Characterization of the Ultrathin HfO$_2$ and Hf-Silicate Films Grown by Atomic Layer Deposition

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Abstract—The physical properties of HfO$_2$ and Hf-silicate layers grown by the atomic layer chemical vapor deposition are characterized as a function of the Hf concentration and the annealing temperature. The peaks of Fourier transform infrared spectra at 960, 900, and 820 cm$^{-1}$ originate from Hf-O-Si chemical bonds, revealing that a Hf-silicate interfacial layer began to form at the HfO$_2$/SiO$_2$ interface after postdeposition annealing process at 600 °C for 1 min. Moreover, the intensity of the peak at 750 cm$^{-1}$ can indicate the degree of crystallization of HfO$_2$. The formed Hf-silicate layer between HfO$_2$ and SiO$_2$ is also confirmed by X-ray photoelectron spectroscopy.

Index Terms—Fourier transform infrared (FTIR), HfO$_2$, Hf-silicate, high-$k$, X-ray photoelectron spectroscopy (XPS), X-ray reflectivity (XRR).

I. INTRODUCTION

In order to meet the International Technology Roadmap for Semiconductor [1] requirements for equivalent oxide thickness (EOT) and gate leakage current, the conventional SiO$_2$ gate dielectric might need to be replaced by higher dielectric constant materials [2]. Using the “high-$k$ dielectric” allows the device to maintain an EOT of 1 nm or less, while having a larger physical thickness to reduce the tunneling current. Among the various high-$k$ dielectric materials, hafnium-based dielectrics are being widely investigated due to their high dielectric permittivity, high melting point, and acceptable thermal and chemical stabilities [3]–[6]. However, the hafnium-based dielectrics still have some critical issues, such as mobility degradation [7] and large flatband voltage shift [8], which impede their industrial application. Furthermore, it is hard to maintain the amorphous state for HfO$_2$ due to its low crystallization temperature (300–400 °C) [9]. The pseudobinary materials, such as Hf-aluminate and Hf-silicate, combine the advantages of acceptable dielectric constant and desirable higher crystallization temperature [10]. Therefore, the material change of high-$k$ dielectrics after the thermal process is a significant issue for the future CMOS applications. In this paper, we investigate the material and electrical modification of Hf-based dielectrics at different annealing conditions and different Si incorporations.

II. EXPERIMENT

The high-$k$ films were on the 15–25 Ω·cm p-type Si wafers. All samples were treated with an SC-1 preclean process before high-$k$ dielectrics deposition. This cleaning process typically results in a chemical oxide layer between high-$k$ dielectrics and the Si substrate to enhance initial growth of the high-$k$ dielectrics. The HfO$_2$ and Hf-silicate films were deposited by hot-wall atomic layer chemical vapor deposition [11] with a reaction temperature of 300 °C, using alternating surface-saturation reactions of HfCl$_4$, SiCl$_4$, and H$_2$O. Note that Hf-silicate films with different Hf/Si ratios (Hf$_{0.36}$Si$_{0.62}$O$_2$, Hf$_{0.5}$Si$_{0.5}$O$_2$, and Hf$_{0.66}$Si$_{0.34}$O$_2$) were grown using alternated nanomixed HfO$_2$/SiO$_2$ [12]. After deposition, a silicon nitride cap to form a thin passivation layer (<0.5 nm) was deposited at 600 °C for 10 s using NH$_3$ and SiCl$_4$ precursors. The samples were annealed in the furnace at 600 °C for 1 min and 1000 °C for 5 min in N$_2$ ambient for postdeposition annealing (PDA). The furnace was kept at the atmospheric pressure and purged by nitrogen. The electrical properties were studied using metal-insulator-semiconductor (MIS) capacitors with a 50-nm-thick Pt electrode deposited by E-gun and a circular area of 2.5 × 10$^{-4}$ cm$^2$ defined by the shadow mask. Another Al contact is deposited on the back of the sample. The postmetalization annealing (PMA) was done in forming gas, N$_2$ (90%) + H$_2$ (10%), at 400 °C for 30 min before the electrical measurement. Fourier transform infrared (FTIR) spectroscopy was used to observe transmission spectra of the different chemical bonds and the change of bonding state after thermal processing. Each spectrum was measured with a resolution of 4 cm$^{-1}$ and a range of 370–1800 cm$^{-1}$ and transformed from transmission

Manuscript received May 8, 2006; revised December 19, 2006. The work of the National Taiwan University group was supported by the National Science Council, Taiwan, R.O.C., under Contract 93-2215-E-002-003 and Contract 93-2215-E-002-017. The review of this paper was arranged by Editor G. Groeseneken.

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Digital Object Identifier 10.1109/TED.2007.892012
Fig. 1. (a) Scheme of FTIR measurement structure. (b) FTIR spectra of HfO$_2$ after PDA at 600°C for 1 min in flowing N$_2$ measured by “face-to-face” structure. The intensity of IR signal with ultrathin high-$k$ layer can be enhanced by the “face-to-face” method.

Fig. 2. FTIR spectra of ultrathin HfO$_2$ films as-deposited, annealed at 600°C for 1 min, and annealed at 1000°C for 5 min in N$_2$ ambient. The positions of the peaks in the three curves are indicated by dashed lines. The intensity of the peak at 750 cm$^{-1}$ is clearly seen to increase the thermal budget.

Fig. 3. FTIR absorption spectra of Hf-silicate. The samples in (a) were not annealed, and in (b) and (c), the samples were annealed in N$_2$ ambient for 1 min at 600°C and for 5 min at 1000°C, respectively. There are only two peaks (at 600 and 512 cm$^{-1}$) in the as-deposited nanomixed HfO$_2$/SiO$_2$, indicating no Hf-silicate formation.

to absorption. High-resolution transmission electron microscope (HRTEM) and X-ray photoelectron spectroscopy (XPS) were used for physical thickness inspection and observation of the chemical composition of the gate dielectrics. X-ray reflectivity (XRR) using CuK$_\alpha$ source was used to study the constituent thickness and roughness of these films. The thickness obtained by XRR was calibrated with HRTEM measurements for layer thickness and atomic force microscopy (AFM) for surface roughness. The electrical properties of HfO$_2$ and Hf-silicate films on chemical oxide with different PDA conditions were also studied. The capacitance–voltage ($C$–$V$) and current–voltage ($I$–$V$) characteristics for electrical properties were measured with HP 4284A and Keithley 4200 instruments, respectively.
Fig. 4. XPS results of the (a) Hf 4f, (b) O 1s, and (c) Si 2p peaks for HfO$_2$ films as-grown and annealed at 1000 °C for 5 min in N$_2$ ambient. The shift of the Hf 4f, O 1s, and Si 2p peaks to higher binding energy is due to the formation of a Hf-silicate layer.

III. RESULTS AND DISCUSSION

A. FTIR Results

FTIR analysis is a reliable and powerful method due to its convenient, rapid, and nondestructive measurement. However, the high-$k$ gate dielectrics are too thin to detect in FTIR measurement, and the characteristics of a thin HfO$_2$ layer may be quite different from those of a thick one due to the crystallization [13]. Previous work has shown that it is possible to detect the chemical bonding vibrations of SiO$_2$, HfO$_2$, and hydrogen defects in layers as thin as several nanometers using attenuated total reflection and multiple internal reflection measurements [14]–[16]. Those techniques use a complicated method to adjust the incident angle of the IR beam to enhance the signal. A simple method to detect the weak signal from the ultrathin film and from the interface between the high-$k$ layer and the oxide is reported here. A schematic cross section of our “face-to-face” measurement structure is shown in Fig. 1(a). The absorption is enhanced in the “face-to-face” structure due to the doubling of the film thickness and the reflection at the interface between the surfaces of two samples. Note that there is no observable absorption signal if we use only one sample in our measurement system. Fig. 1(b) shows the FTIR spectra of HfO$_2$ after annealing at 600 °C for 1 min by the “face-to-face” measurement structure. Fig. 2 shows the FTIR spectra of the as-deposited HfO$_2$ sample and the HfO$_2$ samples annealed at 600 °C (1000 °C) in N$_2$ ambient for 1 min (5 min). There are three peaks, at 750, 600, and 512 cm$^{-1}$, attributed to the Hf–O chemical bonds in the spectra, and the peaks at 960, 900, and 820 cm$^{-1}$ are assigned to Hf–O–Si stretching vibrations [17]–[19]. The peak at around 1120 cm$^{-1}$ may result from the absorption by the Si–N bond [20] formed by surface nitridation or from Si–O–Si bond absorption in the chemical oxide layer. The as-deposited HfO$_2$ film spectrum exhibits peaks at 600 and 512 cm$^{-1}$ due to Hf–O chemical bonds, and these two peaks increase with annealing temperature, so does the 750 cm$^{-1}$ peak. The intensity of the 750 cm$^{-1}$ peak increases with the thermal budget of the HfO$_2$ due to the increasing degree of crystallization [21]. Comparing the three spectra (as-deposited, annealed at 600 °C, and annealed at 1000 °C), the intensities of the peaks at 960, 900, and 820 cm$^{-1}$ are seen to increase with the thermal budget. This is due to the Hf–O–Si chemical bonds formed at the HfO$_2$/SiO$_2$ interface. The formation of silicate cannot be avoided during the thermal process. During the annealing process, Hf-silicate is formed by the atomic diffusion mechanism [22]. As a result of Si diffusion into HfO$_2$, the Hf-silicate should be formed in the original HfO$_2$ layer, thus increasing the interfacial layer thickness. The silicate interfacial layer shows no obvious contrast with the initial chemical oxide in the transmission electron microscopy (TEM) image (Fig. 5), indicating that the interfacial silicate might be Si rich. In Fig. 3, the FTIR absorption spectra of Hf-silicate are shown as a function of Hf concentration at different thermal annealing conditions. In Fig. 3(a), the as-deposited samples show no apparent peaks from 700 to 1000 cm$^{-1}$, which indicates that the as-deposited nanomixed HfO$_2$/SiO$_2$ does not intermix, whereas the peaks at 600 and 512 cm$^{-1}$ are detected in as-deposited nanomixed HfO$_2$/SiO$_2$, indicating Hf–O bond formation. The annealing at 600 °C and 1000 °C generates absorption peaks due to Hf–O–Si stretching vibrations [Fig. 3(b) and (c)], indicating the intermixture and formation of Hf-silicate after the thermal annealing of the nanomixed...
HfO$_2$/SiO$_2$. Moreover, the intensity of the peak at 750 cm$^{-1}$ also increases the Hf concentration in Fig. 3(b) and (c), indicating slight occurrence of phase separation and crystallization at the high Hf concentration [23]. Due to the variation in each measurement, in Fig. 3, the intensity of oxide has been normalized. The integration of the Hf–O–Si peak area is only studied as a function of temperature in the Hf$_{0.66}$Si$_{0.34}$O$_2$ samples. The ratio of this sample with PDA at 600 °C for 1 min and PDA at 1000 °C for 5 min is 2, which indicates the increase of Hf–O–Si bonds with the increase of temperature. Note that, although the HfO$_2$ sample seems to have more pronounced Hf–O–Si peak (Fig. 2) than the nanomixed HfO$_2$/SiO$_2$ samples [Fig. 3(c)], the integration of the Hf–O–Si peak area (filtering the background of the broad signal) is slightly lower than the nanomixed HfO$_2$/SiO$_2$ samples. The quantitative analysis of the FTIR signal is not obtained by the difference of the optical alignment and environmental condition for each measurement.

B. Structural Analysis

The HfO$_2$ film on SiO$_2$ following PDA at 1000 °C is also characterized by XPS measurements, as shown in Fig. 4. In Fig. 4(a), the peak of the XPS of HfO$_2$ after the PDA process is at about 17.9 eV. The shift of Hf peak to higher binding energy is attributed to the formation of Hf-silicate film, which is 0.5 eV higher than that of the as-grown HfO$_2$ film (17.4 eV). Note that the two peaks (Hf 4f$/7/2$ and Hf 4f$/5/2$) of XPS in Hf element cannot be distinguished due to the limit of resolution of the XPS equipment. Furthermore, the O 1s spectrum [Fig. 4(b)] and Si 2p spectrum [Fig. 4(c)] of the annealed samples are also shifted to higher energy as compared to those of as-grown sample, indicating a strong signature of Hf-silicate formation. The intensity of reflected X-ray is dependent on the surface and near-surface electron density. Consequently, XRR has been used to study a variety of surface and thin film properties. In order to understand the effects of the PDA process, it is important to realize the effect on the chemical reaction at interface and the growth of the interfacial layer due to the increasing thermal budget. XRR and TEM have been utilized to analyze the physical characteristics of as-grown and post-annealed HfO$_2$. The TEM images of HfO$_2$ thin films as-deposited, annealed at 600 °C for 1 min, and annealed at 1000 °C for 5 min are shown in Fig. 5(a), (b), and (c), respectively. Fig. 5(a) shows that the as-grown HfO$_2$ partially crystallizes only after 600 °C for 10 s for the Si$_3$N$_4$ cap. The degree of crystallization of HfO$_2$ is clearly increased when the sample was annealed at 1000 °C, which is also indicated by the peak at 750 cm$^{-1}$ in Fig. 2. The thickness of the interfacial layer between the HfO$_2$ and the Si substrate increases with the thermal budget. Evidently, the HfO$_2$ film is partially consumed by the interfacial
silicate, since the HfO$_2$ thickness decreases after annealing. Note that the Si$_3$N$_4$ cap is not visible in the TEM picture, which may be due to the poor contrast between Si$_3$N$_4$ and the TEM bonding glue or too thin thickness of the Si$_3$N$_4$ cap. Fig. 6 depicts the XRR response of the HfO$_2$ film before and after thermal annealing. The period of oscillation in the XRR plot depends on the thickness of the layer with the highest electron density, which is HfO$_2$ in our samples. The HfO$_2$ sample response has a longer period after N$_2$ annealing, indicating the shrinkage of the HfO$_2$ layers. This is confirmed by the TEM image in Fig. 5. Note that the XRR curves of annealed HfO$_2$ are obviously different from the as-deposited one due to the formation of the Hf-silicate layer and the increase of the interface roughness between each layer, which is obtained by XRR simulation. The HfO$_2$/SiO$_2$ interfacial roughness after annealing at 1000 °C for 5 min, which was obtained from the XRR fitting (not shown here), showed an increase of 0.3–0.4 nm as compared to the as-deposited sample. The inset of Fig. 6 is the surface roughness of the HfO$_2$, which is measured by AFM. The surface roughness of samples increases slightly after PDA [24]. The XRR of the annealed HfO$_2$ is fitted by the four-layer model (model 2 in Table I) that includes (in sequence): substrate Si, initial chemical oxide layer, Hf-silicate interfacial layer, and HfO$_2$ [25], and the as-deposited sample is also fitted with the structure without a Hf-silicate layer (model 1 in Table I). Note that although the layer of Hf-silicate is not clearly observed in the TEM picture, a Hf-silicate layer should be reasonably assumed between HfO$_2$ and SiO$_2$. Table I lists the corresponding layer thickness $T$, film density $D$, and surface roughness $R$, obtained by XRR fitting, TEM, and AFM. The surface roughness calculated by simulation is quite similar to that obtained from AFM measurement. The interface roughness in TEM is observed in extremely local region on the scale of nanometers. However, the roughness measured by XRR is an average on a large area (in square millimeters). The correlation between TEM roughness and XRR roughness is not known. The error bar of TEM thickness can be roughly estimated from each TEM micrograph. The thickness of the interfacial layer between the Si and the HfO$_2$ increases significantly when the thin film was annealed at 1000 °C for 5 min (Table I). The oxygen needed for the growth of the interfacial oxide may have originated from the trace oxygen in the flowing N$_2$ ambient and/or the oxygen in HfO$_2$ [26].

### C. Electrical Properties

The high-frequency (100 kHz) $C$–$V$ curves measured at room temperature are plotted in Fig. 7; the electrode area

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**TABLE I**

<table>
<thead>
<tr>
<th>As grown</th>
<th>PDA 600°C 1min</th>
<th>PDA 1000°C 5 min</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Simulation (model 1)</strong></td>
<td><strong>TEM</strong></td>
<td><strong>Simulation (model 2)</strong></td>
</tr>
<tr>
<td>SiO$_2$ ($T$)</td>
<td>1.3 nm</td>
<td>1.4 nm</td>
</tr>
<tr>
<td>HfO$_2$ ($T$)</td>
<td>3.4 nm</td>
<td>3.4 nm</td>
</tr>
<tr>
<td>Density ($D$)</td>
<td>HfO$_2$: 8.2 g/cm$^3$</td>
<td>Hf-silicate: 3 g/cm$^3$</td>
</tr>
<tr>
<td>Surface Roughness ($R$)</td>
<td>0.41 nm (XRR)</td>
<td>0.42 nm (XRR)</td>
</tr>
<tr>
<td></td>
<td>0.37 nm (AFM)</td>
<td>0.44 nm (AFM)</td>
</tr>
</tbody>
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is $2.5 \times 10^{-4}$ cm$^2$. The interfacial chemical oxide is grown by SC-1 before the insulator to restrict the interface trap density. The capacitance of the accumulation region increases, indicating an increase in the dielectric constant density. The gate leakage current reduction as compared to the SiO$_2$ device shows a $10^2$ order of magnitude or less as the Hf concentration (38% to 100%) increases, indicating an increase in the dielectric constant. The gate leakage current reduction as compared to the SiO$_2$ device shows a $10^2$ order of magnitude or less leakage current reduction as compared to the SiO$_2$ device, and the Hf-silicate devices show about one order of magnitude or less leakage current reduction as compared to the SiO$_2$ device.

IV. Conclusion

In summary, we find that the weak FTIR signal from thin Hf$_{1-x}$Si$_x$O$_2$ films can be detected by using a “face-to-face” structure. When the HfO$_2$ thin film on oxide is annealed at high temperature (600 °C and 1000 °C), the formation of a Hf-silicate layer in the HfO$_2$/SiO$_2$ interface is evidenced by the occurrence of the FTIR peaks at 960, 900, and 820 cm$^{-1}$, attributed to Hf–Si–O stretching vibrations. Moreover, XPS results also indicate a great signature of the formation of a Hf-silicate layer. The annealed nanomixed HfO$_2$/SiO$_2$ sample has the same FTIR peaks, indicating that the nanomixed HfO$_2$/SiO$_2$ transformed into Hf-silicate after the thermal process.

Acknowledgment

The authors would like to thank Dr. M. Temple for proof-reading this paper.

References

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