

Atomic Layer Deposition of HfO₂ Thin Films on Si and GaAs Substrates

Justin C Hackley¹, J. Derek Demaree², and Theodosia Gougousi¹

¹Physics, UMBC, 1000 Hilltop Circle, Baltimore, MD, 21250

²Weapons and Materials Research Directorate, Army Research Laboratory, Aberdeen Proving Ground, MD, 21005-5069

ABSTRACT

The atomic layer deposition of HfO₂ thin films is studied on Si(100) and GaAs(100) surfaces. The films are grown using tetrakis(dimethyl)amino hafnium (TDMAH) and H₂O precursors at a deposition temperature of 275°C. The Si surfaces used include a H-terminated surface and an OH-rich chemical oxide. GaAs substrates are subjected to two different pre-deposition treatments involving an HF and a NH₄OH wet chemical etch that has been shown to remove most of the Ga and As native oxides. Spectroscopic ellipsometry (SE) confirms linear growth rates of 1.05±0.05 Å/cycle for all surfaces. Rutherford backscattering spectrometry (RBS) shows that steady-state growth of 2.6×10¹⁴ Hf/cm²/cycle is reached after 10 ALD cycles for the HF-etched GaAs surface. X-ray photoelectron spectroscopy (XPS) indicates the presence of native oxides on both GaAs starting surfaces after 10 cycles due to postdeposition surface oxidation. However, the presence of the native oxide is not detected for thicker 15 and 20 cycle samples indicating passivation of the surface and suppression of the interfacial layer formation.

INTRODUCTION

Atomic Layer Deposition (ALD) is currently considered an enabling technology for the deposition of high quality films in applications that require high accuracy in the film composition and thickness.¹ It is based on a self-limiting, complementary surface reaction that depends on the presence of “reactive” functional groups on the surface that is to be coated.² For example, OH- terminated Si surfaces (Si-OH) have been shown to be amenable to the growth of high quality oxides while H-terminated Si (Si-H) surfaces have been shown to be unfavorable to such growth resulting in rougher and less dense films.³ This view has been challenged recently from results that have shown efficient growth of HfO₂ films on Si-H at 100°C using amide precursors and heavy water.⁴

Hf-based oxides have received increased attention in the past few years as potential replacements of SiO₂ as gate dielectrics in Metal Oxide Semiconductor Field Effect Transistors (MOSFET).⁵ However, one of the major issues with the application of alternative higher k-dielectrics on Si for MOSFET devices is the reduced mobility of the carriers.⁶ As a result, alternative channel materials such as strained Si, Ge and even III-IV semiconductors such as GaAs are currently under investigation. GaAs has electrical properties significantly superior to those of Si but its native oxides are of very poor quality rendering them unusable for high quality devices.⁷ High-k dielectrics have been successfully deposited on various starting surfaces using an array of techniques such as ALD, chemical vapor deposition, physical vapor deposition,

etc.^{8,9,10} As a result, one of the road blocks for the use of alternative substrates to Si may have been removed. In this manuscript we present some of our results on the ALD of HfO₂ films on Si and GaAs surfaces.

EXPERIMENT

The HfO₂ films were deposited using a home built hot-wall flow type reactor that is computer-controlled via a Labview ® routine. The tetrakis(dimethyl)amino hafnium (TDMAH) was purchased from Sigma-Aldrich in a sealed glass ampoule and transferred in a stainless steel vessel in a nitrogen atmosphere. The TDMAH container was then attached to a modular delivery system that was placed in an oven to ensure uniform heating of all surfaces and lines. H₂O was used as the oxidizing agent. The air and or nitrogen were removed from the storage vessels using several freeze, pump, and thaw cycles at liquid nitrogen temperature. Both reagents were delivered using the fixed volume approach described by Hausmann et al.¹¹ To ensure sufficient vapor pressure the TDMAH container was heated to 70°C degrees and the water vessel was kept at room temperature.

Si substrates were prepared by degreasing in J.T. Baker 100 solution (JTB-100) (5min), de-ionized (DI) water rinse (5 min) and either i) 20s etch in Buffered Oxide Etch (BOE) to produce Si-H surfaces or ii) growth of a 15-18 Å high quality chemical oxide using the SC1 recipe.¹² GaAs substrate were prepared by degreasing in JTB-100 solution (5min), DI water rinse (DI) (5 min) and either i) 20s etch in BOE or ii) 3 min etch in a 30% NH₄OH solution. All samples were blown-dry by nitrogen prior to loading in the reactor. The reactor is equipped with a turbo pump that allows quick pump down after venting. Deposition on the differently prepared Si and GaAs surfaces was performed simultaneously for each substrate to minimize the effect of run-to-run process variation.

Film thickness was measured using fixed-angle (70°) spectroscopic ellipsometry (380-900 nm), and the values reported represent the mean of five measurements over a typical sample size of 1.5x1.5 cm. XPS of the interface region was performed using an Al achromatic source, $h\nu=1486.6\text{eV}$. The energy scale was calibrated against the As 3d substrate peak, assigned to a binding energy of 41.1 eV.¹³ High resolution scans were obtained at 0.1 eV step size. Hf surface coverage was measured by RBS using a 1.2 MeV He⁺ beam obtained from a National Electrostatics 5SDH-2 positive ion accelerator.

RESULTS AND DISCUSSION

Spectroscopic ellipsometry has been used to determine the ALD window¹ and Figure 1 shows the growth rate per cycle (GPC) on a Si native oxide surface as a function of substrate temperature and purge time. The GPC reaches a minimum at 275°C and that process temperature was chosen for all the samples examined in this work. The dependence of the GPC on the purge

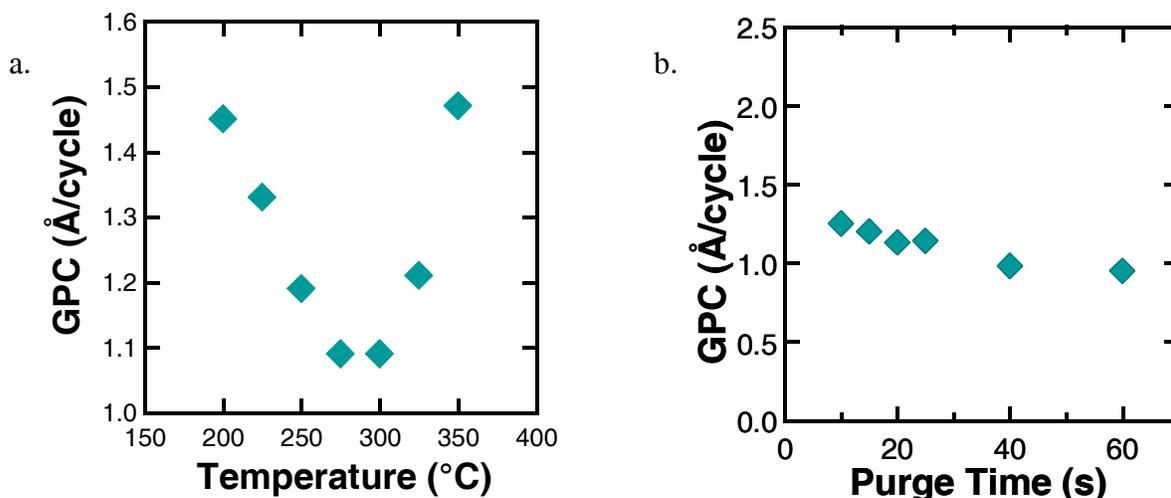


Figure 1. Determination of the ALD conditions for growth on Si surfaces. (a) GPC as a function of substrate temperature, (b) GPC at 275°C vs. purge time.

time has been investigated at well. Figure 1b shows the dependence of the GPC at 275°C on the purge time; after 30s it has practically stabilized and a purge time of 30s has been used for the samples deposited on Si. For the samples deposited on GaAs surfaces a 20s purge time between precursor pulses was found sufficient.

Growth of HfO₂ films on the various starting surfaces was studied using spectroscopic ellipsometry and the results are shown on Figure 2. Figure 2 a shows HfO₂ films thickness as a function of ALD cycles for Si-H and Si-OH while Figure 2b shows similar results for GaAs surfaces treated in BOE and NH₄OH solutions. For depositions that result in coalesced films the GPC is identical at 1.0Å/cycle for both Si starting surfaces, although deposition on Si-OH results

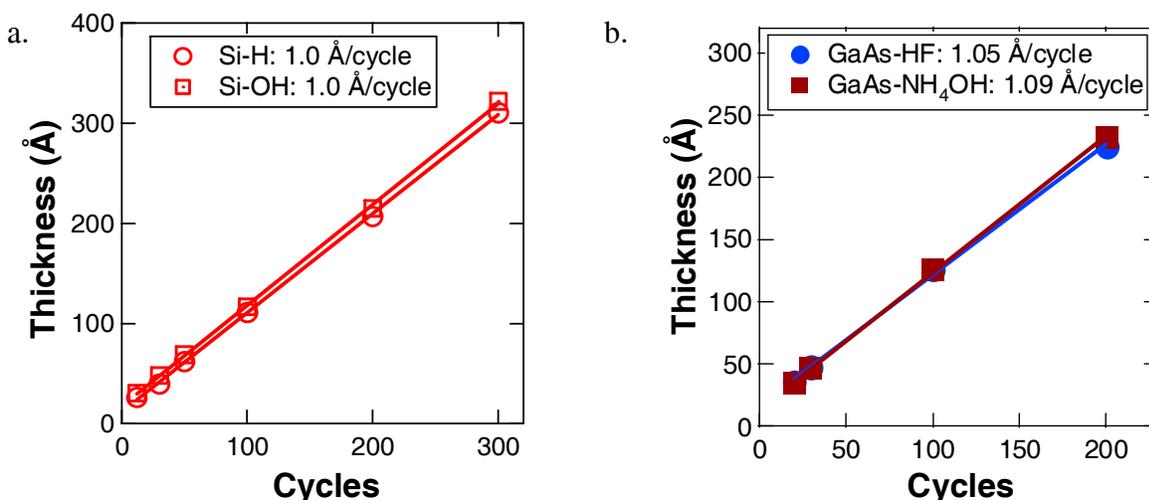


Figure 2. HfO₂ thickness as a function of ALD cycle number measured by for (a) Si surfaces, and (b) GaAs surfaces.

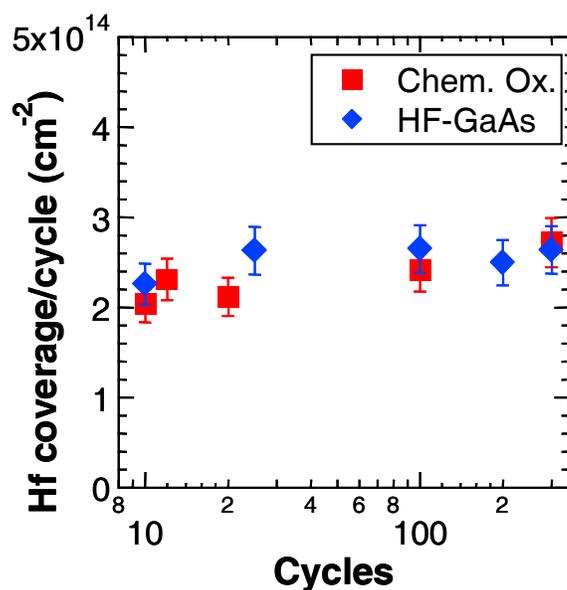


Figure 3. Hf surface coverage per ALD cycle as measured by RBS for Si-OH (squares) and HF (BOE) treated GaAs (diamonds) surfaces. After 10 cycles the Hf coverage reaches its steady state value.

in marginally thicker films. This is probably due to the fact that Si-H surfaces have been shown to present a nucleation barrier for this set of precursors resulting in lower Hf coverage for the initial 4 process cycles.¹⁴ Once the deposition reaches steady state the growth rate is similar for both surfaces. The GPC achieved for the two GaAs surfaces is similar albeit somewhat higher than that obtained for Si. An average GPC of $1.05 \pm 0.05 \text{ \AA/cycle}$ can be reported for all starting surfaces in good agreement with the results reported by Kukli et al.¹⁵

Figure 3 shows the Hf atomic surface coverage per cycle as measured by RBS for samples ranging from 10 to 300 cycles and deposited on Si-OH and GaAs etched in BOE. At 10 cycles the GPC for both surfaces has practically reached its steady state value indicating that both surfaces are amenable to efficient film growth. Our recent results on the surface treatment of GaAs surfaces has shown that after the 20 s BOE etch the surface is covered by approximately a monolayer of the native oxides and it appears that the presence of that is sufficient to ensure efficient film nucleation.¹⁶ By contrast, we have shown that the BOE treated Si surfaces (Si-H) present a barrier to film growth and for the first 4-7 cycles the Hf coverage is significantly lower than that obtained for Si-OH (SC1) surfaces. On Si-H surfaces steady state growth is achieved after 20 process cycles and is accompanied by the formation of an 8-10 Å interfacial layer.¹⁴ The HfO₂/GaAs interface was examined for both BOE and NH₄OH treated starting surfaces and the As 3d and Ga 2p regions for films of 5, 10, 15 and 20 cycles are presented on Figure 4. One can observe the presence of As oxides for the 5 and 10 cycle films while no such observation can be made for the thicker 15 and 20 cycle films. Since we have already established that both BOE and NH₄OH etches practically remove the native As oxides, the reappearance of these peaks in the XPS spectrum for the low cycle films can be explained in terms of postdeposition reoxidation of the interface due to the presence of a non-coalesced HfO₂ film. The broadening of the Ga 2p peaks for the 5 and 10 cycle samples can be explained similarly. In the As 3d region the growth

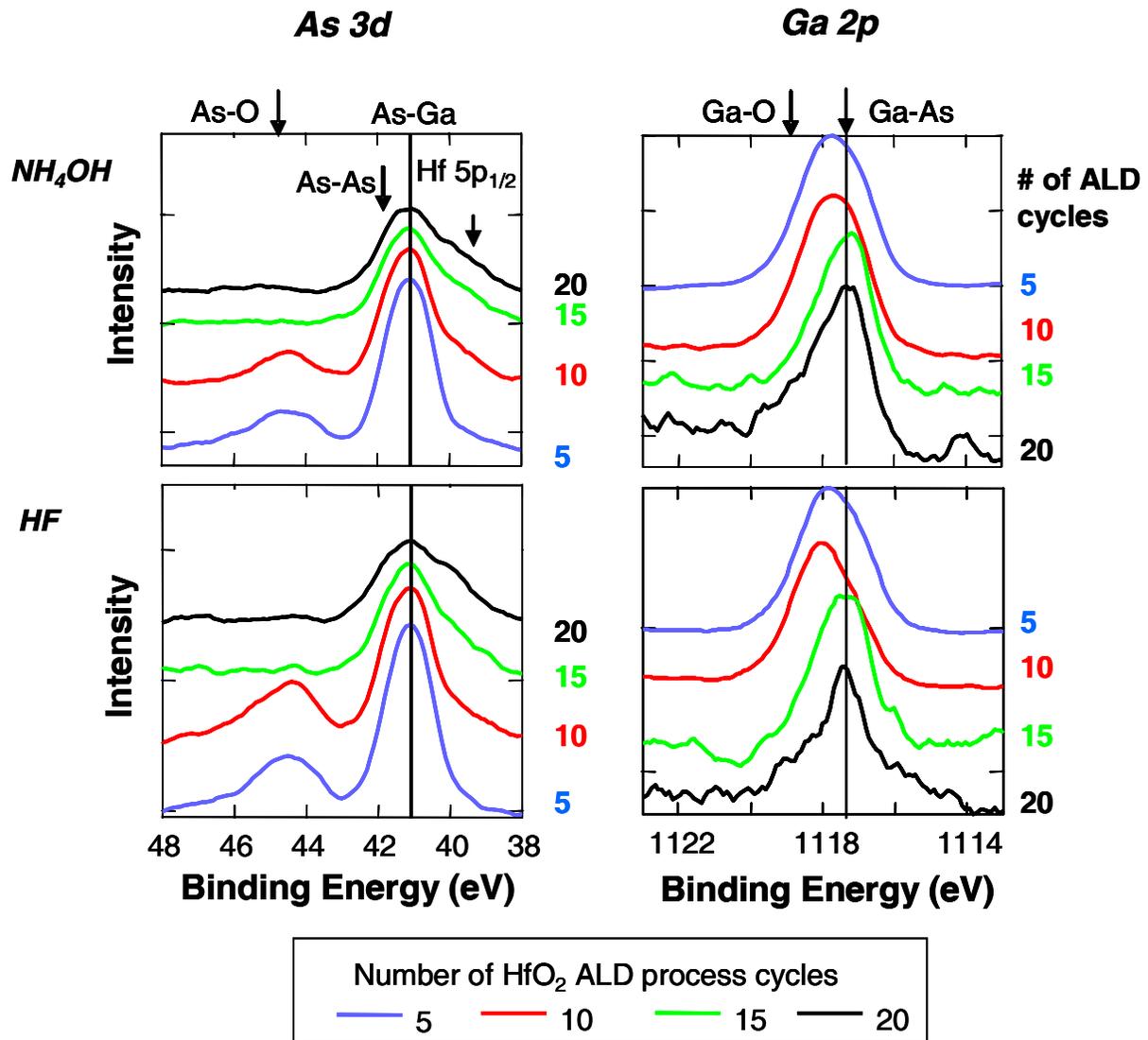


Figure 4. High resolution XP spectra for the As 3d and Ga 2p regions for a series of HfO₂ films deposited on HF(BOE) and NH₄OH treated surfaces. The presence of native oxides is detected after 5 and 10 ALD HfO₂ cycles but not for the 15 and 20 cycle samples. As the starting surface is practically native-oxide free, the above observations can be explained in terms of postdeposition oxidation of the interface. For coalesced HfO₂ films the passivated GaAs surface is protected from either in-process or postdeposition oxidation.

of the HfO₂ film can be observed by the appearance of a shoulder at 39.5 eV due to the Hf 5p_{1/2} photoelectrons. After 15 ALD cycles the HfO₂ overlayer is sufficiently thick to ensure complete surface coverage and the passivated GaAs surface is protected from further oxidation. Deposition of similar HfO₂ films on native oxide GaAs surfaces has resulted in complete consumption of the As-oxides after 15 ALD cycles indicating the presence of an “interfacial cleaning” mechanism.¹⁶

CONCLUSIONS

The ALD of HfO₂ films from TDMAH/H₂O precursors at 275°C has been studied on Si and GaAs surfaces. Both Si-H and Si-OH surfaces as well as HF and NH₄OH-etched GaAs surfaces result in a similar GPC of 1.05±0.05 Å/cycle. RBS shows that the growth on Si-OH and HF-GaAs reaches its steady state after 10 process cycles. Both the HF and NH₄OH treatment passivate the GaAs surface and prevent the formation of interfacial layers for coalesced HfO₂ films.

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