High-field study of muonium states in HfO$_2$ and ZrO$_2$

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Abstract. We present high-transverse field measurements, as a function of temperature, in monoclinic ZrO$_2$ and HfO$_2$. In monoclinic zirconia and hafnia, a diamagnetic component had been previously reported in low-transverse-fields, but a significant fraction of the total muon polarization was missing in these experiments. We now characterize this missing fraction using the high-field capabilities at TRIUMF: a high relaxation component (above 100 $\mu$s$^{-1}$ in monoclinic ZrO$_2$, about 10 $\mu$s$^{-1}$ in HfO$_2$) is observed, which we relate to the formation of compact muonium in these materials. A model for the formation of muonium in these materials is presented.

1. Introduction

Oxides with high dielectric permittivity (high-κ) are currently under intense scrutiny in order to find adequate solutions for the insulator layer in the gates of MOSFET devices. ZrO$_2$ and HfO$_2$ are among the most prominent candidates and HfO$_2$-based transistors have already reached the commercialization stage [1]. Processing of the oxides, whereby hydrogen is often incorporated, is known to have a big impact in its electrical performance. Hydrogen is a strong candidate defect in order to explain the positive fixed charges in the ZrO$_2$ and HfO$_2$ layer [2]. Fundamental studies on the effect of hydrogen in the electrical properties of semiconductors and insulators have known major advances due to the analogy with muonium, a light pseudo-isotope of hydrogen [3].

Previous μSR measurements on monoclinic HfO$_2$ and ZrO$_2$ [4] revealed the formation of a diamagnetic component with a temperature dependent relaxation, which was attributed to the ionization of a (shallow) neutral muonium state at an oxygen-bonded position. However, most of the muon spin polarization was not observed at these ISIS measurements at room temperature: a missing fraction of about 80 – 90% was reported, which was correlated to the formation of a deep muonium state through longitudinal-field repolarization measurements.

Lyons et al. [2] have calculated the stable configurations for hydrogen in monoclinic ZrO$_2$ and monoclinic HfO$_2$ and found negative-U behaviour (indicating compensating character of the impurity). H$^+$, bonded to a threefold-coordinated oxygen atom, was found to be the stable configuration for lower values of the Fermi level, donating its electron to the oxygen atom and acting as a donor. In the negative charged state, stable for higher values of the Fermi level, hydrogen was found to sit interstitially, being coordinated by three Hf atoms. In these calculations, hydrogen was also found to be possibly incorporated on an oxygen site in the so-called multieenter bond configuration [5].
2. Experimental details
Muon spin rotation experiments were performed using the HiTime instrument of the M15 beamline at TRIUMF. High-transverse field experiments (up to 7 T) were performed on high-purity powder samples of monoclinic HfO$_2$ and ZrO$_2$, obtained commercially from Alfa-Aesar. Data analysis was done using the WiMDA program [6]. The data reveal the presence of two components precessing at the diamagnetic Larmor frequency $\omega_L$, with very different relaxations. The data were therefore fitted with two relaxing components, according to

$$A(t) = f_{\text{fast}}e^{-\lambda_{\text{fast}}t}\cos(\omegaLt + \phi_{\text{fast}}) + f_{\text{slow}}e^{-\lambda_{\text{slow}}t}\cos(\omegaLt + \phi_{\text{slow}})$$

We present in Figures 1(a) and 1(c) the first 50 ns of the time spectra obtained at $T = 2$ K, for $B = 2$ T. In Figures 1(b) and 1(d) we show the same spectrum after removal of the slowly relaxing component, fitted as described above. Calibration experiments at room temperature were done with a silver sample in order to extract the maximum instrumental muon spin polarization, as well as the phase of the calibration signal.

![Image](image.png)

**Figure 1.** Time spectra at 2T (detail of first channels showing the fast relaxation) for HfO$_2$ (left) and ZrO$_2$ (right) at $T = 2$ K and for transverse magnetic field $B = 2$ T. The full time spectra are shown in (a) and (c). In (b) and (d) only the fast component is shown, as discussed in the text.

The analysis of the slow component was first performed in the time interval $0.3 - 2.89 \mu s$ and the corresponding parameters were henceforth fixed and used in the two component analysis in the interval $0 - 0.3 \mu s$. In the final fits, the relaxation $\lambda_{\text{fast}}$ of the fast component was fixed to the low-temperature ($T = 2$ K) value. Table 1 summarizes the fitting results for the lowest temperature ($T = 2$ K).

3. Results and discussion
We present in Fig. 2 the temperature dependence of the fraction of the muon spin polarization corresponding to each configuration, for HfO$_2$ and for ZrO$_2$, after normalizing to the maximum
Table 1. Low-temperature (2 K) fit parameters, as discussed in the text.

|       | $\lambda_{\text{slow}}$ | $\lambda_{\text{fast}}$ | $\phi_{\text{slow}}$ | $\phi_{\text{fast}}$ | $f_{\text{slow}}$ | $f_{\text{fast}}$ | missing fraction |
|-------|---------------------------|---------------------------|-----------------------|-----------------------|------------------|------------------|------------------|
| HfO$_2$ | 0.220(4) $\mu s^{-1}$ | 11.1(7) $\mu s^{-1}$ | 151.8(3) | 152(2) | 54.9(4)% | 20.9(9)% | 24(1)%          |
| ZrO$_2$ | 0.272(7) $\mu s^{-1}$ | 101(8) $\mu s^{-1}$ | 152.6(5) | 153(2) | 25.8(3)% | 43(3)% | 31(3)%          |

instrumental asymmetry obtained with the silver calibration. The corresponding temperature dependence of the phase $\phi_{\text{slow}}$ of the slow component is shown in fig. 3. The dashed line in fig. 3 represents the value $\phi_{\text{Ag}} = 140(1)$ deg obtained for the phase of the calibration measurement with silver at room temperature.

**Figure 2.** Temperature dependence of the fraction $f_{\text{slow}}$ and $f_{\text{fast}}$, for ZrO$_2$ and HfO$_2$, for a transverse field $B = 2$ T.

**Figure 3.** Temperature dependence of the phase $\phi_{\text{slow}}$ of the slowly relaxing component, for ZrO$_2$ and HfO$_2$, for a transverse field $B = 2$ T. The dashed line indicates the value obtained for the silver calibration measurement.

3.1. Slow component

We assign the slowly relaxing diamagnetic component to muons thermalizing at an oxygen-bonded position, Mu$_{Ob}$, forming an $O - \mu$ bond. This site was already discussed at length by Cox et al. [4] and a possible reinterpretation is discussed in an accompanying paper [7]. Ab-initio
calculations in similar systems [2, 8] also show that this configuration is the more stable for the positively charged H\(^+\)/\(\mu^+\).

However, the observed phase-shift (Fig. 3) indicates that this state results from the conversion of a previous (unobserved) state. As mentioned already, previous longitudinal-field repolarization measurements in both monoclinic ZrO\(_2\) and HfO\(_2\) reveal the formation of a deep muonium state at room temperature [4]. The slowly relaxing diamagnetic component is thus likely to arise from delayed formation of a precursor deep muonium state, as observed in other semiconductors [9, 10].

The precursor muonium state is likely to sit at an interstitial position. However, at the lowest temperatures, the lattice has insufficient time to relax around the impurity and the neutral precursor muonium at the interstitial position thus corresponds to a metastable interstitial configuration [9, 10, 11]. From this metastable interstitial configuration, the muon can quickly convert to the oxygen-bonded position, Mu\(\text{O}_6\).

The alternative conversion of the metastable interstitial configuration to its true minimum at an interstitial site does not appear to dominate at the lowest temperatures. This process leads to the formation of the missing fraction, where the stable interstitial state is strongly dephased due to line broadening in the conversion process. However, the temperature dependence of the slow component and of the missing fraction suggest that temperature increases the conversion rate of the metastable interstitial configuration to its true minimum. This process thus becomes a more competitive alternative to the conversion to the oxygen-bonded configuration. This is also evidenced by the temperature dependence of the phases in Fig. 3, where a strong dephasing of the slow component is observed for the lowest temperatures, which gradually approaches the value obtained for the silver calibration as the temperature increases, suggesting a suppression of the process responsible for the phase-shift.

In the stable interstitial configuration, the barrier for the conversion to the oxygen-bonded site is larger. The final fraction of muons in the slowly relaxing diamagnetic component therefore decreases as temperature increases, with a corresponding increase of the missing fraction.

We propose that this increase with temperature of the competing formation of the true interstitial configuration is mediated by optical phonons in these ionic compounds. When these modes are activated, the formation process of the true interstitial configuration is enhanced. We have thus modelled the decrease of the slow component with a phenomenological Boltzmann-like functional dependence [4, 12, 13]:

\[
f_{\text{slow}} = \frac{f_{\text{slow}}^0}{1 + N \exp \left(\frac{-E_a}{k_B T}\right)}
\]

where \(E_a\) is the activation energy, \(k_B\) the Boltzmann constant and \(f_{\text{slow}}^0\) is the low temperature value of the slowly relaxing fraction. \(N\) is a parameter associated to the effective density of phonon modes.

The lines in fig 2 are fits with this phenomenological Boltzmann-like dependence. We get an activation energy of 79(7) meV for the decrease of the slow fraction in HfO\(_2\) above 100 K. We note that the phonon modes in monoclinic HfO\(_2\) are calculated in the range 10 – 100 meV [14]. We also note that the fraction of muons stopping at the slowly relaxing diamagnetic fraction is seen to be relatively temperature independent in ZrO\(_2\) (Fig. 2), which is consistent with the much smaller value (around 10 meV) of the phonon mode with maximum density of states in monoclinic zirconia [15].

3.2. Fast component

In Fig. 4 we show the field dependence of the fast relaxation \(\lambda_{\text{fast}}\) in ZrO\(_2\), for \(T = 20\) K. \(\lambda_{\text{fast}}\) is seen to be fairly field independent, suggesting that it corresponds to lifetime broadening associated to delayed muonium formation. We suggest that it corresponds to muons stopping
at the interstitial position in a charged state (either \( \text{Mu}^+ \) or \( \text{Mu}^- \)) and converting to \( \text{Mu}^0 \), where the neutral configuration is known to be stable \([2, 8]\). In the \( \text{Mu}^+ \) case, the electron is captured from the radiolysis products; in the \( \text{Mu}^- \) case, the second electron is either lost to the conduction band or to the valence band (hole capture).

![Figure 4. Field dependence of the relaxation \( \lambda_{\text{fast}} \) of the fastly relaxing component in ZrO\(_2\), in the transverse geometry, for a temperature \( T = 20 \, \text{K} \).](image)

We note that the fast component disappears as the temperature is increased (above 250 K for HfO\(_2\); above 50 K for ZrO\(_2\)). It is not clear from the fits whether this is by line broadening or by a reduction in the fraction \( f_{\text{fast}} \) of muons stopping in this configuration. In the delayed muonium formation model, it is more likely that the fraction is reduced, so we choose to fix the fast relaxation throughout the temperature dependence.

We note that the relaxation of the fast component is almost one order of magnitude higher for ZrO\(_2\) with respect to HfO\(_2\). Also, the temperature stabilities of these components are very different: whereas in HfO\(_2\) the fast component is observed up to 250 K, in ZrO\(_2\) it disappears at about 100 K, with an activation energy of 46(13) meV (again fitting the fast fraction in fig 2 with a Boltzmann-like dependence such as that of eq. 2).

We recall that it is not possible to distinguish \( \text{Mu}^+ \) from \( \text{Mu}^- \) in \( \mu \)SR measurements, so it is not possible to establish definitively whether the diamagnetic component associated to the fast fraction is positively or negatively charged. It is however likely that it sits at (or close to) the same interstitial position than \( \text{Mu}^0 \). If the fast relaxing diamagnetic component corresponded to \( \text{Mu}^+ \), this would imply delayed electron capture, with an average time of 10 ns (for ZrO\(_2\)) or 100 ns (for HfO\(_2\)). This seems to be unlikely high.

It seems therefore plausible that the fastly relaxing diamagnetic fraction corresponds to \( \text{Mu}^- \). In this case, a small fraction of the incoming muons would capture two electrons in the thermalization process (as suggested for other systems \([12, 13, 16]\)) and would end up in the corresponding stable position at the interstitial site.

4. Conclusions

Fig. 5 summarizes our tentative interpretation in a potential-well diagram \([4]\), representing the potential energy for the neutral muonium atom as a function of the configuration coordinate along the path from the interstitial site to the oxygen-bonded site. Muons in HfO\(_2\) and ZrO\(_2\) may stop at the interstitial configuration or at the oxygen-bonded configuration. The formation is however a complex process \([9, 10]\), where a precursor muonium is involved. This precursor is likely at the interstitial position, albeit unrelaxed, and may have an electron or not. The delayed formation of neutral muonium from the charged precursor constitutes the fast component. The precursor stopping as neutral Mu may either relax to the true relaxed interstitial position (missing fraction) or tunnel to the oxygen bonded position. This latter case is progressively hindered as the former case progresses.
**Figure 5.** Schematic potential energy diagram for the neutral Mu states in ZrO$_2$ and HfO$_2$: a precursor neutral muonium state Mu$_I^{0*}$ is formed in a metastable interstitial position. It either converts from there to the oxygen-bound configuration (corresponding to the slowly relaxing component), or to the stable interstitial configuration Mu$_I^{0}$ (unobserved due to dephasing or line broadening). The potentials of the charged states are not presented here.

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