Electrical study of ZrO_2/Si system formed at different oxidation/nitridation temperatures for extended duration in N_2O ambient

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Electrical properties of ZrO_2 formed by simultaneous oxidation and nitridation of sputtered Zr thin films on Si have been systematically investigated. Various oxidation/nitridation temperatures (500, 700, 900, and 1100 °C) have been carried out in N_2O ambient for an extended time of 20 min. Results indicated that the sample oxidized and nitrided at 700 °C possessed the highest effective dielectric constant of 18.22 and electrical breakdown field of 10.7 MV/cm at a current density of 10^{-6} A/cm^2. This is attributed to the lowest effective oxide charge, interface-trap density, and total interface-trap density. The Fowler–Nordheim tunneling mechanism has been investigated for all samples and the highest value of barrier height extracted between the conduction band edges of oxide and semiconductor was 1.22 eV.

I. INTRODUCTION

Utilization of high dielectric constant metal-oxide systems has been widely investigated as an essential component in metal-oxide-semiconductor (MOS)-based devices as a gate dielectric for decades.[1–3] In particular, ZrO_2 has gained great interest due to its high enough κ value (22–25), suitably large band gap (5.8–7.8 eV), good thermodynamic stability when in contact with Si up to ~900 °C of processing temperature, and minimal lattice mismatch with Si(100). Moreover, it can be easily stabilized in the form of cubic or tetragonal polymorphs, which may further enhance its effective κ value.[1,2,4]

Various methods have been used by several groups of researchers to form ZrO_2 thin films on Si substrate, for example, thermal evaporation, pulsed laser deposition, atomic layer deposition, metalorganic chemical vapor deposition, and sputtering.[5–9] Highly dependent on the deposition techniques, various characteristics and quality of ZrO_2 thin films can be fabricated. Based on the reported literature, a combination of metallic Zr sputtering and thermal oxidation process in O_2 ambient is able to produce stoichiometric ZrO_2 thin films.[2,10–12] However, this process initiates the diffusion and reaction between oxygen, silicon, and zirconium, causing an inevitable formation of undesirable interfacial layer (IL) in between ZrO_2 thin film and Si substrate. As a result, capacitance of the MOS capacitor was reduced, and performance of the MOS-based devices was deteriorated.

The presence of nitrogen in the film may help to reduce the IL thickness in between ZrO_2 and Si. It is believed that nitrogen content in the film can help to suppress the out-diffusion of Si by passivating the dangling bonds of the Si surface and improve the hot carrier resistance at the Si-dielectric interface.[13–15] Based on several reported papers,[15–17] ZrO_2 films have shown well-behaved electrical characteristics in the presence of nitrogen. To perform oxidation and nitridation simultaneously, NO and N_2O are the typical gases used.[13] As compared to NO, N_2O is more suitable and preferable to be used due to its nontoxic property.[18] Extending from the previous reported works,[19–22] N_2O has been used to act as the oxidation as well as nitridation source to form tetragonal-ZrO_2 thin films on the Si substrate. Electrical performance of the tetragonal-ZrO_2/Si system formed in N_2O ambient has been studied up to 15 min. The studies provided high enough effective dielectric constant values of 10.58–21.82, with relatively low densities of effective oxide charge, slow-trap, and interface-trap. However, up to date, no investigation has been carried out on the electrical performance for tetragonal-ZrO_2/Si system formed in N_2O ambient for an extended time. It has been reported that a complete catalytic decomposition of N_2O on ZrO_2 happens at a temperature of 700 °C; hence, this particular temperature was chosen in this study.[19] The purpose of the time

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extension is to ascertain whether time extension could help in improving the electrical properties of the tetragonal-ZrO_2/Si system as compared to previous works.[19,21] Therefore, in this work, tetragonal-ZrO_2 was formed by simultaneous oxidation and nitridation of sputtered Zr thin film on Si at various temperatures for an extended time of 20 min in N_2O ambient. Capacitance–voltage (*C–V*) and current–voltage (*I–V*) measurements have been conducted to investigate the electrical properties of tetragonal-ZrO_2 thin films fabricated in this work.

II. EXPERIMENTAL PROCEDURES

(100)-oriented n-type Si substrates (1–10 Ω cm) were subjected to a standard RCA cleaning and diluted HF solution treatment (1 HF:50 H_2O) for 15 s to remove native oxide from the surface prior to metallic Zr sputtering. Edwards Auto 500 RF sputtering system was used to deposit an ultrathin 5-nm Zr metal thin film on the cleaned Si substrates by using a Zr metal target (Alfa Aesar, 99.5%, Alfa Aesar, UK). RF power, working pressure, inert Ar gas flow, and deposition rate were regulated at 170 W, 1.2×10^{-7} Torr, 20 cm^3/min, and 2 Å/s respectively. After the deposition, samples were placed into a horizontal tube furnace and heated up from room temperature to a set of temperatures (500, 700, 900, and 1100 °C) in an Ar flow ambient and the heating rate was constant at 10 °C/min. Once the set temperature was reached, N_2O gas was then introduced with a flow rate of 150 mL/min for 20 min. Samples were eventually taken out at room temperature after the furnace was cooled down to room temperature in an Ar ambient.

MOS capacitors were fabricated to conduct electrical characterization. A layer of 100-nm thick Al was thermally evaporated on top of the films. Subsequently, an array of 9×10^{-4} cm^2 of Al gate electrode was patterned by photolithography process using a shadow mask. Last, an Ohmic back contact was fabricated by depositing a 100-nm thick Al film on backside of the Si substrate after removal of native oxide. The electrical properties of the MOS capacitors were then characterized by high-frequency (1 MHz) capacitance–voltage (*C–V*) and current–voltage (*I–V*) measurements using a computer-controlled Agilent HP4284 LCR meter (Agilent Technologies, Santa Clara, CA) and HP4155-6C semiconductor parameter analyzer (SPA; Agilent Technologies, Santa Clara, CA), respectively.

III. RESULTS AND DISCUSSION

High-frequency *C–V* characteristics of MOS capacitors with ZrO_2 thin film oxidized and nitrided at different processing temperatures (500–1100 °C) for 20 min are shown in Fig. 1. Different saturation capacitance can be observed at the accumulation level. The highest capacitance is attained by the sample oxidized/nitrided at 700 °C, followed by 500, 900 °C, and the lowest capacitance is

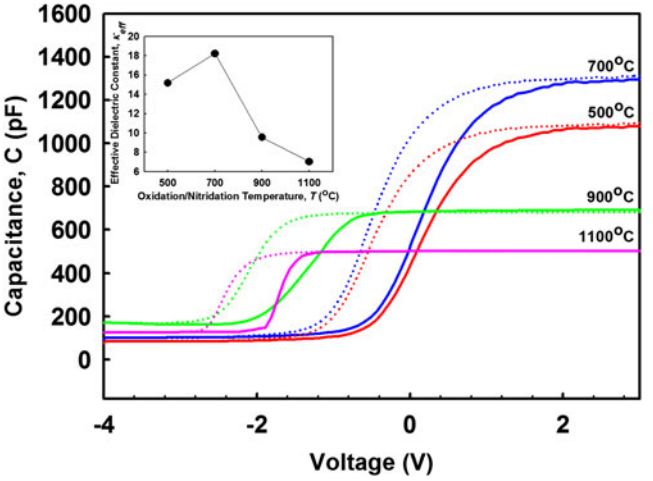


FIG. 1. *C–V* characteristics of the investigated samples oxidized/nitrided at various temperatures. The inset shows the calculated κ_{eff} values as a function of oxidation/nitridation temperature.

obtained by 1100 °C oxidized/nitrided sample. This could be due to the formation of IL that may aggravate the dielectric polarization of the oxidized/nitrided sample, thus reducing the capacitance. The effective dielectric constant (κ_{eff}) can be calculated based on the following general equation[3]:

$$C_{ox} = \kappa_{eff}\varepsilon_0 A/t_{ox} \quad , \qquad (1)$$

where C_{ox} is the capacitance of the oxide, ε_0 is the permittivity of free space, A is the area of the capacitor, and t_{ox} is the total oxide thickness (ZrO_2 + IL). C_{ox} was obtained from the saturation capacitance at the accumulation level (Fig. 1), and the total oxide thickness was obtained from the energy-filtered transmission electron microscope image in Ref. 19. The total oxide thickness of 20-min oxidized/nitrided sample was approximately 11 nm. The calculated κ_{eff} values are in the range of 7.04–18.22 (inset of Fig. 1), depending on the oxidation/nitridation temperature. The highest κ_{eff} value (18.22) is attained by 700 °C oxidized/nitrided sample. This obtained value is comparable with the value reported in Ref. 23 and slightly lower than the values reported in Refs. 24 and 20.

Depletion region is generally observed in the negative bias, and flatband voltage is shifted (ΔV_{FB}) negatively for all characterized capacitors. This indicates the existence of positive effective oxide charges (Q_{eff}) in the oxide.[25] The formation of positive oxide charges might be due to the presence of traps in the oxide, contributed by the Zr and Si dangling bonds. The Q_{eff} contained in the samples can be calculated by the following equation[25]:

$$Q_{eff} = (\Delta V_{FB})C_{ox}/qA \quad , \qquad (2)$$

where q is the electronic charge. The calculated Q_{eff} for each sample is presented in Fig. 2. The lowest Q_{eff} is

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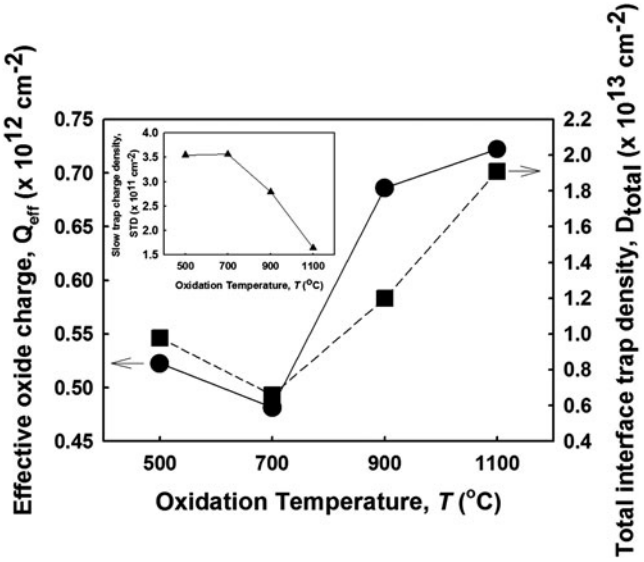


FIG. 2. Effective oxide charge and total interface-trap density in the investigated sample as a function of oxidation/nitridation temperature. The inset shows STD in the investigated sample as a function of oxidation/nitridation temperature.

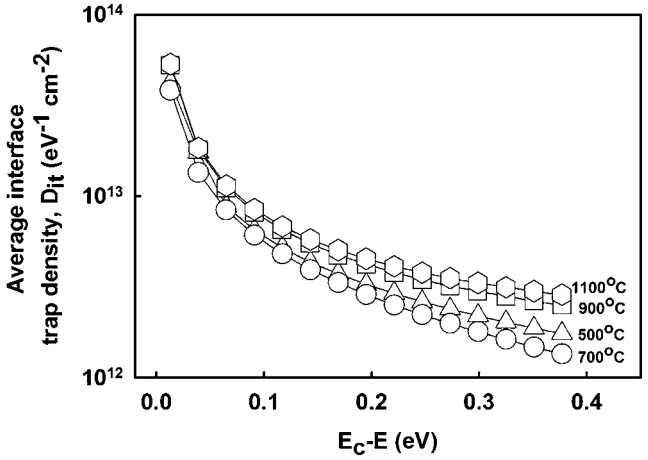


FIG. 3. Interface-trap density of the investigated sample oxidized/nitrided at various temperatures.

acquired by 700 °C oxidized/nitrided sample (4.81×10^{11} cm^{-2}), which is lower than the value reported in Ref. 26.

Hysteresis of the C–V measurements between forward and reverse bias is detected in all samples. As explained by Tanner et al.[27] and Dimitrijev et al.,[28] 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:

$$\mathrm{STD} = (\Delta V) C_{ox}/qA \quad , \tag{3}$$

where ΔV is the difference between flatband voltages of a hysteresis curve. Based on the calculated value (inset of Fig. 2), it is revealed that 700 °C oxidized/nitrided sample has the highest STD (3.57×10^{11} cm^{-2}). The change in STD as a function of oxidation/nitridation temperature is in the reverse trend of Q_{eff}. The oxide charge and hysteresis of the films formed at different temperatures show differences that could be due to the IL thickness change, as reported in Ref. 21.

Figure 3 shows the oxide-semiconductor interface-trap density (D_{it}) of the investigated samples with respect to the energy level of the trap. The D_{it} value was estimated from high frequency C–V measurements using Terman method that had been performed at room temperature[25]:

$$D_{it} = (C_{ox}/qA) \cdot [\mathrm{d}(\Delta V_g)/\mathrm{d}(\phi_s)] \quad , \tag{4}$$

where ϕ_s is the surface potential of Si at a specific gate voltage, V_g. The surface potential of a particular capacitance is taken from an ideal MOS capacitor. The gate voltage is then acquired from the experimental C–V curve of the same capacitance as that of ϕ_s. The steps are repeated for other data points until a relevant D_{it} against (E_c–E) curve is obtained.

From the D_{it} curves, 700 °C oxidized/nitrided sample shows the lowest D_{it}. The D_{it} value obtained at an energy level of 0.2 eV from this experiment is comparable to other reported works, which is in the order of $\sim 10^{12}$ per eV per cm^2.[24,29] To determine the total interface-trap density (D_{total}) of the energy range (E_c–E), the area under the D_{it} – (E_c–E) plot was calculated (Fig. 2). The variation of D_{total} as a function of oxidation time is similar to the changes of Q_{eff}. The reduction of D_{total} is most probably due to incorporation of nitrogen in the ILs. The lowest total interface-trap density obtained in this experiment is 7.21×10^{12} cm^{-2}, which is obtained from 700 °C oxidized/nitrided sample. The D_{it} and D_{total} increase with temperature could be due to the concentration of Si–N, which is too high or much higher than the concentration of Zr–N in the sample, as reported in Ref. 21.

Figure 4 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) measurements obtained from the computer-controlled SPA system. The E value was estimated by[25]:

$$E = (V_g - V_{FB})/t_{ox} \quad . \tag{5}$$

There is a two-step oxide breakdown (E_B and E_{HDB}) observed in the J–E plot for all investigated samples (Fig. 4), due to the presence of interfacial and ZrO_2 layers in the sample.[30] The breakdowns can be explained as follows. One of the layers may experience an electrical breakdown at a lower field, which is labeled as E_B. Subsequently, another layer would block the carriers. Due to increment of electric

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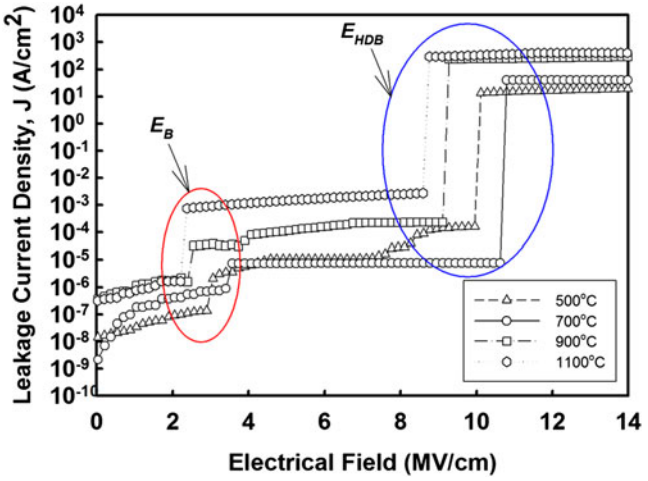


FIG. 4. *J–E* characteristics of investigated sample oxidized/nitrided at various temperatures.

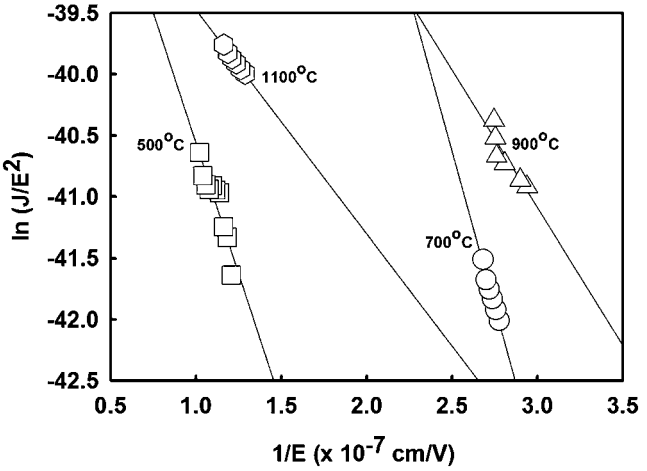


FIG. 5. F–N tunneling linear regression plot [$\ln(J/E^2)$ – $1/E$] of investigated sample oxidized/nitrided at various temperatures.

field, the concentration of the carrier increases until the layer is electrically broken down at a higher electric field at E_{HDB}. The instantaneous increment of leakage current density at E_B is relatively small when compared with others and it is defined as soft breakdown. In contrast, the instantaneous increment of current density at E_{HDB} is large and this is considered as hard breakdown. The trend of E_{HDB} as a function of oxidation/nitridation temperature is reverse when compared with the trend of effective oxide charge (Fig. 2) and of total interface-trap density (Fig. 2) with respect to the oxidation/nitridation temperature. As the density of effective charge and that of interface trap reduce, electrical breakdown field increases. In addition, the breakdown field is also affected by STD (inset of Fig. 2). It is observed that as the trap density is higher, a larger breakdown field can be obtained. The highest dielectric breakdown field, which is referred to as hard breakdown, is attained by 700 °C oxidized/nitrided sample (10.7 MV/cm). The lowest one is recorded by

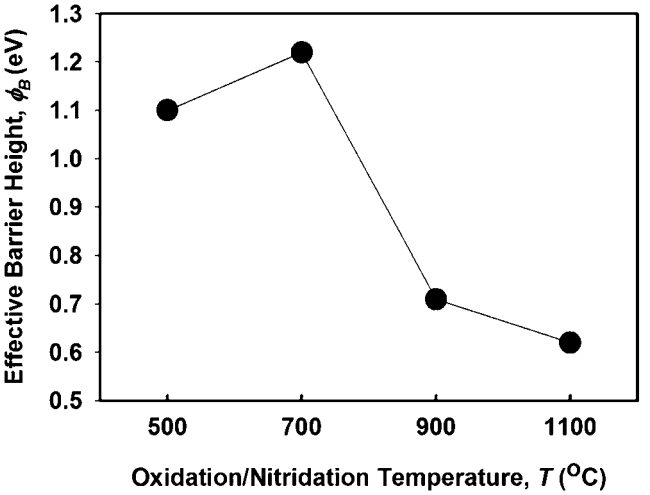


FIG. 6. Barrier height values as a function of oxidation/nitridation temperature.

1100 °C oxidized/nitrided sample (8.6 MV/cm). In comparison, the highest breakdown field recorded in this work is higher than the previous reported works.

Barrier height (ϕ_B) of conduction band edge between Si and the oxidized layer was extracted from Fowler–Nordheim (FN) tunneling model. FN tunneling is referred to the flow of electron through a triangular potential barrier into the conduction band of an insulator.[25] The J attributed to FN tunneling (J_{FN}) can be defined as follows[25]:

$$J_{FN} = AE^2 \exp(-B/E) \quad , \tag{6}$$

where

$$A = 1.54 \times 10^{-6}(m/m_{ox}\phi B) \quad , \tag{7}$$

and

$$B = 6.83 \times 107(m_{ox}\phi B^3/m)^{1/2} \quad , \tag{8}$$

where m_{ox} is the effective electron mass in the oxidized layer, and m is the free electron mass. A linear FN plot of $\ln(J_{FN}/E^2)$ versus $1/E$ is presented in Fig. 5. The intercept of the plot yields A and the gradient of the slope yields B. To calculate ϕ_B, the electron effective mass of the investigated oxide is assumed to be $0.3m$.[23] The calculated ϕ_B as a function of oxidation/nitridation temperature is presented in Fig. 6. The extracted ϕ_B values are ranging from 0.62 to 1.22 eV. The highest value was attained by 700 °C oxidized/nitrided sample (1.22 eV). Comparatively, the highest value obtained in this work is comparable to the value reported (1.23 eV) by thermally evaporated ZrO_2 on Si.[5]

IV. CONCLUSION

In conclusion, ZrO_2 has been formed by simultaneous oxidation and nitridation of sputtered Zr thin film on n-type Si at different temperatures (500–1100 °C) in N_2O environment for an extended time of 20 min. The electrical

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properties of the thin films were investigated. Results indicated that the highest effective dielectric constant of 18.22 and electrical breakdown field of 10.7 MV/cm at 10^{-6} A/cm^2 were attained by 700 °C oxidized/nitrided sample. This is attributed to the lowest effective oxide charge, interface trap density, total interface trap density, and increment of barrier height between conduction band edge of the film and the semiconductor.

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