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Impact of different dopants on the switching properties of ferroelectric hafniumoxide

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1NaMLab gGmbH, Noethnitzer Str. 64, 01187 Dresden, Germany   
2Fraunhofer IPMS-CNT, Koenigsbruecker Str. 180, 01099 Dresden, Germany   
3Imec, Kapeldreef 75, 3001 Leuven, Belgium   
4IHM, TU Dresden, Noethnitzer Str. 64, 01187 Dresden, Germany   
5The Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN 37831, U.S.A.

E-mail: Uwe.Schroeder@namlab.com

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| The wake-up behavior of ferroelectric thin film capacitors based on doped hafnium oxide dielectrics in TiN-based metal–insulator–metal structures is reported. After field cycling a remanent polarization up to 40 µC/cm2and a high coercive field of about 1 MV/cm was observed. Doping of HfO2 |

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| by different dopants with a crystal radius ranging from 54 pm (Si) to 132 pm (Sr) was evaluated. In all cases, an improved polarization–voltage |

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| 1. | hysteresis after wake-up cycling is visible. For smaller dopant atoms like Si and Al stronger pinching of the polarization hysteresis appeared with increasing dopant concentration and proved to be stable during cycling. © 2014 The Japan Society of Applied Physics | |
| Introduction | thanum (2,2,6,6-tetramethyl-3,5-heptanedionato) [La(thd)3], and trimethylaluminium (TMA) as precursors for Hf-, Si-, |

Ferroelectric materials have a high potential as a storage layer for non-volatile memory applications.30)Typically, materials like strontium bismuth tantalate (SBT) or lead zirconate titanate (PZT) are implemented.1,19)The integration into capacitor structures was realized, but an introduction into transistor devices is only possible with interfacial barriers.20) As a consequence, ferroelectric layers thicker than 100 nm need to be used in order to achieve non-volatility.21)Hence, scaling of the devices according to current technology node requirements is hindered.

Recently, ferroelectric properties of doped hafnium oxide were reported2,22)when thin films with a certain composition at the boundary between the monoclinic and the tetragonal/ cubic phases are crystallized. In this paper, we present an (MIM) overview of HfO2 based metal–insulator–metal   
capacitors exhibiting ferroelectric polarization hysteresis for various dopants3)(Si,2)Al,4)Y,10)Gd,5)La,7)Sr6)) and the

Al-, Y-, Gd-, Sr-, and La-oxide deposition, respectively. Ozone or water was used as oxidant and argon or nitrogen as purge and carrier gas. TiN electrodes were deposited by a chemical vapor deposition process based on TiCl4 and NH3 at a deposition temperature of 450 °C or by physical vapor deposition of Ti in nitrogen plasma at 200 °C. Metal–ferroelectric–metal (MFM) stacks with a doped HfO2 thick-ness of 10 nm (unless different thicknesses are mentioned) were annealed in a rapid thermal anneal chamber in N2 at 650–1000 °C to crystallize the whole material stack. Pt dots were deposited on the MFM stack and used as a hard mask to structure the TiN top electrode. The capacitor area was 0.01 mm2. Transistor structuring is described elsewhere.11) Dielectric layer thickness and doping content were evaluated by inline spectral ellipsometry and X-ray photoelectron spectroscopy (XPS), calibrated by Rutherford backscattering (RBS) and proton-induced X-ray emission (PIXE). Standard

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| impact of dopant type and concentration on the ferroelectric | and | high | resolution | transmission | electron | microscopy |

properties. Ferroelectricity can also be achieved in mixed hafnium–zirconium oxides (HfxZr1¹xO2).8,9,23,24)These will not be discussed at this point due to the different composition range of this system compared to the dopants mentioned above. In addition, Si:HfO2 is used as a model system to explain wake-up and fatigue behavior of this new ferro-electric material system. The discovery of ferroelectric HfO2

(HRTEM) was utilized to confirm film thickness and crystallinity. Polarization–voltage (P–V) measurements and positive-up negative-down (PUND) measurements were performed using an aixACCt Systems TF Analyzer 3000. Small signal capacitance–voltage (C–V) measurements were obtained using an Agilent LCR meter at 20 kHz with 3 V amplitude after 1000 wake-up cycles.

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| opens up an interesting pathway to build highly scalable ferroelectric capacitors25)or transistors7,11,26,27)for various  high-density non-volatile memory concepts. | | 3. | Results and discussion | | | | | | |
| 3.1 | Ferroelectric polarization of Si:HfO2 | | | | | | |
| 2. | Methods | The | polarization | hysteresis | of | Si | doped | HfO2 | MFM |
| capacitors was evaluated for a dopant range from 0 to | | | | | | | |

Planar MIM capacitors were processed on 300 mm Si wafers and structured into 4 © 4 cm samples. Si:HfO2, Al:HfO2, Y:HfO2, Gd:HfO2, and Sr:HfO2 films were deposited in a single wafer atomic layer deposition (ALD) reactor using

12 mol % SiO2 on fresh samples and after field cycling. Pure HfO2 showed zero or very low remanent polarization below 3 µC/cm2,10)depending on the deposition process. With

increasing Si dopant content different pinched hysteresis

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| tetrakis(ethylmethylamino)hafnium | (TEMAHf ), | hafnium | curves with changing polarization values were determined |

tetrachloride (HfCl4), silicon tetrachloride (SiCl4) tetrakis(di-

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| methylamino)silane | (4DMAS), | tris(dimethylamino)silane |

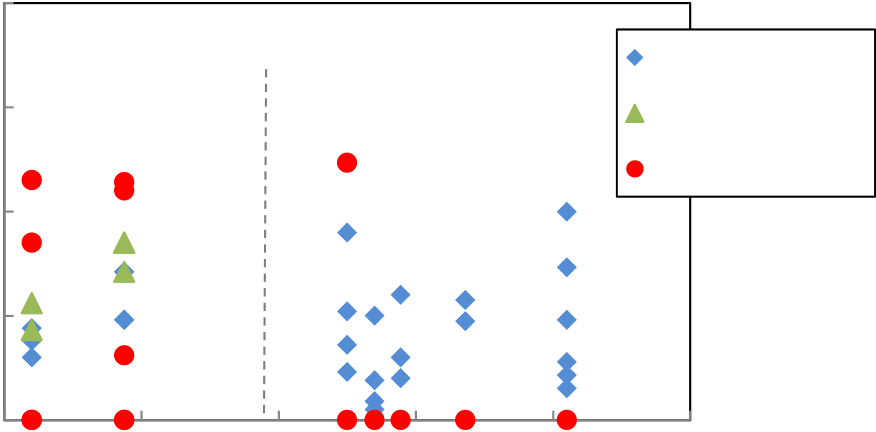
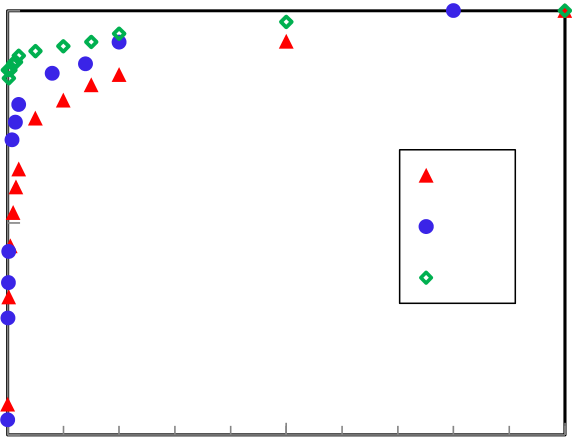
(3DMAS), tris(isopropylcyclopentadienyl)gadolinium [Gd-(iPrCp)3], tris(methylcyclopentadienyl)-yttrium [Y(MeCp)3], strontium di-tert-butylcyclopentadienyl [Sr(tBu3Cp)2], Lan-

[Fig. 1(a)]. A maximum polarization could be verified for 4.4 mol % SiO2 content. For higher SiO2 content the pinching of the hysteresis increased and the remanent polarization reduced. Above 7 mol % the remanent polarization is reduced to zero and only field induced polarization was present. The

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| 2) | 20 | |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | | | | | | |  |  |  |  |  |  |  |
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| Jpn. J. Appl. Phys. 53, 08LE02 (2014) | | | | U. Schroeder et al. | | | | | | | | | |
| Material | Crystal radius29)  (pm) | | | Table I. | Overview of dopant materials used in this study. | | | | | | | | |
| Absolute radius mismatch to Hf | | Crystal phase for | | | | | Coercive field | | Valence |
| (pm) | | high dopant content | | | | | (MV/cm) | |
| Si | 54 | | | 31 | | Tetragonal | | | | | 0.8–1 | | 4 |
| Al | 68 | | | 18 | | Tetragonal/cubic | | | | | 1.3 | | 3 |
| Y | 104 | | | 19 | | Cubic | | | | | 1.2–1.5 | | 3 |
| Gd | 108 | | | 23 | | Cubic | | | | | 1.75 | | 3 |
| La | 117 | | | 32 | | Cubic | | | | | 1.2 | | 3 |
| Sr | 132 | | | 47 | | tbd | | | | | 2 | | 2 |
| 1 | | | | Pr | | **Dopant Concentration (mol%)** | 20 | **Si Al Hf YAYP Gd La Sr** | | | | | FE after cycling |
| **norm. Pr , MW, Ec** | | 0.8 | | 15 |
| pinched hysteresis |
| 10 | paraelectric |
| MW | |
| Ec | | 5 |
| 0.6 | | | | 0 |
| 5000 | | 50 | | | 70 | 90 | 110 | 130 | 150 |
| 0 | | | 2500 |
| **Crystal Radius (pm)** | |
| **cycles** | | | |

Fig. 7. (Color online) Evolution of relative remanent polarization Pr (Fig. 3), the coercive field Ec of a MFM capacitor as well as the memory window MW of a FeFET memory device as a function of field cycles.

the coercive field (Ec) as long as a sufficient remanent polarization is present17)

MW ¼�2 � Ec � dFE; ð1Þ with dFE thickness of the ferroelectric layer. A measurement of the MW with field cycling for a FeFET device is depicted in Fig. 7. The same diagram contains the normalized polarization value and the coercive field from measurements on MFM capacitors. As expected from Eq. (1), the MW should be mainly impacted by the coercive field of the ferroelectric material. Since cycling showed a stronger effect on the MW than it could be calculated from the coercive field other parameters need to play a role. Trapping in the SiO2 interface and the HfO2 should shift both program and erase threshold voltage with minor impact on the MW. As can be seen from Fig. 7, the remanent polarization can be correlated to the memory window as well. Further investigations are required to separate the effects.

3.2 Ferroelectric polarization for various HfO2 dopants Similar measurements as described for Si dopant were performed on MFM capacitors using dopant atoms with a crystal radius larger than Si and different valences (see

Fig. 8. (Color online) Dopant concentration for the formation of the different hysteresis shapes in doped HfO2 layers as a function of the crystal radius of the used dopants. For pure HfO2 and highly doped HfO2 layers a paraelectric behavior is visible. YA = ALD deposited Y2O3; YP = PVD Y2O3.

with higher crystal radius (see Table I). After cycling the samples for at least 1000 wake-up cycles a de-pinching is visible and most samples converted to a ferroelectric material with clean hysteresis (see Fig. 8 square dots). The wake-up effect and fatigue is very similar to the Si doped HfO2 sample with 4.4 mol % SiO2. With increasing dopant concentrations for dopants materials larger than Hf a clear reduction of the remanent polarization is detected.

Only a small dopant content range for Si and Al doped samples remained stable in the pinched hysteresis shape (Fig. 8 triangle dots). The appearance of the stable pinched hysteresis for Si and Al:HfO2 can be related to the phase transition determined for the characterized dopant materials according to

Si, Al monoclinic ! orthorhombic   
 ! tetragonal ! cubic;   
 Y, Gd, La, ðSrÞ monoclinic ! orthorhombic ! cubic: An apparent correlation was visible: only for the dopants with a smaller crystal radius than Hf a transition from a monoclinic to the tetragonal phase via the orthorhombic lattice is seen. Only these dopants indicated stable pinched

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| Table I). | Dopant | atoms | with | different | valences | were | hysteresis. |

evaluated, but the different binding configurations resulting in different oxygen vacancy levels had no effect on the general ability to form a ferroelectric phase of the HfO2. Hence, expected different oxygen vacancy levels in HfO2 did not impact the ferroelectric behavior. A pure field driven oxygen vacancy movement as the main driving root cause for the detected ferroelectric effects can be ruled out. The coercive field slightly increased for most dopant materials

Depicting the measured remanent polarization values for various dopant concentrations and crystal radius resulted in contour plot in Fig. 9. For most samples a maximum polarization between 15–25 µC/cm2could be reached. La doping showed significant higher Pr of about 40 µC/cm2. The dopant content with maximum polarization is almost stable with ³3–6 mol % for most dopants. For all measured samples with highest Y, Gd, and Sr doping content a

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4. Conclusions

The wake-up behavior of doped hafnium oxide MFM capacitors was evaluated during field cycling. All samples started in a more or less pinched polarization–voltage hysteresis shape which opened up during cycling. Only antiferroelectric- or relaxor-like hysteresis curves with zero remanent polarization as detected for Si and Al:HfO2 where stable during cycling. Remanent polarization values im-proved during cycling which could be explained by release of pinned domain walls, which also lead to reduced polarization relaxation. This improvement in the capacitor switching behavior is also visible as an enlarged memory window in FeFET devices. The coercive field slightly increased for most dopant materials with higher crystal radius. Fatigue started to occur typically after 107cycles when field cycling is performed at 1 MHz. Dopant materials with increasing crystal radius showed an almost constant dopant range and that a similar dopant amount was necessary to form the ferroelectric phase.

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