Metal-Oxide-Semiconductor Characteristics of Zr-Oxynitride Thin Film on 4H-SiC Substrate

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Sputtered Zr on 4H-SiC substrate and followed by simultaneous oxidation and nitridation in nitrous oxide ambient at various temperatures (400−900 °C) for 15 min have been systematically investigated. The structural and electrical properties of the samples were evaluated. Energy-filtered transmission electron micrographs demonstrated that an interfacial layer (IL) of 1.44 to 4.20 nm had been formed in between a bulk oxide of 14.63 to 18.53 nm and the SiC substrate, depending on the temperature. The calculated activation energies for the bulk oxide, which was Zr-oxynitride, IL, and total oxide growth were ~0.0535 eV, 0.1543 eV, and ~0.0078 eV, respectively. Supportive results were obtained from X-ray diffractometer, Raman spectrometer, and atomic force microscope. The electrical results revealed that 500 °C oxidized/nitrided sample has demonstrated the highest breakdown field and reliability. This was attributed to the lowest total interface trap, effective oxide charge, and highest barrier height between conduction band edge of oxynitride and semiconductor.

The current progress in semiconductor industry is mainly focusing on high performance devices with high transistor density and low leakage currents. One of the most promising materials for high power and/or high radiation applications is Silicon carbide (SiC) due to its wide bandgap (5.8–7.8 eV), and easily stabilized in the form of cubic or tetragonal polymorphs, which may further enhance its effective k value (22–25), large energy bandgap (5.8−7.8 eV), and easily stabilized in the form of cubic or tetragonal polymorphs, which may further enhance its effective k value.

Generally, the interfaces of high-k gate oxide/SiC semiconductor are often neglected due to the presence of interface defects. These defects may be originated from surface-structural defects, oxidation-induced defects, or radiation-induced defects. The interface trap has a considerable impact or effect on the reliability and lifetime of a MOS device because it is a main source causing leakage current apart from the characteristics of the oxide itself. Hence, it is important to control the thickness and composition of interfacial layer (IL) in between the gate oxide and semiconductor, so that the interface trap density can be minimized to an acceptable level. As a result, good electrical properties of a MOS device can be attained. In our previous works, bulk ZrO2 and IL of Zr-silicate oxynitride (ZrSiON) have been formed on Si substrate via simultaneous thermal oxidation and nitridation of sputtered Zr on Si using N2O gas. The nitridation effect in the process has provided improved electrical properties to the MOS device.

In our recent study, the same technique has been employed on sputtered Zr on SiC substrate. Chemical properties of simultaneously oxidized and nitrided sputtered Zr thin film on SiC substrate using N2O gas have been entailed. Based on the X-ray photoelectron spectrometer (XPS) analysis, it is reported that Zr-oxynitride and its IL of mixed Zr-O, Zr-N, Zr-O-N, Si-N, and/or C-N compounds were formed on SiC substrate. In addition, band alignment of Zr-oxynitride/IL/SiC system has been reported. With the corresponding conduction-band offsets of Zr-oxynitride to IL of 1.1–2.0 eV, depending on the oxidation/nitridation temperature, it is believed that this oxynitride may serve well as gate dielectric in SiC-based MOS capacitors. However, structural and electrical properties of Zr-oxynitride/IL/SiC system have yet to be reported. In this paper, further analyzes on structural and electrical properties will be reported and the correlations with chemical and electronic properties will be explored.

Experimental

0.8 cm × 0.8 cm pre-cut, n-type, (0001) oriented, Si-faced 4H-SiC wafers with 4.09° off axis, 0.020 Ωcm of resistivity, and 1-µm thick n-type epitaxial layer doped with nitrogen at concentration of (1−4) × 1018 cm−3, which were commercially purchased from CREE Inc. (USA), were used as the starting substrates. Ultrasonic and standard RCA (Radio Corporation of America) cleaning method were first used to clean the n-type 4H-SiC substrates. Subsequently, it was followed by dipping it into a diluted HF solution with a ratio of 1 HF : 50 H2O to remove native oxide on the surface. A 5-nm thick Zr film was sputtered on the cleaned SiC substrates using an Edwards Auto 500 RF sputtering system. During the sputtering, working pressure, RF power, inert Ar gas flow, and deposition rate were configured at 1.2×10−3 Torr, 170 W, 20 cm3/min, and 0.2 nm/s, respectively. Samples were placed into a horizontal tube furnace and heated up from room temperature to a set of temperatures (400, 500, 700, and 900 °C) in an Ar flow ambient and the heating rate was set constant at 10 °C/min. Once the set temperature was achieved, N2O gas was then
introduced with a flow rate of 150 mL/min for 15 min. Samples were then taken out at room temperature after the furnace was cooled down to room temperature in an Ar ambient.

Structural and electrical properties of the samples were evaluated by various characterization techniques. Cross-sectional images of the films were examined using Zeiss Libra 200 energy-filtered transmission electron microscopy (EFTEM). Prior to this, a protective layer of resist was deposited on the top most layer of a sample. Then it was ion-milled by a focused ion beam system. Interplanar spacing, \( d \), of the polycrystalline structure was measured from the EFTEM images with the help of ImageJ software, which gives the accuracy of measurements in three decimal places. The surface topography and root-mean-square (RMS) roughness of the investigated samples were analyzed by Nano Navi SPI3800N atomic force microscope (AFM) using a noncontact mode. In order to characterize the crystallinity of the films, X-ray diffraction (XRD) patterns were recorded in a grazing-incident mode, on a PANalytical X’Pert PRO MRD PW3040 diffractometer. Copper (Cu Kβ) radiation was used as the X-ray source, with wavelength (\( \lambda \)) of 1.5406 nm operating at 40 kV and 30 mA. Jobin Yvon HR 800 UV Raman spectrometer with an Ar\(^+\) incident beam and wavelength of 514.5 nm, were conducted to ascertain the stability of chemical bonding upon thermal oxidation and nitridation process.

To characterize the electrical properties of the film, Al-gate MOS capacitors with photolithographically defined square area of \( 9 \times 10^{-4} \) cm\(^2\) (0.03 cm × 0.03 cm) were fabricated on top of the films. Al film was also deposited on back side of the SiC substrate after removal of native oxide in order to obtain an Ohmic back contact. High-frequency (1 MHz) capacitance-voltage (C-V) and current-voltage (I-V) measurements were conducted by a computer-controlled Agilent HP4284 LCR meter and HP4155-6C semiconductor parameter analyzer (SPA), respectively.

**Results and Discussion**

**Structural Characterizations.**—The EFTEM cross-sectional images of films oxidized/nitrided at various temperatures (400–900 °C) are displayed in Fig. 1. Based on these images, the boundaries of bulk oxide, IL, and SiC substrate are clearly defined. Polycrystalline structure of bulk oxide has been observed in all investigated samples, as patches of lattice fringes with interplanar spacing, \( d \), of 0.258 to 0.305 nm. The range of values was measured from the images and it is in agreement with the \( d \) value of ZrO\(_2\).\(^{29,30,31}\) Based on the XPS results in Ref. 29, it is revealed that bulk Zr-oxynitride, which consists of Zr-O, Zr-N, and/or Zr-O-N, has been formed. Therefore, by inference, Zr-N and Zr-O-N may be in amorphous structure which embedded in the polycrystalline ZrO\(_2\). Besides, it is also inferred that IL may be comprised of sub- or non-stoichiometric Zr-O, Zr-N, Zr-O-N, Zr-Si-O, Si-N, and C-N, which are in amorphous structure. The measured physical thickness of the bulk Zr-oxynitride is approximately ranging from 14.63 to 18.53 nm for all investigated samples and the thickness decreases as the oxidation/nitridation temperature increases (Fig. 2). In contrast, thickness of IL that formed in between the bulk Zr-oxynitride and SiC substrate increases from 1.44 to 4.20 nm as the oxidation/nitridation temperature is increased. Generally, the total thickness of the combined oxide (bulk and IL) reduces with the increasing of oxidation/nitridation temperature. From the images with lower magnification (Fig. 1), it is noticeable that sample oxidized/nitrided at 300 °C has the smoothest surface. This observation can be further proven by AFM results in later paragraphs.

Fig. 3 shows the Arrhenius plot of Zr-oxynitride, IL and total (Zr-oxynitride + IL) growth in the N\(_2\)O ambient. The Zr-oxynitride, IL, and total growth rate are identified to be governed by:

\[
t = t_0 \exp \left(-\frac{E_a}{kT}\right)
\]

where, \( E_a \) is the activation energy for a reaction; \( k \) is the Boltzmann constant; \( t \) and \( t_0 \) are the final and initial thicknesses, respectively, of Zr-oxynitride, IL, and a total of Zr-oxynitride + IL, at a given temperature, \( T \), in Kelvin. The calculated \( E_a \) for the Zr-oxynitride, IL, and total growth are \(-0.0335 \) eV, \( 0.1543 \) eV, and \(-0.0078 \) eV, respectively. The negative values of \( E_a \) indicate that the rate of reaction decreases with increasing temperature. In other words, the densification happens with increasing temperature. The positive value of \( E_a \) indicates an increment of reaction rate as the temperature increases. It may indicate an expansion of the investigated layer happens with increasing temperature. On the other hand, the magnitude determines the tendency of a reaction or growth to happen. A small magnitude indicates a slow growth, while a large magnitude indicates a fast growth. In this work, the \( E_a \) value for IL growth in between the Zr-oxynitride and SiC substrate is comparable with the report demonstrated by Lai et al.\(^{33}\) In that report, the Zr-oxynitride was produced by sputtering of Zr metal based on Si substrate, followed by N\(_2\)O plasma...
oxygenitridation using plasma enhanced chemical vapor deposition (PECVD) technique. The reported $E_a$ value for the IL growth was 0.19 eV.

Fig. 4a–4e demonstrates the close-up XRD patterns of as-deposited Zr on SiC and oxidized/nitrided samples at different temperatures within the 2$\theta$ range of 25° to 35° in order to clearly identify the characteristic peaks of tetragonal phase of ZrO$_2$ (t-ZrO$_2$). A very strong intensity of diffraction peak at 35.5° and a minor peak at 43.2° (inset of the figure) were recorded in all investigated samples and the peaks were matched with 4H-SiC(004). These peaks were confirmed by The International Conference for Diffraction Data (ICDD) card number 00-022-1317.

The featureless pattern of as-deposited Zr metal on SiC verifies the amorphous dominance in the sample, as shown in spectrum (a) in Fig. 4. Upon oxidation/nitridation at temperatures of 400 to 900°C, all investigated films transform to crystalline structure. Two peaks from tetragonal (011) and (002) planes appear at 30.2° and 33.8°, respectively, indicating the formation of a dominantly tetragonal phase, as depicted in patterns (b)–(e) in Fig. 4. These two peaks of t-ZrO$_2$ were confirmed by ICDD card numbers, 00-050-1089 and 00-024-1164, respectively. According to the ICDD files, interplanar spacing of t-ZrO$_2$(011) and t-ZrO$_2$(002) are 0.2950 nm and 0.2635 nm, respectively. Therefore, from the XRD analysis, it suggests that crystalline t-ZrO$_2$ has been formed. This result is also supported by the measured interplanar spacing obtained from EFTEM images (Fig. 3). By correlating the XRD analysis with XPS results in Ref. 29, the remaining undetected compounds by XRD are Zr-O, Zr-N, Zr-O-N, Zr-Si-O, Si-N, and C-N and are appear in amorphous structure.

Fig. 5a–5f shows the Raman spectra of bare 4H-SiC substrate, as-deposited Zr on Si, and oxidized/nitrided samples at various temperatures (400–900°C). Two peaks located at 204 cm$^{-1}$ and 777 cm$^{-1}$ are originated from the 4H-SiC substrate in all investigated samples. In as-deposited Zr on SiC sample, except for the two peaks originated from 4H-SiC substrate, the Raman spectrum shows an amorphous phase without significant characteristic bonding peaks. On the other hand, presence of a peak at 471 cm$^{-1}$ and 641 cm$^{-1}$ are identified to be t-ZrO$_2$ in all oxidized/nitrided samples. Based on this result, it has again confirmed that t-ZrO$_2$ has been formed in all oxidized/nitrided samples, which is consistent with the results of XRD.
Figure 6. Two-dimensional AFM surface topography of (a) bare SiC substrate, (b) sputtered Zr on SiC substrate, and oxidized/nitrided samples at (c) 400 °C, (d) 500 °C, (e) 700 °C, and (d) 900 °C.

Two-dimensional (2D) surface topographies of bare 4H-SiC substrate, sputtered Zr metal on SiC substrate, and oxidized/nitrided samples at 400 to 900 °C were recorded on a 3 μm × 3 μm scanned area (Fig. 6). The corresponding surface root-mean-square (RMS) roughnesses of these samples are shown in Fig. 7. The bare SiC substrate has a considerably smooth surface with RMS roughness value of 3.91 nm. After Zr was sputtered on the SiC substrate, a rougher surface with RMS value of 4.67 nm was obtained. This is probably due to the non-uniform distribution of Zr atoms on the SiC surface. However, after samples were oxidized/nitrided at 400 to 900 °C, smoother surfaces with RMS values of 2.45 to 4.08 nm were obtained. The observed surface topographies of the oxidized/nitrided samples are in wavy form with different waviness. It is worth noting that sample oxidized/nitrided at 500 °C has the smoothest surface with wavy topography with RMS roughness value of 2.45 nm, which is matching with the observation made based on EFTEM results (Fig. 1). When the sample was heated up, the sputtered Zr layer on the surface might start to transform into visco-elastic form. At the same time, the arriving oxygen and nitrogen atoms from the ambient might arrange themselves with the Zr atoms on the surface, thus smoother surface can be obtained. At higher temperature of 700–900 °C, there will be more oxygen and nitrogen atoms arrived on the surface, causing uneven distribution of atoms and a rougher surface. As a result, at 900 °C, topography with higher waviness can be observed.

Electrical Characterizations.— Typical high-frequency (1 MHz) C-V curves measured at room temperature are presented (Fig. 8) for samples oxidized/nitrided at various temperatures (400–900 °C), in which the gate bias is bi-directionally swept from −1 to +13 V. It is observed that the capacitance at accumulation level increases with the increasing oxidation/nitridation temperature from 400 to 700 °C and a reduction is observed when the temperature reached 900 °C. This can be explained based on the following formula:

\[
C_{ox} = \kappa \varepsilon_0 A / t_{ox}
\]  

where, \(C_{ox}\) is the oxide capacitance (Zr-oxynitride + IL), \(\kappa\) is effective dielectric constant, \(\varepsilon_0\) is permittivity of free space \((8.85 \times 10^{-12} \text{ F/m})\), \(A\) is area of capacitor, and \(t_{ox}\) is total thickness of Zr-oxynitride and IL.
Apparently, the increment of capacitance may be attributed to higher κ value, larger A, and/or reduced \( t_{ac} \). Since \( \varepsilon_r \) is constant and A in this work is constant, the increment of capacitance is attributed to higher effective κ value (inset of Fig. 8) and reduced \( t_{ac} \) (Fig. 2).

Using Eq. 3, effective dielectric constant (\( \kappa_{eff} \)) of the oxides (Zr-oxynitride + IL) was estimated. \( C_{ox} \) was obtained from C-V measurements and the total oxide thickness was measured from EFTEM images. The relationship of the κ value and oxidation/nitridation temperature is shown in the inset of Fig. 8. The κ values obtained in this study range from 42.32–50.20, which is double the κ value of bulk ZrO\(_2\) (22–25). As reported by Li et al.,\textsuperscript{25} the dielectric constant of ZrO\(_2\) on Si substrate lies in between 7.5–55.0. Based on our previous report,\textsuperscript{24} the dielectric constant of ZrO\(_2\) on Si substrate is in the range of 10.58–21.82. It is strongly dependent on the oxide-substrate interface characteristics, nature of the substrate, electrode material, and oxide deposition method.

In the C-V measurements, depletion region is generally observed in the positive bias of all characterized capacitors. In other words, flatband voltage is shifted (\( \Delta V_{FB} \)) positively. This ascribes to the accumulation of negative effective oxide charges (\( Q_{eff} \)) in the oxynitride during the oxidation/nitridation process.\textsuperscript{30} This parameter was calculated based on the following equation:

\[
Q_{eff} = (\Delta V_{FB})C_{ox}/qA
\]  

where, \( q \) is the electronic charge. The calculated \( Q_{eff} \) for each sample is presented in Fig. 9. The source of negative \( Q_{eff} \) may be due to the existence of acceptor interface traps that act as fixed charges when not located in the majority band edge.\textsuperscript{37} In this work, the lowest \( Q_{eff} \) was obtained by film oxidized/nitrided at 500°C (5.0 \( \times \) 10\(^{13}\) cm\(^{-2}\)), which was relatively small as compared to the post-oxidation annealed film (8.0 \( \times \) 10\(^{13}\) cm\(^{-2}\)).\textsuperscript{38}

Hysteresis of the C-V measurements between forward and reverse bias is detected in all samples. As explained by Tanner et al.\textsuperscript{39} and Dimitrijev et al.\textsuperscript{40}, this phenomenon occurs due to slow traps located at some distance from the interface. The slow trap density (STD) can be indirectly associated with the hysteresis based on the following equation:

\[
STD = (\Delta V)C_{ox}/qA
\]

where, \( \Delta V \) is the difference between flatband voltages of a hysteresis curve. Based on the calculated value (Fig. 9), it is revealed that film oxidized/nitrided at 500°C has the lowest STD (6.0 \( \times \) 10\(^{12}\) cm\(^{-2}\)). The change in STD as a function of oxidation/nitridation temperature demonstrates the same trend as \( Q_{eff} \).

\[\text{Figure 8. C-V characteristics of MOS capacitors with Zr-oxynitride oxidized/nitrided at various temperatures (400–900°C). The inset shows effective dielectric constant of the investigated samples as a function of oxidation/nitridation temperatures (400–900°C).}\]

\[\text{Figure 9. Effective oxide charge and slow trap density contained in the investigated samples as a function of oxidation/nitridation temperatures (400–900°C).}\]

\[\text{Figure 10. Interface-trap density of the investigated samples oxidized/nitrided at various temperatures (400–900°C). The inset shows total interface-trap density of the investigated samples as a function of oxidation/nitridation temperatures (400–900°C).}\]
Dielectric breakdown (EB) of the sample is related to the attainment of the lowest negative Dit (Fig. 12). The trend of the reliability plot is similar to the trend of tested and cumulative failure percentage of the breakdown is presented at 500°C as compared to SiO2/SiC system, Zr-oxynitride on SiC of this work comparable or higher than previous reported work.9, 42–44 However, reliability tests had been performed.45 A total of 25 capacitors were produced a higher leakage current and a lower breakdown field.

Figure 11. J-E characteristics of investigated samples oxidized/nitrided at various temperatures (400–900°C).

~ 3.7 × 1013 cm−2, which is obtained from the film oxidized/nitrided at 500°C.

Fig. 11 shows the leakage current density-electric field (J-E) characteristics of the investigated samples. The J-E plot was transformed from current-voltage (I-V) measurement obtained from the computer-controlled SPA system. The E value was estimated by:28

\[ E = V_B - V_{FB}/t_{ox} \]  

Dielectric breakdown (EB) is defined as electrical breakdown experienced by the dielectric due to an instantaneous increment of leakage current density at a specific field. Of the four investigated samples, the sample oxidized/nitrided at 500°C possesses the highest \( E_B \) (5.05 MV/cm), whereas the lowest \( E_B \) is shown by the sample oxidized/nitrided at 900°C. The highest \( E_B \) in the 500°C oxidized/nitrided sample is related to the attainment of the lowest negative \( \Delta E_C \) ST D T, Ds and \( D_{total} \). In comparison, breakdown field recorded in this work is comparable or higher than previous reported work.9, 42–44 However, as compared to SiO2/SiC system, Zr-oxynitride on SiC of this work has produced a higher leakage current and a lower breakdown field.

From J-E measurements, time-zero dielectric breakdown (TZDB) reliability tests had been performed.45 A total of 25 capacitors were tested and cumulative failure percentage of the breakdown is presented (Fig. 12). The trend of the reliability plot is similar to the trend of \( E_B \) (Fig. 11) with sample oxidized/nitrided at 500°C demonstrates the highest reliability.

Barrier height (\( \phi_B \)) of conduction band edge between SiC and the interfacial layer of the oxide was extracted from Fowler-Nordheim (FN) tunneling model. FN tunneling is referred to the flow of electron through a triangular potential barrier into conduction band of an insulator.23 The \( J \) attributed to FN tunneling (\( J_{FN} \)) can be defined as follow:

\[ J_{FN} = A E^2 \exp (-B/E) \]  

where,

\[ A = (q^3/8\pi h\phi_B)/(m/m_{ox}) \]  

and

\[ B = [8\pi(2m_{ox}\phi_B^3)^{1/2}]/3qh \]  

where, \( h \) is Planck’s constant (4.135 × 10−15 eV-s), \( m_{ox} \) is effective electron mass in the oxidized layer, and \( m \) is free electron mass. By replacing all constants into Eqs. 9 and 10, \( A \) and \( B \) can be rewritten as,

\[ A = 1.54 \times 10^{-6} (m/m_{ox}\phi_B^3) \]  

and

\[ B = 6.83 \times 10^7 (m/m_{ox}\phi_B^3)^{1/2} \]  

By rearranging Eq. 8, it gives

\[ \ln (J_{FN}/E^2) = \ln (A) - B/E \]  

A linear FN plot of \( \ln (J_{FN}/E^2) \) versus \( 1/E \) is presented in Fig. 13. The intercept of the plot yields \( A \) and gradient of the slope yields \( B \). In order to calculate \( \phi_B \), electron effective mass of high \( k \) oxide is assumed to be 0.3m.23, 47 The calculated \( \phi_B \) as a function of oxidation time is presented in Fig. 14. The extracted \( \phi_B \) values are ranging from 1.06 to 1.67 eV. The highest value was attained by 500°C oxidized/nitrided sample (1.67 eV). The extracted \( \phi_B \) values in this work are having the same trend as the conduction-band offsets (\( \Delta E_C \)) extracted from XPS as a function of oxidation/nitridation temperature, with the highest value achieved by 500°C oxidized/nitrided sample (2.00 eV).29 Comparatively, the highest \( \phi_B \) value obtained in this work is also higher than the value reported (1.33 eV) by our previous report of ZrO2 on Si substrate using same technique.
Figure 14. Barrier height values as a function of oxidation/nitridation temperatures.

Conclusions

Structural and electrical properties of oxidized/nitrided Zr thin film on 4H-SiC substrate in N2O ambient for different oxidation/nitridation temperatures (400–900 °C) were presented. EFTEM images demonstrated that bulk Zr-oxynitride which consists of a polycrystalline ZrO2 with embedment of amorphous Zr-N and/or Zr-O-N. The IL may be comprised of sub- or non-stoichiometric Zr-O, Zr-N, Zr-O-N, Zr-Si-O, Si-N, and C-N, which are in amorphous structure. This result is then supported by XRD and Raman results, concluding that the ZrO2 was in tetragonal phase. These properties were subsequently related to the electrical characteristics of the films evaluated by MOS structures. From the electrical characterization, it was verified that 500°C oxidized/nitrided sample gave the best result, owing to the highest electrical breakdown field of 5.05 MV/cm at 10⁻⁶ A/cm². This is attributed to the reduction in interface trap density, total interface trap density, effective oxide charge, and increment of barrier height between conduction band edge of the film and the semiconductor.

Acknowledgments

This work has been supported by Universiti Sains Malaysia (USM) and the Academy Sciences for the Developing World (TWAS). The authors acknowledge USM fellowship, USM-RU-PRGS (8032051), and TWAS-COMSTECH Research grant (09-105 RG/ENG/AS_C) for the financial support during the study.

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