Electronic structure of $\delta$-Ta$_2$O$_5$ with oxygen vacancy: ab initio calculations and comparison with experiment

Maxim V. Ivanov,$^1$ Timofey V. Perevalov,$^1$ Vladimir S. Aliiev,$^1$ Vladimir A. Gritsenko,$^1$ and Vasily V. Kaichev$^2$

$^1$A. V. Rzhanov Institute of Semiconductor Physics SB RAS, Novosibirsk, 630090, Russia
$^2$Boreskov Institute of Catalysis SB RAS, Novosibirsk, 630090, Russia

(Received 4 April 2011; accepted 27 May 2011; published online 28 July 2011)

Electronic structure of oxygen vacancies in Ta$_2$O$_5$ have been studied theoretically by first-principles calculations and experimentally by x-ray photoelectron spectroscopy. Calculations of $\delta$-Ta$_2$O$_5$ were performed using density functional theory within gradient-corrected approximation with the +U approach. Results indicate that the oxygen vacancy causes a defect level in the energy gap at 1.2 eV above the top of the valence band. To produce oxygen vacancies, amorphous films of Ta$_2$O$_5$ were bombarded with Ar$^+$ ions. XPS results indicate that the Ar-ion bombardment leads to the generation of the oxygen vacancies in Ta$_2$O$_5$ that characterize the peak at 2 eV above the valence band. The calculated spectrum of crystalline $\delta$-Ta$_2$O$_5$ demonstrates qualitative correspondence with the XPS spectrum of the amorphous Ta$_2$O$_5$ film after Ar-ion bombardment. © 2011 American Institute of Physics. [doi:10.1063/1.3606416]

INTRODUCTION

Transition metal oxides have wide application in various fields of science and technology such as electronics, optics, metallurgy, and medicine. In particular, tantalum oxide is used as antireflection coating for silicon solar cells and in the multilayer interference filters because of its high thermodynamic stability and high refractive index. Moreover, Ta$_2$O$_5$ was a first nonsilicon oxide that has been applied in a new generation of integrated memory devices. High dielectric constant of 25–50 and its excellent step coverage characteristics have made tantalum oxide a suitable alternative to SiO$_2$ for high density DRAM application. Besides, Ta$_2$O$_5$ films were applied as a storage medium in novel high-k SONOS memory with a TaN/Al$_2$O$_3$/Ta$_2$O$_5$/HfO$_2$/Si structure. Such devices exhibit a better trade-off between long retention and fast programming in comparison with traditional SONOS devices.

In the absence of defects, the current through an isolator is determined by the Fowler-Nordheim mechanism and exponentially depends on the effective tunnel masses of charge carriers. In real isolators, there always are defects that reduce the effective tunnel masses of charge carriers. These traps are responsible for charge transport and therefore can be a reason for high leakage currents. The high leakage current is one of the obstacles to the wide application of Ta$_2$O$_5$ in technology. The oxygen vacancy is considered to be one of the causes of the leakage current. Fortunately, it can be reduced by annealing in ozone, O$_2$-plasma or N$_2$O. However, the origin of the leakage current is still unclear. It was shown that there is a strong correspondence between the leakage current and the local structure around a Ta atom.

To the best of our knowledge, there are three stable low-temperature modifications of tantalum oxides: amorphous Ta$_2$O$_5$, orthorhombic $\beta$-Ta$_2$O$_5$, and hexagonal $\delta$-Ta$_2$O$_5$. The electronic structure of bulk $\beta$- and $\delta$-Ta$_2$O$_5$ and the electronic structure of oxygen vacancy in $\beta$-Ta$_2$O$_5$ have been theoretically investigated by several groups. However, there are few studies that describe correspondence of first-principles calculations with experimental data. In the present work, we investigated the electronic structure of $\delta$-Ta$_2$O$_5$ with oxygen vacancies by means of ab initio calculations along with experimental study of amorphous Ta$_2$O$_5$ by x-ray photoelectron spectroscopy (XPS). It is well known that most physical properties of solids are determined by the short-range order; that makes it reasonable to compare spectra of amorphous Ta$_2$O$_5$ with crystalline Ta$_2$O$_5$. It will be shown in the following section that the local structure of crystalline $\delta$-Ta$_2$O$_5$ is consistent with the local structure of amorphous Ta$_2$O$_5$ films. To produce oxygen vacancies, amorphous films of Ta$_2$O$_5$ were bombarded with Ar$^+$ ions. The experimental XPS spectrum of the valence band of the bombarded Ta$_2$O$_5$ films was compared with the calculated spectrum of $\delta$-Ta$_2$O$_5$ with an oxygen vacancy.

Experimental details

The film of Ta$_2$O$_5$ was deposited on a single-crystal silicon (100) p-type substrate ($\rho \approx 10 \Omega \cdot \text{cm}$) using sputtering of a tantalum target with a reactive ion beam in oxygen. The experimental set-up was described in detail elsewhere. Before the deposition, the Si(100) substrate was cleaned with diluted HF acid to remove the native SiO$_2$ layer, then rinsed with acetone, and then was immediately put into a vacuum chamber. The film was deposited at a substrate temperature of 500 °C. The deposited film was amorphous, with a refractive index around 2.1 at $\lambda = 2.0$ eV. The film thickness was 36 nm.

The core-level and valence band spectra were obtained using a SPECS's XPS machine equipped with an x-ray source XR-50M with a twin Al/Ag anode, an ellipsoidal crystal monochromator FOCUS-500, a hemispherical electron energy analyzer PHOIBOS-150, and an ion source.
Refs. 26 and 27. In contrast, Atanassova and Spassov found this oxide after the Ar-ion bombardment was observed in tors.27 The binding energies were determined with respect XPS peak area together with their relative sensitivity factors and a non-linear Shirley-type background subtraction using FitXPS software with a Gaussian-Lorentzian product Curve-fitting of the core-level spectra was carried out observed in our previous work32 for HfO2 in spite of very formation of the oxide (ΔG°f) was below 60 kcal/mol.28,29 And since for Ta2O5 ΔG°f = −471 kcal/mol, no reduction of this oxide after the Ar-ion bombardment was observed in Refs. 26 and 27. In contrast, Atanassova and Spassov found that the spattering by Ar+ (0.5–5 keV) preferentially removed oxygen from tantalum pentoxide that led to the formation of tantalum suboxides.30,31 A similar effect was also observed in our previous work32 for HfO2 in spite of very high Gibbs free energy of formation of this oxide. The partial reduction of HfO2 to hafnium suboxide HfOx due to the Ar-ion bombardment (3 keV) was detected by XPS. Unfortunately, the theory of sputtering of solids with two or more elements is very poorly developed. However, it is possible to speculate; because the coordination number of Ta cations is higher than the coordination number of O anions in the Ta2O5 lattice, the oxygen vacancies or polyvacancies are mainly generated after a few minutes of the Ar-ion bombardment of Ta2O5.

**Calculation method**

The calculations were performed with the Quantum-ESPRESSO simulation package33 within a DFT framework in the approximation of pseudopotentials with plane waves as a basis set. We used a gradient-corrected approximation with the +U approach (GGA + U) and the PW91 exchange-correlation functional. For determination of U correction, a linear response approach was applied.34 The calculated value of U for Ta atoms is equal to 1.35 eV. Optimization of the lattice constants and the atomic positions for δ-Ta2O5 was based on the BFGS quasi-Newton algorithm. The convergence criterion was satisfied when all components of all forces were smaller than 10−4 a.u.

Oxygen vacancy was created by the removing of one oxygen atom closest to the cell center. In order to minimize defect-defect interactions, we constructed a supercell by 2 × 2 × 3 translating the unit cell along the crystallographic axes. Then we relaxed the structure with the force convergence threshold of 10−3 a.u.

The Brillouin zone was sampled with a 5 × 5 × 5 k-points grid for the primitive unit cell and with a 2 × 2 × 2 k-points grid for the supercell with the cutoff energy of 35 Ry for both cells.

**Electronic structure and chemistry of amorphous Ta2O5: XPS measurements**

The Ta4f spectrum of the as-prepared amorphous Ta2O5/Si film consists of the strong spin-orbit doublet Ta4f7/2-Ta4f5/2 with splitting of 1.89 eV (Fig. 1). Maximum of the Ta4f7/2 peak is located at 26.05 eV. This value is in reasonable agreement with literature for fully oxidized stoichiometric Ta2O5 (26.2–26.3 eV).30,31 The Ar-ion bombardment of the film results in the appearance of new features in the Ta4f spectra at the lower binding energy side. All these spectra are well described with four doublets with the Ta4f7/2 binding energies of 22.0 ± 0.1, 23.2 ± 0.1, 24.6 ± 0.1, and 26.05 eV. The curve-fitting was done using fixed spin-orbit splitting (1.9 eV)

**TABLE I.** Atomic ratio [O]/[Ta], Ta4f binding energies (eV), and percentage of these states (%) for amorphous Ta2O5/Si film before and after Ar-ion bombardment.

<table>
<thead>
<tr>
<th>Spattering Time, min</th>
<th>[O]/[Ta]</th>
<th>Ta4f-2</th>
<th>Ta4f-2</th>
<th>Ta4f-2</th>
<th>Ta4f-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>26.05 (100%)</td>
</tr>
<tr>
<td>5</td>
<td>1.35</td>
<td>21.93 (17.9%)</td>
<td>23.13 (17.2%)</td>
<td>24.51 (13.1%)</td>
<td>26.05 (51.8%)</td>
</tr>
<tr>
<td>15</td>
<td>1.55</td>
<td>22.06 (15.7%)</td>
<td>23.29 (14.0%)</td>
<td>24.62 (13.1%)</td>
<td>26.05 (57.2%)</td>
</tr>
<tr>
<td>35</td>
<td>1.53</td>
<td>22.05 (13.9%)</td>
<td>23.27 (13.5%)</td>
<td>24.60 (13.2%)</td>
<td>26.05 (59.4%)</td>
</tr>
</tbody>
</table>

**FIG. 1.** Core-level Ta4f spectra of amorphous Ta2O5/Si film obtained before (1) and after Ar-ion bombardment during 5 (2), 15 (3), and 35 (4) mins.
and fixed peak area ratio (3:4) in the doublets as well as the same line shape for all peaks. The results of curve-fitting analysis are depicted in Fig. 1. Comparing with published data, these doublets can be attributed to Ta$^{1+}$, Ta$^{2+}$, Ta$^{3+}$/Ta$^{4+}$, and Ta$^{5+}$, respectively. The effect of the partial reduction of tantalum pentoxide is also confirmed by a strong decrease in the [O]/[Ta] atomic ratio after the Ar-ion bombardment. The binding energies and the percentage of these states, as well as the [O]/[Ta] atomic ratio, are listed in Table I.

Figure 2 shows the valence band spectra of the amorphous Ta$_2$O$_5$/Si film obtained before and after the Ar$^+$ bombardment. One can see that the spectrum of fully oxidized stoichiometric Ta$_2$O$_5$ consists of a broad band between 10 and 3 eV below the Fermi level. This band is mainly composed of the Ta$5d$ orbitals that are hybridized with O$2p$. After the Ar-ion bombardment, a new feature at 0.75 eV below the Fermi level appears. According to Ref. 34, this band can be assigned to Ta$5d$ orbitals in the defects like Ta in the metallic state. Hence, these XPS results unambiguously indicate that the Ar-ion bombardment leads to the generation of the oxygen polyvacancies (2.4 eV) that characterize the peak at 0.75 eV below the Fermi level in the valence band spectra.

**Electronic structure of δ-Ta$_2$O$_5$**

δ-Ta$_2$O$_5$ has a hexagonal structure (space group P6/mmm) with the lattice constants $a = b = 7.248$ Å and $c = 3.880$ Å. The calculated lattice constants for δ-Ta$_2$O$_5$ are in good agreement with the experimental values (Table I). The unit cell consists of 10 O and 4 Ta atoms. Local structure of δ-Ta$_2$O$_5$ corresponds well with the local structure of amorphous films as the average coordination number of Ta atoms in amorphous films is in the 6.1–7.8 range.

Figure 4 shows a calculated band diagram of δ-Ta$_2$O$_5$. Here and below, the zero energy corresponds to the top of the valence band. Hexagonal tantalum oxide has an indirect bandgap that is equal to 1.31 eV with the valence band top at $A = (0, 0, 0.5) = A_2$ and the conduction band bottom at the center of the Brillouin zone. The experimental value of $E_g$ for amorphous Ta$_2$O$_5$ is 4.2 eV. As far as we know, there are no experimental values of the energy gap for crystalline

![FIG. 3. Crystal structure of δ-Ta$_2$O$_5$. Light circles correspond to Ta atoms; dark circles correspond to O atoms.](http://jap.aip.org)

**TABLE II.** The optimized lattice constants (in angstroms) and the energy gaps (in eV) of δ-Ta$_2$O$_5$.

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>$E_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>This work</strong></td>
<td>7.316</td>
<td>7.316</td>
<td>3.875</td>
<td>1.31</td>
</tr>
<tr>
<td>Ref. 23</td>
<td>7.118</td>
<td>7.118</td>
<td>3.797</td>
<td>1.18</td>
</tr>
<tr>
<td>Ref. 25</td>
<td>7.338</td>
<td>7.338</td>
<td>3.88</td>
<td>1.06</td>
</tr>
<tr>
<td>Exp.</td>
<td>7.248$^a$</td>
<td>7.248</td>
<td>3.88</td>
<td>4.2$^b$ (amorphous)</td>
</tr>
</tbody>
</table>

$^a$Ref. 21.

$^b$Ref. 24 and 35.
Ta$_2$O$_5$; therefore, it is impossible to judge the accuracy of the obtained value. Nevertheless, we provide the list of theoretical values published in literature (Table II).

Table III shows calculated maximal and minimal effective masses of electrons and holes in $\delta$-Ta$_2$O$_5$. The effective masses of charge carriers were calculated using square approximation of energy dispersion $E(k)$ near the edges of valence and conduction bands. The diverse values of effective masses along the single directions demonstrate strong anisotropy for both electrons and holes.

The partial density of states (PDOS) of perfect $\delta$-Ta$_2$O$_5$ is shown in Fig. 5. It demonstrates the contribution of 5$d$, 2$s$, and 2$p$ orbitals of O atoms. The Ta6$s$ orbitals refer to deep states, and since Ta6$p$ has negligible contribution to the total density of states, these states are not shown in the figure. The upper subband of the valence band is formed mostly by 2$p$ orbitals of oxygen with a small contribution of Ta5$d$ states, while the conduction band is formed by Ta5$d$ states with an addition of O2$p$ states.

**Electronic structure of $\delta$-Ta$_2$O$_5$ with oxygen vacancy**

To simulate oxygen vacancy in $\delta$-Ta$_2$O$_5$, we used a supercell with 168 atoms after $2 \times 2 \times 3$ translation of the unit cell. Since the aim of this work is to demonstrate the correspondence of theoretical spectrum with experimental XPS spectrum, one type of oxygen vacancy was considered. The removed O atom has coordinates (0.5, 0.5, 0.5) in crystallographic axes. Figure 6 shows PDOS calculated for Ta and O atoms that are the closest to the vacancy. The oxygen vacancy causes a defect level in the energy gap. This electron-occupied level is situated 1.2 eV above the top of the valence band. The defect level is formed by 5$d$ and 6$s$ states of tantalum atoms.

Figure 7 shows the valence band spectrum of the amorphous Ta$_2$O$_5$ film bombarded with Ar-ions and the theoretical spectrum calculated by summing up the partial density of states with coefficients corresponding to the photoionization cross-sections. After Ar-ion bombardment, a wide defect peak appears at 2 eV above the top of the valence band, whereas the theoretical level is 1.2 eV above the valence band. Such discrepancy can be explained by a possibility of appearing of polyvacancies in the bombarded films, which were not considered in our theoretical model.

To clarify whether the oxygen vacancy in $\delta$-Ta$_2$O$_5$ can capture electrons or holes, we calculated localization energy for both electrons and holes. The benefit in energy after the capture of a charge carrier can be calculated by formulas

$$
\Delta E^e = E_{q=-1}^{\text{perfect}} - E_{q=0}^{\text{perfect}} - E_{q=-1}^{\text{defect}} - E_{q=0}^{\text{defect}},
$$

$$
\Delta E^h = E_{q=+1}^{\text{perfect}} - E_{q=0}^{\text{perfect}} - E_{q=+1}^{\text{defect}} - E_{q=0}^{\text{defect}}.
$$

![FIG. 5. Partial density of states of $\delta$-Ta$_2$O$_5$.](image)

![FIG. 6. Partial density of states of Ta and O atoms closest to the vacancy. Solid curve for ideal $\delta$-Ta$_2$O$_5$; dashed curve for $\delta$-Ta$_2$O$_5$ with the oxygen vacancy.](image)

![FIG. 7. Valence band spectra of Ta$_2$O$_5$. Solid curve for XPS spectrum of Ta$_2$O$_5$ after Ar-ion bombardment; dashed curve for calculated spectrum of $\delta$-Ta$_2$O$_5$ with the oxygen vacancy.](image)
Here \( E_{\text{perfect}}^{q=0} \), \( E_{\text{defect}}^{q=-1} \), and \( E_{\text{defect}}^{q=-1} \) are total energies of neutral, negatively, and positively charged supercells without the defect; \( E_{\text{defect}}^{q=-1} \), \( E_{\text{defect}}^{q=0} \), and \( E_{\text{defect}}^{q=-1} \) are total energies of neutral, negatively, and positively charged supercells with the defect.

It was obtained that electron and hole captures on the oxygen vacancy are energetically favorable processes with the energy gain of 0.3 and 1.75 eV, respectively. This result is inconsistent with experimental results on the transport properties of Al-Ta₂O₅-Si structures. It was ascertained that in amorphous Ta₂O₅ films a charge transport is conducted by electrons while holes do not contribute to the conductivity. This discrepancy may be explained by the following reasoning. A barrier for electrons at the Si-Ta₂O₅ border is equal to 0.8 eV, while the barrier for holes is equal to 2.3 eV. The 1.31 eV bandgap was found to be consistent with other reported results. To simulate oxygen vacancy supercell approach was applied. The oxygen vacancy produces shallow occupied level at 1.2 eV above the valence band top. Although, the theoretical calculations predict the defect level at 1.2 eV above the top of the valence band, the calculated spectrum of crystalline \( \delta \)-Ta₂O₅ demonstrates qualitative correspondence with the XPS spectrum of the amorphous Ta₂O₅ film after Ar-ion bombardment.

**CONCLUSIONS**

In conclusion, we performed GGA+U electronic structure calculation of bulk and defect \( \delta \)-Ta₂O₅. The optimized lattice constants are in reasonable agreement with the experimental values. The band structure of \( \delta \)-Ta₂O₅ was calculated and theoretical values of effective masses of electrons and holes were obtained. The 1.31 eV bandgap was found to be indirect, that is in agreement with other reported results. To simulate oxygen vacancy supercell approach was applied. The oxygen vacancy produces shallow occupied level at 1.2 eV above the valence band, the defect level is formed by \( 5d \) and \( 6s \) states of Ta atoms.

Besides, electronic structure of amorphous Ta₂O₅ thin films was studied with x-ray photoelectron spectroscopy. To produce oxygen vacancies Ta₂O₅ film was bombarded with Ar⁺ ions. XPS data show a wide defect peak at 2 eV above the valence band top. Although, the theoretical calculations predict the defect level at 1.2 eV above the top of the valence band, the calculated spectrum of crystalline \( \delta \)-Ta₂O₅ demonstrates qualitative correspondence with the XPS spectrum of the amorphous Ta₂O₅ film after Ar-ion bombardment.

**ACKNOWLEDGMENTS**

The work was partly supported by Siberian Branch of Russian Academy of Science through Integration Project No. 70.

37. J. J. Yeh, Atomic Calculation of Photoionization Cross-Section and Asymmetry Parameters (Gordon and Breach Science, Amsterdam, 1993).