Characterization of Hafnium Oxide Thin Films Prepared By MOCVD

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Abstract. Hafnium oxide thin films deposited by MOCVD were annealed in nitrogen at various temperatures. The as-deposited films and annealed films were characterized using Auger electron spectroscopy (AES), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The films were found to be slightly oxygen deficient. Angle-resolved XPS revealed oxygen to be residing in two different chemical states, that of oxygen in hafnium oxide, and possibly, a hafnium silicate. Auger depth profiling revealed nitrogen enrichment in an interfacial layer at the film-substrate interface, which could be the result of an ammonia pre-treatment prior to deposition. The thickness of this interfacial layer was determined to be ~ 15 Å from TEM. Progressively larger grains were found from AFM measurements with increasing annealing temperature.

INTRODUCTION

Until recently, improvements in device performance and functionality have been achieved chiefly by scaling down channel lengths and gate dielectric thickness. However, this reduction in gate dielectric thickness cannot continue indefinitely. While the International Technology Roadmap for Semiconductors (ITRS) predicts that an equivalent oxide thickness of < 1.5 nm is necessary for 0.1 μm technology, the gate leakage current for SiO₂ becomes unacceptably high as its thickness is scaled below 2 nm [1]. In addition, there are concerns with boron penetration and reliability in ultrathin SiO₂ [2].

Many high-κ materials such as Ta₂O₅, Y₂O₃, CeO₂, ZrO₂ and HfO₂ have been studied as alternative gate dielectrics [3]. Their higher dielectric constant compared to SiO₂ allows a greater physical thickness while retaining an equivalent gate capacitance [4]. Of these, HfO₂ appears most promising due to its high κ value (~25), relatively large bandgap (~5.8 eV) and high heat of formation (~ 271 kcal/mol) [1, 5]. Hafnium oxide films have been prepared by many methods, including sputtering [6-8], atomic layer deposition (ALD) [9-11], chemical vapour deposition (CVD) [12] and ion-beam assisted deposition (IBAD) techniques [13,14]. However, post-deposition annealing is often required to improve film quality and reduce leakage current.

Several authors have found the interfacial layer (between HfO₂ and silicon) to be composed of hafnium silicate [3,6,15], but the actual thickness of this layer has not been determined. Although several aspects of hafnium oxide films have been investigated, there are limited studies on the structural and surface characteristics of the films after post-deposition annealing in nitrogen.

In this work, hafnium oxide films prepared by MOCVD were annealed in nitrogen at 700°C, 800°C and 900°C. Auger electron spectroscopy (AES) and angle-resolved X-ray Photoelectron Spectroscopy (ARXPS) were used to study the surface composition and their variation with depth. Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) were employed to study the...
surface roughness and structure of the films, respectively.

**EXPERIMENTAL**

Hafnium oxide films were deposited onto p-type Si (100) substrates by MOCVD. Prior to deposition, the substrates were subjected to HF-last cleaning process followed by a NH₃ pre-gate treatment at 700°C for one minute. HfO₂ film deposition was then carried out using Hf[OC(CH₃)₃]₄ precursor (20 mg/s) and argon (450 sccm) as carrier gas. The chamber temperature and pressure was maintained at 400°C and 400 mTorr respectively during deposition. After deposition, the HfO₂ films were annealed in nitrogen at 700°C, 800°C and 900°C for one minute and their thicknesses measured using spectroscopic ellipsometry (Jusung Eureka-2000).

Auger spectra and depth profiles were acquired using a JEOL JAMP 7800F Scanning Auger Microprobe equipped with a 0.5 keV argon ion gun. An accelerating energy of 10 keV and a probe current of 10 nA were employed for all spectra. For XPS, a VG Escalab 220iXl system with a monochromatized Al Kα (1486.6 eV) source was employed. A constant analyzer energy (CAE) of 100 eV was used and the C 1s peak (assigned a binding energy of 284.6 eV), was used as an internal reference for charge shift corrections. Both survey and narrow scan spectra were acquired using take-off angles of 90° and 30°.

The structure and surface roughness of the films were investigated using a Philips CM200 FEG HRTEM and a DI Dimension 3000 Atomic Force Microscope, respectively. For the latter, the images (three or more scans) were acquired using silicon nitride probes in tapping mode over 1 × 1 μm² area.

**RESULTS AND DISCUSSION**

**Auger Analysis**

Auger spectra were acquired from the hafnium oxide films in the as-received condition and after ~ 1 minute of ion etching. All four films consisted of carbon, oxygen and hafnium in the as-received state, with partial or total removal of adventitious carbon after ion etching. The spectra for sample S1, which is representative of the other samples, are presented in Figure 1 below.

![FIGURE 1. Auger spectra of hafnium oxide film annealed at 700°C in nitrogen (S1). Top: as-received, Bottom: after ~1 min ion etching.](image)

Due to peak overlap between Si KLL and Hf MNN Auger peaks, the low energy Si LVV and Hf NVV peaks were monitored in the depth profiles. Relative sensitivity factors (RSFs)¹ as provided by JEOL, were used to quantify the spectra.

Figure 2 shows a typical depth profile obtained. A sharp drop in oxygen intensity can be seen after ~1 minute of ion etching. A nitrogen peak can also be clearly seen at the hafnium oxide-silicon interface; this peak could have resulted from the ammonia pre-gate treatment. Carbon contamination on the film was minimal. Table 1 shows the relative concentration of the elements found. The corresponding RSFs are given in parentheses. All films have a Hf/O ratio of ~0.56 after ion etching and are slightly oxygen deficient.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (Å)</th>
<th>Anneal Temp /°C</th>
<th>C (0.128)</th>
<th>O (0.371)</th>
<th>Hf NVV (0.104)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S4</td>
<td>57.6</td>
<td>-</td>
<td>9</td>
<td>61</td>
<td>30</td>
</tr>
<tr>
<td>S1</td>
<td>50.0</td>
<td>700</td>
<td>4</td>
<td>62</td>
<td>34</td>
</tr>
<tr>
<td>S2</td>
<td>56.0</td>
<td>800</td>
<td>8</td>
<td>61</td>
<td>31</td>
</tr>
<tr>
<td>S3</td>
<td>59.3</td>
<td>900</td>
<td>6</td>
<td>63</td>
<td>31</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>After Ion Etching</th>
</tr>
</thead>
<tbody>
<tr>
<td>S4</td>
</tr>
<tr>
<td>S1</td>
</tr>
<tr>
<td>S2</td>
</tr>
<tr>
<td>S3</td>
</tr>
</tbody>
</table>

¹ Use of RSFs is only semiquantitative and for comparison purposes.
FIGURE 2. Depth profile of sample S4 (as-deposited).

As seen from Table 1, all four hafnium oxide films have similar surface compositions before and after ion etching and have carbon contents from 4 to 9 at.%.

XPS Analysis

The chemical bonding of hafnium oxide was evaluated qualitatively by XPS. A typical survey spectrum of sample S1 annealed at 700°C at normal incidence is shown in Figure 3. The spectrum reveals the presence of carbon, oxygen, hafnium and silicon. Carbon probably arose from adventitious surface contaminants or from residues of the carbon-containing precursors used [11], while the presence of a silicon signal from the substrate suggests a film thickness of around 5 nm. This is consistent with the observation that the Si 2p intensity varies directly with the film thickness (see Figure 4).

Figure 4 shows the narrow scan spectra of O 1s, Hf 4f and Si 2p for S1 at 90° take-off angle. While the binding energies (BE) of the Hf 4f peaks remain relatively constant with annealing temperature, the BEs of O 1s varied with annealing temperature. Samples S2 and S3 have relatively lower BE compared to Sample S1 and S4 (indicated by diamonds and squares respectively). A small hump, suggestive of a second component, is also visible at X. Similarly, the Si 2p spectra revealed the presence of at least two peak components, as indicated by A and B. Table 2 lists the BEs of Si, SiO2, Hf, HfO2 and HfSi2O5 with those of the hafnium oxide films obtained here.

It can be seen from Table 2 that the BE of oxygen in these films are fairly close to that of HfO2. XPS spectra were also acquired at 30° take-off angle to probe the topmost surface of the films. An example of the peak-fitted O 1s spectrum for this take-off angle is given in Figure 5. Silicon peaks were not observed.

FIGURE 3. A wide scan survey spectrum of Sample S1 at 90° take-off angle.

<p>| TABLE 2. Comparison of the binding energies of our films (at 90° take-off angle), Hf, Si, SiO2 and HfSi2O5. |</p>
<table>
<thead>
<tr>
<th>Sample /Material</th>
<th>O 1s</th>
<th>Hf 4f</th>
<th>Si 2p</th>
<th>Bond</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>530.2</td>
<td>16.2</td>
<td>98.2</td>
<td></td>
<td>this work</td>
</tr>
<tr>
<td>S2</td>
<td>529.7</td>
<td>16.3</td>
<td>98.2</td>
<td></td>
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</tr>
<tr>
<td>S3</td>
<td>529.6</td>
<td>16.3</td>
<td>98.0</td>
<td></td>
<td>this work</td>
</tr>
<tr>
<td>S4</td>
<td>529.9</td>
<td>16.2</td>
<td>98.0</td>
<td></td>
<td>this work</td>
</tr>
<tr>
<td>HfO2</td>
<td>530.4</td>
<td>16.7</td>
<td>-</td>
<td>Hf-O</td>
<td>[16]</td>
</tr>
<tr>
<td>Hf</td>
<td></td>
<td>14.4</td>
<td>-</td>
<td>Hf-Hf</td>
<td>[16]</td>
</tr>
<tr>
<td>SiO2</td>
<td>533.0</td>
<td>-</td>
<td>103.6</td>
<td>Si-O</td>
<td>[16]</td>
</tr>
<tr>
<td>Si</td>
<td></td>
<td>-</td>
<td>99.3, 99.5</td>
<td>Si-Si</td>
<td>[16], [17]</td>
</tr>
<tr>
<td>HfSi2O5</td>
<td>~532</td>
<td>-</td>
<td>-</td>
<td>Hf, Si-O</td>
<td>[17]</td>
</tr>
</tbody>
</table>
The O 1s spectrum consisted of two different chemical states. The main component at 530.3 eV and a smaller component at 531.7 eV were assigned to hafnium oxide (530.2 eV) [18] and non-stoichiometric hafnium silicate (~532 eV) respectively [19]. The feature at 531.7 eV lies between that of SiO$_2$ (533.0 eV) and HfO$_2$ (~530 eV), and is closer to that of HfO$_2$. It is thus reasonable to attribute it to a chemical state intermediate between that of HfO$_2$ and SiO$_2$, i.e. a non-stoichiometric silicate Hf$_x$Si$_{1-x}$O$_y$. The formation of a compound between hafnium oxide and SiO$_2$ is supported by the small Si feature at B (Figure 4), which is distinct from that of SiO$_2$ and Si.

**TEM Results**

Figure 6 gives the TEM cross-section of the four hafnium oxide films. The hafnium oxide layer was polycrystalline for all samples and an amorphous interfacial layer of ~13 – 17 Å was found. Unfortunately, it was not possible to determine the composition of the interfacial layer by electron energy loss spectroscopy (EELS) due to mechanical and thermal shifts. However, given the clear indication of nitrogen enrichment at the film-substrate interface from AES depth profiles, it is likely that this layer is a form of nitride or oxynitride.

**AFM Results**

The AFM images for the as-deposited film and films annealed at different temperature are shown in Figure 7. Films annealed at 700°C and 800°C exhibit smaller grains and pin holes. Both films appeared to be smoother (rms <3 Å) as compared to as-deposited film (rms~3.6Å). Annealing at 900°C led to significant change in surface morphology of the film. Grain growth was observed (image rms~3.3 Å), and the...
maximum grain diameter was measured to be approximately 50 nm.

FIGURE 7. AFM 3D images of hafnium oxide films.

CONCLUSION

Hafnium oxide films prepared by MOCVD and annealed in nitrogen were found to be oxygen deficient. Oxygen was found to exist in two chemical environments, that of hafnium oxide and possibly, hafnium silicate. A nitrogen-rich amorphous interfacial layer (~13-17 Å thick) was formed in all samples, which was not possible to confirm with TEM. More work needs to be done to develop electron microscopy techniques for such analyses. Films annealed at 700°C and 800°C were smoother than the as-deposited film and that annealed at 900°C, where significant grain growth was observed. Work is currently on-going to confirm the grain size of the latter using grazing angle XRD.

ACKNOWLEDGMENTS

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REFERENCES


