Supporting Information


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β-(Ga\textsubscript{(1-x)}Al\textsubscript{x})\textsubscript{2}O\textsubscript{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\textsubscript{(1-x)}Al\textsubscript{x})\textsubscript{2}O\textsubscript{3} we reported in Figure S2 the experimental $E_{g,opt,dir}$ values of $\beta$–(Ga\textsubscript{(1-x)}Al\textsubscript{x})\textsubscript{2}O\textsubscript{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\textsubscript{(1-x)}Al\textsubscript{x})\textsubscript{2}O\textsubscript{3} films ($x < 0.51$).

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

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

From Eq. S1 an extrapolated ($x = 1$) hypothetical $E_{g,dir}$ value of 6.95 eV is derived for monoclinic $\theta$–Al\textsubscript{2}O\textsubscript{3}. The limited range of Al composition exploited ($x_{Al} \leq 0.51$) could affect the extrapolated $E_{g,opt,dir}$ value of $\theta$–Al\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{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): χ_{Al} =1.50; B_{0-Al2O3} = -2.225 eV; A_{0-Al2O3} = 2.3; χ_{Ga} =1.60; B_{β-Ga2O3} = -2.31 eV; A_{β-Ga2O3} =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 $4.85 \pm 0.05 \text{ eV}$ was assumed for the direct band gap value of $β$–Ga$_2$O$_3$ from which the value of $A_2 = 1.98$ was derived according to Eq. 1 with $B = -2.31 \text{ eV}$. In Figure S2 we report, together with the experimental data, the theoretical values estimated by Eq. 8 providing the following equation:

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

A value of $A_{Al2O3} = 2.30$, slightly higher (+6%) than the average one of Eq. 3, was derived for $θ$–alumina in front of a slightly lower (-8%) value, used for $β$–Ga$_2$O$_3$. From Eq. S2 a value of 6.96 eV is obtained for the direct band gap of $θ$–Al$_2$O$_3$ 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.\cite{2}
**Figure S3.** Non-direct optical band gap values vs Al content ($0 \leq x_{Al} \leq 0.8$) (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.
<table>
<thead>
<tr>
<th>Polymorph/phase</th>
<th>$\chi_1$</th>
<th>$A_1$</th>
<th>$B_1$ [eV]</th>
<th>$\chi_2$</th>
<th>$A_2$</th>
<th>$B_2$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-(Ga$_{(1-x)}$Al$_x$)$_2$O$_3$</td>
<td>1.50</td>
<td>2.80</td>
<td>-2.71</td>
<td>1.60</td>
<td>2.22</td>
<td>-2.71</td>
</tr>
<tr>
<td>$\beta$-(Ga$_{(1-x)}$Al$_x$)$_2$O$_3$</td>
<td>1.50</td>
<td>2.23</td>
<td>-2.225</td>
<td>1.60</td>
<td>1.96</td>
<td>-2.31</td>
</tr>
<tr>
<td>Am (Nb$_{(1-x)}$Al$_x$)$<em>2$O$</em>{(5-2x)}$</td>
<td>1.50</td>
<td>1.67</td>
<td>-2.25</td>
<td>1.60</td>
<td>1.302</td>
<td>-1.35</td>
</tr>
<tr>
<td>Am (Ta$_{(1-x)}$Al$_x$)$<em>2$O$</em>{(5-2x)}$</td>
<td>1.50</td>
<td>1.67</td>
<td>-2.25</td>
<td>1.50</td>
<td>1.35</td>
<td>-1.125</td>
</tr>
<tr>
<td>Am (W$<em>{(1-x)}$Al$</em>{2x}$)O$_3$</td>
<td>1.50</td>
<td>1.68</td>
<td>-2.25</td>
<td>1.70</td>
<td>1.35</td>
<td>-1.15</td>
</tr>
</tbody>
</table>

**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.
References

(1) Schmidt-Grund, R.; Kranert, C.; Von Wenckstern, H.; Zviagin, V.; Lorenz, M.; Grundmann, M. Dielectric Function in the Spectral Range (0.5-8.5)EV of an (Alx Ga1-x)2O3 Thin Film with Continuous Composition Spread. J. Appl. Phys. 2015, 117 (16), 165307.


