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Theoretical study of hyperfine interactions at the Ta site in Hafnia polymorphs

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Abstract

The electric field gradient resulting from Ta substitutional defect in normal monoclinic phase is studied using all-electron ab initio NFP-LMTO method. Hyperfine parameters in *Pbca* and *Pnma* phases have also been calculated to determine the usefulness of quadrupolar interactions in the investigation of phase diagrams under hydrostatic pressure. Predictions for hyperfine parameters in high temperature *P*42*nmc* and *Fm*3*m* phases were also developed. Given the donor behavior of Ta in HfO_2, two charge states, 0 and +1, have been studied for each phase. Although HFI do not vary significantly with charge, it was determined that for a Ta+1 in *P*21/*c* phase hyperfine parameters is consistent with experimental results. Quadrupolar interactions for transitions to denser phases show important variations with respect to that of the normal phase: asymmetry parameter for *Pbca* and the electric field gradient for *Pnma* both increase substantially. At high temperature phases, drastic decrease in both EFG and asymmetry parameter in *P*42*nmc* is observed, while they almost vanish in *Fm*3*m*.
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1. Introduction

The perturbed angular correlations (PAC) technique in conjunction with external physical excitations imparted to the sample such as uniaxial stresses, electric fields applied to junctions, variable temperatures, provide microscopic information about the interaction of probe atom with its nearest neighbors. It allows to infer local symmetries, charge states of the defect and information of static and dynamic processes such as the exchange of charge of the defect with the bulk [1,2]. The presence of other nearby defects and microstructures that are different in symmetry from the rest of the bulk can be also detected and could serve as indicators of phase transitions. It is not standard the use of PAC technique as a tool for the investigation of phase diagrams. In condensed matter field, the combination of X-ray diffraction (XRD), Raman optic spectroscopies and thermal differential analysis are employed to obtain structural information and to discover phase changes. Compared with XRD technique the information provided by the electric field gradients (EFG) measured by PAC is indirect and it is not possible to determine the crystal structure starting from the determination of these EFG's. However, PAC could, (with the help of ab initio calculations such as the present), be used to give information about the phase transitions under external stresses such as hydrostatic pressure [3] and/or temperature.

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Hafnia together with zirconia are good candidate's materials for the gate dielectric layers in future sub-micrometric MOSFET transistors. In the construction of the gate oxides grown on silicon, the SiO_2 has been the dominant material in the last 30 years due to its extraordinary properties such as thermal stability, appropriate band-offsets, low concentrations of interface traps centers, etc. However, its low dielectric constant and consequently the dielectric leakage due to the tunnel effect of miniaturized narrow thin films (with thickness in the order of 26 Å for the 120 nm technology), its replacement with a higher dielectric constant material in such sub-micrometric devices make a must. Refractory oxides as the HfO_2, ZrO_2 and Al_2O_3 are important compounds in the search of substitute materials of SiO_2 and they presently attract considerable attention, not only due to its higher dielectric constant but also due to their excellent insulating properties, structural stability and simple crystalline structures.

The phase diagram of HfO_2 under the effects of pressures shows the following sequences from the low to high pressure: monoclinic (*P*21/*c*, m), orthorhombic I (*Pbca*, OI) and orthorhombic II (*Pnma*, OII), also called cotunnite (Fig. 1). On the other hand at high temperature and normal pressures conditions, pure HfO_2 has three polymorphic structures: cubic fluorite (*Fm*3*m*) above 2640 K, tetragonal (*P*42*nmc*) between 1400 and 2640 K, and the monoclinic (*P*21/*c*) phase below 400 K. At the tetragonal to monoclinic transition it is known that cannot stabilize the *P*42*nmc* tetragonal phase to ambient temperature. There is an abrupt change in the lattice parameters during this transformation. It is found that the monoclinic HfO_2, is strongly anisotropic in the thermal expansion, since the *b* axis exhibits a negligible expansion while in the *a* and *c* axes the expansion is substantial. The transformation to the tetragonal phase is associated with an expansion in volume, shear efforts and micro-twining [4].

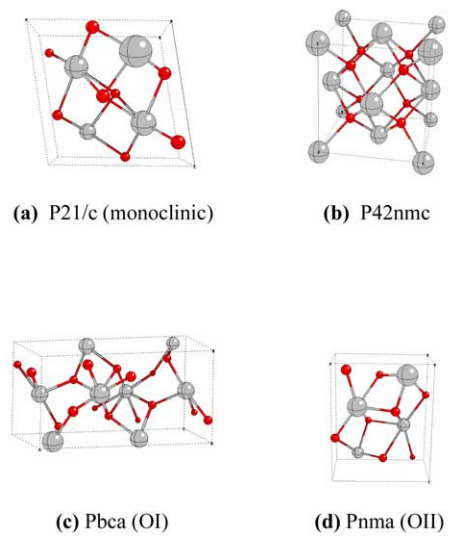

Fig. 1. Units cells of the HfO_2 phases at the equilibrium volumes after internal atomic relaxations took place. Dark circles represent Hf atoms and gray and small circles represent to oxygen atoms. The impurity of Ta is located at substitutional place to Hf.

Abundant experimental information exists related to perturbed angular correlations in the system monoclinic Hafnia doped with $^{181}Hf/^{181}Ta$. At temperature about 300 K, EFG is found with a quadrupolar constant ν_Q in the range of 789–807 MHz and an asymmetry parameter $\eta = 0.35$ [5] and $\nu_Q = 812$ MHz and $\eta = 0.34$ [1]. In both cases, this interaction is assigned to a substitutional site (first site or monoclinic site) free of defects. In the work of Ayala et al. [1], the hyperfine interactions were determined when the temperature was raised from 300 to 800 K and it was observed about 580 K that a 30% of the substitutional site changes its microscopic environment and gives place to a higher electric field gradient EFG in the order of 1300 MHz and $\eta = 0.75$. This effect begins to diminish at 600 K until a complete recovery of the EFG of the substitutional site is observed at 840 K. Increasing the temperature from ambient temperature values to 1300 K, a smooth decrease in EFG corresponding to the first site is observed along with a smooth increase of the asymmetry parameter. In the work of Luthin et al. [2] it is mentioned that at high temperatures a great numbers of intrinsic defects are expected. However, these defects are not trapped by the probe for long enough time to generate a different static EFG. Thus the EFG at high temperatures is assigned to the substitutional site, too.

2. Theoretical approaches

The ab initio all-electron new-full-potential linear-muffin-tin-orbitals (NFP-LMTO) [6,7] method is based on smooth Hankel functions. This method uses the density functional theory in the local approach (LDFT) to account the many body electronic interaction. The system oxide-defect is here simulated by means of periodic cells with 24–48 atoms of the perfect compound containing the defect/complex. The delocalized valence states in our self-consistent calculation are provided by: $5d^2$, $6s^2$ and $6p^0$ for Hf, $5d^3$, $6s^2$ and $6p^0$ for Ta and $2s^2$, $2p^4$ for oxygen, respectively. As done in previous pseudopotential calculations, the 4f electrons of Hf are maintained in the core. However, in our NFP-LMTO core electrons are relaxed during the each self-consistent iteration contrarily to pseudopotential approach. The wave functions basis set are here constructed with s, p, d, f blocks for the Hf and Ta atoms and s, p, d blocks for the O atom, respectively. The smooth radio and the decay of each block were optimized individually in the fluorite phase to obtain total energies converged to a few mRyd/atom.

In the present implementation of the FP-LMTO, the wave functions are represented by means of gaussians in the core and uses Hankel functions for the interstitial region.

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