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# LED lighting: oxidation of GaN from *ab initio* thermodynamic modelling



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## Sustainable lighting with GaN

Lighting is a fundamental and powerful part of modern life. LED lighting is a disruptive technology, which can not only offer exceptional energy efficiencies in a convenient package, but is easily driven by solar-powered lamps in rural “off-grid” locations. This has been shown to lead to improvements in education, health and even gender equity.<sup>1</sup>

Currently, high-performance LED technology is dominated by GaN-based doped semiconductors. While the supply of gallium is limited, improvements in technology can reduce the quantity required and the dependence on rare earth metals.<sup>2</sup>



## Methods

We examined the impact of oxygen, which can enter as a contaminant during the production of GaN by vapour deposition. Density functional theory (DFT) was used to calculate relaxed geometries, formation energies and electronic structures for a variety of hypothetical O-containing GaN crystals. FHI-aims, a highly-parallel all-electron *ab initio* code with an atom-centred basis set, was used with the PBEsol functional.<sup>3</sup>

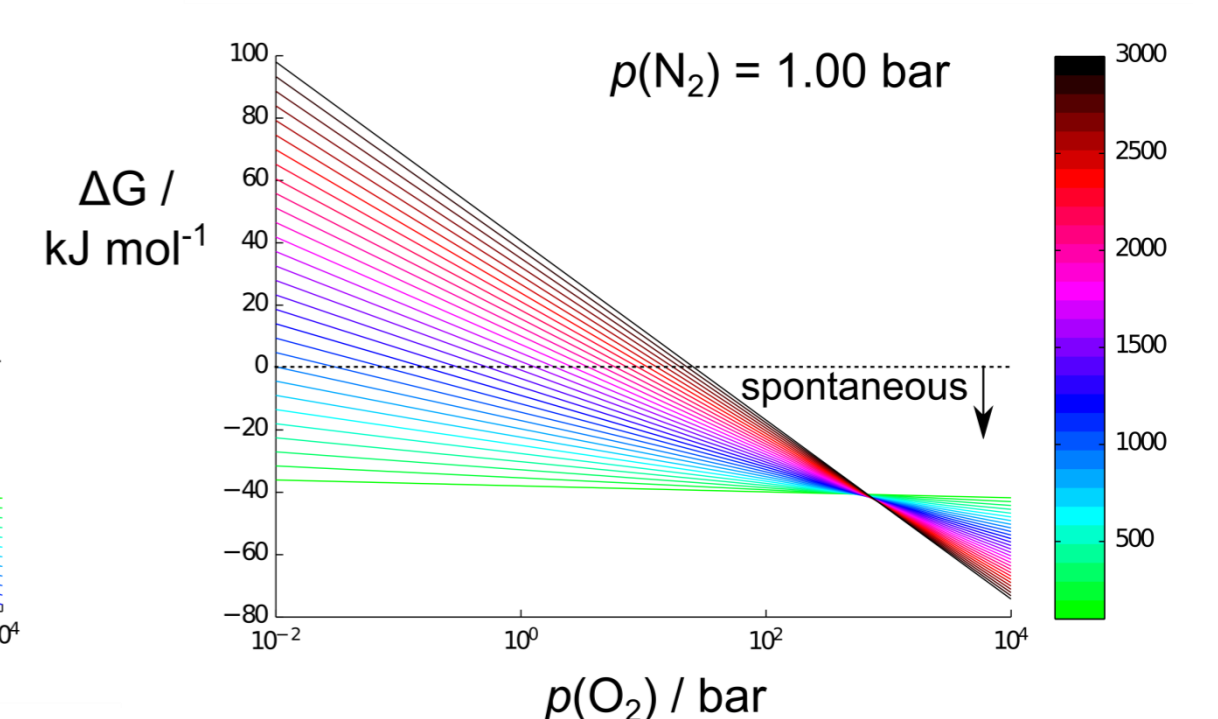
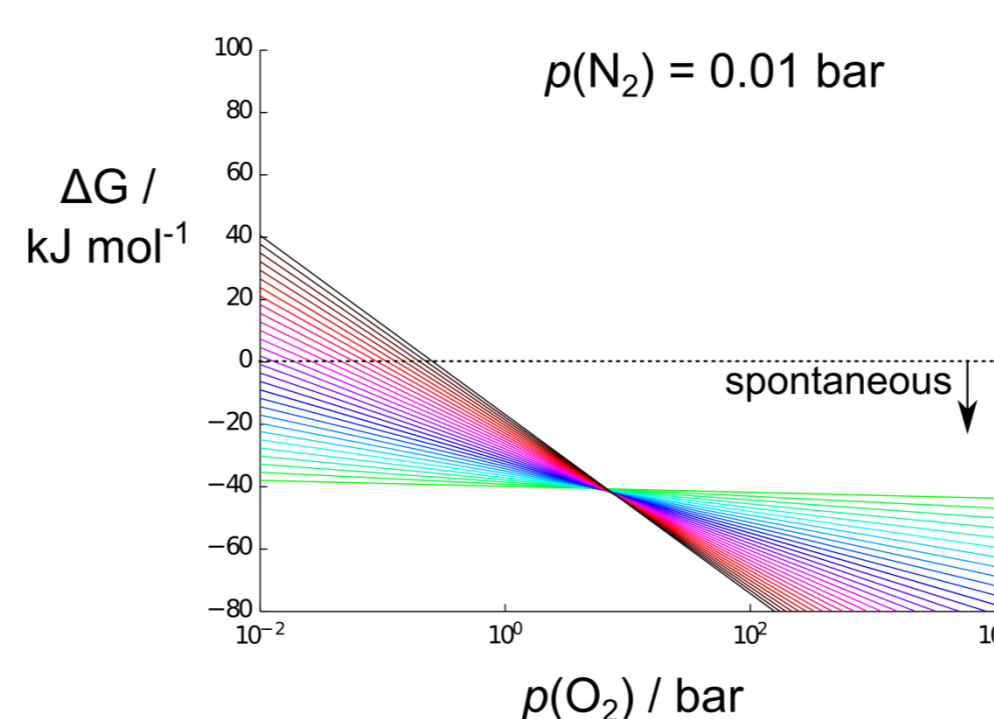
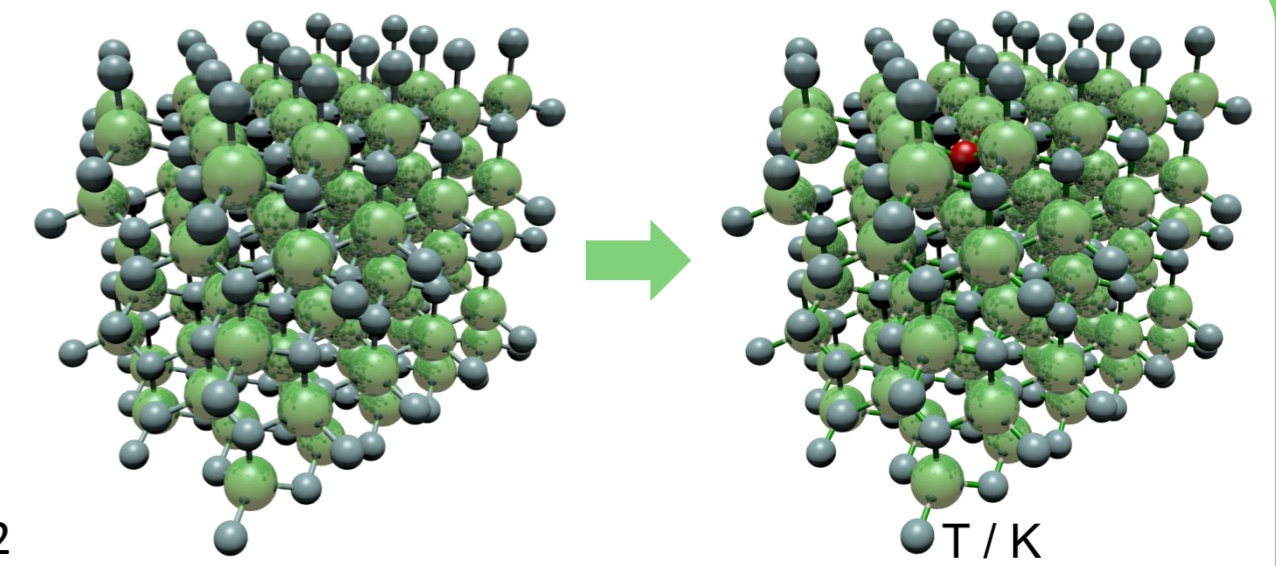
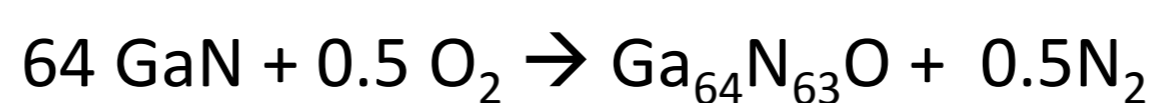
The formation energies from DFT calculations were combined with classical thermodynamics and standard gas-phase data to form a thermodynamic model of a deposition system.

## Key results

- Standard enthalpies of formation were calculated from first principles.
- A range of bulk defects were modelled for an ideal solid formation from gallium metal and gaseous oxygen and nitrogen.
- The calculations suggest that oxidation is favourable at ambient pressure and 1000 K. This is lower than typical operating conditions, but of the same order of magnitude. It is likely that a barrier step has not been included; oxidation does not occur spontaneously in the bulk, but at interfaces.
- Electronic structure calculations confirmed that oxygen acts as an n-type dopant. These properties are important for GaN's role as a semiconductor.

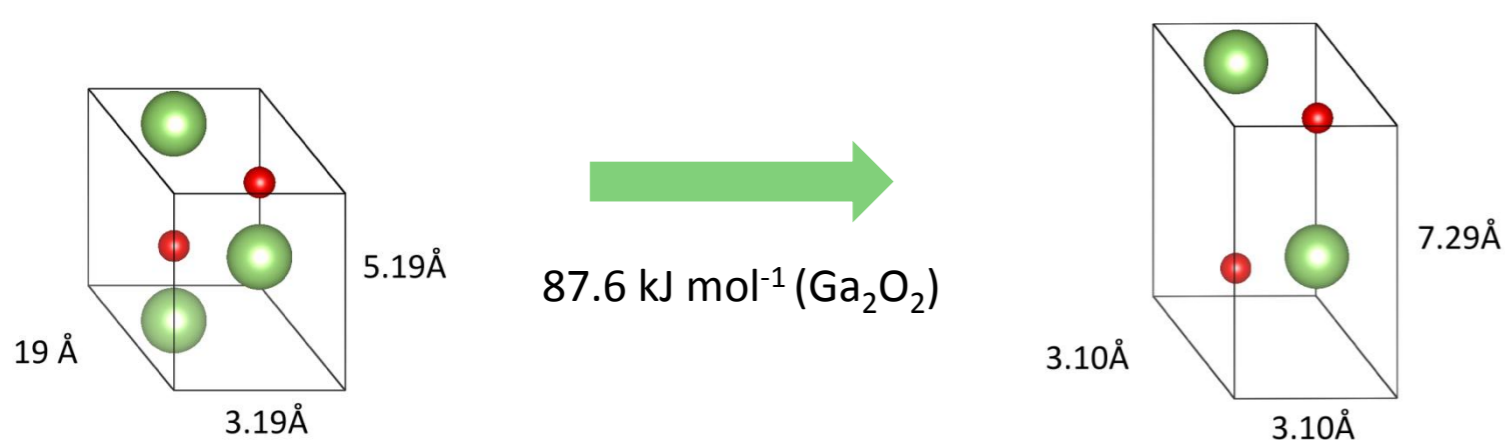
### Onset of oxidation

Energy changes were calculated for the substitution of a single atom in a GaN “supercell”



Gibbs free energy calculated using *ab initio* thermodynamics: reaction spontaneity and equilibrium constant varies based on temperature (T) and ratio of gas partial pressures  $p(\text{O}_2)$  and  $p(\text{N}_2)$ .

### GaO(s): hypothetical structure



Experiments in the literature have suggested that the presence of oxygen does not have to lead to a change in structure.<sup>4</sup> However, this relaxation shows that there could be considerable strain on an oxidised surface.

## Future work

- Behaviour at the surface can be examined with a “slab” model. This approach is often used to calculate adsorption energies which may give further insight into the process.
- The *ab initio* thermodynamic model relies heavily on the ideal gas equation. The model can be developed to use alternative equations of state to model high-pressure systems.
- Hybrid functionals may be used for highly-accurate electronic structures, permitting deeper exploration of the effect of oxygen doping on the bandgap. This can be used to predict optical properties.

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