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Nanomechanical properties of sputter-deposited HfO₂ and HfₓSi₁₋ₓO₂ thin films

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The mechanical properties of sputter-deposited HfO₂ and HfₓSi₁₋ₓO₂ films were studied as a function of composition using nanoindentation. The elastic modulus and hardness were measured at room temperature for as-deposited films of varying Hf content and for films subjected to annealing at 1000 °C. The elastic modulus and hardness of as-deposited films were found to increase monotonically with increasing HfO₂ content, with the hardness increasing from 5.0 ± 0.3 GPa for pure SiO₂ to 8.4 ± 0.4 GPa for pure HfO₂. All films were found to be harder after annealing at 1000 °C, with the increase for SiO₂ films attributed to densification of the SiO₂ network and that for the HfₓSi₁₋ₓO₂ films to a combination of phase separation, densification, and crystallization. © 2011 American Institute of Physics. [doi:10.1063/1.3627155]

I. INTRODUCTION

Hafnium-oxide (HfO₂)-based materials have drawn wide research interest due to their excellent optical and electrical properties. Pure hafnium oxide is a high refractive index, low absorption material used for dielectric mirrors and optical coatings and, in combination with silicon dioxide in microelectronic applications due to its high dielectric-constant (κ ~ 25) and its interface stability with silicon. The use of high-k dielectrics is critical for future microelectronic-scaling to reduce gate leakage and dielectric breakdown and increase the capacitance density and voltage linearity in metal-insulator-metal (MIM) capacitors. However, the low crystallization temperature of pure amorphous hafnium oxide films is a limitation in this application, as current CMOS processing requires film stability during annealing to 1000 °C for 5 s.³–⁶ Emerging devices therefore employ amorphous hafnium silicate films, which have a higher crystallization temperature.⁷,⁸

The electrical and optical properties of HfO₂ and HfₓSi₁₋ₓO₂ thin films have been widely investigated, and considerable effort has been devoted to understand the preparation and thermal stability of such films.⁵,⁸–¹⁰ In contrast, very little has been reported on the mechanical properties of these materials, even though such properties are of critical importance for many applications. For example, the elastomechanical response and process-induced stress evolution of the high-k dielectric films during thermal cycling has a direct effect on process integration and long-term reliability. The dielectric in high-k MIM capacitors is stressed by Coulomb interactions between the charges on the two electrodes, causing capacitance-voltage nonlinearity, an effect called Maxwell stress (σₘₑₓ),¹¹ which depends on the elastic properties of the dielectric thin film. Thus, knowledge of the mechanical properties of the dielectric film is clearly important in understanding and modeling such behavior.

In this study, we have used nanoindentation to measure the hardness and elastic modulus of sputter-deposited HfO₂ and HfₓSi₁₋ₓO₂ thin films. Nanoindentation is an established tool for the measurement of hardness and elastic modulus of surfaces and thin films.¹² Its attractiveness stems from the fact that mechanical properties at small scales can be determined directly from the indentation load and displacement measurements without the need to image the residual impression. Such measurements are commonly performed with a Berkovich three-sided pyramid indenter tip (face angle of 65.3°), but here the measurements are performed with a sharper cube-corner tip (face angle of 35.3°). Cube-corner tips induce plastic deformation in thin films at lower indenta- tion loads than Berkovich tips. The films used in this study are of a thickness range 100–150 nm deposited on a silicon substrate. This system is similar to investigating a soft-film on a harder substrate, in which high indentation loads will have a significant contribution from the underlying substrate. Also, Chudoba et al.¹³ have shown that reliable thin-film hardness and modulus values can be measured with cube-corner tips by an appropriate choice of unload data fit range.

II. EXPERIMENTAL DETAILS

HfO₂ and HfₓSi₁₋ₓO₂ films were deposited onto 100 mm diameter, prime-grade p-type Si (100) wafers at room temperature by radio frequency (RF) sputtering using a commercial sputter deposition system (AJA International ATC 2400-V). The deposition chamber was evacuated to a pressure of 0.133 mPa and back-filled with Ar gas to a pressure of 0.53 Pa for deposition. Pure (99.99%) HfO₂ and SiO₂ targets were used as source materials, and the composition of the films was varied from pure HfO₂ to pure SiO₂ by varying the relative deposition rates of the HfO₂ and SiO₂ sources. The average deposition rate was maintained at around 1.3 nm/s, and

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the wafer was rotated at 25 rpm during deposition to achieve uniform thickness across its 100 mm diameter. After deposition, the wafers were diced into 1 × 1 cm square samples, with one sample of each film composition subsequently subjected to thermal annealing at 1000 °C for 60 min in a quartz-tube furnace. The furnace tube was flushed with Ar at a flow rate of 1650 ml/min and sealed from the atmosphere by passing the Ar gas through an oil-filled backflow preventer at the tube exit. The Ar was dried prior to entering the furnace by passing it through a laboratory drying canister filled with anhydrous CaSO4.

The composition and thickness of as-deposited and annealed films were measured by Rutherford backscattering spectrometry (RBS) using 2 MeV He⁺ ions incident normal to the sample surface and detected with a surface-barrier detector at a scattering angle of 168°. The thickness and refractive index of the films was also measured using a spectroscopic ellipsometer. The crystal structure of the films was determined by glancing-incidence x ray diffraction (GI-XRD) using a Panalytical Xpert Pro™ system with Cu Kα radiation at 1.545 Å. The angle of incidence of the monochromated x ray beam was maintained at 0.5° to the sample surface to minimize contributions from the Si substrate.

The mechanical properties of the films were determined from nanoindentation measurements using a Hysitron Triboindenter™ fitted with a cube-corner diamond tip. Fifty indents were performed on each sample within a load range between 10 and 1200 μN to obtain data at a range of maximum depths. The elastic modulus and hardness were determined by analyzing individual load-unload curves using the Oliver-Pharr method. The technique uses the slope of the tangent to the unloading data at maximum load in conjunction with the derivative of the elastic equations of contact for an equivalent conical indenter to determine the depth of the circle of contact (contact depth). Once this is known, the contact area is extracted from the tip area function, allowing the mechanical parameters to be extracted. Many indent curves are measured over a range of maximum loads to extract depth profiles of modulus and hardness. The tip area function and compliance were generated by indentation in fused silica immediately after the nanoindentation data on the samples was collected. The calibration parameters were confirmed by measuring the mechanical properties of both fused silica and crystalline silicon using the identical experimental set-up. The mechanical properties are well known, allowing the area to be extracted as a function of contact depth. The Oliver-Pharr method is well established but requires slight modification when not using the conventional Berkovich type indenters. The tangent to the unloading data is determined by first fitting the unloading data with a power law curve, thus allowing the tangent to be calculated. The recommended range of the unloading data to use for fitting is 80% (0.9 to 0.1 of maximum load). However, Chudoba et al. found that features sometimes observed in the unloading data from indents made using a cube corner caused inaccurate fitting. Therefore, to ensure reliable hardness and modulus data when using a cube corner tip, fitting should be performed using only the upper portion of the unloading curve. In this study, the upper 95%-60% of data from the unloading curve was used to calculate the hardness and modulus.

III. RESULTS AND DISCUSSION

Figure 1 shows a typical RBS spectrum for an as-deposited Hf$_x$Si$_{1-x}$O$_2$ film together with a fit to the experimental data using the RUMP code. The composition and thickness of this particular film were determined to be Hf$_{0.6}$Si$_{0.4}$O$_2$ and 1.5 × 10$^{18}$ at.cm$^{-2}$ and 194 nm, respectively.

![RBS spectrum](image)

**TABLE I. Summary of the film composition and thickness measured by Rutherford backscattering spectrometry and spectroscopic ellipsometry.**

<table>
<thead>
<tr>
<th>Thin film</th>
<th>Nominal x</th>
<th>Measured thickness (nm)</th>
<th>Ellipsometer</th>
<th>RBS$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfO$_2$ (A)</td>
<td>1.00</td>
<td>1.00 ± 0.05</td>
<td>159 ± 4</td>
<td>154 ± 8</td>
</tr>
<tr>
<td>Hf$<em>{0.75}$Si$</em>{0.25}$O$_2$ (B)</td>
<td>0.75</td>
<td>0.83 ± 0.04</td>
<td>138 ± 3</td>
<td>140 ± 7</td>
</tr>
<tr>
<td>Hf$<em>{0.5}$Si$</em>{0.5}$O$_2$ (C)</td>
<td>0.50</td>
<td>0.60 ± 0.03</td>
<td>208 ± 5</td>
<td>194 ± 10</td>
</tr>
<tr>
<td>SiO$_2$ (D)</td>
<td>0.00</td>
<td>0.00</td>
<td>118 ± 3</td>
<td>110 ± 6</td>
</tr>
</tbody>
</table>

$^a$Assumed bulk density of HfO$_2$ = 9.68 g.cm$^{-3}$ and SiO$_2$ = 2.26 g.cm$^{-3}$. 

The thicknesses measured by RBS and ellipsometry measurements. The thicknesses measured by the two techniques are in excellent agreement, with differences being within the...
uncertainty of the measurements. Note that the error associated with RBS measurements is estimated to be around 5% for both the thickness and composition, while that for the ellipsometry is estimated to be 2%.

GI-XRD spectra from as-deposited and annealed samples are shown in Fig. 2. The spectra from as-deposited films (presented in Fig. 2(a)) exhibit broad peaks centered at 2h values of 32° and 55°, consistent with the films being amorphous. In contrast, spectra from the annealed samples (presented in Fig. 2(b)) show well-defined diffraction peaks from HfO2. This is consistent with previous studies, in which HfxSi1-xO2 films have been shown to undergo phase separation during annealing to produce crystalline HfO2 precipitates within an amorphous SiO2 matrix. Indexing the diffraction patterns shows that the annealed HfO2 film is composed primarily of the monoclinic phase (C2/h, 90% vol. fraction), with a smaller volume fraction of the orthorhombic phase (10% vol. fraction), while the annealed HfxSi1-xO2 films are composed mainly of the orthorhombic phase (∼70% vol. fraction) and a smaller volume fraction of the monoclinic phase (30% vol. fraction). From this data and results from previous studies,16–18 it is clear that, while as-deposited films can be regarded as a homogenous mixture of HfO2 and SiO2, annealed HfxSi1-xO2 are composites of c-HfO2 in an amorphous SiO2 matrix and annealed HfO2 films have a mixed phase crystalline structure.

Typical nanoindentation load-unload curves are shown in Fig. 3. For a maximum indentation load of 1200 μN, the depth of penetration in HfO2 and SiO2 was found to be 155 nm and 205 nm, respectively, comparable to or greater than the film thickness. The smooth load-displacement curve suggests that no cracking or delamination of the films was induced by the indentation process.

Figure 4 shows the reduced elastic modulus (E) and hardness (H) measured as a function of indentation contact depth (hc) for each of the films. Measurements at low loads, contact depths less than ∼25 nm, show very high E and H values that are generally attributed to indentation size effects13,19 and difficulties with obtaining accurate tip area functions. Hardness increase toward the surface due to indentation size effect depends on the preparation of the films, indenter tip radius, and agglomeration of dislocations at the very beginning of the plastic deformation. The measured hardness gradient in the low depth range is, therefore, inevitably a combination of several effects. At higher loads, contact depths greater than 50 nm, the modulus of the thinner SiO2 film gradually increases with increasing depth. Such effects arise from increasing contributions from the substrate. Interestingly, the extracted hardness values seem less sensitive to the penetration depth, remaining reasonably constant for penetration depths over the range 50–150 nm. In order to summarize the mechanical properties, E and H values were determined by averaging measurements over the contact depth in the range 50 to 100 nm in this study. The validity of this approach is supported by the fact that the measured modulus of deposited SiO2 is similar to that measured for bulk SiO2, and comparison of data extracted over other ranges had little effect on the results.

The extracted elastic modulus values are shown in Fig. 5(a) as a function of the film composition. The modulus of the as-deposited films increases with increasing Hf content, from around 68 ± 4 GPa for SiO2 to 152 ± 13 GPa for HfO2.
In contrast to SiO$_2$, Hf oxides and silicates interact strongly with diffusing oxygen during deposition. This interaction occurs throughout the bulk of the film, thereby increasing the density of the films. This increase in density contributes to the increase in hardness and modulus values of the as-deposited films. A similar trend is observed for the annealed films, with the modulus increasing from $76 \pm 4$ GPa for SiO$_2$ to $166 \pm 8$ GPa for HfO$_2$. Within the measurement error, no difference in the modulus was observed after annealing; however, the modulus was observed to increase linearly with increasing HfO$_2$ content.

Extracted hardness values are shown in Fig. 5(b) as a function of the film composition. The data show a monotonic increase in hardness with increasing HfO$_2$ content and an increase in the hardness of films with the same composition after annealing at 1000 °C. The solid and dashed lines represent upper and lower bounds on the hardness calculated from iso-strain and iso-stress models, respectively.

The hardness of the as-deposited SiO$_2$ film was measured to be $5.0 \pm 0.3$ GPa, considerably lower than that of the bulk-fused silica reference sample, which is expected, given that deposited films are generally less dense than bulk material. The hardness of this film increased to $6.7 \pm 0.3$ GPa after annealing at 1000 °C, consistent with some densification of the film. In contrast, the increase in the hardness of the HfO$_2$ film is most likely associated with crystallization, which transforms from an amorphous phase to a mixture of monoclinic and orthorhombic phases. This also involves densification of the film, as the crystalline phases are generally more dense (density 9.68 g/cm$^3$) than the amorphous phase (density 9.38 g/cm$^3$), with stable monoclinic phase being denser than the metastable orthorhombic phase. On this basis, the increase in hardness of the Hf$_x$Si$_{1-x}$O$_2$ films after annealing is attributed to phase separation of the SiO$_2$ and HfO$_2$, densification of the SiO$_2$, and crystallization.
of the HfO$_2$ fraction to form a composite material. The data in Fig. 5(b) for as-deposited and annealed samples are well described by the iso-stress model, which is to be expected given their microstructure.

IV. CONCLUSIONS

The elastic modulus and hardness of amorphous Hf$_x$Si$_{1-x}$O$_2$ thin films deposited by sputter deposition have been shown to increase monotonically with increasing Hf content, with the hardness increasing from 5.0 $\pm$ 0.3 GPa for $x = 0$ (pure SiO$_2$) to 8.4 $\pm$ 0.4 GPa for $x = 1$ (pure HfO$_2$). All films were shown to be harder after annealing at 1000°C, with the increase for SiO$_2$ films attributed to densification of the SiO$_2$ network and that for the Hf$_x$Si$_{1-x}$O$_2$ films to a combination of phase separation, densification, and crystallization.

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12See http://www.genplot.com for information about comprehensive analysis and simulation of RBS spectra.