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Nature of chemical states of sulfur embedded in atomic-layer-deposited HfO_2 film on Ge substrate for interface passivation

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Sulfur was embedded in atomic-layer-deposited (ALD) HfO_2 films grown on Ge substrate by annealing under H_2S gas before and after HfO_2 ALD. The chemical states of sulfur in the film were examined by S K-edge X-ray absorption spectroscopy. It was revealed that the valences of S-ions were mostly –2 at Ge/HfO_2 interface (GeS_x or $HfO_{2-y}S_y$ to passivate the interface), while they were mostly +6 in HfO_2 layers (sulfates; $HfO_{2-z}(SO_4)_z$). The leakage current density in post-deposition-treated film was lower than that in pre-deposition-treated one. This suggests that the passivation of defects in oxide layer by sulfate ions is more effective to lower the leakage current rather than the interface defect passivation by S^{2-} ions.

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1 Introduction Nowadays, oxides with high dielectric constant (high-*k*) are widely used as the insulating barrier that prevents direct electrical leakage between gate and channel in metal–insulator–semiconductor field-effect transistor (MISFET) devices [1]. The electrical properties as a gate insulator (GI) can be degraded due to the presence of defects including oxygen nonstoichiometry in the gate oxide or dangling bonds of the channel material surface, necessitating certain "healing" of the defects [1, 2]. However, when germanium rather than silicon is used as a channel material for next generation MISFETs, it is more difficult to heal such defects; annealing at high temperature would aggravate the electrical properties of the high-*k*/Ge system because Ge is thermally unstable [3, 4].

Recently, it has been reported that passivation of the defects by injecting sulfur ions into Ge, is effective in improving the electrical properties [5, 6]. Along with a conventional wet process in which the Ge substrate is immersed in aqueous $(NH_4)_2S$, a dry process in which the Ge substrate is exposed to H_2S gas environment with heat, is newly developed [7–9]. The S ions injected by these methods have been simply regarded as to fill the defects by occupying the oxygen sites or form Ge–S bonding at the interface. In both cases, the S ions should have valence of –2 similar to O ions [6, 7]. However, the S ions incorporated in the high-*k* GI layers can, in principle, be further oxidized due to abundance of oxygen ions [10]. In spite of the possible oxidation of sulfur, as far as we know, studies on the oxidation states of sulfur have not been reported. This is mainly because the concentration of sulfur embedded in the high-*k*/Ge system, would be too low (<1%) to be observable in conventional chemical analysis techniques such as X-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy [7, 11].

Therefore, in this work, we focused on examining the oxidation states of S ions in high-*k*/Ge system. For the representative high-*k* GI, we chose the most well-known oxide, HfO_2, which can be prepared by a well-established technique of atomic layer deposition (ALD) [6, 8, 12, 13]. To enhance the measurability of the S signals, we used a

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bulk-sensitive and element-specific technique, X-ray absorption spectroscopy (XAS) at S K-edge (photon energy, $h\nu \sim 2470$ eV) [14]. From the XAS analysis of the sulfur chemistry in samples prepared under various conditions, we found a clear evidence of oxidation of sulfur ions incorporated due to H_2S treatment.

2 Experimental ALD HfO_2 films were grown on clean Ge substrate using TEMAHf [tetrakis(ethylmethylamino) hafnium] and O_3 as the metal organic precursor and oxygen source, respectively, at a substrate temperature of 280 °C. H_2S treatment was performed at 400 °C for 30 s, under H_2S (5%)/N_2 (95%) atmosphere with the working pressure of 500 Torr. The S K-edge XAS was performed at the 16A1 beamline in Taiwan Light Source. Data were collected in fluorescence yield mode with a Lytle detector at room temperature. The probing depth of S K-edge XAS is much larger than 10 nm, deep enough to detect the signals from the buried interface as well as the ALD-grown oxide layers. To fabricate MIS capacitor for the leakage current measurement, 100 nm-thick TiN gate electrode was deposited on the Ge/HfO_2 stack using DC magnetron sputter. Leakage current density–voltage (*J–V*) characteristic was examined using HP4156A Precision Semiconductor Parameter Analyzer. The density-functional-theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package with projector-augmented wave pseudopotential. The hybrid functional of the Heyd–Scuseria–Ernzerhof type with the screening parameter of 0.2 $Å^{-1}$ was employed to calculate the exchange correlation energy, because it gives reasonable band gaps [15]. We made the model structure of $Hf(SO_4)_2$ by substituting Hf for Zr of $Zr(SO_4)_2$ [16].

We first examined the sulfur chemistry of the samples annealed in H_2S environment prior to HfO_2 deposition. Figure 1a shows the S K-edge XAS spectra from Ge substrate after H_2S treatment, after a 6 nm-thick HfO_2 deposition on it [Ge(H_2S)/HfO_2], and after a 2 nm-thick TiN electrode deposition on top of HfO_2 [Ge(H_2S)/HfO_2/TiN]. We can assess the chemical states of sulfur ions according to $h\nu$, since the energy cost to create a core hole differs naturally depending on the screening of the valence electrons; the first peaks at $h\nu \sim 2471$ eV and the second peaks at $h\nu \sim 2482$ eV indicate the valences of –2 and +6, respectively [10]. It is clearly shown that for the Ge substrate, only a signal from –2 valence is observed, while for the two HfO_2-deposited films, both of the signals (i.e. from –2 and +6 valences) are observed. The similarity in overall peak intensities of the two films signifies the negligible role of TiN deposition on the chemical evolution of S-ions embedded in the specimens.

Since XAS reflects the unoccupied electronic structure projected on specific atomic sites, the XAS peak intensity should be roughly proportional to the abundance of empty electron states [14]. Therefore, peak intensity from a single S^{6+} ion, in which all of the 3sp shell electron states are empty, should be much more intense than that from a single S^{2-} ion, in which 3 sp shell states are almost filled. This signifies that the concentration of S^{6+} is very small (<10%) compared to that of S^{2-} for all specimens. The high intensities of the first peaks highlight the dominance of S^{2-} in the three specimens. The magnified view of the first peaks is shown in Fig. 1b. In the case of Ge substrate (H_2S-treated), S^{2-} feature can be attributed to the formation of GeS_x or remaining H_2S at the Ge surface [17]. The Ge–S bonds can passivate the active interfaces [7], lowering the electrical leakage current across the Ge/HfO_2 interface.

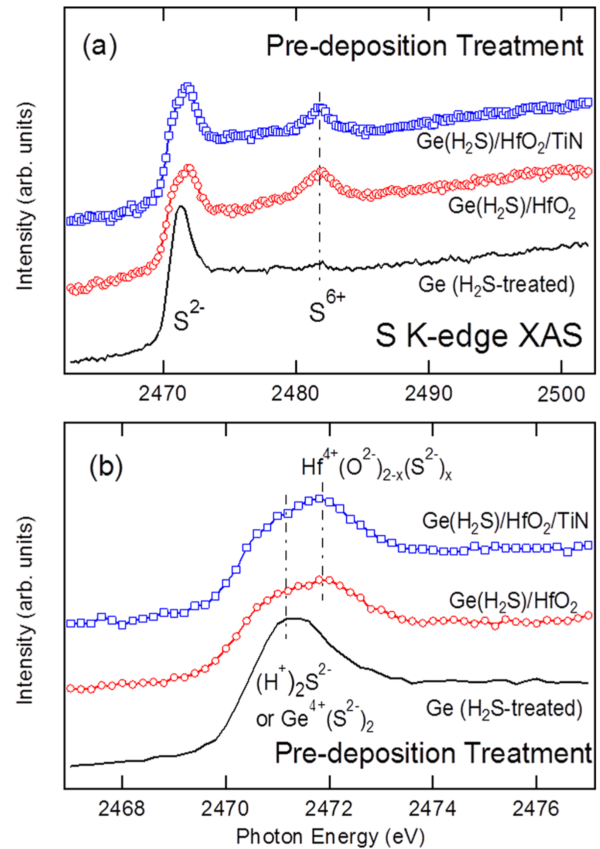

Figure 1 (a) S K-edge XAS spectra from Ge substrate after annealing under H_2S gas environment, after a 6 nm-thick HfO_2 deposition, and after a TiN electrode deposition on top of HfO_2. (b) The magnified plot near the edges.

Meanwhile, in the case of HfO_2-deposited films, the peak widths are rather larger than that of Ge substrate and the lineshapes of features are not reproducible from a simple combination of Lorentzian/Gaussian shapes with certain arctangential backgrounds. Therefore, we divided the features into two: One at ~2471 eV should be attributed to the Ge–S bonds at the Ge surface. The other one at ~2472 eV from the indirect Hf–S bonds in $HfO_{2-z}S_z$ in the oxide layers. This assignment is reasonable because the valence of S ions in $HfO_{2-z}S_z$ can be slightly higher than the nominal value of –2 due to lower electronegativity of S compared to O.

The S^{2-} ions might either form Ge–S bonds to passivate the interface or fill the oxygen vacancy in the oxide

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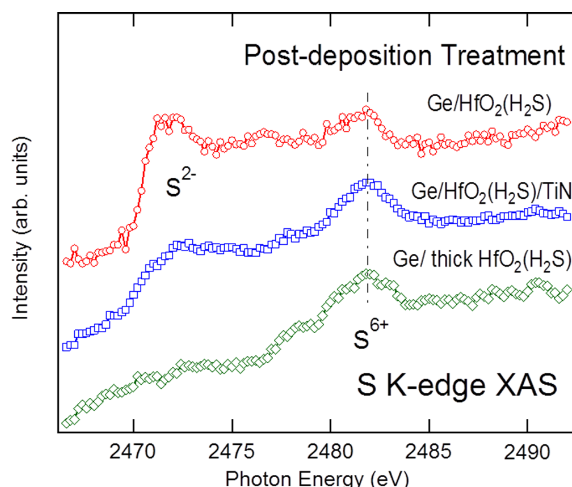

Figure 2 S K-edge XAS spectra of Ge/HfO_2 (6 nm) after annealing under H_2S gas environment and after 2 nm-thick TiN electrode deposition on top of it. The spectrum from a thick HfO_2 film (20 nm) after H_2S treatment is appended for comparison.

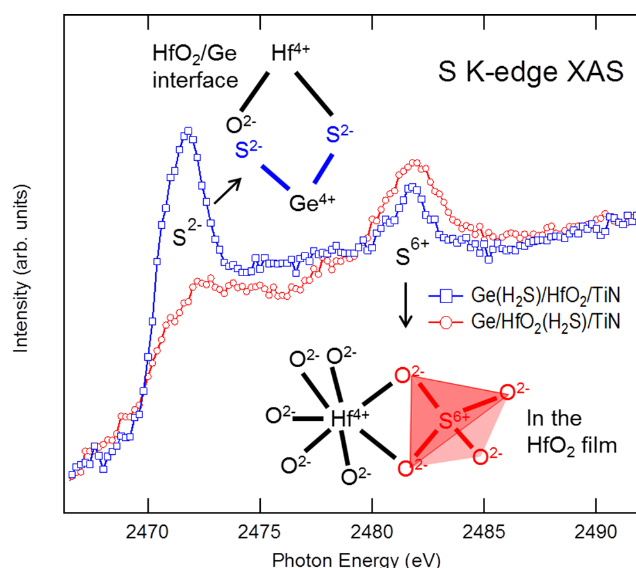

Figure 3 Comparison of the pre-deposition and post-deposition annealing effects. Weaker (stronger) intensity of S^{2-} (S^{6+}) in the post-deposition treatment strongly suggests the dominance of S^{2-} at the interface and prevalence of SO_4^{2-} in the HfO_2 layers. The schematics of the atomic structures at the interface and in the HfO_2 layers are appended.

layers to diminish the electrical leakages [6, 7]. To resolve which of these mechanisms is dominant, we need a control experiment with complementary set of samples in which a different depth profile of S ions is implemented. We prepared Ge/HfO_2 films first and then annealed the samples under H_2S exposure. As will be discussed in Fig. 3, the sulfur ions in the films annealed after the deposition remained mostly in the oxide layers.

Figure 2 shows the XAS spectra of Ge/HfO_2 (6 nm) film after H_2S treatment [Ge/HfO_2(H_2S)] and the same film except additional 2 nm-thick TiN electrode on top of it [Ge/HfO_2(H_2S)/TiN]. In the spectrum of Ge/HfO_2(H_2S), at least three peaks were observed and each of them can be attributed to S^{2-} (~2471 eV), S^{4+} (~2477 eV), or S^{6+} (~2482 eV) [10]. The S^{2-} signals can be attributed to the presence of GeS_x or $HfO_{2-z}S_z$, as in the case of pre-deposition annealed samples (Fig. 1). Meanwhile, S^{4+} and S^{6+} signals should be attributed to sulfite (SO_3^{2-}) and sulfate (SO_4^{2-}) ions, respectively. Since the ALD HfO_2 layers contain abundant O, it is not surprising that the S-ions embedded in HfO_2 are highly oxidized.

The intensities of sulfite and sulfate peaks are not less than that of sulfide (S^{2-}). Regardless of the TiN deposition, the concentration ratios of sulfite/sulfate over sulfide overall were increased, when we applied the post-deposition treatment rather than the pre-deposition treatment. In fact, after the TiN deposition the features of the high oxidation numbers (2477–2482 eV) became slightly more intense, whereas the S^{2-} features (~2471 eV) became weaker. This suggests that the deposition of TiN on top of HfO_2 layers might promote the sulfur oxidation. In the post-deposition treatment, S is injected from H_2S gas environment. Thus, highly oxidized S-ions in post-deposition-annealed samples should mostly be near the surface of HfO_2 layers. Therefore, the impact of TiN deposition can be maximized in the case of post-deposition-annealed samples.

In Fig. 2, the spectrum of a thick HfO_2 film (~20 nm) after H_2S exposure is appended for comparison. No clear features of S^{2-} but only the sulfite/sulfate features are observed in the spectrum. This evidently shows that the S-ions in HfO_2 layers are mostly oxidized. The absence of prominent S^{2-} features in the thick film implies that the S^{2-} ions in the Ge/HfO_2 thin films should be mostly buried underneath the film, namely, at the Ge/HfO_2 interface. Therefore, we can tell that S embedded in the Ge/HfO_2 films constitute sulfide at the interface and sulfite or sulfate in the oxide layers.

Figure 3 comparatively shows the spectra of Ge(H_2S)/HfO_2/TiN and Ge/HfO_2(H_2S)/TiN. The peak intensity of S^{6+} (S^{2-}) in the latter increased (decreased) compared to the former, reflecting the difference in depth profiles of the two ionic species. The bonding structures for the S^{2-} and S^{6+} ions are schematically described in the insets. At the interface, S^{2-} ions should either fill the oxygen defects or form Ge–S bonds, possibly improving the characteristics of the high-*k* films [6, 18]. On the other hand, SO_4^{2-} (S^{6+}) or SO_3^{2-} (S^{4+}) radicals can be coordinated mostly in the oxide layers so as to constitute locally a sulfate or sulfite. The oxygen ions in those radicals might fill the oxygen defects in the oxides grown by ALD, which would reduce the leakage current as well [19].

Since the electronic structure or stability of the local structures of sulfates/sulfites has been rarely reported so far [20], it is not easy to predict whether the incorporation of such sulfate/sulfite bonds might improve the characteristics as high-*k* oxide or not. Our DFT calculation showed that a model structure of $Hf(SO_4)_2$ would have a larger

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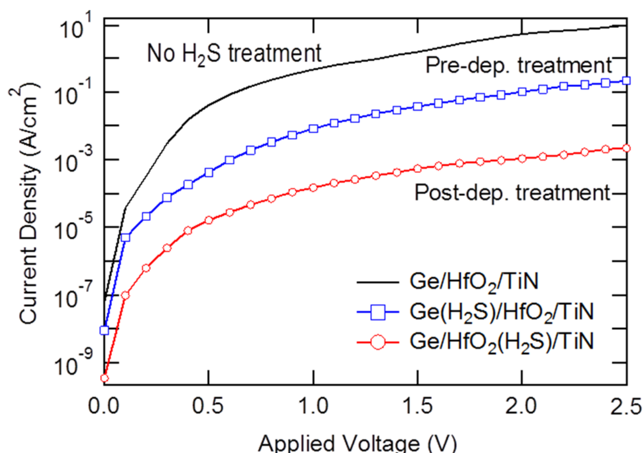

Figure 4 Typical *J–V* curves for TiN/HfO_2/Ge MIS capacitors with the pre-deposition and post-deposition H_2S treatments.

bandgap (by +0.4 eV) than HfO_2 (~5.7 eV). This suggests that partial formation of Hf-sulfate would slightly increase the bandgap of the entire film. The larger bandgap implies lower possibility of thermal electronic excitation. Although the actual S concentration in the system, judged from XPS [21] appears to be very low (<1%) so that the electrical leakage is mostly relevant to the defect states in bandgap rather than the bandgap itself in these large bandgap oxides, this theoretical result is consistent with our experimental observation of reduced leakage current in S^{6+}/S^{4+}-embedded HfO_2 (see Fig. 4). This signifies that the incorporation of the high-oxidation-number S ions (sulfate or sulfite ions) can effectively play a significant role in determining the insulating properties of Hf-composites.

Figure 4 shows the typical *J–V* curves for Ge/HfO_2/TiN, Ge(H_2S)/HfO_2/TiN and Ge/HfO_2(H_2S)/TiN capacitors. It evidently shows an improvement in the electrical leakage in the cases with H_2S treatment. This can be attributed to passivation of the electrical defects in the film and/or the interface by sulfur ions. Interestingly, the *J* values for Ge/HfO_2(H_2S)/TiN is overall lower than that for Ge(H_2S)/HfO_2/TiN. In the case of Ge(H_2S)/HfO_2/TiN, the passivation of Ge surface should work as to lower the interface defect densities while the defects in HfO_2 layers could not be removed. In contrast, in Ge/HfO_2(H_2S)/TiN, the sulfur ions can migrate into the system down to the Ge substrate, so that the defects both at the interface and in the oxide layers can be healed. Thus, the lower leakage current in Ge/HfO_2(H_2S)/TiN suggests that the healing of defects in the film by the sulfate or sulfite ions had a greater impact on the electrical properties of the high-*k* GI than the passivation of the interface by sulfide ions. The strong covalent nature of the S–O bonds will efficiently prohibit donating charges to the HfO_2 host to minimize the effects of the defects. Therefore, sulfur oxidation in the high-*k* GI should be considered in future theoretical and experimental studies to explore its passivation effects.

3 Conclusion

XAS studies of H_2S treatments on the Ge/HfO_2 films showed the dominance of S^{6+} in the HfO_2 layers, indicating that the sulfur ions from H_2S gas can effectively incorporate and oxidize in the oxide as to locally form sulfate ions (SO_4^{2-}). The low leakage current in the H_2S-treated HfO_2 films suggests that the incorporation of sulfate radicals can effectively lower the defect density in the oxide and interface. Comparative studies of pre-deposition-treated and post-deposition-treated films revealed that the H_2S exposure after HfO_2 ALD is more efficient to form sulfates, whereas the same H_2S exposure before HfO_2 ALD would mostly form sulfides at the HfO_2/Ge interfaces.

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