Effect of oxidation temperature on physical and electrical properties of ZrO₂ thin-film gate oxide on Ge substrate

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Abstract

The effects of oxidation temperatures on metal-oxide-semiconductor characteristics of sputtered zirconium thin films on germanium systematically investigated in an oxygen ambient. The samples were oxidized for 15 min at temperatures varying between 300 °C and 800 °C. The sample oxidized at 500 °C has demonstrated the highest electrical breakdown field of 16.6 MV cm⁻¹. The crystallinity of the film was evaluated by X-ray diffraction, Fourier-transform infrared, Raman, and X-ray photoelectron spectroscopy analyses were also performed. The crystallite size and microstrain of the films were estimated by Williamson-Hall plot analysis. Optical microscopy was used to examine the sample surfaces and high-resolution transmission electron microscopy was carried out to investigate the cross-sectional structure. GeO₂ was detected in samples oxidized at temperature above 600 °C. A possible thermal oxidation mechanism related to the diffusion of oxygen through the ZrO₂ layer and formation of germanium dioxide has been proposed and discussed.

1. Introduction

For decades, silicon has dominated the semiconductor complementary metal oxide (CMOS) process because its native oxide, SiO₂, has excellent insulating properties for metal-oxide-semiconductor field-effect transistor (MOSFET) devices and especially has low interface trap level density of the order of 1 × 10¹⁰ cm⁻² eV⁻¹ [1–4]. For the past few decades the semiconductor industry have reduced the scaling of MOSFET to improve device performance. However, at current MOSFET scaling, major difficulties emerge due to physical and technology limitations; issues related to non stationary transport, fundamental limits of binary devices switching, issues in supply voltage down scaling and others [5].

Both p-MOSFET and n-MOSFET devices are essential components in CMOS devices, where the mobility of majority carrier of p-MOSFET (hole) is lower than its n-MOSFET majority carrier (electron). Hence, for high-speed applications, p-MOSFET, is the bottleneck for further improvement. In that context, germanium has emerged as a promising candidate for a channel material to be used in high-speed CMOS devices, mainly because germanium has the highest hole mobility in groups IV and III-V semiconductor materials with a hole mobility 1900 cm² V⁻¹ s⁻¹, which is more than 4 times that of Si [6].

For MOSFET scaling, higher capacitance value between the gate and the substrate with smaller area is required. For decades, the industry standard has reduced the thickness of dielectrics to achieve this purpose [7]. According to the International Technology Roadmap for Semiconductors (ITRS) and several reports, as the oxide is thinned down to 1.2 nm, current direct tunneling through the oxide may increase tremendously. To overcome the aforementioned problem, high dielectric constant (κ) gate has been proposed as an alternative gate dielectric [8–10]. ZrO₂ as a high κ material has been widely studied as dielectric in the Si channel due to its excellent properties, such as high κ value, large energy bandgap, and easy stabilization in the form of cubic or tetragonal polymorphs [11–13]. It is valuable to also study Ge channel. Some reports have stated that the interface layer (IL) between ZrO₂ gate dielectric and Ge wafer disappeared when heat-treated at certain conditions; however, the mechanism still remains an open question [6,14]. The understanding of this mechanism is essential because it may enable this type of oxide-semiconductor structure, that is, ZrO₂/Ge, to be applied in the semiconductor industry, owing to IL-free structure, which may prevent premature electrical breakdown [15].

Compared with the counterpart Si, Ge is considerably unstable at high-temperature process because its melting temperature is lower than Si and Ge surface is unstable when expose to O₂ environment. This research will focus on how the oxygen penetrates through the dielectric layer and chemically react with Ge.

2. Experimental procedures

To prepare impurity-free samples, germanium wafer (n-type, (100)-
oriented, 0.01 Ω cm to 0.05 Ω cm, 1 cm × 1 cm was dip-cleaned in hydrofluoric acid (HF) solution (1:50 HF:H2O) and DI water. By using TF 450 physical vapor deposition (PVD) radiofrequency (RF) sputtering system, metallic zirconium (Zr) film was sputtered from a Zr target (Kurt J. Lesker, USA, 99.999% purity) at room temperature. Pressure, RF power, and argon gas flow rate were set at 3 × 10^{-5} mbar, 170 W, and 25 cm^3 min^{-1}, respectively. Experimental oxidation temperatures were set at 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, and 800 °C using Carbolite CTF tube furnace. Samples of sputtered Zr on Ge wafer were placed into the tube furnace with an O2 flow rate of 150 mL min^{-1} at each experimental temperature for 15 min. The oxidized samples were cooled down in the tube furnace before removal.

The properties of the samples were characterized by various measurement methods as discussed below. Film crystallinity was characterized using a PANalytical Empyrean X-ray diffractometer (XRD) system in the 2θ scan ranging from 10° to 80°. Copper radiation (Cu Kα) with a wavelength (λ) of 0.15406 nm was used as an X-ray source. The chemical compositions of the films were analyzed by X-ray photoelectron spectrometer (XPS) on ULVAC-PHI Quantera II (Al-Kα radiation). The X-ray tube was operated at 23.8 W. The analyzed area had a diameter of 100 μm. During XPS measurements, the pressure in UHV chamber was about 3 × 10^{-7} Pa. Survey scan was measured at 280 eV (energy resolution, 1 eV per step) pass energy, this was for elemental analysis. Narrow scan (with high resolution) was measured at 112 eV (energy resolution, 0.1 eV per step) pass energy, and it was for chemical states analysis. All data were recorded at a 45° take-off angle. To study geometry structure, film samples were sent for deposition of platinum (Pt) on surface for protection from ion bombardment damage caused by the focused ion beam during lamella preparation, followed by cross-sectioning using TECNAI G2 F20 high-resolution transmission electron microscope (HRTEM). The interplanar spacing (d) of the polycrystalline structure was measured from HRTEM images using ImageJ software. PerkinElmer Spectrum 400 Fourier-transform infrared (FTIR) spectrometer was used to study the chemical function of the films. Horiba Xplora One Raman spectrometer was used to measure chemical bonding. Optical microscope from Raman spectrometer was used to examine sample surfaces.

To study the electrical properties of the films, MOS capacitor test structures with area of 300 μm × 300 μm were fabricated. Aluminum (Kurt J. Lesker, USA, Al 99.9995% purity) sputtered with 200-nm-thick Al film to form an Ohmic back contact. BPW-800 8" probe station with a Keithley 4200 semiconductor characterization system (SCS) was used to measure current–voltage (I–V).

3. Results and discussion

3.1. J–E characteristics

J–E characteristics were used to study the effects of oxidation temperature on the electrical properties of the samples. Fig. 1 shows the J–E characteristics of samples oxidized at various temperatures. In the results, 300 °C, 400 °C, and 500 °C samples showed typical J–E curve. To determine the best sample, the highest electric breakdown field (E) with the lowest leakage current density (J) must be attained. Electrical characterization revealed that 500 °C samples yielded the highest electrical breakdown fields. The electrical breakdown fields were 14.3 MV cm^{-1}, 13.1 MV cm^{-1}, and 16.6 MV cm^{-1}, respectively. The recorded leakage current density for these three samples were in the order of 10^{-6} A cm^{-2} up to the applied electric field of 10 MV cm^{-1}. Beyond this applied electric field, the 500 °C sample demonstrates the lowest leakage current at the same order of magnitude of 10^{-6} A cm^{-2} up to the highest electric breakdown field, that is, 16.6 MV cm^{-1}. Therefore, 500 °C sample has the best electrical properties for application in CMOS technology. For 600 °C samples, it was observed that the breakdown electric field was 11.8 MV cm^{-1}. However, the leakage current of 600 °C samples before breakdown was unusually high, this may be because the ZrO2 dielectric was damaged by GeO gas which was generated at Ge wafer surface during oxidation. The 700 °C and 800 °C samples showed almost a short circuit in J–E curve measurement results. For further study, physical analysis will be performed in next section.

3.2. XRD analysis

Fig. 2 shows XRD patterns of samples oxidized at various temperatures. For the 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C samples, the peak at 51.22° (Fig. 2, red dotted line) was identified as monoclinic ZrO2 (22 1) peak [16]. The tetragonal Ge, t-Ge (004) was found at 52.39° (Fig. 2, blue dotted line) in 300 °C, 400 °C, 500 °C, and 600 °C samples [17]. The tetragonal trizirconium germanium oxide, t-GeO2Zr3 (220) was found at 51.61° (Fig. 2, green dotted line) in 700 °C and 800 °C samples [18]. The hexagonal GeO2, h-GeO2 (011) peak was observed at 25.94° in 600 °C samples. It could be contributed to the diffusion of O2 through ZrO2 layer, which reacted with Ge and formed crystallization of GeO2. The numbers of GeO2 peak increased as the oxidation temperature increased. The peaks of h-GeO2 found in the 700 °C and 800 °C samples were 20.54°, 25.94°, 35.98°, 39.02°, 39.46°, 41.79°, 44.90°, 48.66°, 53.35°, 56.31°, 58.84°, 61.65°, 66.04°, 67.03°, 70.00°, 73.81°, 76.32°, 77.27°, 77.60°, and 78.50° corresponding to (010), (011), (110), (102), (111), (020), (021), (112), (202), (210), (310), and (211), respectively.
(211), (113), (122), (031), (014), (302), (220), (213), (114), and (221) planes, respectively [19].

Williamson–Hall (W–H) plot analysis is used for evaluating the crystallite size \( D \) and microstrain \( \varepsilon \). The W–H as Eq. (1) [20]:

\[
(\beta_0 + \beta) \cos \theta = \frac{K \lambda}{D} + 4\varepsilon \sin \theta
\]

where \( \lambda \) is the wavelength of the radiation; \( K \) is a constant, which is equal to 0.9; \( \theta \) is the peak position; \( \beta_0 \) is the peak width at half-maximum intensity; and \( \beta \) is the peak width at half-maximum intensity. Based on Eq. 1, one plots a graph of \((\beta_0 + \beta) \cos \theta \) versus \( 4 \sin \theta \). Microstrain is the gradient, whereas \( S \) is the intercept of the graph, from which \( D \) can be calculated as Eq. (2):

\[
D = \frac{K \lambda}{y \text{ intercept}}
\]

Crystallite sizes of ZrO\(_2\) and GeO\(_2\)Zr\(_3\) of all samples were not calculated by using W–H plot because the number of peaks was insufficient for the study purposes. Because 600 °C samples only had one peak of h-GeO\(_2\), hence, only crystallite sizes and microstrain of 700 °C and 800 °C samples were calculated by using W–H plot. Fig. 3 shows the W–H plot of h-GeO\(_2\) for the 700 °C and 800 °C samples. According to Fig. 3, the points were distributed well in the two groups. Thus, it is better to draw two well-fitted regression lines (correlation coefficient, ~0.95) instead of one regression line with a correlation coefficient value less than 0.1. For the solid and dashed regression lines, they were defined as type 1 for the 700 °C and 800 °C samples, respectively. The crystallite size of h-GeO\(_2\) (type 1) of the 700 °C and 800 °C samples were 26.55 nm and 26.24 nm, respectively. The microstrain of h-GeO\(_2\) (type 1) of the 700 °C and 800 °C samples were 0.0026 and 0.0035, respectively. For the dotted and dashed-dotted regression lines, they were defined as type 2 for 700 °C and 800 °C samples, respectively. The crystallite size of h-GeO\(_2\) (type 2) of the 700 °C and 800 °C samples were 18.35 nm and 19.07 nm, respectively. The microstrain of h-GeO\(_2\) (type 2) of 700 °C and 800 °C samples were 0.011 and 0.0095, respectively. Two different locations of h-GeO\(_2\) films were inferred because of the two type dimensions of h-GeO\(_2\) crystallite size that were obtained. This inference will be verified and discussed in a later section.

3.3. Raman spectroscopy analysis

Fig. 4 shows the Raman analysis of oxidized samples at various temperatures. The peak that belonged to Ge was detected at 309 cm\(^{-1}\) [21,22] for all the samples. The peak that belonged to monoclinic ZrO\(_2\) was detected at 181 cm\(^{-1}\) [23] in 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C samples. Two peaks, 171 cm\(^{-1}\) and 454 cm\(^{-1}\), in 600 °C, 700 °C, and 800 °C samples of GeO\(_2\) were detected. For 800 °C samples, the extra peaks of GeO\(_2\) were detected at 130 cm\(^{-1}\), 221 cm\(^{-1}\), and 270 cm\(^{-1}\) [24,25]. The numbers of GeO\(_2\) peak increased as the oxidation temperature increased. These results were in conformity with the J-E characteristics and XRD analysis results where the GeO\(_2\) was detected for the samples oxidized above 600 °C.

3.4. FTIR analysis

Fig. 5 shows the FTIR analysis of the samples oxidized at various temperatures. FTIR analysis detected the presence of GeO\(_2\) trace in all the samples which were oxidized above 600 °C. This finding was in conformity with the J-E characteristics and XRD analysis results. Ge peak at 1044 cm\(^{-1}\) [26] was detected for all the samples. The ZrO\(_2\) peak at 570 cm\(^{-1}\) [27] was detected in the 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C samples. For 600 °C samples, the peaks of GeO\(_2\) were detected at 518 cm\(^{-1}\) and 903 cm\(^{-1}\). For the 800 °C samples, the peaks of GeO\(_2\) were detected at 518 cm\(^{-1}\), 589 cm\(^{-1}\), 927 cm\(^{-1}\), and 959 cm\(^{-1}\) [28,29]. The numbers of GeO\(_2\) peak increased as the oxidation temperature increased.

3.5. Optical microscope analysis

Optical microscope was used to examine samples surface condition at various temperatures as shown in Fig. 6. Fig. 6(a) shows the 300 °C to 500 °C samples, the surfaces were found to be smooth and defect-free. Fig. 6(b) shows the 600 °C samples, the blisters were found scattering.
Fig. 6(c) shows the 700 °C samples, where higher levels of blister defects and film discoloration were observed. Fig. 6(d) shows the 800 °C samples, where severe blister defects and film discoloration were observed.

3.6. XPS analysis

XPS analysis was performed for the evaluations of the structural and chemical properties of the ZrO₂ dielectric. By performing XPS wide scans for 300 °C, 400 °C, 500 °C, and 600 °C samples, core-level spectra of Zr 3d, Zr 3p, Zr 3s, Ge 3d, Ge 3p, Ge 3s, C 1s, and O 1s were detected. Narrow scans on Zr 3d, Ge 3d, and O 1s were also performed for 300 °C, 400 °C, 500 °C, and 600 °C samples. For comparison purpose, the signals of corresponding measurements were normalized to filter off the noise. Each spectrum was calibrated in respect to the carbon 1s (284.8 eV) state which was shown at Fig. 7(a).

Fig. 7(b) shows the narrow scan of Zr 3d for samples oxidized at various temperatures from 300 °C to 600 °C. Two peaks that belonged to ZrO₂ were detected from the Zr 3d narrow scan. The peak positions of lower binding energy belonged to Zr 3d₅/₂ in 300 °C, 400 °C, 500 °C, and 600 °C samples were 182.41 eV, 182.58 eV, 182.38 eV, and 182.78 eV, respectively. The peak positions for the higher binding energy that belonged to Zr 3d₃/₂ were 184.78 eV, 184.95 eV, 184.75 eV, and 185.15 eV, respectively [9,31,32]. The distance of peak to peak for all samples was 2.37 eV. The binding energy increased when the oxidation temperature increased except for the 500 °C samples.

Fig. 7(c) shows the narrow scan O 1s of samples oxidized at various temperatures from 300 °C to 600 °C. The ZrO₂ peak was the main peak in the 300 °C, 400 °C, 500 °C, and 600 °C samples, and the peak positions were 530.83 eV, 531.01 eV, 530.91 eV, and 531.34 eV, respectively [33–35]. The peak positions of GeO₂ were 532.13 eV, 532.44 eV, 532.24 eV, and 532.55 eV, respectively [36]. The component of GeO₂ was undetectable due to insignificant level. Similar with Zr 3d, the binding energy increased when the oxidation temperature increased except for the 500 °C samples.

Fig. 7(d) shows the narrow scan Ge 3d of samples oxidized at various temperatures, from 300 °C to 600 °C. The higher intensity of Ge–O peak was detected in 300 °C, 400 °C, 500 °C, and 600 °C samples which are located at 32.24 eV, 32.40 eV, 32.17 eV, and 32.71 eV, respectively. The lower intensity of Ge–O peak was detected which is located at 30.21 eV, 30.15 eV, 29.74 eV, and 30.59 eV, respectively. According to the reported literature [32,37,38], the peak positions of Ge, GeO, and GeO₂ were about 29.3 eV, 30.9 eV, and 32.5 eV, respectively. Fig. 8 shows the oxidation temperature versus binding energy of GeO₂ and GeOₓ. The peak position of higher intensity was near 32.5 eV, and should be the GeO₂, and the peak position of lower intensity was between 29.3 eV and 30.9 eV, which were assumed to be GeOₓ where x were valued in between 0 and 1.

In summary, the binding energy of ZrO₂ and GeO₂ shifted to higher binding energies when the oxidation temperature increased except for 500 °C samples. The shifting of binding energy indicated the certain level of overoxidation. The 500 °C samples did not linearly increased with temperature because the Ge atoms had sufficient energy to diffuse into ZrO₂. This assumption was based on temperature activation of dopant in Ge was 400 °C to 500 °C [6] which means the Ge atoms were active at 500 °C. The diffused Ge will combine with oxygen atom of existing ZrO₂ and formed Ge–O. Hence, binding energy of ZrO₂ shifted toward lower energy. Based on the reported literature [6], Ge may diffuse into the ZrO₂ dielectric layer. Ge was diffused in its solid state and bonded with the dangling bonds of atom O to become Ge–O in solid...
state, hence this temperature does not harm the electrical performance of the sample. On the other hand, for the 600 °C sample, GeO is in gaseous state, which will be demonstrated by Eq. (5) in the later Section 3.8, where gas pressure will increase at the hermetic space causing damage to the dielectric layer and thus leading to leakage current to outer layers. In other words, in 600 °C samples, the GeO2 generated between ZrO2 and Ge wafer. This prevented the diffusion of Ge into ZrO2. Hence, the peak position will be shifted toward higher energy and in linearity with 300 °C and 400 °C samples. Fig. 9 shows the narrow scan peak position of Zr 3\textit{d}_5/2 versus oxidation temperatures. The slope of the regression line was 1.2 × 10^{-3} eV °C^{-1}, and the correlation coefficient was 0.98. Compared with the \( J-E \) characteristics which were discussed previously, the overoxidation will reduce the breakdown field. The 500 °C samples had the lowest oxidation rate and the highest electrical breakdown field.

3.7. HRTEM analysis

HRTEM analysis was performed to study the cross-section of the samples. Fig. 10 shows the cross-section of HRTEM images of 300 °C and 500 °C samples. The thickness of ZrO2 dielectric for 300 °C and 500 °C samples were 5 nm and 8 nm, respectively. Assuming the thicknesses are in linear relationship with oxidation temperatures [39], by using 300 °C and 500 °C thicknesses, a regression line was shown at Fig. 11. Therefore, the thicknesses of the oxidized Zr thin films approximately range from 5 nm to 12.5 nm at 300 °C to 800 °C. Based on the results discussed in Section 3.6, increment of oxidation temperature may increase the level of overoxidation, and Ge atoms may have sufficient energy to diffuse into ZrO2 at 500 °C samples. This may be the reason why the induced ZrO2 dielectric of the 500 °C samples was thicker than the 300 °C samples. The ZrO2 dielectric showed as an amorphous structure and no IL were found between Ge wafer and ZrO2 dielectric layers. The phenomenon of IL free may due to the Ge diffusion into ZrO2 dielectric. The details of the behavior may need to be determined by the relative gain between the entropy arising from the intermixing and interface energy associated with the phase separation [6].
3.8. Thermal oxidation mechanism

Fig. 12(a) shows the schematic diagram of sputtered Zr film on Ge wafer before thermal oxidation. For the 300 °C, 400 °C, and 500 °C samples, the O2 directly reacted with the Zr film which was deposited by sputtering according to the Eq. (3) and formed the ZrO2 dielectric as shown in Fig. 12(b).

\[ Zr + O_2(g) \rightarrow ZrO_2 \]  

For the 600 °C, 700 °C, and 800 °C samples, the samples thermally oxidized according to the 3-step reactions as shown in Fig. 12(c). In high temperature ambient, the O2 received enough energy to diffuse through ZrO2 dielectric layer and reacted with the Ge wafer. GeO2 film formed on the surface of Ge wafer as shown in Eq. (4). After the GeO2 formed, GeO2 will react with Ge wafer, and GeO gas was generated according to Eq. (5) [6]. GeO gas will damage ZrO2 film where the blisters were observed on the top surface of the samples as shown in Fig. 6. The GeO gas diffused outward and reacted with O2 in atmosphere. After that, another GeO2 film was formed on the ZrO2 according to Eq. (6). Hence, this explained the reason why two crystallite sizes of h-GeO2 were observed at Section 3.2.

\[ Ge + O_2(g) \rightarrow GeO_2 \]  
\[ 3GeO_2 + 3Ge \rightarrow 6GeO(g) \]  
\[ 2GeO(g) + O_2(g) \rightarrow 2GeO_2 \]  

For 700 °C and 800 °C samples, the GeO gas and O2 may react with ZrO2 dielectric, and GeO3Zr3 was generated according to Eq. (7).

\[ 6ZrO_2 + 2GeO(g) + O_2(g) \rightarrow 2GeO_2Zr_3 \]  

From the analysis of two GeO2 layers, the absolute value of microstrain for the top layer will be less than the bottom layer, which is the reason why the bottom layer was compressed by the upper layer and Ge wafer. Because the compressive stress of bottom layer was higher than the top layer, the crystallite size of top layer was larger than bottom layer. Therefore, h-GeO2 (type 1) at Fig. 3 was assumed to be the top...
layer and h-GeO₂ (type 2) as the bottom layer. For the 800 °C samples, the microstrain of GeO₂/Zr₂O₅ was −0.0075, a value between the two microstrain values of GeO₂ layers, indicating it as the middle layer. Therefore, it is convenient to assume that GeO₂ (type 1) is located at the top most layer.

4. Conclusions

Pure Zr metal layers sputtered on Ge substrates were oxidized by a thermal oxidation process at various temperatures, from 300 °C to 800 °C for 15 min. J-E characteristics results showed that the leakage current was unacceptably high for oxidation temperature above 600 °C. FTIR, Raman, and XRD found GeO₂ components for samples with oxidation temperatures above 600 °C. The fact that two types of crystallite size and microstrain were found by W-H plot analysis indicates that there are two generating sources for GeO₂. It can be concluded that ZrO₂ dielectric film was unstable for oxidation temperature above 600 °C on Ge wafer. A possible thermal oxidation mechanism related to diffusion of O₂ through the ZrO₂ layer and formation of GeO₂ has been proposed and explicated. For ZrO₂ dielectric, the overoxidation will reduce the breakdown field. The samples oxidized at 500 °C have the lowest oxidation rate and has shown the highest electrical breakdown field.

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References