

COMPUTATIONAL AND EXPERIMENTAL STUDIES OF DIFFUSION IN MONOCLINIC HfO₂

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Research on hafnia and zirconia has received a boost in the last two decades, mainly because of their electrical properties. As materials with high dielectric permittivity and a wide band-gap, they can replace SiO₂ in Si-based semiconductor devices as the gate dielectric, and they can be employed as the insulator in metal—insulator—metal structures, showing memristive behavior.^[1,2] Anion, and possibly cation, transport is of fundamental importance for the annealing of such devices and the proposed mechanism of resistive switching (filament switching in the case of HfO₂).^[2,3] In this study, we investigated both cation and anion diffusion in HfO₂ using diffusion experiments, with subsequent determination of the diffusion profiles by Secondary Ion Mass Spectrometry (SIMS). For the diffusion of oxygen in dense ceramics of monoclinic HfO₂, (¹⁸O/¹⁶O) isotope exchange anneals were performed in the temperature range $573 \leq T / K \leq 973$ at an oxygen partial pressure of $p_{O_2} = 200$ mbar.^[4] All measured isotope profiles exhibited two features: the first feature, closer to the surface, was attributed to slow oxygen diffusion in an impurity silicate phase; the second feature, deeper in the sample, was attributed to oxygen diffusion in a homogeneous bulk phase. The activation enthalpy of oxygen tracer diffusion in bulk HfO₂ was found to be $\Delta H_{D^{\bullet}} \approx 0.5$ eV.

In contrast to oxygen diffusion, diffusion of cations in HfO₂ and other oxide-ion conductors is experimentally much more challenging. It is slow, requiring, therefore, high temperatures and long diffusion times. In the case of HfO₂, there is also the problem of Si impurities (see above), which are hard to get rid of in ceramic samples. To alleviate these problems somewhat, we directly investigated the diffusion of Zr in thin films of nanocrystalline, monoclinic HfO₂, prepared by Atomic Layer Deposition (ALD) and coupled with a sputtered top layer of ZrO₂ as a diffusion source. Diffusion experiments were performed in the temperature range $1173 \leq T / K \leq 1323$ in air. All measured diffusion profiles exhibited bulk diffusion and fast grain-boundary diffusion. Using numerical simulations, we were able to describe the profiles and extract diffusion coefficients for Zr diffusion in bulk HfO₂ and along its grain boundaries. The activation enthalpies of diffusion in both cases were, surprisingly, the same at $\Delta H_{D_{b/Dgb}} \approx 2.1$ eV. They are also much lower than activation energies predicted by static atomistic simulations.^[5]

In order to aid the interpretation of the experimental data, we conducted atomistic simulations of cation diffusion in HfO₂. Specifically we performed Molecular Dynamics (MD) simulations using the empirical pair potentials derived by Catlow and Lewis.^[6,7] These potentials are suitable for describing defect behaviour in HfO₂.^[8,9] The activation enthalpy of Hf diffusion in bulk HfO₂ we obtained from the MD simulations agrees exceedingly well with the experimental results: $\Delta H_{D^{\bullet}} \approx 2$ eV. The reasons for this behaviour are discussed.

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