Electronic structure of aluminum oxide: ab initio simulations of $\alpha$ and $\gamma$ phases and comparison with experiment for amorphous films

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Abstract. The electronic structure of $\gamma$-Al$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ has been investigated by means of the density functional theory. A comparison of the calculation results with experimental data for amorphous alumina films is also presented. The electronic structure is described in terms of band structure and density of states. It has been found that $\gamma$-Al$_2$O$_3$ have similar electronic structure with $\alpha$-Al$_2$O$_3$ and amorphous Al$_2$O$_3$. Effective electron masses in $\gamma$-Al$_2$O$_3$ as well as in $\alpha$-Al$_2$O$_3$ equal to $m_e^* \approx 0.4 m_0$ that is in a good agreement with the experimentally found tunnel electron mass in amorphous Al$_2$O$_3$. The heavy holes in both alumina crystals are explained by the valence band top forming by O 2$p_z$ nonbonding orbitals.

1 Introduction

Aluminum oxide (Al$_2$O$_3$) is an important material that is widely used in many technological applications. It is well known that Al$_2$O$_3$ exists in various metastable polymorphs (transition aluminas like $\gamma$, $\eta$, $\delta$, $\theta$ and $\chi$ phases) in addition to the thermodynamically stable $\alpha$-Al$_2$O$_3$ phase (corundum) [1]. The transition aluminas (especially the $\gamma$ phase) have fine particles size with high surface area, and find industrial applications as adsorbents, catalysts or catalysts supports, coatings and soft abrasives [2]. $\alpha$-Al$_2$O$_3$ mainly used as electrical insulators, tunneling barriers, and radiation-resistant materials as well as an optical material. In the last years aluminas also attracted much attention as an alternative dielectric for future applications in silicon devices. This fact is explained by high dielectric constant of Al$_2$O$_3$ which is at least 2 times higher than the one of silicon dioxide [3]. Correspondingly, thin alumina films are considered as gate dielectric layers in Complementary Metal-Oxide-Semiconductor (CMOS) devices that allows to suppress the gate leakage current arising due to direct tunneling of electrons [4,5]. Another new important application of alumina is a blocking dielectric in Silicon-Oxide-Nitride-Oxide-Silicon (SONOS) flash memory [6,7]. In the last case replacement of traditional SiO$_2$ by high-$k$ dielectric opens possibilities for increasing of the performance, reliability, production yield and for reducing of the flash memory devises production cost. Nowadays TaN-Al$_2$O$_3$-Si$_3$N$_4$-SiO$_2$-Si (TANOS) structures are also are intensively investigated in order to develop the flash memory devices of giga- and terabit scales [8]. These new directions in the semiconductor microelectronics stimulate high interest to theoretical and experimental studies of the electronic structure of the different Al$_2$O$_3$ polymorphs [9,10].

For practical usage in the microelectronics alumina is usually evaporated in the amorphous phase by Atomic Layer Deposition (ALD) technique [11]. The following thermal annealing, which is used for a densification of the alumina films, results in a crystallization to $\gamma$-Al$_2$O$_3$ [12,13]. Upon crystallization, the bandgap and band offsets of Al$_2$O$_3$ increase significantly [14]. This point out that the crystal structure of Al$_2$O$_3$ layers affects characteristics of the blocking dielectric in the flash memory devices, in spite of the fact that $\gamma$-Al$_2$O$_3$ atomic coordination is quite close to amorphous phase coordiniation [15-17]. Unfortunately, alumina is characterized by unacceptably large leakage current density that limits its application in the flash memory devices [8,18]. In the polycrystalline oxide films high level of the leakage current density is mainly determined by the presence of grain boundaries. In the defects absence the charge transfer is specified by tunneling injection of electrons and holes. It could be described with Fowler-Nordheim tunneling mechanism. The current magnitude is exponentially depending on effective masses of charge carriers in dielectric. Hence,
the determination of electron and hole effective masses allows estimating acceptable characteristics of corresponding structures. It should be noted that the alumina importance has motivated intensive experimental and theoretical investigations. At the same time, the great number of the works is devoted to the study of the corundum electronic properties, while the electronic structure of $\gamma$-Al$_2$O$_3$ is studied much more modestly [19–24]. The deficiency of the experimental studies of $\gamma$-Al$_2$O$_3$ is associated with a difficulty of obtaining pure samples due to the metastable nature of this phase. For theoretical researches, difficulties come from the complexity of the $\gamma$-Al$_2$O$_3$ crystal structure. According to crystallographic data $\gamma$-Al$_2$O$_3$ has a pseudoamorphous defective spinel structure in which Al cations and vacancies are randomly distributed among the tetrahedral and octahedral sites within a perfect fcc sublattice of oxygen atoms [25,26]. In contrast some authors suggest that 40% of the cations in the $\gamma$-Al$_2$O$_3$ structure occupy nonspinel positions [27]. Controversy over the structures of $\gamma$-Al$_2$O$_3$ is widely discussed in the literature [27]. Nevertheless, for our study we pick out a spinel-related structure of $\gamma$-Al$_2$O$_3$.

In this contribution, we used the Quantum-ESPRESSO code [28] based on the density functional theory (DFT), plane waves, and pseudopotentials (both norm-conserving and ultrasoft) in order to investigate the electronic structure of bulk $\gamma$-Al$_2$O$_3$ in details. For calibration of our calculating technique we produced a thorough simulation of the well-studied $\alpha$-Al$_2$O$_3$ electronic structure. The results were also compared with available experimental data, including data on amorphous alumina. The differences between the $\alpha$, $\gamma$ and amorphous phases were discussed.

2 Theoretical and experimental techniques

The theoretical results were obtained using the QUANTUM-ESPRESSO code based on DFT within the plane-wave as a basis set and pseudopotential approximation [28]. The ion-electron interactions were described using the ultrasoft pseudopotentials [29] in both a generalized gradient approximation (GGA) exchange-correlation functional in the Perdew-Burke parameterization and a local density approximation (LDA) functional in the Perdew-Zunger parameterization [28,30]. These pseudopotentials were chosen from a reason of the best description of structural parameters of the $\alpha$-Al$_2$O$_3$ cell. The Brillouin Zone of the unit cell was sampled with a $7 \times 7 \times 7$ $k$-points grid for $\alpha$-Al$_2$O$_3$ and a $5 \times 5 \times 3$ $k$-points grid for $\gamma$-Al$_2$O$_3$. The grids were generated by the Monkhorst-Pack algorithm. The plane-wave cutoff energy was selected in such way that the convergence in the total unit-cell energy was not worse than 0.0001 Ry/atom and was taken equal to 40 Ry. The geometry optimization was performed using the BFGS algorithm [31].

To test our approach, bulk properties of $\alpha$-Al$_2$O$_3$ were modeled and compared with literature data. The perfect crystal of $\alpha$-Al$_2$O$_3$ has a trigonal unit cell containing two Al$_2$O$_3$ molecules (space group R-3cR). Each Al cation is bonded to six O anions in the form of a distorted octahedron and each O anions is bonded to four Al cations in the form of a distorted tetrahedron. The calculated lattice constants show an agreement level with experiment, which is typical for solid-state DFT calculations: the LDA calculations underestimate the lattice constant by $\sim 2\%$ relatively to the experimentally observed value, whereas the GGA calculations overestimate the lattice constants by $\sim 1\%$. The equilibrium lattice constants of $\alpha$-Al$_2$O$_3$ calculated with the GGA pseudopotential equal $a_1 = 5.160$ Å and $\theta_1 = 55.286^\circ$, calculated with the LDA pseudopotentials equal $a_i = 4.981$ Å and $\theta_i = 55.238^\circ$, whereas experimental values are: $a_i = 5.1284$ Å, $\theta_i = 55.28^\circ$ [32]. Previous ab initio calculations of $\alpha$-Al$_2$O$_3$ carried out with different techniques had similar agreement with experiment [33].

The crystal structure of $\gamma$-alumina has been a long-standing interest. A review of the main experimental results can be found in reference [27]. At present, there are two principal theoretical models of bulk $\gamma$-Al$_2$O$_3$: spinel-related structure and nonspinel structure. Most of researchers suggest that $\gamma$-alumina structure resembles a close packed oxygen (fcc) lattice with Al cations and vacancies statistically distributed among the tetrahedral and octahedral sites. It can be generated either from a strained hausmannite or a spinel structure by removing Al cations to achieve Al$_2$O$_3$ stoichiometry. The spinel-related structure is well described by model proposed by Sohlberg et al. [34] and worked out in future by Gutierrez et al. [35]. Minimal structure of $\gamma$-Al$_2$O$_3$ has 16 Al cations and 24 O anions in the unit cell is derived from the spinel with two cation vacancies at octahedral sites that are farthest from each other. This structural model is widely used in the literature [21,22,26]. Another computational model proposed by Paglia et al. [27] are referred to 160-atoms supercells with significant portions of occupied nonspinel positions. These unit cells must not be regarded as the actual structures, but as representative of a rather large number of structures that have very close energies. As mentioned in the introduction, due to the statistical distribution of vacancies, the structure can be regarded as pseudoamorphous. Nonspinel Paglia structure reproduce a number of experimental features of $\gamma$-Al$_2$O$_3$. However, Proupin and Gutierrez compared the electronic properties, calculated for both Sohlberg and Paglia $\gamma$-Al$_2$O$_3$ models, and found that the band structure of the nonspinel model shows some additional information [23]. Moreover, the calculated total energy of the nonspinel structure is 5 meV/atom higher than the one of the spinel structure. The authors associate this result with systematic errors inherent to DFT.

Thereby in current investigations we take the minimal 40-atoms defective spinel structure of $\gamma$-Al$_2$O$_3$. In this model the coordination numbers for O anions can be either three or four, and the Al cations can be four- or sixfold coordinated. The equilibrium unit cell constants for $\gamma$-alumina, calculated with the GGA pseudopotentials are $a_1 = 5.661$ Å, $a_2 = 5.625$ Å, $a_3 = 13.625$ Å and $\theta_1 = 89.456^\circ$, $\theta_2 = 90.015^\circ$ $\theta_3 = 120.213^\circ$. It is close...
to monoclinic structure (space group C2/m) obtained by Pinto et al. [21]: \( a_1 = a_2 = 5.663 \text{ Å}, a_3 = 13.712 \text{ Å}, \theta_1 = \theta_2 = 90.6^\circ, \theta_3 = 119.60^\circ \) and almost coincident with calculated structural data of Proupin and Gutierrez [23].

X-ray photoelectron spectra of amorphous \( \text{Al}_2\text{O}_3 \) were measured on a SPECS’s spectrometer equipped with a X-ray source XR-50M with a twin Al/Ag anode, FOCUS-500 ellipsoidal crystal monochromator, and hemispherical electron energy analyzer PHOBIOS-150. The valence band spectra as well as O 1s and Al 2p core-level spectra were typically obtained using monochromatic Al K\( \alpha \) radiation and a fixed analyzer pass energy of 10 eV. Both O 1s and Al 2p core-level spectra were used for determination of the bulk plasma oscillations energy and bandgap [36–38]. Ultraviolet-induced electron emission spectra of valence band were also obtained using He lamp capable of producing He II (40.8 eV) radiation.

The electron energy loss spectrum (EELS) of amorphous \( \text{Al}_2\text{O}_3 \) was measured at the energy of the monochromatic electron beam equal to 200 eV. The amorphous \( \text{Al}_2\text{O}_3 \) samples were synthesized by ALD method from trimethylaluminum Al(CH\(_3\))\(_3\) and water vapor H\(_2\)O. The p-type silicon with (100) orientation and \( \approx 10 \Omega \text{ cm} \) resistance was used as substrate.

### 3 Results and discussion

The band structure of \( \gamma\text{-Al}_2\text{O}_3 \) calculated along the high-symmetry lines of the BZ is typical for an insulator material. The obtained results are in agreement with earlier calculations [20–23]. \( \gamma\text{-Al}_2\text{O}_3 \) has a direct bandgap with valence band (VB) top and conduction band (CB) bottom at the \( \Gamma \)-point, like in \( \alpha \)-phase. Both upper and lower valence bands calculated for \( \gamma\text{-Al}_2\text{O}_3 \) are slightly widened in comparison with \( \alpha\text{-Al}_2\text{O}_3 \). At the same time, the energy gap between upper and lower valence band as well as bandgap between VB top and CB bottom for \( \gamma\text{-Al}_2\text{O}_3 \) are reduced against \( \alpha\text{-Al}_2\text{O}_3 \). The bandgaps values for \( \gamma\text{-Al}_2\text{O}_3 \) calculated with the GGA pseudopotential is 3.9 eV and calculated with the LDA pseudopotential is 5.1 eV. Correponding values for \( \alpha\text{-Al}_2\text{O}_3 \) are 6.0 eV and 7.3 eV. The bandgaps obtained using both methods are noticeably smaller than the correspondent experimental values. The reported experimental bandgap values for \( \alpha\text{-Al}_2\text{O}_3 \) is 8.8 eV [39], and for \( \gamma\text{-Al}_2\text{O}_3 \) is 7.0–8.7 eV [19,39].

Figure 1 shows the results of X-ray emission spectroscopy (XES) taken from reference [40]. One can see spectra of the valence band as well as Al \( L_\alpha \), Al \( K \) and O \( K \) emission and quantum yield spectra of \( \alpha\text{-Al}_2\text{O}_3 \) and \( \gamma\text{-Al}_2\text{O}_3 \). The respective calculated partial densities of states (PDOS) are represented on the same plots in dashed lines. All spectra are reduced to a common energy scale and the position of the valence band top is taken as zero energy. According to the dipole selections rules, the Al \( L_{\alpha III} \) spectra reveal the transitions between the 2p and 3s, 3d orbitals of Al, the Al K – the transitions between the 1s and 3p orbitals of Al, and the O K – transitions between the 1s and 2p orbitals of O. To an accuracy of the matrix elements dependence from energy one should suppose that the experimental XES spectra reflect the PDOS in valence band.

Calculated PDOS of \( \alpha \)- and \( \gamma\text{-Al}_2\text{O}_3 \) is in acceptable qualitative agreement with published experimental X-ray emission and absorption spectra. The agreement of calculations with the XES Al \( K \) spectrum for both \( \alpha\text{-Al}_2\text{O}_3 \) and \( \gamma\text{-Al}_2\text{O}_3 \) is observed for the upper valence band only. The calculated relative intensities of the peaks corresponding to the partial density of Al 3p states in the lower valence band exceed the peak intensities in the upper valence band. Previously, similar discrepancy for Si 3p peaks was observed in SiO\(_2\) and Si\(_3\)N\(_4\) [41]. The structure of the experimental Al \( L_{\alpha III} \) spectrum can not be adequetly described using the calculated partial density of the Al 3s states. In particular, the upper peak in the Al \( L_{\alpha III} \) at energy of \( \approx 3 \text{ eV} \) for both crystalline alumina is absent in the Al 3s spectrum. This is due to the fact that Al 3d orbitals are ignored in our theoretical model. The calculation of the \( \text{Al}_2\text{O}_3 \) electronic structure with a correct consideration of the contribution of aluminum 3d orbitals for the description of X-ray emission spectra was beyond the scope of this work. The PDOS calculations for \( \gamma\text{-Al}_2\text{O}_3 \) made by Proupin and Gutierrez [23] show Al 3d peak exactly at energy of \( \approx 3 \text{ eV} \). For SiO\(_2\) and Si\(_3\)N\(_4\) resembling discrepancy of calculations with experiments is associated with nonlocal (two-center) transitions [41].

Based on presented XES data the energy diagram which reflects the electron transitions in \( \alpha\text{-Al}_2\text{O}_3 \) was constructed (Fig. 2). The diagram has been constructed within a framework of approach which was developed for SiO\(_2\) [42]. The energy level of electron in vacuum is taken as zero energy. The vacuum level locates on \( \phi^e = 2.0 \text{ eV} \) above conduction band bottom [43,44]. The horizontal lines in the valence and conduction bands correspond to density of states peaks position which were observed in X-ray transition. The Al 1s and Al 2p energy levels are evaluated from the X-ray emission spectra published in.
Fig. 2. The empirical energy diagram reflecting the electron transitions in α-Al₂O₃ are observed in the emission and ionization spectra of the core levels.

The O 2s and O 2p energy levels were taken from reference [45].

It is known that solid states electronic structure is determined by the short range atomic order. In reference [40] with XES it was found that crystalline α and γ-Al₂O₃ have very similar electronic structure and, moreover, it is close to electronic structure of Al(OH)₃. On that ground in current work we compare our calculated results for α- and γ-Al₂O₃ with experimental data for amorphous alumina. Figure 3 presents a comparison of experimental valence band spectra obtained with ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) for amorphous alumina (α-Al₂O₃) with corresponding theoretically calculated spectra of α- and γ-Al₂O₃. The calculated spectra are obtained by summing the PDOS with regard to the corresponding photoionization cross sections [46]. The calculated relative intensities of major UPS and XPS peaks are in satisfactory fit with experimental relative intensities. Due to low photoionization cross section of Al 3s and Al 3p the main contribution to the UPS at excitation energy of 40.8 eV is from the O 2p orbitals. In contrast the XPS obtained at excitation energy of 1486.74 eV exhibits two distinct structures at 17–18 eV and 1–7 eV binding energy, which mainly correspond to photoemission from the O 2s and Al 3s orbitals, respectively. The variance in experimental and calculated peaks position causes by underestimation of DFT calculated bands width. In turn the variance in experimental and calculated peaks width could be caused by limited...
Table 1. Calculated maximum and minimum values of effective electron $m_e^*$ and hole $m_h^*$ masses in $\alpha$- and $\gamma$-$\text{Al}_2\text{O}_3$.

<table>
<thead>
<tr>
<th>Effective mass</th>
<th>$\alpha$-$\text{Al}_2\text{O}_3$</th>
<th>$\gamma$-$\text{Al}_2\text{O}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron mass</td>
<td>$m_e^*/m_0 \approx 0.4$</td>
<td>$m_e^*/m_0 \approx 0.4$</td>
</tr>
<tr>
<td>Hole mass</td>
<td>7.5</td>
<td>1.3</td>
</tr>
<tr>
<td>$m_h^*/m_0$</td>
<td>0.4</td>
<td>$\gtrsim 1$</td>
</tr>
</tbody>
</table>

hole’s lifetime on the core levels which leads to widening of experimental peaks.

Thus the satisfactory qualitative agreement between experimental and calculated data suggests that indeed our theoretical model provides a correct description of the electronic structure of both alumina modifications. Moreover, it is seen that $\alpha$- and $\gamma$-$\text{Al}_2\text{O}_3$ have qualitatively equivalent electronic structures, which is rather close to electronic structure of amorphous alumina. It confirm that the major features of the $\text{Al}_2\text{O}_3$ electronic structure are determined by the short range atomic order.

Table 1 presents calculated maximum and minimum values of effective electron and hole masses in $\alpha$- and $\gamma$-$\text{Al}_2\text{O}_3$. Effective masses were calculated by means of quadratic approximation of highest occupied and lowest unoccupied bands $E(\vec{k})$:

$$m_{\alpha/\gamma}^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E(\vec{k})}{\partial k^2}.$$  \hspace{2cm} (1)

Effective electron masses both in $\alpha$- and $\gamma$-$\text{Al}_2\text{O}_3$ are isotropic and their values $m_e^* \approx 0.4 m_0$ are coinciding. This value should be compared with the experimental values of the tunneling effective mass for electrons in $\text{Al}_2\text{O}_3$: $m_e^* = 0.3 m_0$ [47], $m_e^* = (0.22 - 0.42) m_0$ [48], $m_e^* = 0.5 m_0$ [49], and $m_e^* = 0.2 m_0$ [49]. In both alumina polymorphs light and heavy holes are presented. For both alumina polymorphs the strong anisotropy effective hole mass tensors was observed. Unfortunately, there is no experimental data about alumina effective hole masses.

The presence of the heavy holes masses in alumina can be explained by the fact that the VB top for $\alpha$- and $\gamma$-$\text{Al}_2\text{O}_3$ is mainly formed by the nonbonding O 2p$_\pi$ orbitals. This is proved by the plot of valence charge densities in an O-Al-O bonding plane presented in Figure 4. One can see the charge density of the highest part of upper VB (Fig. 4a) has the preferential orientation perpendicular to the Al–O bond that corresponds to the O 2p nonbonding $\pi$ states. The similar electronic density map of the top band in the upper VB for $\gamma$-$\text{Al}_2\text{O}_3$ was obtained in reference [21]. The presence of the light holes is explained by an admixture of the bonding O 2p and Al 3s, 3p orbitals. Figure 4b shows the charge density of O 2p-like character which lies along the Al–O bond. This implies that it is $\sigma$ bonding Al–O orbital. The similar valence charge density distribution were found for SiO$_2$ [50].

Figure 5 shows the experimental EELS spectra for amorphous and $\alpha$- phase of alumina. The zero energy corresponds to the energy of elastical scattered electrons. The experimental spectrum of $\alpha$-$\text{Al}_2\text{O}_3$ has the major peak at 23.7 eV which corresponds to the valence-electron plasma oscillations ($\hbar\omega_p$). The EELS spectrum of $\alpha$-$\text{Al}_2\text{O}_3$ (taken from Ref. [51]) gives $\hbar\omega_p = 26$ eV. This experimental peak is very close to peak 26.5 eV calculated for the energy loss function $-\text{Im}(1/\varepsilon)$ for $\alpha$-$\text{Al}_2\text{O}_3$ presented on the same plot. Our calculations of the dielectric function ($\varepsilon$) allow taking into account the bandgap underestimation by adding rigid shift of the conduction band enhancing the energy bandgap. Thus we used rigid shift 1.8 eV for calculations $\alpha$- and $\gamma$-$\text{Al}_2\text{O}_3$. Because of the calculated $\varepsilon$ for both $\alpha$- and $\gamma$-$\text{Al}_2\text{O}_3$ are almost isotropic, we present averaged values. The function $-\text{Im}(1/\varepsilon)$ is proportional to the probability that fast electrons traversing the bulk material will lose energy. One would expect the peak of $-\text{Im}(1/\varepsilon)$ for our systems to be in the vicinity of the plasma energy.

The calculated plasma oscillations energy is in good agreement with experimental measured values. In this work we also use X-ray photoelectron spectroscopy for determination of $\hbar\omega_p$. It is well-known that the photoelectrons emitted within the solids may suffer inelastic
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Fig. 6. Al 2p and O 1s core level XPS spectra of amorphous Al₂O₃. The satellites at the higher binding energy correspond to the plasmon loss peaks.

Fig. 7. Energy loss spectrum of O 1s photoelectrons for amorphous Al₂O₃ film.

losses due to plasmon and band-to-band excitations. The plasmon loss signals are usually observed with a rather broad spectrum shifted toward the higher binding energy side (the lower kinetic energy side) of the primary core-level peak by a value of plasma oscillations energy. For amorphous Al₂O₃ one can see extrapeaks in the O 1s as well as in the Al 2p core-level spectra shifted toward the higher binding energy side by 23.4 eV (Fig. 6). It means that for α-Al₂O₃ the energy of bulk plasma oscillations is about 23.4 eV. According to literature data, calculated (Refs. [19,52–55]) and experimental measured (Refs. [55,56]) values of \( h\omega_p \) for different phases of alumina are in the range from 23 eV to 26 eV.

From the threshold energy of the energy loss spectra of photoelectrons the bandgap energy could be determined as well. Figure 7 shows O 1s photoelectrons energy loss spectrum of amorphous Al₂O₃ film with thickness of 15 nm. The onset of band-to-band excitation of amorphous Al₂O₃ film which corresponds to the bandgap was defined as an intercept of the linear extrapolation of the leading edge to the background level. For this amorphous film the bandgap is about 6.5 eV. It is close to 6.2 eV value measured for 15-nm-thick amorphous alumina film obtained by the atomic layer chemical vapor deposition (ALCVD) using the photoconductivity technique [44] and to 6.7 eV measured for 9-nm-thick ALCVD alumina film with XPS [38].

4 Conclusion

γ-Al₂O₃ has considerable technological importance for modern microelectronics. We have presented a comparative study of the electronic properties of γ-Al₂O₃ with α-Al₂O₃ and amorphous Al₂O₃. The comparisons with experimental results for α- and amorphous alumina shows that our calculation technique and crystal structures provide correct description of the electronic structure and interatomic interaction of both Al₂O₃ modifications. We have shown that γ-Al₂O₃ and α-Al₂O₃ have similar electronic structure. It can be concluded that the electronic properties of Al₂O₃ are determined by the short-range atomic order.

For both crystals the electron effective mass are isotropic and equal to 0.4m₀. This value comparable to most semiconductors and is smaller than the hole effective mass. This indicates that the electronic conduction in these crystals is possible, if somehow the electrons can be promoted to CB by overcoming the large bandgap. The top of the highest VB for both α- and γ-Al₂O₃ is formed by the nonbonding O 2pₓ orbitals preferentially. In all probability, it explains the presence of the heavy effective hole masses in α- and γ-Al₂O₃. The light holes are explained by the admixture of bonding O 2pₓ and Al 3s, 3p orbitals. The calculated values of the plasmon energy for both α- and γ-Al₂O₃ are equal to 26.5 eV which is in a good agreement with previous calculated values and experimental data for α-Al₂O₃.

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