Reliability of Al₂O₃-doped ZrO₂ high-k dielectrics in three-dimensional stacked metal-insulator-metal capacitors

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Received 24 June 2010; accepted 27 October 2010; published online 20 December 2010

In this paper, we report reliability evaluation results for nanomixed amorphous ZrAl₂O₅ and symmetrically or asymmetrically stacked ZrO₂/Al₂O₃/ZrO₂ dielectric thin films grown by atomic layer deposition method in cylindrical metal-insulator-metal capacitor structure. Clear distinctions between their I-V asymmetry and breakdown behavior were correlated with the differences in compositional modification of bottom interface, defect density, and conduction mechanism of the film stacks. The thermochemical molecular bond breaking model was found to explain the dielectric constant dependent breakdown field strength and electric field acceleration parameter of lifetime very well. © 2010 American Institute of Physics. [doi:10.1063/1.3520666]

I. INTRODUCTION

In recent generation of gigabit scale dynamic random access memory (DRAM) technology, the storage capacitor adopts the three-dimensional metal-insulator-metal (MIM) cylindrical architecture. High-permittivity (high-k) dielectrics have been introduced to replace SiO₂ or SiON as insulator material, and TiN is used as the mainstream electrode material. The atomic-layer-deposition (ALD) is a method of choice to ensure a good uniformity and low defectivity of the thin films.¹,²

Among various high-k dielectrics being intensively studied so far, ZrO₂ and its corresponding Al or Si doped films are of the most industrial interest for current and near future generation technology nodes.³–⁵ The dielectric constant of ZrO₂ thin films depends strongly on their phase and crystallinity, which can be regulated via control of the growth temperature and film thickness. The highest k value of ~46 has been predicted for pure ZrO₂ crystallized to tetragonal phase.⁶ However, the high negative biased leakage current makes it inapplicable.³ The leakage can be significantly suppressed by interlaying Al₂O₃ or SiO₂ into ZrO₂ to interrupt the grain boundary channels, which were found to be the leakage paths of crystalline ZrO₂.⁷ However, the addition of interlayer will sacrifice the effective k value due to the low permittivity of the dopants. Recently, it was reported that heavily doped, amorphous ZrAl₂O₅ (x = 30 at. %) could also meet the leakage current density criterion of 1 fA/cell (at ±1 V) for DRAM applications.³

For a successful introduction of new type of dielectrics into storage node capacitor, besides the stringent requirements of performance (i.e., permittivity and leakage), manufacturability, and production cost, the issue of long-term reliability plays a crucial role in all phases of product development. One strict reliability specification is that the time dependent dielectric breakdown (TDDB) behavior must satisfy the ten year lifetime criteria at accumulated fail rate of 10 ppm. Therefore, the main tasks of dielectric reliability assessment are to (1) perform the accelerated lifetime testing; (2) identify an extrapolation model which can be used for lifetime prediction at operation conditions appropriately; (3) understand the causes for reliability degradation; (4) and finally feedback the results to material processing to improve the quality of films.

In this work, we report a comparison study of the TDDB behavior for nanomixed, amorphous ZrAl₂O₅ thin film and stack systems of ZrO₂/Al₂O₃/ZrO₂ (ZA), where a thin Al₂O₃ monolayer is inserted symmetrically or asymmetrically between two ZrO₂ layers. The results will be helpful to understand the correlation between the conduction mechanisms and breakdown behavior of ZrO₂-based high-k dielectrics.

II. EXPERIMENTAL PROCEDURES

The TiN–ZrAl₂O₅–TiN MIM capacitors with cylindrical structure were fabricated using 65nm DRAM technology. The TiN electrodes were formed by pulsed chemical vapor deposition using TiCl₄ and NH₃ as reactants. The dielectrics of ZrO₂ and Al₂O₃ were deposited, respectively, from Zr(CH₃C₂H₅)₄-ozone (O₃) and Al(CH₃)₃-ozone (O₃) at 275 °C by ALD. The deposition temperature of 450 °C for the TiN top electrode is the highest thermal budget for the ZrAl₂O₅ thin films, which contain the main impurity of about 3% carbon.

Three different film stacks were evaluated in this work. The first one is denoted by amorphous ZrAl₂O₅, in which about 30 at. % Al₂O₃ was homogeneously doped into ZrO₂ with a total thickness of ~6 nm. A k value of ~24 was
obtained from capacitance measurements, indicating the amorphous nature of the film. The second one is denoted by crystalline ZAZ, in which ZrO$_2$ was symmetrically separated by insertion of a monolayer of Al$_2$O$_3$ to form 5.2 nm ZrO$_2$/0.35 nm Al$_2$O$_3$/5.2 nm ZrO$_2$ sandwich structure. The measured $k$ value of about 40 indicates both upper and bottom ZrO$_2$ layers have been crystallized. In the third sample, asymmetric ZAZ, a ~0.35 nm thick Al$_2$O$_3$ layer was inserted between ~5.5 nm bottom ZrO$_2$ layer and ~2.2 nm thick upper ZrO$_2$ layer, forming the crystalline ZrO$_2$/amorphous Al$_2$O$_3$/amorphous ZrO$_2$ laminate structure. The $k$ value of this film stack is about 35.

Electrical characterization was performed at different temperatures. The time-to-breakdown ($t_{BD}$) and breakdown voltage ($V_{BD}$) were measured using the conventional constant voltage stress (CVS) procedure and a voltage ramp stress (VRS) with additional monitor current measurement at a fixed low voltage. In particular, the long-term ($t_{BD} > 10^4$ s) CVS measurements were carried out using in-house developed testing setup, which can simultaneously stress 16 capacitors at one touch-down of the needle card.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the current-voltage (I-V) characteristics obtained from VRS measurements at 125 °C, noting that all three film stacks satisfy the leakage criteria of 1 fA/cell (at ±1.0 V) for DRAM applications. It is of practical interest to compare the evolution of their monitor current recorded at a fixed low voltage and correlate it to the microstructural features of the films. Amorphous ZrAl$_2$O$_5$ first shows a rather flat monitor current, indicating quite low density of bulk defects to trap electrons. At high stress voltages, the monitor current exhibits a clear increase especially in negative bias direction, followed by a hard breakdown. Similar to the observation for HiSiO films, such a current increase without breakdown can be explained by Coulomb barrier lowering effect. Recent work from Weinreich et al. revealed a thin interfacial layer growth between amorphous or crystalline ZrO$_2$ and the bottom TiN electrode. Due to the use of O$_2$ oxidant during the ALD process of ZrO$_2$, the TiN is oxidized to form TiO$_2$N$_x$ and even TiO$_2$. The amount of TiO$_2$ was found to increase significantly after crystallization of ZrO$_2$. Formation of ZrO$_2$N$_x$ compound was also identified, because TiN removed oxygen from ZrO$_2$ and simultaneously released nitrogen. The pronounced barrier lowering effect seen for amorphous ZrAl$_2$O$_5$ at negative bias should be most likely attributed to the incorporation of N into ZrO$_2$, which results in more O vacancies at the bottom interface. Trapping of positively charged vacancies into ZrO$_2$ bulk will effectively enhance the electric field near the cathode and therefore cause an increase in tunneling current. No significant oxidation of TiN and incorporation of N into ZrO$_2$ have been detected between ZrO$_2$ and top TiN electrode. Thus, a weak barrier lowering effect seen for positive bias appears to be due to less oxygen vacancies existing at the upper interface.

Crystalline ZAZ shows apparent decrease in monitor current before breakdown at both polarities. This can be explained by the existence of high defect density due to the formation of grain boundaries and resultant large amount of electron trapping in the material. For asymmetric ZAZ, only the thicker bottom ZrO$_2$ layer has been crystallized. In contrast to the symmetrically crystallized ZAZ films, the fact of less grain boundaries causes relatively weaker electron trapping effect especially for positive bias. It should be kept in mind that higher dielectric constant of the crystalline bottom ZrO$_2$ layer results in lower internal electric field drop across it. Similar to the discussion for amorphous samples, the barrier lowering effect seen at negative polarity can be explained by compositional modifications at bottom interface.

To compare their polarity asymmetry, the leakage currents of three film stacks were plotted as a function of average electric field across the dielectric (average field = stress voltage divided by the physical thickness of high-$k$) in Fig. 1(b). The amorphous ZrAl$_2$O$_5$ exhibits higher leakage for positive biasing on top electrode, i.e., electron injection from bottom to top. In contrast the crystalline and asymmetric ZAZ stacks show higher leakage at negative polarity. Crystallization of the ZrO$_2$ layer causes the leakage to increase slightly at negative polarity, however, to decrease aggressively at positive polarity. A similar effect of crystallization on the polarity asymmetry of leakage has also been observed in the work of Weinreich et al. It is worthy to note the breakdown field strengths ($E_{bd}$) of amorphous ZrAl$_2$O$_5$ ($E_{bd} = 5.5$ MV/cm) and crystalline ZAZ ($E_{bd} = 3.6$ or ~3.7 MV/cm) are quite close to the thermochemical model predictions $^{11}$ for ZrO$_2$ in cubic phase ($E_{bd} = 5.7$ MV/cm) and tetragonal phases ($E_{bd} = 3.3$ MV/cm), respectively. In this model proposed by McPherson et al., the breakdown strength of material is predicted to show an approximate ($k$)$^{-12}$ dependence. According to Clausius-
Mossotti equation $E_{pd}=(2+k)E_{ox}^{1/3}$, larger dielectric constant results in higher local electric-field $E_{loc}$ that distorts and weakens the molecular bond. The $E_{pd}$ versus $(k)^{-1/2}$ plot given in Fig. 2 shows the $\text{Al}_2\text{O}_3$-doped $\text{ZrO}_2$ thin films investigated in this work follow nicely such a relationship.

To further understand their conduction mechanisms, I-V measurements were performed for three film stacks at temperatures from 25 up to 175 °C. Figure 3 shows the Arrhenius plot of leakage current measured at different stress voltages.

For amorphous $\text{ZrAl}_2\text{O}_4$, measured at temperatures below 85 °C, defect levels of 0.45 eV and 0.6 eV with respect to the conduction band in the dielectric were extracted at negative and positive polarities, respectively. Such shallow trap depths should be related to high carbon contamination content in the material. At higher temperatures, leakage current at positive bias is dominated by the electrons activated from deeper defects at 1.05 eV below conduction band edge. However, the leakage does not obey PF conduction under negative bias. In this case, trap-assistant tunneling might be the dominant transport mechanism. As discussed for the barrier lowering effects of amorphous $\text{ZrAl}_2\text{O}_4$, large amount of oxygen vacancies exist at bottom interface. When subjected to negative bias at high temperatures, these O vacancies may be easily trapped into the oxide bulk. An increase in concentration of traps makes the TAT process possible. The polarity asymmetry of I-V curve should be attributed to the differences in trap level, conduction mechanism, and especially defect density at bottom and upper interfaces.

The crystalline $\text{ZAZ}$ films obey exclusively the PF conduction. Defect level of 1.2 eV is obtained for negative polarity. Under positive bias, trap levels of 0.9 eV and 1.4 eV are extracted at low and high measurement temperatures, respectively. Due to evolving of grain boundaries, the TAT mechanism, which depends strongly on trap density, may also exist but hide under the dominant PF emission.

For asymmetric $\text{ZAZ}$ at both polarities, deep trap level of ~1.3 eV is obtained at temperatures above 85 °C, which is attributed to bulk defects most likely caused by oxygen vacancies. When the electron injection is from top amorphous $\text{ZrO}_2$ layer side (negative bias), electron emission from shallow trap level of 0.6 eV becomes dominant at low temperatures, which is consistent with the observation for amorphous $\text{ZrAl}_2\text{O}_4$. For injection from the crystalline $\text{ZrO}_2$ side evolving grain boundaries, the TAT conduction dominates at low temperatures which is also in agreement with the existence of higher trap density.

The I-V asymmetry of $\text{ZAZ}$ film stacks should be mainly attributed to the formation of $\text{TiO}_2$ and diffusion of nitrogen into the $\text{ZrO}_2$ layer at the bottom interface. Due to lower band gap and offset of $\text{TiO}_2$ compared to $\text{ZrO}_2$, a band offset lowering is formed between the dielectric and bottom TIN electrode. The resultant internal field favors electron tunneling under negative bias.

Figure 4 shows typical stress and monitoring current traces during CVS. The aforementioned discussion of conduction mechanisms is helpful for understanding the transient current features. For amorphous $\text{ZrAl}_2\text{O}_4$ at negative bias.
different stress voltages. In Fig. 5, the logarithm of electric field.

dependence of the lifetime in the accessed stress range follows an exponential law, 

due to the barrier lowering effect; while positive bias causes almost a direct hard breakdown without transition phase. At both polarities, crystalline ZAZ shows a decrease in current at first due to electron trapping. After that, stress induced leakage current (SILC) can be seen clearly before the final hard breakdown. The noisy current increase is thought to correlate to repeated process of electron trapping/detrapping and local creation of additional defects. Asymmetric ZAZ exhibits the features of barrier lowering and SILC under negative and positive biases, respectively. The observation of SILC for the ZAZ film stacks is correlated with defects with an energy level deeper than 1.2 eV. This is consistent with the study of degradation mechanism for the metal/high-k gate stacks by Bersuker et al. They identified that the SILC of HfO$_2$ thin films was attributed to deep traps at 1.1–1.6 eV.

Characteristic lifetime parameter $t_{63}$ (breakdown time at 63.2% failures) is extracted from CVS measurements at different stress voltages. In Fig. 5, the logarithm of $t_{63}$ is plotted as a function of average electric field over the dielectrics. For crystalline and asymmetric ZAZ stacks, the electric field dependence of the lifetime in the accessed stress range follows an exponential law,

$$t_{BD} = t_0 e^{-nE},$$

where $E_0$ is the external field across the dielectric, $n$ is the dipole moment, and $k_B=8.63 \times 10^{-5}$ eV is the Boltzmann constant. This equation predicts that the field-acceleration parameter $\gamma$ should increase with increasing dielectric constant. A summary of electrical properties of three film stacks is given in Table I, in which the field-acceleration parameters of amorphous ZrAl$_2$O$_x$ were obtained by fitting its TDDB data to the linear-E model. We can see clearly a higher dielectric constant results in a larger $\gamma$ value, supporting that the TDDB behavior of ZrO$_2$-based high-$k$ dielectrics can be described well by the thermochemical model at least in a certain voltage range.

It is worthy to note that, for both symmetric and asymmetric ZrO$_2$–Al$_2$O$_3$–ZrO$_2$ film stacks, positive bias on top electrode gives rise to more aggressive voltage acceleration (i.e., larger $\gamma$ parameters) than negative bias. This might be attributed to higher crystallinity of the bottom ZrO$_2$ layer and resultant relatively higher $k$ value of it. For amorphous ZrAl$_2$O$_x$, almost identical $t_{63}$ values are obtained at positive and negative biases with the same stress magnitude.

IV. CONCLUSIONS

Electrical properties of Al$_2$O$_3$-doped ZrO$_2$ dielectric thin films in three-dimensional MIM capacitors were investigated by means of I-V and CVS measurements. Amorphous ZrAl$_2$O$_x$ exhibits higher leakage at positive gate bias and pronounced barrier-lowering effect at negative polarity. Both phenomena are due to incorporation of N into ZrO$_2$, which

$$t_{BD} = aE^{-n},$$

is found to best describe the field dependence of the breakdown time. Figure 5 also depicts the feature of dielectric constant dependent breakdown strength, i.e., at the same time to breakdown, the breakdown of thin film with larger $k$ value happens at lower electric field. The thermochemical model considers the dielectric breakdown is a field-driven thermal-chemical bond breakage process. The relationship between the field-acceleration parameter $\gamma$ (in unit of centimeter per megavolt) and the dielectric constant is given by,

$$\gamma = \frac{\partial \ln t_{BD}}{\partial E_{ext}} = \frac{(2 + k)\rho}{3k_B T},$$

where $E_{ext}$ is the external field across the dielectric, $\rho$ is the dipole moment, and $k_B=8.63 \times 10^{-5}$ eV is the Boltzmann constant. This equation predicts that the field-acceleration parameter $\gamma$ should increase with increasing dielectric constant. A summary of electrical properties of three film stacks is given in Table I, in which the field-acceleration parameters of amorphous ZrAl$_2$O$_x$ were obtained by fitting its TDDB data to the linear-E model. We can see clearly a higher dielectric constant results in a larger $\gamma$ value, supporting that the TDDB behavior of ZrO$_2$-based high-$k$ dielectrics can be described well by the thermochemical model at least in a certain voltage range.

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results in more O vacancies at the bottom interface. For crystalline films, higher leakage current at negative polarity is due to formation of TiO₂ at the bottom interface and resultant band offset asymmetry; the observation of electron trapping and SILC are attributed to grain-boundary related high defect density. In the accessed CVS measurement time frame between 10⁻¹ and 10⁶ s, the power-law model is appropriate for lifetime extrapolation of amorphous ZrAl₂O₇. Since both symmetric and asymmetric ZrO₂–Al₂O₃–ZrO₂ stacks follow the conservative linear-E model and show more aggressive field-acceleration of lifetime for positive bias on TE, it may be concluded that the reliability of sandwiched ZAZ stack is dominated by the crystalline ZrO₂ layer. As predicted by the thermochemical model, larger dielectric constant results in lower breakdown electric field but higher field-acceleration parameter of lifetime. All three films satisfy the leakage criteria of 1 fA/cell (at ±1.0 V) and the reliability specification of ten year lifetime for DRAM storage capacitor applications.

ACKNOWLEDGMENTS

This work was financially supported by the Federal Ministry of Education and Research of the Federal Republic of Germany (Project: MEGAEP, Grant No. 13N9264A). The authors are grateful to Qimonda Dresden GmbH & Co. OHG I.N. for processing and providing of wafers.