Quantitative Modeling of Point Defects in β-Ga_2O_3 Combining Hybrid Functional Energetics with Semiconductor and Processes Thermodynamics

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Supplementary Materials

Grouping of similar defects to simplify plots

Because of the enormous number of somewhat similar complexes included in our calculations, we grouped similar defects together to simplify plots. For example, the slightly different configurations of Ga vacancies V^{ia}_{Ga}, V^{ib}_{Ga} and V^{ic}_{Ga} all have similar formation energy diagram structure thus behave similarly. Grouping their concentrations together as V^{i}_{Ga} allows plots to be more intelligible. Figure S1 shows Figure 1(a) without this grouping.

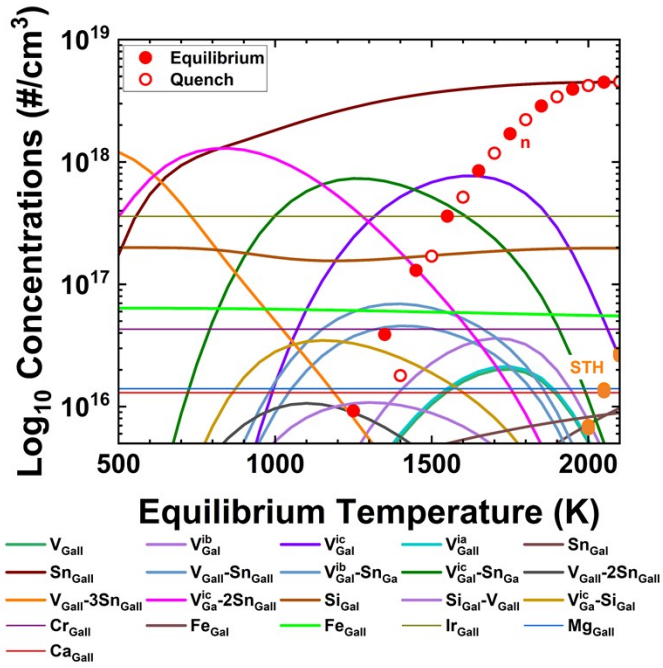

Figure S1. Same as Fig. 1 (a) but including all of the individual defects and complexes without grouping.

Including Hydrogen

Figure S2 shows the calculation of the concentration of defects including hydrogen related defects. Figure S2(a) shows the same calculation as shown in figure 1 (a) (EFG grown, p_{O2}=0.02 atm, f=0.40) in the main paper with inclusion of H-related defects. Figure S2(b) shows the same calculation as shown in figure 3(c) (O_2 annealing scenario of EFG grown Ga_2O_3, p_{O2}=1 atm, f=0.40). These plots comparing with figure 1(a) and figure 3(c) in the main paper, shows that including H-related defects doesn't change any conclusion.

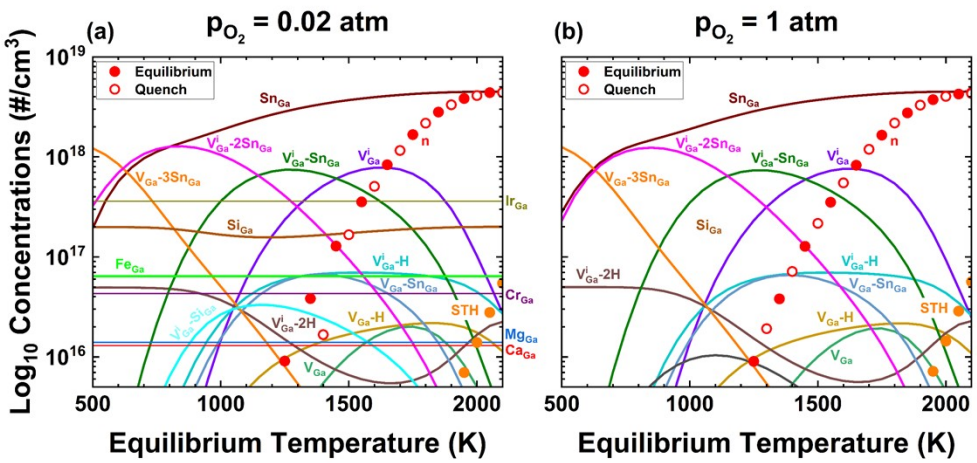

Figure S2. Defects concentrations calculated for Sn-doped wafer (a) same as figure 1(a) in the main paper and (b) same as figure 3(c) in the main paper. Both of these calculations are done with inclusion of hydrogen related defects.

Effect of band edge temperature dependencies

In the body of the paper, calculations held f = 0.40. Figure S3, S4, S5 & S6 shows results for Fig. 3b, 3c, 5a & 5c but with f = 0, 0.5 & 1, respectively.

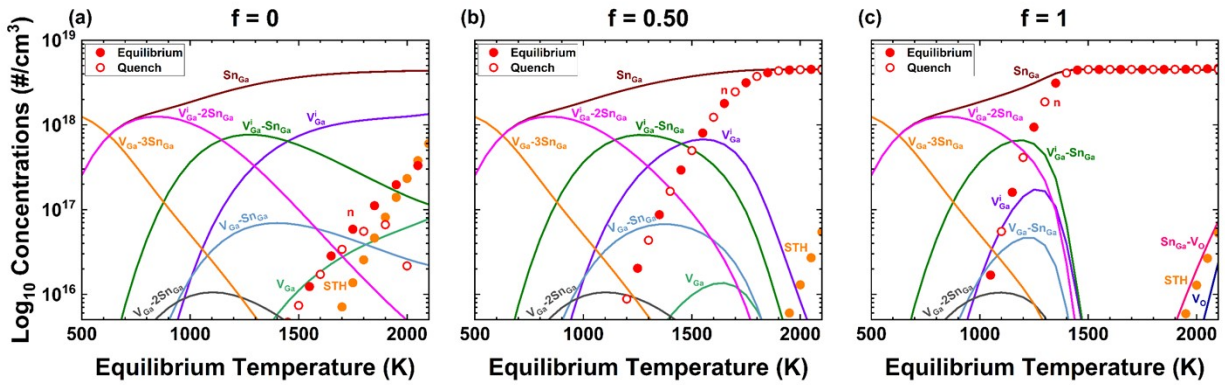

Figure S3. Similar as Fig. 3b (EFG grown, p_{O2}=0.02 atm, f=0.40) but for f = 0, 0.5 & 1, to see what happens by varying f from 0 to 1, meaning 0/100, 50/50 & 100/0 split of Eg(T) between conduction and valence bands, respectively.

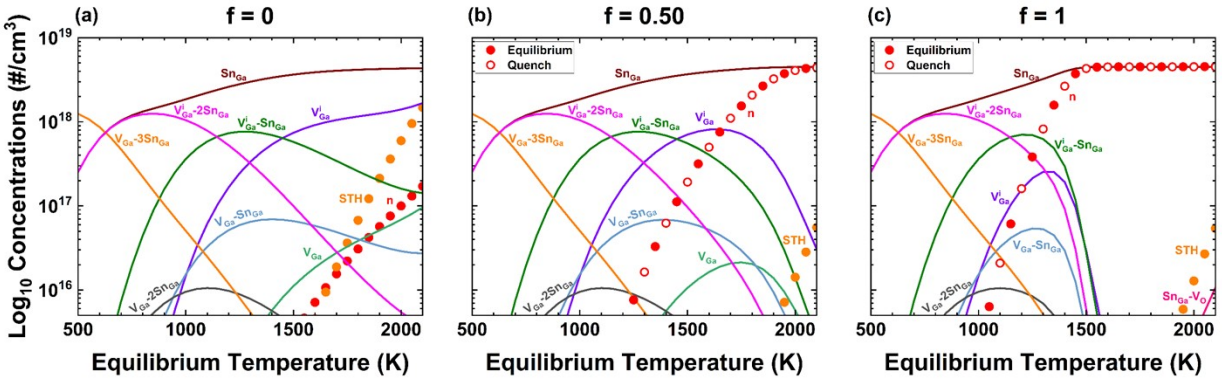

Figure S4. Similar as Fig. 3c (O_2 annealing, p_{O2}=1 atm, f=0.40) but for f = 0, 0.5 & 1, to see what happens by varying f from 0 to 1, meaning 0/100, 50/50 & 100/0 split of Eg(T) between conduction and valence bands, respectively.

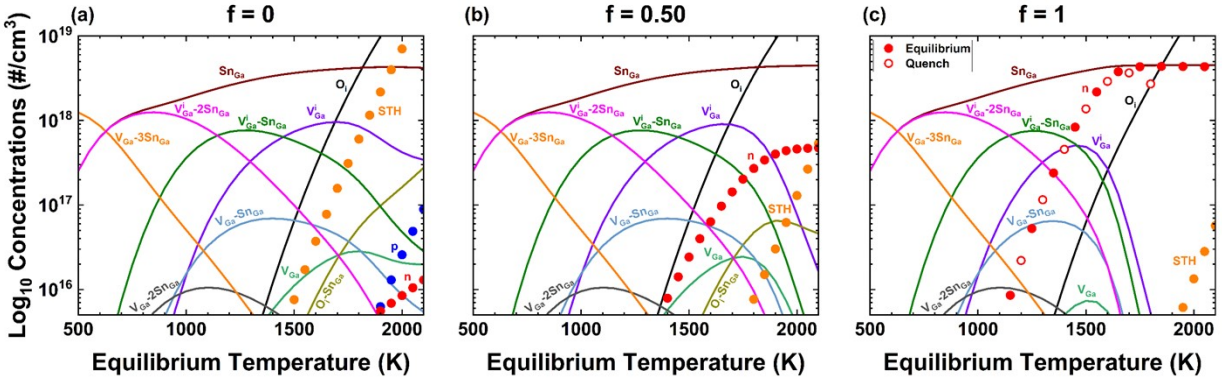

Figure S5. Similar as Fig. 5a (without μ(T) scenario) but for f = 0, 0.5 & 1, to see what happens by varying f from 0 to 1, meaning 0/100, 50/50 & 100/0 split of Eg(T) between conduction and valence bands, respectively.

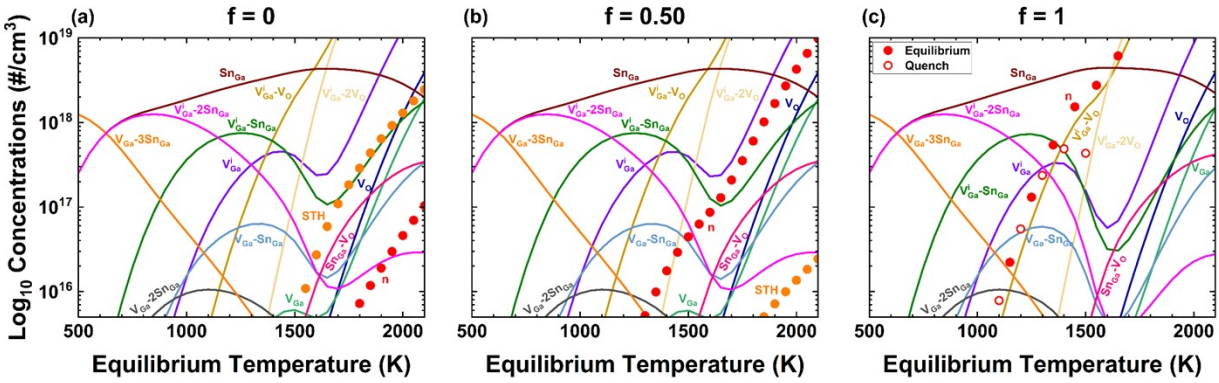

Figure S1. Similar as Fig. 5c (without $\Delta S_{vib}(T)$ scenario) but for f = 0, 0.5 & 1, to see what happens by varying f from 0 to 1, meaning 0/100, 50/50 & 100/0 split of Eg(T) between conduction and valence bands, respectively.

Bridgman Method

Figure S7 presents the calculated defect concentrations for Sn-doped β-Ga_2O_3 crystals grown via the Bridgman method under conditions of p_{O2} = 0.20 atm and f = 0.40. This calculation shows excellent agreement with the experimental data reported by Hoshikawa et al. [1], where the calculated carrier concentrations aligns closely with the measured value of 3.6×10^{18} /cm^3 for a doping concentration of 5.1×10^{18} /cm^3 [Sn] at 1950-2000 K. The impurity values used in this calculation were consistent with those reported in the same study. Similar to the EFG calculation (Fig. 1(a)), the Bridgman method indicates that both equilibrium and quenching conditions lead to Sn-doped wafers remaining n-type with <1% compensation, provided that the native defect system is frozen-in at approximately 1950 K. This prediction reinforces the findings of the EFG scenario, demonstrating a consistent theoretical understanding of the defect behavior in Sn-doped β-Ga_2O_3 across different growth methods.

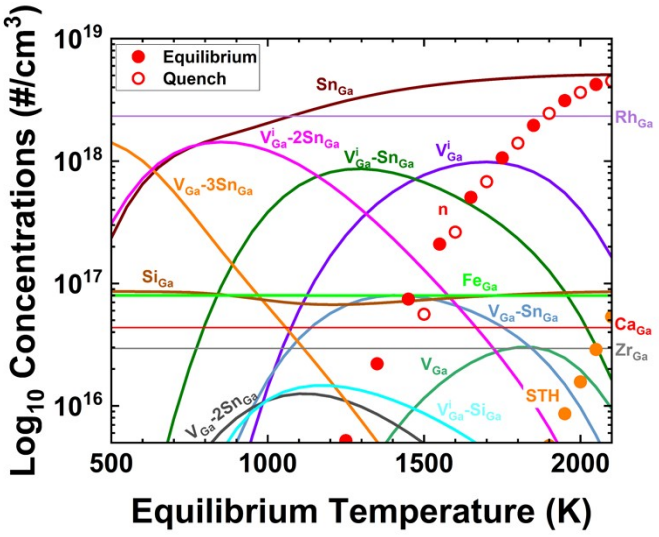

Figure S7. defect concentrations calculated for the Bridgman grown Sn-doped β-Ga_2O_3 (p_{O2} = 0.20 atm and f = 0.40)

Defect Structures

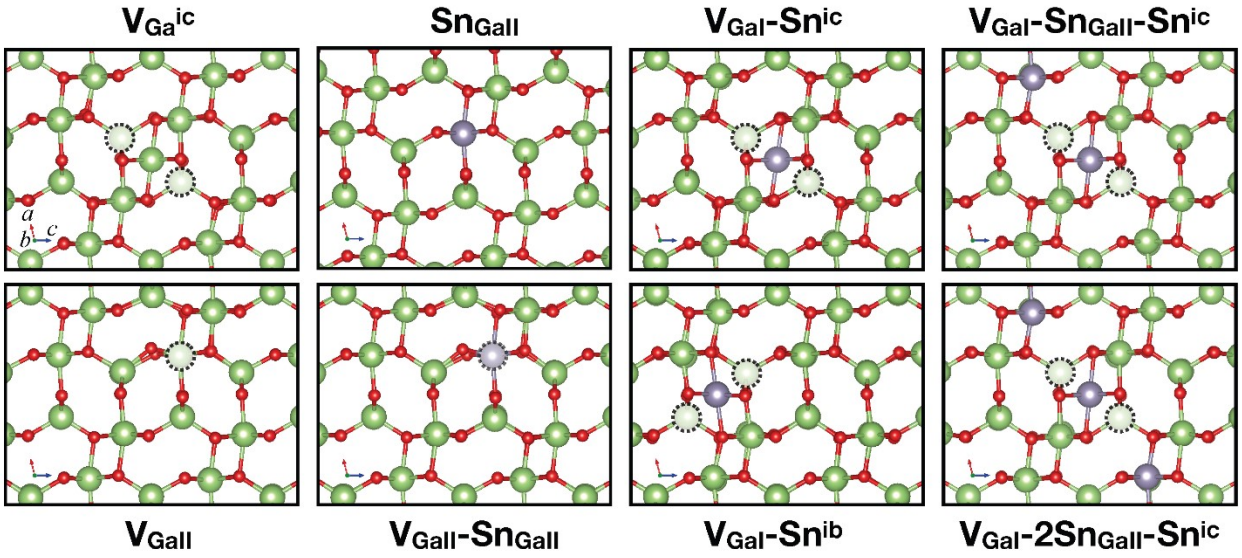

Figure S2. Structures of the defects dominating the β-Ga_2O_3 defect equilibria discussed in this work.

Figure S8 shows the defect structures of the defects that are crucial for the paper formatting the whole defects scenarios. From Fig. 1, (a) V_{Ga}^{ic} represents a split vacancy configuration where one V_{Ga} is shared between two Ga sites with one Ga_i residing between them[2]; (b) V_{GaII} shows the conventional Ga vacancies on the Ga(II) sublattice; (c) Sn_{GaII} shows substitutional Sn atom replacing one Ga atom; (d) V_{GaII}-Sn_{GaII} shows a complex consisting of a Ga vacancy and a substitutional Sn atom; (e) and (f) V_{Ga}-Sn_{Ga} represents two symmetry-distinct configurations of split-vacancy complexes with Sn occupying the central site replacing Ga, (g) V_{GaI}-Sn_{GaII}-Sn^{ic} represents larger complex involving one split vacancy with Sn replacing the central Ga atom and one substitutional Sn atom, and finally (h) V_{GaI}-$2Sn_{GaII}$-Sn^{ic} shows an extended version of (g) with one more substitutional Sn atom.

Workflow of KROGER

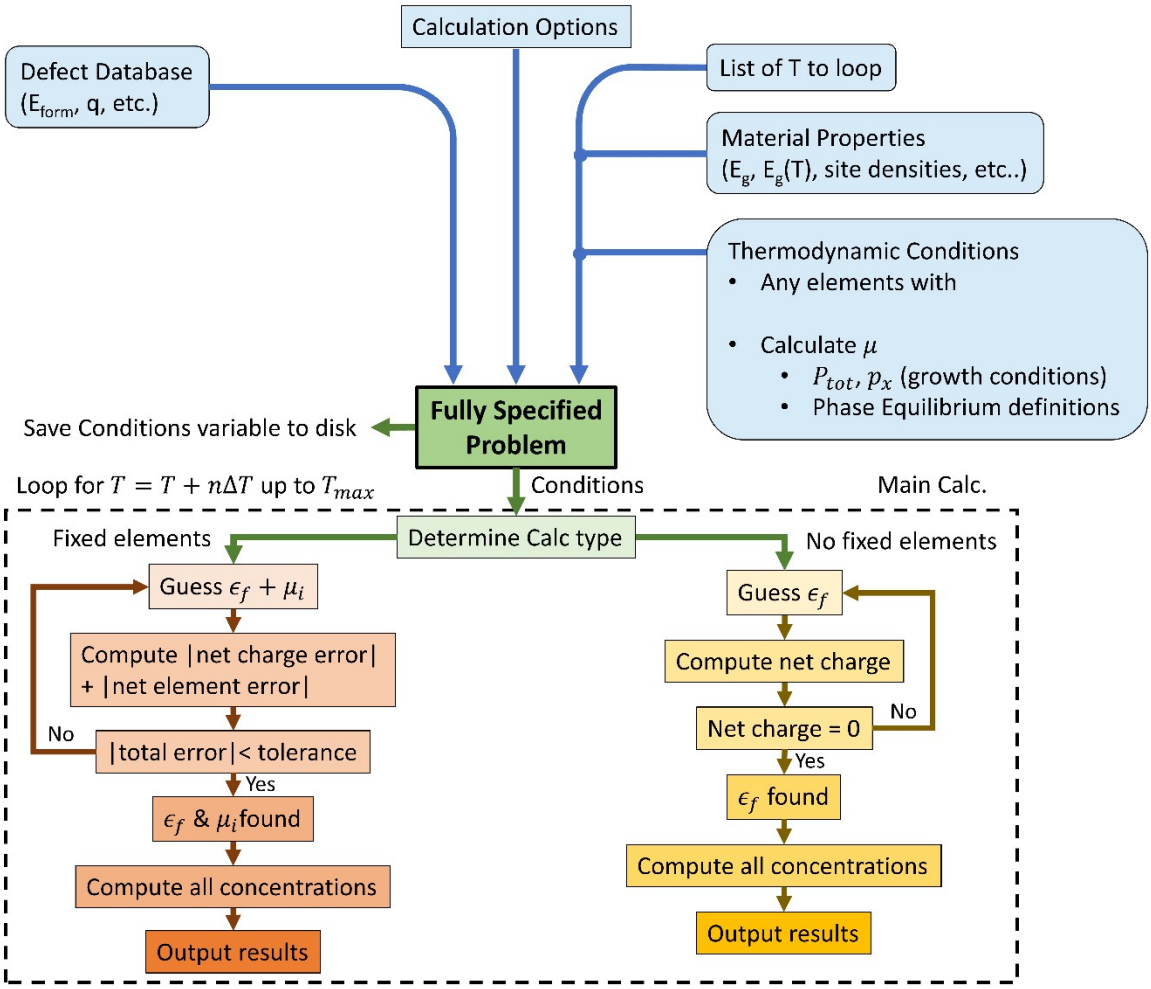

Figure S9. Workflow diagram of KROGER program. Light blue boxes represent user inputs required to fully define the problem, leading to the green box that consolidates all conditions. Within the dotted box, KROGER performs two types of calculations to determine the final concentrations of defects. The sequential flow from input to output is outlined step by step.

References

(1) Hoshikawa, K.; Kobayashi, T.; Ohba, E.; Kobayashi, T. 50 Mm Diameter Sn-Doped (0 0 1) β-Ga2O3 Crystal Growth Using the Vertical Bridgeman Technique in Ambient Air. *J. Cryst. Growth* **2020**, *546*, 125778. https://doi.org/10.1016/j.jcrysgro.2020.125778.

(2) Frodason, Y. K.; Varley, J. B.; Johansen, K. M. H.; Vines, L.; Van De Walle, C. G. Migration of Ga Vacancies and Interstitials in β − Ga 2 O 3. *Phys. Rev. B* **2023**, *107* (2), 024109. https://doi.org/10.1103/PhysRevB.107.024109.