Solid State Phenomena
ISSN: 1662-9779, Vol. 359, pp 29-34
doi:10.4028/p-yZ4Fux
© 2024 The Author(s). Published by Trans Tech Publications Ltd, Switzerland.
Submitted: 2023-08-21
Revised: 2024-02-09
Accepted: 2024-02-24
Online: 2024-08-22

Improving HfO_2 Thick Films for SiC Power Devices by Si, Y and La Doping

Sandra Krause[1,a*], Thomas Mikolajick[1,b] and Uwe Schroeder[2 c]

[1]TU Dresden, 01062 Dresden, Germany

[2]NaMLab Noethnitzer Str. 64a, 01187 Dresden, Germany

[a]sandra.krause@mailbox.tu-dresden.de, [b]thomas.mikolajick@tu-dresden.de, [c]uwe.schroeder@namlab.com

Keywords: doped HfO_2, dielectric stack, high-k, crystallization behavior, breakdown field, leakage current, dielectric constant, grain size

Abstract. We investigated the electrical and structural effects of silicon (Si), yttrium (Y) and lanthanum (La) doping in 10-45 nm thick hafnium dioxide (HfO_2) films on silicon carbide (SiC) and Si substrates. We show that the introduction of Si dopants leads to a significant enhancement of the electric breakdown field and a reduction of the leakage current density by elevating the crystallization temperature. This effect becomes stronger with higher Si content. In contrast, Y and La doping does not raise T_C but increases the tetragonal and orthorhombic phase portion within the crystalline films and therefore enhances the dielectric constant k. Furthermore, we show that larger grains in crystalline films are associated with a higher leakage current density.

Introduction

Silicon carbide (SiC) offers distinct advantages over silicon (Si) due to its wider bandgap, enabling higher electric fields and higher temperatures in SiC devices. However, the conventional silicon dioxide (SiO_2) gate oxide limits the full exploitation of these benefits as it cannot withstand the high electric fields present in the dielectric of such a device [1]. Replacing SiO_2 (dielectric constant k = 3.9) by dielectrics with a higher k alters the electric field distribution in the device. The reduced electric field strength within the gate dielectric allows for higher applied voltages or further device downscaling [1]. Hafnium dioxide (HfO_2) is a promising alternative with a dielectric constant of 20-40 [2], depending on the crystalline phase content. Yet, it has low band offsets to the conduction and valence band of SiC (ΔE_C = 0.7 eV and ΔE_V = 1.7 eV) [3], leading to high leakage currents [3,4]. In recent years HfO_2 thin films have shown significant advantages over SiO_2 in low power devices [1]. Thus, it is reasonable to adapt the properties of HfO_2-based films for high power applications [5,6]. Current research has shown that introducing dopants into HfO_2 films can significantly enhance their electrical properties [2,7,8].

This study focuses on the electrical and structural properties of stacks of Si / Y / La-doped HfO_2 deposited on a thin thermally grown SiO_2 layer on SiC and Si substrates. The objective is to find a stack with a high dielectric constant k, high electric breakdown field (E_{BD}) and low leakage current density (J_{leak}).

Methods

The HfO_2-based films with a thickness ranging from 15 to 45 nm were deposited by plasma-enhanced atomic layer deposition (PE-ALD) at 300°C. Si doping was incorporated using specific ALD cycle ratios, resulting in a percentage of Si cations of 4% and 6% in the HfO_2 film. For Y doping, the cation percentage was 5% and 7%, and for La doping it was 9%. A sketch of the samples along with a TEM image of the pure HfO_2 film is presented in Fig. 1. The samples were annealed at ~500°C or ~1000°C for one minute in Argon ambient, and the layer thickness was determined by X-ray reflectometry (XRR) or transmission electron microscopy (TEM). The crystallographic phase was determined from the peak positions in Grazing-incidence X-ray diffraction measurements (GIXRD),

This article is an open access article under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0)

and the size of the crystal grains was estimated from the peak width using the Scherrer relation [9]. The dielectric constant k was calculated from the MOS capacitance in the accumulation regime. The obtained k value represents an "effective" k that accounts for the entire dielectric stack including SiO_2 and the HfO_2-based layer. The k value of the HfO_2-based layer was calculated using an equivalent circuit model consisting of two capacitors in series, the measured layer thicknesses, and the k value of SiO_2. The leakage current density J_{leak} at an applied electric field of 2 MV/cm was determined using current-voltage (IV) measurements. The electric breakdown field E_{BD} was defined at a current density of 10 mA/cm^2.

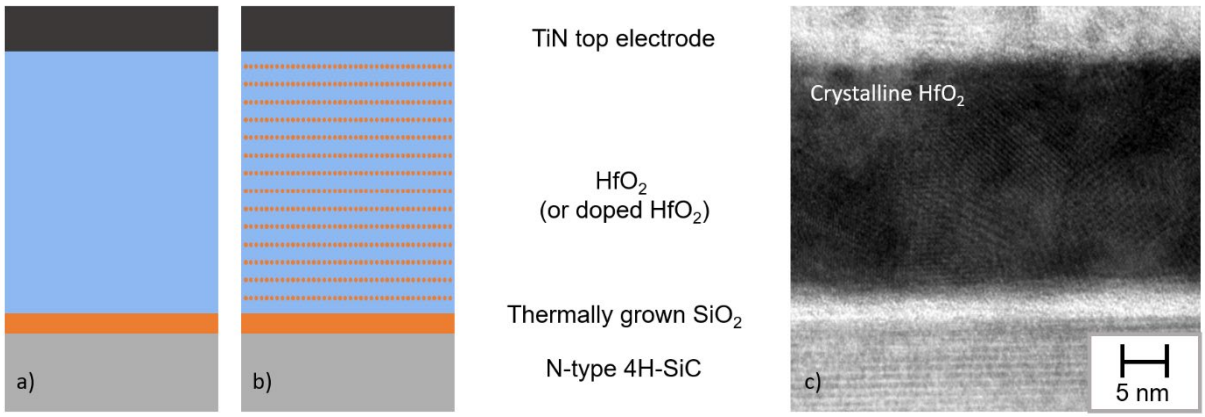

Fig. 1. Schematics of the sample with a) pure HfO_2 and b) doped HfO_2. The blue layer represents the ALD-deposited oxide, and the orange dots resemble the dopants. The TEM image c) shows the sample with pure HfO_2 after annealing. The features in the HfO_2 film are the lattice planes allowing for differentiation of individual crystal grains, while the amorphous SiO_2 interlayer lacks this texture.

Results and Discussion

Fig. 2 shows the relationship between J_{leak} at 2 MV/cm and the k value for the different capacitor structures. For the samples annealed at 1000°C, J_{leak} was enhanced by four to eight orders of magnitude, rendering them unsuitable as gate dielectrics. Moreover, the high leakage inhibits the saturation of the accumulation capacitance during the CV measurement, which makes the k determination unreliable for these samples [10]. Consequently, these samples are excluded from further evaluation.

In contrast, the samples annealed at ~500°C show promising results. For SiC samples, J_{leak} is typically one order of magnitude higher than for Si samples, which can be attributed to the lower conduction band offset between SiC and HfO_2. This is supported by the dependence of E_{BD} on the leakage behavior (Fig. 3): samples with higher leakage demonstrate a lower breakdown voltage. The higher J_{leak} for the SiC samples draws a distinction between the two datasets and shifts the graph for SiC to the right. For a SiC power device in operation, typically, a leakage current of less than 100 nA/cm^2 is desirable [11], which is fulfilled for all samples. Additionally, the ranking of high-k materials remains consistent for both substrates. The Si-doping enhances E_{BD}, while Y and La-doping result in a lower E_{BD} and higher J_{leak} as compared to the pure HfO_2 films. This observation is expected given that the high-k material was deposited on an interfacial SiO_2 layer for both substrates which effectively eliminates the effects of possibly different ALD growth behavior on the different substrates.

The difference in the atomic radii of the dopant and the Hf atoms induces internal tensile stress in the HfO_2 lattice, which affects the T_C and the resulting crystalline phase [12,13]. GIXRD measurements confirm that pure HfO_2 crystallizes in the monoclinic phase [2] (Fig. 4). Consequent annealing experiments revealed T_C of about 375°C for the 30 nm undoped HfO_2 film, which ranks at the lower end of values reported in literature [3–5]. Fig. 1c shows a TEM image of the crystalline HfO_2. For the Si-doped films, GIXRD indicates the presence of randomly oriented nanocrystallites

within a predominantly amorphous matrix. This can be concluded from the broad peak observed in the measurements performed on both as deposited and annealed films. T_C is increased to approximately 650°C and 750°C for the 4 % and 6 % Si-doped films, respectively. In contrast, La or Y doping does not increase T_C above 500°C and leads to a mixture of crystallographic phases present in the crystalline films. This goes along with an increase in the k value, as tetragonal or orthorhombic HfO_2 have k values of 30-40 compared to approximately 20 for the monoclinic HfO_2 [2].

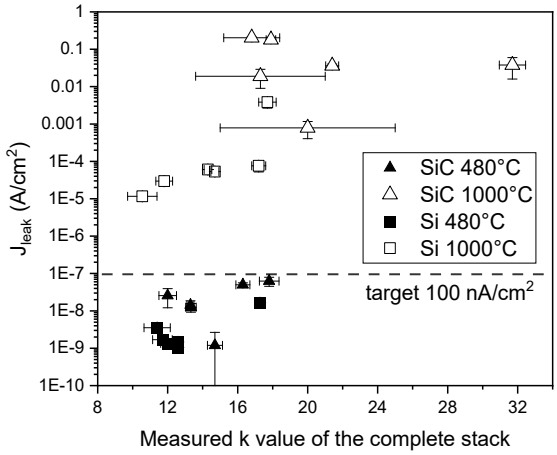

Fig. 2. Dependence of J_{leak} at 2 MV/cm on the dielectric constant of the (doped-)HfO_2/SiO_2 stack on Si or SiC substrates after annealing. J_{leak} is higher for SiC samples and increases with higher annealing temperature and higher k value.

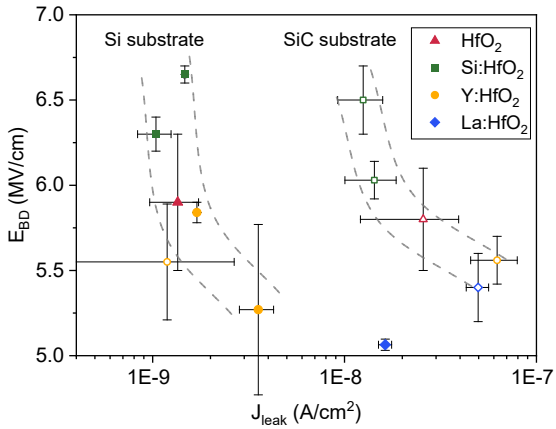

Fig. 3. Dependence of E_{BD} on J_{leak} at 2MV/cm. Samples with lower J_{leak} exhibit a higher E_{BD}. Empty datapoints stand for SiC, filled for Si samples, the shape of the datapoints indicates the material. Dotted lines are a guide to the eye.

Fig. 5 shows that stacks with HfO_2 layers with higher k have a lower E_{BD}, which is consistent with [1,3,4]. Furthermore, these results reveal that the amorphous films have a significantly higher E_{BD} than the crystalline films. At the same time, they exhibit a lower k value since they do not profit from the higher k of the tetragonal or orthorhombic phase portion. Generally, amorphous oxides are advantageous as insulators because they lack grain boundaries, which could provide leakage paths for charge carriers [6,13].

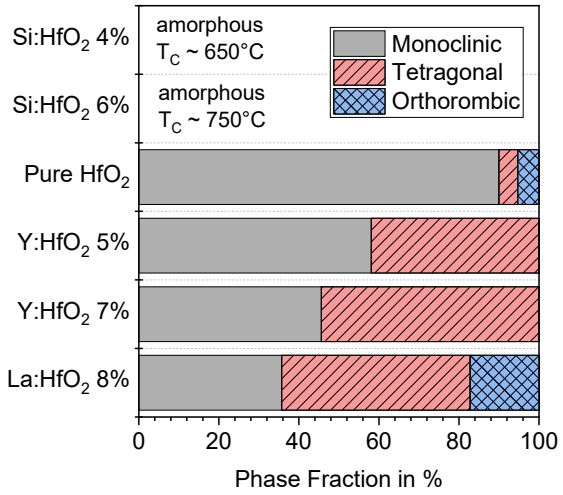

Fig. 4. Crystalline phases present in the HfO_2-based films after annealing at 500°C as confirmed by GIXRD. While the monoclinic phase is prominent in pure HfO_2, introducing dopants leads to an increase in the tetragonal phase portion. Si-doping increases T_C of the films and keeps them amorphous.

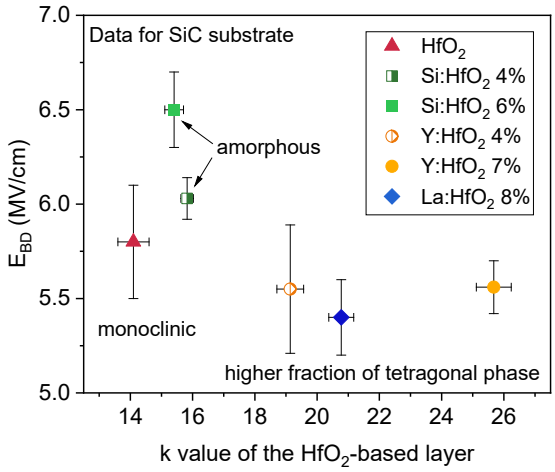

Fig. 5. Dependence of E_{BD} on k. E_{BD} is generally higher for the amorphous films. The highest E_{BD} was measured for the HfO_2 film with the highest Si doping. The k value of the HfO_2-based layer was calculated from the k value of the entire stack and the physical thicknesses of the layers as measured by XRR or TEM.

Fig. 6 further illustrates the relationship between crystallographic structure and charge carrier conduction. Samples with larger crystal grains exhibit a higher leakage current. Although this effect

may seem negligible at an electric field of 2 MV/cm, the difference becomes significant at higher fields. We assume that the amorphous films or films with a high number of small grains provide much more complex leakage paths compared to films with fewer large grains, subsequently reducing the probability of carrier conduction [14]. Notably at 5 MV/cm, a few nanometers reduction in crystal grain size results in a J_{leak} almost four orders of magnitude lower. This observation highlights the critical impact of crystal grain size on charge carrier conduction mechanisms in our HfO_2-based films.

For a better understanding of the doping impact, Fig. 7 illustrates the E_{BD} dependence on the doping concentration for the three doping materials. The HfO_2-based film with the highest Si doping exhibits the highest E_{BD}. For the Y and La-doped HfO_2 films E_{BD} decreased compared to the pure HfO_2. The advantage of Si doping can be attributed to two factors. Firstly, the Si-doped layers are amorphous when annealed at 500°C in contrast to the other films. Secondly, the Si atom is four-valent, which matches Hf, in contrast to Y and La, which are tri-valent. The mismatch of valency results in dangling bonds within the film, leading to an increased defect density in the bulk of the material [8,13]. Such defects can accumulate charge, resulting in higher J_{leak} and lower E_{BD} [12,13].

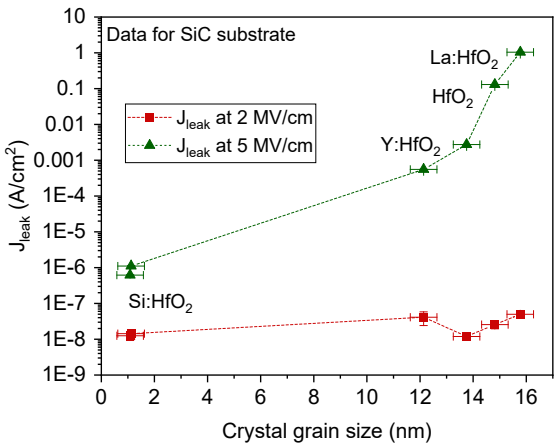

Fig. 6. Dependence of J_{leak} on the size of crystalline grains at two different applied fields. Samples with larger crystal grains exhibit higher J_{leak} at higher applied voltages.

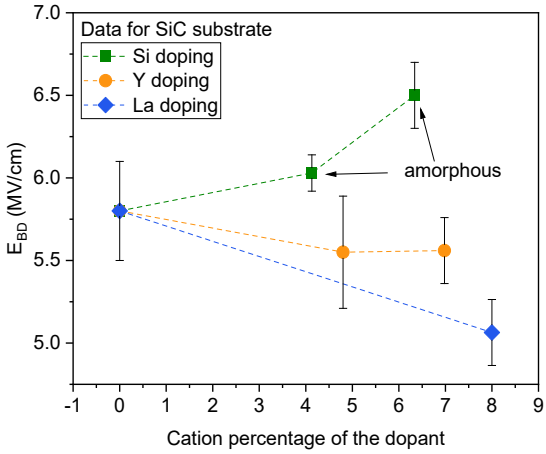

Fig. 7. Dependence of E_{BD} on Si, Y, and La doping concentration in HfO_2. E_{BD} increases with Si content and decreases with Y and La content.

To explore the trade-off between E_{BD} and k, Fig. 8 displays their product as a figure of merit (FOM). The plot demonstrates that E_{BD}*k is higher for the stack with pure HfO_2 compared to a stack with pure SiO_2, and it can be further enhanced by introducing the dopants investigated in this study. Notably, all the presented stacks surpass the value of 39 for SiO_2 (with literature values of k = 3.9 and E_{BD} = 10 MV/cm) [3]. This FOM provides a powerful tool to rank the films, but to decide whether a specific film is suitable for a specific application, one must consider which of the two factors, E_{BD} or k, is more critical.

Si-doped films demonstrate the most promising characteristics regarding high E_{BD}, low J_{leak} and increased T_C. To further investigate the breakdown behavior, Si-doped films of various thicknesses were deposited on Si substrates. Fig. 9 illustrates that thicker Si-doped layers have a lower E_{BD}, which is consistent with [15,16]. This observation could provide another explanation for the higher E_{BD} exhibited by the Si-doped films. Assuming that the diffusion of dopants is negligible after deposition, then the doping is not uniformly distributed within the stack. Each Si ALD cycle creates a Si-rich layer, dividing the bulk pure HfO_2 into thinner layers. For instance, in case of the highly Si-doped film, this would lead to HfO_2 layers with a thickness of about 1.2 nm. This phenomenon also explains the increase in T_C, as several researchers have reported an exponential rise of T_C by reducing layer thickness down to a few nanometers [17–19]. In their work [17] Zacharias et al presented a calculation for T_C of SiO_2 films depending on their thickness. By adapting this equation to HfO_2, we derived equation (1), where T_{Cbulk} represents the T_C of HfO_2 thick films (375°C) and d is the layer thickness of the film under investigation (1.2 nm for 6 % and 1.8 nm for 4 %). Our calculated T_C values of 774°C and 688°C for the 6% and 4% Si-doped films, respectively, align well with our

measured values. It is important to note that T_C for the Si-doped films was determined through annealing in steps of 100°C, leading to an uncertainty of about 50°C in the measured values.

$$T_C = T_{Cbulk} + 663\, e^{-d/2.43nm}\ ^\circ C \quad (1)$$

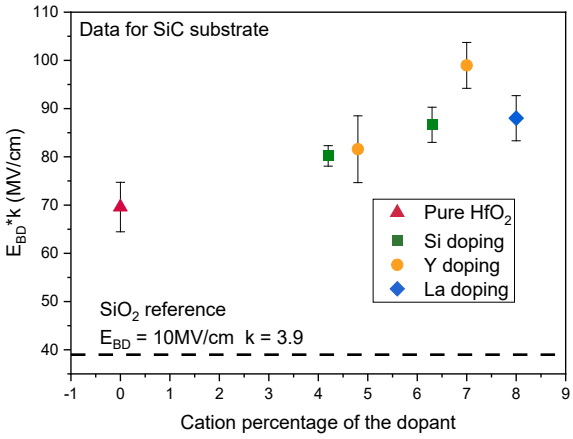

Fig. 8. All investigated HfO_2-based films have a higher E_{BD}*k than SiO_2, with a tendency for an increased E_{BD}*k with higher doping levels. The sample with the highest Y-doping did not exhibit the highest E_{BD} (Fig. 4) but it has the highest E_{BD}*k due to its high k value.

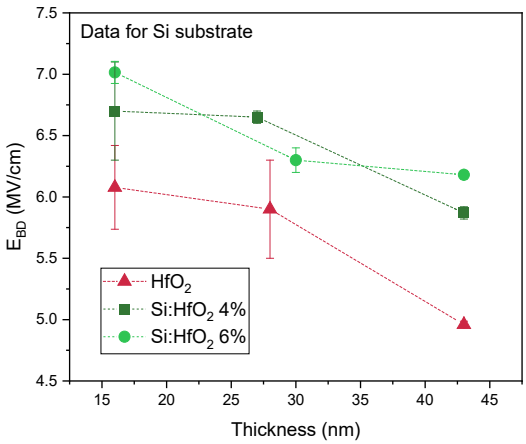

Fig. 9. Dependence of E_{BD} on the physical thickness of the stack for Si-doped HfO_2 films on Si substrate. Thicker layers have a higher J_{leak} and a lower E_{BD} value.

Summary

This study demonstrated that amorphous doped HfO_2-based films exhibit higher electric breakdown fields and lower leakage current density than corresponding crystalline films. The small atomic radius of Si enables increasing the crystallization temperature and the Si-doped HfO_2 films remain amorphous after annealing at ~500°C. As a result, Si-doped films demonstrate lower leakage current densities and higher electric breakdown fields. In contrast, La- and Y-doped HfO_2 films do not show a significant increase in the crystallization temperature but exhibit a higher dielectric constant, which can be attributed to the presence of the tetragonal and orthorhombic phases within the crystalline films. In summary, Si doped amorphous HfO_2 films demonstrate superior electrical performance, making them more suitable as gate dielectrics than their crystalline counterparts. This can be attributed to the size and valency of the Si-atoms. Moreover, it is noteworthy that the investigated films exhibit consistent structural and electrical behavior on both Si and SiC substrate. This finding enhances their potential for application versatility across various semiconductor platforms.

Our study demonstrates that while pure HfO_2 may not be a viable replacement for SiO_2 as gate dielectric in SiC power devices, Si-doping significantly enhances the structural and electrical properties of a 30 nm HfO_2 film. To further enhance the suitability of Si-doped HfO_2 films for the integration into state-of-the-art SiC power devices, future research should focus on increasing the thermal budget that the stack can withstand during the fabrication processes.

References

[1] Kol,S., Oral,A. Hf-Based High-κ Dielectrics: A Review. Acta Phys. Pol. A 136, 873-881 (2019).

[2] Richter, C., Schenk, T., Park, M. H., Tscharntke, F. A., Grimley, E. D., LeBeau, J. M., et al. Si Doped Hafnium Oxide—A "Fragile" Ferroelectric System. Adv. Electron. Mater. 3, 1700131 (2017).

[3] Siddiqui, A., Khosa, R. Y., Usman, M. High-k dielectrics for 4H-silicon carbide: present status and future perspectives. J. Mater. Chem. C 9, 5055–5081 (2021).

[4] Robertson, J. Band offsets of wide-band-gap oxides and implications for future electronic devices. J. Vac. Sci. Technol. B 18, 1785 (2000). https://doi.org/10.1116/1.591472

[5] Nawaz, M. On the Evaluation of Gate Dielectrics for 4H-SiC Based Power MOSFETs. Active and Passive Electronic Components 2015, 1–12 (2015). https://doi.org/10.1155/2015/651527

[6] Narayanan, V., Frank, M. M., eds. Thin films on silicon: electronic and photonic applications. (World Scientific, 2017).

[7] Lomenzo, P. D., Takmeel, Q., Moghaddam, S., Nishida, T. Annealing behavior of ferroelectric Si-doped HfO2 thin films. Thin Solid Films 615, 139–144 (2016).

[8] Materlik, R., Künneth, C., Falkowski, M., Mikolajick, T., Kersch, A. Al-, Y-, and La-doping effects favoring intrinsic and field induced ferroelectricity in HfO2: A first principles study. Journal of Applied Physics 123, 164101 (2018).

[9] Holzwarth, U., Gibson, N. The Scherrer equation versus the 'Debye-Scherrer equation'. Nature Nanotech 6, 534–534 (2011).

[10] Lu, Y., Hall, S., Tan, L. Z., Mitrovic, I. Z., Davey, W. M., Raeissi, B., et al. Leakage current effects on C-V plots of high-k metal-oxide-semiconductor capacitors. J. Vac. Sci. Technol. B 27, 352 (2009).

[11] Weckbrodt, J., Ginot, N., Batard, C., Azzopardi, S. Monitoring of Gate Leakage Current on SiC Power MOSFETs: An Estimation Method for Smart Gate Drivers. IEEE Trans. Power Electron. 36, 8752–8760 (2021).

[12] Park, M. H., Lee, Y. H., Kim, H. J., Kim, Y. J., Moon, T., Kim, K. D., et al. Ferroelectricity and Antiferroelectricity of Doped Thin HfO_2 -Based Films. Adv. Mater. 27, 1811–1831 (2015).

[13] Schroeder, U., Mueller, S., Mueller, J., Yurchuk, E., Martin, D., Adelmann, C., et al. Hafnium Oxide Based CMOS Compatible Ferroelectric Materials. ECS J. Solid State Sci. Technol. 2, N69–N72 (2013).

[14] Chiu, F.-C. A Review on Conduction Mechanisms in Dielectric Films. Advances in Materials Science and Engineering 2014, 1–18 (2014).

[15] DiMaria, D. J. Explanation for the oxide thickness dependence of breakdown characteristics of metal-oxide-semiconductor structures. Microelectronic Engineering 36, 317–320 (1997).

[16] Kauerauf, T., Degraeve, R., Cartier, E., Govoreanu, B., Blomme, P., Kaczer, B., et al. Towards understanding degradation and breakdown of SiO/sub 2//high-k stacks. in Digest. International Electron Devices Meeting, pp. 521–524 (IEEE, 2002).

[17] Zacharias, M., Bläsing, J., Veit, P., Tsybeskov, L., Hirschman, K., Fauchet, P. M. Thermal crystallization of amorphous Si/SiO2 superlattices. Applied Physics Letters 74, 2614–2616 (1999).

[18] Navrotsky, A. Thermochemical insights into refractory ceramic materials based on oxides with large tetravalent cations. J. Mater. Chem. 15, 1883 (2005).

[19] Ushakov, S.V., Navrotsky, A., Yang, Y., Stemmer, S., Kukli, K., Ritala, M., et al. Crystallization in hafnia- and zirconia-based systems. Phys. Stat. Sol. (b) 241, 2268–2278 (2004).