Structural and Dielectric Characterization of Atomic Layer Deposited HfO₂ and TiO₂ as Promising Gate Oxides

Qian Tao, 1 Gregory Jursich, 2,3 and Christos Takoudis 1,2

1 Department of Chemical Engineering, University of Illinois at Chicago, IL, 60607
2 Department of Bioengineering, University of Illinois at Chicago, IL, 60607
3 Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, IL, 60607

Abstract - Tetrakis (diethylamino) hafnium (TDEAH), tetrakis (diethylamino) titanium (TDEAT) and H₂O were used for the atomic layer deposition of HfO₂ and TiO₂ films on silicon substrates. X-ray Photoelectron Spectroscopy showed that after a short Ar⁺ sputtering for removing surface contaminants, both HfO₂ and TiO₂ films were found to be essentially carbon free. While HfO₂ remained at +4 chemical state after the surface sputtering, TiO₂ partially changed into Ti³⁺ (Ti₂O₃) and Ti²⁺ (TiO), suggesting a preferential sputtering of O over Ti. Phase-shift interferometry (PSI) was applied to probe the surface morphology of both as-deposited and post annealed films, which were later examined by Grazing Incidence X-ray Diffraction (GIXRD). From both PSI and GIXRD results, as-deposited HfO₂ and TiO₂ films were found to be amorphous with smooth surfaces but began to crystallize with roughened surfaces after annealing at 600 °C, with HfO₂ crystallizing into a monoclinic structure and TiO₂ crystallizing into an anatase structure. C-V and I-V measurement were performed after electron beam evaporation of Al metal contacts on the dielectric layers. The calculated dielectric constant (k) value of TiO₂ is almost three times higher than that of HfO₂ and the measured leakage current densities for the metal oxides are below 10⁻⁵ A/cm² at the applied voltage of 1 V.

I. Introduction

Atomic layer deposition (ALD) has gained increasing popularity as robust means for coating thin films because of its precise film thickness control, conformal growth on complex structures, low growth temperature and low pinhole density. Such advantages make ALD an important technique for applications in gate insulator of metal oxide semiconductor field effect transistors and in capacitor dielectric of dynamic random access memories. So far, many candidate gate dielectric materials for the replacement of SiO₂ have been studied such as Ta₂O₅, TiO₂, Al₂O₃, Y₂O₃, ZrO₂ and HfO₂. From all these materials, HfO₂ and TiO₂ seem to be promising candidates due to their favorable properties. For instance, the reported dielectric constant of HfO₂ and TiO₂ could be 15-30 and 7-80 or even higher. The large variation in dielectric constants of both HfO₂ and TiO₂ has been attributed to differences in film thickness, impurities such as carbon, and to crystallization from amorphous phases after high temperature annealing. Another issue of integrating HfO₂ and TiO₂ as gate dielectrics is their low crystallization temperature of about 550 °C, since crystallization introduces defects into the structure and therefore may lead to higher gate leakage current density.

High quality thin films of HfO₂ and TiO₂ have been formed by using different systems, such as metal organic chemical vapor deposition, reactive sputtering and atomic layer deposition. In general, these studies show that amorphous HfO₂ and TiO₂ films could be produced at relatively low temperatures with good deposition rates. Previous studies have focused on film qualities, such as film thickness/deposition rate, structural/compositional properties, morphology and electrical properties. In this paper, we studied Ar⁺ surface sputtering effects exerted on as-deposited HfO₂ and TiO₂ films, film morphology before and after annealing as well as the dielectric properties of as-deposited films. Although Ar⁺ is not routinely used in silicon processing, it is still analogous to many implant processes employed in industry since high energy ions such as nitrogen implantation through the gate oxide into the silicon substrate are used to adjust the threshold voltage.
II. Experimental

HfO₂ and TiO₂ thin films were deposited using tetrakis (diethylamino) hafnium (TDEAH) and tetrakis (diethylamino) titanium (TDEAT) as metal precursors with H₂O as the oxidizer. Prior to deposition, Si substrates (20x20 mm) were cleaned using Radio Corporation of America (RCA) standard cleaning (SC-1) to remove organic contaminants followed by 1% HF dip for 10 s to remove native oxide down to 1 nm as measured by spectral ellipsometry immediately after cleaning. Each of these two steps was followed by thorough DI water rinsing and drying in N₂. Immediately after cleaning, the substrates were loaded into a hot wall ALD reactor to deposit HfO₂ or TiO₂ films. The metal precursors were contained in stainless steel vessels with the TDEAH reservoir kept at 65 ºC and the TDEAT reservoir at 67 ºC during deposition. Moisture was supplied into the reactor as pulses of wet N₂ taken from a continuous flow of N₂ going through a bubbler of water maintained at 0 ºC. Further description of the ALD reactor along with other process parameters is reported in reference 15.

In this study, the ALD film thickness was measured with a spectral ellipsometer (J. A. Woollam Co., Inc., model M-44), and for each thickness determination, multiple measurements across the film were made with mean values representing the film thickness. In order to study film crystallization temperature, targeting samples were further annealed in N₂ (99.996%) for 5 min at temperature of 600 and 800 ºC at 1 atm in a preheated quartz horizontal furnace (Lindberg Blue STF) with N₂ flow rate of 40 sccm. Film structures were probed by an x-ray photoelectron spectrometer (XPS; Kratos AXIS-165) equipped with a monochromatic Al Kα (1486.6 eV) x-ray source operating at 15 kV and 10 mA. High-resolution spectra of the elements-of-interest were collected using pass energy of 20 eV, step size of 0.1 eV and dwell time of 200 ms. Semi-quantitative analysis of peak intensities was performed through spectral peak-fitting where peaks were subtracted from Shirley-typed backgrounds and deconvoluted using Gaussian-Lorentzian peak shape functions. The binding energy scales of all XPS spectra were calibrated with reference to the adventitious carbon 1s position at 285 eV. Phase-shifting interferometry (PSI) was performed by using non-contact optical profiler (Wyko NT3300 system) to examine the surface roughness before and after annealing. A high resolution x-ray diffractometer (Philips X’pert) was used to obtain grazing incidence x-ray diffraction (GIXRD) spectra of HfO₂ and TiO₂ films. The GIXRD spectra were collected at a low angle of incidence at 0.7º with an overall diffraction angle resolution of 0.15º. The use of grazing incidence x-ray allows high resolution diffraction patterns with enhanced sensitivity of films without interference of diffraction lines from the single crystal Si (100) substrate. Before conducting Capacitance-Voltage (C-V) and Current-Voltage (I-V) measurements, about 150 nm Al metal contacts were coated on top of HfO₂ and TiO₂ by electron beam evaporation (Varian model # NRC3117) at the voltage of 10 kV and current of 175 mA. C-V and I-V measurements were performed at the frequency of 100 kHz using Agilent 4980 equipped with MDC model 802B Mercury Probe. The area of metal contacts is 1.6x10⁻³ cm².

III. Results and Discussion

Table I shows the elemental composition of Hf, Ti, O, C, Si from 6-nm-thick HfO₂ and TiO₂ samples probed by XPS before and after sputtering for 300 s at 4 kV/15 mA (voltage/emission). Before sputtering, the atomic ratio of O to Hf is larger than 2 due to the existence of other oxygen species, such as, O-H, C-O (on the surface) and Si-O (at the interface). After sputtering, the atomic ratio of O to Hf becomes smaller because of the removal of the hydro oxygen and carbon oxygen species on the surface (as discussed later). Comparatively, the atomic ratio of O to Ti is observed larger than 2 for the unsputtered TiO₂ film, which becomes only about 1.5 after sputtering, suggesting the formation of titanium suboxides. The detected atomic concentrations of carbon from the unsputtered films are as high as above 20%, which are reduced to less than 4% after surface sputtering, indicating the carbon is mostly adventitious and contamination from air. A higher atomic concentration of silicon is observed after sputtering, due to the attenuated oxide film after sputtering.

<table>
<thead>
<tr>
<th>Elements</th>
<th>HfO₂ (BS at. %)</th>
<th>HfO₂ (AS at. %)</th>
<th>TiO₂ (BS at. %)</th>
<th>TiO₂ (AS at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf</td>
<td>19</td>
<td>24</td>
<td>——</td>
<td>——</td>
</tr>
<tr>
<td>Ti</td>
<td>——</td>
<td>——</td>
<td>21</td>
<td>31</td>
</tr>
<tr>
<td>O</td>
<td>53</td>
<td>58</td>
<td>53</td>
<td>49</td>
</tr>
<tr>
<td>C</td>
<td>22</td>
<td>3</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>Si</td>
<td>6</td>
<td>15</td>
<td>6</td>
<td>16</td>
</tr>
</tbody>
</table>

Table I Elemental compositions (at. %) on 6 nm HfO₂ and TiO₂ determined by XPS before and after sputtering (BS and AS) for 300 s.
Figure 1 shows XPS core scans of Hf, O and C of HfO$_2$ sample before and after sputtering. The core spectrum of Hf 4f, before sputtering, consists of two features: 4f$_{5/2}$ at 19.1 eV and 4f$_{7/2}$ at 17.4 eV with the standard spin-orbital splitting (SOS) of 1.7 eV, indicative of HfO$_2$ formation; peaks at lower binding energies are not observed, indicating an absence of HfSix formation during ALD. After sputtering, the Hf 4f peak positions remain the same, while peak intensity decreases due to the removal of HfO$_2$ layers. Oxygen 1s spectrum of the unsputtered HfO$_2$ film exhibited three peaks, which were associated with Hf-O-Hf (529.7 eV), O-H (530.8 eV) and Si-O (531.7 eV); after sputtering, the O-H peak disappeared, indicating O-H species resulted from the surface absorbed water vapor (considering no O-H group in the precursor ligands). Meanwhile, it is observed that the peak intensity of Hf-O-Hf decreased compared with the slightly increased Si-O peak intensity, suggesting that Si-O comes from the 1 nm SiO$_2$ at the interface. Substantial amount of carbon was found in the unsputtered HfO$_2$ film with the strongest C 1s orbital at 285 eV designated as the adventitious carbon, the intermediate peak at 286 eV corresponds to the C-OH next to the smallest peak at 289.2 eV assigned as O=C-OH species; after sputtering, only a small amount of adventitious carbon residues is left on the surface, which could also be the result of the sputtering process.

Figure 2 shows XPS core scans for Ti, O and C of TiO$_2$ sample before and after sputtering. The unsputtered Ti 2p (Ti 2p$_{1/2}$ at 462.7 eV, Ti2p$_{3/2}$ at 457.0 eV) with the standard SOS of 5.7 eV, is assigned to the Ti$^{4+}$ in TiO$_2$. After sputtering, the original Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ peaks appeared as six primary peaks, and those peaks, based on earlier observation of XPS of TiO$_{2-x}$, are assigned as TiO$_2$ (463.8 eV and 458.6 eV), Ti$_2$O$_3$ (461.4 eV and 457.0 eV) and TiO (460.4 eV and 455.1 eV). It is known that argon ion bombardment may alter the chemical state and composition of compounds such as TiO$_2$, NiO, Ta$_2$O$_5$, CuO etc. For instance, McCurdy, et al found that TiO$_2$ could be reduced into Ti$_2$O$_3$ and TiO depending on the duration of argon sputtering or the temperature of post-deposition annealing; Hashimoto, et al also reported the appearance of Ti$^{2+}$ and Ti$^{3+}$ in addition to Ti$^{4+}$ after ion bombardment at 2 kV (4 kV in the present report) and a sufficient sputtering time would result in an equilibrium state between the sputtered atoms and implanted ions. However, in both mentioned reports, analyses lacked differentiation of Ti (at different chemical states) associated with O; figure 2 (b) shows that, Ti-O-Ti peak (at 530.0 eV before sputtering) resulted into three peaks assigned to oxygen in titanium dioxide and suboxides next to the Si-O peak at 531.8 eV, which is found to shift by 0.3 eV to higher binding energy than that for the unsputtered film. The O-H species from the unsputtered TiO$_2$ (530.5 eV) is, again, no longer observed after sputtering. The amount of carbon is largely reduced to less than 4% after sputtering with the removals of C-OH and O=C-OH species, but it now shows two shoulders at the lower binding energy on the adventitious carbon peak, which could be assigned to newly formed Ti-carbon (TiC$_x$) species after sputtering; these species might result from the redeposition of sputtered Ti and carbon atoms. XPS results show a preferential sputtering of O over Ti, while such
preferential sputtering did not occur to HfO₂ films.

The surface roughness of both as-deposited and post-annealed films is important because it affects shifts in electronic energy levels and degrades electrical characteristics. Change of surface roughness may also reveal structural changes in the film. From phase-shift interferometry calibration results of 28 nm-thick as-deposited TiO₂ and HfO₂, the RMS (root mean square) roughness is found to be 0.22 nm for HfO₂ and 0.34 nm for TiO₂. Upon annealing at 600 °C and 800 °C, the RMS roughnesses increase to 0.93 nm and 0.97 nm, respectively, for the annealed HfO₂, compared to 0.97 nm and 1.06 nm for the annealed TiO₂, suggesting a change of the film structure. From the GIXRD insets of figures 3 and 4, the lack of any diffraction peaks for two-theta between 20 to 40° suggests amorphous nature of the as-deposited HfO₂ and TiO₂ films. Upon post deposition annealing, HfO₂ crystallized into the monoclinic structure while TiO₂ appeared to start crystallizing into the anatase structure. Also, these results show that film crystallization structures are independent of the annealing temperature at 600 - 800 °C.

C-V measurements were performed over a voltage range of -2 to +2 V at 100 kHz, while I-V measurements were performed over a voltage range of 0 to 5 V at 100 kHz. Relative dielectric constant values are computed from the maximum capacitance observed in the accumulation region of C-V curves as well as film thicknesses from spectral ellipsometry. The dielectric constant values of the overall films are found to be 35 for TiO₂ and 12 for HfO₂, and the corresponding equivalent oxide thickness (EOT) values are 1.6 nm for TiO₂ and 3.6 nm for HfO₂. It should be noted that both dielectric constants are lower than reported values of TiO₂ and HfO₂; 6, 7 this is possibly because the measured samples were as-deposited and amorphous without any post-
deposition treatments such as in forming gas/high temperature annealing, which could enhance dielectric properties and result in crystalline phases with higher dielectric constants.\textsuperscript{7, 28} Also, there is 1 nm SiO\textsubscript{2} at the interface as buffer layer, which results in compromised overall dielectric constants for both metal oxides. From I-V curves, in the insets of figures 5 and 6, the leakage current density increased steeply when the applied voltage increased from 0 to 1.6 V for HfO\textsubscript{2} (1 V for TiO\textsubscript{2}); slight increases were found when the applied voltage was further increased to 5 V. The leakage current densities at 1 V are 1.1x10\textsuperscript{-6} A/cm\textsuperscript{2} for HfO\textsubscript{2} and 1.5x10\textsuperscript{-5} A/cm\textsuperscript{2} for TiO\textsubscript{2}, respectively. The achieved leakage current densities of TiO\textsubscript{2} are four orders of magnitude lower than that of SiO\textsubscript{2} at similar EOT levels.\textsuperscript{29}

V. Conclusion

In this work, HfO\textsubscript{2} and TiO\textsubscript{2} were successfully synthesized by atomic layer deposition from TDEAH, TDEAT and H\textsubscript{2}O. XPS results of thin HfO\textsubscript{2} and TiO\textsubscript{2} films show that both films are practically free from carbon contamination after 5 min Ar\textsuperscript{+} surface sputtering. A preferential sputtering of O over Ti was found to cause the transition of Ti\textsuperscript{4+} into Ti\textsuperscript{2+} and Ti\textsuperscript{3+}, while such transitions did not occur to Hf\textsuperscript{4+} under similar conditions. Based on GIXRD analyses, both as-deposited HfO\textsubscript{2} and TiO\textsubscript{2} were found to be amorphous and crystallized after annealing at 600 °C for 5 minutes in N\textsubscript{2} environment, which were also manifested by the increased surface roughness of the annealed films. Dielectric constant values resulting from C-V measurements of as-deposited films are 12 and 35 for HfO\textsubscript{2} and TiO\textsubscript{2}, respectively, with EOT values of 3.6 nm for HfO\textsubscript{2} and 1.6 nm for TiO\textsubscript{2}. Even though HfO\textsubscript{2} film exhibits lower dielectric constant and larger EOT value than those of TiO\textsubscript{2}, it may be superior to TiO\textsubscript{2} in terms of confining leakage current density, i.e., 1/10 of that of TiO\textsubscript{2} at the applied bias of 1 V. Both ALD HfO\textsubscript{2} and TiO\textsubscript{2} exhibit promising dielectric properties as gate oxide for CMOS application.

The authors would like to thank Dr. Barton Gordon from Materials Development Corporation for assisting C-V and I-V measurement. Metal precursors were provided by American Air Liquide. Financial support by the National Science Foundation (Grant EEC 0755115) is also gratefully acknowledged.

References