

# Chapter 1

## Theory

### 1.1 Sesquioxides

Transparent Conductive Oxides (TCOs) are materials that combine the properties of having low absorption coefficient in the visible spectrum and being conductive at the same time [1]. The interest in these materials is motivated by possible usage in portable and flexible electronics, displays, solar cells and more [2]. Due to the restriction on only a few materials in the industry (e.g.  $\text{SnO}_2$  and  $\text{In}_2\text{O}_3$ ), investigations of new materials are required [2]. This includes fabrication of *p*-type TCOs as well as compounds with even larger band gaps than 3 eV, called Ultrawide-bandgap (UWBG) materials. A candidate for the latter is  $\text{Ga}_2\text{O}_3$  with its several polymorphs [3], where the corundum structured  $\alpha$ - $\text{Ga}_2\text{O}_3$  gained interest, even though its deposition has to account for parasitic growth of the thermodynamically more stable  $\beta$ -phase [4].

At this point,  $\text{Cr}_2\text{O}_3$  comes in handy being a possible *p*-type TCO as well as being isomorphic to group-III sesquioxide  $\alpha$ - $\text{Ga}_2\text{O}_3$  with quite similar lattice parameters (cf. Tab. 1.1). This enables the use of  $\text{Cr}_2\text{O}_3$  as a buffer layer between  $\alpha$ - $\text{Ga}_2\text{O}_3$  and isomorphic  $\alpha$ - $\text{Al}_2\text{O}_3$  (sapphire) substrates to improve the deposition process [5]. Furthermore,  $\text{Cr}_2\text{O}_3$  exhibits increased conductivity upon doping [6] and could thus serve as *p*-type component in a *p-n*-heterojunction with  $\alpha$ - $\text{Ga}_2\text{O}_3$ . In the following, an overview of the two mentioned sesquioxides will be provided with focus on the physical properties being relevant to this work.

#### 1.1.1 Chromium Oxide

“Chromia” or “Eskolaite” is a sesquioxide composed of the transition metal chromium and oxygen with formula unit  $\text{Cr}_2\text{O}_3$ . Among other chromium oxides (e.g. metallic  $\text{CrO}_2$ , toxic  $\text{CrO}_3$  etc.), it is the thermodynamically most stable phase [7–9], making it the abundant chromium oxide on earth [10].  $\text{Cr}_2\text{O}_3$  occurs mainly in the  $\alpha$ -phase (described below), but a cubic spinel  $\gamma$ -phase with random missing Cr point defects has also been reported [7]. Henceforth, “ $\text{Cr}_2\text{O}_3$ ” will refer to the  $\alpha$ -phase.

As coating material,  $\text{Cr}_2\text{O}_3$  is commonly used due to its high hardness and resistance against corrosion [8, 11], also explaining its use-case as component of stainless steel to form passive films [9].  $\text{Cr}_2\text{O}_3$  thin films absorb electromagnetic waves with wavelengths smaller than 400 nm, making it opaque in the UV-spectrum [12, 13]. It is transparent in

	$a$	$c$	Ref.
$\alpha\text{-Al}_2\text{O}_3$	4.76 Å	13.00 Å	Pishchik, Lytvynov, and Dobrovinskaya (2009) [17]
$\alpha\text{-Cr}_2\text{O}_3$	4.96 Å	13.59 Å	Mi et al. (2018) [10]
$\alpha\text{-Ga}_2\text{O}_3$	4.98 Å	13.43 Å	Marezio and Remeika (1967) [18]

Table 1.1: Lattice constants of selected corundum structured compounds.

the visible spectrum with, e.g., a reported transmittance of 40 % at 700 nm for 0.5  $\mu\text{m}$  thick films by Cheng, Gomi, and Sakata (1996) [12].

$\text{Cr}_2\text{O}_3$  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 [9]. The oxygen atoms arrange in a hexagonal close-packed manner, where two thirds of the formed octahedrons are filled with Cr atoms [14]. 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 [1, 5, 10, 15, 16], and we will use the values in Tab. 1.1.

Several techniques were applied for depositing chromia thin films, including: Chemical Vapor Deposition (CVD) [19–21] on silicon and glass, Molecular Beam Epitaxy (MBE) on sapphire [1, 22], thermal evaporation on platinum [7], electron-beam evaporation on glass [8], spray pyrolysis on glass [23], radio-frequency (RF) sputtering on sapphire [5, 24, 25], reactive direct current (DC) sputtering on glass [13], reactive Pulsed Laser Deposition (PLD) on silicon [26] and sapphire [27], and non-reactive PLD on sapphire [1, 11, 28].

**Electronic Structure** Experimental and theoretical studies reveal that chromia exhibits a band gap of 3.2 to 3.4 eV [7, 9, 10, 16] making it a wide band gap material. This predicts insulating behavior [16], 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> [9, 10, 14]: 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 [9, 10]. Thus,  $3d \rightarrow 3d$  band transitions are possible, favoring the Mott-Hubbard model of this compound [9]. Furthermore, the O- $2p$  states are mainly present in the valence band, at similar energies as the Cr- $3d$  states, which leads to hybridization and thus favoring the charge-transfer model [9].

However, several studies agree on  $\text{Cr}_2\text{O}_3$  being a semiconductor with  $p$ -type conductivity<sup>3</sup> at room temperature and atmospheric conditions [9–12, 24, 26, 29]. 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”

<sup>1</sup>The spins of the Cr atoms along this direction are alternating  $3 \uparrow$  and  $3 \downarrow$  [1], making the crystal antiferromagnetic [9, 14].

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

<sup>3</sup>Cheng et al. (2001) actually find  $\text{Cr}_2\text{O}_3$  to be insulating. It is noted that they examined  $\text{Cr}_2\text{O}_3$  as an 2 nm thick oxide surface on  $\text{CrO}_2$  films deposited by CVD [20]. Farrell et al. (2015) also find that their high quality epitaxial films of  $\text{Cr}_2\text{O}_3$  grown by MBE exhibit no  $p$ -type conductivity [22]. Similar results were found by Kehoe et al. (2016) for MBE and PLD deposited films [1].

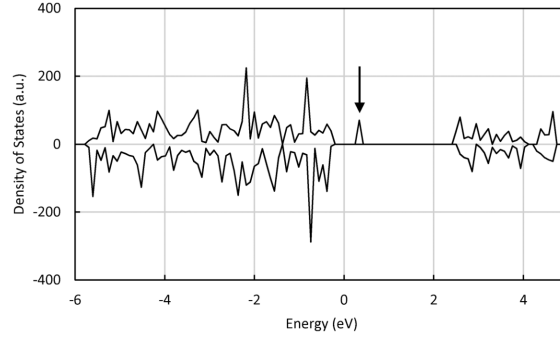


Figure 1.1: Calculated density of states (DOS) of chromia, taking a  $V_{\text{Cr}}$  into account. The arrow marks the new acceptor level. Image taken from [9].

$V_{\text{Cr}}$ ) the band structure changes in two ways: The band gap itself is reduced [10], but not in a way that it would make excitations of valence electrons into the conduction band much more probable than for defectless chromia. But additionally, there is a new band introduced slightly above the Fermi level (cf. Fig. 1.1), which acts as an unoccupied acceptor level [10]. This defect state is mainly composed of O-2*p* orbitals of the oxygen anions surrounding the vacancy [9]. From a more intuitive point of view, a missing neutral chromium atom effectively removes the  $\text{Cr}^{3+}$  cation as well as three electrons bound to the adjacent  $\text{O}^{2-}$  anions, thus creating three holes [9] 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 [9]. A similar defect state is introduced by oxygen vacancies [10]. 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-2*p* acceptor states) rather than electrons via Cr Frenkel defects and O vacancies (Cr-3*d* donor states).

**Doping** Several attempts have been made to alter the conductivity of chromia thin films deliberately, including incorporation of magnesium, nickel, or lithium to achieve better *p*-type conductivity [22]. On the other hand, incorporating titanium seems to yield electrons as majority carriers [30] due to the higher valent state of Ti when substituting Cr sites ( $\text{Ti}_{\text{Cr}}$ ) [29].

Due to interest in the electrical properties of *p*-type TCOs, the influence on Mg-doped  $\text{Cr}_2\text{O}_3$  thin films has been investigated by several studies [1, 6, 16, 22, 23, 28, 30]. 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  $V_{\text{Cr}}$  [1]. 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 [6]. This result can be further improved by postan-

nealing [22] and deposition at higher oxygen partial pressures [22, 30]. 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 [6, 16]. 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 [16, 23].

### 1.1.2 Gallium Oxide

$\text{Ga}_2\text{O}_3$  is a group-III sesquioxide with four different polymorphs, of which  $\beta\text{-Ga}_2\text{O}_3$  is the thermodynamically most stable one at ambient conditions [3, 4, 31]. The corundum-structured  $\alpha\text{-Ga}_2\text{O}_3$  phase, which is of more relevance for this work, is isomorphic to  $\text{Cr}_2\text{O}_3$  (cf. section 1.1.1), with lattice parameters as listed in Tab. 1.1.  $\alpha\text{-Ga}_2\text{O}_3$  is metastable [32], i.e. not favored in the first place, but remains irreversibly after formation, e.g., after phase transition from  $\beta$ - to  $\alpha$ -phase at high temperatures [33]. The thermodynamic equilibrium – which determines the favored phase – can also be changed by strain due to lattice mismatch occurring during heteroepitaxy<sup>4</sup> [31]. This approach is of particular interest due to the possibility of deposition on cheap<sup>5</sup> and readily available sapphire substrates which are isomorphic to  $\alpha\text{-Ga}_2\text{O}_3$  [25, 32, 33]. Note that deposition of  $\beta\text{-Ga}_2\text{O}_3$  on sapphire is also possible, but only with restriction to formation of more than one crystal domain [34]. On the other hand, highly crystalline [33]  $\alpha\text{-Ga}_2\text{O}_3$  thin films should be able to be grown without rotational domains [34].

Deposition of  $\alpha\text{-Ga}_2\text{O}_3$  on sapphire has been done by several deposition techniques, including [34]: Halide Vapor Phase Epitaxy (HVPE), mist CVD [35], MBE [31], Atomic Layer Deposition and metalorganic CVD. Phase-pure deposition via PLD has also been achieved [4, 31]. Despite being isomorphic to each other,  $\alpha\text{-Ga}_2\text{O}_3$  and sapphire still exhibit a lattice mismatch of around 4.8% along the *a*-axis [32]. This induces semi-coherent growth with a fairly high dislocation density, which has been reported to be around  $7 \times 10^{10} \text{ cm}^{-2}$  [35]. In particular, this becomes a problem regarding carrier mobility which is tremendously hindered by dislocation scattering [32].

To overcome the problems of lattice mismatch between sapphire substrates and  $\alpha\text{-Ga}_2\text{O}_3$  thin films, quasi-continuous gradients from  $\text{Al}_2\text{O}_3$  to  $\alpha\text{-Ga}_2\text{O}_3$  have been applied, utilizing the capability of alloying the respective compounds [36]. Furthermore, buffer layers of isomorphic  $\text{Cr}_2\text{O}_3$  have been used to decrease the high dislocation density for deposition on *c*-oriented [5, 24] as well as *r*-oriented sapphire [25]. Deposition on other than *c*-oriented substrates also seems to decrease parasitic phases, because the suppression of crystal facets perpendicular to the principal *c*-axis may increase phase purity [37]. It has to be noted that despite the difficulties occurring upon lattice mismatch, coherent growth seems to be feasible without buffer layers for different deposition techniques, at least for some monolayers [31].

<sup>4</sup>However, the possibility of formation of parasitic  $\beta$ -phase still has to be taken into account [4].

<sup>5</sup>Compared to bulk  $\beta\text{-Ga}_2\text{O}_3$  substrates [32, 34].

With 5.0 to 5.3 eV [34],  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> has the highest band gap of the four polymorphs [33]. Increasing or decreasing the band gap is possible by alloying with Al<sub>2</sub>O<sub>3</sub> [37] or In<sub>2</sub>O<sub>3</sub> [38], respectively. The crystal structure also allows for alloying with other corundum structured compounds [34], in particular other transition metal oxides such as Cr<sub>2</sub>O<sub>3</sub> [24, 25]. The conduction band is mainly composed of Ga-4s states with an effective electron mass of 0.3  $m_e$ . The valence band is very flat and mainly composed of O-2p orbitals, yielding a high effective electron mass and thus strong localization [33]. Next to band gap engineering, *n*-type doping via Sn or Si incorporation has been accomplished [34].



# Bibliography

- [1] Aoife B Kehoe et al. “Assessing the potential of Mg-doped  $\text{Cr}_2\text{O}_3$  as a novel  $p$ -type transparent conducting oxide”. In: *Journal of Physics: Condensed Matter* 28.12 (2016), p. 125501. ISSN: 0953-8984, 1361-648X. DOI: [10.1088/0953-8984/28/12/125501](https://doi.org/10.1088/0953-8984/28/12/125501).
- [2] David S. Ginley, ed. *Handbook of Transparent Conductors*. Boston, MA: Springer US, 2011. ISBN: 978-1-4419-1637-2 978-1-4419-1638-9. DOI: [10.1007/978-1-4419-1638-9](https://doi.org/10.1007/978-1-4419-1638-9).
- [3] Anna Hassa, Marius Grundmann, and Holger Von Wenckstern. “Progression of group-III sesquioxides: epitaxy, solubility and desorption”. In: *Journal of Physics D: Applied Physics* 54.22 (2021), p. 223001. ISSN: 0022-3727, 1361-6463. DOI: [10.1088/1361-6463/abd4a4](https://doi.org/10.1088/1361-6463/abd4a4).
- [4] Clemens Petersen et al. “PLD of  $\alpha\text{-Ga}_2\text{O}_3$  on  $m$ -plane  $\text{Al}_2\text{O}_3$ : Growth regime, growth process, and structural properties”. In: *APL Materials* 11.6 (2023), p. 061122. ISSN: 2166-532X. DOI: [10.1063/5.0149797](https://doi.org/10.1063/5.0149797).
- [5] S.I. Stepanov et al. “HVPE growth of corundum-structured  $\alpha\text{-Ga}_2\text{O}_3$  on sapphire substrates with  $\alpha\text{-Cr}_2\text{O}_3$  buffer layer”. In: *Materials Physics and Mechanics* 47 (2021), pp. 577–581. DOI: [10.18149/MPM.4742021\\_4](https://doi.org/10.18149/MPM.4742021_4).
- [6] N. Uekawa and K. Kaneko. “Dopant Reduction in  $p$ -Type Oxide Films upon Oxygen Absorption”. In: *The Journal of Physical Chemistry* 100.10 (1996), pp. 4193–4198. ISSN: 0022-3654, 1541-5740. DOI: [10.1021/jp952784m](https://doi.org/10.1021/jp952784m).
- [7] P. S. Robbert et al. “Novel electronic and magnetic properties of ultrathin chromium oxide films grown on  $\text{Pt}(111)$ ”. In: *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 16.3 (1998), pp. 990–995. ISSN: 0734-2101, 1520-8559. DOI: [10.1116/1.581283](https://doi.org/10.1116/1.581283).
- [8] M.F. Al-Kuhaili and S.M.A. Durrani. “Optical properties of chromium oxide thin films deposited by electron-beam evaporation”. In: *Optical Materials* 29.6 (2007), pp. 709–713. ISSN: 09253467. DOI: [10.1016/j.optmat.2005.11.020](https://doi.org/10.1016/j.optmat.2005.11.020).
- [9] François Lebreau et al. “Structural, Magnetic, Electronic, Defect, and Diffusion Properties of  $\text{Cr}_2\text{O}_3$ : A DFT+ $U$  Study”. In: *The Journal of Physical Chemistry C* 118.31 (2014), pp. 18133–18145. ISSN: 1932-7447. DOI: [10.1021/jp5039943](https://doi.org/10.1021/jp5039943).
- [10] Zhishan Mi et al. “The effects of strain and vacancy defects on the electronic structure of  $\text{Cr}_2\text{O}_3$ ”. In: *Computational Materials Science* 144 (2018), pp. 64–69. ISSN: 09270256. DOI: [10.1016/j.commatsci.2017.12.012](https://doi.org/10.1016/j.commatsci.2017.12.012).

- [11] Jarnail Singh et al. “Structural, optical and electrical characterization of epitaxial  $\text{Cr}_2\text{O}_3$  thin film deposited by PLD”. In: *Materials Research Express* 6.10 (2019), p. 106406. ISSN: 2053-1591. DOI: [10.1088/2053-1591/ab3543](https://doi.org/10.1088/2053-1591/ab3543).
- [12] Chun-Shen Cheng, H. Gomi, and H. Sakata. “Electrical and Optical Properties of  $\text{Cr}_2\text{O}_3$  Films Prepared by Chemical Vapour Deposition”. In: *Physica Status Solidi (a)* 155.2 (1996), pp. 417–425. ISSN: 00318965, 1521396X. DOI: [10.1002/pssa.2211550215](https://doi.org/10.1002/pssa.2211550215).
- [13] Cecilia Guillén and José Herrero. “Structural Changes Induced by Heating in Sputtered NiO and  $\text{Cr}_2\text{O}_3$  Thin Films as  $p$ -Type Transparent Conductive Electrodes”. In: *Electronic Materials* 2.2 (2021), pp. 49–59. ISSN: 2673-3978. DOI: [10.3390/electronicmat2020005](https://doi.org/10.3390/electronicmat2020005).
- [14] M. Catti et al. “Electronic, magnetic and crystal structure of  $\text{Cr}_2\text{O}_3$  by theoretical methods”. In: *Journal of Physics and Chemistry of Solids* 57.11 (1996), pp. 1735–1741. ISSN: 00223697. DOI: [10.1016/0022-3697\(96\)00034-0](https://doi.org/10.1016/0022-3697(96)00034-0).
- [15] Larry W. Finger and Robert M. Hazen. “Crystal structure and isothermal compression of  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{V}_2\text{O}_3$  to 50 kbars”. In: *Journal of Applied Physics* 51.10 (1980), pp. 5362–5367. ISSN: 0021-8979, 1089-7550. DOI: [10.1063/1.327451](https://doi.org/10.1063/1.327451).
- [16] Elisabetta Arca et al. “Effect of Chemical Precursors On the Optical and Electrical Properties of  $p$ -Type Transparent Conducting  $\text{Cr}_2\text{O}_3:(\text{Mg},\text{N})$ ”. In: *The Journal of Physical Chemistry C* 117.42 (2013), pp. 21901–21907. ISSN: 1932-7447. DOI: [10.1021/jp404230k](https://doi.org/10.1021/jp404230k).
- [17] Valerian Pishchik, Leonid A. Lytvynov, and Elena R. Dobrovinskaya. *Sapphire: Material, Manufacturing, Applications*. Boston, MA: Springer US, 2009. ISBN: 978-0-387-85694-0 978-0-387-85695-7. DOI: [10.1007/978-0-387-85695-7](https://doi.org/10.1007/978-0-387-85695-7).
- [18] M. Marezio and J. P. Remeika. “Bond lengths in the  $\alpha\text{-Ga}_2\text{O}_3$  structure and the high-pressure phase of  $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$ ”. In: *The Journal of Chemical Physics* 46.5 (1967), pp. 1862–1865. ISSN: 0021-9606, 1089-7690. DOI: [10.1063/1.1840945](https://doi.org/10.1063/1.1840945).
- [19] Ruihua Cheng, C.N. Borca, and P.A. Dowben. “Selective Area Chemical Vapor Deposition of Chromium Oxides”. In: *MRS Proceedings* 614 (2000), F10.4.1. ISSN: 0272-9172, 1946-4274. DOI: [10.1557/PROC-614-F10.4.1](https://doi.org/10.1557/PROC-614-F10.4.1).
- [20] Ruihua Cheng et al. “Characterization of the native  $\text{Cr}_2\text{O}_3$  oxide surface of  $\text{CrO}_2$ ”. In: *Applied Physics Letters* 79.19 (2001), pp. 3122–3124. ISSN: 0003-6951, 1077-3118. DOI: [10.1063/1.1416474](https://doi.org/10.1063/1.1416474).
- [21] Ruihua Cheng et al. “Potential phase control of chromium oxide thin films prepared by laser-initiated organometallic chemical vapor deposition”. In: *Applied Physics Letters* 78.4 (2001), pp. 521–523. ISSN: 0003-6951, 1077-3118. DOI: [10.1063/1.1343846](https://doi.org/10.1063/1.1343846).
- [22] L. Farrell et al. “Conducting mechanism in the epitaxial  $p$ -type transparent conducting oxide  $\text{Cr}_2\text{O}_3:\text{Mg}$ ”. In: *Physical Review B* 91.12 (2015), p. 125202. ISSN: 1098-0121, 1550-235X. DOI: [10.1103/PhysRevB.91.125202](https://doi.org/10.1103/PhysRevB.91.125202).



- [23] E. Arca, K. Fleischer, and I. V. Shvets. “Magnesium, nitrogen codoped  $\text{Cr}_2\text{O}_3$ : A  $p$ -type transparent conducting oxide”. In: *Applied Physics Letters* 99.11 (2011), p. 111910. ISSN: 0003-6951. DOI: [10.1063/1.3638461](https://doi.org/10.1063/1.3638461).
- [24] Alexander Polyakov et al. “Electrical properties of  $\alpha$ - $\text{Ga}_2\text{O}_3$  films grown by halide vapor phase epitaxy on sapphire with  $\alpha$ - $\text{Cr}_2\text{O}_3$  buffers”. In: *Journal of Applied Physics* 131.21 (2022), p. 215701. ISSN: 0021-8979, 1089-7550. DOI: [10.1063/5.0090832](https://doi.org/10.1063/5.0090832).
- [25] Alexander Polyakov et al. “Effects of sapphire substrate orientation on Sn-doped  $\alpha$ - $\text{Ga}_2\text{O}_3$  grown by halide vapor phase epitaxy using  $\alpha$ - $\text{Cr}_2\text{O}_3$  buffers”. In: *Journal of Physics D: Applied Physics* 55.49 (2022), p. 495102. ISSN: 0022-3727, 1361-6463. DOI: [10.1088/1361-6463/ac962f](https://doi.org/10.1088/1361-6463/ac962f).
- [26] Anna Caricato et al. “Deposition of chromium oxide thin films with large thermoelectromotive force coefficient by reactive pulsed laser ablation”. In: *Journal of Optoelectronics and Advanced Materials* 12 (2010), p. 427.
- [27] Sandhyarani Punugupati, Jagdish Narayan, and Frank Hunte. “Room temperature ferromagnetism in epitaxial  $\text{Cr}_2\text{O}_3$  thin films grown on r-sapphire”. In: *Journal of Applied Physics* 117.19 (2015), p. 193907. ISSN: 0021-8979, 1089-7550. DOI: [10.1063/1.4921435](https://doi.org/10.1063/1.4921435).
- [28] Elisabetta Arca et al. “Valence band modification of  $\text{Cr}_2\text{O}_3$  by Ni-doping: creating a high figure of merit  $p$ -type TCO”. In: *Journal of Materials Chemistry C* 5.47 (2017), pp. 12610–12618. ISSN: 2050-7534. DOI: [10.1039/C7TC03545D](https://doi.org/10.1039/C7TC03545D).
- [29] P. Kofstad and K. P. Lillerud. “On High Temperature Oxidation of Chromium: II. Properties of and the Oxidation Mechanism of Chromium”. In: *Journal of The Electrochemical Society* 127.11 (1980), pp. 2410–2419. ISSN: 0013-4651, 1945-7111. DOI: [10.1149/1.2129481](https://doi.org/10.1149/1.2129481).
- [30] A Holt and P Kofstad. “Electrical conductivity and defect structure of  $\text{Cr}_2\text{O}_3$ . II. Reduced temperatures ( $< \sim 1000^\circ\text{C}$ )”. In: *Solid State Ionics* 69.2 (1994), pp. 137–143. ISSN: 01672738. DOI: [10.1016/0167-2738\(94\)90402-2](https://doi.org/10.1016/0167-2738(94)90402-2).
- [31] Robert Schewski et al. “Epitaxial stabilization of pseudomorphic  $\alpha$ - $\text{Ga}_2\text{O}_3$  on sapphire (0001)”. In: *Applied Physics Express* 8.1 (2015), p. 011101. ISSN: 1882-0778, 1882-0786. DOI: [10.7567/APEX.8.011101](https://doi.org/10.7567/APEX.8.011101).
- [32] Kentaro Kaneko et al. “Progress in  $\alpha$ - $\text{Ga}_2\text{O}_3$  for practical device applications”. In: *Japanese Journal of Applied Physics* 62 (SF 2023), SF0803. ISSN: 0021-4922, 1347-4065. DOI: [10.35848/1347-4065/acd125](https://doi.org/10.35848/1347-4065/acd125).
- [33] S. J. Pearton et al. “A review of  $\text{Ga}_2\text{O}_3$  materials, processing, and devices”. In: *Applied Physics Reviews* 5.1 (2018), p. 011301. ISSN: 1931-9401. DOI: [10.1063/1.5006941](https://doi.org/10.1063/1.5006941).
- [34] Duyoung Yang et al. “Epitaxial growth of alpha gallium oxide thin films on sapphire substrates for electronic and optoelectronic devices: progress and perspective”. In: *Electronic Materials Letters* 18.2 (2022), pp. 113–128. ISSN: 1738-8090, 2093-6788. DOI: [10.1007/s13391-021-00333-5](https://doi.org/10.1007/s13391-021-00333-5).

- [35] Kentaro Kaneko et al. “Evaluation of misfit relaxation in  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> epitaxial growth on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrate”. In: *Japanese Journal of Applied Physics* 51 (2R 2012), p. 020201. ISSN: 0021-4922, 1347-4065. DOI: [10.1143/JJAP.51.020201](https://doi.org/10.1143/JJAP.51.020201).
- [36] Riena Jinno et al. “Reduction in edge dislocation density in corundum-structured  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> layers on sapphire substrates with quasi-graded  $\alpha$ -(Al,Ga)<sub>2</sub>O<sub>3</sub> buffer layers”. In: *Applied Physics Express* 9.7 (2016), p. 071101. ISSN: 1882-0778, 1882-0786. DOI: [10.7567/APEX.9.071101](https://doi.org/10.7567/APEX.9.071101).
- [37] Riena Jinno et al. “Crystal orientation dictated epitaxy of ultrawide-bandgap 5.4-to 8.6-eV  $\alpha$ -(AlGa)<sub>2</sub>O<sub>3</sub> on m-plane sapphire”. In: *Science Advances* 7.2 (2021), eabd5891. ISSN: 2375-2548. DOI: [10.1126/sciadv.abd5891](https://doi.org/10.1126/sciadv.abd5891).
- [38] Anna Hassa et al. “Control of phase formation of (Al<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> thin films on c-plane Al<sub>2</sub>O<sub>3</sub>”. In: *Journal of Physics D: Applied Physics* 53.48 (2020), p. 485105. ISSN: 0022-3727, 1361-6463. DOI: [10.1088/1361-6463/abaf7d](https://doi.org/10.1088/1361-6463/abaf7d).