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|  | PAPER | | **[View Article Online](http://dx.doi.org/10.1039/C6TC04807B)**  **[View Journal](http://pubs.rsc.org/en/journals/journal/TC)  [| View Issue](http://pubs.rsc.org/en/journals/journal/TC?issueid=TC005002)** |
| lished on 14 December 2016. Downloaded by Georgia Institute of Technology on 13/04/2017 06:35:07. | Cite this: *J. Mater. Chem. C,* 2017, | An extensive study of the influence of dopants on the ferroelectric properties of HfO2 | |
| 5, 333 | S. Starschich\* and U. Boettger | |
| The ferroelectric properties of hafnium oxide based thin films prepared by chemical solution deposition (CSD) are investigated. In this extensive study, a wealth of strongly different dopants (size and valence) and dopant concentrations is used to induce ferroelectricity in 42 nm thin films. Using the same precursors and preparation conditions for all dopants a good comparability is given. In particular, the dopant size appears to have a crucial impact on the resulting ferroelectric properties. For smaller dopants only a small ferroelectric | | |
| Received 4th November 2016, | response is observed whereas for larger dopants the remanent polarization is increased significantly. The | |
| Accepted 1st December 2016 | crystal phase for varying dopant concentrations and dopant sizes is investigated by grazing incidence X-ray | |
| DOI: 10.1039/c6tc04807b | diffractions (GI-XRD). A dominating cubic phase is found for doping concentrations showing the highest | |
| remanent polarization. Similar to first CSD studies on Y:HfO2, this is reflected in a prominent wake-up | | |
| www.rsc.org/MaterialsC | behavior, which is attributed to a phase transition from cubic to orthorhombic during field cycling. | |
| Introduction | | prepared by sputter deposition,19pulsed layer deposition20and CSD,21indicating that the stabilization of the ferroelectric |
| Recently discovered unconventional ferroelectric materials based on | | phase is independent of the layer preparation technique. |
| doped hafnium oxide1have attracted a lot of attention. Hafnium | | Furthermore, it was shown that in the case of yttrium doping |
| oxide is completely compatible with known semiconductor | | almost an identical doping dependence was observed for CSD |
| fabrication processes and therefore is a promising candidate | | and ALD prepared devices.22 |
| for future high density, nonvolatile memory devices.2–4Aside | | The influence of different dopants on the ferroelectric |
| from the memory application, Park et al. also discussed the | | switching properties of hafnium oxide was reported earlier |
| energy-related applications such as pyroelectric energy harvesting, | | by Schroeder et al.23They showed that dopants with a |
| electrocaloric cooling and electrostatic energy storage.5–7The | | smaller ionic radius compared to hafnium show a pinched |
| Pub | ferroelectricity is attributed to the non-centrosymmetric orthor- | | hysteresis, which is stable even after wake-up and was thus |

hombic phase with a Pca21 space group, which was recently found by Sang et al.,8but the origin of the stabilization of the ferroelectric phase in these films is not completely understood yet. The stabilization of higher symmetric phases in HfO2 (cubic, tetragonal) compared to the monoclinic bulk phase was found earlier to depend on the thermal treatment,9growth temperature,10 surface energy effects11and mechanical encapsulation realized by the electrodes.12Furthermore, doping with various elements leads to the stabilization of a higher symmetric phase as summarized by Mueller et al.4After the first discovery of ferroelectricity in silicon doped hafnium oxide in 2011 by Boescke et al.,1it was shown that ferroelectricity can be induced by several dopants which are also known to stabilize a higher symmetric phase in hafnium oxide (Y,13 Gd,14Al,15Sr,16and La17). Furthermore, a mixture of hafnium and zirconium oxide (HZO) does also stabilize the ferroelectric phase.18 Ferroelectricity was not only observed for layers prepared by atomic layer deposition, but also observed for yttrium doped samples

attributed to an antiferroelectric-like behaviour. Later this behaviour could be explained by a field-induced phase tran-sition from tetragonal to orthorhombic in an applied field.24 Moreover, it was shown in a previous work that there is no significant difference in the suitability to induce ferroelectric properties in HfO2 for different dopants from the lanthanoid group.22   
 In this work the influence of several dopants with varying ionic radii between 54 pm and 135 pm on the ferroelectric properties is investigated (Mg, Ba, Sr, Y, La, Nd, Sm, Er, Al, Ga, In, Co, and Ni). For a good comparability of all dopants the same type of precursor is used during solution preparation as well as the preparation conditions are the same. GI-XRD is used to determine the crystal phase for different dopants and varying doping concentrations. The ionic radii shown in this work are based on the results of Shannon.25For the Hf1�xZrxO2 system the concentration window where ferroelectricity appears was reported to be much wider compared to the dopants mentioned

Institut fu¨r Werkstoffe der Elektrotechnik 2, RWTH Aachen University, above,18,26and therefore HZO is not taken into account for

D-52074 Aachen, Germany. E-mail: Starschich@iwe.rwth-aachen.de this work.

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*J. Mater. Chem. C,* 2017, 5, 333--338 | 333

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| Experimental |  | |
| The sample preparation by chemical solution deposition was |
| carried out as described in detail in a previous work.22For all |
| samples a final crystallization step of 800 1C for 90 s was realized in |
| an argon/oxygen (1:1) atmosphere leading finally to the following |
| layer stack: SiO2\TiO2\100 nm Pt\42 nm X:HfO2\50 nm Pt. |
| The polarization measurements were carried out using an |
| aixACCT Systems TF Analyzer 2000, whereas an HP4284A LCR meter |
| was used to record the capacitance. For the GI-XRD measurements a |
| PANalytical XPert Pro with a wavelength of 0.154 nm was used. The |
| P–V and C–V curves were measured at a frequency of 1 kHz with a |
| 50 mV ac probing signal for the capacitance measurements on |
| device areas of 2.5 � 10�4cm2. As reported previously, a certain amount of wake-up cycles are necessary to exhibit ferroelectric |
| properties.21,27For all electrical data shown here 1000 rectangle |
| cycles with a frequency of 1 kHz at an electrical field of 3.25 MV cm�1 |
| were performed beforehand. To achieve comparable hysteresis |
| curves an identical electrical field of 3.25 MV cm�1was also |
| applied for all measurements. |
| Results and discussion | Fig. 1 | Ferroelectric hysteresis with the corresponding current curves for |
| three different elements from the alkaline earth metal group. | |
| Published on 14 December 2016. Downloaded b | The dependence of the ferroelectric hysteresis on the yttrium |  | |
| doping concentration was already shown in a previous work for |
| CSD prepared samples.22A maximum remanent polarization |
| was found for a yttrium concentration of 5.2 mol%. For a |
| higher and lower concentration the remanent polarization is |
| reduced and vanishes completely at 0 mol% and 11 mol%, |
| respectively. Such a window for the doping concentration is |
| found for all dopants mentioned in the introduction. The origin |
| of this behaviour is not fully understood yet. The influence of |
| several parameters on stabilizing the ferroelectric phase like |
| oxygen vacancies, electrical fields, surface energy and strain |
| was considered by several groups.24,28,29 |
| The doping dependence for three elements (Mg, Sr, and Ba) |
| from the alkaline earth metal group is shown in Fig. 1. This |
| group of elements is extremely interesting, because the elements |
| Fig. 2 | The remanent polarization Pr depending of the doping concen- |
| show similar chemical properties but the ionic radii strongly vary |
| tration for Mg, Sr and Ba. | |
| between 72 pm (Mg) and 135 pm (Ba). Doping with magnesium |

shows a very small ferroelectric response with a remnant polariza-

tion of 3 mC cm�2but is evidenced by the ferroelectric switching current peaks.30Strontium and barium exhibit a significantly larger polarization with a comparable maximum remanent polarization of 12.8 mC cm�2and 12 mC cm�2, respectively. The doping dependence of the remanent polarization for the alkaline earth metals is summarized in Fig. 2.

As for yttrium doping a window for the doping concentration is given, whereas the maximum of the remanent polarization is found for all three elements at 7.5 mol% instead of 5.2 mol% as found for yttrium. Another difference is the larger doping window where ferroelectricity appears. At 11 mol% for strontium and barium still a relative high remanent polarization of 11 mC cm�2 and 7.2 mC cm�2can be observed, respectively. For strontium even at 15 mol% a remanent polarization of 8.3 mC cm�2remains, whereas for barium the remanent polarization almost completely vanishes.

334 | *J. Mater. Chem. C,* 2017, 5, 333--338

The larger process window of strontium is not understood yet. The most significant result is that strontium and barium show a much higher remanent polarization compared to magnesium. The influence of the ionic radius on the remanent polarization will be discussed later.

The crystal phases for the varying doping concentrations are exemplarily shown for barium in Fig. 3. For pure hafnium oxide a dominating monoclinic phase is found indicated by the double peak around 301. For increasing barium content the cubic phase is stabilized. The phase evaluation from monoclinic to a high-k cubic phase is also visible for the relative permittivity as shown in the inset in Fig. 3. The relative permittivity increases with increasing barium content from 18 to 27 and saturates for concentrations above 7.5 mol%. It is worth mentioning that the highest remanent polarization is found for 7.5 mol% where

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| Fig. 4 | Ferroelectric hysteresis and the corresponding current curves for |
| 7.5 mol% barium doped hafnium oxide before and after the wake-up with | |
| 1000 cycles at 1 kHz. | |
| wnloaded by Ge | The ferroelectric hysteresis for aluminium, gallium and indium | |
| Fig. 3 | GI-XRD pattern for varying barium content. The inset shows the |
| relative permittivity depending of the barium concentration. The values for | |
| (boron group) doping with ionic radii varying from 54 pm (Al) | |
| the relative permittivity are taken at 0 V before the wake-up. | |
| to 80 pm (In) is shown in Fig. 5. A doping concentration of | |
| Published on 14 December 2016. Do | the cubic phase is dominant. This was also observed for CSD | | 5.2 mol% is used for the comparison of all dopants showing the | |
| highest remanent polarization for these elements. A small | |
| prepared layers with yttrium doping, where initially no ferroelectric | | hysteresis can be measured for all elements, whereby the | |
| hysteresis could be measured.21It was shown that an electrical | | remanent polarization slightly increases with increasing ionic | |
| field cycling is necessary to exhibit a ferroelectric hysteresis. | | radius from 3 mC cm�2(Al) to 5.2 mC cm�2(In) which can also | |
| The wake-up was observed in hafnium oxide for several dopants | | be indicated by the increasing switching current peaks. | |
| (Si,31Gd,14and Sr16) as well as for the Hf1�xZrxO2 system.26 Furthermore, for different deposition techniques (sputtering,19 | | Fig. 6 illustrates the remanent polarization depending of the | |
| ionic radius for several dopants. The values for the rare earth | |
| chemical solution deposition,21and pulsed layer deposition32) | | metals are taken from a recent publication.22The hysteresis | |
| initial cycling was also necessary to exhibit the maximum | | for cobalt and nickel is not shown here but both elements have | |

remanent polarization. Therefore, it can be concluded that the wake-up is an intrinsic property of the hafnia and zirconia based ferroelectrics. Park et al. assumed a phase transition during wake-up from a tetragonal to ferroelectric orthorhombic phase as the origin of the observed wake-up for 8 nm Hf0.5Zr0.5O2.33 Such a phase transition from the cubic to orthorhombic phase is also assumed for our samples. A field induced phase transition is attributed to the movement of oxygen vacancies27,34and was recently found by Grimley et al. for gadolinium doped hafnium oxide.35As exemplarily shown for barium doping in Fig. 4 the wake-up behaviour is observed for all dopants used in this work. During the first cycle, almost no switching currents are visible, whereas after the wake-up the ferroelectric hysteresis splits up and two current peaks are visible. For the layers in this work a very strong wake-up is observed where initially no ferroelectric phase can be found. It was shown in a previous work that for a higher crystallization temperature the orthorhombic phase is also initially present for CSD deposited layers.22Unfortunately, due to the high temperature no electrical characterization of the layers was possible.

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almost identical ionic radii and show a similar remanent polarization of around 3.8 mC cm�2. It should be mentioned that the remanent polarization for yttrium reported earlier is higher than that shown in this work.22This is due to the higher electrical field applied during wake-up and hysteresis measure-ments. From Fig. 6 a strong dependence of the remanent polarization on the ionic radius can be found. Larger dopants induce an almost four times larger remanent polarization compared to smaller ones. The edge where the remanent polarization increases is not as perhaps would be expected at the hafnium ion radius, but rather for ions larger than approxi-mately 85 pm. A further increase of the ionic radius seems to result in a slight reduction of the remanent polarization. For lanthanum doping recently a value for the remanent polarization of 40 mC cm�2was observed,17which could not be reproduced in this work similar to the recent results by Chernikova et al.36For hafnium oxide a maximum remanent polarization of approxi-mately 50 mC cm�2was simulated by ab initio calculations.24,29 Therefore, the grains given in this work are either random oriented or not all grains exhibit the ferroelectric orthorhombic

*J. Mater. Chem. C,* 2017, 5, 333--338 | 335

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|  | | silicon doping during crystallization to obtain ferroelectricity |
| as also shown by Boescke et al.39Possibly, for higher annealing |
| temperatures and/or capsuling also for the smaller dopants used |
| with CSD a higher remanent polarization could be achieved. As |
| mentioned before, for a higher crystallization temperature no |
| electrical characterization was possible. A crystallization after |
| deposition of the top electrode is also not possible, because |
| during crystallization, the layer is densified and therefore the top |
| electrode is not stable. In contrast to the ALD prepared layers no |
| thickness dependence is found for doped hafnium oxide pre- |
| pared by CSD. As mentioned in the introduction, in a previous |
| work Schroeder et al. observed a stable constricted hysteresis |
| also after wake-up for dopants with a smaller radius compared to |
| hafnium.23No such stable constricted hysteresis was found for |
| the CSD prepared layers. There are some differences between |
| ALD and CSD, which may have a strong influence on the |
| resulting ferroelectric properties. On the one hand, during |
| CSD, except the crystallization step, a maximum temperature |
| of 215 1C is applied after spin coating, whereas for ALD a |
| Fig. 5 | Ferroelectric hysteresis and the corresponding current curves for | temperature of up to 300 1C is used during deposition.38On |
| 5.2 mol% doped hafnium oxide for elements of the boron group. | | the other hand, for the CSD process most of the organic parts are |
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| during the heating step leading to a strong compression of |
| the layer.22Whereby for the ALD process after deposition an |
| amorphous layer is present which is crystallized without such a |
| strong change in density. Therefore, still strong differences can |
| be found between ALD and CSD prepared samples, although for |
| yttrium doping a very similar behaviour was found.22 |
| It is worth mentioning that lead doping was also investigated. |
| However, no ferroelectric response was found for a concentration |
| of 5.2 mol%. GI-XRD measurements revealed a strong monoclinic |
| phase where apparently no phase transition took place to the |
| ferroelectric orthorhombic phase during cycling (data not shown |
| here). Therefore, many dopants but not all are suitable to induce |
| ferroelectricity in hafnium oxide. |
| Fig. 7 shows the exemplary GI-XRD results for two larger (Ba, Y) |

Fig. 6 Remanent polarization depending of the ionic radius for different dopants (a coordination number of VI is used for all elements for the ionic radius). The data points for the rare earth metals are taken from a previous publication.22For the shown data the maximum remanent polarization is used. For the alkaline earth metals the maximum remanent polarization is found at a concentration of 7.5 mol%, whereas for all other dopants a maximum remanent polarization is depicted at 5.2 mol%.

phase after wake-up, leading to a lower remanent polarization as possible theoretically. A relatively low remanent polarization of 6 mC cm�2for aluminium doping was also found for ALD prepared films.15In another work by Polakowski et al. an optimized aluminium doping process was presented with a remanent polarization of 20 mC cm�2.37Also for silicon doping, whereby silicon is the smallest dopant used so far, a strong dependence on the layer thickness and crystallization temperature was found by Yurchuk et al.38The best results were found for a relatively high crystallization temperature of 1000 1C and a layer thickness of 9 nm, whereby for thicker films, the ferroelectricity vanishes. Furthermore, an encapsulation was necessary for

336 | *J. Mater. Chem. C,* 2017, 5, 333--338

and smaller (Ni, Mg) dopants, respectively. A very similar pattern is found for the larger and smaller dopants. This is kind of unexpected since it is known that dopants smaller than hafnium preferentially stabilize the tetragonal phase, whereas larger dopants tend to stabilize the cubic phase in hafnium oxide.40–44Although a cubic phase is present for all films, still a difference between smaller and larger dopants can be found. For the smaller dopants the peaks are shifted towards larger 2theta values which indicates smaller lattice constants. This is also expected if a smaller ion is incorporated into the lattice. Furthermore, a small shift of the platinum peaks at 811 and 461 can be observed towards smaller values, which indicates a change in the lattice constants of the platinum electrode. Therefore, it seems that the oxide layer slightly influences the crystal structure of the platinum during crystallization. These small differences in the lattice constants could hinder the transformation from the cubic into ferroelectric orthorhombic phase during wake-up cycling for the smaller dopants.

Although the chemical properties within one group (e.g. Mg, Sr, Ba) are similar, the different elements still show some differences e.g. in their electronegativity which could influence

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|  | | ferroelectricity in hafnium oxide is proven for the first time. All |
| devices were prepared by CSD using the same precursors and |
| preparation conditions to achieve a good comparability. For the |
| elements of the alkaline earth metals, the maximum remanent |
| polarization was found for a doping concentration of 7.5 mol%, |
| whereas for all other dopants a concentration of 5.2 mol% |
| showed the largest ferroelectric response. Furthermore, for the |
| alkaline earth metals a larger doping window was found where |
| ferroelectricity appears. In particular for strontium doping even |
| at 15 mol% a significant remanent polarization remains. Most |
| interesting is the strong dopant size dependence found in this |
| work for CSD prepared samples. For doping elements with an |
| ionic radius larger than 85 pm a significantly higher remanent |
| polarization is given. |
| Acknowledgements |
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| thank Tony Schenk (Namlab Dresden) for the careful correction of |
| the present work. |
| Fig. 7 | GI-XRD results for two smaller (Mg, Ni) and two larger (Y, Ba) doping | Notes and references |
| elements. For barium the pattern for a doping concentration of 7.5 mol% is | |
| used, whereas for the other elements the pattern for a doping concentration | |
| of 5.2 mol% is drawn showing the highest remanent polarization from the | | 1 T. S. Boescke, J. Mueller, D. Braeuhaus, U. Schroeder and |
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the dopant size is not the only parameter which is needed to consider for understanding the stabilization of the ferroelectric phase in hafnium oxide. Furthermore, it is still unclear why for the alkaline earth metals a maximum of the remanent polariza-tion is found for a doping concentration of 7.5 mol%, whereas for all other dopants shown here the maximum is given at 5.2 mol%. If the amount of induced oxygen vacancies due to the doping would play a role, then it would be expected that for the divalent alkaline earth metals the maximum remanent polarization should be shifted towards lower concentration compared to for example the trivalent yttrium. In addition, the larger doping window where ferroelectricity appears is not understood yet.

Conclusions

In conclusion, we have shown that many divalent and trivalent

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