Evidence of GeO volatilization and its effect on the characteristics of HfO_2 grown on a Ge substrate*

Fan Ji-Bin(樊继斌)†, Liu Hong-Xia(刘红侠), Fei Cheng-Xi(费晨曦), Ma Fei(马 飞), Fan Xiao-Jiao(范晓娇), and Hao Yue(郝 跃)

School of Microelectronics, Key Laboratory of Wide Band-Gap Semiconductor Materials and Devices, Xidian University, Xi'an 710071, *China*

(Received 18 June 2012; revised manuscript received 19 September 2012)

HfO_2 films are deposited by atomic layer deposition (ALD) using tetrakis ethylmethylamino hafnium (TEMAH) as the hafnium precursor, while O_3 or H_2O is used as the oxygen precursor. After annealing at 500 °C in nitrogen, the thickness of Ge oxide's interfacial layer decreases, and the presence of GeO is observed at the H_2O-based HfO_2 interface due to GeO volatilization, while it is not observed for the O_3-based HfO_2. The difference is attributed to the residue hydroxyl groups or H_2O molecules in H_2O-based HfO_2 hydrolyzing GeO_2 and forming GeO, whereas GeO is only formed by the typical reaction mechanism between GeO_2 and the Ge substrate for O_3-based HfO_2 after annealing. The volatilization of GeO deteriorates the characteristics of the high-κ films after annealing, which has effects on the variation of valence band offset and the *C–V* characteristics of HfO_2/Ge after annealing. The results are confirmed by X-ray photoelectron spectroscopy (XPS) and electrical measurements.

Keywords: GeO volatilization, H_2O-based HfO_2, O_3-based HfO_2, thermal stability

PACS: 77.55.D–, 82.80.Pv **DOI:** 10.1088/1674-1056/22/3/037702

1. Introduction

High-κ/Ge gate stacks are very promising for future nanoscale devices because both electron and hole mobilities of Ge are higher than those of Si. Recently developed high-κ materials have reopened the door to Ge as the channel material in metal–oxide–semiconductor field effect transistors (MOSFETs).[1–5] One of the main concerns for high-κ/Ge gate-stack devices is that Ge–O bonds inevitably exist at the interface between Ge and the high-κ films. The volatilization of GeO occurs even below 500 °C, which is required for the source/drain activation in the CMOS fabrication process. The volatilization of GeO out of the air will generate a huge amount of defects and traps in the high-κ film after GeO desorption and volatilization.[6,7] It tends to deteriorate the interface and the high-κ film quality.[8,9] Many research has been done to investigate the origin of GeO volatilization and its effects on dielectric materials.[8,10–13] However, the studies performed so far are focused on the HfO_2 films obtained using single oxygen precursors. The effects of the volatilization of GeO on the characteristics of HfO_2 grown on high mobility semiconductor substrates using different oxygen precursors (H_2O or O_3) need to be further studied. Therefore, in the present work, HfO_2 films are deposited using O_3 or H_2O as the oxygen precursors with tetrakis ethylmethylamino hafnium (TEMAH) as the hafnium precursor by atomic layer deposition (ALD). After a compatible annealing process for source/drain activation in CMOS fabrication, the differently processed HfO_2 films are investigated by X-ray photoelectron spectroscopy (XPS) and electrical measurements.

2. Experiments

Before the deposition, the gallium-doped p-type (100) Ge wafers with resistivity 0.3–1.0 Ω·cm were obtained after RCA cleaning and dipped in dilute HF (hydrofluoric acid: deionized water =1:50) to remove the Ge native oxides. Then, *in-situ* O_3 oxidation of the Ge surface in ALD was carried out to grow GeO_2 at 200 °C. After that, HfO_2 films were deposited by ALD at 280 °C using H_2O or O_3 on the Ge substrates. Liquid TEMAH was used as the hafnium precursor. The container of the Hf precursor was heated to 95 °C, corresponding to the vapor pressure of 10–15 hPa. When H_2O was used as the oxidant, the container was set at room temperature, corresponding to a vapor pressure of 7 hPa. The ozone generator used the ultra pure O_2 (99.999%) to obtain O_3, the concentration was 200 g/N·m^3. After all the films were annealed in nitrogen at 500 °C for 60 s, XPS and electrical measurements were carried out. The XPS using monochromatic Al K_α X-ray ($h\nu = 1486.7$ eV) and all the XPS spectra were calibrated against the adventitious C 1s peak at 285.0 eV to correct the differential charging.

3. Results and discussion

Figure 1 shows the thicknesses of Ge oxides for 4 nm HfO_2 films measured by a Woollam M2000D spectroscopic

*Project supported by the National Natural Science Foundation of China (Grant Nos. 60976068 and 61076097) and the Cultivation Fund of the Key Scientific and Technical Innovation Project of the Ministry of Education of China (Grant No. 708083).

†Corresponding author. E-mail: jbfan@mail.xidian.edu.cn

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ellipsometer. For the as-deposited films, the thicknesses of the Ge oxides are 1.98 nm and 2.17 nm for H_2O-based HfO_2 and O_3-based HfO_2, respectively. The O_3-based HfO_2 has a thicker interfacial layer compared with the H_2O-based HfO_2. This can be explained by further oxidization that occurs during the deposition process because O_3 has a strong oxidization ability. After annealing, the thicknesses of the Ge oxides change to 1.68 nm and 2.11 nm for H_2O-based HfO_2 and O_3-based HfO_2, respectively. A 0.3 nm reduction of the Ge-oxide thickness is obtained for H_2O-based HfO_2 before and after annealing, whereas only 0.06 nm of that is obtained for O_3-based HfO_2 on the Ge substrate. The decrease of the Ge-oxide thickness is mainly attributed to the volatilization of GeO after annealing.[8] Therefore, the desorption and volatilization of GeO are more likely to occur in the H_2O-based HfO_2 compared with the O_3-based HfO_2 after annealing due to its larger variation of the Ge-oxide thickness.

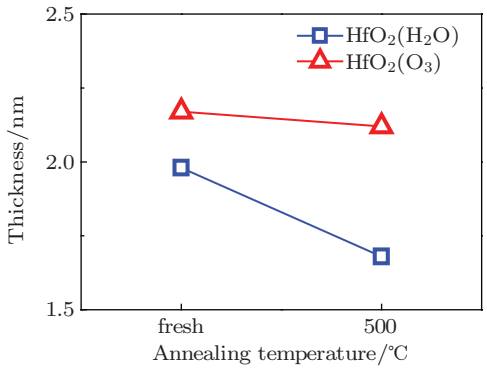


Fig. 1. (color online) Thicknesses of Ge oxides for H_2O-based and O_3-based HfO_2 grown on Ge after annealing.

In order to confirm that the volatilization of GeO occurs after annealing, two identical Si substrates are face-to-face covered with 4 nm H_2O-based HfO_2 and 4 nm O_3-based HfO_2 films during annealing, respectively. Then, an XPS measurement is carried out immediately on the surfaces of the Si substrates after annealing. If the GeO out-diffusion occurs during annealing, it can be detected by the XPS. Figure 2 shows the Ge-2p spectra of H_2O-based HfO_2 and O_3-based HfO_2 on Ge substrates before and after annealing. As shown in Fig. 2(a), for the Si substrate covered with the H_2O-based HfO_2, two significant peaks located at 1219.06 eV and 1250.14 eV are observed after annealing. They are attributed to GeO.[14] For the Si substrate covered with the O_3-based HfO_2, two peaks located at 1219.04 eV and 1250.13 eV are observed, and the magnitudes of these peaks are much weaker. They are also attributed to GeO.[14] These results indicate that the desorption and volatilization of GeO occurs and GeO diffuses out to the air after annealing. This is further confirmed by the results of the Ge-2p spectra for H_2O-based HfO_2 or O_3-based HfO_2 on Ge substrates after annealing, as shown in Fig. 2(b). The GeO peak intensities of H_2O-based HfO_2 on Ge decrease significantly after annealing, while no obvious change is observed for the O_3-based HfO_2. The Ge-2p spectra show that the volatilization of GeO is more serious for H_2O-based HfO_2 compared with O_3-based HfO_2, which is consistent with the thickness measurements.

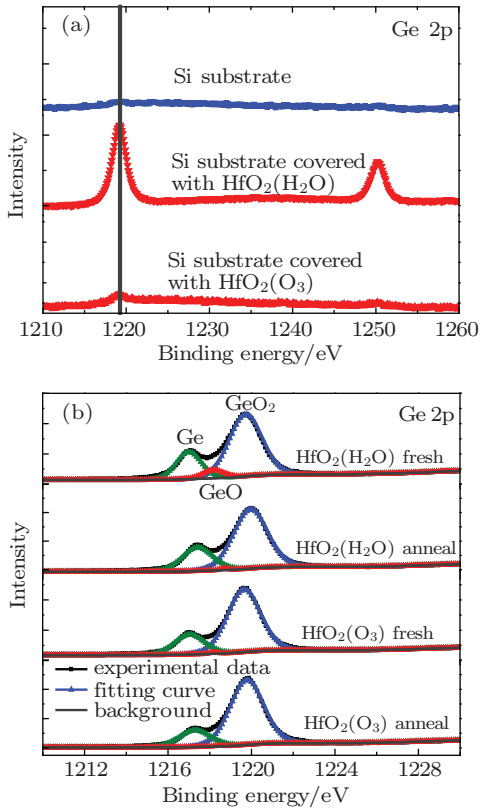


Fig. 2. (color online) Ge-2p spectra for (a) Si substrates covered with H_2O-based and O_3-based HfO_2 films, (b) Ge substrates covered with H_2O-based and O_3-based HfO_2 films before and after annealing.

In order to explain the different changes of HfO_2 films after annealing, the formation mechanism of GeO should be investigated. Typically, the reduction of GeO_2 through the reaction between GeO_2 and the Ge substrate generates volatile GeO at the GeO_2/Ge interface.[15,16] This occurs for both H_2O-based HfO_2 and O_3-based HfO_2 on Ge substrates after annealing. Furthermore, for H_2O-based HfO_2, there may be a residue of a high concentration of hydroxyl groups or H_2O molecules in the films because H_2O tends to physisorb on the surface strongly and it is hard to clean even though the purge time is sufficient.[17] GeO_2 is hydrolyzable in H_2O. The formation and the dissolution of GeO_2 occurs simultaneously, and the oxide mainly consists of Ge suboxide (GeO).[18] The rates of formation and dissolution increase quickly because the annealing temperature is high enough. The residual hydroxyl groups or H_2O molecules enhance the generation of GeO and reduce GeO_2 during annealing for H_2O-based HfO_2 grown on the Ge substrate. Both GeO generation mechanisms occur for the H_2O-based HfO_2 grown on the Ge substrate, which can lead to more GeO being generated and volatilized during

the annealing. However, for O_3-based HfO_2 on Ge, the O_3 is easy to purge, and it provides a high Ge^{4+} density and a good Ge/GeO_2 interface. Therefore, for H_2O-based HfO_2 grown on the Ge substrate, the interfacial layer thickness decreases significantly and GeO volatilizes more seriously compared with O_3-based HfO_2 after annealing.

The volatilization of GeO out of the air can generate a lot of defects and traps in the high-κ film, resulting in the deterioration of the characteristics of the high-κ film.[8,9] In order to use high-κ/Ge gate stacks in devices, the valence-band and the conduction-band offsets are required to be higher than 1 eV to reduce the leakage current due to tunneling through the barrier energy at the interface between the high-κ film and the Ge substrate.[19,20] Thus, the effects of GeO volatilization on the valence-band offset (VBO) should be evaluated. The valence band offset ΔE_v is determined using the photoelectron-based method[21]

$$\Delta E_v = (E_{CL}^{Ge_{2p}} - E_v^{Ge})_{bulk} - (E_{CL}^{Hf_{4f}} - E_v^{HfO_2})_{bulk} + (E_{CL}^{Hf_{4f}} - E_{CL}^{Ge_{2p}})_{HfO_2/Ge}, \quad (1)$$

where $E_{CL}^{Ge_{2p}}$ and $E_{CL}^{Hf_{4f}}$ are the binding energies of Ge-2p and Hf-4f shallow core levels, respectively, E_v^{Ge} and $E_v^{HfO_2}$ are determined in bulk Ge and thick HfO_2 films, which are the binding energies corresponding to the valence band maximum (VBM) values in Ge and HfO_2, respectively. The position of the VBM is determined using the linear method.[22] In order to obtain accurate VBO values, the cleaned bulk P-type (0.3–1.0 Ω·cm) Ge(100) substrate is measured by XPS, as shown in Fig. 3. The VBM is 0.26 eV, determined by the linear method. The energy difference between Ge 2p and VBM is 1217.12 eV.

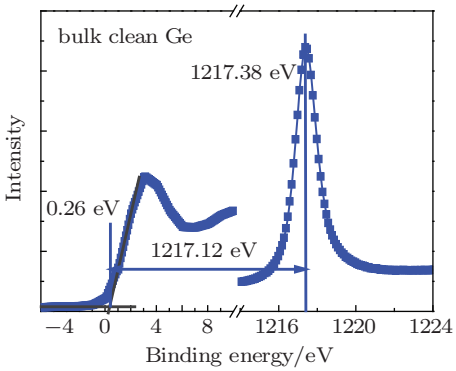


Fig. 3. (color online) XPS core-level spectrum of Ge 2p for clean Ge substrate.

Figure 4 shows the XPS core level spectra of Ge 2p and Hf 4f for H_2O-based HfO_2 films. The core level energies are obtained by curve fitting to ensure a high accuracy. For a 10 nm HfO_2 film, the energy difference between Hf 4f and VBM is 15.39 eV. It changes to 15.37 eV after annealing, as shown in Fig. 4(a). The energy difference between Hf 4f and Ge 2p is 1199.22 eV in a 4 nm HfO_2 film and 1200.14 eV for the as-deposited and annealed films. Using these values with Eq. (1), we can obtain the VBOs of 2.51 eV and 1.61 eV for the as-deposited and the annealed HfO_2 films, respectively. The VBO variation is as large as 0.90 eV for the H_2O-based HfO_2 after annealing. For O_3-based HfO_2 films, the differences in Hf 4f level energy and the VBM value between the as-deposited and the annealed O_3-based HfO_2 films are 15.00 eV and 15.15 eV, respectively, as shown in Fig. 4(b). Furthermore, the energy differences between the Hf 4f and the Ge 2p signals for 4 nm HfO_2 are 1199.48 eV and 1199.57 eV, respectively. The VBO values of O_3-based HfO_2 films are 2.64 eV and 2.40 eV for the as-deposited and the annealed O_3-based HfO_2 films, respectively. The VBO variation is 0.24 eV after annealing. The results indicate that the variation of VBO is affected by the volatilization of GeO because it deteriorates the Ge oxide interfacial layer and the high-κ film properties. More volatilization of the GeO leads to a larger VBO variation after annealing. In addition, the binding energy of Hf 4f for as-deposited H_2O-based HfO_2 shows a shift of 0.66 eV to a lower binding energy, which is in agreement with the formation of $HfGeO_x$.[23] The results indicate that Ge (or GeO) is incorporated in the HfO_2 films, which is consistent with the first-principles quantum-mechanical calculations.[9]

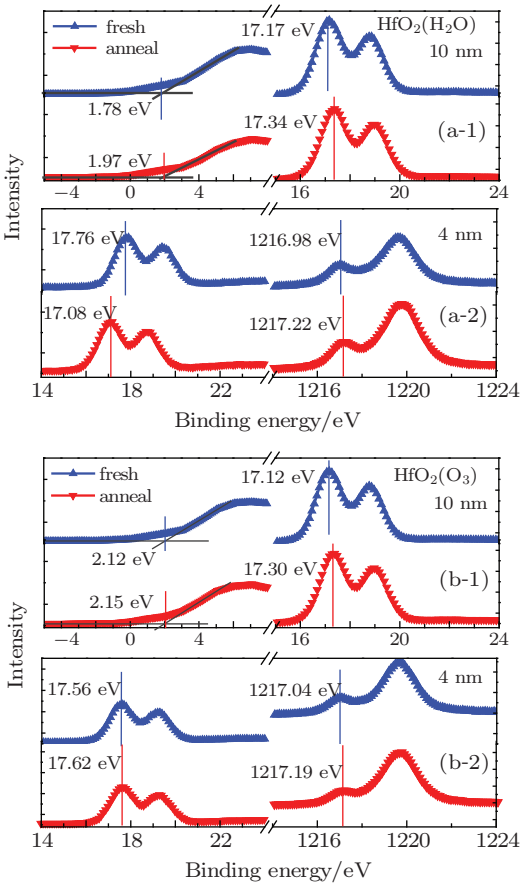


Fig. 4. (color online) XPS core-level spectra of Ge 2p and Hf 4f for (a) H_2O-based (b) O_3-based HfO_2 films before and after annealing.

Figure 5 shows the C–V characteristics of H_2O-based HfO_2 and O_3-based HfO_2 (f = 100 kHz). The gate voltage

(V_G) is swept from accumulation to inversion and then back. The dispersion between positive and negative scanning *C–V* curves is observed for both as-deposited and annealed H_2O-based HfO_2 films, indicating that the slow interface state density is still large. The capacitance increases a lot after annealing due to the volatilization of GeO which decreased the thickness of the low permittivity interfacial layer. Furthermore, after annealing, the *C–V* curve degrades at a lower negative voltage due to excessive leakage, suggesting that the volatilization of GeO deteriorates the characteristics of high-κ films. For O_3-based HfO_2, a relatively good *C–V* characteristic is observed before and after annealing. A slight increase of the capacitance is observed and the hysteresis decreases after annealing. Those *C–V* characteristics indicate that HfO_2 films deposited using O_3 as the oxygen precursor have advantages compared to those deposited with H_2O. A cap layer, formed on the top of the GeO_2 film, may help to suppress the GeO desorption and volatilization for the H_2O-based ALD process.[8]

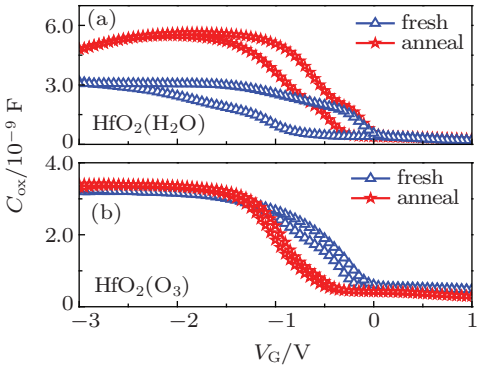


Fig. 5. (color online) The *C–V* characteristics of (a) H_2O-based (b) O_3-based HfO_2 films on Ge substrates before and after annealing.

4. Conclusion

In this paper, the volatilization of GeO is investigated for the HfO_2 films deposited with different oxidants (H_2O or O_3) by ALD. The volatilization of the GeO is detected by XPS after annealing, which leads to the thickness of the Ge-oxide interfacial layer decreasing. The thickness measurement results and the XPS spectra indicate that the volatilization of GeO is more serious for H_2O-based HfO_2 compared to O_3-based HfO_2. The different changes are attributed to another GeO formation mechanism occurring for H_2O-based HfO_2 due to the residual hydroxyl groups or H_2O molecules after annealing, whereas only the typical reaction mechanism between GeO_2 and the Ge substrate occurs for O_3-based HfO_2. Further testing results indicate that the volatilization of the GeO affects the VBO and the electrical properties of the HfO_2/Ge gate stack because it deteriorates the properties of HfO_2 films and the interface layer.

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