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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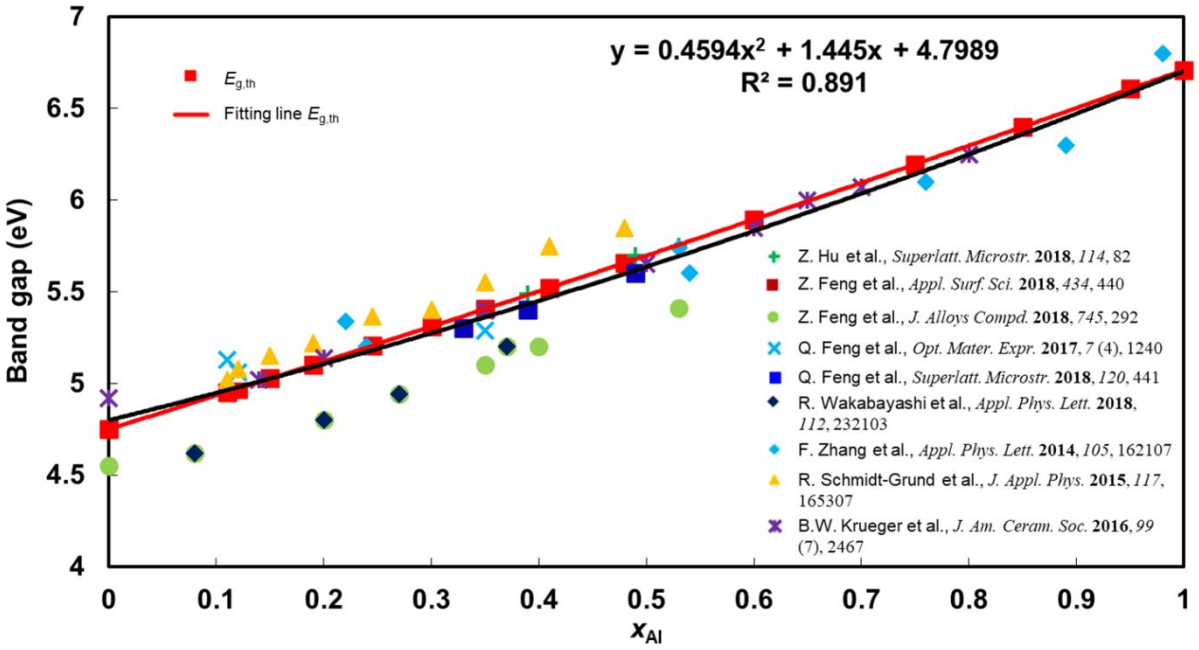

Figure S1. Fitting of all the experimental data pertaining β-$(Ga_{(1-x)}\ Al_x)_2O_3$ mixed oxides system, regardless of band gap measure technique.

β–($(Ga_{(1-x)}Al_x)_2O_3$) 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 β–$(Ga_{(1-x)}Al_x)_2O_3$ we reported in Figure S2 the experimental $E_{g,opt.dir}$ values of β–$(Ga_{(1-x)}Al_x)_2O_3$ derived by using the Tauc's plot approximation[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 β–$(Ga_{(1-x)}Al_x)_2O_3$ films ($x < 0.51$).
According to the authors, the best fitting linear equation of the experimental data of Figure S2 follows the equation:

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

From Eq. S1 an extrapolated (x = 1) hypothetical $E_{g,dir.}$ value of 6.95 eV is derived for monoclinic θ–Al_2O_3. The limited range of Al composition exploited ($x_{Al} \leq 0.51$) could affect the extrapolated $E_{g,opt.dir}$ value of θ–Al_2O_3, but it agrees nicely with the DFT estimated E_g values[2–5] and with experimental E_g value measured by REELS for crystalline Atomic Layer Deposited (ALD)[6] or sputtered Al_2O_3 films.[7]

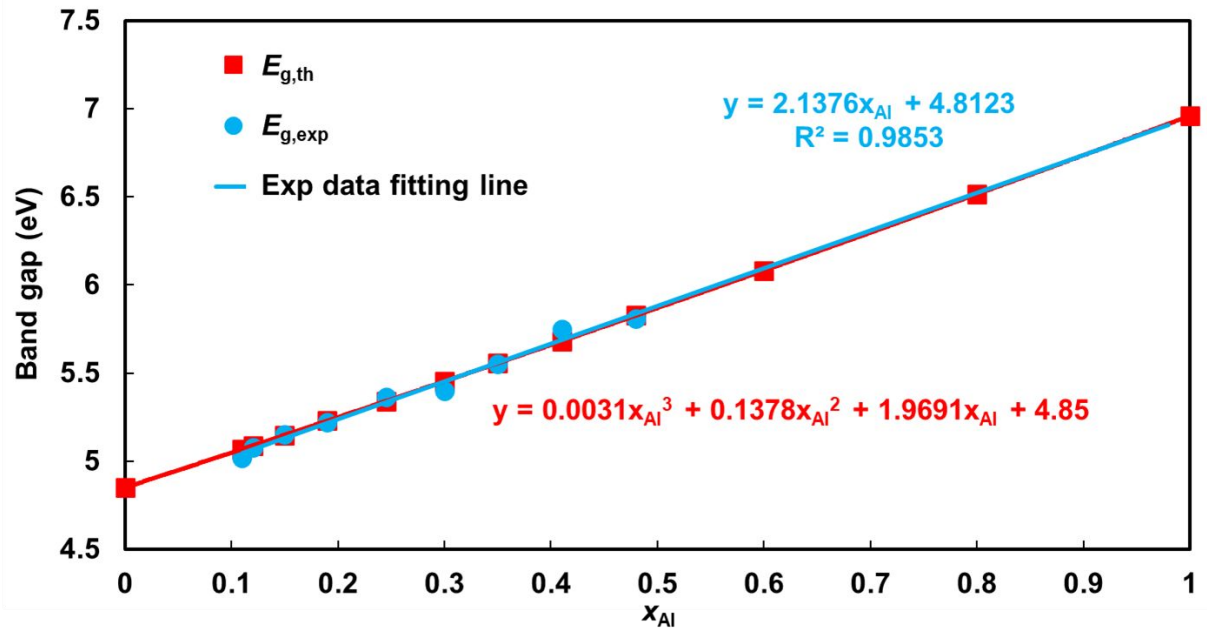

Figure S2. Direct optical band gap values vs Al content ($0.11 \leq x_{Al} \leq 0.48$) for PLD polycrystalline films[1] derived from Tauc plots (azure circles). Theoretical band gap values derived according to eqs.8 by assuming (see text): χ_{Al}=1.50; $B_{\theta-Al2O3}$ = -2.225 eV; $A_{\theta-Al2O3}$ = 2.3; χ_{Ga}=1.60; $B_{\beta-Ga2O3}$ = -2.31eV; $A_{\beta-Ga2O3}$ =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[8] a value of 4.85 ± 0.05 eV was assumed for the direct band gap value of β–Ga_2O_3 from which the value of A_2= 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:

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

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_2O_3. From Eq. S2 a value of 6.96 eV is obtained for the direct band gap of θ–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.[2]

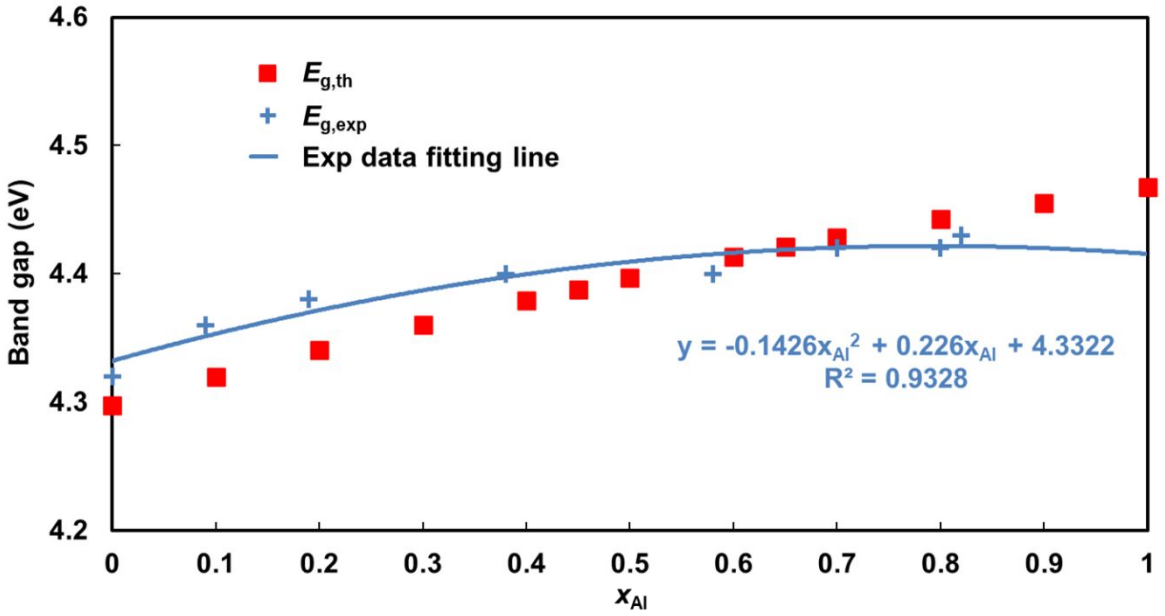

Figure S3. Non-direct optical band gap values vs Al content ($0 \leq x_{Al} \leq 0.8$) (blue plus) for amorphous anodic film grown up to 5 V Hg/HgO at 10 mV s^{-1} in borate buffer solution on Al-Ta magnetron sputtered alloys of various compositions derived from Tauc plots.

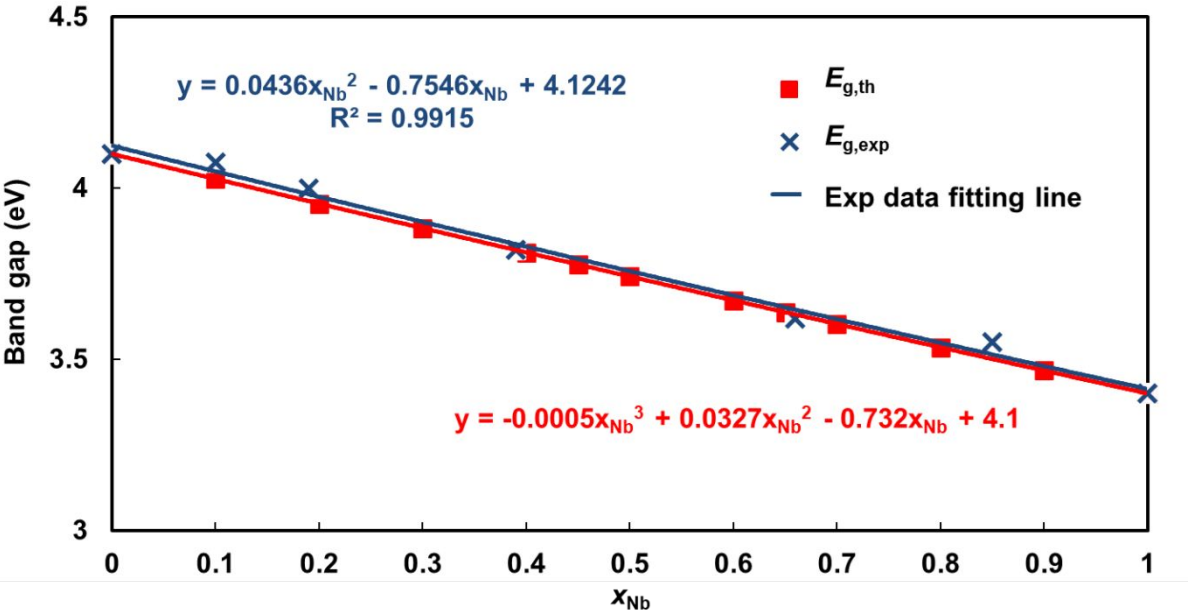

Figure S4. Non-direct optical band gap values vs Nb content (blue times symbols) for amorphous anodic film grown up to 5 V Ag/AgCl at 10 mV s^{-1} in NaOH solution on Nb-Ta magnetron sputtered alloys of various compositions derived from Tauc plots.

Polymorph/ phase	χ_1	A_1	B_1 [eV]	χ_2	A_2	B_2 [eV]
α-$(Ga_{(1-x)}Al_x)_2O_3$	1.50	2.80	-2.71	1.60	2.22	-2.71
β-$(Ga_{(1-x)}Al_x)_2O_3$	1.50	2.23	-2.225	1.60	1.96	-2.31
Am $(Nb_{(1-x)}Al_x)_2O_{(5-2x)}$	1.50	1.67	-2.25	1.60	1.302	-1.35
Am $(Ta_{(1-x)}Al_x)_2O_{(5-2x)}$	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.

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.

(2) Peintinger, M. F.; Kratz, M. J.; Bredow, T. Quantum-Chemical Study of Stable, Meta-Stable and High-Pressure Alumina Polymorphs and Aluminum Hydroxides. *J. Mater. Chem. A* **2014**, *2* (32), 13143–13158.

(3) Liu, D.; Guo, Y.; Lin, L.; Robertson, J. First-Principles Calculations of the Electronic Structure and Defects of Al2O3. *J. Appl. Phys.* **2013**, *114* (8), 083704.

(4) Wang, T.; Li, W.; Ni, C.; Janotti, A. Band Gap and Band Offset of Ga2O3 and (AlxGa1-x)2O3 Alloys. *Phys. Rev. Appl.* **2018**, *10*, 011003.

(5) Peelaers, H.; Varley, J. B.; Speck, J. S.; Van De Walle, C. G. Structural and Electronic Properties of Ga2O3-Al2O3 Alloys. *Appl. Phys. Lett.* **2018**, *112* (24), 242101.

(6) Franchy, R.; Schmitz, G.; Gassmann, P.; Bartolucci, F. Growth of Thin, Crystalline Oxide, Nitride, and Oxynitride Films on NiAl and CoGa Surfaces. *Appl. Phys. A Mater. Sci. Process.* **1997**, *65* (6), 551–566.

(7) Fares, C.; Ren, F.; Lambers, E.; Hays, D. C.; Gila, B. P.; Pearton, S. J. Valence- and Conduction-Band Offsets for Atomic-Layer-Deposited Al2O3 on (010) (Al0.14Ga0.86)2O3. *J. Electron. Mater.* **2019**, *48* (3), 1568–1573.

(8) Hinuma, Y.; Gake, T.; Oba, F. Band Alignment at Surfaces and Heterointerfaces of Al2O3, Ga2O3, In2O3, and Related Group-III Oxide Polymorphs: A First-Principles Study. *Phys. Rev. Mater.* **2019**, *3* (8), 084605.