Band alignment and enhanced breakdown field of simultaneously oxidized and nitrided Zr film on Si

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Abstract
The band alignment of ZrO$_2$/interfacial layer/Si structure fabricated by simultaneous oxidation and nitridation of sputtered Zr on Si in N$_2$O at 700°C for different durations has been established by using X-ray photoelectron spectroscopy. Valence band offset of ZrO$_2$/Si was found to be 4.75 eV, while the highest corresponding conduction offset of ZrO$_2$/interfacial layer was found to be 3.40 eV; owing to the combination of relatively larger bandgaps, it enhanced electrical breakdown field to 13.6 MV/cm at 10$^{-6}$ A/cm$^2$.

Keywords: oxidation, sputtered-Zr, nitrous oxide, band alignment, electrical breakdown field

Background
Application of high dielectric constant ($\kappa$) materials as future gate dielectrics on Si-based metal oxide semiconductor (MOS) devices has driven a tremendous research to realize an ultra-large-scale integrated circuitry with high performance and low power consumption [1-3]. Of various investigated high $\kappa$ materials, ZrO$_2$ is being considered as a potential gate dielectric for the near future generation technology nodes. It has been reported that excellent electrical properties of MOS capacitors that incorporated ZrO$_2$ thin film as gate dielectric [4,5]. Putkonen et al. [5] and Niinisto et al. [4] have obtained the breakdown fields of ZrO$_2$ at 6.0 and 9.5 MV/cm, respectively, at leakage current density of 10$^{-2}$ A/cm$^2$. In order to attain excellent electrical properties of a device, interfacial properties of dielectric/Si play an indispensable role [6,7]. The leakage characteristic and electrical breakdown field of gate dielectric are basically dependent on the bandgap of the dielectric and on the band alignment with Si [8,9]. Hence, to use ZrO$_2$ as gate dielectric in MOS capacitors, it should have sufficiently high band offsets with Si ($>1.00$ eV) for both holes (valence band offset) and electrons (conduction band offset), so that an ultralow leakage current can be acquired [2,3]. Therefore, it is crucial to quantify these energy band offsets. Additionally, it is necessary to consider an interfacial layer (IL) that is inevitably formed in between ZrO$_2$ and Si in the evaluation of band alignment. Works along this direction were reported by a number of researchers (Table 1). It is summarized that band alignment of the ZrO$_2$/IL/Si system can be categorized into two types, depending on the oxide deposition techniques rather than the types (n or p) of semiconductor: type (i), alignment of ZrO$_2$ bandgap in between the IL bandgap [10-13] and type (ii), alignment of ZrO$_2$ conduction band outside the IL bandgap [14]. In this work, using simultaneous oxidation and nitridation of sputtered Zr on n-type Si in N$_2$O, alignment of ZrO$_2$ valence band outside the IL bandgap has been revealed [type (iii) in Table 1] (Figure 1). Owing to this type of alignment, dielectric electric breakdown field at low leakage current density has been enhanced.

Results and discussion
Figure 2a shows typical X-ray photoelectron spectroscopy (XPS) valence band spectra of ZrO$_2$ and IL for all investigated samples. The valence band edges ($E_v$) of ZrO$_2$ and IL were estimated by an intercept of linear extrapolation of a maximum negative slope near the edge to the minimum horizontal baseline [10]. As a result, valence band offsets ($\Delta E_v$) of ZrO$_2$ and IL with
respect to Si substrate were 4.75 ± 0.05 eV and 3.75 ± 0.05 eV, respectively, for all investigated samples. To determine conduction band offset ($\Delta E_c$) of ZrO$_2$/IL/Si system, the bandgaps ($E_g$) of ZrO$_2$ and IL were first deduced from O 1s plasmon loss spectra [15,16] of ZrO$_2$ and IL, respectively. Figure 2b representatively demonstrates the XPS O 1s plasmon loss spectra of ZrO$_2$ and IL for a 15-min sample. Whilst for other samples, the $E_g$ values of ZrO$_2$ and IL extracted from their respective O 1s plasmon loss spectra are shown in Figure 3. As explained earlier, values of $E_g$ were also approximated by an intercept of linear extrapolation. The extracted $E_g$ values of ZrO$_2$ and IL were 6.20 to 6.50 eV and 8.20 to 8.80 eV, respectively, for all investigated samples. To determine conduction band offset ($\Delta E_c$) of ZrO$_2$/IL/Si system, the bandgaps ($E_g$) of ZrO$_2$ and IL were first deduced from O 1s plasmon loss spectra [15,16] of ZrO$_2$ and IL, respectively. Figure 2b representatively demonstrates the XPS O 1s plasmon loss spectra of ZrO$_2$ and IL for a 15-min sample. Whilst for other samples, the $E_g$ values of ZrO$_2$ and IL extracted from their respective O 1s plasmon loss spectra are shown in Figure 3. As explained earlier, values of $E_g$ were also approximated by an intercept of linear extrapolation. The extracted $E_g$ values of ZrO$_2$ and IL were 6.20 to

| Type | Deposition method | $E_g$(ZrO$_2$) | $E_g$(IL) | $\Delta E_v$ | $\Delta E_c$ | Reference |
|------|------------------|----------------|------------|--------------|-------------|-----------|
| (i)  | Evaporation      | 5.50           | 8.60       | 1.00         | 1.90        | [10]      |
|      | Sputtering       | 5.40           | 7.60       | 1.00         | 1.20        | [11]      |
|      | Atomic layer chemical vapor deposition | 5.80 | 7.60 | 1.15 | 1.05 | [12] |
|      | Electron beam deposition of Zr + oxidation in O$_2$ | 5.80 | 9.00 | 1.80 | 1.40 | [13] |
| (ii) | PLD              | 5.70           | 4.70       | 3.30 to 3.50 | 1.50        | [14]      |
| (iii)| Sputtering of Zr + oxidation and nitridation in N$_2$O | 6.20 to 6.50 | 8.20 to 8.80 | 4.75 | 3.40 | This work |

Type (i) defines alignment of ZrO$_2$ bandgap in between the IL bandgap and type (ii) defines alignment of ZrO$_2$ conduction band outside the IL bandgap. Type (iii) defines ZrO$_2$ valence band outside the IL bandgap which is obtained from this work.

Figure 1 Band alignment of ZrO$_2$/IL/Si system. $E_g$(ZrO$_2$) = bandgap of ZrO$_2$, $E_g$(IL) = bandgap of IL, $E_g$(Si) = bandgap of Si, $\Delta E_v$(ZrO$_2$/Si) = valence band offsets of ZrO$_2$ to Si, $\Delta E_c$(ZrO$_2$/IL) = conduction band offset of ZrO$_2$ to IL.

Figure 2 XPS valence band spectra of ZrO$_2$ and IL for all investigated samples. (a) XPS valence band spectra of ZrO$_2$ and IL for all investigated samples. (b) XPS O 1s plasmon loss spectra of ZrO$_2$ and IL for 15-min sample.
6.50 eV and 8.20 to 8.80 eV, respectively, with tolerance of 0.05 eV, dependent on the oxidation time (Figure 3). Ultimately, conduction band offset of ZrO₂ to IL, \( \Delta E_c(ZrO_2/IL) \), for the ZrO₂/IL/Si system can be eventually derived [17]:

\[
\Delta E_c(ZrO_2/IL) = E_g(IL) - \Delta E_c(IL/Si) + \Delta E_v(ZrO_2/IL) - E_g(ZrO_2),
\]

where, \( E_g(ZrO_2) \) and \( E_g(IL) \) are the bandgaps of ZrO₂ and IL, respectively. \( \Delta E_v(ZrO_2/Si) \) and \( \Delta E_v(IL/Si) \) are the valence band offsets of ZrO₂ and IL, respectively, with respect to Si substrate. The calculated values of \( E_g(ZrO_2) \), \( E_g(IL) \), \( \Delta E_c(ZrO_2/Si) \), \( \Delta E_c(IL/Si) \), and \( \Delta E_c(ZrO_2/IL) \) are presented in Figure 3. The highest value of \( \Delta E_c(ZrO_2/IL) \), i.e., 3.40 eV, was attained by sample oxidized/nitrided for 15 min (Figure 3) when compared to other samples. A schematic of the band alignment of the ZrO₂/IL/Si system is illustrated in Figure 1. The \( E_g \) value of Si substrate is obtained from literature [3,18]. It is found that values of \( E_g(ZrO_2) \), \( E_g(IL) \), \( \Delta E_c \), and \( \Delta E_v \) obtained in this study are higher than the values reported in literatures (Table 1).

Figure 4 shows typical leakage current density electric field (J-E) characteristics of the investigated samples. The J-E plot was transformed from current-voltage (I-V) measurement. The \( E \) value was estimated by first determining the flatband voltage (\( V_{FB} \)) shift from the applied gate voltage (\( V_g \)) and then dividing the total thicknesses of ZrO₂ and IL (\( t_{ox} \)) measured by energy filtered transmission electron microscopy (EFTEM) (images are not shown here). The acquired \( J \) value in this study is \( \sim 10^{-8} \) A/cm² at \( E = 2.0 \) MV/cm, which is lower than the other studies [4,5,14].

A two-step oxide breakdown (BK-1 and BK-2) is being recorded in the J-E plot for all investigated samples (inset of Figure 4). The existence of interfacial and ZrO₂ layers in the sample is the main cause of this two-step breakdown [19]. The breakdowns can be explained as follows. One of the layers may experience an electrical breakdown at a lower field, which is labeled as BK-1. Subsequently, another layer would block the carriers. Due to the increment of the electric field, the concentration of the carrier increases until the layer is electrically broken down at a higher electric field at BK-2. The instantaneous increment of leakage current density at BK-1 is relatively small when compared with others, and it is defined as soft breakdown. The magnitude of BK-1 increases gradually as the oxidation time is increased (inset of Figure 4). In contrast, the instantaneous increment of current density at BK-2 is large, and this is considered as hard breakdown. The highest dielectric breakdown field, which is referred to as hard breakdown, is attained by sample oxidized/nitride for 15 min (13.6 MV/cm at \( 10^{-6} \) A/cm²). The lowest one is recorded by sample oxidized/nitride for 10 min (4.8 MV/cm at \( 10^{-6} \) A/cm²). In comparison, dielectric breakdown field recorded in this work is higher than the previous reported works [4,5,14].

**Conclusions**

In summary, the band alignment of ZrO₂/IL/Si structure produced by simultaneous oxidation and nitridation of sputtered Zr thin film on Si in N₂O has been established. Via this method, higher \( \Delta E_c \) and \( \Delta E_v \) values have been attained. Hence, a higher electrical breakdown field at low leakage current density has been achieved.

**Methods**

The n-type Si(100) substrate with a resistivity of 1 to 10 Ω cm was used in this study. After undergoing a
standard wafers cleaning process, a 5-nm thick Zr film was sputtered on the cleaned Si substrates by an RF sputtering system. Following that, samples were loaded into a horizontal tube furnace and were heated up from room temperature to 700°C in an Ar flow ambient, and the heating rate was fixed at 10°C/min. Once the set temperature was achieved, N2O gas was introduced with a flow rate of 150 mL/min for a set of durations (5, 10, 15, and 20 min). After the furnace was cooled down to room temperature in an Ar ambient, the samples were withdrawn from the furnace. To experimentally determine band alignment of the dielectric/semiconductor structure, XPS measurements were conducted using Kratos Axis Ultra DLD (Kratos Analytical, Chestnut Ridge, NY, USA). with a monochromatic Al-Kα X-ray source (hv = 1,486.69 eV) performed at the Research Center for Surface and Materials Science, The Auckland University, New Zealand. The spectra of survey or wide scan (binding energy of -5 to 25 eV) were collected at a take off angle of 0° with respect to surface normal, with low pass energy of 20 eV and small step size of 0.1 eV. Due to the onset of single particle excitation and band-to-band transition, the energy loss spectrum of O 1s photoelectron provides further insight on the bandgaps of ZrO2 and IL [20]. Subsequently, a detail scan of O 1s was carried out using the same pass energy and step size of 1.0 eV. Ar ion gun (5 keV) was employed to etch the sample in order to perform chemical depth profiling (results are not shown here), in order for the boundary of ZrO2 and IL to be identified. A Shirley background function, which is proportional to the integrated photoelectron peak area, was subtracted from all of the XPS spectra to correct for the inelastic photoelectron scattering effect [21]. Band alignment extraction was based on Kraut method [15,16]. As to characterize the leakage characteristic and electrical breakdown field of the film, MOS capacitor test structure was formed by thermally evaporated a 100-nm thick aluminum (Al) film, acting as a gate electrode, on top of the films. The area of a capacitor was photolithographically defined at 9 × 10⁻⁴ cm². In order to obtain an Ohmic back contact, a 100-nm thick Al film was thermally evaporated on the backside of the Si substrate after removal of native oxide. I-V measurements were performed by a computer-controlled Agilent HP4155-6C semiconductor parameter analyzer (Agilent Technologies, Santa Clara, CA, USA).

Acknowledgements
The authors would like to acknowledge the support provided by USM fellowship, USM-PRGS (8032051), and The Academy of Sciences for the Developing World (TWAS) through the TWAS-COMSTECH research grant (09-105 RG/ENG/AS_C) during the study.

Authors’ contributions
YHW has been involved in the experimental design, data acquisition, data interpretation and analysis, and drafting and revision of the manuscript. KYC has been involved in revising the manuscript critically for important intellectual content and has given final approval to the version to be submitted for publication.

Competing interests
The authors declare that they have no competing interests.

Received: 11 April 2011 Accepted: 10 August 2011
Published: 10 August 2011

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doi:10.1103/1556-276X-6-489

Cite this article as: Wong and Cheong: Band alignment and enhanced breakdown field of simultaneously oxidized and nitrided Zr film on Si. Nanoscale Research Letters 2011 6:489.