

|  | $a$    | $c$     | Ref.                 |
|--|--------|---------|----------------------|
| $\alpha$ -Al <sub>2</sub> O <sub>3</sub> |        |         |                      |
| $\alpha$ -Cr <sub>2</sub> O <sub>3</sub> | 4.96 Å | 13.59 Å | Mi et al. (2018) [4] |
| $\alpha$ -Ga <sub>2</sub> O <sub>3</sub> |        |         |                      |

Table 1: Lattice constants of selected corundum structured compounds.

“Chromia” or “Eskolaite” is a sesquioxide composed of the transition metal chromium and oxygen with formula unit Cr<sub>2</sub>O<sub>3</sub>. Among other chromium oxides (e.g. metallic CrO<sub>2</sub>, toxic CrO<sub>3</sub> etc.), it is the thermodynamically most stable phase [1–3], making it the abundant chromium oxide on earth [4]. Cr<sub>2</sub>O<sub>3</sub> occurs mainly in the  $\alpha$ -phase (described below), but a cubic spinel  $\gamma$ -phase with random missing Cr point defects has also been reported [1]. Henceforth, “Cr<sub>2</sub>O<sub>3</sub>” will refer to the  $\alpha$ -phase.

As coating material, Cr<sub>2</sub>O<sub>3</sub> is commonly used due to its high hardness and resistance against corrosion [2, 5], also explaining its use-case as component of stainless steel to form passive films [3]. Cr<sub>2</sub>O<sub>3</sub> thin films absorb electromagnetic waves with wavelengths smaller than 400 nm, making it opaque in the UV-spectrum [6, 7]. It is transparent in the visible spectrum with, e.g., a reported transmittance of 40 % at 700 nm for 0.5  $\mu$ m thick films by Cheng, Gomi, and Sakata (1996) [6].

Cr<sub>2</sub>O<sub>3</sub> crystallizes in the corundum structure, which has trigonal symmetry (space group  $R\bar{3}c$ ) and belongs to the hexagonal crystal family. One unit cell contains six formula units, i.e. 12 chromium cations and 18 oxygen anions [3]. The oxygen atoms arrange in a hexagonal close-packed manner, where two thirds of the formed octahedrons are filled with Cr atoms [8]. The unit cell is spanned by a principal axis, called  $c$ -axis<sup>1</sup>, and a hexagonal basal plane with lattice constant  $a$ . The numerical values for those lattice parameters differ depending on the publication [4, 9–12], and we will use the values in Tab. 1.

Several techniques were applied for depositing chromia thin films, including: Chemical Vapor Deposition (CVD) [13–15] on silicon and glass, Molecular Beam Epitaxy (MBE) on sapphire [9, 16], thermal evaporation on platinum [1], electron-beam evaporation on glass [2], spray pyrolysis on glass [17], radio-frequency (RF) sputtering on sapphire [12, 18, 19], reactive direct current (DC) sputtering on glass [7], reactive Pulsed Laser Deposition (PLD) on silicon [20] and sapphire [21], and non-reactive PLD on sapphire [5, 9, 22].

**Electronic Structure** Experimental and theoretical studies reveal that chromia exhibits a band gap of 3.2 to 3.4 eV [1, 3, 4, 11] making it a wide band gap material. This predicts insulating behavior [11], classified as both Mott-Hubbard type and charge-transfer type, which are models to describe the electronic behavior of compounds containing transition metals with partly filled  $3d^n$  orbitals<sup>2</sup> [3, 4, 8]: Density Functional Theory (DFT) calculations show that the Cr- $3d$  states are almost solely responsible for electronic states in the conduction band and that they are also present in the valence band [3, 4]. Thus,  $3d \rightarrow 3d$  band transitions are possible, favoring the Mott-Hubbard model of this compound [3]. Furthermore, the O- $2p$  states are mainly present in the

<sup>1</sup>The spins of the Cr atoms along this direction are alternating  $3 \uparrow$  and  $3 \downarrow$  [9], making the crystal antiferromagnetic [3, 8].

<sup>2</sup> $n = 5$  for Cr

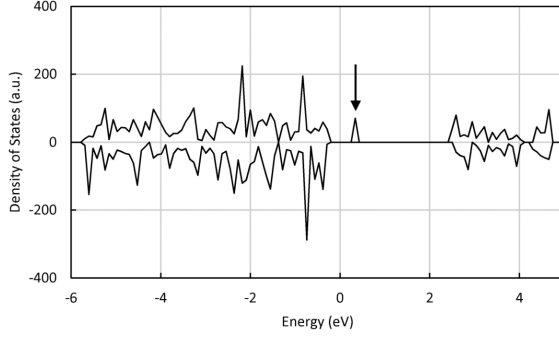


Figure 1: Calculated density of states (DOS) of chromia, taking a  $V_{Cr}$  into account. The arrow marks the new acceptor level. Image taken from [3].

valence band, at similar energies as the Cr-3d states, which leads to hybridization and thus favoring the charge-transfer model [3].

However, several studies agree on  $Cr_2O_3$  being a semiconductor with *p*-type conductivity<sup>3</sup> at room temperature and atmospheric conditions [3–6, 18, 20, 23]. Calculating the impact of different crystal point defects on the band structure may give insight into these observations. Indeed, when considering a missing chromium atom (“vacancy”  $V_{Cr}$ ) the band structure changes in two ways: The band gap itself is reduced [4], but not in a way that it would make excitations of valence electrons into the conduction band much more probable than at room temperature. But additionally, there is a new band introduced slightly above the Fermi level (cf. Fig. 1), which acts as an unoccupied acceptor level [4]. This defect state is mainly composed of O-2p orbitals of the oxygen anions surrounding the vacancy [3]. From a more intuitive point of view, a missing neutral chromium atom effectively removes the  $Cr^{3+}$  cation as well as three electrons bound to the adjacent  $O^{2-}$  anions, thus creating three holes [3] explaining the *p*-type conductivity.

Note that there are also other possible defects with different effects: a chromium Frenkel point defect describes a Cr atom leaving its position and occupying a formerly unoccupied cavity in one of the oxygen-octahedrons. This Frenkel defect actually creates a new band right below the Fermi level, acting as an occupied donor level [3]. A similar defect state is introduced by oxygen vacancies [4]. But note that the Fermi level is located only slightly above the Valence Band Maximum (VBM) and thus the new occupied donor level is not significantly closer to the Conduction Band Minimum (CBM), which means that electrons still have to overcome the band gap energy to get into conducting states. This favors the formation of holes via Cr vacancies (O-2p acceptor states) rather than electrons via Cr Frenkel defects and O vacancies (Cr-3d donor states).

**Doping** Several attempts have been made to alter the conductivity of chromia thin films, including incorporation of magnesium, nickel, or lithium to achieve better *p*-type

<sup>3</sup>Cheng et al. (2001) actually find  $Cr_2O_3$  to be insulating. It is noted that they examined  $Cr_2O_3$  as an 2 nm thick oxide surface on  $CrO_2$  films deposited by CVD [14]. Farrell et al. (2015) also find that their high quality epitaxial films of  $Cr_2O_3$  grown by MBE exhibit no *p*-type conductivity [16]. Similar results were found by Kehoe et al. (2016) for MBE and PLD deposited films [9].

conductivity [16]. On the other hand, incorporating titanium seems to yield electrons as majority carriers [24] due to the higher valent state of Ti when substituting Cr sites ( $\text{Ti}_{\text{Cr}}$ ) [23].

Due to interest in the electrical properties of *p*-type Transparent Conductive Oxides (TCOs), the influence on Mg-doped  $\text{Cr}_2\text{O}_3$  thin films has been investigated by several studies [9, 11, 16, 17, 22, 24, 25]. Substituting Cr atoms with less valent hole providers – compared to structural defects of pure  $\text{Cr}_2\text{O}_3$  – does not only allow for a more controlled defect incorporation, but is also energetically more favorable due to a lower formation energy of  $\text{Mg}_{\text{Cr}}$  compared to  $V_{\text{Cr}}$  [9]. Uekawa and Kaneko (1996) report an increase in conductivity of five orders of magnitude for  $\text{Cr}_2\text{O}_3\text{:Mg}$  thin films [25]. This result can be further improved by postannealing [16] and deposition at higher oxygen partial pressures [16, 24]. These effects are attributed to homogenization of magnesium inside the thin films and increased MgO incorporation during deposition, respectively. An observed side-effect of Mg-doping is a color change to a brownish tint [11, 25]. Uekawa and Kaneko (1996) discuss that this may be the result of a mixed valence state of chromium ( $\text{Cr}^{4+}$  or  $\text{Cr}^{6+}$ ), formed upon doping, as observed by X-ray Photoelectron Spectroscopy (XPS). This may establish an unoccupied state, favoring charge-transfer transitions from O-2*p* orbitals to this low-energetic state, resulting in a different visual appearance of the thin films. However, it has been shown that the overall transparency can be increased by codoping of Mg with nitrogen which also reduces the decolorization substantially [11, 17].

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