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Interface states for HfO$_2$/Si structure observed by x-ray photoelectron spectroscopy measurements under bias

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A 1.0 nm silicon nitride (SiN) layer can prevent reaction between HfO$_2$ and Si completely. In this case, the interface state spectra obtained from x-ray photoelectron spectroscopy measurements under bias have two peaks above and below the midgap, attributable to Si dangling bonds interacting weakly with an atom in SiN, indicating a high atomic density of the SiN layer. When a HfO$_2$ layer is deposited on a 1.0 nm SiO$_2$ layer, the SiO$_2$ thickness increases to 1.6 nm. For this structure, one interface state peak is present near the midgap, attributable to isolated Si dangling bonds, indicating a low atomic density. © 2006 American Institute of Physics.

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A decrease in the leakage current density flowing through gate dielectrics is one of the most serious and urgent problems to be solved for further miniaturization of large scale integration. High dielectrics (high $\kappa$) such as HfO$_2$ (Refs. 1–15) and ZrO$_2$ (Refs. 15 and 16) are extensively studied for gate insulating layers alternative of silicon dioxide (SiO$_2$). HfO$_2$ is one of the most promising candidates because of its high dielectric constant, thermal stability, wide band-gap energy, etc. HfO$_2$ layers can be formed using several methods such as chemical vapor deposition, atomic layer deposition, sputter deposition of Hf metal followed by annealing, and reactive sputtering. However, the interface characteristics of high $\kappa$ dielectric/Si interfaces are not so good as those of SiO$_2$/Si interfaces, e.g., high interface state density. Moreover, in most cases, an interfacial layer is formed due to the reaction between HfO$_2$ and Si, which degrades the electrical characteristics. In the case of Hf deposition followed by heat treatments, the interfacial layer thickness is small but Hf silicate and/or silicide are formed at the interface. To avoid these phenomena, buffer layers such as silicon oxynitride (SiON), silicon nitride (SiN), and SiO$_2$ (Refs. 7, 11, and 13) are inserted between Si and HfO$_2$.

In the present study, interface state spectra for HfO$_2$/Si interfaces have been obtained from x-ray photoelectron spectroscopy (XPS) measurements under bias and the effect of buffer layers (SiN and SiO$_2$) on the interface state spectra has been investigated. XPS measurements under bias have already been found to give interface state spectra of ultrathin SiO$_2$ layers through which a high density leakage current flows and thus to which electrical measurements such as capacitance-voltage and conductance-voltage methods are not applicable.

Phosphorus-doped n-type Si(100) wafers with an $\sim$10 $\Omega$ cm resistivity were cleaned using the RCA method and etched with dilute hydrofluoric acid. For some specimens, 1.0 nm thick SiO$_2$ buffer layers were formed by heat treatments at 900 °C for 30 s in dry oxygen. For other specimens, 1.0 nm thick SiN layers were formed by direct Si nitridation by means of the low energy electron impact method. In this case, nitrogen plasma was generated by heating tungsten filament in 1 Pa nitrogen atmosphere and 40 V was applied between the filament and a grid. The plasma nitridation was performed at 400 °C for 1 min. $\sim$2 nm thick HfO$_2$ films were deposited at 400 °C by means of the electron-beam evaporation method using a HfO$_2$ target. For XPS measurements under bias, an $\sim$3 nm thick platinum (Pt) layer was deposited using the thermal evaporation method. During XPS measurements under bias, the Pt layer was earthed and a bias voltage was applied to the rear Si electrode.

Figure 1 shows the XPS spectra in the Hf 4f region. When a HfO$_2$ layer was directly deposited on the Si sub-

![FIG. 1. XPS spectra in the Hf 4f region for the HfO$_2$-deposited specimens on the following surfaces: (a) HF-etched Si(100) and (b) 1.0 nm SiN-covered Si(100).](image-url)
Strate, peaks due to Hf silicide$^{8,9,25}$ were observed at 13.6 and 15.2 eV (spectrum a). In this case, the metal-oxide semiconductor (MOS) diodes showed poor electrical characteristics such as a high leakage current density and the presence of hysteresis in the current-voltage curves. When the HfO$_2$ layers were deposited on 1.0 nm SiN layer-covered Si substrate, these peaks due to silicide were not observed (spectrum b). A similar result was also obtained in the case of the HfO$_2$ deposition on the 1.0 nm SiO$_2$ layer. The main peaks at 16.8 and 18.4 eV are attributable to Hf 4f$_{7/2}$ and 4f$_{5/2}$ levels due to HfO$_{2.5}$. These results clearly show that the 1.0 nm SiN and SiO$_2$ layers effectively prevent the Hf silicide formation.

The leakage current density of the MOS diodes with the SiN buffer layer was lower than that of the MOS diodes without buffer layer although the effective oxide thickness $E_{ot}$, for the MOS diodes was slightly decreased by insertion of the SiN buffer layer. When HfO$_2$ was directly deposited on Si in our experiments, SiO$_2$-rich Hf silicate was formed at the interface, resulting in an increase in $E_{ot}$. The SiN buffer layer prevents this interfacial layer formation as described below, leading to a slight decrease in $E_{ot}$.

Figure 2 shows the XPS spectra in the Si 2p region for the HfO$_2$/Si structure. Spectra (a) and (b) are for the SiO$_2$/Si(100) structure before and after the HfO$_2$ deposition, respectively. From the ratio in the area intensity between the SiO$_2$ peak and the Si substrate peak,$^{26,27}$ the SiO$_2$ thicknesses before and after the deposition were estimated to be 1.0 and 1.6 nm, respectively. In the estimation, 3.2 and 2.7 nm are adopted as the photoelectron mean free paths in SiO$_2$ and Si, respectively. Spectra (c) and (d) are for the SiN/Si(100) structure before and after the HfO$_2$ deposition, respectively. The SiN thickness was estimated to be 1.0 nm for both the specimens. This result clearly shows that the interfacial reaction was completely prevented by the 1.0 nm SiN layer, but not completely by the 1.0 nm SiO$_2$ layer.

The SiN layer included a small concentration of oxygen, and the atomic concentration ratio of oxygen, O/(N+O), for the as-formed SiN layers was estimated to be 0.35 from the intensity ratio between the N 1s and O 1s peaks. Due to the high nitrogen concentration ratio of 65%, the SiN structure is very dense, resulting in the complete prevention of the reaction between HfO$_2$ and Si. The SiN thickness did not increase at all even after heat treatments at 400 °C in nitrogen.

Figure 3 shows interface state spectra obtained from XPS measurements under bias for the following MOS diodes: (a) (Pt/2 nm HfO$_2$/1.6 nm SiO$_2$/Si(100)) and (b) (Pt/2 nm HfO$_2$/1.0 nm SiN/Si(100)).
(e.g., thermal oxide formed at 450 °C and chemical oxide formed in hydrochloric acid plus hydrogen peroxide solutions) possess a low atomic density and, consequently, an interface state peak near the midgap.\(^{20,29}\) Although the SiO\(_2\) layers were formed at 900 °C, the SiO\(_2\) thickness increased from 1.0 to 1.6 nm by HfO\(_2\) deposition at 400 °C. This result indicates that the final SiO\(_2\)/Si interface was formed at 400 °C during HfO\(_2\) deposition. Due to the low temperature formation, the SiO\(_2\) interfacial region is thought to possess a low atomic density.

For the HfO\(_2\)/SiN/Si(100) specimens, on the other hand, two interface state peaks, one above and the other below the midgap, were observed (spectrum b). On the basis of the theoretical calculations, the peak above the midgap is attributable to Si dangling bonds interacting weakly with an atom in the SiN layer having lone-pair electrons, while that below the midgap to Si dangling bonds interacting weakly with a Si atom having an unpaired electron.\(^{28}\) It is well known that SiN layers possess high atomic density and therefore effectively act as a diffusion barrier. In fact, the 1.0 nm SiN layer inserted between Si and HfO\(_2\) completely prevents diffusion from HfO\(_2\). When the atomic density of the insulating layer is high, the Si dangling bonds at the interface possess a smaller space, resulting in the weak interaction between the Si dangling bonds and atoms in SiN.

For the HfO\(_2\)/SiO\(_2\)/Si(100) structure, the interface state density near the valence and conduction bands are high, while those for the HfO\(_2\)/SiN/Si(100) structure are much lower. The U-shaped interface states arise from deviations of bond angles and lengths in Si near interfaces from the bulk Si values.\(^{30}\) The present results may indicate that stress at the SiN/Si interface is lower than that at the SiO\(_2\)/Si interface.

As a summary, SiO\(_2\) and SiN buffer layers between HfO\(_2\) and Si have been investigated. The thickness of the 1.0 nm SiO\(_2\) layers increases to 1.6 nm after the HfO\(_2\) deposition. In this case, the interface state spectrum possesses a peak near the midgap due to isolated Si dangling bonds and it is attributed to a low atomic density of SiO\(_2\) near the interface. The 1.0 nm SiN layer formed by the low energy electron impact method possesses a high nitrogen concentration of 65%. When this SiN layer is inserted between HfO\(_2\) and Si, the reaction between them is completely prevented. The interface state spectrum for the HfO\(_2\)/SiN/Si(100) structure has two peaks, one above and the other below the midgap, and they are attributed to Si dangling bonds interacting weakly with atoms in the SiN layers. The two peaked interface state spectrum arises from the high atomic density of the SiN layer.


