaks. Due to the complexity of the Ga $2p_{3/2}$ region the spectra were fitted using 2 peaks, one corresponding to the substrate peak (Ga-As), and another representing the total contribution of the gallium oxides.

Rutherford backscattering spectrometry (RBS) measurements were made using a 1.2 MeV He$^+$ beam obtained from a National Electrostatics 5SDH-2 positive ion accelerator. The backscattering angle was 170 degrees, and the spectra were collected using a surface barrier detector subtending approximately 5 millisteradians. The raw RBS data was fitted using the simulation program RUMP.[15]

RESULTS

TEMAHf + H₂O

Figure 1 shows high resolution XP spectra for the As 3d and Ga $2p_{3/2}$ regions for the starting surface and after 25 ALD cycles that result in the deposition of ~30Å of HfO_2 film. The starting surface is cleaned GaAs (100) covered with ~26Å of native oxide. The presence of the HfO_2 layer in sample (b) reduces the overall intensity of both the substrate and the oxides peaks. However the ratio of the integrated oxide intensity to the integrated substrate As 3d or Ga $2p_{3/2}$ intensity is independent of the overlayer thickness as the photoelectrons from both regions are attenuated by the same exponential factor when crossing the HfO_2 layer. For the As 3d
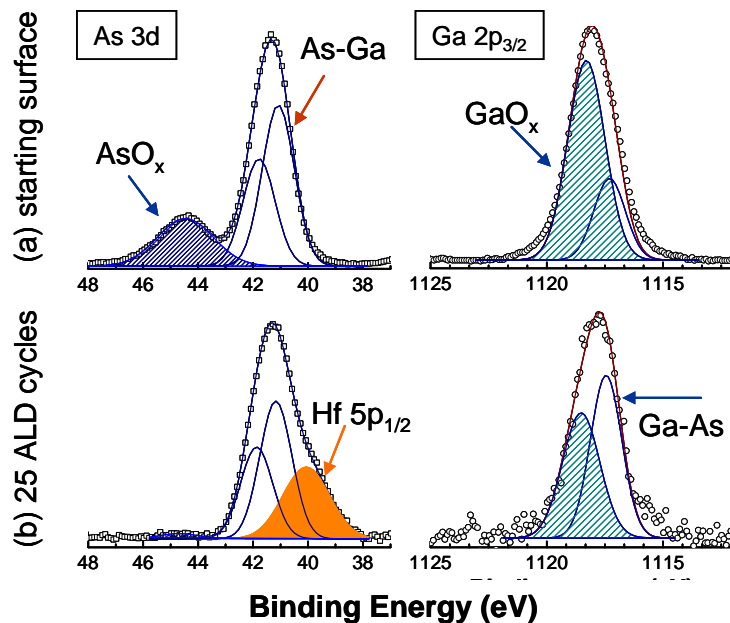

Figure 1. As 3d and Ga $2p_{3/2}$ high resolution XP spectra for (a) the starting native oxide GaAs (100) surface, and (B) after the deposition of ~30Å of HfO_2 from TEMAHf and H_2O.

region the ratio of the oxide to the substrate peak decreases from 0.31±0.04 for the starting surface to 0.03±0.01 after the deposition of ~30Å of HfO_2.This reduction is clearly evident in comparing spectra (a) and (b). The very small separation in the binding energy of the Ga substrate peak and that of the oxides makes direct observation of the Ga oxide intensity reduction harder. However, upon closer inspection clear differences are seen in the shape of the peak between samples (a) and (b). Peak (a) exhibits a low BE tail while peak (b) exhibits a high BE tail indicating a change in the mixture of the constituent peaks. Peak deconvolution reveals that the ratio of the integrated Ga oxide intensity to that of the substrate changes from 2.9±0.4 for the starting surface to 0.9±0.1 after 25 ALD cycles. The validity of the parameters used in the peak deconvolution especially for the Ga $2p_{3/2}$ is demonstrated in Figure 2 that shows the same spectral regions for 20 cycle films (~25Å of HfO2) deposited on etched GaAs surfaces. Both treatments ("HF" and "NH4OH") have been shown to remove most of the surface native oxides.[11] After the deposition of a small amount of interfacial oxide is detected but the FWHM of the Ga $2p_{3/2}$ peak is clearly smaller providing the essential parameters to deconvolve the rest of the Ga $2p_{3/2}$ peaks.
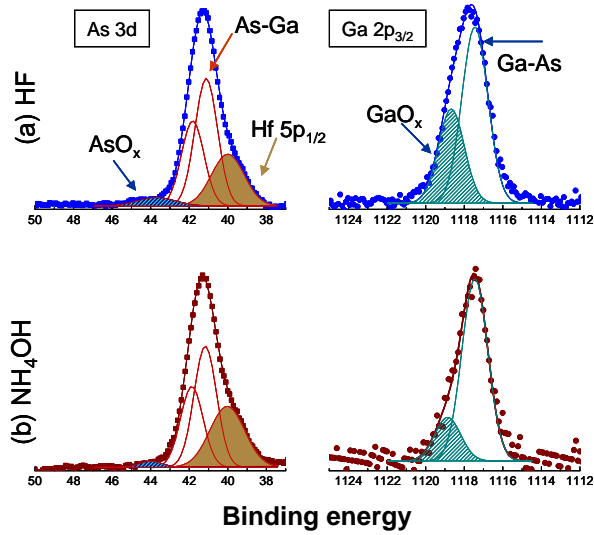
Figure 2. As 3d and Ga $2p_{3/2}$ spectra for samples of ~25Å of HfO_2 deposited on GaAs surfaces treated in HF and NH4OH solutions..
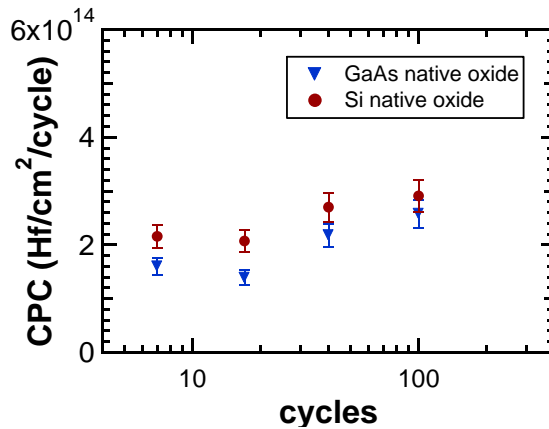
Figure 3. Hf atom surface coverage per cycle for cleaned native oxide GaAs (100) surfaces and Si native oxide control samples.

Figure 3 shows Hf atom coverage per cycle measured by RBS for films deposited simultaneously on GaAs cleaned native oxide and Si control samples. Similar to previous observations the Hf atom coverage per cycle (CPC) is initially low but appears to reach a steady state value of ~2.7×10^{14} cm^{-2} after ~40 process cycles.

TDMAHf + H$_2$O

Figure 4 shows high resolution XP spectra for the As 3d and Ga $2p_{3/2}$ regions for 15, 20 and 100 cycle films deposited on native oxide starting surfaces similar to those shown on Figure 1 (a). The nominal HfO_2 thickness of these samples is 15, 20 and 100 Å.[16] For the 100 cycle film the HfO_2 layer was ion etched in the XPS chamber until the substrate peaks were clearly visible. As evidenced by the presence of the Hf $5p_{1/2}$ peak some of the HfO_2 layer was left to preserve the integrity of the interface. The sequence of the data shows a gradual removal of the interfacial Ga and As oxides. As oxides are removed easier; there is practically zero intensity for the 20 cycle film. Ga oxides persist longer and even after 100 ALD cycles a monolayer or two is still present in the interface.
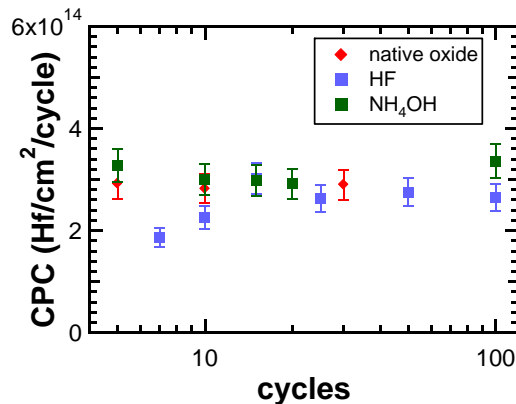
Figure 5 shows Hf atom coverage per cycle (CPC) measured by RBS for films deposited on GaAs native oxide, "HF" and "NH4OH" surfaces. The coverage reached reaches a steady state value of $\sim2.9 \times 10^{14}$ cm^{-2} for all three starting surfaces after ~20 process cycles.

TDMATi + H_2O

Figure 6 shows high resolution XP spectra for the As 3d and Ga $2p_{3/2}$ regions for the starting surface and after 60 ALD cycles that result in the deposition of ~35Å of TiO_2 film. For the As 3d region the ratio of the oxide to the substrate peak decreases from 0.53 ± 0.08 for the starting surface to 0.19 ± 0.03 for the ~35Å TiO_2 sample. This reduction is clearly evident in comparing spectra (a) and (b). For
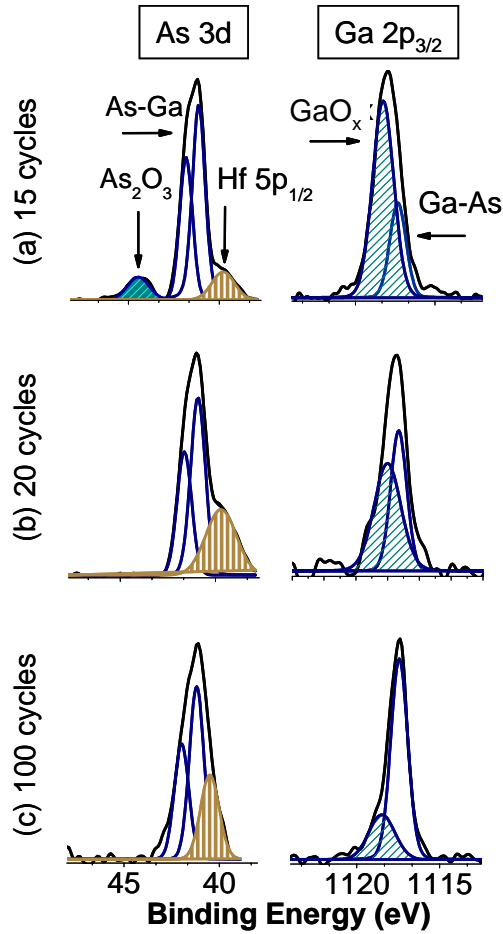
Figure 4. As 3d and Ga $2p_{3/2}$ high resolution XP spectra for 15, 20, and 100 cycle HfO2 films deposited on native oxide GaAs (100) surfaces from TDMAHf and H_2O.

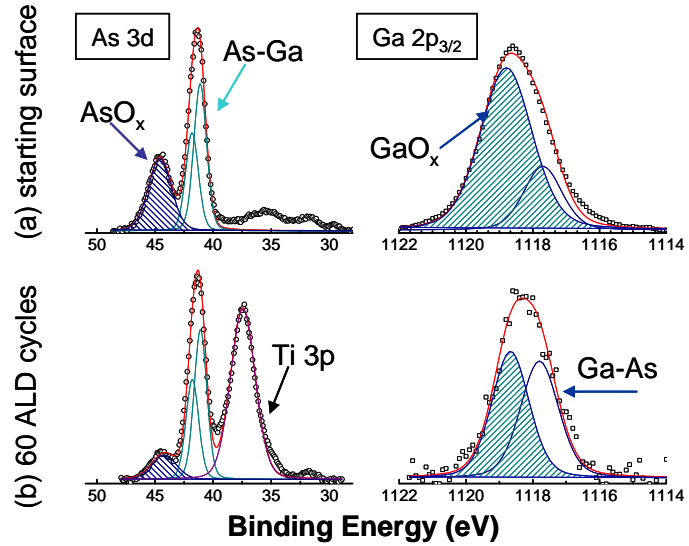**Figure 5.** Hf atom surface coverage per cycle on various GaAs surfaces measured by RBS.

the Ga 2p 3/2 peak, deconvolution reveals that the ratio of the integrated Ga oxide intensity to that of the substrate changes from 3.4±0.5 for the starting surface to 1.1±0.2 after 60 ALD cycles.

Figure 7 shows Ti atom coverage per cycle (CPC) measured by RBS for films deposited on Si native oxide surfaces. The coverage is has a steady state value of ~1.4 x10^{14} cm^{-2}. The Ti atom surface coverage on GaAs surfaces can not be measured by RBS. However, based on the results for the ALD of HfO$_2$ on GaAs we do not expect significant difference in surface coverage between the Si native oxide and GaAs native oxide.
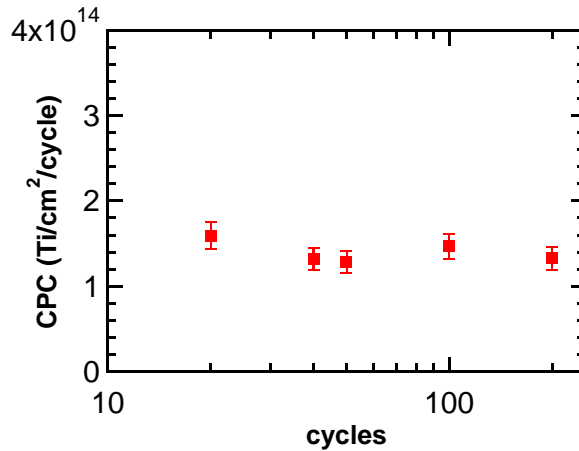

Figure 6. As 3d and Ga 2p$_{3/2}$ high resolution XP spectra for (a) the starting native oxide GaAs surface, and (b) after the deposition of ~40Å of TiO$_2$ from TDMATi and H$_2$O.

DISCUSSION

When native oxide GaAs substrates are used as a starting surface, the ALD of HfO$_2$ and TiO$_2$ results in the gradual thinning of the surface As and Ga oxides. Arsenic oxides are easier to remove while a monolayer or two of the gallium oxides remains at the interface even after 100 Å of HfO$_2$ has been deposited. The common feature behind these observations is the use of amide metal organic precursors. Two of the precursors (TDMAHf and TDMATi) have exactly the same structure while the

Figure 7. Ti atom coverage per cycle on Si native oxide surfaces measured by RBS.

third (TEMAHf) is a common variant in which one of the methyl ligands has been replaced by an ethyl ligand. It appears that one of the ALD reaction byproducts, an amine HNR$_1$R$_2$ where R$_1$ and R$_2$ are either ethyl of methyl groups may be responsible for the etching reaction. Evidence in support of this are:

a. A gradual reduction in the oxide intensity (relative to the substrate intensity) as a function of film thickness is observed for coalesced TiO$_2$ and HfO$_2$ films. High-k films coalescence is required to prevent postdeposition oxidation of the interface.

b. For the three ALD processes examined in this work, the process that results in the lowest film growth rate requires more ALD cycles to complete the oxide removal. The TiO$_2$ process that achieves the lowest metal surface coverage requires in excess of 60 ALD cycles to reach ~60% decrease in the As oxide signal intensity. By contrast the TDMAHf process that has a

substantially higher growth rate requires only about 20 ALD cycles to reach almost complete removal of the As oxide.

Further supporting evidence can be found in the reports of surface oxide removal caused by the thermal decomposition of metal organic molecules such as tris dimethyl amino arsenic on GaAs surfaces.[17-18]

ACKNOWLEDGMENTS

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