

Pseudopotential study of PrO<sub>2</sub> and HfO<sub>2</sub> in fluorite phaseJ. Dąbrowski<sup>1,a</sup>, V. Zavodinsky<sup>a,b</sup>, A. Fleszar<sup>c</sup><sup>a</sup>IHP, Im Technologiepark 25, D-15236 Frankfurt(Oder), Germany<sup>b</sup>Institute for Automation and Control Processes, 5 Radio str., Vladivostok 690041, Russia,<sup>c</sup>Würzburg University, Würzburg, Germany**Abstract**

Praseodymium and hafnium oxides are prospective candidates to substitute SiO<sub>2</sub> in decanano MOSFET transistors. We report first *ab initio* pseudopotential band structure calculations for these materials. We find that fluorite phases of PrO<sub>2</sub> and HfO<sub>2</sub> have similar electronic structures. The important difference is a narrow subband forming the conduction band bottom in PrO<sub>2</sub> but absent in HfO<sub>2</sub>. Electrons in this *f*-type subband have large masses. This explains why ultrathin epitaxial Pr oxide films have low leakage in spite of a relatively small conduction band offset ( $\sim 1$  eV) between the oxide and the Si substrate.

**1 Introduction**

Scaling of CMOS [1-4] requires MOSFET gate oxide equivalent thicknesses  $t_{eq} < 1.5$  nm for channel lengths below 100 nm. But a 1.5 nm thick SiO<sub>2</sub> is leaky and unreliable. It fails because direct tunneling current depends exponentially on the insulator physical thickness  $t$ , determined in turn by scaling rules for gate capacitance  $C$ . Since  $t = K/C$ , where  $K$  is the dielectric constant, one can increase the film thickness  $n$  times by replacing SiO<sub>2</sub> by an insulator with  $K$  which is  $n$  times larger than that of SiO<sub>2</sub> ( $K$  of SiO<sub>2</sub> is  $\sim 4$ ). This new dielectric should have  $K$  above  $\sim 20$  but, for practical reasons [6], lower than  $\sim 40$ . Other key parameters determining the leakage current are: band offsets with respect to Si, and electron and hole effective masses. The purpose of this work is to obtain fundamental data on band structures of important candidates for epitaxial high- $K$  dielectrics: Hf and Pr oxides [5].

These oxides can be produced in a number of

crystallographic structures, with unit cells of various shapes. Si(001) substrate imposes symmetry constraints on the epitaxial film (Fig. 1), so that it grows in an orthorhombic structure closely related to the fluorite structure. The latter is very simple (Fig. 1, top) and therefore suited for exploratory calculations as those presented here.

We report results for HfO<sub>2</sub> and PrO<sub>2</sub> in the fluorite structure, obtained within the Density Functional Theory (DFT) by the pseudopotential *ab initio* fhi97md package [7]. RPA dielectric function of HfO<sub>2</sub> has been computed from the LDA bands and quasiparticle calculations were done within the GW approximation [12, 13].

**2 Computational details**

We used the *ab initio* pseudopotential plane wave code fhi97md [7], extended for atoms with valence electrons of *f* type. We applied Local Density Approximation (LDA) for the exchange and correlation energy [8, 9] and nonlocal pseudopotentials [10, 11]. Most of the results presented

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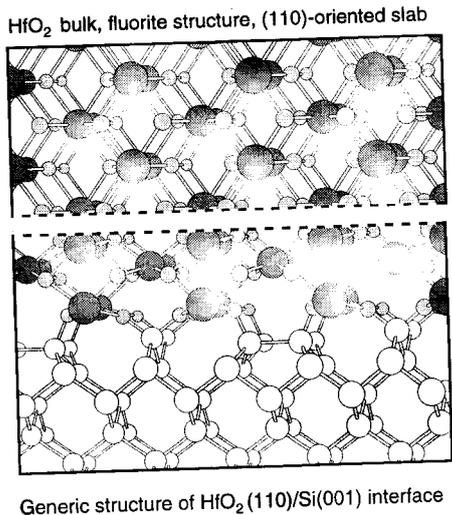


Figure 1: Si(001) substrate imposes symmetry constraints on the film. Epitaxial praseodymium and hafnium oxide layers (bottom) have structure related to fluorite (top) and a (110) orientation [14, 15].

are obtained with 40 Ry cutoff for plane waves and with two special  $k$ -points:  $(1/4, 1/4, 1/4)$  and  $(3/4, 1/4, 1/4)$ . Tests have been performed for 10 and 20  $k$ -point schemes and for energy cutoffs between 30 Ry and 60 Ry. We also verified the influence of a Generalized Gradient Correction [16] and Nonlinear Core Correction [17].

An important part of this work is the construction of a pseudopotential for Pr atoms. The electronic configuration of Pr is  $[\text{Xe}]4f^3 5d^0 6s^2$ . We split these electrons into core and valence electrons. As core electrons we take  $[\text{Xe}]4f^1$ , but without  $5p$  electrons which we treat as belonging to the valence group. This procedure is consistent with suggestions to divide the  $f$ -electrons of Pr into localized and delocalized groups [18] and with strong  $f$ - $d$  superposition of Pr valence states [18, 19, 20]. The core density of states is computed for a given excited configuration of the valence electrons  $4f^x 5p^6 5d^{2-x+y} 6s^{2-y}$  of the free atom and kept frozen during calculations for the solid. The valence electrons are confined to their excited configuration when the pseudopotential is created, but allowed to fully relax in the solid.

We found that reliable pseudopotentials can be obtained with  $p$  locality and  $0.2 < x < 0.5$  and with  $y = 0$ . Other choices resulted in pseudopo-

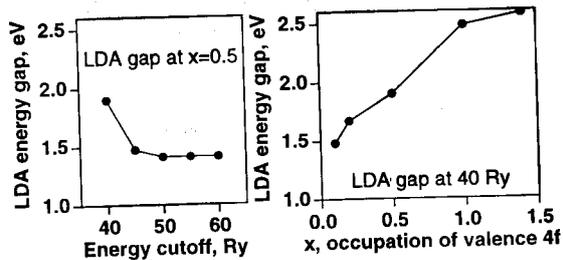


Figure 2: Left: Energy cutoff dependence of the band gap of PrO<sub>2</sub>. LDA, 40 Ry,  $x=0.5$ . Right: Dependence of LDA band gap on the pseudopotential at 40 Ry.

tentials with ghost states [21] at energies comparable with the conduction band energies of PrO<sub>2</sub>. These ghosts (nonphysical eigenstates) are produced by the specific form of  $s$  nonlocality in the pseudopotential. They disappear when the  $s$  term is chosen as local. However,  $s$ -local pseudopotentials cannot be transferred to the PrO<sub>2</sub> environment: the computed lattice constant  $a_0$  of PrO<sub>2</sub> becomes then too large. On the other hand,  $a_0$ , obtained with any higher  $l$  term chosen as local is about 2% less than experimental, independently of the presence of ghost states above the valence band. Overbinding of this magnitude is typical for LDA. The computed bulk modulus is about 250 GPa, as expected for hard ceramics.

The band structure of PrO<sub>2</sub> depends somewhat on the choice of the pseudopotential (Fig. 2, right), but this dependence is mostly due to relatively rigid shift of the conduction bands. As the valence band and the density of occupied states are only weakly affected, the computed bulk modulus is not strongly affected by the choice of the pseudopotential. Similarly, the main effect of increasing the plane wave cutoff above 40 Ry is a certain reduction of the band gap (Fig. 2, left). Since it is well known that LDA underestimates band gaps (cf. the next Section and Fig. 2, top), we will use the  $x=0.5$  pseudopotential and 40 Ry cutoff, which produce the widest band gap among the pseudopotentials free from ghost states.

### 3 Discussion of results

This Section compares *ab initio* electronic structures computed for HfO<sub>2</sub> and PrO<sub>2</sub>. First, we consider DFT (LDA) and quasiparticle-corrected

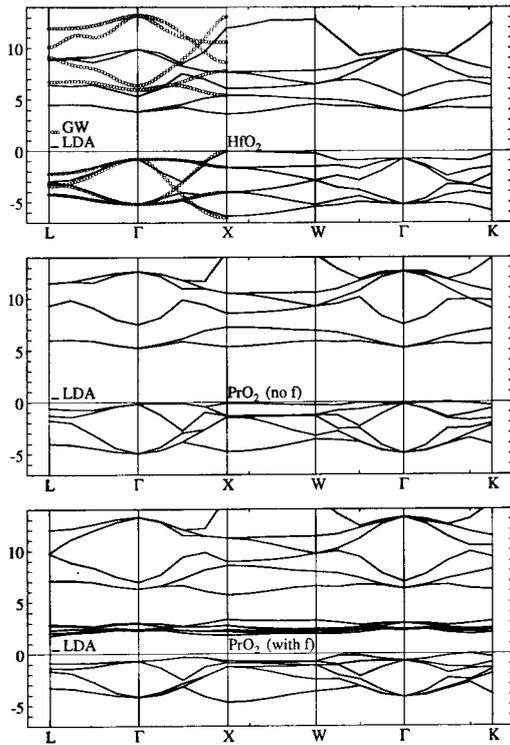


Figure 3: Band structures of Hf and Pr dioxide, fluorite phase. Energy zero is at top of the valence band. Top: HfO<sub>2</sub> computed with LDA (solid lines) and true excitation energies obtained with GW (circles). LDA yields a good valence band and a principally correct structure of the conduction band, but the gap width is underestimated. Mid: PrO<sub>2</sub> computed with no *f* states; essentially the same as HfO<sub>2</sub>. Bottom: PrO<sub>2</sub> computed with *f* states; a narrow *f*-band is formed at the CB bottom.

(GW) band structures of HfO<sub>2</sub>. In contrast to DFT, which is designed to yield the correct electron density and total energy of the electronic ground state, the quasiparticle correction formalism aims for realistic electronic excitation energies. Second, we compute LDA band structures of PrO<sub>2</sub> with and without the contribution from *f* electrons and discuss differences to the HfO<sub>2</sub> case. Third, we address implications for the gate leakage currents of transistors with gate dielectrics containing high Pr concentration. Finally, we mention the effect of pressure on PrO<sub>2</sub> band gap.

An interesting feature of the electronic structure of HfO<sub>2</sub> (Fig. 3, top) is that the valence band (VB) top is displaced from the Brillouin

zone (BZ) center towards the BZ edge at X. This result is independent of the choice of pseudopotentials and of numerical conditions (plane wave basis set, BZ sampling scheme) and is seen also in GW excitation energies. We obtain a direct band gap close to X; its width is about 3.5 eV in LDA. Quasiparticle correction (GW) opens the forbidden gap to nearly 5.5 eV and changes some distances between the conduction band (CB) states, but the overall CB structure remains the same as in LDA. The VB structure is much less affected.

The LDA band structure of PrO<sub>2</sub> computed with neglect of Pr *f* electrons (Fig. 3, mid) resembles that of HfO<sub>2</sub>. The main difference is that the VB top becomes flatter, resulting in increased hole effective masses. Inclusion of *f* electrons (Fig. 3, bottom) leads to narrowing of the VB and to more pronounced maxima in the VB top. They remain outside the BZ center but are located further away from the BZ edge than for HfO<sub>2</sub>.

But the most important effect is the appearance of a narrow subband under the CB bottom. This band is responsible for a much smaller forbidden gap in PrO<sub>2</sub> when compared to that of HfO<sub>2</sub>. It is built mostly of *f*-states of Pr atoms and is rather narrow, that is, quite localized.

Does this *f*-band remain at the CB bottom also in the quasiparticle spectrum, i.e., in the real spectrum of electronic excitation energies? We are not yet able to answer this question by a GW calculation. But we performed a simple estimate of the contribution to the difference between the true excitation energy and the LDA eigenvalue from the LDA self-interaction term. This contribution can be large because the band is quite localized. To estimate the correction, we computed the band structure of a degenerate material with one conduction electron per unit cell. The *f* states did move close to the rest of the CB, but still forming a separate band below these other states. Therefore, we have reasons to believe that the CB bottom of PrO<sub>2</sub> is indeed built of *f* states.

This result has a consequence for our understanding of leakage currents through some transition metal oxide dielectrics. Note that the band gap of a lanthanide row (i.e., *f*-electron) transition metal oxide (PrO<sub>2</sub>) is considerably smaller than that of a *d*-electron transition metal oxide (HfO<sub>2</sub>) where *f* electrons play little role. Recent experiments [22] indicate that the actual band gap of a Pr<sub>2</sub>O<sub>3</sub>/Si(001) film (which has an atomic

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structure similar to that of  $\text{PrO}_2$ ) is only 2-3 eV. But from the point of view of the tunneling current, this narrowing of the band gap and, most probably, the corresponding reduction of the CB offset with respect to silicon, is compensated by large electron masses in the oxide CB.

Finally, we note that the results reported here have been obtained for bulk material. An epitaxial film is under high strain caused by lattice mismatch to the substrate. We have not yet computed the influence of the epitaxial, lateral stress on the electronic structure of the oxide. But we observed that the influence of hydrostatic stress on  $\text{PrO}_2$  band gap is not dramatic: when the lattice constant is varied from 5.1 to 5.5 Angstroms, the band gap decreases only by 0.4 eV. This means that a lateral stress of the magnitude of a few percents would induce changes in the band gap of the order of 0.1 eV. In our opinion, this result indicates that our conclusions remain valid also for epitaxial material.

#### 4 Summary and conclusions

We reported results of *ab initio* calculations for fundamental electronic properties of  $\text{HfO}_2$  and  $\text{PrO}_2$  in their fluorite-structure phases, i.e., those related to films grown epitaxially on silicon substrates. We described a method to construct a working pseudopotential for Pr and presented results of first pseudopotential *ab initio* DFT-LDA calculations for the electronic structure of bulk  $\text{PrO}_2$ . We compared them to LDA and first GW electronic structures of  $\text{HfO}_2$ .

We found that both materials have a rather similar band structure, with exception of a narrow *f*-band which forms the bottom of the conduction band in  $\text{PrO}_2$  but is missing in  $\text{HfO}_2$ . This *f*-band is responsible for low leakage of Pr oxide gate dielectrics in spite of relatively small band gap of this material.

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#### References

- <sup>1</sup> S. M. Sze. *Physics of Semiconductor Devices*. Wiley, 1981.
- <sup>2</sup> L. Manchanda. In: W. M. Bullis, D. G. Seiler, and A. C. Diebold (Eds.) *Semiconductor Characterization*. Woodbury, New York 1996, p. 123.
- <sup>3</sup> J. Dąbrowski, H.-J. Müssig, M. Duane, S. T. Dunham, R. Goossens, H.-H. Vuong. *Advances in Solid State Physics* 38 (1999) 565. Postscript file available from [www.ihp-ffo.de/chipps/97/Ddoc/dpg.html](http://www.ihp-ffo.de/chipps/97/Ddoc/dpg.html)
- <sup>4</sup> J. Dąbrowski, H.-J. Müssig. *Silicon Surfaces and Formation of Interfaces*. World Scientific, Singapore, 2000; see [www.ihp-ffo.de/chipps/Dbook2000](http://www.ihp-ffo.de/chipps/Dbook2000)
- <sup>5</sup> H. J. Osten, J. P. Liu, P. Gaworzewski, E. Bugiel, and P. Zaumseil, *Techn. Dig. IEDM* 2000.
- <sup>6</sup> B. Cheng, M. Cao, R. Rao, A. Inani, P. Vande Voorde, W. M. Greene, J. M. C. Stork, Z. Yu, P. M. Zeitzoff, and J. C. S. Woo. *IEEE Transactions on Electron Devices* 46 (1999) 1537.
- <sup>7</sup> M. Bockstedte. *Comp. Phys. Commun.* 107 (1997) 187.
- <sup>8</sup> D. M. Ceperley, B. J. Alder. *Phys. Rev. Lett.* 45 (1980) 567.
- <sup>9</sup> J. P. Perdew, A. Zunger. *Phys. Rev. B* 23 (1981) 5048.
- <sup>10</sup> D. R. Hamann. *Phys. Rev. B* 40 (1989) 2980; G. B. Bachelet, D. R. Hamann, M. A. Schlüter. *Phys. Rev. B* 26 (1982) 4199.
- <sup>11</sup> L. Kleinman, D. M. Bylander. *Phys. Rev. Lett.* 48 (1982) 1425.
- <sup>12</sup> L. Hedin, S. Lundqvist. In: H. Ehrenreich, F. Seitz, D. Turnbull (Eds.) *Solid State Physics*. Academic, New York, 1969, Vol. 23, p. 1; W. G. Aulbur, L. Jonsson, J. W. Wilkins. H. Ehrenreich, F. Spaepen (Eds.) *Solid State Physics*, Academic, New York, 2000, Vol. 54, p. 1.
- <sup>13</sup> A. Fleszar, W. Hanke. *Phys. Rev. B* 56 (1997) 10228.
- <sup>14</sup> H. J. Osten, J. P. Liu, E. Bugiel, and P. Zaumseil, submitted to *Phys. Rev. Lett.*
- <sup>15</sup> J. Dąbrowski and V. Zavodinsky, unpublished.
- <sup>16</sup> J. P. Perdew, K. Burke, and Y. Wang. *Phys. Rev. B* 54 (1996) 16533.
- <sup>17</sup> S. G. Louie, S. Froyen, and M. L. Cohen. *Phys. Rev. B* 26 (1982) 1738.
- <sup>18</sup> U. Lundin, I. Sandalov, O. Eriksson, B. Johansson. *Physica B* 259-261 (1999) 231.
- <sup>19</sup> P. K. De Molle, S. K. Sinharoy. *Phys. Lett. A* 249 (1998) 147.
- <sup>20</sup> C. Hwang, J. W. Lee, S. T. Kim, B. H. Lee, and M. Onellion. *Solid State Comm.* 103 (1997) 229.
- <sup>21</sup> X. Gonze, R. Stumpf, and M. Scheffler. *Phys. Rev. B* 44 (1991) 8503.
- <sup>22</sup> J. P. Liu and H. J. Osten, unpublished.