Microelectronic Engineering 178 (2017) 275–278

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Research paper

Atomic and electronic structure of oxygen polyvacancies in ZrO_2

T.V. Perevalov *, D.R. Islamov

Rzhanov Institute of Semiconductor Physics SB RAS, 13 Lavrentiev ave., 630090 Novosibirsk, Russia
Novosibirsk State University, 2 Pirogov str., 630090 Novosibirsk, Russia

ARTICLE INFO

Article history:
Received 20 February 2017
Received in revised form 26 April 2017
Accepted 12 May 2017
Available online 15 May 2017

Keywords:
Zirconia
Oxygen vacancy
Polyvacancy
Density functional theory
Defect states
Localization

ABSTRACT

We investigate oxygen-deficient crystalline zirconia using quantum-chemical simulation within the hybrid density functional theory. It was shown that the oxygen vacancy in ZrO_2 is the amphoteric defects and it can act as the electron and hole trap. The most energetically favorable spatial configuration of oxygen polyvacancies in ZrO_2 were calculated. It was found that each subsequent vacancy forms near the already existing one, and no more than 2 removed O atoms, related to Zr atom. The ability of oxygen polyvacancy to act as a conductive filament and to participate in the resistive switching is discussed.

1. Introduction

Zirconia (ZrO_2) is a perspective high-κ dielectric for a wide range of technological applications in microelectronics [1]. There is an increasing interest in exploring ZrO2 as a material for nonvolatile memory. As well as for many other high-k oxides, the key characteristics of zirconia are defined by oxygen vacancies. Oxygen vacancies can act as traps for charge carriers and, therefore, they can be responsible for the not negligible leakage current through the thin zirconia oxide [2]. On the other hand, the presence of the oxygen vacancies in high concentration, is able to access the possibility of using zirconia as an active storage medium in Resistive Random Access Memory (RRAM) [3], Magnetoresistive Random Access Memory (MRAM) [4] and charge-trapping flash memory [5]. Thus, oxygen vacancies play a pivotal role in the dominant-to-date model of resistive switching in high-κ oxides based on the filament formation/dissociation. The switching is generally discussed in terms of generation and recovery processes of oxygen vacancy defects within the filament region. While RRAM is intensively investigated, little is reported on the physical assessment of such models. The simplest filament model is a chain of oxygen vacancies, i.e. oxygen polyvacancy.

Understanding the oxygen vacancy-related properties in ZrO_2 is extremely important for microelectronic devices. Particularly, studying the possibility of oxygen vacancies chain formation possibility (energy benefit) in ZrO_2 and their ability to participate in conduction is of great theoretical and practical interest. Zirconia films in resistive switching devices are generally nano-crystalline in the as-deposited state or after annealing prior to the investigation [6]. This gives grounds to investigate the physics of resistive effect by means of quantum-chemical modeling of the oxygen vacancies and polyvacancies atomic and electronic structure in crystalline phase ZrO_2. There have been many efforts in the first principles calculation of electronic structure of the oxygen vacancy in crystalline ZrO_2 [7–12]. Most of them [7–10] used the standard density functional theory based on the local density approximation (LDA) or the generalized gradient approximation (GGA), in which the dielectric bandgaps are appreciably underestimated. That approach did not show vividly the bandgap oxygen vacancy levels. Furthermore, the authors confine themselves to modeling one of the three ZrO_2 crystal phases: cubic [9,10], tetragonal [12] and monoclinic [7,8,11]. As far as we know, the properties of oxygen polyvacancies in ZrO_2 have not been investigated yet.

In this paper, we have investigated the atomic and electronic structure of oxygen vacancy and polyvacancy in the cubic Fm3m (c-), tetragonal P42/nmc (t-) and monoclinic P21/c (m-) phases of ZrO_2 using an approach that provides the bandgap value close to the experimentally measured one.

2. Methods

Simulations were performed in the framework of the periodic supercell formalism in terms of the spin-unrestricted hybrid DFT using the B3LYP functional [13] in the Quantum-ESPRESSO code [14]. The use of hybrid functional is crucial for the objectives of the study because they reproduce the defect levels position in the bandgap without any artificial corrections. Moreover, this approach correctly considers the structural relaxation compared to the standard DFT, especially when

---

* Corresponding author.
E-mail address: timson@isp.nsc.ru (T.V. Perevalov).

http://dx.doi.org/10.1016/j.mee.2017.05.036
0167-9317/

the latter predicts a shallow level, weak charge localization on the defect and a small atomic relaxation (as in the case of negatively charged oxygen vacancy [7]).

The 192-atom c-, t-ZrO_2 and 96-atom m-ZrO_2 supercells were used to simulate the oxygen polyvacancy. Calculations were made using the following electronic configuration of the constituent elements: Zr [Kr] $4s^24p^64d^25s^2$ and O [He] $2s^22p^4$, where the core configurations are shown in the parentheses. The potentials of nuclei and core electrons are described by atomic norm-conserving nonlocal pseudopotentials of the Troullier-Martins type. The pseudopotentials and the correctness of the method itself is confirmed by the agreement between the calculated and experimental values of the structural parameters for c-, t - and m-ZrO_2 [7,8]. The plane-wave cutoff energy was taken equal to 60 Ry, the kinetic energy cutoff for the exact exchange operator was taken equal to 140 Ry.

The bandgap calculated as the energy difference between the highest occupied and lowest unoccupied one-electron states of perfect neutral ZrO_2, and also as a difference of the total energies of perfect ZrO_2 with a different total charge by the formula:

$$E_g = E^- + E^+ - 2E^0 \tag{1}$$

Here E^0 is the total energy of the perfect neutral structure, E^- and E^+ are the total energies of the perfect structure with an electron added and removed, respectively.

The polyvacancies simulations were determined by the following procedure. The choice of the second oxygen atom for the removal was made by trying all the possible positions and identifying the minimum defect formation energy. The three-vacancy atomic structure is determined for a fixed vacancies pair on the same principle, and so on for the N-vacancy. The vacancy formation energies were calculated as follows:

$$E_{form}(\mathrm{Nvac}) = E_{Nvac} - E^0 + N\mu_O \tag{2}$$

Here E_{Nvac} is the total energy of the supercell with the N oxygen vacancy, and μ_O is the oxygen atom chemical potential, which is determined as half of the total energies of an isolated oxygen molecule in the triplet state. This model reflects a gradual increase in the polyvacancy size. In the calculations of searching the polyvacancy atomic structure, the geometry optimization was performed using the local exchange-correlation functional in the Perdew-Burke generalized gradient approximation.

We considered five charge states ($q = +1, 0, -1$ and -2) of oxygen monovacancy (V^q) for the trap thermal E_{th} and optical E_{opt} ionization energies to the conduction band calculation by the formulas [15]:

$$E_{th}(V^q) = \left[E^- + E^{q+1}_{q+1}\right] - \left[E^0 + E^q_q\right] \tag{3}$$

$$E_{opt}(V^q) = E_{th}(V^q) + E_{relax}\left(V^{q+1}\right) = E_{th}(V^q) + \left[E^{q+1}_q - E^{q+1}_{q+1}\right] \tag{4}$$

E_{opt} corresponds to a vertical Frank–Condon transition from the occupied defect ground state to the excited empty state (non-relaxed final state). E_{th} corresponds to a transition to the ground (relaxed) state. $E^0$and E^- are defined in the formulas above, E^q_q and E^{q+1}_{q+1} are the total energies of the supercell with the defect in charge state q and $q + 1$ in the optimized geometry. E^{q+1}_q is the total energy of the supercell with the vacancy in a charge state $q + 1$, but with the equilibrium geometry corresponding to charge state q. The compensating (neutralizing) uniform background potential method was used for charged defects calculations. Due to the complexity, these calculations were carried out only for m-ZrO_2 as the most stable and close to amorphous.

3. Results

The bandgap values, calculated as the energy difference between the highest occupied and lowest unoccupied one-electron states, are 5.7, 6.1 and 5.6 eV for c-, t- and m-ZrO_2, respectively, are consistent with the corresponding experimental values 5.1, 5.78 and 5.83 eV [16]. For m-ZrO_2 the 4- and 3-fold coordinated (4f and 3f) oxygen vacancy formation energies, 6.11 and 6.17 eV, predict the 4f vacancies prevalence in the real structure. This values are in excellent agreement with the previous results [9], despite the use of another calculation technique, and in the qualitative agreement with the results of [7,8]. The neutral oxygen vacancy formation energy for c- and t-ZrO_2 are 5.61 and 5.72 eV, whereas a different theoretical approach predicts 6.63 eV [10] and 7.2 eV [12], respectively. Thus, according to our results, crystalline zirconia oxide is not so scarcely reducible material, as was predicted [10,12].

Different charged states of 3f and 4f oxygen vacancies in m-ZrO_2 form filled and empty defect states in the bandgap as shown in Fig. 1. The neutral oxygen vacancy forms a state occupied by two electrons near the middle of the bandgap. The negatively charged oxygen vacancy levels are positioned about 1 eV below from CBM and that is consistent with experiments [17]. The 4f oxygen vacancy localization of the extra electron on the VO^{-1} level is stronger than for the 3f vacancy. The second added electron leads either to the singlet (V^{-2}(s)) or triplet (V^{-2}(t)) defect state, and the latter is 0.06 eV lower in energy. The significant depth of negatively charged defect levels is the result of significant structure atomic relaxation (about 0.1 Å vs. 0.01 Å in [7]) and charge density redistribution and it indicates a strong polaronic effect. In the +1 charged oxygen vacancy (one electron is removed from the vacancies), the remaining electron is localized near the middle of the m-ZrO_2 bandgap. The fully ionized oxygen vacancy gives one empty state VO^{+2} in the bandgap and near the conduction band bottom.

The defect peaks depth and width (lower than 0.1 eV) in the total density of states (TDOS) spectra indicate the charge localization in space. The charge density spatial distribution of the excess charge in the m-ZrO_2 supercell also confirms the charge localization (Fig. 2). Both positive and negative charges are localized in the oxygen vacancy region and its first coordination sphere. The electron density of the oxygen vacancy in state $q = +1$ (or remaining on the defect level electron) is distributed evenly between the nearest Zr atoms and it can be described as a bonding combination of atomic orbitals of all Zr neighboring the vacant site. Strong localization with its maximum in the center of the vacancy and the behavior of the lattice relaxation have the typical structure of an *F* center. A similar result was obtained previously [7]. An additional electron localized is much weaker and it leads to a charge density distribution among two Zr atoms closest to each other. It reflects the bonding character of the charge density corresponding

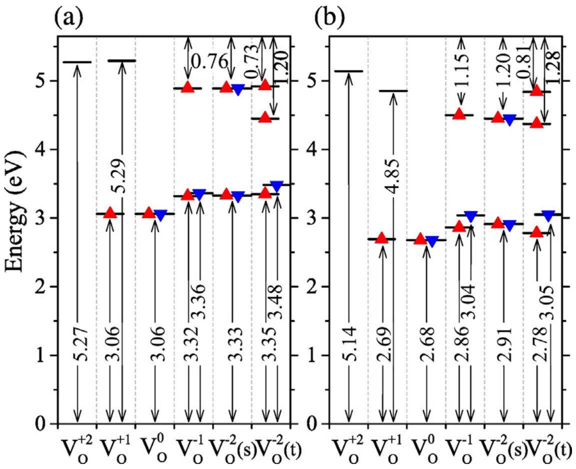

Fig. 1. Defect energy levels in the bandgap of m-ZrO_2 for 3f (a) and 4f (b) oxygen vacancy in different charge states.