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Electronic structure of bulk and defect α- and γ-Al_2O_3

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ABSTRACT

Electronic structure of bulk and oxygen vacancies of high-k dielectric Al_2O_3 (α- and γ- phases) was calculated from the first principles. It was found, that oxygen vacancy can be both electron and hole trap in α- and γ-Al_2O_3. High leakage current trough thin films of Al_2O_3 can be caused by oxygen vacancies.
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1. Introduction

Nowadays Al_2O_3 is intensively studied as dielectric of relatively high dielectric permittivity $\varepsilon \approx 10$ (high-k dielectric) for application in silicon devices [1]. Amorphous film alumina (a-Al_2O_3) is considered as a gate dielectric in CMOS devices to suppress the tunnel current [2]. Also a-Al_2O_3 was proposed as a blocking dielectric in Silicon-Oxide–Nitride-Oxide–Silicon (SONOS) flash memory [3]. Now TaN-Al_2O_3–Si_3N_4–SiO_2–Si (TANOS) structures are investigated for developing of giga- and terabit scale flash memory devices [4]. For application in flash devices alumina is evaporated in amorphous phase by atomic layer deposition (ALD) method. Thermal annealing, which is used for alumina densification in flash devices results in crystallization to γ-Al_2O_3 [5]. One of the main unsolved problems of flash memory with alumina blocking dielectric it is not long enough retention of information [6]. Defects, which can play the role of electron and hole traps in Al_2O_3 can result in charge loss from Si_3N_4 layer to gate in TANOS flash devices. The most common defect in high-k dielectrics is the oxygen vacancy (so called F-centre). Thus the exploration of oxygen vacancy ability to capture the charge carriers in γ-Al_2O_3 is an important task for the optimization of flash memory devices memory properties. In this paper we perform an ab-initio calculation of electronic structure of α- and γ-Al_2O_3 with oxygen vacancy to determine oxygen vacancy ability to localize charge carriers. We compare our calculated results with experimental data.

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2. Computational procedure and model systems

The calculations were performed using the Quantum-ESPRESSO program package [7]. The program is based on the density functional theory and a plane-wave basis set. The core electrons were described using the ultrasoft generalized gradient approximation (GGA) pseudopotential in Perdew-Burke (PB) parameterization and norm-conserving local density approximation (LDA) one in Perdew-Zunger (PZ) parameterization. The plane-wave cutoff energy in the self-consistent field calculations was taken equal to 40 Ry. The k-point mesh density in the reciprocal space was chosen 2×2×2 in Monkhorst-Pack grid sampling. The convergence in the total unit-cell energy was not worse than 0.001 Ry/atom.

The perfect crystal of α-Al_2O_3 has a rhombohedral structure of space group R-3cR. Each Al atom is bonded to six O in the form of a distorted octahedron and each O is bonded to four Al atoms in the form of a distorted tetrahedron. The common assumption is that γ-Al_2O_3 is a defective spinel, in which cation vacancies are required to maintain the charge balance. In current research we use a minimal structure containing 40 atoms derived from the spinel as proposed in Ref. [8]. For defect calculation in Al_2O_3, one has to use a supercell of sufficient size in order to avoid the possible defect–defect interaction. The α- and γ-Al_2O_3 supercell contains a total of 80 and 160 atoms, respectively, in which one of the interior O atoms is removed to create an anion vacancy.

3. Simulation results and discussions

The band structures of bulk α- and γ-Al_2O_3 were calculated. Both α- and γ-Al_2O_3 have direct band gap at the Γ point. The band gaps are 6.0 eV and 4.0 eV for α- and γ-Al_2O_3, respectively. Band

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Table 1
Calculated effective electron and hole masses for α-Al_2O_3 and γ-Al_2O_3 crystals.

	α-Al_2O_3	γ-Al_2O_3
Effective electron masses m_e^*/m_0	0.40 ($\Gamma \to A$) 0.38 ($\perp\Gamma \to A$)	0.40
Effective hole masses m_h^*/m_0	7.5($\perp\Gamma \to A$) 0.35 ($\Gamma \to A$)	1.3 ($\Gamma \to K$) >>1 ($\perp\Gamma \to K$)

gaps are calculated as a difference of the systems total energies with N, $N+1$ and $N-1$ electrons with equation

$$E_g = \left(E_{\text{total}}^{q=0} - E_{\text{total}}^{q=+1}\right) - \left(E_{\text{total}}^{q=-1} - E_{\text{total}}^{q=0}\right),$$

gives values 8.2 eV for α-Al_2O_3 and 6.0 eV for γ-Al_2O_3. The reported experimental band gap value for α-Al_2O_3 is 8.7 eV and for γ-Al_2O_3 is 7.2 eV [9].

Table 1 presents calculated maximum and minimum values of effective electron and hole masses in α- and γ-Al_2O_3. Electron effective mass tensor for both crystals is almost isotropic with $m_e^* \approx 0.4m_0$. This value is in agreement with experimental value for electron tunneling effective mass in amorphous Al_2O_3 $m_e^* = (0.22{-}0.42)m_0$ [5]. In both crystal modifications both light and heavy holes are presented.

Fig. 1 presents comparison of experimental ultraviolet photoelectron spectra (UPS) and X-ray photoelectron spectra (XPS) of amorphous alumina oxide, with corresponding theoretically calculated values for α- and γ-Al_2O_3. Al_2O_3 films 150 Å thick were deposited on Si by ALD from trimethyl aluminum $Al(CH_3)_3$. X-ray and ultraviolet photoelectron spectra were measured on a Phi Quantum 2000 spectrometer. The calculated relative intensities of major peaks are in good agreement with experimental relative intensities.

Calculated partial densities of states (PDOS) of α- and γ-Al_2O_3 is in qualitative agreement with published experimental X-ray emission and absorption spectra [10] (Fig. 2). The features of the structure of the experimental Al $L_{II,III}$ spectrum can not be adequately described using the calculated partial density of the Al 3s states. In SiO_2 and Si_3N_4, where a similar discrepancy is observed, the upper peak in the valence band originates from Si 3d orbitals and is associated with nonlocal (two-center) transitions [11]. Agree-

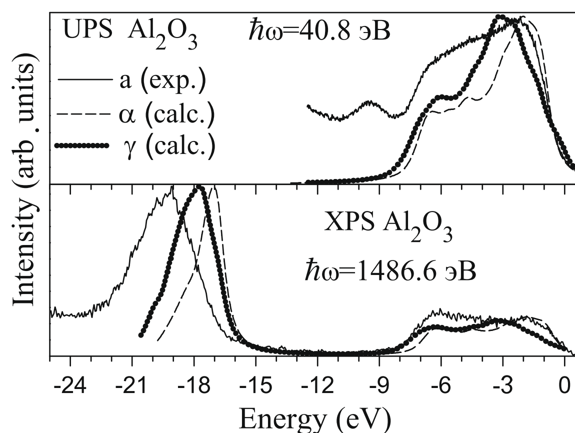

Fig. 1. Experimental UPS and XPS spectra for amorphous Al_2O_3 (solid lines). Dashed and dotted lines designate correspondent calculated spectra for α-Al_2O_3 and γ-Al_2O_3, respectively.

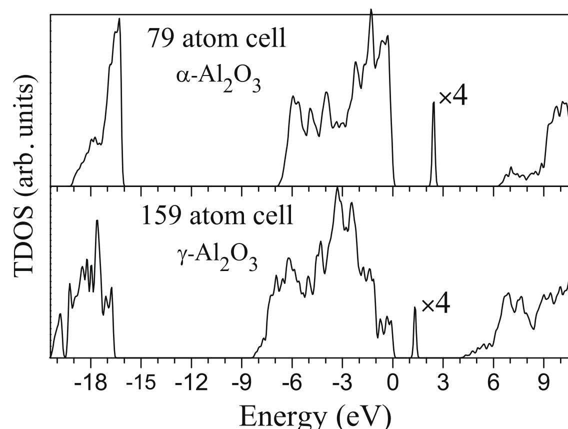

Fig. 3. Total density of electron states of α-Al_2O_3 and γ-Al_2O_3 with oxygen vacancy.

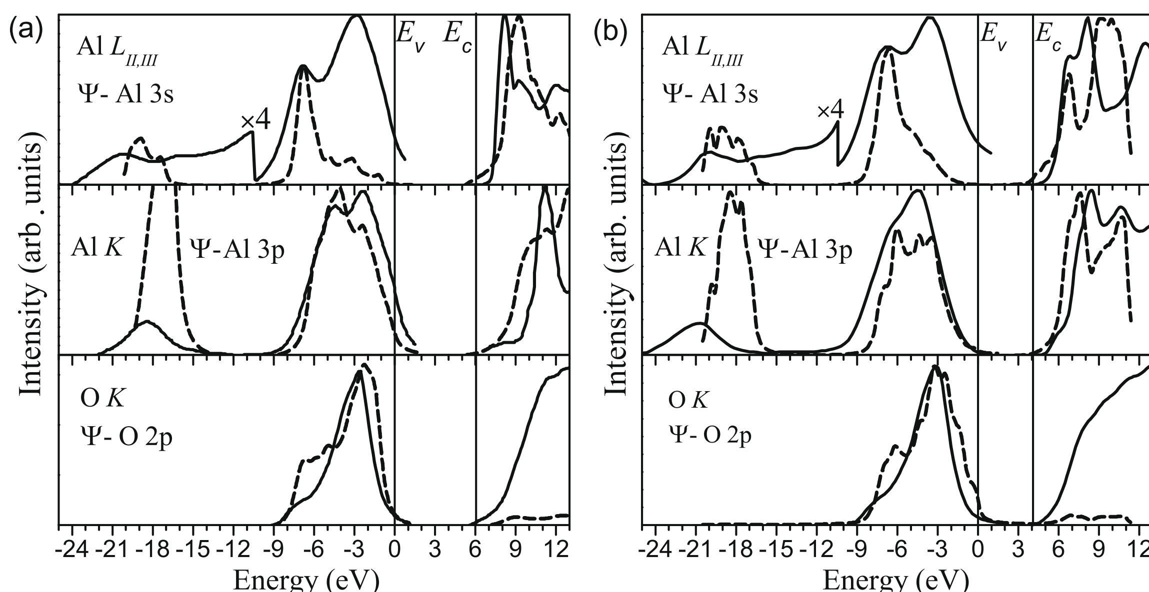

Fig. 2. Experimental X-ray emission and absorption spectra for α-Al_2O_3 (a) and γ-Al_2O_3 (b) (solid lines) with correspondent calculated PDOS in the valence and conduction bands (dashed lines).

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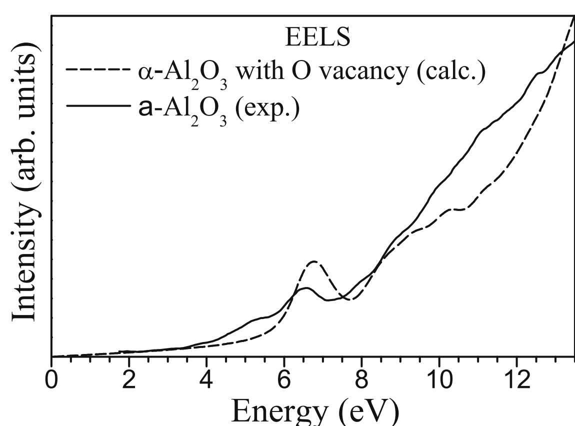

Fig. 4. Experimental EELS spectra for a-Al_2O_3 (solid line) and calculated EELS specter for α-Al_2O_3 with oxygen vacancy (dashed line).

ment between experimental and calculated data suggests that our theoretical model indeed allows a correct description of the electronic structure of both modifications. It was found that α- and γ- phases of Al_2O_3 have qualitatively similar electronic structures. Therefore, the major features of the Al_2O_3 electronic structure are determined by the nearest atomic order.

The calculated electronic structures α- and γ-Al_2O_3 with oxygen vacancy defect show that oxygen vacancy introduces a series of energy levels in the crystal band structure (Fig. 3). One occupied energy level appears above valence band in the band gap. Vacant energy levels appear close and above the bottom of conduction band. The charge localization energies were estimated as difference between perfect and defect electron affinities and ionization energies, as follows:

$$\Delta\varepsilon^{e/h} = \left(E_{\text{perfect}}^{q=-1/+1} - E_{\text{perfect}}^{q=0}\right) - \left(E_{\text{defect}}^{q=-1/+1} - E_{\text{defect}}^{q=0}\right).$$

It was obtained that electron capture on oxygen vacancy both in α- and γ-Al_2O_3 is an energetically favorable process with energy gain of 0.5 eV and 0.1 eV, respectively. So an oxygen vacancy can play the role of electron localization centre. The hole capture on oxygen vacancy is also an energetically favorable process with energy gain of 2.9 eV for α-Al_2O_3 and 1.3 eV for γ-Al_2O_3. It should be noted that calculated electron localization energies are underestimated. It is caused by the wrong position of the bottom of the conduction band and by the well-known tendency of DFT to underestimate the degree of localization of electron states in shallow traps.

Experimental EELS spectra of amorphous Al_2O_3 contains absorption peak at 6.2 eV, which is generally attributed to an F center. Our calculated EELS spectra for cells with oxygen vacancies shows peak at 6.3 eV very close to the experimental value, thus confirming theory above (Fig. 4).

Acknowledgements

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