First-principles study of manganese-stabilized hafnia

I.V. Maznichenko a, S. Ostanin b,*, A. Ernst b, I. Mertig a

a Martin-Luther-Universität Halle-Wittenberg, Institut für Physik, D-06099 Halle (Saale), Germany
b Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle (Saale), Germany

1. Introduction

For the last decade, a rich expertise has been built up on how to integrate ferromagnetism into semiconductor materials [1] and, therefore, to advance toward novel spintronics devices, which possess the ability both to generate and manipulate electronic spin at room temperature and above. As well as a high Curie temperature, $T_C$, a useful attribute for any appropriate spintronics material is a large difference between the majority and minority spin density of states at the Fermi energy so that it can act as the source of a spin injection. In the best-characterized dilute magnetic semiconductors (DMS), such as Ga(Mn)As, a variety of factors continue to keep the measured Curie temperature below 173 K [2]. For this reason and in the wake of theoretical predictions [3] that ZnO should become ferromagnetic when doped with a transition metal, most of the experimental studies are currently focusing on magnetic oxides. So far, the room temperature ferromagnetism was experimentally detected in thin films of cobalt doped TiO$_2$ [4], HfO$_2$ [5,6] and Cr-doped In$_2$O$_3$ [7]. However, the picture here is also complicated. For instance, Zn$_{1-x}$Mn$_x$O is not ferromagnetic unless additional hole doping is provided [3]. Regarding the Co-doped TiO$_2$ and HfO$_2$ ceramics, their magnetic properties are heavily dependent on the structure and defects [8,9]. The magnetic oxide-based materials suitable for spintronics are scarce, indeed. They must be easy to fabricate, stable, and compatible with conventional semiconductors and metals. Ostanin and coworkers [10] have recently predicted that Mn-stabilized cubic zirconia to be half-metallic and ferromagnetic at 500 K. ZrO$_2$ is well known both as a catalyst and as an imitation diamond. Besides, ZrO$_2$ is one of few high dielectric constant and wide-gap insulators and is known to be thermally stable on SiGe and, therefore, it meets the criteria of spintronics. In ZrO$_2$, the concentration of manganese, $x_{\text{Mn}}$, can exceed 40% while the theoretically estimated $T_C$ increases with $x_{\text{Mn}}$ above room temperature when $x_{\text{Mn}} > 20\%$ [10]. For experimental verification, Clavel et al. [11] have synthesized the 5% Mn-doped ZrO$_2$ nanoparticles. It was found that the coexistence of Mn(II) and Mn(III), tends to antiferromagnetic interactions and that a higher oxidation state is more likely to support ferromagnetism. The theory [10] anticipates that the presence of Mn(IV) in Mn–ZrO$_2$ can keep $T_C > 300\,\text{K}$. In this paper, from the basis of state-of-the-art ab initio electronic structure calculations we propose that Mn-doped cubic HfO$_2$ matches extremely demanding spintronics criteria. Pure HfO$_2$ is being investigated as a high dielectric constant insulating gate for field effect transistor technology. Although the upper limit of solubility of manganese in hafnia is unknown, it might be compatible with that of Mn–ZrO$_2$. The fundamental nature of DMS and magnetic oxides is far from being well understood. We believe that magnetically doped ceramics such as Mn–HfO$_2$ provide an ideal opportunity for the study of ferromagnetism associated with the carrier mediated half-metallicity.

2. Calculation details

Our propositions are based on extensive density functional theory calculations, within the local density approximation (LDA) to the exchange-correlation energy. In principle, ab initio calculations should result in a parameter-free picture, and the conventional LDA has been proven reliable in predicting ground-state properties of metallic systems and semiconductors. There are numerous applications of the LDA to calculations of $T_C$ in DMS (for a recent review, see Ref. [12] and references therein).
For DMS, a key issue is the energy position of the 3d states of a magnetic impurity. When the LDA tends to underestimate the localized character of the magnetic impurity states, the \textit{ab initio} calculations are not entirely successful in describing all experimental findings and, therefore, much work is required to properly deal with the on-site Coulomb correlations in the framework of density functional theory. In particular, LDA+U \cite{13} and the self-interaction-corrected (SIC) local spin-density approaches \cite{14} can improve the picture of DMS \cite{15,16}. For Mn-doped hafnia, the use of LDA was motivated by our previous experience with LDA+U calculations for Mn-doped zirconia \cite{10}, which demonstrate that the correlation effects cannot significantly change the magnetic properties of the material.

We use the multiple scattering Korringa–Kohn–Rostoker (KKR) theory, with the coherent-potential approximation (CPA) \cite{17} to describe the motion of the electrons through the system. The CPA handles the location of the randomly distributed magnetic impurities. Alternatively, the effect of short-range order of impurities is studied using the 12-atom fluorite \textit{Hf}_3\textit{Mn}_1\textit{O}_8 supercell, shown in Fig. 1, which corresponds to the 25\% Mn–HfO$_2$ composition. The $T_C$ value is extracted from the energy difference $\Delta E$ between total energies of the paramagnetic and ferromagnetic solutions: $k_B T_C = 2/3 \Delta E / x_{\text{Mn}}$. For the supercell modeling the 25\% Mn–HfO$_2$ composition we estimated interatomic Heisenberg exchange parameters by using magnetic force theorem \cite{18} within a supercell approach. The estimated Curie temperature in the mean field approximation is 682 K and in a good agreement with the CPA result. This indicates that the CPA approximation is the appropriate tools to study the electronic structure of this material. Furthermore, the obtained exchange parameters were used for the calculation of the Curie temperature within the RPA \cite{19,20}. The RPA is based on the Green function formalism for magnons and provides more reliable critical temperatures. For the 25\% Mn–HfO$_2$ composition we found the RPA $T_C$ to be 578 K. Since the RPA underestimates usually the critical temperature, we expect the experimental $T_C$ to be between the RPA and mean field results.

Previously, Coey et al. \cite{6} have reported that thin films of HfO$_2$ produced by pulsed-laser deposition on sapphire, ytttria-stabilized ZrO$_2$ and silicon substrates show ferromagnetic magnetization curves with Curie temperature of the order of 400 K. Oxygen vacancy is the defect which is known to be presented in doped oxides. Until recently, the effect of the oxygen vacancy defects in ceramics on their possible high-$T_C$ ferromagnetism was not studied. Here, we model the presence of oxygen vacancy in Mn–HfO$_2$ using the CPA. The inset of Fig. 2 illustrates the dependence of Curie temperature of 25\% Mn–HfO$_2$ upon the number of oxygen vacancies $\delta$. It is shown that the system is a room temperature ferromagnet when $\delta<1/8$. It means that to keep $T_C$ above 300 K the upper limit for the O vacancies accommodated in Mn–HfO$_2$ is one vacancy per two manganese atoms. Formally, it corresponds to Mn 3+ oxidation state. If $x_{\text{Mn}}<0.25$ then the O vacancy limit becomes smaller. We suggest that the coexistence of Mn(IV) and Mn(III) in Mn-doped HfO$_2$ is essential for the issue of high $T_C$.

### 3. Results and discussion

Using the KKR-CPA technique we computed, first, the equilibrium volume for several compositions of \textit{Hf}_1-x\textit{Mn}_x\textit{O}_2 between 0<x_{\text{Mn}}<0.5. The volume decreases with increasing $x_{\text{Mn}}$. In Fig. 2, we plot the calculated $T_C$ versus $x_{\text{Mn}}$. $T_C$ increases to well above room temperature when $x>5\%$. For Mn–ZrO$_2$, the similar effect was found \cite{10}.

Surprisingly, in the case of Mn–HfO$_2$ we find that its Curie temperature increases more rapidly with the Mn concentration than that estimated for Mn-doped zirconia. In Mn–HfO$_2$ at $x=0.25$ the estimated $T_C$ is 694 K compared to 660 K which is predicted for Mn–ZrO$_2$. At this concentration we calculated the interatomic Heisenberg exchange parameters by using magnetic force theorem \cite{18} within a supercell approach. The estimated Curie temperature in the mean field approximation is 682 K and in a good agreement with the CPA result. This indicates that the CPA approximation is the appropriate tools to study the electronic structure of this material. Furthermore, the obtained exchange parameters were used for the calculation of the Curie temperature within the RPA \cite{19,20}. The RPA is based on the Green function formalism for magnons and provides more reliable critical temperatures. For the 25\% Mn–HfO$_2$ composition we found the RPA $T_C$ to be 578 K. Since the RPA underestimates usually the critical temperature, we expect the experimental $T_C$ to be between the RPA and mean field results.
Another important property of magnetic oxide to be appropriate for spintronics is its half-metallicity. Our calculations clearly demonstrate that Zr\textsubscript{0.125}Mn\textsubscript{0.875}O\textsubscript{2} can obey such a behavior. Fig. 3 shows the electronic density of states (DOS) calculated for the 25% Mn–HfO\textsubscript{2} composition, using both the supercell and CPA approaches. The spin-resolved DOS shows the metallic character for majority spin (Fig. 3a) and the band gap of ~1 eV for minority spin (Fig. 3b). Hence, the 25% Mn–HfO\textsubscript{2} as well as Mn-stabilized zirconia can be half-metallic at 0 K.

The lowest unoccupied electronic states for the minority spin channel of 25% Mn–HfO\textsubscript{2} are composed by the Mn 3d states, namely, the \(e_g\) and \(t_{2g}\) subbands, which are separated from each other by the crystal field. Because of well known strong localization of the \(e_g\) and \(t_{2g}\) states, it is unlikely that the half-metallic behavior of Mn–HfO\textsubscript{2} can be significantly affected at the finite temperatures. This makes this material very appealing.

The Mn magnetic moments calculated for \(x_{\text{Mn}} = 0.25\) using the CPA and supercell approaches are 3.35 and 3.41 \(\mu_B\), respectively. The total magnetization calculated per cell shows rather different values: 2.37 \(\mu_B\) in the case of CPA and 2.99 \(\mu_B\) when the 12-atom supercell is used. Hence, the induced magnetic moments are directed antiparallel to the Mn magnetic moment. It is clear that the widely used local CPA cannot properly treat the long-range interactions, which can play an important role in the system. The Mn magnetic moment weakly depends on \(x_{\text{Mn}}\) while it notably increases with the O vacancy concentration \(\delta\). For \(x_{\text{Mn}} = 0.25\) and \(\delta = 0.25\) we obtain 4.21 \(\mu_B\) on the Mn site and 4.69 \(\mu_B\) per cell. It seems that at the presence of unrelaxed oxygen vacancy in Mn–HfO\textsubscript{2} some induced magnetic moments being aligned parallel to the Mn moment, contribute to the total magnetic moment. The sign of the O magnetic moments is negative between 0<\(\delta<0.5\) and then it vanishes at \(\delta = 0.5\) while the Mn moment adopts its integer value of 4 \(\mu_B\). However, in search for high-\(T_c\) Mn-doped oxide the researches must keep the number of oxygen vacancies below \(b\).

**Fig. 3.** (a), (b) Spin-resolved DOS of Hf\textsubscript{0.75}Mn\textsubscript{0.25}O\textsubscript{2}, calculated using the supercell and CPA approaches. The DOS of pure HfO\textsubscript{2} is shown for comparison. (c)-(e) The corresponding site-resolved DOS curves.

### 4. Summary

From the ab initio basis of our work we anticipate that Mn-stabilized cubic hafnia, Hf\textsubscript{0.75}Mn\textsubscript{0.25}O\textsubscript{2}, can become a room temperature half-metallic ferromagnet when \(x_{\text{Mn}}>0.2\) and \(\delta<0.125\). This means that the Mn/Hf ratio is larger than 1:5 and, simultaneously, the ratio between the number of possible oxygen vacancies and Mn impurities must be less than 1:2, providing the coexistence of Mn(IV) and Mn(III) in the system. Thus, we find the key electronic and structural factors for optimal magnetic doping of Mn–HfO\textsubscript{2}.

### Acknowledgement

This work was supported from the DFG SFB 762 “Funktionalität Oxidischer Grenzflächen”.

### References


