Online APS March Meeting 2021

Computational Fermi level engineering and doping-type conversion of Ga_2O_3 via three-step processing

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NREL/PR-5K00-81057

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Fermi Level Engineering of Mg-doped Ga_2O_3 with Hydrogen

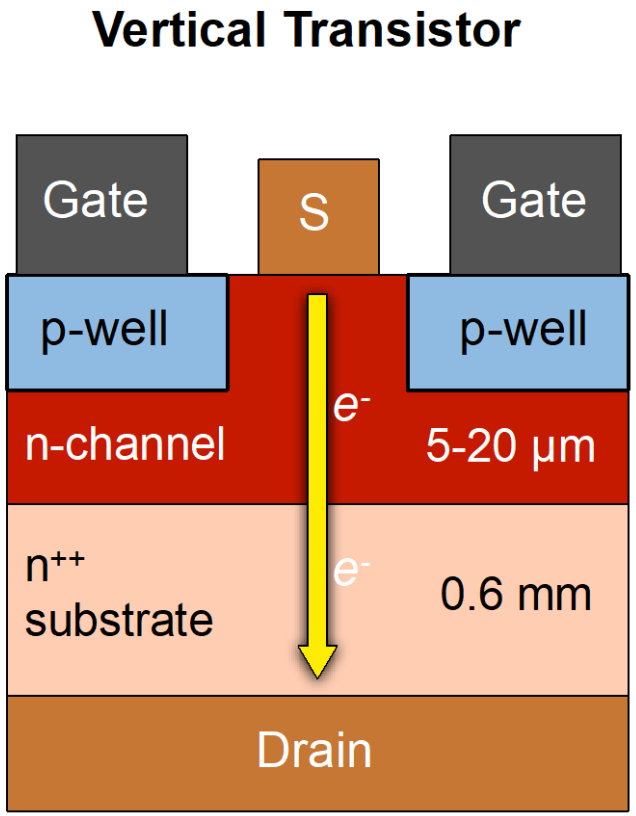
- **Ga_2O_3 is intrinsically n-type** and using extrinsic dopants its n-type conductivity can easily be tuned[1,2]
- However, **p-type doping faces obstacles[3,4]**

Motivation:

- P-type doping of Mg:GaN with hydrogen[5]
- Potential application of Ga_2O_3 in devices[1,6]

Key results:

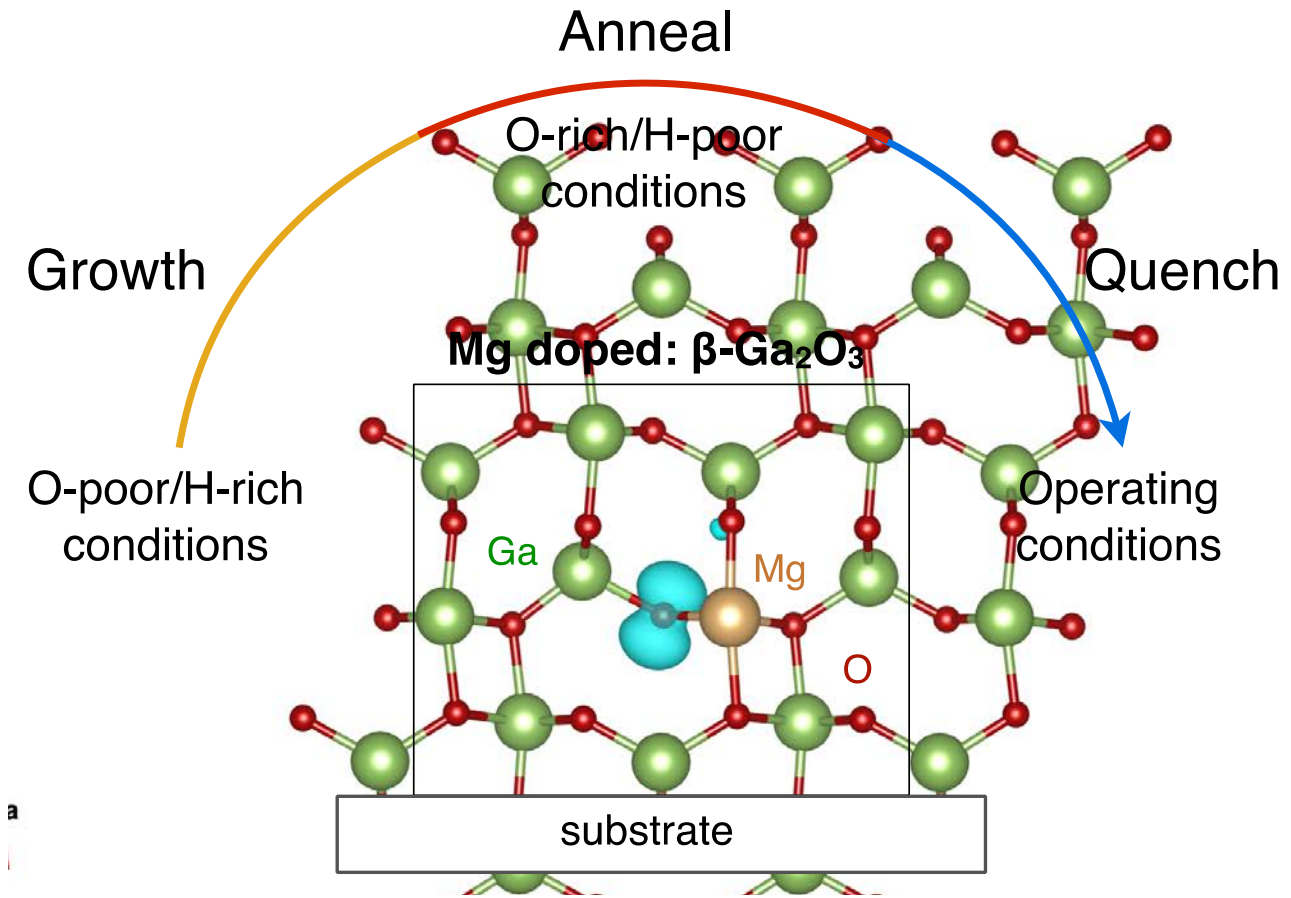
- Type conversion ($N_A > N_D$) of Mg-doped Ga_2O_3
- Fermi level pushed below mid gap
- Free electron density greatly suppressed



[1]S. J. Pearton et al., *Appl. Phys. Rev.*, **2018**, **5**, 011301
[2]S. Lany, *APL Mater.*, **2018**, 6, 046103
[3]J. L. Lyons, *Semicond. Sci. Technol.*, **2018**, 33, 05LT02
[4]J. B. Varley et al., *J. Phys. Condens. Matter*, **2011**, 23, 334212
[5]S. Nakamura et al., *Jpn. J. Appl. Phys.*, **1992**, 31, 1258–1266
[6]S. B. Reese, A. Zakutayev et al., Joule **2019**, 3 903-907

Three-Step Processing Applied to Mg-doped Ga_2O_3 with H

- **Estimate thermodynamic conditions (*T*, pO_2, pH_2O) that maximizes net acceptor concentrations**

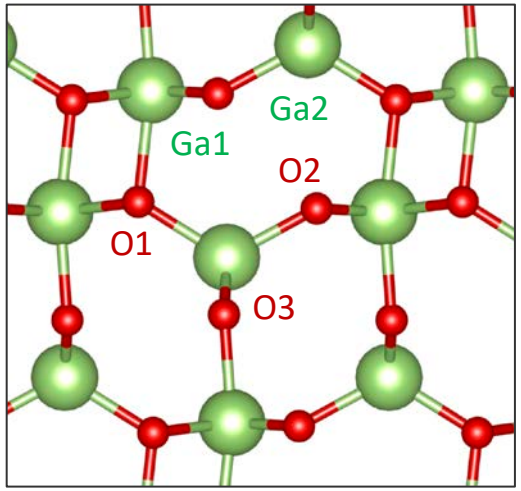


Methodology: Thermodynamic Modeling Workflow

1. Relax atomic structure

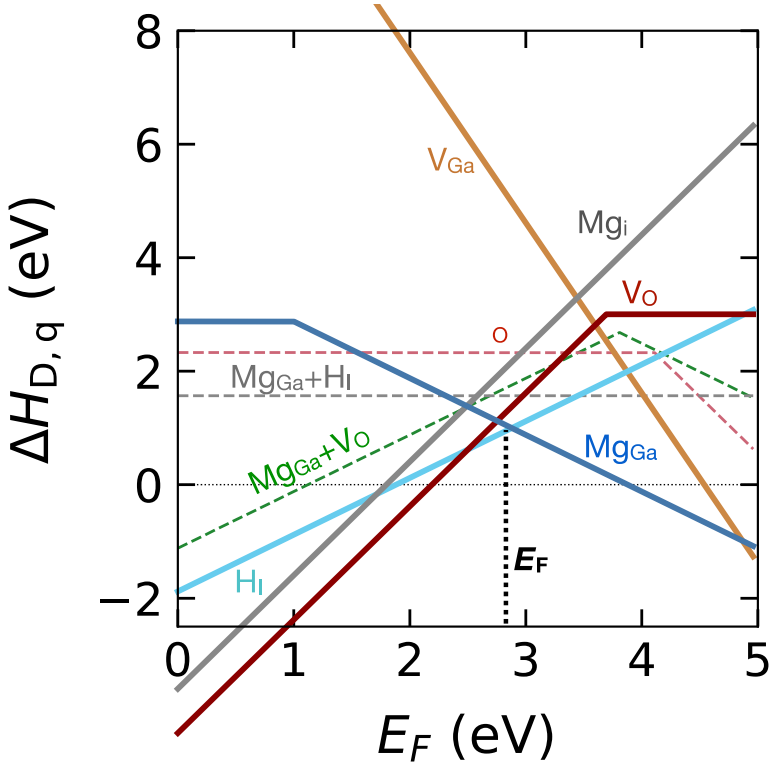
Atomic and electronic structure relaxation using DFT

β-Ga_2O_3



2. Calculate defect formation energy

Identify important intrinsic defects, dopants, impurities and defect-pairs



S. Lany, *APL Mater.*, **2018**, 6, 046103
A. Goyal, V. Stevanovic et al. *Comp. Mater. Sci.,* **2017**, 130

Methodology: Thermodynamic Modeling Workflow

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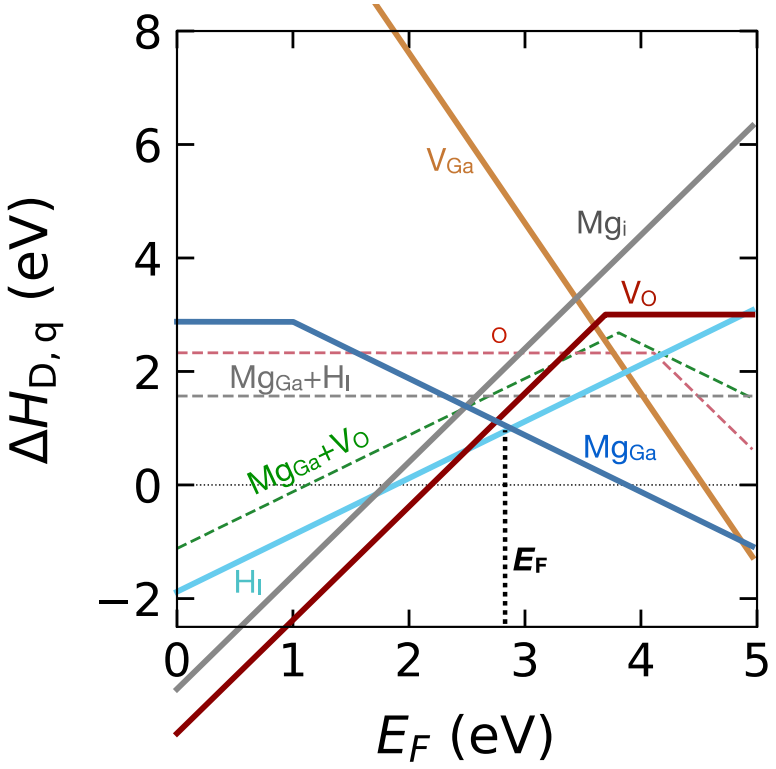


3. Model thermodynamic properties

Defect and free carrier concentrations as function of T and pO_2 , pH_2O

(Courtesy: S. Lany)

Defect formation energy	$\Delta H = \Delta H_{D,q}(\mu, E_F)$
Defect concentration	$c_D \approx N_{site} \times \exp(-\Delta H/kT)$
Electron/hole density	$c_e = \int f_{FD}(E-E_F)\, g(E)\, dE$
Charge neutrality	$-c_e + c_h + \Sigma\,[q \cdot c(D^q)] = 0$
Self-consistent solution	$\Delta H(E_F) \longrightarrow c_D(\Delta H) \longrightarrow E_F$
pO_2 dependence of μ_O (ideal gas)	$\Delta\mu_O(T,P_0) = \frac{1}{2}[H_0+\Delta H(T)] - \frac{1}{2}T\cdot[S_0+\Delta S(T)]$ $\Delta\mu_O(T,P) = \Delta\mu_O(T,P_0) + \frac{1}{2}kT\ln(P/P_0)$

O, H chemical potentials outcome of equilibrium $H_2 + \frac{1}{2}\,O_2 \leftrightarrow H_2O$ gas

K. Biswas and S. Lany *PRB*, **2009**, 115206
S. Lany J. *Chem. Phys.*, **2018**, 071101

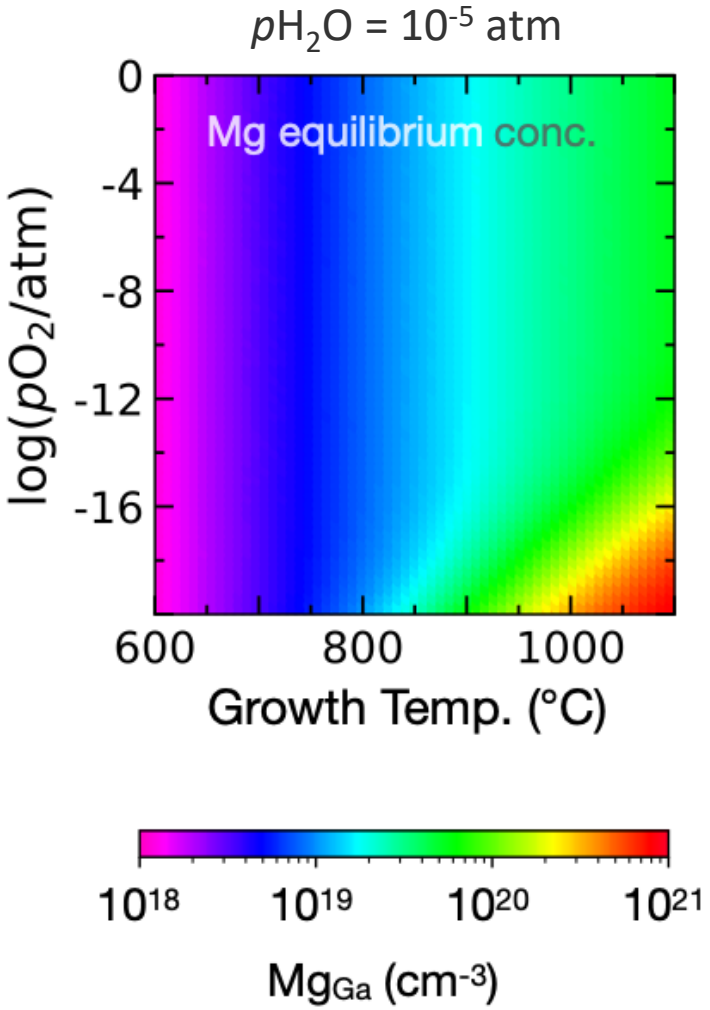
Growth at O-poor and H-rich Conditions

Typical thin-film growth conditions:

Typical Like-Process	Temp. (°C)	range pO_2 (atm)	max pH_2O (atm)[1,2]
PVD	600 - 800	10^{-13} – 10^{-5}	10^{-5}
CVD	800 - 1100	10^{-18} - 10^{0}	10^{0}

Under H-rich conditions (pH_2O = 10^{-5} atm) Mg solubility less sensitive to pO_2

Mg conc. under Growth

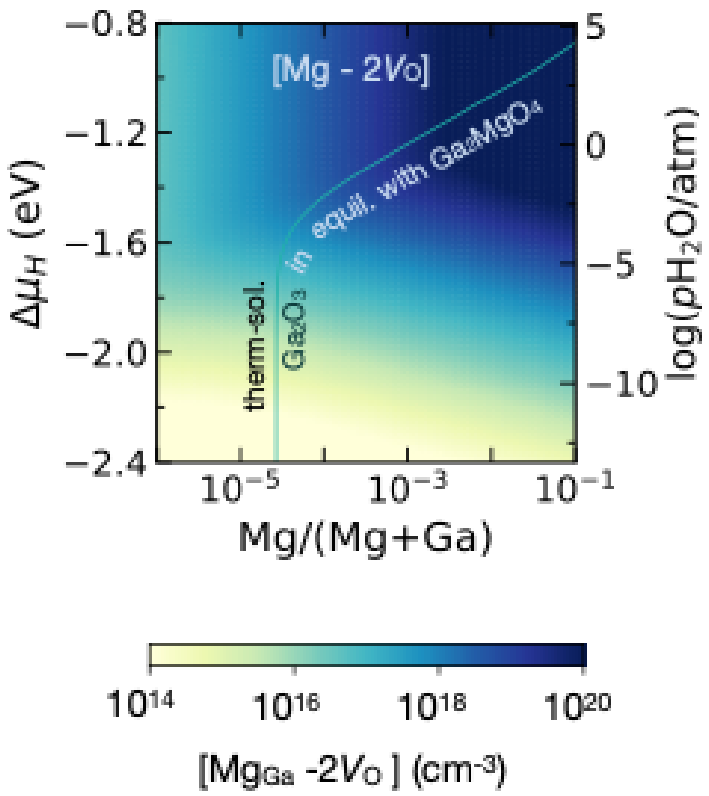


[1]Upper limit of ballistic particle transfer across chamber in PVD process such as MBE or PLD
[2]In APCVD if H_2O is used as oxygen precursor for Ga_2O_3 growth

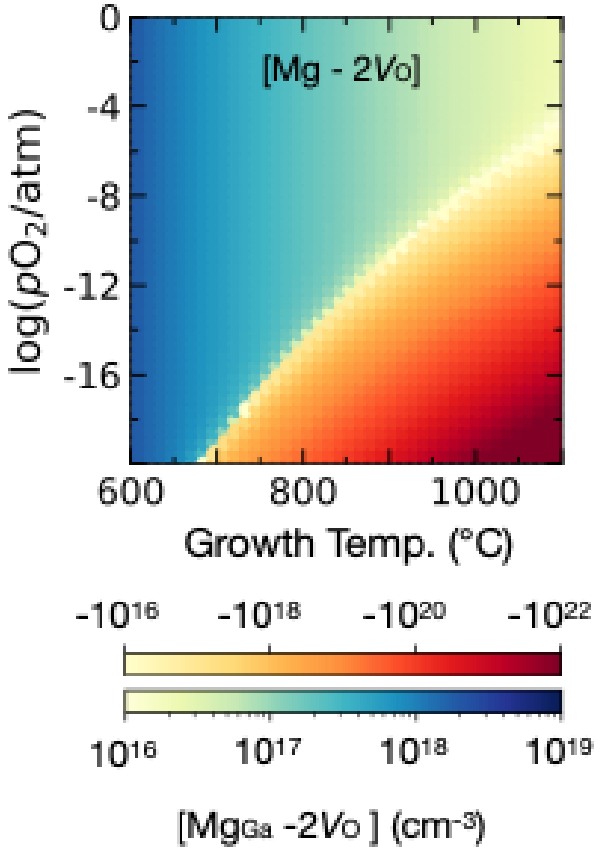
Growth Step: Beyond Mg Equilibrium Solubility

- Beyond equilibrium Mg solubility feasible in thin-film growth[1,2] and under atmospheric pressure chemical vapor (APCVD) process[3]
- Even higher Mg solubility possible under hydrogen plasma source[4]

T = 600C, pO_2 = 10^{-9} atm



pH_2O = 10^{-5} atm, Mg = 1%



Lower growth T and H-rich conditions required to maximize [Mg – $2V_O$] defect concentration

[1]G. B. Gonzalez et al., *J. Am. Ceram. Soc*. 95, **2012**, 809-815
[2]M. H. Wong et al., *Appl. Phys. Lett*. **2018**, 113 102103
[3]T. Terasako et al., *Phys. Status Solidi C 12,* **2015**, *985-988*
[4]L. Tian et al., *Surface & Coatings Tech*. 347, **2018**, 181-190

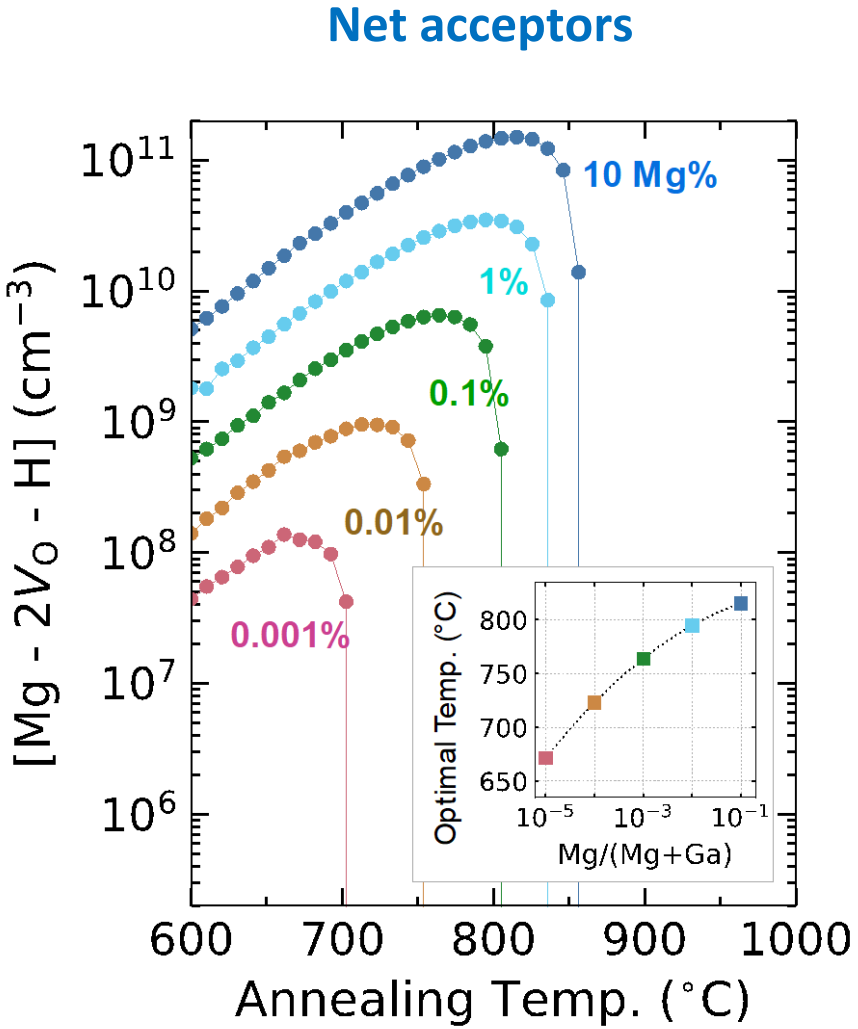
Equilibrium Anneal at O-rich and H-poor Conditions

- Allow for O vacancies and H to equilibrate
- Conditions analogous to Mg:GaN[1,2] (N-rich/H-poor)
- O-rich: pO_2 = 1 atm
- H-poor*: $pH_2O = 10^{-8}$ atm

*Choice of pH_2O:

- Research grade gas typically contains 1 ppm $pH_2O = 10^{-6}$ atm
- Gases can be further purified (gas chromatography)
- Impurity level 10 ppb possible = 10^{-8} atm

Optimal annealing temperature that maximizes net acceptors for Mg-doping level

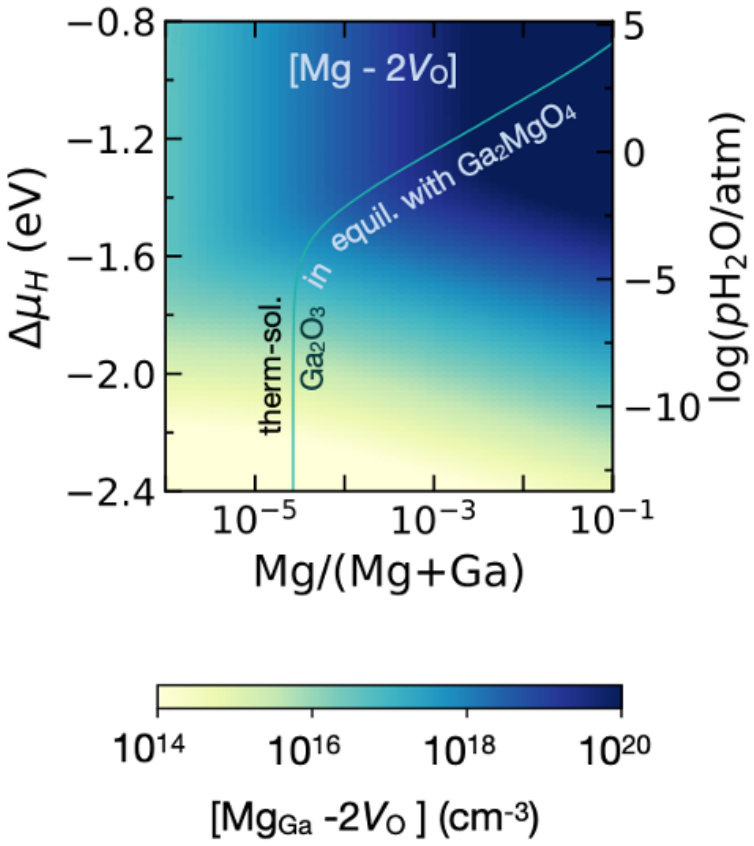


[1]S. Nakamura et al., *Jpn. J. Appl. Phys.*, **1992**, 31, 1258–1266
[2]S. Nakamura et al., *Jpn. J. Appl. Phys.*, **1992**, 31, L139–L142

Non-Equilibrium Anneal at Fixed V_O Concentration

Growth

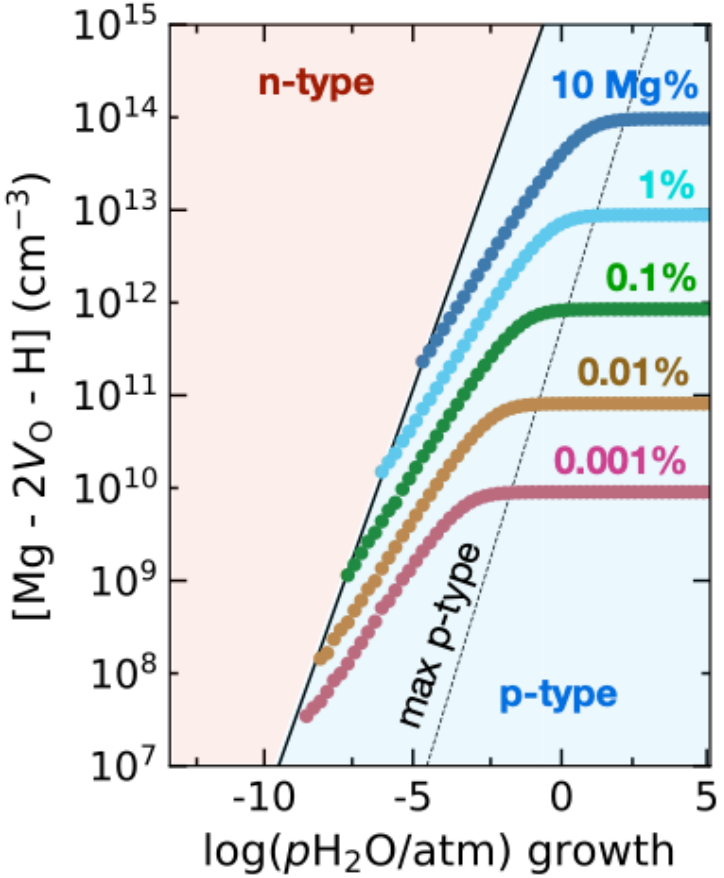
T = 600°C, pO_2 = 10^{-9} atm



Fix V_O conc.

Non-equilibrium Anneal

T = 600 °C, pO_2 = 1 atm, pH_2O = 10^{-8} atm



Higher conc. of net acceptors than at the equilibrium annealing

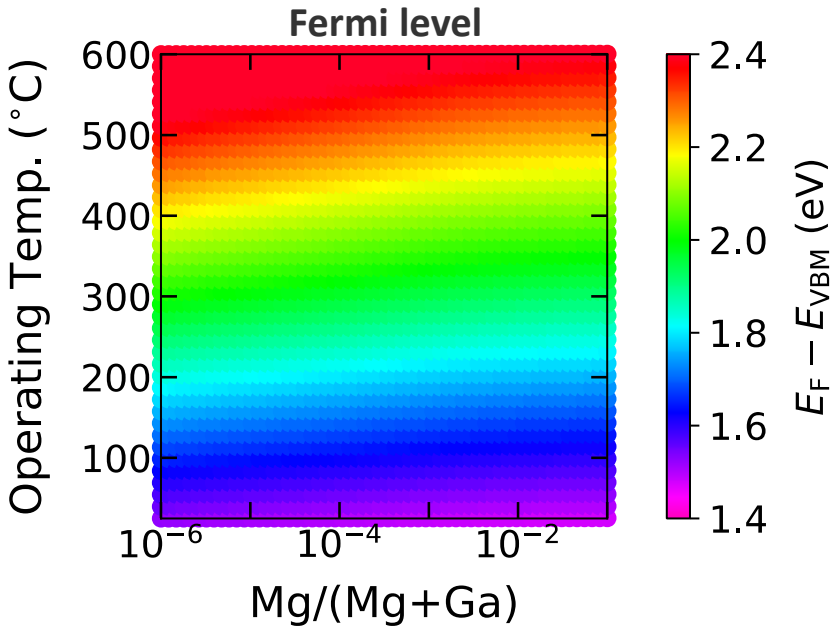
Kyrtsos et al. Phys. Rev. B, **2017**, 95, 245202
M. H. Wong et al., *Appl. Phys. Lett*. **2018**, 113 102103
H. Peelaers et al. *APL Mater.* **2019**, 7, 2022519

Minimum pH_2O needed during growth for conversion (N_A>N_D)

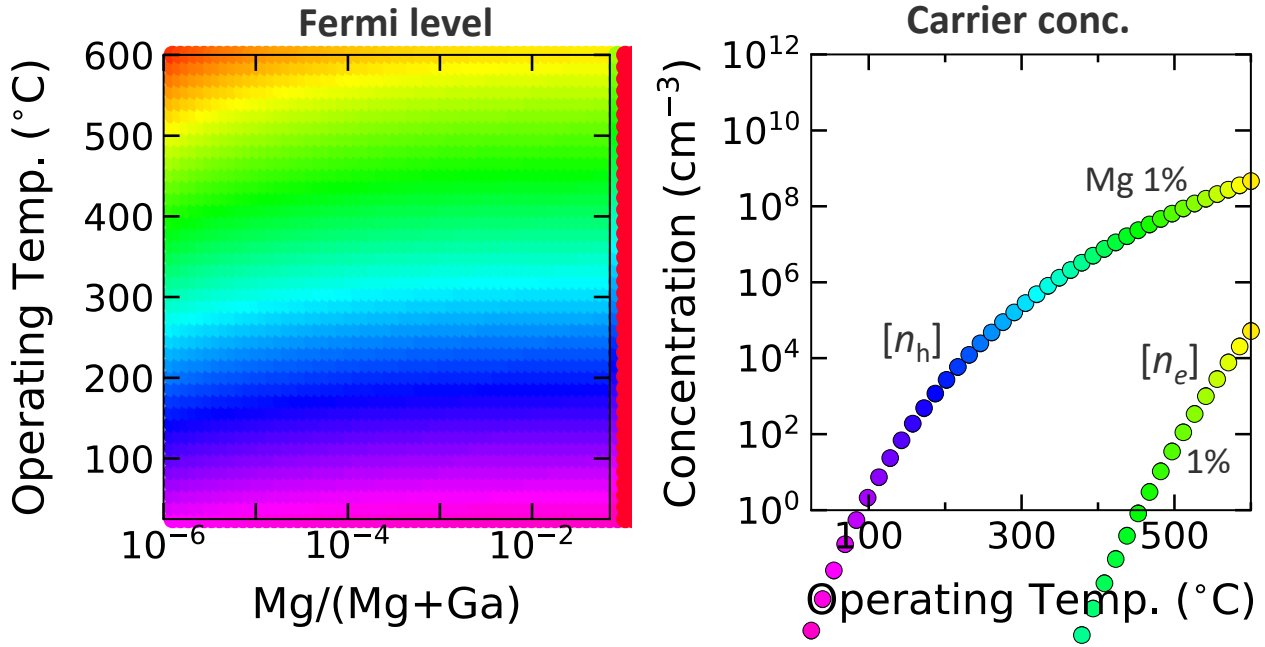
Quench From the Preceding Annealing Step

- Quenched from the preceding anneal step at pO_2 = 1 atm, pH_2O = 10^{-8} atm
- Freeze defect concentrations and allow for Fermi level, electrons and holes to equilibrate

Quench from equilibrium anneal



Quench from non-equilibrium anneal

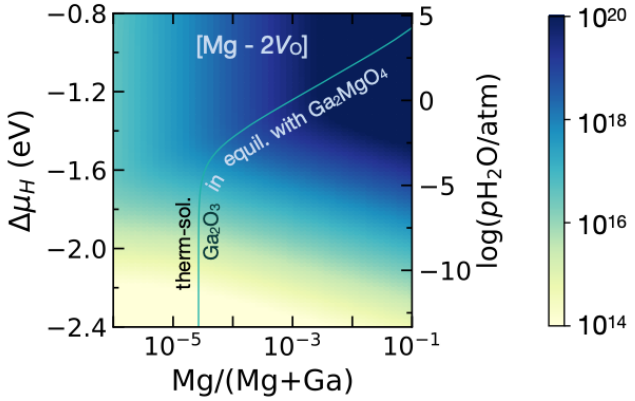


Fermi level has stronger dependence on operating temperature and [n_e] greatly suppressed

Three-step Processing of Ga_2O_3 with H

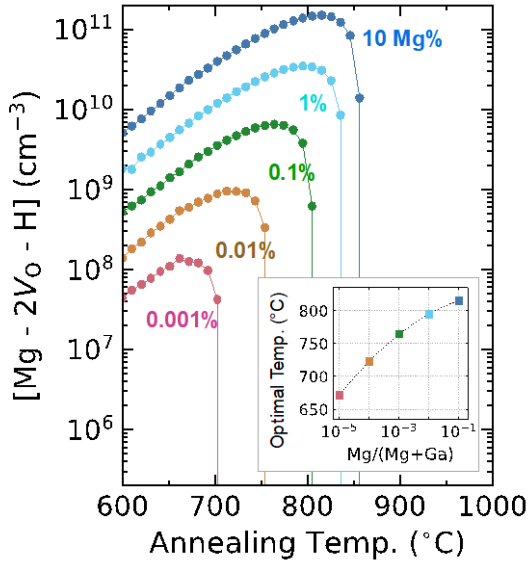
Growth:

- **Lower growth *T* is better**
- **H-rich $pH_2O > 10^{-7}$ atm needed to enable type conversion ($N_A > N_D$)**



Equilibrium Anneal:

- **Optimal anneal temperature to maximize net acceptors ~ 10^7-10^{11} cm^{-3}**



Non-equilibrium Anneal:

- **If achievable, result in higher net acceptors ~10^{10} - 10^{14} cm^{-3} than equilibrium annealing**

Quench:

- **E_F below mid gap value**
- **Electron concentrations can be greatly suppressed**