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## Effects of transition metal impurities in alpha alumina: a theoretical study

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**Abstract.** Ab-initio calculations based on density functional theory have been employed to study the electronic and some optical properties of Y and Nb doped  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with corundum structure. The Nd presence elevates the static dielectric constant of the pure alumina, but changes significantly its band offset. Doping with Y preserves the band gap value and increases slightly the dielectric constant of the pure alumina, thus showing a potential to be used in semiconductor industry.

### 1. Introduction

In recent years the semiconductor industry has been searching for a material which could substitute the silicon dioxide (SiO<sub>2</sub>) in order to construct a new type of dielectric gate in transistors [1,2]. The new material should meet two fundamental criteria: it needs to possess a wide band gap and a high dielectric constant at the same time. Various studies indicate the alumina (Al<sub>2</sub>O<sub>3</sub>) as one of the most promising candidates for such a substitution [3]: it has a wide band gap, similar band offset as the SiO<sub>2</sub> and high dielectric constant ( $\kappa = 9$ ), which can be elevated even more by appropriate doping of the pure material.

In 2002 the theoretical study of Haverty et al [4] showed that a presence of certain transition metals (Y, Sc) in the alumina with orthorhombic structure ( $\kappa$ -Al<sub>2</sub>O<sub>3</sub>) maintains the gap value and increases the dielectric constant, while the presence of others (Zr, Nb) diminishes the gap. In 2003 these theoretical predictions have been confirmed by Lee et al [5], who studied experimentally the amorphous alumina doped with 6,25 % of Y, Sc, Zr and Nb.

The objective of the present work is to verify if the presence of the same impurities induces the same effects in the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with corundum structure, which is a common material with a large scale of applicability. For this purpose we calculated the electronic and some optical properties of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> doped with the Y (as a representative of the first group of impurities) and with the Nb (representing the second group of impurities). The principal goal is to estimate if the doped materials satisfy the fundamental criteria of semiconductor industry or not.

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## 2. Calculations

The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallizes in a corundum structure, with the hexagonal Bravais lattice and the space group R-3C (167). The unit cell contains two molecular formulas, i.e. 10 atoms. The local coordination of the Al consists of 6 oxygen atoms arranged in the vertices of distorted octahedron [6].

The pure alumina has been modeled by infinite repetition of a supercell comprising the 8 original cells (80 atoms). This has been done in order to compare the calculated properties with the doped systems, and to be able to extract the impurity effects. The doped alumina crystals were simulated by substitution of one Al in the center of pure alumina supercell by Y and Nb respectively.

The self-consistent band-structure calculations were performed by density-functional theory [7] based, full potential linear augmented plane wave (FP-LAPW) method [8] as embodied in WIEN2k computer code [9]. In this method, the electronic wave functions, charge density and crystal potential are expanded in spherical harmonics inside the non-overlapping spheres centered at each nuclear position (atomic spheres), and in plane waves in the rest of the space (interstitial region). The choice for the atomic sphere radii (in atomic units) was 1.8 for the Al, Y and Nb, and 1.5 for O. Inside atomic spheres the partial waves were expanded up to  $l_{\max}=6$ , while the number of plane waves in the interstitial was limited by the cut-off at  $K_{\max}=7.5/R_{\text{MT}}$ . The augmented plane waves were utilized as a basis set. The charge density was Fourier expanded up to  $G_{\max}=14$ . For the k-space integration a mesh of 6 k-points in the irreducible part of the Brillouin zone was used. Exchange and correlation effects were treated by generalized-gradient approximation (GGA96) [10]. The Al 2p, 3s and 3p, the O 2s and 2p, the Nb 4s, 4p, 4d and 5s, and the Y 4s, 4p, 4d and 5s electronic states were considered as valence ones, and treated within the scalar-relativistic approach, whereas the core states were relaxed in a fully relativistic manner.

The crystal structure of the pure and the doped systems was computationally optimized: all atomic positions around the impurities were allowed to relax until the equilibrium position were reached, while the unit cell parameters were optimized only for the pure crystal and kept unchanged for the doped systems.

The optical response of the studied systems is determined by calculating their complex dielectric tensors  $\epsilon$ . Imaginary part of this tensor is directly proportional to the optical absorption spectrum of the materials. It can be computed from knowledge of the electronic band structure. In the limit of linear optics, neglecting electron polarization effects and within the frame of random phase approximation, the expression for the imaginary part of  $\epsilon$  is the following [11]:

$$\text{Im} \epsilon_{\alpha\beta}(\omega) = \frac{4\pi^2 e^2}{m^2 \omega^2} \sum_{i,f} \int_{\text{BZ}} \frac{2dk}{(2\pi)^3} \left| \langle \varphi_{fk} | P_{\beta} | \varphi_{ik} \rangle \right| \left| \langle \varphi_{fk} | P_{\alpha} | \varphi_{ik} \rangle \right| \cdot \delta(E_f(k) - E_i(k) - \hbar\omega) \quad (1)$$

for a vertical transition from a filled initial state  $|\varphi_{ik}\rangle$  of energy  $E_i(k)$  to an empty final state  $|\varphi_{fk}\rangle$  of energy  $E_f(k)$  with the same wave vector  $k$ .  $\omega$  is the frequency of the incident radiation,  $m$  the electron mass,  $P$  the momentum operator, and  $\alpha$  and  $\beta$  stand for the projections x,y,z.

We computed the  $\text{Im}(\epsilon)$  up to incident radiation energy of  $\hbar\omega = 40$  eV. The real part of dielectric tensor is then determined using Kramers-Kronig relation. Both real and imaginary parts of  $\epsilon$  were calculated with a mesh of 38 k-points in the irreducible wedge of the first Brillouin zone, for all three studied systems. Owing to the hexagonal symmetry the dielectric tensor is diagonal, with two different values:  $\epsilon_{zz}$  (along the c-axis of the crystal) and  $\epsilon_{xx}=\epsilon_{yy}$  (in the plane perpendicular to the hexagonal c-axis).

## 3. Results and discussions

### 3.1. Electronic structure

The figure 1 shows the calculated total electronic density of states (TDOS) of the pure and doped alumina in the energy interval around the Fermi level. The electronic structure of the pure Al<sub>2</sub>O<sub>3</sub> is

characterized by 3 blocks of electronic states, two of them in the valence and one in the conduction region. A more detailed analysis [12] shows that the bands in the valence region are dominated by the oxygen's states: s- (lower energy block) and p- (higher energy block). The conduction band is composed of the hybridized s- and p- states of Al and O. The band gap value is calculated to be 6.0 eV, underestimated in comparison with the experimental value (8.7 eV [13]) due to approximate treatment of exchange and correlation effects (GGA) in the practical application of DFT.

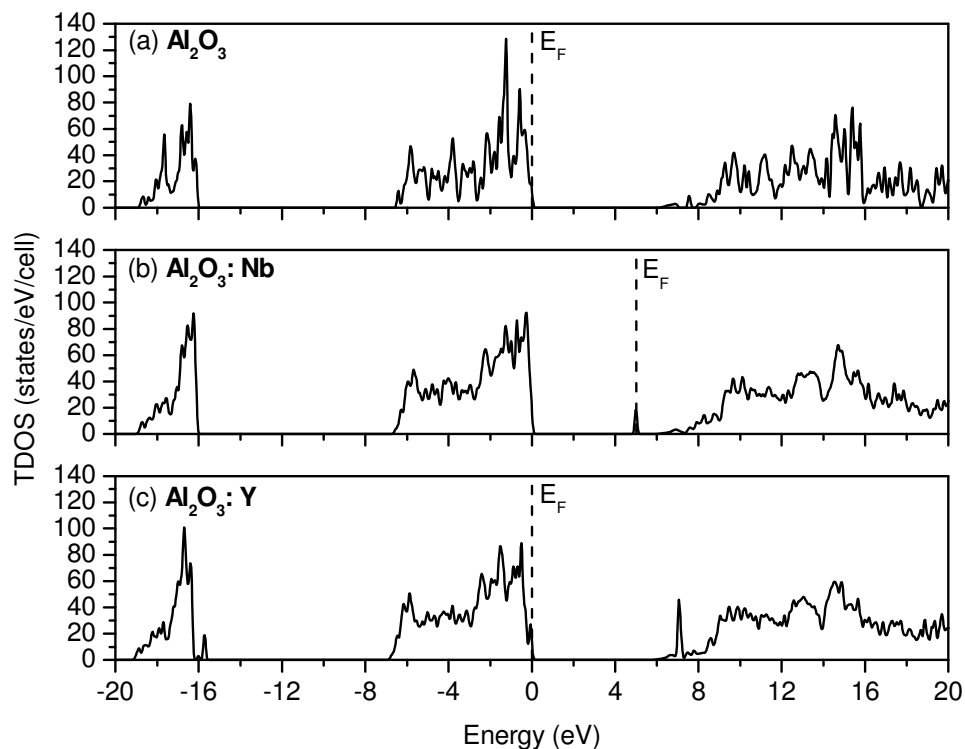


Figure 1: Total density of electronic states of (a) pure  $\text{Al}_2\text{O}_3$ , (b)  $\text{Al}_2\text{O}_3$  doped with Nb and (c)  $\text{Al}_2\text{O}_3$  doped with Y. Dashed lines denote Fermi levels.

Insertion of the Nb into the  $\text{Al}_2\text{O}_3$  changes significantly its band structure (fig. 1b). The calculated band gap value is 4.8 eV, diminished in comparison with the gap value of the pure alumina. The Nb introduces one shallow band within the gap and one broad band at the bottom of the conduction band. These bands are composed of the Nb d-states, strongly hybridized with the nearest neighbour O's p-states [12]. The shallow band is situated approximately 1 eV below the bottom of the conduction band.

In the case when the  $\text{Al}_2\text{O}_3$  is doped with Y, its electronic structure is much less changed (fig. 1c). The calculated gap value is practically the same as for the pure alumina (~6.0 eV), in accordance with the previously published theoretical value [14]. The Y introduces one sharp band situated at the very bottom of the conduction band. It is composed of Y d-states hybridized with the neighbouring O's p-states [12].

### 3.2. Dielectric constants

Figure 2 shows the calculated real part of dielectric tensor of the three studied alumina systems along the x- and z-directions.

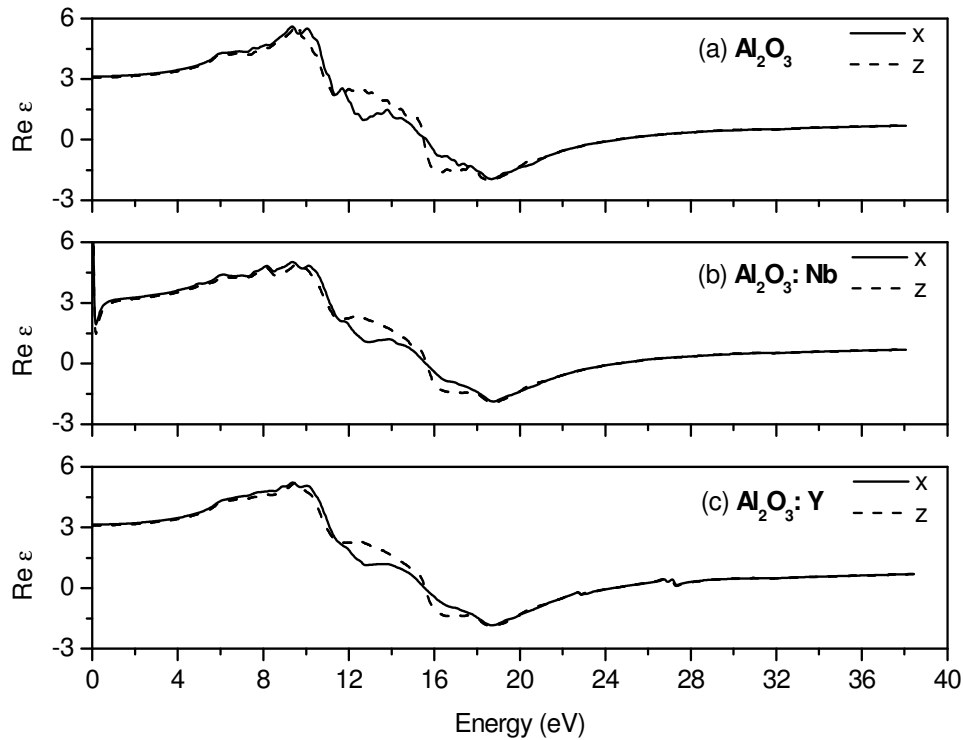


Figure 2: The real part of the dielectric tensor along the x- and z-axis of (a) pure  $\text{Al}_2\text{O}_3$ , (b)  $\text{Al}_2\text{O}_3$  doped with Nb and (c)  $\text{Al}_2\text{O}_3$  doped with Y.

The static dielectric constant  $\epsilon(0)$  is calculated as a zero energy limit of the real part of dielectric tensor. For the pure  $\text{Al}_2\text{O}_3$  the  $\epsilon_x(0)$  along the x-axis is calculated to be 3.12, in satisfactory agreement with the experimental value of 3.27 [6]. For the Y doped alumina  $\epsilon_x(0)$  is calculated to be 3.15, while for the Nb doped alumina 12.92. The similar conclusions were found for the static dielectric constant  $\epsilon_z(0)$  along the z-axis. For the pure alumina we calculated  $\epsilon_z(0)=3.08$ , in good agreement with the already published value of 2.98 [6]. For the Y and Nb doped alumina  $\epsilon_z(0)$  is calculated to be 3.11 and 15.84 respectively.

The results show that the alumina exhibits a slight increase of its static dielectric constant when doped with Y, while this increase is drastic in the case of doping with the Nb. The latter originates from the intra-band electronic transitions between the populated and the empty part of the shallow band within the gap (Nb d-electrons are transferred to O-p states), and it is highly exaggerated by the approximate form of the formula (1).

#### 4. Conclusions

We performed a theoretical study of the Y and Nb doped  $\alpha\text{-Al}_2\text{O}_3$  with corundum structure. The electronic and optical properties of the pure and doped systems were calculated on the basis of the first-principles, density functional theory based full potential augmented plane wave method. The principal goal was to verify if the doped materials satisfy some basic conditions for application in semiconductor industry, concerning their band gap values and the static dielectric constants.

The results of our study strongly indicate that the Nb presence elevates the dielectric constant value, but shrinks significantly the band gap of the pure alumina. Consequently, this system does not

attend the semiconductor industry demands due to its low band gap value. On the other hand, the Y presence does not alter the band gap value and increases the dielectric constant of the alumina at the same time. This increase is rather small due to a low concentration of impurities in our computational model (1/80 or 1.25% versus 6.25 % used in experiment with  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> [5]). It, however, indicates that the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> doped with the Y has a potential to serve for a construction of new generation of dielectric gates in transistors.

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