Abstract: In this research, the hafnium titanate oxide thin films, Ti$_x$Hf$_{1-x}$O$_2$, with titanium contents of $x = 0, 0.25, 0.9$, and $1$ were deposited on germanium substrates by atomic layer deposition (ALD) at 300 °C. The approximate deposition rates of $0.2$ Å and $0.17$ Å per cycle were obtained for titanium oxide and hafnium oxide, respectively. X-ray Photoelectron Spectroscopy (XPS) indicates the formation of GeO$_x$ and germanate at the interface. X-ray diffraction (XRD) indicates that all the thin films remain amorphous for this deposition condition. The surface roughness was analyzed using an atomic force microscope (AFM) for each sample. The electrical characterization shows very low hysteresis between ramp up and ramp down of the Capacitance-Voltage (CV) and the curves are indicative of low trap densities. A relatively large leakage current is observed and the lowest leakage current among the four samples is about $1$ mA/cm$^2$ at a bias of $0.5$ V for a Ti$_{0.9}$Hf$_{0.1}$O$_2$ sample. The large leakage current is partially attributed to the deterioration of the interface between Ge and Ti$_x$Hf$_{1-x}$O$_2$ caused by the oxidation source from HfO$_2$. Consideration of the energy band diagrams for the different materials systems also provides a possible explanation for the observed leakage current behavior.

Keywords: Ge substrate; titanium-doped hafnium oxide; XPS; XRD; AFM
Metal-Oxide-Semiconductor Field Effect Transistor (MOSFET) and a variety of dielectric materials were attempted. Among the various candidates, hafnium-based gate stacks, such as HfO₂, HfON, and LaHfOₓ, have proven to be possible solutions for Ge MOS devices and transistors due to their relatively good reliability and high performance [6–9]. However, the reported dielectric constants of hafnium-based gate stacks varied from 11.5 to 21, which limited further scaling into the sub-nanometer regime [10,11]. In order to overcome this problem, a number of trials were carried out to further increase the permittivity of the dielectrics. One approach was to add a smaller amount of rare earth materials to the oxides to stabilize the crystal phase with a higher relative dielectric constant, such as lanthanum doped zirconium oxide [12,13]. Similar trials were performed on the hafnium oxide deposited on the silicon substrates, although the increase in the dielectric constant was not significant [14,15]. Another possible solution was to mix hafnium oxide with other dielectric materials with higher permittivity, such as titanium oxide (with \( k \approx 50–80 \)). The high dielectric constant of the titanium oxide originates from the soft phonons of titanium, and an increase in the overall dielectric constant of gate oxides after mixing HfO₂ and TiO₂ was achieved [16,17]. Although the addition of TiO₂ improved the dielectric constant of an HfO₂-based material, the small energy band gap of TiO₂ [18], which would result in a large leakage current, remained an issue to be considered [17]. Thus, the influence of different amounts of titanium oxide on the properties of the HfO₂-based material is of great interest. In addition, the deterioration of the interface due to the oxidation source borne by the high-\( \kappa \) materials was observed, and the effective passivation of the germanium surface is still an open question [3]. In order to minimize the deterioration of the interface and suppress the growth of the unstable native oxide of germanium, a number of methods have been conceived to passivate the germanium surface, such as NH₃ and sulfur treatment [19,20], or inserting an interfacial layer, such as aluminum oxide [21] between the high-\( \kappa \) thin film and the germanium substrate.

In this work, a 0.3 nm Al₂O₃ interfacial layer was deposited on the germanium substrate by atomic layer deposition (ALD) to passivate the surface. Subsequently, the thin films with different content levels of the TiO₂ in HfO₂ were deposited by ALD. The effect of TiO₂ content in hafnium oxide was explored in terms of physical and electrical properties. Furthermore, the interface quality and chemical structure between the oxides and substrates were investigated. The results of the measurements and the performance of the thin films of TiO₂-HfO₂ deposited on Ge substrate are presented and discussed in this paper.

2. Results and Discussion

X-ray Photoelectron Spectroscopy (XPS) was used to characterize the quality of the interface and the thin films in the stacks. Firstly, the XPS was performed on the 5 nm and 10 nm HfO₂ thin films to find out the chemical structure of the HfO₂ samples in the depth direction. XPS is a surface sensitive technique so the interface was probed by using a 5 nm nominal thickness film on the germanium substrate. As shown in Figure 1a,b, the Hf 4f line shape is typically composed of a 4f⁷/₂ and 4f⁵/₂ spin-orbit doublet [22]. With respect to the Hf 4f⁷/₂ peak positions, there is a clear difference between the two thin films with different thicknesses. The sample with a thickness of 10 nm has the lower binding energy (BE) peak at the position of 16.5 eV, which is tentatively assigned to stoichiometric HfO₂. For the sample with a thickness of 5 nm, the binding energy of the peak is centered at 17.3 eV, a difference of 0.8 eV in comparison to the 10 nm one. This shift is indicative of the greater interaction between the HfO₂ and Ge, and suggests stoichiometric and chemical changes at the interface. This is in accord with previous research, which has reported that the binding energy of Hf 4f⁷/₂ peak in HfSiₓOᵧ was 1 eV higher than that from HfO₂, which has a binding energy in the range of 16.5–17 eV [23,24]. Similar results have also been found for the Ge MOS device, which stated that about a 0.5 eV shift of binding energy existed for the Hf 4f⁷/₂ peak from HfGeOₓ compared with that from HfO₂ [25,26]. We can thus tentatively assign the shift in the Hf 4f binding energy to the formation of a germinate, HfGeOₓ. In contrast, the XPS results in Figure 2a,b for the TiO₂ samples in...
this experiment show that the Ti 3p\(3/2\) peaks for the 5 nm and 10 nm thickness samples are centered at the same position with binding energy of 36.9 eV, suggesting that no chemical structure change occurs for the TiO\(2\) samples in depth direction. Based upon the above analysis, it is inferred that HfO\(2\) will react with the Ge atoms at the interface without an effective passivation of the substrate. Formation of HfGeO\(x\) at the interface deteriorates the interface and possibly increases the leakage current in the stack [26].

**Figure 1.** The XPS line shape for HfO\(2\) thin films with the thickness of (a) 10 nm and (b) 5 nm. The sample with a thickness of 10 nm has the lower bonded peak at the position of 16.5 eV for Hf 4f\(7/2\) spectra. For the sample with a thickness of 5 nm, the bonded peak for Hf 4f\(7/2\) spectra is centered at 17.3 eV, with a difference of 0.8 eV in comparison to 10 nm one. This shift is probably due to the reaction of HfO\(2\) with the germanium for the 5 nm HfO\(2\) sample.

**Figure 2.** The Ti 3p spectra from: (a) 5 nm TiO\(2\); (b) 10 nm TiO\(2\); and (c) 5 nm Ti\(_{0.9}\)Hf\(_{0.1}\)O\(2\) thin films. The 5 nm and 10 nm thickness TiO\(2\) samples share the same Ti 3p\(3/2\) binding energy centered at the 36.9 eV. A small difference, 0.4 eV, is observed in binding energy of Ti 3p spectra between TiO\(2\) at 36.9 eV and in the Ti\(_{0.9}\)Hf\(_{0.1}\)O\(2\) samples at 37.3 eV.

Figure 2c compares the Ti 3p spectrum from the Ti\(_{0.9}\)Hf\(_{0.1}\)O\(2\) sample with the Ti 3p from a pure TiO\(2\) film on germanium, while Figure 3 shows the Hf 4f\(7/2\) spectra from the same 5 nm thick Ti\(_{0.9}\)Hf\(_{0.1}\)O\(2\) sample and compares it to Hf 4f\(7/2\) from a pure HfO\(2\) film. It is clear that the Hf 4f\(7/2\) binding energy from Ti\(_{0.9}\)Hf\(_{0.1}\)O\(2\), 17 eV, has a smaller difference in comparison to the pure HfO\(2\) at 17.3 eV (Ti\(_{0.25}\)Hf\(_{0.75}\)O\(2\) has the same Hf 4f\(7/2\) binding energy as Ti\(_{0.9}\)Hf\(_{0.1}\)O\(2\), 17 eV, not shown here).
In addition, Figure 2a,c show that there is also a difference of 0.4 eV in the binding energy of the Ti 3p spectra between TiO₂ (36.9 eV) and Ti₀.₉Hf₀.₁O₂ (37.3 eV). For the Ti₀.₂₅Hf₀.₇₅O₂ sample, the Ti 3p spectrum was found shifted to a higher binding energy by about 0.2 eV, while Hf 4f shifted to lower binding energy by about 0.3 eV. The shift of the Hf 4f 7/2 peak in the TiₓHf₁₋ₓO₂ samples to a lower binding energy and the Ti 3p to a higher binding energy suggests that an electron transfer from HfO₂ to TiO₂ takes place as a result of chemical mixing between TiO₂ and HfO₂.

**Figure 3.** The Hf 4f spectra from 5 nm thick films of (a) HfO₂ and (b) Ti₀.₉Hf₀.₁O₂ on Ge. The Hf 4f 7/2 binding energy from Ti₀.₉Hf₀.₁O₂ is 17 eV with a smaller shift compared to the HfO₂ with a shift of 17.3 eV.

In addition, from the analysis of the Ge 3d spectra from the four samples with a thickness of 5 nm shown in Figure 4, more information about the Ge surface can be deduced. The corresponding O 1s spectra from the four samples are shown in Figure 5. The peaks corresponding to Ge from elemental Ge and GeOₓ are labeled in the figures. The presence of Ge²⁺, Ge³⁺, and Ge⁴⁺ is due to the oxidation of the germanium substrate at the interfacial region, as well as possible germinate formation. Table 1 shows the compositions extracted from the line fits, relative to the bulk substrate Ge⁰ peak, of the various components at the interface for the four samples. It is clear that the oxidation is much less in the samples with TiO₂ (Figure 4a) compared with the other samples, while the oxidation of the substrate in the case of HfO₂ is much greater (Figure 4d). The fitting of the spectra shows an absence of Ge⁴⁺ in the TiO₂ sample, while an incremental increase of the GeOₓ intensity, especially Ge³⁺, is observed with the increasing HfO₂ content. This suggests that increasing the amount of HfO₂ in the dielectric films provides more oxidation sources to the interface [27]. This has also been observed in other research, which states that Ge atoms were oxidized by the oxygen atoms provided by the HfO₂ layer [3]. Furthermore, the Hf 4f 7/2 binding energy difference for the HfO₂ samples with different thickness, shown in Figure 1a,b and discussed above, also supports this finding. Therefore, it is inferred that the HfO₂ is a factor in the oxidation and has a deteriorating effect on the interface. With regard to the significant binding energy shift of the Ge 3d spectra from the samples, it is partially attributed to the presence of a mixture of oxides of GeOₙ (where x < 2) and GeO₂ at the interfacial region. The GeOₓ, referred to as a suboxide in the following discussion, consists of a structure with less than four oxygen atoms attached to one Ge. GeO is known to exhibit a signal at a binding energy lower than that of GeO₂ [28]. In this experiment, the concentration of GeO₂ and the x value differ from each other for the four samples. For Ge⁴⁺, it is absent in the pure TiO₂ layer on the germanium, and it is minimal for the Ti₀.₉Hf₀.₁O₂, while it is at a maximum for the pure HfO₂ layer. Therefore, this behavior causes the resultant intensity of the spectral component due to GeO₂ increasing, with
a concomitant decrease in intensity of the peak of GeO$_x$ for oxygen rich samples, and this intensity variation leads to a shift of the overall peak [28,29]. A similar phenomenon of Ge 3d spectra shift was also observed by Caymax in the interface study of the HfO$_2$ gate dielectric deposited on Ge [30]. In addition, the formation of HfGeO$_x$ due to the reaction between HfO$_2$ and Ge is also a possible contributing factor to the shift of the Ge 3d spectra [25,31].

Figure 4. Ge 3d spectra from 5 nm thin films of: (a) TiO$_2$; (b) Ti$_{0.9}$Hf$_{0.1}$O$_2$; (c) Ti$_{0.25}$Hf$_{0.75}$O$_2$; and (d) HfO$_2$ samples. The presence of Ge$^{2+}$, Ge$^{3+}$, and Ge$^{4+}$ is due to the Ge oxidation at the interfacial region. There is an increment of GeO$_x$ peak intensity, especially for Ge$^{4+}$ peaks, with the increase of the HfO$_2$ concentration.

Figure 5. Cont.
An atomic force microscope (AFM) was used to examine the surface roughness of the samples and the results for a scan area of 100 nm × 100 nm are presented in Figure 6. The surface roughness of the samples is quantitatively determined by the root-mean-squared roughness (\(R_{rms}\)), defined as

\[
R_{rms} = \sqrt{\frac{\sum_{n=1}^{N} (z_n - \bar{z})^2}{N - 1}}
\]

where \(z_n\) is the measured height, \(\bar{z}\) is the average height of the sample, and \(N\) is the number of measurements.

| Materials       | Ge\(^{+2}\) | Ge\(^{+3}\) | Ge\(^{+4}\) |
|-----------------|-------------|-------------|-------------|
| TiO\(_2\)       | 0.06        | 0.12        | –           |
| Ti\(_{0.9}\)Hf\(_{0.1}\)O\(_2\) | 0.06        | 0.24        | 0.14        |
| Ti\(_{0.25}\)Hf\(_{0.75}\)O\(_2\) | 0.17        | 0.24        | 0.41        |
| HfO\(_2\)       | 0.13        | 0.45        | 0.79        |

Figure 5. O 1s spectra from 5 nm films of: (a) TiO\(_2\); (b) Ti\(_{0.9}\)Hf\(_{0.1}\)O\(_2\); (c) Ti\(_{0.25}\)Hf\(_{0.75}\)O\(_2\); and (d) HfO\(_2\).

Table 1. Compositions extracted from the line fits shown in Figure 4, relative to the bulk substrate Ge\(^0\) peak for the four samples.

Figure 6. Cont.
Figure 6. Atomic force microscope (AFM) images of the samples: (a) TiO$_2$; (b) Ti$_{0.9}$Hf$_{0.1}$O$_2$; (c) Ti$_{0.25}$Hf$_{0.75}$O$_2$; and (d) HfO$_2$. The roughness ($R_{\text{rms}}$) for each sample is 0.325 nm, 0.431 nm, 0.425 nm, and 0.202 nm.

As can be seen, all the samples exhibit good surface morphology with a roughness $R_{\text{rms}}$ of 0.325 nm, 0.431 nm, 0.425 nm, and 0.202 nm for TiO$_2$, Ti$_{0.9}$Hf$_{0.1}$O$_2$, Ti$_{0.25}$Hf$_{0.75}$O$_2$, and HfO$_2$ respectively. The roughness of the thin films less than 0.5 nm demonstrates a nearly atomically smooth surface [32].

Figure 7 shows the XRD patterns for the four samples with different compositions of TiO$_2$ and HfO$_2$. The measurement was performed on the samples with a nominal thickness of 10 nm (the actual thickness was in the range 8 to 11 nm determined by ellipsometer). For all the samples, no noticeable diffraction peaks are observed, except for the one coming from the substrate centered at around 31.5°. According to the results of the XRD patterns only, it seems that all the thin films remained amorphous under these deposition conditions. However, due to the small thickness of the thin films, around 10 nm, the sensitivity of the XRD is probably not sufficient to detect a limited amount of the crystalline phase if it is present in the thin films, as has been previously pointed out [33,34]. It is possible that TEM (or SEAD) could further prove the exact morphology of the thin films.

Figure 7. XRD patterns for the 10 nm HfO$_2$, Ti$_{0.25}$Hf$_{0.75}$O$_2$, Ti$_{0.9}$Hf$_{0.1}$O$_2$, and TiO$_2$ thin films deposited on the germanium substrate. No noticeable diffraction peaks are observed, except for the one from the substrate.
The Capacitance-Voltage (CV) curves were obtained by sweeping the gate voltage from -1 V to 0.5 V in both directions (ramp up and ramp down) at a frequency of 1 MHz using an Agilent 4284A LCR meter (Agilent, Santa, CA, USA). Due to an unacceptable distortion of the CV characteristics caused by a large leakage current for the TiO₂ sample, reported below, only the CV curves extracted from HfO₂, Ti₀.₂₅Hf₀.₇₅O₂, and Ti₀.₉Hf₀.₁O₂ samples are presented in Figure 8. The high frequency CV measurements on the three as-grown thin films show that the samples have low trap densities because there is almost no hysteresis between the ramp up and ramp down of the CV curves. Due to the dielectric relaxation, likely caused by parasitic effect, lossy interfacial layer, and surface roughness of the samples, the obvious frequency dispersion of the samples is observed. Therefore, the vertical change of the CV characteristics is not discussed in this paper [35–37]. Regarding the CV characteristics of the Ti₀.₂₅Hf₀.₇₅O₂ sample, it is noted that saturation in the accumulation region is not obtained, regardless of the bias voltage level. This behavior is attributed to the large leakage current for this sample, which is possibly partially related to the deterioration of the interface as discussed above in the section for XPS analysis. Further comments regarding the leakage current are made in the following section.

Figure 8. CV characteristics for the three samples of Ti₀.₉Hf₀.₁O₂, Ti₀.₂₅Hf₀.₇₅O₂, and HfO₂. The gate voltage was swept from -1 V to 0.5 V at a frequency of 1 MHz, and no horizontal shift is observed. For the CV characteristics of the Ti₀.₂₅Hf₀.₇₅O₂ sample, saturation in the accumulation region is not obtained regardless of the bias voltage level, which is attributed to the large leakage current observed in this sample.

Figure 9 illustrates the relationship between the gate leakage current density (\( J_g \)) and the bias voltage (\( V_g \)) of the samples. The maximum current limit on our instrument was set at 2 mA. From observations drawn from Figure 9, it is apparent that the titanium oxide has the highest leakage current level, followed by hafnium oxide and Ti₀.₂₅Hf₀.₇₅O₂ thin films, both of which have similar leakage current levels. The Ti₀.₉Hf₀.₁O₂ sample has the lowest leakage current, with less than 1 mA/cm² at a bias voltage of 0.5 V. The large leakage current for the TiO₂ sample is attributed to the small band gap of TiO₂ as shown in Figure 10a and discussed further below. For the Ti₀.₉Hf₀.₁O₂, Ti₀.₂₅Hf₀.₇₅O₂, and HfO₂ samples with a larger band gap, it is clear that the leakage current increases with greater amounts of HfO₂. Previous research has also reported that a large leakage current was caused by the formation of HfGeO₄ at the interface between HfO₂ and Ge, and the leakage current was reduced if a germanium nitride barrier layer was first introduced, preventing the formation of HfGeO₄ [3]. High leakage current behavior, therefore, is probably due to the deterioration of the interfacial layer caused by the interaction of HfO₂ and Ge, which is consistent with the results shown in Figure 4. Thus, the increase in the leakage current clearly correlates with the hafnium oxide rich samples. For the TiO₂ doped samples, the TiO₂ would react with HfO₂ to form HfTiOₓ, consuming
the HfO$_2$, which would otherwise have reacted with the Ge at the interface. It is also possible that other mechanisms may also exist to suppress the leakage current, as has been observed in the titanium doped tantalum oxide. Titanium doping was found to suppress the oxygen vacancies in tantalum oxide capacitors, which resulted in a significant reduction in the leakage current [38]. For the HfO$_2$ capacitors, there are also a considerable number of oxygen vacancies [39–42], which could potentially be suppressed when titanium is doped in the HfO$_2$.

![Image](image_url)

**Figure 9.** Gate leakage current density ($J_g$) versus gate voltage ($V_g$) for samples of HfO$_2$, Ti$_{0.25}$Hf$_{0.75}$O$_2$, Ti$_{0.9}$Hf$_{0.1}$O$_2$, and TiO$_2$. The titanium oxide occupies the highest leakage current level followed by hafnium oxide and Ti$_{0.25}$Hf$_{0.75}$O$_2$ thin films with similar leakage current levels. The Ti$_{0.9}$Hf$_{0.1}$O$_2$ sample has the lowest leakage current.

Although the titanium incorporation seems to suppress the leakage current, the leakage current is still relatively large. The energy band diagram [18,19] in Figure 10 attempts to provide a possible explanation in conjunction with the XPS results discussed above. From the energy band diagram in Figure 10a, titanium oxide has a relatively small band gap (3.2 eV), and the conduction band minimum is at 4.21 eV, while the band gap and conduction band minimum for germanium are 0.66 eV and 4.13 eV, respectively. The thin aluminum oxide with the thickness of about 0.3 nm is used to passivate the germanium surface and it has almost no contribution to suppressing the leakage current. If a voltage was applied at the gate on the TiO$_2$/Al$_2$O$_3$ stack, a dramatic leakage current should be induced, considering the energy band diagram in Figure 10a. For the energy band diagram of the hafnium oxide shown in Figure 10b, the band gap is wider and the conduction band minimum is higher than that of the TiO$_2$. Thus, the HfO$_2$ sample has a higher potential barrier across the oxide. Therefore, the leakage current of the HfO$_2$ is five times smaller than that of the TiO$_2$, regardless of the deterioration of the interface caused by the oxidation of the substrate. When TiO$_2$ is doped in HfO$_2$, the reaction of TiO$_2$ and HfO$_2$ should adjust the energy band diagram as shown in Figure 10c, and the leakage current should be between that of TiO$_2$ and HfO$_2$ from the point view of energy band diagram. However, as mentioned above, HfO$_2$ is considered to be an oxidation source and contributes to the interface deterioration, which enhances the leakage current for the HfO$_2$ rich samples. Fortunately, the formation of HfTiO$_3$ in TiO$_2$ doped HfO$_2$ reduces the reaction between the HfO$_2$ and the germanium and suppresses the deterioration of interface, which results in the significant reduction of leakage current. Therefore, in our case, the Ti$_{0.25}$Hf$_{0.75}$O$_2$ dielectric sample has almost the same leakage current as the HfO$_2$ sample while the Ti$_{0.9}$Hf$_{0.1}$O$_2$ sample with much less HfO$_2$ has the smallest leakage current among all samples.
3. Experimental Section

Before mixing HfO$_2$ with TiO$_2$ to form Ti$_x$Hf$_{1-x}$O$_2$, the ALD growth rates of TiO$_2$ and HfO$_2$ were tested individually. Titanium isopropoxide and methoxymethyl hafnium were used as the ALD precursors and heated to 40 °C and 100 °C, respectively. Deionized water was used as an oxygen source and argon was employed as carrier gas in all the experiments. All the deposition was performed at the substrate temperature of 300 °C. The sequence for ALD deposition was precursor pulse/purge/water pulse/purge. For both precursors, the precursor pulse duration of 3 s was...
followed by a purge time of 6 s. Water pulse times of 0.01 s were followed by 3 s purge times. The thickness of thin films with different ALD cycles was measured by an ellipsometer. The relationship between the film thickness and corresponding ALD cycles is shown in Figure 11. From the slopes of the fitting straight line, it was found that the deposition rates for the TiO$_2$ and the HfO$_2$ were approximately 0.203 Å/cycle and 0.166 Å/cycle, respectively. Based on these growth rates, the cycle ratio of the titanium oxide to the hafnium oxide was evaluated to obtain the required dielectric oxides, with the ratio of TiO$_2$ to HfO$_2$ being 1:3 and 9:1 (Ti$_{0.25}$Hf$_{0.75}$O$_2$ and Ti$_{0.9}$Hf$_{0.1}$O$_2$), respectively, in terms of thickness. For example, for Ti$_{0.25}$Hf$_{0.75}$O$_2$, two TiO$_2$ cycles (0.4 Å) were followed by seven HfO$_2$ cycles (1.2 Å). The content of TiO$_2$ is equal to 0.4 Å/(0.4 Å + 1.2 Å) = 25%. According to the cycle ratio and deposition rates, the total cycles for each oxide were designed to produce the required thickness of the thin films. The $p$-type germanium wafers were used as the substrates of ALD Ti$_x$Hf$_{1-x}$O$_2$ thin films. The Ge wafer was cleaned ultrasonically in acetone followed by an O$_2$ plasma treatment. The germanium oxide on the surface was removed by cyclically rinsing with deionized water (DI water) and diluted 2% HF. The clean wafers were transferred to the ALD chamber (Oxford Instruments OpAL™, Oxford, UK) immediately to deposit an Al$_2$O$_3$ passivation layer (~0.3 nm) by ALD using trimethylaluminum (TMA) as precursor. The TiO$_2$, Ti$_{0.9}$Hf$_{0.1}$O$_2$, Ti$_{0.25}$Hf$_{0.75}$O$_2$, and HfO$_2$ thin films were then deposited on the Al$_2$O$_3$ passivated germanium substrates, respectively. XPS measurements were carried out in a UHV system consisting of Al Kα X-ray (1486.6 eV) source and a PEP vacuum systems 5-channel HSA electron energy analyzer. Due to an impurity in the carbon in the samples the C 1s peak in the spectra at 284.6 eV was used to calibrate any charging effects during measurements. The experimental XPS spectra were fitted using a Gaussian-Lorentzian line shape doublet to account for the spin-orbit splitting, using the CASAXPS fitting package. Grazing Incident X-ray diffraction (GIXRD) was carried out using a Bruker diffractometer (Bruker, Karlsruhe, Germany) with a Cu Kα radiation source (40 kV, 40 mA), spanning a 20 range from 20° to 50° at a scan rate of 1°/s for all measurements. The surface morphology and roughness of the thin films were analyzed using an atomic force microscope (AFM) (Bruker, Karlsruhe, Germany). The thickness of each thin film was measured by an ELLIP-SR-1 ellipsometer with the incident angle of 65° and wavelength from 300 nm to 900 nm with a step of 20 nm. The electrode contacts with a diameter of 0.3 mm and thickness of 350 nm were deposited by E-beam evaporation (TEMD-600, Beijing, China). The back surfaces of the samples were deposited with aluminum to form ohmic contact. An Aglient 4284A precision LCR meter and a Keithley 487 picomammeter (Keithley, Cleveland, USA) were employed to investigate the electrical properties of the samples. All the electrical measurements were performed in the dark at room temperature with a Faraday Cage surrounding the prober station.

Figure 11. The thin film thickness versus ALD cycles for titanium oxide and hafnium oxide, respectively. The slopes of the two fitting straight lines ($y = 0.0203x + 2.0008$ and $y = 0.0166x$) represent the corresponding deposition rates, and $R^2$ is the coefficient of determination. The deposition rates for TiO$_2$ and HfO$_2$ are approximately 0.203 Å/cycle and 0.166 Å/cycle, respectively.
4. Conclusions

Hafnium titanate oxide thin films, Ti$_x$Hf$_{1-x}$O$_2$, with a titanium content of $x = 0, 0.25, 0.9,$ and 1 were deposited on alumina passivated germanium substrates. XPS was used to analyze the interface quality and chemical structure. The results indicated that the HfO$_2$ deteriorates the interface quality, leading to an enhanced leakage current. The surface roughness was analyzed with an atomic force microscope, and all the samples exhibited relatively good surface morphology with the roughness RMS of 0.202 nm, 0.425 nm, 0.431 nm, and 0.325 nm for HfO$_2$, Ti$_{0.25}$Hf$_{0.75}$O$_2$, Ti$_{0.9}$Hf$_{0.1}$O$_2$, and TiO$_2$, respectively. XRD analysis shows that all the samples are amorphous under these deposition conditions. By using electrical characterization, it is found that there is almost no hysteresis between ramp up and ramp down of the CV curves, suggesting low trap densities. A relatively large leakage current is observed, with the lowest leakage current being about 1 mA/cm$^2$ at the bias of 0.5 V for Ti$_{0.9}$Hf$_{0.1}$O$_2$. The largest leakage current is attributed to the deterioration of the interface caused by the oxidation source borne by HfO$_2$, and the small band gap of the dielectric materials.

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