Mater. Res. Soc. Symp. Proc. Vol. 996 © 2007 Materials Research Society 0996-H03-09

Nucleation Studies of HfO_2 Thin Films Produced by Atomic Layer Deposition

Justin C. Hackley[1], J. Derek Demaree[2], and Theodosia Gougousi[1]
[1]Physics, UMBC, 1000 Hilltop Circle, Baltimore, MD, 21250
[2]Weapons & Materials Research Directorate, Army Research Laboratory, Aberdeen Proving Ground, Aberdeen, MD, 21005-5069

ABSTRACT

A hot wall Atomic Layer Deposition (ALD) flow reactor equipped with a Quartz Crystal Microbalance (QCM) has been used for the deposition of HfO_2 thin films with tetrakis (dimethylamino) hafnium (TDMAH) and H_2O as precursors. HfO_2 films were deposited on H-terminated Si and SC1 chemical oxide starting surfaces. Spectroscopic ellipsometry (SE) and QCM measurements confirm linear growth of the films at a substrate temperature of 275°C. FTIR spectra indicate the films are amorphous as-deposited. Two distinct growth regimes are observed: from 1-50 cycles, both surfaces display similar growth rates of about 1.0 Å/cycle; from 50-200 cycles, HfO_2 growth is decreased by about 15% to ~0.87 Å/cycle on both surfaces. Nucleation and initial growth behavior of the films on Si-H were examined using X-ray photoelectron spectroscopy (XPS). Angle-resolved XPS, at take-off angles of θ=0, 15, 30, 45 and 60° measured from the normal to the sample surface, is used to probe the interfacial region of thin films (4, 7, 10, 15 and 25 cycles) on H-terminated samples. Initially, an interfacial layer comprised of a SiO_x/$HfSiO_x$ mixture is grown between 1-10 ALD cycles. We observe that the Si/HfO_2 interface is unstable, and oxidation continues up to the 25th ALD cycle, reaching a thickness of ~18Å.

INTRODUCTION

As the use of Si based gate oxides are reaching their scaling limitations, hafnium-based oxide materials are the leading candidates to replace them as the insulating layer in transistor gate stacks. Among the desirable properties of the Hf containing insulating materials is a high dielectric constant (k~25), suitable band gaps and offsets, good electrical properties and good resistance to reaction with atmospheric moisture.[1] Atomic layer deposition (ALD) is an excellent technique for depositing such high-k oxides since the low process temperatures and characteristic self-limiting surface reactions provide precise, monolayer growth control and excellent conformal films.[2] The deposition of HfO_2 thin films has been studied on various starting Si surfaces, including different chemical oxides and hydrogen-terminated Si (Si-H).[3] However, a serious problem which plagues most gate oxide processes on Si-H is the formation of an interfacial SiO_x layer during deposition[4], which increases the equivalent oxide thickness (EOT) and degrades the electrical characteristics of the device.[5] In order to maximize the potential of high-k dielectric materials for this application, a stable interface is required between the dielectric and the Si substrate. Metal-organic precursors are popular for HfO_2 deposition due to low toxicity, ease to handle, low deposition temperature and impurity content in the film. In

this article we present an initial study of the HfO_2/Si interface of films deposited from tetrakis(dimethylamino)hafnium (TDMAH) and H_2O, on both chemical oxide and Si-H starting surfaces. Initial results indicate that the Si-H interface is unstable and continues to oxidize up to the 25th process cycle.

EXPERIMENT

A home-made, hot wall flow tube type ALD reactor is used to deposit HfO_2 thin films, with the process automated by a LABVIEW® routine. TDMAH was purchased from Strem Chemicals, and was stored in an air tight stainless steel vessel. The precursor delivery system was placed inside an oven to achieve uniform temperature control of the vessel and delivery lines. The fixed-volume (~15cc in our case) precursor delivery approach of Hausmann et al. was implemented for the precursor and H_2O reagents.[2] The TDMAH precursor was held at ~75°C in order to achieve vapor pressure higher than the 200mtorr process pressure. The H_2O was kept in a stainless steel cylinder at room temperature, ~24°C; air was removed from the cylinder by several freeze, pump and thaw cycles. The reactor is flushed with a constant flow of ~18sccm of ultra-pure N_2 during depositions; a 60 l/s turbo pump maintains a reactor base pressure of 6×10^{-7} torr during idle time. Substrates were prepared by cleaning pieces of Si(100) wafers in JT Baker solution for 5 min followed by a 5 min de-ionized water rinse. The Si-H surface was obtained by dipping the cleaned wafers in BOE for 20-30s, rinsing briefly with de-ionized water, and blow-drying with N_2; the chemical oxide surface was prepared with the standard SC1 recipe[3], resulting in 15-18Å of oxide grown on the Si-H surface. After removal of the native oxide, Si-H (HF-last) samples were loaded into the heated reactor within three minutes, where a 30-minute N_2 purge provided a clean ALD environment. The stability of the Si-H surface was investigated under these circumstances; spectroscopic ellipsometry revealed no oxide growth on the Si-H surface after 30-minute exposures to these ALD process conditions. HfO_2 was deposited simultaneously on Si-H and SC1 surfaces to obtain a valid comparison of the film nucleation on the two starting surfaces. A 380-900nm variable wavelength, fixed-angle spectroscopic ellipsometer (SE) was used to measure film thickness immediately after HfO_2 deposition. A five-point average was taken over the sample surface (typical samples measured 1.5 cm×1.5 cm). A Kratos-Ultra X-ray photoelectron spectrometer (Al source, hυ=1486.6eV) was used to examine elemental composition of the HfO_2 films, and angle-resolved scans from 0-60°(measured from the normal of the sample surface) were used to probe the interfacial layer of the films. To compensate for sample-charging effects, the Si 2p peak was centered at 99.3eV for all of the scans. Fourier transform infra-red spectroscopy (FTIR) was performed with a Nicolet 4700 spectrometer in the far-IR region (600-50 cm^{-1}) on thicker films grown on double-polished Si(100) wafers to investigate crystallinity and purity of the as-deposited films. Anneals were carried out in a ULVAC-RIKO MILA-3000 model annealer at 900°C under an ultra-high purity Ar purge.

RESULTS

In Figure 1a, we show the growth rate on a native oxide surface as a function of substrate temperature, measured by SE. The data show a rather sharp minimum centered between 275-300°C; the lower of these temperatures was chosen for our deposition temperature. Figure 1b shows the HfO_2 growth rate versus reactor purge time. The growth rate decreases slightly from

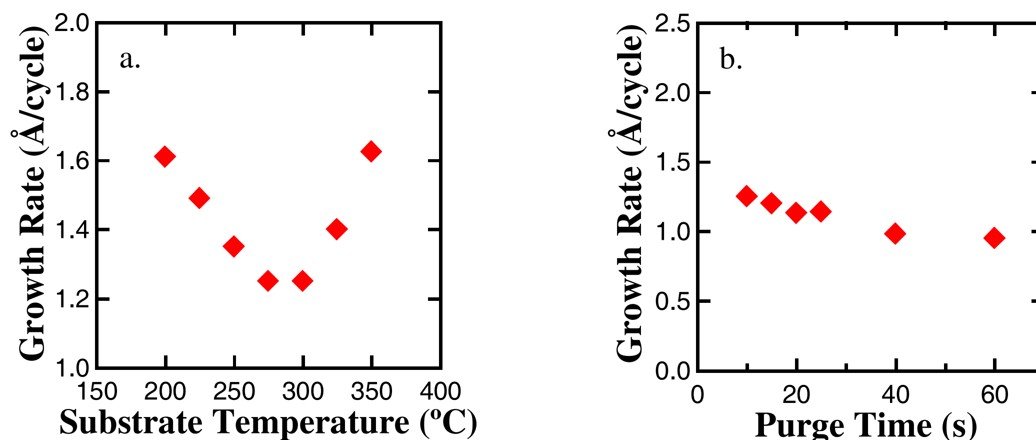

Figure 1. HfO_2 growth rate versus (a) substrate temperature**,** (b) reactor purge time.

10-40s, with a negligible change from 40-60s; a 30s period of ultra-high purity N_2 was chosen as the optimal purge time.

HfO_2 films ranging from 4-200 ALD cycles were grown on both Si-H and SC1 surfaces, and these growth rates are shown in Figures 2a and 2b (the chemical oxide thickness is subtracted out of these plots). SE measurements show two distinct growth regimes: from 4-50 cycles, both surfaces display equal growth rates of about 1 Å/cycle, which is comparable to previous work with TDMAH[6,7], but for films greater than 50 cycles the growth rate decreases by about 15% to 0.87 Å/cycle. The intercept of ~12.4Å on the HF-last data in Figure 2b is indicative of the formation of an interfacial layer. Raw ARXPS scans of the Si 2p peak show an oxide peak centered at about 103eV (Figure 3); this peak does not change substantially between samples of 4, 7 and 10 cycles. However, a dramatic increase in this interfacial peak can be seen in the 15 and 25 cycle samples. Both the oxide peak and Si 2p peak are integrated and fitted to the following equation taken from Powell et al[8],

$$\ln(1+R/K) = d/(\lambda\cos\theta) \qquad (1)$$

where R is the ratio of the two peaks (Si^{4+}/Si^{o}), K=0.7 is the relative sensitivity factor of the peaks, d is the oxide thickness, λ=3.47 nm is the effective attenuation coefficient, and θ is

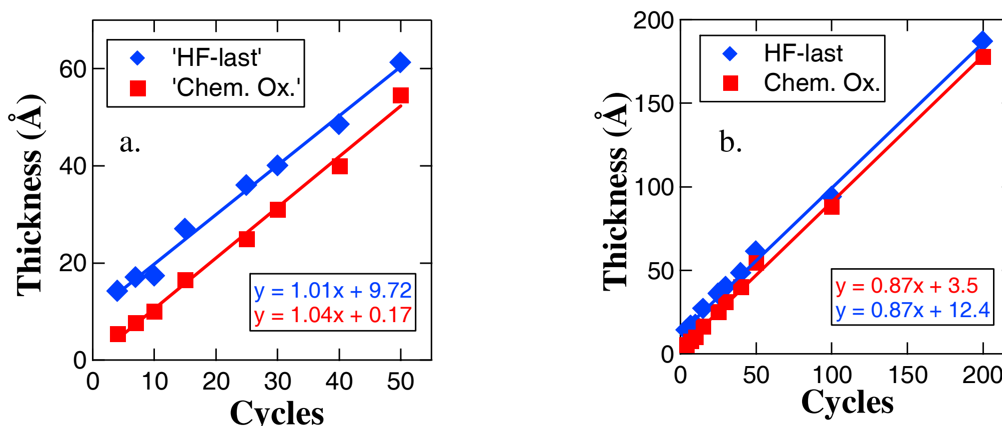

Figure 2. HfO_2 thickness for (a) 4-50 cycles, and (b) 4-200 cycles.

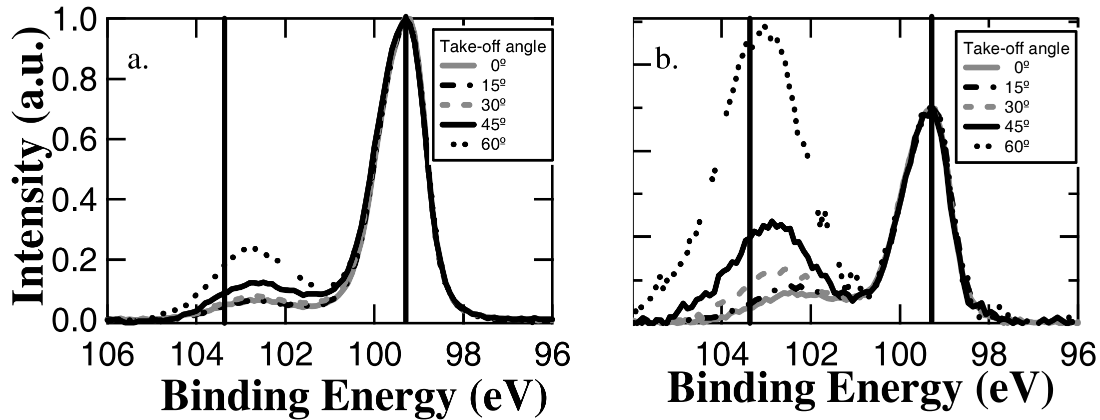

Figure 3. ARXPS of the Si 2p and interfacial oxide peak for (a) 10, (b) 25 ALD cycles; the positions of Si 2p and Si^{4+} are marked by the vertical lines.

the take-off angle which is measured from the surface normal. The fitted data is displayed in Figure 4; a 10% error is assumed in the integrated peak intensities, including both fitting error and noise. Using standard error propagation techniques, we arrive at a 14% error in each data point.

Figure 5 summarizes the results of the interface thickness measurements based on the ARXPS data. The interfacial layer remains nearly constant at 5-7Å for the 4, 7 and 10-cycle samples, then increases to 13Å at 15 cycles, and reaches a thickness of 18Å after 25 ALD cycles. The 25-cycle sample marked the limiting HfO_2 overlayer thickness for the ARXPS technique. HRTEM imaging will be used to study the extent of the interface oxidation for thicker samples.

The purity and morphology of thicker films was examined with FTIR. In Figure 6 we present the far IR spectrum of an as-deposited 200 cycle-film. The spectrum is compared to that of a film annealed at 900°C that is known to be crystalline to a large degree. The difference in the structure of the two films indicates that the as-deposited film is mainly amorphous. [7,9]

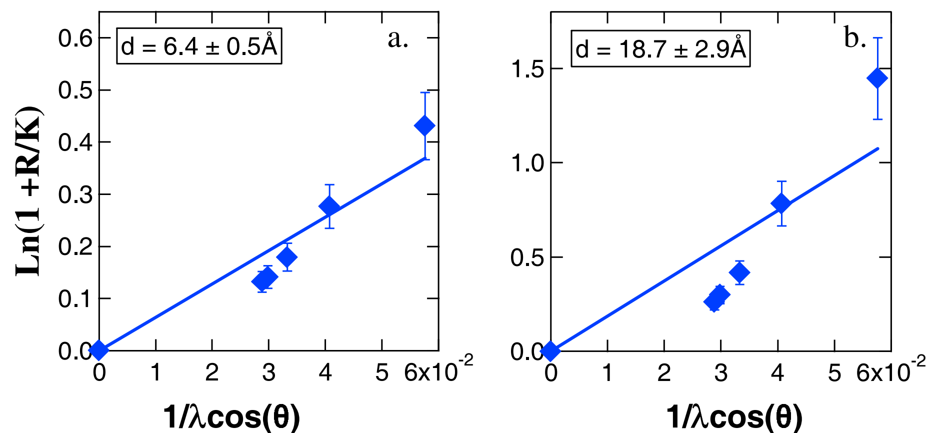

Figure 4. ARXPS data fitted to Equation 1 for (a) 10, (b) 25 ALD cycles.

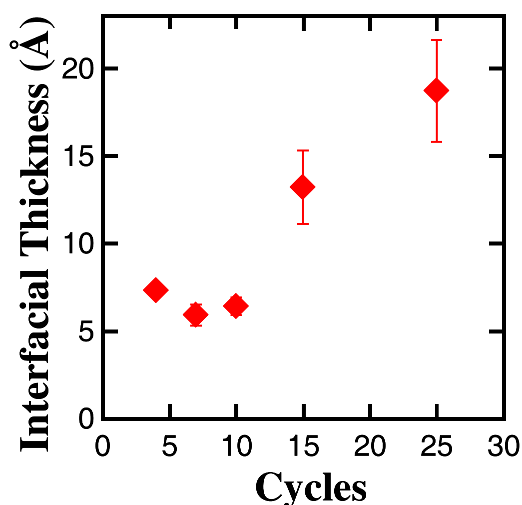

Figure 5. Variation of the interfacial layer thickness with ALD cycles.

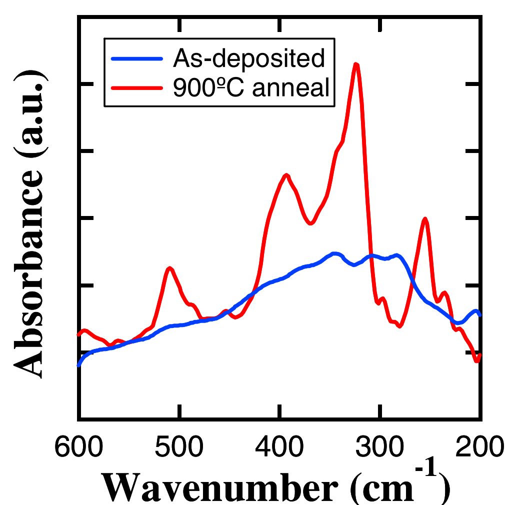

Figure 6. Crystallization of 200 cycle HfO_2 film shown by characteristic FTIR absorbance peaks

DISCUSSION

Film thickness measurements performed by SE show an initial amplified HfO_2 growth region lasting up to 50 cycles for both the chemical oxide and Si-H starting surfaces. Similar observations have been previously documented by Green et al. for HfO_2 deposition from $HfCl_4$ and H_2O at 300°C on SC2 and Si-H starting surfaces and were explained in terms of film density variation with film thickness.[3] This is the first such observation for metal-organic based ALD, however.

ARXPS analysis reveals a primary 5-7Å interfacial layer grown on the Si-H surface during the first few ALD cycles, and the interface appears to be stable. From the oxide peak location, this layer may be composed of a $SiO_x/HfSiO_x$ mixture. However, prolonged exposure to the ALD process environment degrades the HfO_2/Si interface and encourages further oxidation of the substrate above 10 cycles. The FWHM of the oxide peak is observed to increase for the 15 and 25 cycle samples (>2eV), and the peak shifts slightly towards a higher binding energy which implies a nearly stoichiometric SiO_2 layer. The 25-cycle sample represents the thickest HfO_2 film that we could investigate using this technique and ~ 18Å of interface was observed.

FTIR spectra in the far-IR regime show that the as-deposited films are amorphous and crystallize after post-deposition high-temperature anneals. Previously, it has been shown that the interfacial layer associated with as-deposited high-k films increases with high-temperature annealing[10] and a possible mechanism for this growth is enhanced oxygen diffusion along grain boundaries in the film. The as-deposited films are amorphous but extensive studies of the morphology of films deposited on Si-H reveal non-continuous growth and extensive island growth.[11] It is possible that at 25 cycles the films have not coalesced which would allow for a very efficient oxygen transport route to the interface. Kukli et al reports an interfacial layer of

nearly 20Å for a 78Å (90-cycle) HfO_2 film grown on Si-H under similar process conditions.[7] If we take this value to be the limiting thickness of the interfacial layer, then we can conclude that our films coalesce at a thickness of ~20Å. Once a continuous amorphous film is achieved then the interface is protected from further oxidation.

CONCLUSIONS

HfO_2 films were deposited on both SC1 chemical oxide and Si-H starting surfaces from the precursors TDMAH and H_2O in a homemade, hot-wall flow type ALD reactor. SE measurements show an initial enhanced growth rate of ~1 Å/cycle on both surfaces, which slows to a steady-state rate of 0.85 Å/cycle after about the 50th cycle. ARXPS measurements reveal that the HfO_2/Si-H interface is unstable: an initial ~6Å of interfacial oxide is formed during the first 4 ALD cycles and continues to grow up to about the 25th cycle, reaching a thickness of ~18Å.

ACKNOWLEDGEMENTS

Financial support from UMBC and the ACS Petroleum Research Fund (44228-G5) is gratefully acknowledged.

REFERENCES

1. P. Raghu, N. Rana, C. Yim, E. Shero, F. Shadman, *J. Electro. Soc.*, **150** F186-F193 (2003).
2. Dennis M. Hausmann, Esther Kim, Jill Becker, and Roy G. Gordon, *Chem. Mater.*, **14** 4350-4358 (2002).
3. M.L. Green, M.-Y. Ho, B. Busch, G.D. Wilk, T. Sorsch, T. Conard, B. Brijs, W. Vandervorst, P.I. Räisänen, D.Muller, M. Bude, J. Grazul, *J. Appl. Phys.*, **92** 7169 (2002).
4. K.B. Chung, C.N. Whang, H.S. Chang, D.W. Moon, M.-H. Cho, *J. Vac. Sci. Technol. A,* **25**(1) 141 (2007).
5. G.D. Wilk, R.M. Wallace, J.M. Anthony, *J. Appl. Phys.*, **89** 5243 (2001).
6. X. Liu, S. Ramanathan, T.E. Seidel, *Mat. Res. Soc. Symp. Proc.,***765** D3.8.1 (2003).
7. K. Kukli, T. Pilvi, M. Ritala, T. Sajavaara, J. Lu, M. Leskela, *Thin Solid Films*, **491** 328-338 (2005).
8. C.J. Powell, A. Jablonski, *J. Elec. Spec.*, 100 137-160 (1999).
9. K. Tomida, H. Shimizu, K. Kita, K. Kyuno, A. Toriumi, *Mat. Res. Soc. Symp. Proc.*, **811** D10.9 (2004).
10. R.M.C. de Almeida, I.J.R. Baumvol, *Surface Science Reports,* **49** 1-114 (2003).
11. R. L. Puurunen, W. Vandervorst, W. F. A. Besling, O. Richard, H. Bender, T. Conard, C. Zhao, A. Delabie, M. Caymax, S. De Gendt, M. Heyns, M. M. Viitanen, M. de Ridder, H. H. Brongersma, Y. Tamminga, T. Dao, T. de Win, M. Verheijen, M. Kaiser, M. Tuominen *J. Appl. Phys.* **96**(9), 4878 (2004).