Supporting Information

A Generalized Semi-Empirical Approach to the Modelling of the Optical Band Gap of Ternary Al-(Ga, Nb, Ta, W) Oxides Containing Different Alumina Polymorphs.

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Figure S1. Fitting of all the experimental data pertaining $\beta-(Ga_{(1-x)}Al_x)_2O_3$ mixed oxides system, regardless of band gap measure technique.

$\beta-(Ga_{(1-x)}Al_x)_2O_3$ ternary system: $E_g$ vs $x_{Al}$ for direct optical transitions

In order to complete the test on the influence of different parameters on the ability of the proposed correlation to fit the composition dependence of $\beta-(Ga_{(1-x)}Al_x)_2O_3$ we reported in Figure S2 the experimental $E_{g,\text{opt,dir}}$ values of $\beta-(Ga_{(1-x)}Al_x)_2O_3$ derived by using the Tauc’s plot approximation\textsuperscript{1} and pertaining to samples grown by pulsed laser deposition (PLD). A rather limited range of Al composition ($0.11 \leq x \leq 0.48$) was exploited in order to maintain the pure monoclinic structure of $\beta-(Ga_{(1-x)}Al_x)_2O_3$ films ($x < 0.51$).

According to the authors, the best fitting linear equation of the experimental data of Figure S2 follows the equation:

$$E_{g,\text{opt,dir}} = 4.8123 + 2.1376x_{Al} \text{ [eV]} \quad E_{g1} = 6.95 \text{ eV}$$  \[S1\]

From Eq. S1 an extrapolated ($x = 1$) hypothetical $E_{g,\text{dir}}$ value of 6.95 eV is derived for monoclinic $\theta-Al_2O_3$. The limited range of Al composition exploited ($x_{Al} \leq 0.51$) could affect the extrapolated $E_{g,\text{opt,dir}}$ value of $\theta-Al_2O_3$, but it agrees nicely with the DFT estimated $E_g$ values\textsuperscript{2–5} and with experimental $E_g$ value measured by REELS for crystalline Atomic Layer Deposited (ALD)\textsuperscript{6} or sputtered Al$_2$O$_3$ films.\textsuperscript{7}
Figure S2. Direct optical band gap values vs Al content (0.11 ≤ x_{Al} ≤ 0.48) for PLD polycrystalline films derived from Tauc plots (azure circles). Theoretical band gap values derived according to eqs. 8 by assuming (see text): \( \chi_{Al} = 1.50; B_{\theta-Al_2O_3} = -2.225 \text{ eV}; A_{\theta-Al_2O_3} = 2.3; \chi_{Ga} = 1.60; B_{\beta-Ga_2O_3} = -2.31 \text{ eV}; A_{\beta-Ga_2O_3} = 1.983 \) (red squares).

Fitting procedure of experimental data points was carried out by means of Eq. 8 and by assuming the same values of B and electronegativity, previously used, for fitting the experimental \( E_{g,ind.} \) vs \( x_{Al} \) data sets. In agreement with literature data a value of 4.85 ± 0.05 eV was assumed for the direct band gap value of \( \beta-Ga_2O_3 \) from which the value of \( A_\beta = 1.98 \) was derived according to Eq. 1 with \( B = -2.31 \) eV. In Figure S2 we report, together with the experimental data, the theoretical values estimated by Eq. 8 providing the following equation:

\[
E_{g,th} = 0.0031x_{Al}^3 + 0.1378x_{Al}^2 + 1.9691x_{Al} + 4.85 \quad \text{[eV]} \quad \text{[S2]}
\]

A value of \( A_{Al_2O_3} = 2.30 \), slightly higher (+6%) than the average one of Eq. 3, was derived for \( \theta \)-alumina in front of a slightly lower (-8%) value, used for \( \beta-Ga_2O_3 \). From Eq. S2 a value of 6.96 eV is obtained for the direct band gap of \( \theta-Al_2O_3 \) almost coincident with the value derived from fitting the experimental data (see Eq. S1). This last value should be in very good agreement with the value of \( E_g \) reported by Peintinger et al. apart the disagreement on the nature of optical transitions which is reported as indirect.
Figure S3. Non-direct optical band gap values vs Al content (0 ≤ $x_{Al} ≤ 0.8$) (blue plus) for amorphous anodic film grown up to 5 V Hg/HgO at 10 mV s$^{-1}$ in borate buffer solution on Al-Ta magnetron sputtered alloys of various compositions derived from Tauc plots.

Figure S4. Non-direct optical band gap values vs Nb content (blue times symbols) for amorphous anodic film grown up to 5 V Ag/AgCl at 10 mV s$^{-1}$ in NaOH solution on Nb-Ta magnetron sputtered alloys of various compositions derived from Tauc plots.
| Polymorph/phase  | $\chi_1$ | $A_1$  | $B_1$ [eV] | $\chi_2$ | $A_2$  | $B_2$ [eV] |
|-----------------|---------|--------|-----------|---------|--------|-----------|
| $\alpha$-(Ga$_{(1-x)}$Al$_x$)$_2$O$_3$ | 1.50    | 2.80   | -2.71     | 1.60    | 2.22   | -2.71     |
| $\beta$-(Ga$_{(1-x)}$Al$_x$)$_2$O$_3$ | 1.50    | 2.23   | -2.225    | 1.60    | 1.96   | -2.31     |
| Am (Nb$_{(1-x)}$Al$_x$)$_2$O$_{(5-2x)}$ | 1.50    | 1.67   | -2.25     | 1.60    | 1.302  | -1.35     |
| Am (Ta$_{(1-x)}$Al$_x$)$_2$O$_{(5-2x)}$ | 1.50    | 1.67   | -2.25     | 1.50    | 1.35   | -1.125    |
| Am (W$_{(1-x)}$Al$_{2x}$)O$_3$       | 1.50    | 1.68   | -2.25     | 1.70    | 1.35   | -1.15     |

Table S1. Fitting parameters for the different Al-(Ga, Nb, Ta, W) oxides systems studied in the manuscript (see eq. 8). Element 1: Al, Element 2: cationic partner.
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