TiO$_2$/HfO$_2$ Bi-Layer Gate Stacks Grown by Atomic Layer Deposition for Germanium-Based Metal-Oxide-Semiconductor Devices Using GeO$_x$N$_y$ Passivation Layer

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Material and electrical properties of TiO$_2$/HfO$_2$ bi-layer gate stacks were investigated for germanium (Ge) based metal-oxide-semiconductor devices. In situ NH$_3$ plasma treatment was employed to passivate the Ge surface and promising performance including low capacitance-voltage hysteresis and interface trap density was achieved. It shows a superior dielectric breakdown voltage (4.2-3.4 V) for the TiO$_2$/HfO$_2$ bi-layer stacks than HfO$_2$ single layer stack at a similar capacitance equivalent thickness (CET) of 1.6 nm. A minimum CET of 1.4 nm was obtained for capacitors on both p and n-type Ge (100) with a gate leakage current density $< 4 \times 10^{-7}$ A/cm$^2$ at VFB $\pm 1$ V.

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As Silicon based complementary metal-oxide-semiconductor field-effect-transistor (CMOSFET) is approaching its fundamental limit, alternative channel material germanium (Ge) has received intensive interests due to its intrinsic high mobility for both electrons (3900 cm$^2$/V s) and holes (1900 cm$^2$/V s). Various high $k$ gate dielectrics including Al$_2$O$_3$, HfO$_2$, and ZrO$_2$ have been investigated for Ge-based MOS devices. TiO$_2$ exhibits a high dielectric constant ($\sim 80$ for the rutile crystalline phase) and can be considered a potential candidate for a high-$k$ dielectric. However, its low conduction band offset (CBO) makes an additional interfacial layer (IL) with sufficient CBO necessary. Both Al$_2$O$_3$ (Refs. 9 and 10) and HfO$_2$ (Ref. 11) IL have been investigated for implementing TiO$_2$ as gate dielectric on Ge. HfO$_2$ shows superior properties due to its higher $k$ value and less degradation for ultrathin films. Although the band gap of HfO$_2$ is smaller than Al$_2$O$_3$, both CBO and valence band offset (VBO) are already larger than 2 eV for HfO$_2$ with respect to Ge. Among many thin film deposition techniques, atomic layer deposition (ALD) plays a major role for high $k$ dielectrics deposition owing to its intrinsic advantage of growing uniform films with precise thickness control at atomic level. Comparing to conventional thermal ALD, plasma enhanced (PE)-ALD is consider a promising approach to deposit films at lower temperature with high quality and higher density due to the higher reactivity of radicals. For instance, TiO$_2$ deposited by thermal ALD exhibits a $k$ value in the range of 32–35 (Ref. 9) while the TiO$_2$ films grown by PE-ALD possess much higher $k$ value ($\sim 50$). With our control samples, HfO$_2$ grown by PE-ALD also exhibits a higher $k$ value than thermal ALD (24 vs. 18). Prior to high $k$ dielectric deposition, Ge surface passivation is essential to reduce the interface trap density ($D_{it}$). Effective electrical Ge surface passivation has been demonstrated using a variety of methods, e.g., using GeO$_2$. Surface nitridation with thermal NH$_3$, SiH$_4$/NH$_3$ (Ref. 17) or a H$_2$N$_2$/Ar (Ref. 18) gas plasma. While the thermal NH$_3$ treatment approach has been shown to be quite effective, it usually requires high temperature (e.g., $>550^\circ$ C) to form a high quality GeO$_x$N$_y$ IL. Recently, we reported the ultrathin GeO$_x$N$_y$ passivation layer formed by NH$_3$ plasma, which can be performed at ALD process temperature (e.g., $250^\circ$ C). It is promising to limit the total thermal budget by using this plasma passivation technique. In this work, we investigate the properties of TiO$_2$ and HfO$_2$ films grown by PE-ALD on Ge (100) after in situ GeO$_x$N$_y$ passivation with NH$_3$ plasma.

Electrical performance of the capacitors with TiO$_2$/HfO$_2$ bi-layer gate stacks is comprehensively evaluated. Ge (100) wafers with resistivity of 0.05–0.1 $\Omega$ cm were used as substrates. Prior to 5 min rinse in de-ionized water, the Ge wafers were cleaned in a 0.5% HF solution for 1 min. Around 0.3 nm thick GeO$_x$ IL remains on the surface after the cleaning process. Then the samples were immediately loaded into a home-built ALD chamber through a loadlock. The details for the ALD setup were given in our previous work. The Ge surface was passivated by using an NH$_3$ plasma prior to the ALD growth. An inductively coupled plasma source (remote mode, downstream configuration) was used for generating the plasma. The samples remain stationary in the ALD chamber while the plasma source was separated from the ALD chamber through a computer controlled valve during the precursors pulse time to avoid contamination of the ICP source. The power of the NH$_3$ plasma was fixed at 200 W with a pressure around 5 $\times$ 10$^{-3}$ mbar and the exposure time was varied from 15 to 30 s. The HfO$_2$ and TiO$_2$ dielectric was grown by PE-ALD using either Tetakis (ethyldimethylamido)hafnium(IV) (TEMAH) or tetrakis-dimethylamido titanium (DTMAT) and O$_2$ plasma without breaking a vacuum. A shadow mask was used to pattern sputtered Pt gate electrodes. A Ti(20 nm)/Pt(40 nm) architecture was used on sputtering electrode to reduce series resistance. Post metal annealing (PMA) was conducted in a forming gas ambient at 300 $^\circ$C for 30 min. Both spectroscopic ellipsometry and X-ray reflectivity (XRR) were employed to measure the thickness of the films. The chemical composition of the film was analyzed by X-ray photoelectron spectroscopy (XPS) using Al K$_a$ x-rays. The capacitance-voltage (C-V) measurement was carried out using an HP 4192 A impedance analyzer. The current was measured with a Keithley 617 electrometer and the applied voltage to the capacitors was calibrated with a HP 3478 A multimeter.

The Ge surface after NH$_3$ plasma passivation was analyzed by XPS. An ultrathin Al$_2$O$_3$ cap layer (~1 nm) was in situ deposited by PE-ALD to avoid contamination and degradation of the formed GeO$_x$N$_y$ passivation layer. Figure 1 shows the Ge 3d core level spectra. In addition to a doublet attributed to bulk Ge 3d$3/2$ and 3d$5/2$ with a separation of 5 3/4 eV, the spectra were fitted by three components, GeO, GeO$_2$, and GeO$_x$N$_y$. Except for GeO$_x$N$_y$, the chemical shifts of Ge 3d binding energy (BE) for each of these components were fixed according to reported data. The atomic concentration of N in the passivation layer is relatively low and around 8% according to the XPS measurement. Using our current setup for performing the NH$_3$ plasma treatment, it is difficult to tune the O/N ratio. It is found that the binding energy shift of Ge 3p core level is $\sim$2 eV prior to HfO$_2$.
deposition and \( \sim 1.7 \) eV after \( \text{HfO}_2 \) deposition (data not shown), suggesting partial intermixing between the \( \text{GeO}_{x}\text{Ny} \) layer and the subsequent \( \text{HfO}_2 \) film. \( \text{HfO}_2 \) and \( \text{TiO}_2 \) were grown on the passivated Ge (100) using PE-ALD without air exposure. \( \text{Hf}^{4+} \) and \( \text{Ti}^{2+} \) XPS core level spectra are shown in Fig. 2. A doublet with binding energy of 16.4 and 18.1 eV was well fitted for \( \text{Hf}\,{}^{4}\text{f} \) spectra, which shows oxidation state of \( \text{Hf}^{4+} \) and no significant contribution from sub-oxide or defects. \( \text{Ti}^{2+} \) XPS analysis indicates that the films grown by PE-ALD have very low level of sub-oxide and defects and are suitable for the application of gate stacks. It is attributed to the high reactivity of O radicals created by the \( \text{O}_2 \) plasma, therefore, resulting in complete oxidation.

Electrical properties of the MOS capacitors with \( \text{TiO}_2/\text{HfO}_2 \) bi-layer gate stacks are comprehensively evaluated. Figure 3 shows the \( C-V \) and \( J-V \) characteristics for the capacitor on n-Ge (100) with capacitance equivalent thickness (CET) of \( \sim 1.6 \) nm. A \( \sim 1.1 \) nm thick \( \text{GeO}_{x}\text{Ny} \) passivation layer was formed by in situ NH\(_3\) plasma treatment with plasma exposure time of 30 s. The thickness of \( \text{HfO}_2 \) and \( \text{TiO}_2 \) was around 1.2 and 3 nm, respectively. Multiple frequencies (from 200 Hz to 1000 KHz) were used to obtain both flat \( C_{\text{min}} \) at high frequency and response of minority carriers at low frequency (shown in Fig. 3a). Well behaved \( C-V \) curves suggest effective electrical Ge surface passivation using in situ formed \( \text{GeO}_{x}\text{Ny} \) layer. The Berglund method was used to relate the Ge surface potential to the gate bias (data not shown). The range of Ge surface potential change is larger than 0.8 eV, which suggests free movement of the Femi-level at the Ge surface through the entire Ge band gap since the range is already greater than the Ge band gap (0.66 eV). Therefore, the inversion response is not related to interface-trap-dominated generation-recombination of carriers in inversion, but rather a true inversion behavior. The interface trap density (\( \text{D}_{\text{it}} \)) was also estimated by using the high-low frequency method and it was lower than \( 7 \times 10^{11} \) \text{eV}^{-1}\text{cm}^{-2} \) at flat-band condition. Very promising device stability against high voltage gate bias was observed for the capacitor with \( \text{TiO}_2/\text{HfO}_2 \) bi-layer stacks. Figure 3b shows high reproducibility of gate leakage current density (\( J_g \)) when the gate bias repeatedly sweeps from 0 to 4 V back and forth. The dielectric breakdown voltage was increased substantially from \( \sim 3.4 \) V for the capacitor using a \( \text{HfO}_2 \) single layer stack to \( \sim 4.2 \) V for the capacitor using \( \text{TiO}_2/\text{HfO}_2 \) bi-layer stacks with similar \( \text{GeO}_{x}\text{Ny} \) IL and CET of \( \sim 1.6 \) nm. It is related to the fact that one can use a larger...
physical thickness of the TiO2/HfO2 bi-layer stacks while maintaining similar EOT since TiO2 exhibited a higher dielectric constant (~50) than HfO2 (~24). It is worth mentioning that NH3 plasma formed GeOxNy IL shows a higher dielectric breakdown field (~15 MV/cm) than O2 plasma formed GeOx IL (~10 MV/cm). C-V hysteresis was evaluated to be around 80 mV at flat-band voltage. C-V hysteresis is usually attributed to bulk oxide traps related to Ge outdiffusion or interface mixing.\(^6\) The decrease of BE shift of Ge 3p core level after HfO2 deposition (from 2 to 1.7 eV) suggests partial intermixing between the GeOxNy layer and the subsequent HfO2 film, and may cause the hysteresis behavior. However, the outdiffusion of Ge into HfO2 is limited by using GeOxNy IL and in situ PE-ALD HfO2. According to the XPS measurement, the atomic concentration of Ge in the thin HfO2 films is less than 3%, which indicates sufficient suppression of Ge outdiffusion.

A minimum CET of 1.4 nm was obtained for capacitors on both p and n-type Ge (100) by reducing the NH3 exposure time to 15 s, and therefore decreasing the thickness of the GeOxNy layer to ~0.7 nm. It is worth mentioning that the “re-growth” of the IL during the PE-ALD process due to the highly reactive O radicals makes it very difficult to further reduce the IL thickness. As shown in Fig. 4, no severe degradation was observed for the capacitor on n-Ge (100) and well shaped C-V curves remained. However, apparent C-V humps were demonstrated for the capacitor on p-Ge (100) in an ac frequency range from 5 KHz to 500 Hz. An asymmetric D\(_t\) distribution and much higher D\(_t\) at the Ge conduction band side could be the source for such degradation.\(^6\) A similar degradation was observed for TiO2/HfO2 bi-layer gate stacks when using a GeO2 passivation layer.\(^7\) Further investigation is necessary to determine the mechanism of the degradation and for optimizing the capacitors on p-Ge (100). Nevertheless, low J\(_g\) (<4 x 10\(^{-7}\) A/cm\(^2\)) was obtained for both capacitors at \(V_{FB} \pm 1\) V with a CET of 1.4 nm as shown in Fig. 5. It opens perspective for continued EOT scaling while maintaining a low J\(_g\).

In summary, we found that TiO2 and HfO2 thin films grown by PE-ALD exhibit no significant sub-oxide components or defects. Excellent stability was demonstrated for the capacitors with TiO2/HfO2 bi-layer gate stacks against high voltage gate bias. The capacitor can sustain repeated gate bias sweeps from 0 to 4 V at CET around 1.6 nm. With decreasing thickness of the GeOxNy IL, low J\(_g\) (<4 x 10\(^{-7}\) A/cm\(^2\)) was obtained at \(V_{FB} \pm 1\) V for the capacitors on both p and n-type Ge(100) with a minimum CET of 1.4 nm. However, degradation in the inversion region was observed for the capacitor on p-Ge (100).

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