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# Initial growth of interfacial oxide during deposition of $HfO_2$ on silicon

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Interfacial chemistry of Hf/Si, $HfO_2/SiO_2/Si$, and $HfO_2/Si$ is investigated by x-ray photoelectron spectroscopy in order to understand the interfacial layer formation mechanism. Deposition of Hf and $HfO_2$ films was carried out on Si wafers by electron-beam evaporation with oxygen backfill. We show that the interfacial layer formation takes place predominantly at the initial stage of the $HfO_2$ film deposition. Temporary direct bonding between Hf metal and Si is proposed to be the source of the catalytic reaction resuting in formation of interfacial layer. Formation of interfacial layer was suppressed by chemically grown thin oxide blocking the direct Si–Hf bonding. We also demonstrate reduced interfacial layer after modified Shiraki surface etch, compared to the Radio Corporation of America clean. This indicates that a more complete hydrogen termination and atomically smoother surface can delay the onset of interfacial layer formation. © *2004 American Institute of Physics*.
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Scaling of metal–oxide–semiconductor field effect transistor (MOSFET) devices will require high-$k$ gate dielectric materials when very thin (<2 nm) $SiO_2$ layer will no longer be acceptable as gate oxide due to the high leakage current by direct tunneling. $HfO_2$ is one of the most widely studied materials for its high dielectric constant ($k \sim 25$), wide band gap, and thermal stability on silicon at elevated temperature.[1] However, for a replacement of $SiO_2$ with high-$k$ gate dielectrics, several obstacles should be overcome. Interfacial layer (IL) formation is one of them.[2–5] $HfO_2$ film is known to have high permeability to oxygen and metallic Hf films are also very easily oxidized in air.[2] Therefore, growth of the interfacial layer takes place at the $HfO_2/Si$ interface during the deposition process, postdeposition annealing, and exposure to air.[6]

It is still uncertain whether the interfacial layer growth occurs predominantly in the initial stage of the deposition or continues gradually throughout the deposition process. Understanding the mechanisms governing interfacial layer formation is very important in engineering the interface structure for applications of high-$k$ dielectrics. Low dielectric constant of interfacial oxides or silicates reduces the overall dielectric constant of the gate stack. In addition, the uncontrolled nature of the interfacial layer growth results in variations of device parameters such as threshold voltage. In this work, we show that the growth of the interfacial layer takes place predominantly in the initial period of $HfO_2$ deposition, even at room temperature. The effect of pregrown chemical oxide on the formation of the interfacial layer is described. Finally, a cleaning method that reduces the interfacial layer thickness is demonstrated.

$HfO_2$ films were prepared on $p$-type Si(100) substrates with a resistivity of 1–10 Ω cm by electron-beam (e-beam) evaporation at room temperature. E-beam evaporation was performed using $HfO_2$ pellets or Hf metal as source materials. Oxygen backfill (at $5 \times 10^{-5}$ Torr) was applied during the film deposition. Wafers were cleaned by the modified Shiraki procedure.[7] After $HfO_2$ deposition, some samples were subject to 30 min postdeposition anneals at 350 °C in $H_2$ ambient, at 2 Torr. The details of the $HfO_2$ film deposition and wafer cleaning methods were described previously.[7,8] X-ray photoelectron spectroscopy (XPS) spectra were obtained using Al $K\alpha$ radiation excitation at a takeoff angle of 90°. The peak intensities from Si $2p$ core level were normalized to the substrate Si–Si ($Si^0$) peak height and aligned to the substrate peak position which averaged 99.3 eV. Peaks corresponding to Hf $4f$ core level were normalized to the Hf $4f_{7/2}$ peak height.

In order to determine the effect of adsorbed oxygen on the formation of interfacial layer, an as-cleaned sample was introduced into the e-beam evaporation chamber and exposed to oxygen at a partial pressure of $5 \times 10^{-5}$ Torr for 20 min. The oxygen was then turned off and the chamber returned to the base pressure ($<1 \times 10^{-7}$ Torr) and a 6 nm thick Hf metal layer deposited. We designate this sample as $Hf/O_2/Si$. A control sample of $Hf/HfO_2/Si$ was formed by e-beam evaporation of Hf metal at an oxygen partial pressure of $5 \times 10^{-5}$ Torr, forming a 1 nm thick layer, followed by a 5 nm thick layer of Hf metal evaporated without oxygen. A third sample of $HfO_2/Si$ consisted of 6 nm thick $HfO_2$ formed on Si by e-beam evaporation of $HfO_2$ under oxygen partial pressure of $5 \times 10^{-5}$ Torr. The schematic of the sample preparation for experiment is illustrated in Fig. 1.

The Si $2p$ core level and Hf $4f$ core-level XPS spectra obtained from these samples are shown in Fig. 2. In addition to the Si–Si bond at 99.3 eV peaks associated with $SiO_x$, Hf–O, and Hf–Si were observed. We assume that the $SiO_x$ signal is due to interfacial silicon oxide. Indeed, interfacial oxide was not detected from the $Hf/O_2/Si$ sample. This confirms the efficacy of our cleaning procedure and shows that

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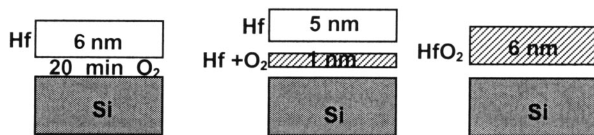


FIG. 1. Schematic illustration of $HfO_2$ and Hf film deposition experiment.

exposure to oxygen prior to Hf evaporation does not result in formation of $SiO_x$. This sample should be thus referred to as Hf/Si, but we retain the original designation for consistency. Interfacial oxide was detected for the $Hf/HfO_2/Si$ and $HfO_2/Si$ sample. For both samples, the calculated thickness [9] of the interfacial $SiO_x$ layer was ~0.7 nm, about equal to 2 monolayer of $SiO_2$. Considering the longer exposure to oxygen for the $HfO_2/Si$ sample and the low temperature of the silicon substrate (<50 °C), this indicates that formation of the IL takes place predominantly at the initial stage of $HfO_2$ deposition. The $SiO_x$ peak from the $Hf/HfO_2/Si$ sample is located at a higher binding energy, ~0.5 eV, than that from the $HfO_2/Si$; it is more $SiO_2$-like. Finally, Hf–Si bonding peaks are detected in $Hf/O_2/Si$ and Hf/HfO2/Si samples. This evidence of direct contact between Hf and silicon substrate may indicate that the IL is in fact hafnium–oxygen silicate ($HfSi_xO_y$).[10] The $HfO_2/Si$ was fully oxidized as confirmed by the presence of Hf–O peaks. Partial oxidation of the $Hf/O_2/Si$ and $Hf/HfO_2/Si$ samples most likely occurred after removal from the evaporator and exposure to air. A binding energy shift of Hf–O bonds to higher energy in these two samples, with respect to the fully oxidized $HfO_2/Si$, is attributed to the presence of Hf–O–Si bonds due to Si outdiffusion into the $HfO_2$.[3,10–12]

Figure 3 shows Si 2*p* core-level spectra of two samples, one with an intentionally grown chemial oxide and the other with a H-terminated Si surface. The experiment was carried out to compare the effect of the oxide intentionally formed on Si with that formed on a clean Si surface by the process of formation of $HfO_2$. Wafers with ~1 nm thick chemical oxide grown in $HCl:H_2O_2:H_2O$ solution and H-terminated Si prepared by modified Shiraki cleaning were introduced into the evaporator at the same time and a 5 nm thick layer of $HfO_2$ was deposited on them. Parts of these samples were annealed in $H_2$. The IL formed on a clean silicon surface exhibits binding energy of 102.2 eV. This is 0.5 eV lower than that

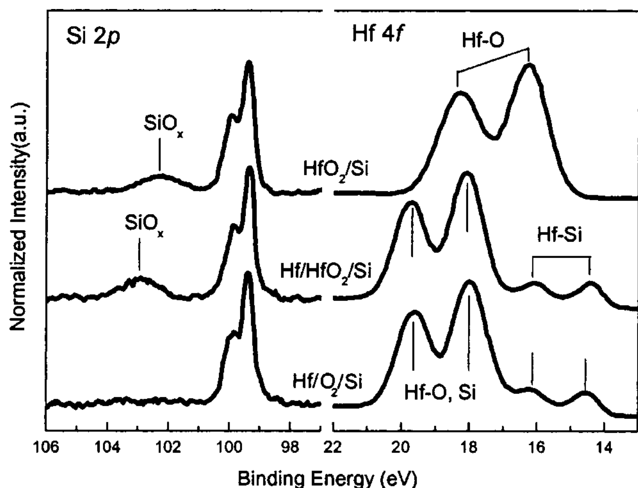


FIG. 2. Si 2*p* core-level and Hf 4*f* core-level XPS spectra of $Hf/HfO_2/Si$ sample and Hf/Si sample.

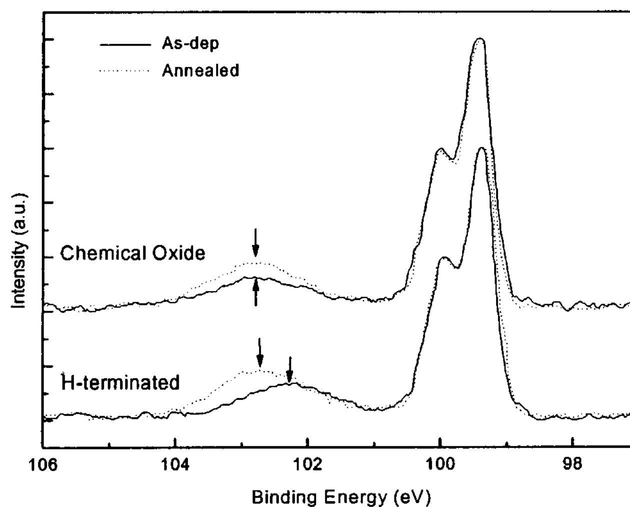


FIG. 3. Si 2*p* core-level XPS spectra obtained from as-grown state and after annealing. $HfO_2$ film has been deposited on pregrown chemical oxide and hydrogen-terminated surface at the same time.

formed on the chemical oxide, indicating a more silicatelike nature of the IL in the former. We interpreted the data of Fig. 2 assuming that the IL formed on oxide-free surfaces contains Hf–O–Si bonds. Formation of a Hf–silicate IL has been reported for $HfO_2$ deposited on $SiO_2$ of similar thickness,[4] and is consistent with its presence in our sample prepared on chemical oxide. Higher binding energy of the IL in this sample may indicate a lower concentration of Hf–O–Si. In $H_2$ annealed samples, the IL peak intensity from both samples increased but the binding energy shift is noticeable only in the H-terminated silicon sample. The intensity increase of the IL peak corresponds to the thickness increase. This indicates that additional oxidation takes place during $H_2$ annealing process at the IL/Si interface and within the IL matrix resulting in creation of Si–O bonds. The source of oxygen, either from residual oxygen in the chamber or oxygen trapped in the film during the deposition process, cannot be decided at this point. However, our result shows that a pregrown oxide layer can reduce the change in the stoichiometry of the IL in subsequent thermal processes. This allows for better control of the process. Therefore, a controlled growth of a high-quality IL can be a valuable tool in the formation of high-*k* gate dielectrics.[13]

The effect of different silicon cleaning methods on the formation of IL is illustrated in Fig. 4. Modified Shiraki (MS) cleaning was compared to the Radio Corporation of America (RCA) clean (Piranha+SC1+diluted HF dip) by evaluating the XPS data. For this purpose, two wafers were separately cleaned by the two methods and a 4 nm thick film of $HfO_2$ was deposited on both of them at the same time. The Si 2*p* core-level spectra were then measured. The normalized intensity of the $SiO_x$ peak at around 102.4 eV from MS-cleaned sample was ~20% lower than that of the RCA-cleaned sample while the remainder of the spectra is identical. This result confirms the trend observed in our previous studies where the combined effect of more complete hydrogen termination and an atomically smoother surface resulting from MS cleaning was to limit the growth of native oxide.[7]

Our XPS data on $Hf/HfO_2/Si$, $HfO_2/Si$, and $Hf/O_2/Si$ samples show that the oxygen physically adsorbed on the surface of silicon does not initiate the formation of the IL. Instead, the IL is formed by the exposure of the surface to the

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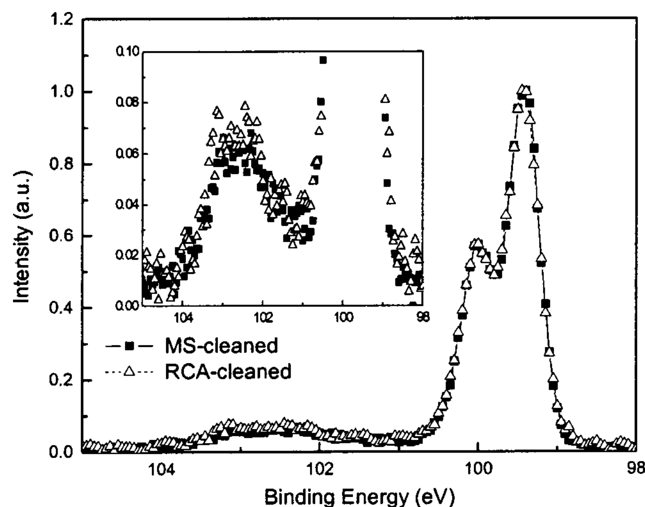


FIG. 4. XPS Si 2*p* core-level spectra of $HfO_2$ film deposited on MS-cleaned sample and RCA-cleaned sample.

hafnium metal together with oxygen. The formation of Hf–Si bonds thus appears to play an important role in the oxidation of silicon under oxygen partial pressure. Since the $HfO_2$ is thermodynamically stable with respect to Si,[14] a kinetic mechanism is needed to account for the experimentally observed formation of interfacial $SiO_x$ layer.[15] When hydrogen-terminated silicon surface is exposed to oxygen, formation of a H–Si dipole moment weakens the Si–Si back bond resulting in the formation of Si–O bond.[16] This is made possible by the large electronegativity of hydrogen (2.1).[17] However, electronegativity of hafnium (1.3) is lower than that of silicon and this mechanism cannot be responsible for Si oxidation on a Hf covered surface. Oxidation accelerated by the catalytic effect of transition metal atoms on a silicon surface has been proposed previously.[15,18,19] The oxidation of the Si–Si back bonds by reactive oxygen atoms would proceed until the surface Hf becomes oxidized. At this point, oxidation of Si stops about formation of $HfO_2$ continues.

The absence of the IL in the $Hf/O_2/Si$ sample deposited under a high vacuum implies that the adsorbed oxygen is unimportant and that a continuous supply of oxygen during Hf deposition is essential for the formation of the IL. The fact that the $SiO_x$ peak in $Hf/HfO_2/Si$ sample is located at higher binding energy, is more $SiO_2$-like, than in the $HfO_2/Si$ sample suggests a higher density of Si–O bonds in the former. However, this sample was prepared by evaporation of Hf metal under partial pressure of $O_2$, in contrast to the $HfO_2/Si$ sample prepared by evaporation of $HfO_2$ under the same partial pressure of $O_2$. This result supports the idea that a higher concentration of Hf–Si bonds at the beginning of the deposition results in more Si–O bonds at the interface, which is consistent with the above discussion. To avoid the IL formation, care must to be taken not to expose the silicon surface to metal and oxygen atoms at the same time.

We have shown that the IL formation takes place predominantly in the initial stage of the $HfO_2$ deposition. The interaction between Hf metal and Si appears to accelerate formation of $SiO_x$. Pregrown chemical oxide suppressed the formation of silicatelike IL during $HfO_2$ deposition and resulted in a more stable IL under subsequent annealing.

Thinner IL growth was observed in the MS-cleaned sample compared to the RCA-cleaned sample. The MS-cleaned samples are flatter and thus present fewer atomic steps and kinks that facilitate chemical reactions. In the future, MOSFET applications which will require EOT values of less than 1 nm, even small differences in IL will be significant.


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