Oxygen polyvacancy in anatas as a filament: first principle investigation

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Abstract. We investigate oxygen-deficient anatase using quantum-chemical simulation within the density functional theory. It was found that the most energetically favorable spatial configuration of an oxygen polyvacancy is a three-dimensional chain in crystallographic direction [100] or [010]. The ability of oxygen polyvacancy in the form of a chain to act as a conductive filament and to participate in the resistive switching is discussed.

1. Introduction
The currently, titanium oxide (TiO\textsubscript{2}) is being intensively studied as an active medium for nonvolatile memory devices, based on the reversible switching of dielectric from a high resistance state to a low resistance state under the current pulse in the metal-insulator-metal (MIM) structure [1, 2]. The most discussed model of the resistive switching is based on the formation and dissociation of a filament - a conductive nanowire with a diameter of 1-10 nm in the dielectric [1, 3]. It is a widespread belief that oxygen vacancies are responsible for such dielectric layer structure transformation [1, 3]. According to the filament model, a conductive channel in the resistive memory element is formed by the oxygen atoms release and migration from the lattice sites in some region of the dielectric film. Thus, the study of the atomic and electronic structure of TiO\textsubscript{2} with the vacancy complexes of closely spaced oxygen vacancies (that is, polyvacancies) is very important for determining their ability to form ordered structures and participate in resistive switching.

Oxygen divacancies and the electronic structure of highly oxygen-deficient rutile (r-TiO\textsubscript{2}) with a concentration up to 5\% were calculated in [4]. When the vacancy concentration is less than 1\%, the defective zone remains rather narrow, which does not agree with experiment and suggests that, perhaps, a defects clustering, i.e. the formation of polyvacancies, occurs. The analysis of the oxygen vacancies location in r-TiO\textsubscript{2} in the (110) plane showed that it is energetically favorable for vacancies to line up in chains [5]: a one-dimensional chain in the direction [110] or two-dimensional in the direction [001]. Titanium ions, separating vacancies in these chains, form a conductive filament. We can assume that similar conclusions are true for anatase (a-TiO\textsubscript{2}). However, the weak point of this model is that the selection of the plane (110), in which oxygen vacancies are created, is arbitrary.

The goal of the present work is to study the atomic and electronic structure of vacancy complexes (oxygen polyvacancies) in a-TiO\textsubscript{2} by means of quantum-chemical simulation and X-ray photoelectron spectroscopy.
2. Computational details
The simulation was carried out using a Quantum ESPRESSO software package within the density functional theory (DFT) in a periodic supercell model. Two types of exchange-correlation functional were used: the generalized gradient approximation in the calculations of the structural parameters optimization and another, correctly describing the value of the band gap of TiO$_2$, hybrid functional B3LYP in the calculations of the density of electronic states. We used $a$-TiO$_2$ supercells of 96, 144, and 192 atoms. To simulate the atomic structure of oxygen divacancy, after removal of the first oxygen atom, followed by relaxation, the second oxygen atom was removed according to the principle of the least energy required for this: all possible options for the location of the second vacancy were tested, and the energies of its formation were compared. The structure of oxygen trivacancy was determined similarly, but for a pair of fixed vacancies, and so on. X-ray photoelectron spectra (XPS) were calculated by summing the partial densities of filled states with weight factors equal to the corresponding values of the photoionization cross section and by smoothing using a Gaussian function with a half-width of 0.8 eV.

3. Results and discussion
First of all, the total density of states (TDOS) and partial density of states (PDOS) spectra of $a$-TiO$_2$ with oxygen monovacancy in 96 atoms supercell were calculated (figure 1). For clarity, PDOS is presented for Ti and O atoms closest to the vacancy, and only part of the spectrum is shown which includes the band gap and the conduction band. The obtained spectra are in qualitative agreement with the results obtained in the framework of close techniques in Ref. [6], as well as with experimental data [7]. The presence of oxygen vacancies leads to the two filled spin-polarized states with the one spin orientation (up) are appearance in $a$-TiO$_2$ band gap. These defective levels are formed mainly by Ti 3$d$ states closest to the vacancy atoms. It was found that the oxygen vacancy ground state is the magnetic (triplet) only in the case of simulation of relatively small supercell size (no more than 108 atoms). The oxygen vacancy ground state is nonmagnetic (singlet) for larger than 108 atoms supercells. The transition from triplet state to singlet state is due to the increase in the distance between oxygen vacancies in neighbouring supercells.

![Figure 1](image)

Figure 1. (a) TDOS spectra for electrons with spin up ($\alpha$) and down ($\beta$) calculated for 96 atom $a$-TiO$_2$ supercell with a neutral O vacancy. (b) PDOS spectra of $a$-TiO$_2$, calculated for the closest to the vacancy titanium and oxygen atoms. The zero of energy is taken the position of valence band top.

An ideal supercell of 96 atoms $a$-TiO$_2$ with the four oxygen atoms that undergo removal as well as the removal sequence is represented in figure 2a. For each subsequent vacancy, formation near the existing vacancies is energetically favorable. However, it should not be as close as possible, but at the diametrically opposite end of the octahedron. The indicated O atoms are arranged in rectangle tops.
The calculated valence band XPS for a perfect $a$-TiO$_2$ and with 1, 2, 3, and 4 O vacancies as well as experimental XPS (from [8]) for $a$-TiO$_2$ before and after Ar$^+$ ions etching are shown in figure 3. The experimental XPS for stoichiometric $a$-TiO$_2$ is in good agreement with published data [9] and is well described by the theoretical spectrum. This demonstrates the correctness of our theoretical model.

The Ar$^+$ ions etching of $a$-TiO$_2$ leads to the formation of a broad peak with a maximum 2.9 eV above the valence band top. The calculated spectra of $a$-TiO$_2$ with oxygen polyvacancies show a similar peak, and its intensity is greater with a higher degree of oxygen deficiency. The position of the maximum of the calculated peak is 2.3-2.6 eV, depending on the size of polyvacancy. Thus the Ar$^+$ ions etching leads to the formation of an oxygen-deficient surface layer in $a$-TiO$_2$. The experimental peak in the band gap is best described by the theoretical one obtained by the calculations for a 96-atom supercell with 4 O vacancies. So the vacancies concentration in the actual structure is about $10^{20}$ cm$^{-3}$.

To determine the potential of an O polyvacancy in $a$-TiO$_2$ for further growing in size, supercells of 144 and 192 atoms were used (figures 1b and 1c). Eight O atoms that are easiest to remove from the 144-atom supercell form a rectangular parallelepiped with a square base, extending along the crystallographic axis [001]. Subsequent O atoms removal is the least energy cost in the [010] or [001] direction. With an arbitrary selection of one of these directions, further increase of a polyvacancy in size will take place in this direction (Fig. 1c). Thus, the formation of O polyvacancies as a directional three-dimensional chain with a cross section diameter of 0.6 nm is energetically favorable for anatase. This calls into question the structure of the chain of oxygen vacancies in r-TiO$_2$ predicted in [5].

The energetic efficiency of the formation of oxygen vacancies chain in $a$-TiO$_2$ is consistent with the filament model of the resistive switching of dielectric. However, these chains have an orientation in the absence of an external field. The directional character of growth of a polyvacancy in size in $a$-TiO$_2$ can be naturally explained by the presence of selected high symmetry directions. In real MIM structures, TiO$_2$ layers are amorphous or polycrystalline. However, since the electronic structure of solids is mainly determined by a short range order, we can assume that amorphous TiO$_2$, as well as rutile and anatase, are characterized by energetic efficiency of the formation of each successive vacancy namely in the proximity of already existing ones, and the external electric field sets the direction of growth of a polyvacancy in the form of a certain chain (filament).
The TDOS spectra in the energy range from the valence band top ($E_r$) to the bottom of the conduction band ($E_c$), for O polyvacancies in a 192-atom $a$-TiO$_2$ supercell are shown in figure 4. For ease of interpretation and visualization of the results, calculations were carried out only for the $Γ$-point. Each removal of O atom adds level in the band gap. These levels are filled with electrons and are distributed on the band gap preferentially near the $E_c$. The growth of an O polyvacancy in size in the form of a chain yields a broad defective band in the energy spectrum of $a$-TiO$_2$ filled with electrons, which eventually intersects with the conduction band. Thus, $a$-TiO$_2$ can acquire conductivity that is implemented through the channel of titanium ions separating vacancies in this chain.

![Figure 4. Fragments of the total density of states spectra, showing the defect states in the band gap, caused by the presence of one, two, three, four, and five oxygen vacancies in a 192-atom $a$-TiO$_2$ supercell. Zero energy corresponds to $E_r$, the upper limit of energy corresponds to $E_c$.](image)

### 4. Summary

In the framework of quantum-chemical simulation, the atomic and electronic structure of oxygen polyvacancies in anatase is studied. It is demonstrated that the calculation method used is correct. We used an original procedure of searching the positions of oxygen atoms in $a$-TiO$_2$ supercells, which are removed for polyvacancies simulating. It is found that the polyvacancies formation in the form of a three-dimensional chain with a diagonal of 0.6 nm is energetically favorable for $a$-TiO$_2$. These chains of oxygen vacancies can act as a conductive shunt.

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### References

[1] Kwon D H, Kim K M, Jang J H, Jeon J H, Lee M H, Kim G H, Li X S, Park G S, Lee B, Han S, Kim M and Hwang C S 2010 Nature Nanotechnology 5 148-153

[2] Hu C Q, McDaniel M D, Posadas A, Demkov A A, Ekerdt J G and Yu E T 2014 Nano Letters 14 4360-4367

[3] Bersuker G, Gilmer D C, Veksler D, Kirsch P, Velli L, Padovani A, Larcher L, McKenna K, Shluger A, Iglesias V, Porti M and Nafria M 2011 Journal of Applied Physics 110 124518

[4] Yu N C and Halley J W 1995 Physical Review B 51 4768-4776

[5] Park S G, Magyari-Kope B and Nishi Y 2011 IEEE Electron Device Letters 32 197-199

[6] Finazzi E, Valentin C Di, Pacchioni G and Selloni A 2008 The Journal of Chemical Physics 129 154113

[7] Henrich V E, Dresselhaus G and Zeiger H J 1976 Physical Review Letters 36 1335-1339

[8] Perevalov T V, Islamov D R and Saraev A A 2016 Technical Physics Letters 42 601-604

[9] Sanjines R, Tang H, Berger H, Gozzo F, Margaritondo G and Levy F 1994 Journal of Applied Physics 75 2945-2951