Time dependent dielectric breakdown of amorphous $ZrAl_xO_y$ high-*k* dielectric used in dynamic random access memory metal-insulator-metal capacitor

Dayu Zhou,[1,a),b)] U. Schroeder,[1,a),c)] G. Jegert,[2] M. Kerber,[3] S. Uppal,[1] R Agaiby,[1] M. Reinicke,[1] J. Heitmann,[1] and L. Oberbeck[1]
[1]*Qimonda Dresden GmbH & Co. OHG, Koenigsbruecker Strasse 180, 01099 Dresden, Germany*
[2]*Qimonda AG, Am Campeon 1-12, 85579 Neubiberg, Germany*
[3]*Infineon Technologies AG, Otto-Hahn-Ring 6, 81739 Munich, Germany*

(Received 9 April 2009; accepted 11 July 2009; published online 26 August 2009)

Reliability is of serious concern for high-*k* dielectrics used in advanced memory applications. In this study, the time dependent dielectric breakdown behavior is investigated for metal-insulator-metal capacitors with amorphous $ZrAl_xO_y$ thin films as insulator and TiN as electrodes. Constant voltage stress measurements over seven orders of magnitude in time show that the power-law model is appropriate for lifetime extrapolation. The voltage acceleration parameter increases with decreasing temperature, and the thermal activation energy, E_a, increases with decreasing stress voltage, both translating to a gain in lifetime under product operation conditions. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3204001]

I. INTRODUCTION

Due to aggressive scaling of the size of dynamic random access memory (DRAM) cells for better performance and higher density, it is mandatory to use high-*k* dielectrics in metal-insulator-metal (MIM) storage capacitors to meet the basic functional requirements, such as leakage criterion and capacitance.[1] In contrast to Ta_2O_5 and HfO_2, ZrO_2-based materials exhibit better thermodynamical stability and therefore have attracted great research efforts in recent years.[2–8] For the sake of achieving highest dielectric constant, all these studies were intended for crystalline ZrO_2 in the tetragonal phase, which requires a certain thermal budget and thickness of the thin film. A highest *k* value of ~40 can be reached in pure crystalline ZrO_2. However, the high leakage current makes it inapplicable.[4,5] The leakage can be significantly suppressed by adding Al_2O_3 or SiO_2 as insulating layers into ZrO_2 to form so-called ZAZ or ZSZ stacks.[3,5–8] The addition of interlayer will, however, sacrifice the effective *k* value due to the low permittivity of the dopants.

Besides the basic requirements of proper functionality, reliability is always of serious concern since the first introduction of high-*k* dielectrics. One strict reliability specification is that the TDDB (time dependent dielectric breakdown) behavior must satisfy the ten-year lifetime criteria at accumulated fail rate of 10 ppm. Therefore, one of the main tasks of dielectric reliability assessment is to identify an extrapolation model using the accelerated lifetime testing, which can be used for lifetime prediction at operation conditions appropriately.

For crystalline $ZrO_2/SiO_2/ZrO_2$ (ZSZ) thin films with thicknesses of 8 and 10 nm,[7] long-term measurements up to 10^5 s demonstrate the voltage dependence of the lifetime follows an exponential law,

$$t_{BD} = t_0 e^{-\gamma V}, \quad (1)$$

which is also called linear-*E* model conventionally due to the yielding of a straight line in the semilog plot of t_{BD} versus voltage. Recently, Seo *et al.*[8] reported their extreme long-term (up to 10^7 s) test results for asymmetric $ZrO_2/Al_2O_3/ZrO_2$ (ZAZ, 8 nm/0.4 nm/4 nm) films. The progressive power law model,

$$t_{BD} = aV^{-n}, \quad (2)$$

was found to best describe the voltage dependence of the breakdown time. It was found in both works that positive bias on top electrode (TE) gave rise to more aggressive voltage acceleration (i.e., larger γ or n parameters) than negative bias. Such a polarity dependent voltage acceleration is consistent with the observation of asymmetric *I-V* characteristic, which has been attributed to different properties of the two dielectric/metal interfaces.

In this work, we report a detailed investigation of the TDDB behavior for amorphous $ZrAl_xO_y$ thin films. The results will be helpful to understand the conduction and breakdown mechanisms of ZrO_2-based high-*k* dielectrics.

II. EXPERIMENTAL PROCEDURES

MIM capacitors with TiN top and bottom electrodes (BEs) and $ZrAl_xO_y$ (ZAO) dielectrics were fabricated on patterned hardware. The TiN electrodes were formed by chemical vapor deposition using $TiCl_4$ and NH_3 as reactants. The ZAO films (<10 nm thick) were grown by atomic layer deposition (ALD) at 275 °C with $Zr[N(CH_3)C_2H_5]_4$ and $Al(CH_3)_3$ as precursors, and ozone (O_3) used as an oxidant. Al_2O_3 (<30 at. %) was doped into ZrO_2 as interlayers to prevent crystallization and suppress the leakage. The deposition temperature of 450 °C for the TiN TE is the highest thermal budget for the ZAO thin films, which contain the

[a)]Authors to whom correspondence should be addressed.
[b)]Electronic mail: dayu_zhou1970@yahoo.com.
[c)]Electronic mail: uwe.schroeder@namlab.com.

 © 2009 American Institute of Physics

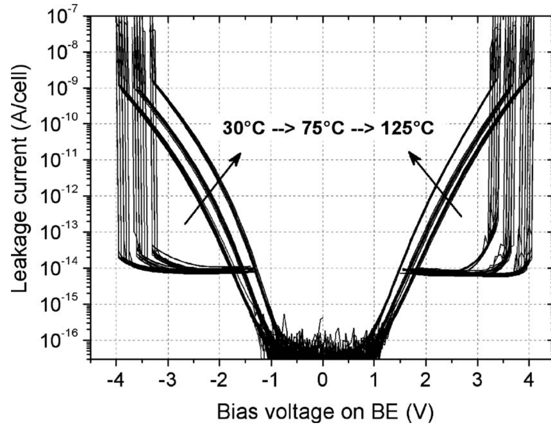

FIG. 1. Temperature dependent *I-V* characteristics with monitor current measured at a fixed low voltage.

main impurity of about 3% carbon. A k value of around 24 was obtained from capacitance measurements, indicating the amorphous nature of the thin films.

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 touchdown of the needle card. For all measurements, the TE was grounded; positive and negative biases were applied on BE.

III. RESULTS AND DISCUSSION

Figure 1 shows the *I-V* characteristics obtained from VRS measurements at 30, 75, and 125 °C. The leakage current and breakdown voltages are rather symmetric, depending only slightly on the polarity of the stress voltage. An increase in temperature results in an increase in leakage current and a corresponding decrease in breakdown voltage. Even at 125 °C, the amorphous ZAO films still satisfy the leakage criteria of 1 fA/cell (at ± 1.0 V) for DRAM applications. For positive bias on BE, the monitor current decreases slightly at low stress voltages, indicating the existence of a small amount of electron trapping. Particularly at 125 °C, a smooth increase in monitor current can be seen clearly before the hard breakdown. Similar to the observation for HfSiO films,[9] this can be explained by Coulomb barrier lowering due to electron detrapping or positive charges trapping into dielectric. Since the detrapping/trapping is a thermally activated process, the barrier lowering effect becomes weaker with a decrease in temperature. In the case of negative stressing on BE, the monitor current exhibits only a slight, temperature independent increase prior to hard breakdown.

Figure 2 shows typical stress and monitoring current traces during long-term CVS, at 125 °C. The measurements are over seven orders of magnitude in time, i.e., from 10^{-1} s up to 10^6 s.

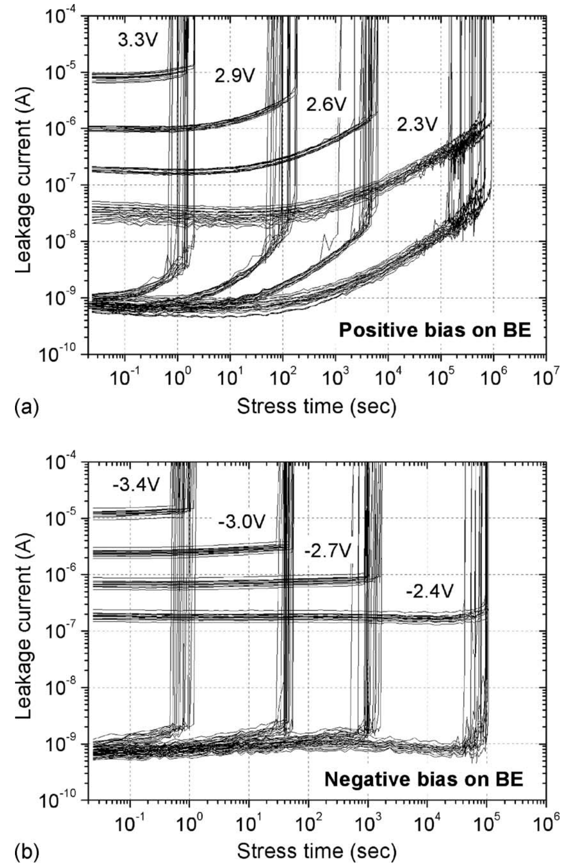

FIG. 2. Leakage current transients during long-term CVS measurements at 125 °C for selected stress voltages. The monitor voltages are 1.8 and −1.6 V, respectively, for (a) positive bias and (b) negative bias on BE.

Similar to barrier lowering effect demonstrated in the *I-V* curve, the monitor current exhibits a smooth increase in the case of positive bias on BE; and the final current level before the onset of hard breakdown becomes even higher with decreasing stress voltage. In contrast, only a slight increase in monitor current can be observed for negative bias on BE. The polarity dependent current characteristics can be attributed to the differences in roughness and chemical composition between the bottom TiN/ZrO_2 and top ZrO_2/TiN interfaces. Gaillard *et al.*[10] found that, for planar MIM capacitors, the bottom interface was 2× rougher compared with the top interface. Recent work from Weinreich *et al.*[3] revealed oxidation of the bottom TiN electrode during the ALD process of ZrO_2. The formation of TiO_2 with smaller band gap results in band offset lowering between ZrO_2 and TiN BE. As a consequence of differences in interface properties, it is easier to generate defects when electrons are injected from TE and loose their energy at the rougher and compositionally modified bottom TiN/ZrO_2 interface. Defect accumulation in dielectric near the cathode provides a positive feedback to the electron tunneling process and therefore results in an increase in monitor current.

Figure 3 demonstrates the Weibull distributions of the time to hard breakdown (t_{BD}) at different stress voltages. The average values of the shape parameter (Weibull slope) are 2.74 and 2.84, respectively, for positive and negative biases on BE. Note that, even for measurements at low stress volt-

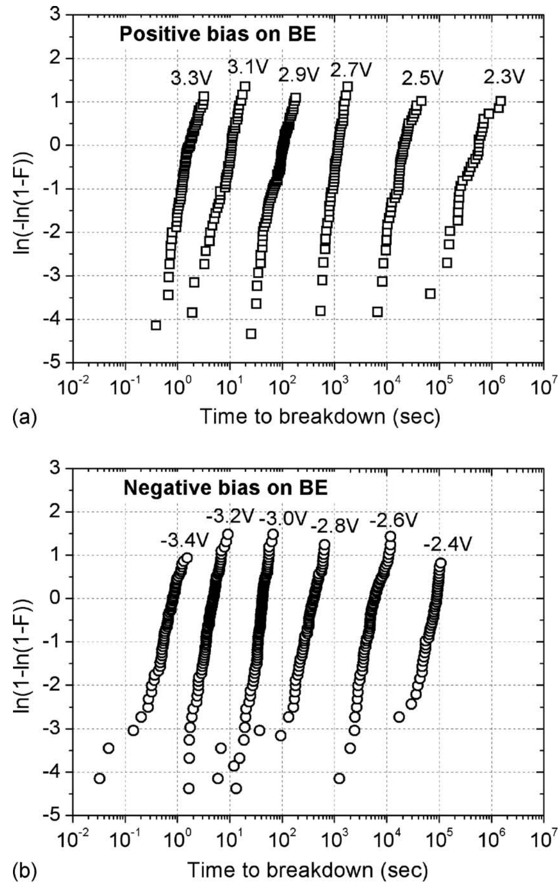

FIG. 3. Weibull distributions of the hard breakdown measured at 125 °C for (a) positive bias and (b) negative bias on BE.

ages (with $t_{BD} > 10^4$ s), each distribution still contains more than 30 points; and all the distributions at high voltages include more than 60 samples. Such a dense sampling ensures a high accuracy of the extracted characteristic parameter t_{63} (t_{BD} at 63.2% failures).

In Fig. 4, the logarithm of t_{63} is plotted as a function of bias voltage for both polarities. Note that almost identical t_{63} values are obtained at positive and negative biases with the

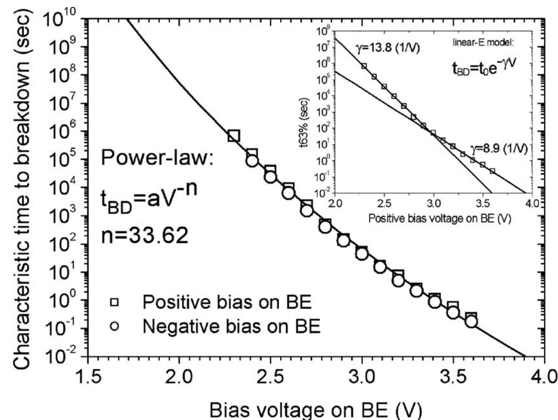

FIG. 4. Voltage acceleration results from long-term CVS measurements at 125 °C, showing an almost symmetric depending on the polarity of the bias voltage. The data can be fitted well using the power-law model. The inset figure shows the fitting to linear-*E* model in high and low voltage regions, respectively.

same stress magnitude. This independence of voltage acceleration on polarity indicates that there is no direct correlation between t_{BD} and the leakage current increase before breakdown. In other words, the defect generation, which causes leakage current increase, is not the main driving force for trigger of breakdown.

In the full measurement time frame from 10^{-1} up to 10^6 s, the data can be fitted very well using the power-law model. The fitting results in a voltage acceleration parameter of $n=33.62$. Such a small exponent has been reported for SiO_2 and SiON gate oxides with a thickness above 5 nm.[11]

Great efforts have been made to understand the physical mechanisms that result in a power-law dependence of the t_{BD} on stress voltage for SiO_2 and SiON dielectrics. Anode hydrogen release and anode hole injection are two most widely accepted explanations. In recent work of Nicollian *et al.*,[12] the former was identified as the primary mechanism for trap generation and breakdown. In contrast to the solid theoretical and experimental investigations for SiO_2 and SiON gate oxides, physical details for the breakdown mechanism of high-*k* dielectrics remain unclear. Controversies, such as linear-*E* and power-law models observed for both crystalline ZSZ and ZAZ stacks, make the debate fairly complex.[7,8] Nevertheless for the amorphous ZAO thin films studied in this work, the doubtless evidence for power law indicates the degradation should be mainly caused by a fluence-driven defect generation process. Electron flowing across the dielectric leads to a continuous buildup of defects. Eventually the damage reaches a limit, and breakdown is triggered at the weakest point.

The inset in Fig. 4 shows that the conventional linear-*E* model can be used only for regional approximation of the voltage acceleration behavior. A γ of 8.9 (1/V) can be obtained in the high voltage region, and it increases drastically to 13.8 (1/V) in the low voltage region. Using Eqs. (1) and (2), the voltage dependence of the acceleration factor (AF) can be derived:

$$\mathrm{AF} = \frac{-\partial \ln t_{BD}}{\partial V} = \gamma(V) = \frac{n}{V}. \quad (3)$$

It is worthy to notice in the inset that the linear-*E* model can sectionally represent the data very well in a quite wide voltage range. This is due to the fact that the power-law exponent n is rather small. Nevertheless for lifetime extrapolation at operation conditions, it should be kept in mind that the power law is the only model leading to prediction with a high degree of accuracy. In contrast, the most conservative linear-*E* model will significantly underestimate the lifetime.

Figure 5 demonstrates the voltage acceleration behavior measured at three different temperature levels. In the accessed voltage range, the measured data can be represented very well by the linear-*E* model. The acceleration parameter γ exhibits a clear temperature dependence, increasing with a decrease in temperature.

The linear-*E* model proposed by McPherson *et al.*[13,14] considers the dielectric breakdown as a field-driven thermal-chemical bond breakage process. The time to breakdown (t_{BD}) can be expressed quantitatively as

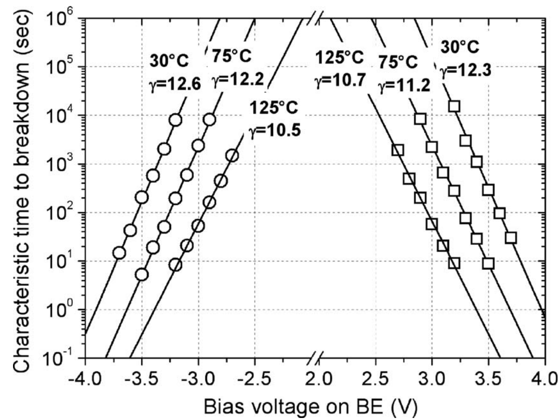

FIG. 5. Voltage acceleration measured at 30, 75, and 125 °C, showing an increase in acceleration parameter, γ (1/V), with decreasing temperature. Solid lines represent fitting to the linear-E model.

$$t_{BD} = A_0 \exp\left(\frac{\Delta H_0 - \rho E_{loc}}{K_B T}\right), \quad (4)$$

where A_0 is a pre-exponential constant, ΔH_0 represents the activation energy required for bond breakage, k_B=8.63 $\times 10^{-5}$ eV is the Boltzmann constant, and ρ is the dipole moment. The local electric filed E_{loc} is given by the Clausius–Mossotti equation: $E_{loc}=(2+k)E_{ext}/3$, where E_{ext} is the external field across the dielectric. Using Eq. (4), temperature dependence of the field acceleration parameter γ (in unit of cm/MV) shown in Fig. 5 can be theoretically predicted:

$$\gamma = -\frac{\partial \ln t_{BD}}{\partial E_{ext}} = \frac{(2+k)\rho}{3K_B T}. \quad (5)$$

The linear-E model explains the function of applied field by its interaction with the dipole moment, which lowers the activation energy required for bond breakage. The so-called apparent activation energy E_a is given by $E_a=\Delta H_0-\rho E_{loc}$, indicating a linear dependence of E_a on the applied field (voltage). Figure 6 shows stress voltage dependence of E_a obtained from aforementioned CVS measurements at different temperature levels. Linear relationship can be observed clearly for both polarities, supporting that the TDDB behavior of amorphous ZAO can be described well by the linear-E model at least in a certain voltage range.

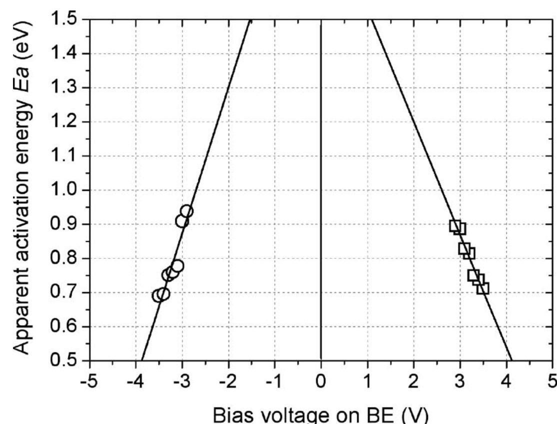

FIG. 6. Stress voltage dependence of the apparent activation energy (E_a) of TDDB lifetime, showing an increase in E_a with decreasing stress voltage.

The slope of linear fitting for E_a-versus-local field plot yields the dipole moment. ρ=2.7 eÅ and ρ=3.4 eÅ were obtained for positive and negative biases on BE, respectively. The values are close to 4.4 eÅ reported for tetragonal ZrO_2,[14] but much smaller than the data reported for HfAlO (11 eÅ).[15]

IV. CONCLUSIONS

I-V characteristics and long-term TDDB reliability measurements are presented for amorphous $ZrAl_xO_y$ (ZAO) thin films in MIM capacitor. The material generally exhibits good polarity symmetry with respect to leakage (stress) current, breakdown voltage, and time to breakdown. In the full measurement time frame from 10^{-1} up to 10^6 s, stress voltage dependence of time to breakdown follows the progressive power-law model. The conservative linear-E model can be used for regional approximation of the voltage acceleration behavior. The dependence of acceleration parameter on temperature and the dependence of activation energy on stress voltage can also be explained very well using the linear-E model. The results show that amorphous ZAO is a promising high-k material 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 No. 01M3171A). The authors are responsible for the content of the paper.

[1] See The International Technology Roadmap for Semiconductors, Semiconductor Industry Association; see also http://www.itrs.net/ for the most recent updates (2008).
[2] T. S. Böscke, S. Govindarajan, P. D. Kirsch, P. Y. Hung, C. Krug, B. H. Lee, J. Heitmann, U. Schröder, G. Pant, B. E. Gnade, and W. H. Krautschneider, Appl. Phys. Lett. **91**, 072902 (2007).
[3] W. Weinreich, R. Reiche, M. Lemberger, G. Jegert, J. Müller, L. Wilde, S. Teichert, J. Heitmann, E. Erben, L. Oberbeck, U. Schröder, A. J. Bauer, and H. Ryssel, Microelectron. Eng. **86**, 1826 (2009).
[4] J.-H. Kim, V. A. Ignatova, P. Kücher, J. Heitmann, L. Oberbeck, and U. Schröder, Thin Solid Films **516**, 8333 (2008).
[5] H.-J. Cho, Y.-D. Kim, D.-S. Park, E. Lee, C.-H. Park, J.-S. Jang, K.-B. Lee, H.-W. Kim, S.-J. Chae, Y.-J. Ki, I.-K. Han, and Y.-W. Song, Proceedings of the 36th European Solid-State Device Research Conference (ESSDERC, 2006), p. 146.
[6] D.-S. Kil, H.-S. Song, K.-J. Lee, K. Hong, J.-H. Kim, K.-S. Park, S.-J. Yeom, J.-S. Roh, N.-J. Kwak, H.-C. Sohn, J.-W. Kim, and S.-W. Park, Tech. Dig. VLSI Symp. **2006**, p. 38.
[7] R. Agaiby, P. Hofmann, D. Zhou, M. Kerber, J. Heitmann, U. Schroeder, E. Erben, and L. Oberbeck, IEEE Electron Device Lett. **30**, 340 (2009).
[8] J.-Y. Seo, J.-E. Seok, H.-J. Kim, H.-J. Kim, H.-S. Park, J.-E. Jeon, and W.-S. Lee, Proceedings of the 26th International Conference on Microelectronics (MIEL, 2008), p. 521.
[9] R. Duschl, M. Kerber, A. Avellan, S. Jakschik, U. Schroeder, and S. Kudelka, Microelectron. Reliab. **47**, 497 (2007).
[10] N. Gaillard, L. Pinzelli, M. Gros-Jean, and A. Bsiesy, Appl. Phys. Lett. **89**, 133506 (2006).
[11] T. Pompl and M. Roehner, Microelectron. Reliab. **45**, 1835 (2005).
[12] P. E. Nicollian, A. T. Krishnan, C. A. Chancellor, R. B. Khamankar, S. Chakravarthi, C. Bowen, and V. K. Reddy, Proceedings of International Reliability Physics Symposium, 2007, p. 197.
[13] J. W. McPherson and H. C. Mogul, J. Appl. Phys. **84**, 1513 (1998).
[14] J. McPherson, J.-Y. Kim, A. Shanware, and H. Mogul, Appl. Phys. Lett. **82**, 2121 (2003).
[15] K. Takeda, R. Yamada, T. Imai, T. Fujiwara, T. Hashimoto, and T. Ando, IEEE Trans. Electron Devices **55**, 1359 (2008).

Journal of Applied Physics is copyrighted by the American Institute of Physics (AIP). Redistribution of journal material is subject to the AIP online journal license and/or AIP copyright. For more information, see http://ojps.aip.org/japo/japcr/jsp