Point defects in Ga_2O_3 as efficient UV-Vis light emission centers

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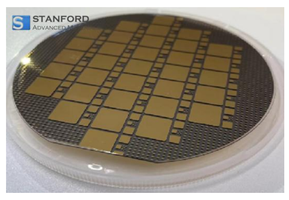
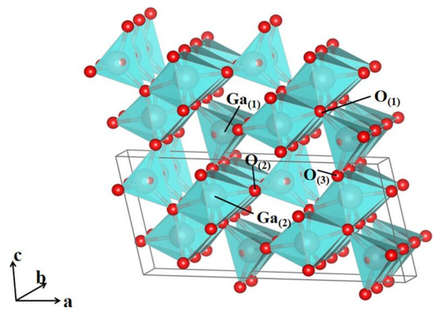
Ga_2O_3 ultra-wide-band-gap oxide

- E_g= 4.8 eV → a member of UWBGO family
- Transparent material; candidate for advanced technology applications (solar-blind UV photodetectors, solar cells, sensors and power electronic applications)
- 5 polymorphs (rhombohedral α, monoclinic β, defected spinel γ, cubic δ and orthorhombic ε)
- Advantages over GaN and SiC: the cost of producing large-area substrates potentially lower (melt growth techniques possible), MOSFET with larger electric field
- Absence of clear demonstration of *p*-type doping (full Ga_2O_3-based bipolar devices are impossible)



Gallium Oxide Wafer
(Stanford Advanced Materials)
https://www.samaterials.com

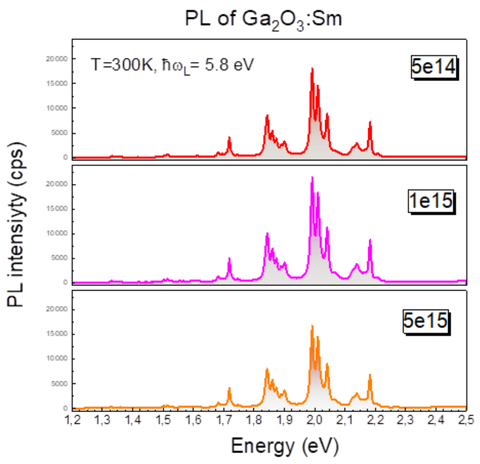


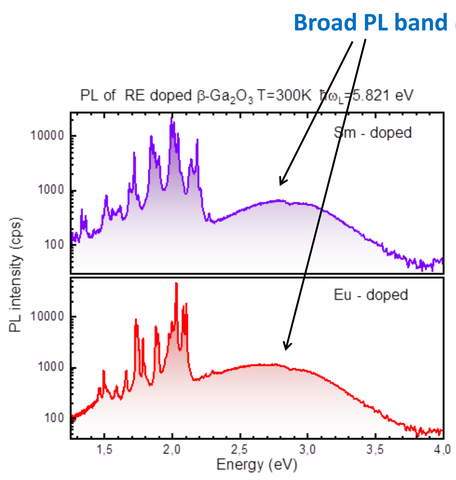
β-Ga_2O_3 monoclinic crystal structure

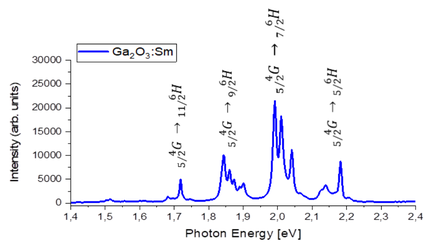
- Monoclinic crystal structure; 3 oxygen sites (O_I, O_{II} – two trigonal, and one O_{III} tetragonal) and 2 Ga sites (tetrahedral & octahedral) → anisotropy of physical, optical and transport properties
- DFT calculations → CBM at the Γ point and fairly flat VB;
  indirect E_g = 4.66 eV, direct E_g = 4.69 eV
- Large m_h ; holes tend to form small polarons localized at lattice imperfections
- Lack of near-band-edge (NBE) photoluminescence
- RT PL dominated by a broad set of transitions @ ~399nm ascribed to oxygen vacancies (V_{OI}, V_{OII} and V_{OIII}) → 416, 442 and 464 nm; but several mechanisms invoked to explain the UVA PL (native defects, self-trapped polarons)
- Ultra-wide E_g → attractive matrix for Rare Earth (RE) dopants

Room temperature PL of β-Ga_2O_3:RE

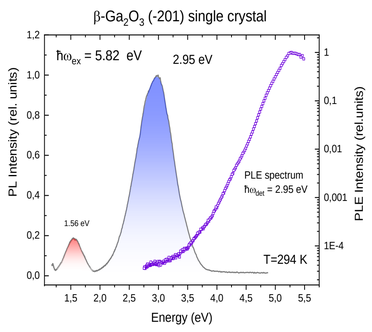
- E_g of 4.9 eV → transparent material, appropriate matrix for Rare Earth-based emitters
- Single β-Ga_2O_3 (010) crystals (from Kyma Co.) implanted with Sm and Eu to a fluence of 4e14, 1e15 and 5e15 at/cm², implantation energy 150 keV
- Implantation performed at UMCS (Marie Curie-Skłodowska University, Lublin, Poland, dr M. Turek)
- Intensive RE-related photoluminescence observed at RT
- WBG of 4.9 eV → weak PL quenching expected; PL does not depend on temperature
- Samarium implantation with a fluence of $4{\cdot}10^{14}$, $1{\cdot}10^{15}$ and $5{\cdot}10^{15}$ at/cm² → intensive PL at RT
- Intensive PL @ RT for high fluences → quenching effect not observed







- Bright PL from defect states appears at 2.4 – 3.2 eV (with excitation above E_g)
- Energy far from E_g = 4.9 eV → intensive RT PL (relatively weak dependence on the Fermi function)
- This PL band is very common and appears in undoped and implanted crystals



- Laser excitation above E_g (5.82 eV) → bright RT PL from defect states appears at 2.2 – 3.4 eV, with max at 2.95 eV (intensity weakly dependent on the Fermi function)
- PL excitation (PLE) with a xenon lamp shows max intensity of the 2.95 eV line at 5 eV (close to bandgap)
- Urbach states near the CB edge

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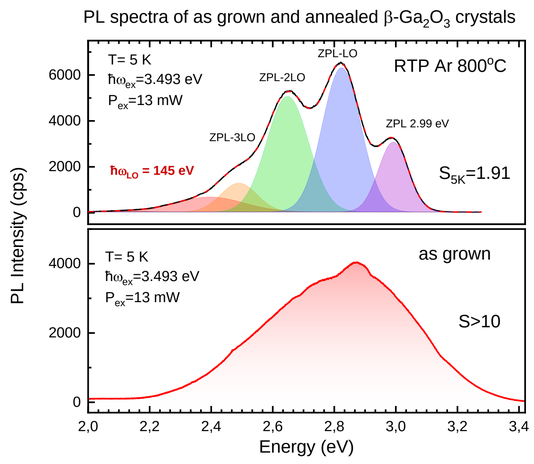
Rapid Thermal Annealing @ 800°C

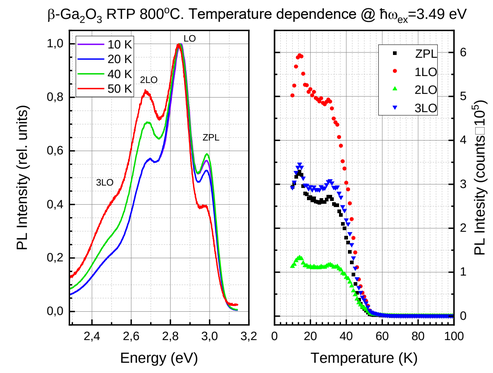
- A significant difference between as grown and annealed β-Ga_2O_3 crystals
- Annealing at 800°C results in evolution of PL spectra → PL fine structure, in which zero-phonon-line (ZPL) at 2.99 eV is accompanied by phonon repetitions separated by 145 meV
- High difference in Huang-Rhys factor S:

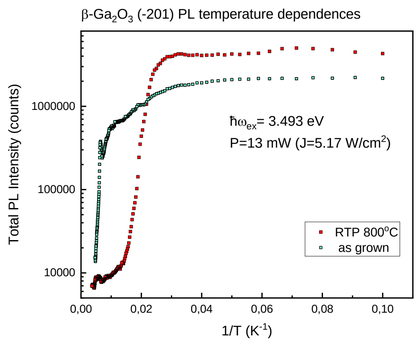
  $S_{asgrown} \geq 10$ $S_{RTP} = 1.91$

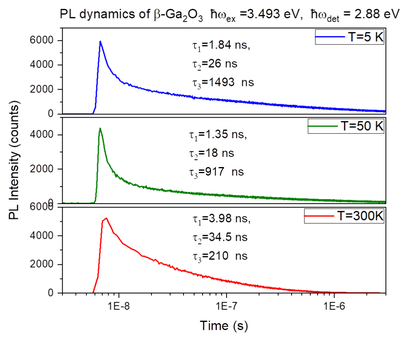


PL temperature dependence

- RTP annealed β-Ga_2O_3 crystals → PL temperature dependence with E_{exc}= 3.49 eV
- PL fine structure, with the ZPL at 2.99 eV accompanied by 3 phonon repetitions is observed at higher temperature







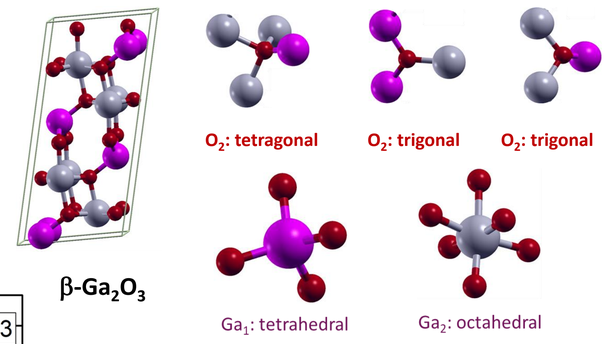
- PL temperature dependence with E_{exc}= 3.49 eV (resonant excitation of PL line)
- Fast atypical PL drop for T≤ 50K for RTP annealed β-Ga_2O_3 crystal and for T ≤ 250K for as grown
- As grown β-Ga_2O_3 crystal → interplay between different transitions; a few PL centers below 30K

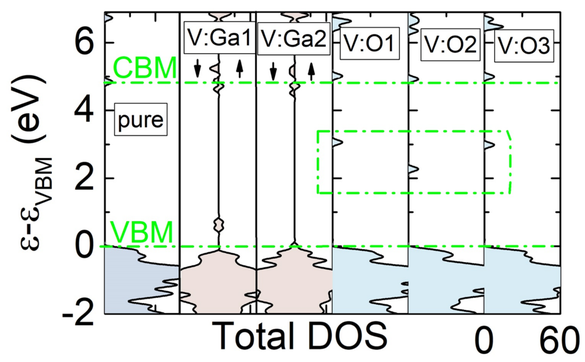
PL decay time

- PL decay time measured for $h\nu_{exc}$= 3.49 eV and $h\nu_{det}$= 2.88 eV
- PL decay is non-exponential → indirect indication of DAP centrum
- Relatively short decay times (~4 ns at RT) indicate isolated centrum → good candidate for a single photon emitter (SPE)?

Density Functional Theory calculations

- DFT: Calculation performed using QUANTUM-ESPRESSO package.
- Within the generalized gradient approximation (GGA)+U.
- Hubbard-like +U terms where applied on the both d(Ga) and p(O).
- U_{Ga} =3 eV, U_O =7 eV give the correct band structure of Ga_2O_3. Calculated E_g = 4.85 eV.
- Defect calculations in the 160-atoms supercell





- Total density of states of Ga_2O_3: without defects (pure) and involving one vacancy at Ga_1, Ga_2, O_1, O_2 and O_3 sites, respectively;
- Ga-vacancies are deep acceptor states;
- O-vacancies are deep donor states with different electronic structure that depends on site –geometry;

Calculated charge transition levels with respect to the VBM:
+2/0 = 2.8 eV (for O_1);
+2/0 = 2.3 eV (O_2);
+2/0 = 2.95 eV (O_3)

Summary

- Single β-Ga_2O_3 crystal is a good candidate for optical applications when doped with RE ions
- Single β-Ga_2O_3 does not show near-band-edge, but bright RT PL from defect states at 2.2 – 3.4 eV, with max at 2.95 eV
- Annealing at 800°C results in evolution of PL spectra → PL fine structure, in which zero-phonon-line (ZPL) at 2.99 eV is accompanied by 3 phonon repetitions
- PL temperature dependence indicates only one transition center
- DFT calculations indicate that this line originate from oxygen vacancy defect (derived from trigonal oxygen)
- PL temperature dependence and short Decay time (about 4 ns at RT) indicate that this state might be promising as a SPE center