Following the seminal work of Cox et al. (J. Phys. Cond. Matt. 18 (2006) 1079) on high-k dielectric oxide muonics, we discuss the electronic structure and electrical activity of the hydrogen impurity, modelled by its lighter pseudo-isotope muonium in high-k oxides. Recent results on the donor and acceptor hydrogen configurations in TeO2 and Y2O3 will be presented, including the apparent coexistence of a shallow-donor configuration with a deep acceptor configuration in TeO2 and the robustness of the acceptor configuration in Y2O3.
Hydrogen in high-k dielectric oxides modeled by muonium

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Outline

• Introduction: H in high-k oxides in the context of current research of H in semiconductors and insulators

• TeO$_2$ and Y$_2$O$_3$: Experimental and computational results

• Discussion / conclusions
A little bit of the history of the early Coimbra/ISIS interaction

- late 1980’s: H in intermetallic compounds, studied by PAC as a major topic of the Applied Nuclear Physics Group in Coimbra led by Nuno Ayres de Campos;
- early 1990’s: visit of Steve Cox to Coimbra and collaboration of the Coimbra group (N. Ayres de Campos, J. M. Gil, P. J. Mendes) in LCR-muSR measurements in aluminum and ice;
- late 1990’s: H in semiconductors studied by muSR becomes a major research topic of the Coimbra group, in close collaboration with A. Weidinger and S. Cox.
H behaving as a shallow donor contributing to n-type conductivity

FIG. 2. Formation energies of interstitial hydrogen in ZnO, as a function of Fermi level, obtained from DFT-LDA calculations and referenced to the energy of a free H₂ molecule. For each charge state, only the lowest-energy configuration is shown. Zero-point energies are included. The zero of Fermi energy is chosen at the top of the valence band, and both the theoretical ($E_{F}^{\text{th}} = 1.91$ eV, dotted line) and experimental ($E_{F}^{\exp} = 3.4$ eV) band gaps are indicated. The energies for H⁰ and H⁺ are shown in dashed lines to indicate they are underestimated in the LDA calculations; after correction, H⁺ is the lowest-energy state throughout the experimental band gap.
A tribute to ISIS sensitivity

Beatings clearly visible for $t>17 \mu s$!
H behaving as a compensating centre
(amphoteric impurity always contradicting conductivity)

CG Van de Walle, Phys Stat Solidi (b) 229 (2002) 221

A key to the problem: band line-ups!

CG Van de Walle and J. Neugebauer,


ε(+/−) predicted to be constant

RC Vilão et al. – University of Coimbra
H in high-k dielectric oxides

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Oxford, September/2012
Hydrogen as a source of conductivity in oxides

<table>
<thead>
<tr>
<th>Material</th>
<th>CB (eV)</th>
<th>VB (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>-1.37</td>
<td>-9.17</td>
</tr>
<tr>
<td>ZnO</td>
<td>-4.05</td>
<td>-7.45</td>
</tr>
<tr>
<td>CdO</td>
<td>-4.35</td>
<td>-6.75</td>
</tr>
<tr>
<td>SnO₂</td>
<td>-4.44</td>
<td>-8.04</td>
</tr>
</tbody>
</table>

+/- pinning level at 3.0±0.4 eV
Oxide muonics: I. Modelling the electrical activity of hydrogen in semiconducting oxides

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Abstract

A shallow-to-deep instability of hydrogen defect centres in narrow-gap oxide semiconductors is revealed by a study of the electronic structure and electrical activity of their muonium counterparts, a methodology that we term ’muonics’.

In CdO, Ag2O and Cu2O, paramagnetic muonium centres show varying degrees of delocalization of the singly occupied orbital, their hyperfine constants spanning 4 orders of magnitude. PrO and RbO, on the other hand, show only electronically diamagnetic muon states, mimicking those of interstitial protons.

Muonium in CdO shows shallow-donor behaviour, dissociating between 50 and 150 K, the effective ionization energy of 0.1 eV is at some variance with the effective-mass model but illustrates the properties of hydrogen doping, indicating n-type conductivity as in the wider-gap oxide, ZnO. For Ag2O, the principal donor level is deeper (0.25 eV) but ionization is nonetheless complete by room temperature. Striking examples of level-crossing and RF resonance spectroscopy reveal a more complex interplay of several metastable states in this case. In CuO, muonium has quasi-atomic character and is stable to 600 K, although the electron orbital is substantially more delocalized than in the trapped-atom states known in certain wide-gap dielectric oxides. Its eventual disappearance towards 900 K, with an effective ionization energy of 1 eV, defines an electrically active level near mid-gap in this material.

Table 1. Hyperfine parameters for relevant muonium defect centres, listed in decreasing order of the isotropic component or contact interaction, \( A_{iso} \). Anisotropy is quantified by the dipolar term \( D \). The sign of the contact interaction is so far unknown for muonium in HgO but, by analogy with bond-centred muonium in Si, could well be negative. Spin density \( \rho_M \) on the muon is expressed as the ratio \( A_{iso}/A_0 \), where \( A_0 = 4463 \text{ MHz} \) is the vacuum-state or free-muon hyperfine constant. Spin density \( \rho_N \) in s, p or d orbitals on the nearest-neighbour nuclei is likewise the ratio of the nuclear hyperfine parameters and the corresponding atomic values, these latter given by Moreton and Preston (1978). Literature references are (i) Patterson (1988), (ii) Schneider et al. (1990) (the \( \rho_N \) s are for Cu neighbours here; these authors also give the values for Cl), (iii) Cox and Symons (1986), (iv) Kiefl et al. (1998), (v) Gil et al. (2001b), (vi) Cox et al. (2001a), (vii) Alberti et al. (2001), and (viii) Lord et al. (2001); a compendium of other literature data for ZnO is given by Cox (2003). Also tabulated are parameters for the silver–hydrogen radical cations: (x, xi) Echau and Symons (1969), (xii) 2006

<table>
<thead>
<tr>
<th>( A_{iso} ) (MHz)</th>
<th>( D ) (MHz)</th>
<th>( \rho_M ) or ( \rho_T )</th>
<th>( \rho_N ) (s)</th>
<th>( \rho_N ) (p or d)</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>SeMnT</td>
<td>2066</td>
<td>0</td>
<td>0.46</td>
<td>0.035</td>
<td>(i)</td>
</tr>
<tr>
<td>Cu2O</td>
<td>1280 ± 20</td>
<td>0.27</td>
<td>0.007</td>
<td>0.14</td>
<td>(ii)</td>
</tr>
<tr>
<td>CuCl</td>
<td>1226</td>
<td>300</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SeMnO</td>
<td>67</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag2O:Me4</td>
<td>37 ± 0.2</td>
<td>10 ± 1</td>
<td>0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag2O:Me3</td>
<td>7.4 ± 0.1</td>
<td>5</td>
<td>0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HgO</td>
<td>0.5 ± 0.2</td>
<td>0.1</td>
<td>10^-4</td>
<td>~10^-4</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>0.05</td>
<td>0.1</td>
<td>10^-5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Ag}^2+ )</td>
<td>0.55</td>
<td>0.14</td>
<td>~0.3</td>
<td></td>
<td>(x)</td>
</tr>
<tr>
<td>( \text{Ag}^2+ )</td>
<td>0.05</td>
<td>0.44</td>
<td>0.05</td>
<td></td>
<td>(xi)</td>
</tr>
</tbody>
</table>

Frontiers of Muon Spectroscopy
Oxford, September/2012
Oxide muonics: II. Modelling the electrical activity of hydrogen in wide-gap and high-permittivity dielectrics

S F J Cox1, 2, J J. Ogunrinle3, J S Lord1, S P. O'Connor2, M J. Gil1, E V. Alberti1, J Prieto Duarte1, R C Vilão1, N Ayres de Campos1, D J. Kreb8, A D. Davis5, M Clarricoats5 and D P. van der Werf6

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Abstract

Following the prediction and confirmation that interstitial hydrogen forms shallow donors in zinc oxide, inducing electronic conductivity, the question arises as to whether it could do so in other oxides, not least in those under consideration as thin-film insulators or high-permittivity gate dielectrics. We have screened a wide selection of binary oxides for this behaviour, therefore, using muon as an accessible experimental model for hydrogen. New examples of the shallow-donor states that are required for n-type doping are inferred from hyperfine broadening or splitting of the muon spin rotation spectra. Electron effective masses are estimated (for several materials where they are not previously reported) although polaronic rather than hydrogenic models appear in some cases to be appropriate. Deep states are characterized by hyperfine decoupling methods, with new examples found of the neutral interstitial atom even in materials where hydrogen is predicted to have negative-U character, as well as a highly amphoteric interstitial donor state assigned to a vacancy-defect complex. Comprehensive data on the thermal stability of the various neutral states are given, with effective isostation temperatures ranging from 10 K for the shallow to over 100 K for the deep states, and corresponding activation energies between tens of meV and several eV. A striking feature of the systematics, rationalized in a new model, is the preponderance of shallow states in materials with band gaps less than 5 eV, atomic states above 7 eV, and their coexistence in the intervening threshold range, 5–7 eV.

Table 2. Results for neutral (paramagnetic) muonium states. The designation Shallow Donor indicates direct observation or reasonable inference; candidate shallow donor (SD) indicates that the current results are suggestive but not conclusive. The designation atomic implies a hyperfine constant within about 20% of the free-atom value in the paramagnetic state. In Co3O4 it is reduced by 30%. Contact terms for the shallow donors are inferred to be smaller by another factor of 5 relative to a magnetic state that would have an isothermal contact term of 15 MHz. The states with hyperfine parameters that are intermediate in value and highly anisotropic, References to these: 1 = our previous papers; 2 = Brown (1983); 3 = Brown et al. (2005); 4 = Cox et al. (2006); 5 = Strooper et al. (1996); 6 = Keiler et al. (1996); 7 = Brown (1983); 8 = Cox et al. (2006). In addition to the data shown here, the atomic states with hyperfine parameters inferred from literature comparisons are included for systematic completeness; see also table 3 (and figure 7).

<table>
<thead>
<tr>
<th>Material</th>
<th>Isotiation range (K)</th>
<th>Fraction at RT</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag2O</td>
<td>125–250</td>
<td></td>
<td>1 2 4 6</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.2</td>
<td></td>
<td>1 2 4 6</td>
</tr>
<tr>
<td>BaO</td>
<td>100–1000</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>BeO</td>
<td>300–1000</td>
<td></td>
<td>1 2 4</td>
</tr>
<tr>
<td>CaO</td>
<td>50–500</td>
<td></td>
<td>1 2 4</td>
</tr>
<tr>
<td>CaF2</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>CdO</td>
<td>500–1000</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>Co3O4</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>Cu2O</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>Dy2O3</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>Eu2O3</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>Ga2O3</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>GeO2</td>
<td>2–3</td>
<td></td>
<td>1 2 4</td>
</tr>
<tr>
<td>HfO2</td>
<td>300–1000</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>In2O3</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>La2O3</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>Li2O</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>MgO</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>NiO</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>PdO</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>Pr2O3</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>PbO</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>Sc2O3</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>SeO2</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>SiO2</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>SrO</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>TiO2</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
<tr>
<td>ZnO</td>
<td>500–800</td>
<td>0.45</td>
<td>1 2 6</td>
</tr>
</tbody>
</table>

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No muonium is seen

Deep acceptors (also In2O3, Ga2O3)

Deep donors (Ag2O and HgO, not represented)

Shallow donors

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H in high-k dielectric oxides

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Why TeO$_2$ and Y$_2$O$_3$?

TeO$_2$ is a promising active material for optical devices and gas sensors; high dielectric constants have also been reported.

Distorted rutile structure, $E_g = 3.5$ eV

H is present during growth of $\alpha$-TeO$_2$: Cr$^{3+}$ - $V_O$ - 2H complex and V$^{4+}$ - 2H centre have been characterized

Y$_2$O$_3$ is widely used in ceramic materials' processing and in rare-earth doped lasers; it is a candidate high-k oxide to replace SiO$_2$.

Cubic bixbyite structure; $E_g = 6$ eV

H impurities are known to play major role both in electronic and ionic conductivities
20% of the muons correspond to a highly relaxed line consistent with a 21 MHz oscillation.

TeO$_2$

Diamagnetic relaxation is observed (electronic origin, not due to nuclear spins).

20% of muon spin polarization missing.
$\text{TeO}_2$

![Graph showing fractions (%) vs. temperature (K) for slow and fast components.](image-url)
**TeO$_2$**
Relaxation of diamagnetic component decreases below 50 K

Electronic origin: typical indirect signature of shallow muonium (relaxation due to unresolved Mu lines)

- strong covalent O-H bond perpendicular to c-axis (0.98 Å)
- nn Te slightly pulled out (0.25 Å)
- also lowest energy for neutral state (“H0”) with extra electron degenerate with CBM

**H$^+$ (shallow) donor configuration**

![Graph showing the energy level as a function of temperature (T) in Kelvin (K) with a peak at 6(2) meV and a field strength (B) of 2 mT.](image)

Relaxation of diamagnetic component decreases below 50 K

**Electronic origin:** typical indirect signature of shallow muonium (relaxation due to unresolved Mu lines)

- strong covalent O-H bond perpendicular to c-axis (0.98 Å)
- nn Te slightly pulled out (0.25 Å)
- also lowest energy for neutral state (“H0”) with extra electron degenerate with CBM
Metastable deep atomic-like (acceptor) configuration

Isotropic $\Lambda \sim 70\%$ of vacuum value
(deep atomic-like Mu state)

$\Lambda = 3.5 (1) \text{ GHz}$

$T = 6 \text{ K}$

TeO$_2$

- lowest energy configuration for H$^-$
- stable configuration for H$^0$ but at higher energy than donor configuration
- distance to nn Te $\sim 1.75 \text{ \AA}$
- distance to 2 nn O (other side of ring) just above 2 \text{ \AA}
Computational formation energies

\[ \varepsilon (+/-) \text{ below CBM, both experimental and computational} \]

\[ \text{H as a negative-U center in TeO}_2 \]

\[ \varepsilon (+/0) \text{ donor level resonant with conduction band} \]

\[ \text{A shallow donor is expected (compensating, not n-type dopant)} \]
~49% of the muons precess at the paramagnetic Mu 21 MHz line

Highly-relaxed component corresponding to ~40% of the total asymmetry

~11% of the muons precess at diamagnetic Larmor frequency

$Y_2O_3$

$T = 300 \text{ K}$
$B = 1.5 \text{ mT}$

$\text{Asymmetry (\%)}$

$\text{Time (\mu s)}$
Y$_2$O$_3$

![Graph showing fractions vs. temperature (K) for various fractions: $f_{\text{slow}}$, $f_{\text{Mu}}$, $f_{\text{fast}}$, and total. The graph includes data points and curves indicating the behavior of these fractions with temperature.]

![Diagram of the Y$_2$O$_3$ crystal structure with labels for H$^0$ and Y$_1$ and Y$_2$.]

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H in high-k dielectric oxides
(d) $Y_2O_3$

2.5(1.5) and 0.3(1) eV

(e) $Y_2O_3$ 300K
H$^+$ (shallow?) donor configuration

$E_A = 13(1)\text{ meV}$
$\text{Y}_2\text{O}_3$

$Mu_C^+ \rightarrow Mu_A^+$?

$Mu_A^+ + e^- \rightarrow Mu_A^0$?

$E_A = 142(10)$ meV

$E_A = 371(16)$ meV

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Conclusions

• H as negative-U amphoteric impurity in TeO₂ and Y₂O₃
• Identification and characterization of both shallow donor and deep acceptor H configurations
• Possible interconversion between configurations (temperature dynamics) or H interaction with intrinsic defects (extended complex suggested by theory)

Thanks!

• ISIS and PSI μSR teams
• Milipeia computational cluster team (Coimbra)
• €€€: FCT (Portugal) - project PTDC/FIS/102722/2008
Questions?