Antiferroelectricity in ZrO2 and Ferroelectricity in Zr, Al, La Doped HfO2 Nanoparticles

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Abstract
The dependence of the polarization P in Hf₁₋ₓZrxO₂ nanoparticles on electric field, dopant concentration x, size and temperature are studied using the transverse Ising model and the Green’s function method. Pure ZrO₂ shows at high electric fields an antiferroelectric behavior. Pure HfO₂ is a linear dielectric in the monoclinic phase. With increasing ZrO₂ content the PE of HZO shows a ferroelectric behavior. The composition dependence of the remanent polarization rP has a maximum for x = 0.5. For x = 0, pure HfO₂, and x = 1, pure ZrO₂, rP = 0. P increases with decreasing HZO nanoparticle size. The influence of Al and La doping on rP in HfO₂ nanoparticles is also studied. The exhibiting of the ferroelectricity in ion doped HfO₂ is due to a phase transformation and to an internal strain effect. The observed results are in good qualitative agreement with the experimental data.

Keywords
ZrO₂ Nanoparticles, Zr, Al, La Doped HfO₂ Nanoparticles, Electric Properties, Microscopic Model, Green’s Function

1. Introduction
ZrO₂ is a wide-band insulating material with a high dielectric constant. With increasing temperature in ZrO₂ exist monoclinic, tetragonal, orthorhombic and cubic phases. Antiferroelectric (AFE)-like double-hysteresis loops are observed in ZrO₂ thin films [1] [2] where the structure is tetragonal at room temperature [3] [4] [5] [6]. Using density functional calculations Reyes-Lillo et al. [7] have studied the experimentally reported field induced phase transition in ZrO₂ thin film [1] [2] which corresponds to an intrinsic effect.
Furthermore, ferroelectricity was found in HfO₂ thin films doped with Zr (HZO) [1] [4] [8] [9] [10] [11] [12] as well as with Si, Y, Al, Gd, La [13] -[20]. It must be noted that pure HfO₂ and ZrO₂ are not ferroelectric. HfO₂ exists with increasing temperature in monoclinic, tetragonal and cubic phases [21]. In nano-materials the tetragonal phase extends to lower temperatures [5]. For different Zr content x the HZO thin films show dielectric (x = 0), ferroelectric (for example x = 0.5) and AFE (for example x = 0.7) properties, which are due to the involvement of monoclinic (m-phase, P₂₁/c-dielectric), orthorhombic (o-phase, Pca2₁-ferroelectric) and tetragonal (t-phase, P₄/nmc-AFE) phases depending on the Hf/Zr ratio [1]. Wei et al. [9] reported that the polarization P increases with decreasing nanoparticle (NP) size. In HZO thin films P increases significantly when the film thickness decreases [22].

Below a critical size of 30 nm pure ZrO₂ is stabilized in the tetragonal phase at room temperature which is considered as a crystallite size effect [23]. There are also reports for critical sizes for the tetragonal to monoclinic transformation between 15 - 20 nm [24] [25] [26]. The tetragonal phase of HfO₂ is stabilized for d < 3.6 - 3.8 nm [27].

The phase stability and the ferroelectricity of orthorhombic HZO ferroelectric material are theoretically investigated by Chen et al. [28] with density functional theory (DFT) computations. Oxygen defect impacts on ferroelectricity in HZO are studied using first-principles calculations by Wei et al. [29]. Also with the DFT Materlik et al. [30] have studied the ferroelectric phase of HfO₂, ZrO₂ and HZO. Batra et al. [31] revealed later that the results of Ref. [30] might not be correct. The experimentally observed stress in HZO films is tensile [32] whereas Batra et al. [31] reported a compressive stress.

The physical origin of the AFE hysteresis in ZrO₂ NPs and the ferroelectricity in HZO and Al, La doped HfO₂ NPs is still under debate. The aim of the present paper is to investigate theoretically these problems using a microscopic model and the Green’s function technique.

2. Model and Green’s Function

The properties of Zr doped HfO₂, Hf₁₋ₓZrxO₂, NPs can be described by the transverse Ising model [33]:

\[ H = -\sum_{ia} \Omega_{a} x_{ia} S_{ia}^{x} - \frac{1}{2} \sum_{iajß} J_{ij}^{aß} x_{ia} x_{jß} S_{ia}^{z} S_{jß}^{z} - \mu E \sum_{ia} S_{ia}^{z} \]  \tag{1}

The pseudo-spin operator \( S_{ia}^{z} \) characterizes the two positions of the ferroelectric unit at the lattice point \( i \). \( J_{ij} \) is the pseudo-spin interaction between the pseudo-spins at sites \( i \) and \( j \) which is positive or negative in the ferroelectric or AFE case, respectively. The dynamics of the model with strength \( \Omega \) is determined by the operator \( S_{ia}^{z} \). \( E \) is an external electric field. Here \( \alpha, \beta \) mean Zr (or Al, La) or Hf. \( x_{ia}^{Zr} = 1 \), \( x_{ia}^{Hf} = 0 \) for pure ZrO₂, and \( x_{ia}^{Zr} = 0 \), \( x_{ia}^{Hf} = 1 \) for pure HfO₂. Thus, \( x_{ia}^{Zr} + x_{ia}^{Hf} = 1 \). \( \Omega_{a} \) has two values—\( \Omega_{Zr}^{Zr} \) and \( \Omega_{Hf}^{Hf} \). The interaction term \( J_{ij}^{aß} \) has three different values—\( J_{ij}^{Zr-Zr} \), \( J_{ij}^{Hf-Hf} \) and \( J_{ij}^{Zr-Hf} \).
The Hamiltonian (1) can be written in explicit form as \( x \equiv x^{Zr} \):

\[
H = -\Omega^{Zr} \sum_i S_i^{Zr} x_i - \Omega^{Hf} \sum_i S_i^{Hf} (1 - x_i) - \frac{1}{2} \sum_{ij} J^{Zr-Zr}_{ij} S_i^{Zr} S_j^{Zr} x_i x_j \\
- \frac{1}{2} \sum_{ij} J^{Hf-Hf}_{ij} S_i^{Hf} S_j^{Hf} (1 - x_i)(1 - x_j) - \sum_{ij} J^{Zr-Hf}_{ij} S_i^{Zr} S_j^{Hf} (1 - x_i) x_j. 
\]  

(2)

We assume that

\[
\langle S_i^{Zr} x_i \rangle \approx \langle S_i^{Zr} \rangle x; \quad \langle S_i^{Hf} (1 - x_i) \rangle \approx \langle S_i^{Hf} \rangle (1 - x),
\]

where \( \langle x_i \rangle = x \). The factor \( x \) gives the concentration of the Zr ions which substitute the Hf ions, whereas \( (1 - x) \) is the concentration of the Hf ions.

The retarded Green’s function is defined as:

\[
G_i(t) = -i \theta(t) \langle [B_i(t), B_j^+] \rangle.
\]

(4)

The operator \( B_i \) stands for the set \( S_i^{Zr}, S_i^{Zr}, S_i^{Hf}, S_i^{Hf} \), where \( S^- \), \( S^+ \) are Pauli operators (\( S = 1/2 \), \( S^z = S^- S^+ \)).

The polarization \( P \) of a HZO NP is obtained as:

\[
P = \frac{1}{2N} \sum_i \tanh \left( \frac{\epsilon_i}{k_B T} \right).
\]

(5)

The mixed transverse pseudo-spin-wave excitations \( \epsilon_i \) in a given shell \( n \) are calculated from the poles of the Green’s function (4) using the method proposed by Tserkovnikov [34]:

\[
\epsilon_{ij} = \frac{1}{2} \left( \epsilon_{ij}^{11} + \epsilon_{ij}^{22} \right) \pm \frac{1}{2} \sqrt{\left( \epsilon_{ij}^{11} - \epsilon_{ij}^{22} \right)^2 + 4 \epsilon_{ij}^{12} \epsilon_{ij}^{21}},
\]

(6)

\[
\epsilon_{ij}^{11} = 2x\Omega^{Zr} \langle S_i^{-Zr} \rangle \delta_{ij} - x(1 - x) J^{Zr-Zr}_{ij} \langle S_i^{Hf} \rangle - \frac{1}{2N'} \sum_{im} (1 - x) J^{Hf-Hf}_{im} \left[ 2 \langle S_i^{Hf} \rangle - 4 \langle S_m^{Hf} \rangle \langle S_i^{Hf} \rangle \delta_{ij} \\
+ 2 \langle S_m^{Hf} S_i^{Hf} \rangle \right]/2 \langle S_i^{Hf} \rangle \delta_{ij},
\]

\[
\epsilon_{ij}^{22} = 2(1 - x) \Omega^{Hf} \langle S_i^{-Hf} \rangle \delta_{ij} - x(1 - x) J^{Zr-Hf}_{ij} \langle S_i^{Zr} \rangle \\
- \frac{1}{2N'} \sum_{im} x J^{Zr-Zr}_{im} \left[ 2 \langle S_i^{Zr} \rangle - 4 \langle S_m^{Zr} S_i^{Zr} \rangle \delta_{ij} \\
+ 2 \langle S_m^{Zr} S_i^{Zr} \rangle \right]/2 \langle S_i^{Zr} \rangle \delta_{ij},
\]

\[
\epsilon_{ij}^{12} = 2x\Omega^{Zr} \langle S_i^{Zr} \rangle \delta_{ij} \langle S_i^{Zr} \rangle \delta_{ij} \\
- \frac{1}{2N'} \sum_{im} x J^{Zr-Zr}_{im} \langle S_m^{Zr} S_i^{Zr} \rangle \langle S_i^{Zr} \rangle \delta_{ij},
\]

\[
\epsilon_{ij}^{21} = 2(1 - x) \Omega^{Hf} \langle S_i^{Hf} \rangle \delta_{ij} \langle S_i^{Hf} \rangle \delta_{ij} \\
- \frac{1}{2N'} \sum_{im} (1 - x) J^{Hf-Hf}_{im} \langle S_m^{Hf} S_i^{Hf} \rangle \langle S_i^{Hf} \rangle \delta_{ij},
\]

\[
\langle S_i^{Zr} \rangle = \frac{1}{2N'} \sum_i \epsilon_{ij} \tanh \frac{\epsilon_{ij}}{2k_B T},
\]

(6)
\[ \langle S_{ij}^{HH} \rangle = \frac{1}{4N'} \sum_j \epsilon_{ij}^{22} \tanh \left( \frac{\epsilon_{ij}}{2k_BT} \right), \]
\[ \langle S_{ij}^{Zr} \rangle = \langle S_{ij}^{Zr} \rangle = \frac{1}{4} \epsilon_{ij}^{12} \tanh \left( \frac{\epsilon_{ij}}{2k_BT} \right), \]
\[ \langle S_{ij}^{Hf} \rangle = \langle S_{ij}^{Hf} \rangle = \frac{1}{4} \epsilon_{ij}^{21} \tanh \left( \frac{\epsilon_{ij}}{2k_BT} \right), \]

where \( N' \) is the number of lattice sites.

### 3. Numerical Results and Discussion

Our NP has an icosahedral symmetry. A certain Hf-spin is fixed in the center of the particle and all other spins are included into shells \( n \). \( n = 1 \) denotes the central spin and \( n = N \) represents the surface shell. Strain effects on the surface of the NP change the number of next neighbors on the surface and reduce the symmetry. Therefore the pseudo-spin interaction constants can take different values on the surface and in the bulk, denoted with the index "s" and "b", respectively. Moreover, \( J \) is proportional to the inverse of the distance between two nearest spins, \( i.e. \) of the lattice parameters.

In order to clarify the AFE behavior in ZrO\(_2\) we will firstly consider the electric field dependence of the polarization in the tetragonal phase of a ZrO\(_2\) NP with \( N = 3 \) shells for \( T = 300 \) K. Materlik et al. [30] showed that AFE behavior of pure ZrO\(_2\) thin films is observed after stabilization of the tetragonal phase for \( d < 35 \) nm. Using the lattice parameters for ZrO\(_2\) from Ref. [30] in the tetragonal phase \( a = 5.06, b = 5.18, c = 5.06 \) (Å) we obtain the following model parameters: \( J = -535 \) K, \( \Omega = 20 \) K, \( J_s = 1.6J_b \), \( \Omega_s = 0.8\Omega_b \). The tetragonal structure is PbZrO\(_3\) (PZO)-like AFE one, the electric dipoles are aligned antiparallel to their nearest neighbors—analogous to the magnetic moments in antiferromagnetic materials, therefore, we chose \( J < 0 \). The results are presented in Figure 1, curve 1. This AFE behaviour is in agreement with the experimental data of Ref. [2] [7] [30] [35] [36]. The polar AFE phase exists under a certain magnitude of the external electric field. When \( T \) increases, above a critical temperature \( T_{crit} \) only paraelectric properties can be observed. So, we can conclude, that one explanation of the origin of the AFE-ty in ZrO\(_2\) NPs is a phase transformation from a tetragonal to an orthorhombic phase induced by an external electric field which is an intrinsic behavior. This is confirmed by the ab-initio study of Reyes-Lillo et al. [7].

Now we will study the electric behaviour for different electric field, temperature, crystal phase and size of Hf\(_{1-x}\)Zr\(_x\)O\(_2\) NPs. By doping of ions with different radius appear different strains which give rise to additive changes (increasing or decreasing) of the pseudo-spin interaction constant \( J_d = J(r_i - r_j) \) in the defect sizes (denoted as \( J_d \)) compared to the undoped samples. The radius of the tetravalent Zr ion (86 pm) is a little larger than that of the Hf ion (85 pm), \( i.e. \) there is a small tensile strain \( (J_d < J_b) \), in agreement with the experimental data.
of Shiraishi et al. [32] for HZO thin films, whereas Batra et al. [31] reported a compressive stress.

The electric field dependence of the polarization in Hf$_{1-x}$Zr$_x$O$_2$ NPs is shown in Figure 1, curves 1-3. ZrO$_2$ and HfO$_2$ have almost equivalent crystal phases, with almost identical lattice parameters. It is seen that pure HfO$_2$ (Figure 1, curve 3) in the monoclinic phase is a linear dielectric with no notable nonlinear response of the polarization curve. As the ZrO$_2$ content increases, the $P(E)$ curve reaches its maximum value for doping concentration $x = 0.5$ (Figure 1, curve 2). ZrO$_2$ displays an AFE-behavior at high fields, where the polarization response becomes non-linear with hysteresis (Figure 1, curve 1). In the non-polar state where the polarization $P = 0$ we obtain a linear dependence in the polarization $P(E)$ below the Curie-Weiss temperature $T_0$ (curve 1). Above $T_0$ with increasing temperature, when the temperature is between $T_0$ and $T_C$ (the ferroelectric phase transition Curie temperature), $T_0 < T < T_C$, there is a polar state, and the hysteresis loop is similar to the ferroelectric one (curve 2, $x = 0.5$). In this temperature region the crystal is in the orthorhombic phase where the electric dipoles are aligned parallel to their nearest neighbors, i.e. $J > 0$. Using the lattice parameters for HZO from [30] $a = 5.06$, $b = 5.14$, $c = 5.27$ Å we have calculated the following model parameters: $J_d = 505$ K, $\Omega_d = 20$ K. We assume $J_z = 1.6J_y$, $\Omega_z = 0.8\Omega_y$. The begin of the polar ferroelectric state corresponds to the monoclinic to orthorhombic phase transformation ($J > 0$). A similar ferroelectric hysteresis curve is obtained also for $x = 0.4$. This ferroelectric behaviour of HZO nanostructures is reported in Ref. [1] [9] [10] [28] [35] [37] [38]. Above $T_C$ in the temperature interval $T_C < T < T_1$, the polar phase becomes to be metastable. Because of this the hysteresis curve shows a ferroelectric behavior. For $T_1 < T < T_4$ (the AFE phase transition temperature), we observe the AFE-like state ($J < 0$) (Figure 1, curve 1), typical for pure ZrO$_2$ NP ($x = 1$), the crystal phase is tetragonal. The polar phase cannot be induced when the temperature $T$ is around $T_N$ even under an external electric field.
field. For temperatures higher than the AFE transition temperature $T_N$ in the cubic phase remain only paraelectric properties. The monoclinic phase decreases with increasing the ZrO$_2$ content. It can be seen from Figure 1 that the remanent polarization $P_r$ is zero for pure HfO$_2$ and ZrO$_2$. $P_r$ reaches at doping concentration $x = 0.5$ its maximum value.

In Figure 2 is shown the composition dependence $x$ of the remanent polarization $P_r$ in HZO NPs. For $x = 0$, for pure HfO$_2$, $P_r = 0$. With increasing of $x$ $P_r$ increases, reaches at $x = 0.5$ its maximum value and then in pure ZrO$_2$, $x = 1$, $P_r$ is again zero. The experimentally reported maximum value of the remanent polarization $P_r$ is in the interval $x = 0.5 - 0.6$ [1] [37] [38] [39]. Mueller et al. [1] have shown that for $x = 0.5$ the ferroelectric phase is stable between 100 - 400 K. In this temperature interval HZO thin films for $x = 0.7$ show a transition to a double-loop hysteresis, whereas pure ZrO$_2$ thin films remain in this double-loop hysteresis starting from low temperatures.

To completely explain the ferroelectric-phase stability in HZO NPs, we want to focus now on the size dependence of the polarization $P$ in HZO NPs which is demonstrated in Figure 3. It must be noted, that the distance between the shells is $\approx$10 Å, i.e. we consider NPs with $N = 2 - 10$, i.e. with size of 2 - 50 nm. It can be seen from Figure 3 that $P$ increases with decreasing NP size, i.e. the ferroelectric properties disappear in large NPs, thick films and bulk materials, in agreement with the experimental data [9] [18] [40] [41]. This behaviour shows that the m-phase (non-ferroelectric), which is absent or very rarely found in the smallest NPs, increases with increasing size whereas the ferroelectric rhombohedral phase is stabilized by the existing surface strain. To conclude, we show that strain can be used in very small NPs of HZO to induce a ferroelectric phase, with a large polarization $P$ and remanent polarization $P_r$. Park et al. [18] reported also that the o-phase increases with decrease thickness in HZO film. Climia et al. [42] show that oxygen vacancies can reduce drastically the polarization reversal barriers.

Finally, we will consider the effect of different ion doping on the electric properties of HfO$_2$ NPs. Variations of Al and La doping concentration influences the crystallographic structure of the NP and therefore the polarization. The insertion of a 3+ (Al) or 4+ (La) cation in the HfO$_2$ lattice leads to the appearance of oxygen vacancies to keep the charge balance. The radius of the Al ion (67.5 pm) is smaller compared to the ionic radius of the Hf ion (85 pm) (i.e. in our model we have $J_d > J_b$). Figure 4 shows the remanent polarization $P_r$ of the HfO$_2$ NP as a function of the Al-concentration (Figure 4, curve 1). The $P_r$ value increases firstly by increasing the Al concentration starting at $x = 0.01$. The maximum ferroelectric polarization is reached at $x = 0.03$ Al, followed by an AFE region between $x = 0.04 - 0.06$ Al. At higher Al-concentrations the doped HfO$_2$ NP behaves as a paraelectric material. Mueller et al. [16] showed that the ferroelectricity is related to the non-centrosymmetric orthorhombic phase which is stabilized at low Al doping concentration.
Figure 2. The remanent polarization of Hf$_{1-x}$Zr$_x$O$_2$ NPs for $J_s = 1.6J_s$, $\Omega_s = 0.8\Omega_s$, $J_d = 0.8J_s$, $\Omega_d = 1.2\Omega_s$, and different Zr concentration $x$.

Figure 3. Size dependence of the polarization of HZO NPs for $J_s = 1.6J_s$, $\Omega_s = 0.8\Omega_s$.

Figure 4. Doping concentration dependence of the remanent polarization $P_r$ of a HfO$_2$ NP for doping with: (1) Al ($J_d = 605$ K); (2) La ($J_d = 451$ K) ions.

A similar behavior for the Al concentration dependence of the dielectric constant in HfO$_2$ thin films is reported by Yoo et al. [43].

The electric properties of La doped HfO$_2$ NPs are also studied. The radius of the La ion (117.2 pm) is larger compared to the ionic radius of Hf (85 pm) (this means $J_d < J_d$). Batra et al. [31] have shown that La doping stabilizes the or-
It can be seen from Figure 4, curve 2, that compared to the Al doping, the ferroelectric region for the La doped HfO$_2$ NP which starts at higher $x$ value, $x \approx 0.05$, is shifted to higher doping concentrations and is broader due to the larger ionic radius of the La ion. In addition, the remanent polarization $P_r$ is larger for the La doping than for the Al doping (Figure 4, curves 2 and 1). The maximum value of $P_r$ is observed for $x = 0.14$. Schroeder et al. [44] reported also that La shows the highest remanent polarization values of all ion doped HfO$_2$ thin films. Our results confirm the experimental data of Ref. [15] [44] for Al and La doped HfO$_2$ thin films. It must be noted that the observed here maximum values of the ion doped HfO$_2$ NPs are comparable to the values reported for Al-doped ($x = 0.025 - 0.03$ [43] [44] and for La-doped ($x = 0.12$ [16]) HfO$_2$ epitaxial thin films.

4. Conclusions

The properties of HZO are theoretically investigated till now with DFT computations. In this paper for the first time is used the microscopic transverse Ising model in order to clarify the physical origin of the AFE hysteresis in ZrO$_2$ NPs and the ferroelectricity in HZO and Al, La doped HfO$_2$ NPs which is still under debate. Therefore, we have investigated the dependence of the polarization $P$ in ion doped HfO$_2$ NPs on electric field, dopant concentration $x$, size and temperature. Different from the DFT we study the behavior of the material at finite temperatures. To that aim we use a Green’s function technique for $T \neq 0$. It can be concluded that the change in the polarization $P_r$ with respect to the doping concentration in HfO$_2$ NPs is the result of the transformation of the crystalline phase due to the internal stress, of the appearance of an orthorhombic phase exhibiting ferroelectricity. Moreover, we try to clarify some discrepancies in the literature, for example about the appearing strain in HZO NPs (it is tensile and not compressible).

We obtain that pure ZrO$_2$ displays in the tetragonal phase an AFE-behavior ($J < 0$) at high fields inducing a t-o phase transformation. Pure HfO$_2$ is a linear dielectric in the monoclinic phase. With increasing the ZrO$_2$ content in HZO the hysteresis loop is consistent with that for ferroelectric materials ($J > 0$). $P_r(x)$ shows a maximum for $x = 0.5$. For $x = 0$ and $x = 1$ $P_r = 0$. It is shown that the properties of these three compounds—ZrO$_2$, HfO$_2$ and HZO—are changed with ion doping and size. The polarization $P$ increases with decreasing NP size, i.e. the non-ferroelectric m-phase disappears with decreasing size. We show that strain can be used in very small NPs of HZO to induce a ferroelectric phase with large $P$ and $P_r$.

The influence of Al and La doping on $P_r(x)$ in HfO$_2$ NPs is also studied. Stress due to the different ionic radii of the doping ions compared to the host ones (which cause different pseudo-spin interaction constants in the defect states) as well as the distribution of oxygen vacancies play a key role for the phase transformations in doped HfO$_2$ nanostructures. Both remanent polarizations...
have a maximum value at $x = 0.03$ and $0.14$, respectively. The $P_r$ curve for La doping is shifted to higher doping concentrations and is broader due to the larger radius of the La ion. Moreover, $P_r$ is larger for La-doped compared with that of Al-doped HfO$_2$ NPs.

There are some differences in the electric properties of ion doped HfO$_2$ and ZrO$_2$ nanostructures [43] [45] [46]. For example Yoo et al. [43] observed that the dielectric constant in Al doped HfO$_2$ thin films undergoes a maximum whereas in Al doped ZrO$_2$ thin films it decreases. The electric properties of ion doped HZO and ZrO$_2$ NPs will be considered in the next paper.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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