High-k dielectric characterization by VUV spectroscopic ellipsometry and X-ray reflection


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Abstract. In this study, we use vacuum UV spectroscopic ellipsometry (VUVSE) to characterize new high dielectric materials. Indeed, all the candidates for high k dielectrics become strongly absorbent when the wavelength is reduced down to 140nm. So, the correlation between thickness and refractive index is reduced in the VUV range and much more precise structural information can be deduced. \( \text{HfO}_2 \), \( \text{Al}_2\text{O}_3 \) and mixed \( \text{HfAlO}_x \) layers have been studied with and without thin \( \text{SiO}_2 \) oxide at the interface. X-ray reflectometry (XRR) has been used to measure precisely the layer thickness and roughness. The two techniques are included in the same automated metrology system dedicated to 300mm technology which is also presented. We show in particular that VUVSE can detect the crystalline character of the layers and their composition can be measured in addition to the layer thickness. Results are compared to those obtained by transmission electron microscopy (TEM), x-ray fluorescence analysis (XRF) and x-ray photoemission (XPS).

INTRODUCTION

The continuous scaling of \( \text{SiO}_2 \) based gate dielectrics to the fundamental limits governed by large gate leakage and oxide reliability requires the introduction of new high-K materials for sub-100nm technology nodes. Most of the current research in high-K dielectrics is concentrated on binary metal oxides and silicates (see review [1] and references therein). The main motivation for exploring these classes of materials is their thermodynamically predicted thermal stability with silicon [2] and wide band gap [3]. Two promising materials are \( \text{HfO}_2 \) and \( \text{Al}_2\text{O}_3 \). Alumina is a very stable and robust material and has been extensively studied. Recently, \( \text{Al}_2\text{O}_3 \) NFETs with 80nm effective gate length have shown more than two a order of magnitude reduction in leakage currents and equal or better reliability than \( \text{SiO}_2 \) at room temperature [4]. \( \text{HfO}_2 \) CMOS devices have also shown interesting properties with low density of interface defects [5]. Both for the development of these processes and for future process control, the optimization of the physical analysis procedures for these materials is necessary [6]. In addition, to be used in a production environment, these new materials will need to be characterized precisely in a non destructive way. In this respect, spectroscopic ellipsometry SE has long been recognized as a leading technique because of its sensitivity to very thin layers. It is now routinely used for the control of different steps of the fabrication procedure in standard silicon microelectronics. For gate dielectrics like silicon oxynitrides, we have already shown that standard spectroscopic ellipsometry in the UV/visible wavelength range is not sufficient to deduce accurately at the same time the layer thickness and nitridation level due to the high correlation between thickness and optical index for these very thin layers. We have proposed a method based on a combined system including SE and x-ray reflectance XRR [7]. The same kind of approach can be applied to new high-K dielectric materials as shown in references [8,9]. In this paper, we show that ellipsometry in the VUV range is very powerful to characterize these new materials. XRR is used to provide absolute thickness values and to build accurately the optical index database and adjust the physical models. Results are compared to transmission electron microscopy (TEM), x-ray fluorescence analysis (XRF), and x-ray photoemission (XPS).
EXPERIMENTAL DETAILS

Metrology tool VUVSE / XRR

A new combined VUVSE-XRR tool dedicated to process control measurements on wafers up to 300 mm in diameter is used in this study. To cover the spectral range from 138 nm to 650 nm (i.e. 2 eV to 9 eV), the SE part of the instrument requires a purged environment. The instrument is fully automated. It includes a load lock, a wafer carrier robot compartment and the main purged box with a goniometer and the metrology, a sample holder with remote alignment capacity and a mapping stage (see general layout of the system in figure 1 and photograph in figure 2).

The VUVSE setup includes a double monochromator in the polarizer arm just after the deuterium lamp. This mounting ensures an optimized stray light rejection with a minimized beam path. The light beam goes through a MgF$_2$ Rochon polarizer mounted on a stepper motor. The reflected beam passes through another Rochon analyzer and is detected by a photomultiplier in photon counting mode. The two arms are mounted on the goniometer. The angle of incidence can be changed automatically in the range from grazing incidence up to 7° from normal. The system works in rotating analyzer mode to avoid parasitic polarization due to the monochromator. Polarization sensitivity of the detector is calibrated in straight line. In addition to ellipsometry, the system can make photometric measurements (reflectance and transmittance versus angle of incidence and/or wavelength) at fixed polarization state.

In addition to the ellipsometer arms, the XRR setup is mounted on the same goniometer. It includes a ceramic fine focus x-ray tube (Copper K-\(\alpha\) line at 0.154nm) cooled with water. A computer controlled stabilized high voltage supply is used at 40KV, 30mA. The beam is defined perpendicular to sample surface using Soller slits located just after the x-ray tube. The beam divergence is limited by interchangeable slits. A curved graphite crystal is used to monochromatize the x-ray beam after reflection on the sample surface. The detection is made using a NaI scintillator with beryllium window and a photomultiplier tube in photon counting mode. The dynamic range of the instrument can be extended to more than $10^6$ using automatic Ni attenuators and optimized integration time. Grazing X-ray reflectometry leads to absolute thickness measurements up to 200 nm, of multilayer structures, and the top or interface roughness up to 2 nm. VUVSE is then used to calculate the refractive index \(n\) and extinction coefficient \(k\) values, taking into account the thickness values given by the XRR option.

The purged environment is obtained by injection of grade nitrogen. An internal blower recycles the glove box atmosphere on molecular sieve to capture the water vapor, and separately on a bed of catalytic copper to filter oxygen. In normal working conditions, the concentrations of remaining H$_2$O and O$_2$ are below 1 ppm. The system is able to work in closed loop for 4 to 6 months. The internal pressure is kept 1 mbar above the atmospheric pressure by injecting fresh nitrogen, or pumping down with the vacuum dry pump of the load lock. The load lock must be evacuated and refilled with nitrogen each time that a new cassette of samples is to be put into the purged box to avoid O$_2$ and H$_2$O introduction. So the consumption of nitrogen is depending on the number of load lock cycles. Periodic reactors regeneration is necessary every six months. The instrument complies with CE and SEMI standards S2 and S8.

FIGURE 1. Schematic diagram of the automated combined VUVSE/XRR system.

FIGURE 2. Photograph of the automated combined VUVSE/XRR system.
Description of the samples

HfO$_2$, Al$_2$O$_3$ and HfAlO$_x$ layers have been deposited at IMEC by Atomic Layer Deposition (ALD) with alternating pulses of HfCl$_4$, Al(CH$_3$)$_3$ and H$_2$O at 300°C [10]. The thinner samples are deposited on a 1 nm silicon oxide grown in situ by rapid thermal oxidation (RTO) and the thick samples on HF-last silicon surfaces. Pure HfO$_2$ and Al$_2$O$_3$ layers have been deposited varying the number of cycles from 5 to 100. In addition layer composition has also been tested for the HfAlO$_x$ layers varying the relative number of HfCl$_4$ and Al(CH$_3$)$_3$ cycles (ratios 2:1, 1:1 and 1:2). Thicker reference layers allow precise determination of the optical indices of the HfO$_2$, Al$_2$O$_3$ and HfAlO$_x$ materials as shown below. Thinner samples are used to analyze the layer and interface behavior of the different systems with thickness. HfO$_2$ samples have been also annealed in a nitrogen ambient at 700°C after the deposition.

EXPERIMENTAL RESULTS

Thick layers and optical index extraction

All the thick samples have been measured by XRR to deduce precisely the layer thickness. As shown in figure 3, the index contrast between silicon and alumina is high at 0.154nm. So, very well defined interference fringes can be detected. The model used for the simulation includes a 0.74nm top surface roughness layer in addition to the 49.18nm thick Al$_2$O$_3$ layer. Then the VUV-SE measurement of figure 4 is used to extract at each wavelength the refractive index $n$ and the extinction coefficient $k$ of the alumina layer fixing the layer thickness and the top surface roughness. Result is reported in Figure 5 and we see that the alumina layer becomes absorbent for energies higher than 6eV (or wavelength lower than 206nm). The same procedure is applied to the other kinds of thick layers (HfO$_2$ and HfAlO$_x$). Results are also reported in Figure 5 and the same increase of the extinction coefficient above 6eV is detected. So, a first conclusion can be made. If the SE measurement is not made in the VUV region, the correlation between thickness and optical index is extremely high for very thin layers as used for gate dielectrics because the layers are completely transparent. The interest of working in the VUV is an enhanced optical contrast and better accuracy on the extracted physical parameters.

figure 3

figure 4

figure 5
**Structural behavior of Al₂O₃ and HfO₂**

Nine Al₂O₃ and nine HfO₂ layers have been deposited on 1nm thick RTO oxide layer. The number of ALCD cycles varies from 5 to 100 to obtain a large range of thickness. All the samples have been measured by XRR. One example is reported in Figure 6. The model used for the XRR simulations includes a RTO layer fixed at 1nm because of its very low contrast with the silicon substrate, a Al₂O₃ or HfO₂ homogenous layer with a fixed composition, and a top surface roughness simulated using a surface layer with variable thickness and a Debye Waller factor. The adjustment is made on the layer thickness, density and roughness. Results are summarized in Figure 7 and 8 for Al₂O₃ and HfO₂ layers respectively. The surface roughness is quite independent of the number of cycles. The layer thickness increases with the number of cycles as expected but the uncertainties are more important for the thinner samples. The layer density is rather independent of the number of cycles for Al₂O₃ layers and increases with the number of cycles for HfO₂ layers. These different behaviors are related to the crystallinity of the layers as demonstrated by TEM. Al₂O₃ layers are amorphous for all the range of thickness explored in this study and their density is independent of the thickness. In contrast for HfO₂ system, very thin layers are amorphous and the crystallinity increases with the layer thickness. A consequence is a substantial increase of the layer density with the thickness. An additional thermal annealing improves the crystallinity and increases the density as shown in Figure 8. This behavior is also detected by VUVSE as shown on the extracted optical indices for as-deposited HfO₂ sample and after thermal annealing at 700°C in figure 9. Better well defined structures in optical transitions are detectable after annealing indicating an increase of the crystalline state of the layer and verified by HRTEM on the same samples (cf. figure 10).
TABLE 1. VUV SE results on HfAlO<sub>x</sub> samples. The last three thicker samples are used to extract the optical indices and their composition is measured by XRF. Composition of the other layers have been measured by XPS for comparison.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Hf:Al Cycle Ratio</th>
<th>Number cycles</th>
<th>Thickness (nm)</th>
<th>HfO&lt;sub&gt;2&lt;/sub&gt; mol frac SE</th>
<th>HfO&lt;sub&gt;2&lt;/sub&gt; mol frac XPS/XRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2:1</td>
<td>9</td>
<td>0.45±0.03</td>
<td>0.75±0.10</td>
<td>0.88 (XPS)</td>
</tr>
<tr>
<td>2</td>
<td>1:1</td>
<td>10</td>
<td>0.93±0.04</td>
<td>0.56±0.09</td>
<td>0.79 (XPS)</td>
</tr>
<tr>
<td>3</td>
<td>1:2</td>
<td>9</td>
<td>0.91±0.06</td>
<td>0.53±0.13</td>
<td>0.67 (XPS)</td>
</tr>
<tr>
<td>4</td>
<td>2:1</td>
<td>27</td>
<td>1.84±0.05</td>
<td>0.64±0.04</td>
<td>0.67 (XPS)</td>
</tr>
<tr>
<td>5</td>
<td>1:1</td>
<td>28</td>
<td>2.00±0.04</td>
<td>0.59±0.03</td>
<td>0.59 (XPS)</td>
</tr>
<tr>
<td>6</td>
<td>1:2</td>
<td>27</td>
<td>2.10±0.03</td>
<td>0.48±0.03</td>
<td>0.44 (XPS)</td>
</tr>
<tr>
<td>7</td>
<td>2:1</td>
<td>90</td>
<td>5.75±0.06</td>
<td>0.66±0.01</td>
<td>0.73 (XPS)</td>
</tr>
<tr>
<td>8</td>
<td>1:1</td>
<td>90</td>
<td>5.61±0.05</td>
<td>0.59±0.01</td>
<td>0.59 (XPS)</td>
</tr>
<tr>
<td>9</td>
<td>1:2</td>
<td>90</td>
<td>5.88±0.05</td>
<td>0.39±0.01</td>
<td>0.37 (XPS)</td>
</tr>
<tr>
<td>10</td>
<td>2:1</td>
<td>909</td>
<td>53.20±0.05</td>
<td>0.263±0.001</td>
<td>0.263 (XRF)</td>
</tr>
<tr>
<td>11</td>
<td>1:1</td>
<td>910</td>
<td>56.10±0.03</td>
<td>0.415±0.001</td>
<td>0.415 (XRF)</td>
</tr>
<tr>
<td>12</td>
<td>1:2</td>
<td>909</td>
<td>58.83±0.03</td>
<td>0.594±0.001</td>
<td>0.594 (XRF)</td>
</tr>
</tbody>
</table>

Composition of HfAlO<sub>x</sub> layers

The HfAlO<sub>x</sub> samples reported in Table 1 have been measured by VUV ellipsometry. The three thicker samples (10, 11 and 12) were used to extract the optical indices for the three different composition of the materials. Results are reported in figure 5. If we compare with those of pure HfO<sub>2</sub> and pure A1<sub>2</sub>O<sub>3</sub> we obtain intermediate curves which vary continuously from one extreme composition to the other. To analyze the other thinner samples, we have applied an alloy model [11] to extract independently the layer thickness and the composition (in terms of relative molecular fraction based on XRF calibration). As shown in figure 11, thin HfAlO<sub>x</sub> with similar number of cycles (90 cycles in figure 11), but variable composition cannot be distinguished outside the VUV range. Figure 11 shows only the Tan Ψ parameters by the same conclusion can be made on the cos Δ parameters. So, composition information cannot be extracted with conventional ellipsometry in visible/UV range. On the contrary, the strong absorption in the VUV range of these new materials, offers a way to extract this kind of very important information. The different results obtained with the alloy model are summarized in Table 1 with the different uncertainties associated with the extracted values (± 1 σ from the Levenberg Marquard algorithm used for the numerical adjustments). One can immediately see that the thickness and layer composition can be extracted independently with a good accuracy except for the thinnest layers around 1nm. For layers as thin as 2 and 5nm, the thickness and composition can be extracted with a reasonable accuracy. Results are also consistent with independent measurements made by X-ray photoemission spectroscopy on the same samples (cf. table 1). These results are important since it is this kind of thickness that will be used for the gate dielectrics of the next generations of IC’s.

Figure 11: VUV SE measurements on the three thin HfAlO<sub>x</sub> samples with variable composition.

CONCLUSIONS

In this paper, we have shown that VUV spectroscopic ellipsometry is the technique of choice to characterize new high K gate dielectrics. This is due to the fact that all these new materials become absorbent when the wavelength is reduced down to 190nm. So, the correlation between thickness and refractive index is reduced in the VUV range and more precise structural information can be deduced. We have shown that the effect of a thermal annealing at 700°C on 4nm thick HfO<sub>2</sub> layers can be detected in addition to the layer thickness. Optical indices of HfO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and mixed HfAlO<sub>x</sub> layers have been
precisely determined on ~50nm thick layers. Then we have shown that an alloy model can be used to extract independently the thickness and composition of layers as thin as 2 to 5nm with a good accuracy. All these results have been confirmed by x-ray reflectometry (XRR) combined on the same system, transmission electron microscopy (TEM) and x-ray photoemission (XPS). In the next generation of IC manufacturing, a metrology with an un-precedented accuracy will be needed to control the critical step of gate dielectric deposition. We think strongly that our combined VUVSE /XRR system will be capable to fulfill these requirements

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