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Oxygen vacancies and donor impurities in β -Ga₂O₃

J. B. Varley,^{1,a)} J. R. Weber,¹ A. Janotti,² and C. G. Van de Walle²

¹Department of Physics, University of California, Santa Barbara, California 93106-9530, USA

²Department of Materials, University of California, Santa Barbara, California 93106-5050, USA

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Using hybrid functionals we have investigated the role of oxygen vacancies and various impurities in the electrical and optical properties of the transparent conducting oxide β -Ga₂O₃. We find that oxygen vacancies are deep donors, and thus cannot explain the unintentional n -type conductivity. Instead, we attribute the conductivity to common background impurities such as silicon and hydrogen. Monatomic hydrogen has low formation energies and acts as a shallow donor in both interstitial and substitutional configurations. We also explore other dopants, where substitutional forms of Si, Ge, Sn, F, and Cl are shown to behave as shallow donors. © 2010 American Institute of Physics. [doi:10.1063/1.3499306]

Of all the wide-band-gap oxide semiconductors, β -Ga₂O₃ is one of the few that remains transparent well into the ultraviolet (UV), making it a promising deep-UV transparent conducting oxide (TCO) for applications in laser lithography, solar cells, and UV optoelectronic devices.^{1,2} Unintentionally doped β -Ga₂O₃ can have carrier concentrations up to 10^{18} cm⁻³.³ Its band gap is 4.9 eV,² considerably larger than that of conventional TCOs such as In₂O₃, SnO₂, and ZnO. β -Ga₂O₃ in single-crystal form⁴ has also been explored as an alternative substrate for epitaxial GaN growth,⁵ despite having a crystal structure that differs from the GaN wurtzite structure. Use of β -Ga₂O₃ is very appealing as it would combine the transparency of sapphire with the electrical conductivity of SiC, the two primary substrates currently used for commercial GaN-based devices.

Currently, the lack of understanding and control of the unintentional n -type conductivity of β -Ga₂O₃ still inhibits its applications. As with many other oxides, this conductivity has historically been attributed to the presence of oxygen vacancies (V_O), largely based on the correlation between conductivity and oxygen partial pressure in annealing environments.⁶ Calculations have offered insight into the migration mechanisms⁷ and the relative energies of oxygen vacancies in the inequivalent sites of the monoclinic structure^{7,8} but only minimal information about the charge states and ionization energies.

In this letter, we report formation energies and charge-state transition levels for oxygen vacancies and donor impurities based on density functional theory (DFT) using novel hybrid functionals that do not suffer from the band-gap problem inherent in traditional DFT. We first discuss the band structure of β -Ga₂O₃, comparing with experiment and previous calculations. We then describe the electronic structure and stability of the oxygen vacancy, showing that it does *not* contribute to the observed conductivity. Finally, we report results for donor impurities, and suggest that silicon and hydrogen are the likely cause of the observed electrical conductivity in unintentionally doped β -Ga₂O₃.

The calculations are based on generalized Kohn–Sham theory with the HSE06 screened hybrid functional⁹ and the projector augmented-wave method, as implemented in the

VASP code.^{10,11} The Hartree–Fock mixing parameter is set to 35%, which reproduces the experimental band gap;² the resulting structural parameters are in good agreement with the experimental values (Table I).

We use a 120-atom supercell, a $2 \times 2 \times 2$ mesh of Monkhorst–Pack k -points, and a plane-wave basis set with a cutoff of 400 eV. The semicore Ga d electrons were treated as core electrons; tests in which these d electrons were explicitly included in the valence produced formation energies that differ by less than 0.1 eV. Corrections due to finite-size effects resulting from the long-range Coulomb interaction of charged defects in a homogeneous neutralizing background were explicitly included following the scheme of Freysoldt *et al.*,¹⁵ with a weighted spatial-averaged static dielectric constant of 10.

Formation energies (E^f) are key quantities from which we can derive impurity and defect concentrations, stability of different charge states, and the related electronic transition levels.¹⁶ The formation energy of V_O in Ga₂O₃ is given by the following:

$$E^f[V_O^q] = E_{\text{tot}}[V_O^q] - E_{\text{tot}}[\text{Ga}_2\text{O}_3] + \mu_O + q\epsilon_F,$$

where $E_{\text{tot}}[V_O^q]$ and $E_{\text{tot}}[\text{Ga}_2\text{O}_3]$ represent the total energy of the supercell containing a vacancy in charge state q , and that

TABLE I. Calculated lattice parameters, formation enthalpy per formula unit, direct and indirect band gaps, and electron effective masses for β -Ga₂O₃, as compared to experiment and previous calculations.

Parameter	HSE06	B3LYP	Experiment
a (Å)	12.25	12.34 ^a	12.23 ± 0.02 ^b
b (Å)	3.05	3.035 ^a	3.04 ± 0.01 ^b
c (Å)	5.84	5.799 ^a	5.80 ± 0.01 ^b
β (deg)	103.9	103.9 ^a	103.7 ± 0.3 ^b
ΔH (eV/f.u.)	-10.40	...	-11.29 ^c
E_g^d (eV)	4.87	4.69 ^a	4.9 ^d
E_g^i (eV)	4.83	4.66 ^a	...
m_c^*/m_e	0.281 ± 0.005	0.342 ^a	$0.5\text{--}2.0$ ^e

^aReference 12.

^bReference 13.

^cReference 14.

^dReference 2.

^eReference 1.

^aElectronic mail: jvarley@physics.ucsb.edu.

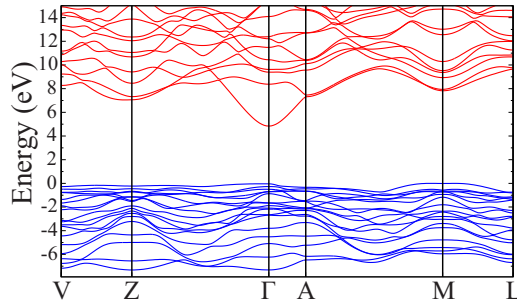


FIG. 1. (Color online) Band structure for β -Ga₂O₃ calculated using the primitive unit cell of base-centered monoclinic β -Ga₂O₃ (see Ref. 12). The VBM, which occurs just off the M point and is only 0.03 eV higher than at Γ , is set to zero on the energy axis.

of a perfect crystal in the same supercell. The O removed from the crystal is placed in a reservoir which we reference to the energy of an O₂ molecule. The chemical potential μ_{O} can vary to represent experimental conditions during growth or annealing, i.e., from O-rich (Ga-poor) to O-poor (Ga-rich) conditions. The electrons are exchanged with the Fermi level ϵ_F , which is conventionally referenced to the valence-band maximum (VBM).

The monoclinic crystal structure of β -Ga₂O₃, space group C2/m, is described by four lattice parameters (Table I); the three lattice vectors and β , the angle between the a and c axes.¹² It possesses three inequivalent O sites and two inequivalent Ga sites. O(I) and O(II) are threefold coordinated, while O(III) is fourfold coordinated. Ga(I) and Ga(II) are tetrahedrally and octahedrally coordinated, respectively. The calculated band structure of β -Ga₂O₃ is shown in Fig. 1. We find an indirect band gap of 4.83 eV, with the VBM located just off of the M point, slightly smaller than the direct band gap of 4.87 eV at Γ . Analysis of the dipole matrix elements reveals that while the vertical transitions are dipole-allowed at the Γ point and at the VBM, they are roughly an order of magnitude weaker at the VBM and rapidly decrease to 0 at the M -point. The weakness of the indirect transitions and the small energy difference between indirect and direct gaps effectively make β -Ga₂O₃ a *direct-gap* material, consistent with the experimentally observed sharp absorption onset at ~ 4.9 eV.² The electron effective mass is small and almost isotropic, with a value of $0.281 \pm 0.005 m_e$. In contrast, the almost flat valence band results in hole effective masses (m_h^*) that can be much larger, in agreement with previous calculations.^{12,17} While the low dispersion along the Γ -Z direction makes it difficult to extract an accurate value, estimated around $40 m_e$ from our fits, we do find a much smaller m_h^* along the Γ -A direction ($0.40 m_e$).

The calculated formation energies for V_{O} in Ga₂O₃ are shown in Fig. 2(a). The $\epsilon(+2/0)$ transition levels, denoted by the kinks in the formation-energy plots, are more than 1 eV below the conduction-band minimum (CBM). We thus conclude that V_{O} acts as a *deep* donor and cannot contribute to n -type conductivity. As seen in Fig. 2(a), V_{O} is stable in the neutral charge state for Fermi-level values in the upper part of the band gap. The different oxygen sites lead to slightly different geometries, formation energies and transition levels: $\epsilon(2+/0)=3.31$ eV for O(I), 2.70 eV for O(II), and 3.57 eV for O(III). V_{O}^0 has the lowest energy on the O(II) site, in which two of the three O-Ga bonds are the longest among all O-Ga bonds. Additionally, the E_f^f of the V_{O} are high for most

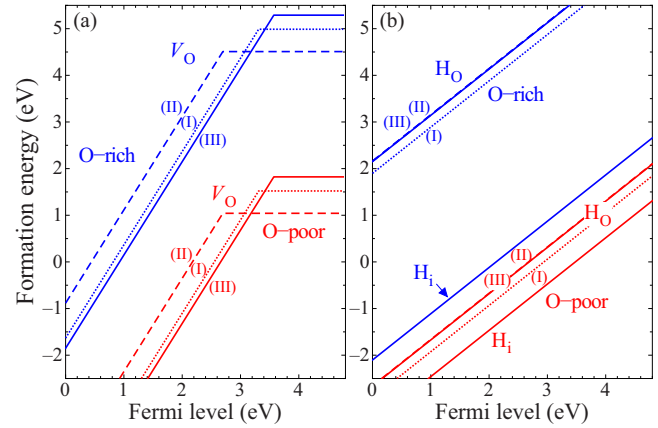


FIG. 2. (Color online) Formation energy vs Fermi level for the oxygen vacancy (a) and H impurities (b) in β -Ga₂O₃. Values for O-rich and O-poor conditions are shown. The labels (I), (II), and (III) refer to the three inequivalent O sites.

values of oxygen chemical potential, indicating a low concentration of vacancies will be present.

The paramagnetic state V_{O}^+ is not stable for any value of the Fermi level but could be generated by photoexcitation. By calculating V_{O}^+ in the geometry of the V_{O}^0 configuration, we predict absorption energies of 2.71, 3.37, and 2.52 eV for O(I), (II), and (III) sites, with corresponding emission energies of 0.67, 1.23, and 0.65 eV. Since the reported electron paramagnetic resonance experiments do not mention intentional photoexcitation, the assignment of the reported EPR signal to oxygen vacancies¹⁸ should be re-examined. Additional emission energies of 2.06, 1.40, and 2.25 eV can result from above-band-gap excitations, due to the recombination of an electron localized on the V_{O}^0 with a photogenerated hole in the valence band. None of these emission energies match the characteristic blue or green luminescence bands of β -Ga₂O₃,¹⁹ suggesting that these bands do not originate from V_{O} .

Turning now to impurities, we first investigated the role of hydrogen. We find that H can occupy either interstitial (H_i) or substitutional sites (H_{O});²⁰ in both configurations, H acts as shallow donor. Due to the complex crystal structure of β -Ga₂O₃, many configurations exist in which H_i^+ forms a strong bond with an O atom and which are all close in energy. In the lowest-energy configuration [included in Fig. 2(b)], H_i^+ bonds to a lone pair of the threefold coordinated O(I). The low formation energy of H_i under both O-rich and O-poor conditions indicates it will be easily incorporated as an unintentional impurity whenever H is present in the growth or annealing environment. In the acceptor charge state, H_i^- , the H atom preferentially sits near two Ga atoms, yielding a transition level $\epsilon(+/-)=4.90$ eV, just above the CBM. Interstitial hydrogen thus behaves exclusively as a shallow donor for any Fermi level within the band gap of β -Ga₂O₃.²¹ Substitutional hydrogen, H_{O} , has a low formation energy only under O-poor conditions.²²

The energy barrier for the dissociation of the H_{O}^+ into H_i^+ and V_{O}^0 is only 1.33 eV, estimated as the sum of the binding energy (0.99 eV) and the migration barrier of H_i^+ (0.34 eV). Such a low barrier indicates that both H_i^+ and H_{O}^+ are mobile at modest temperatures and may be readily removable by thermal annealing.¹³

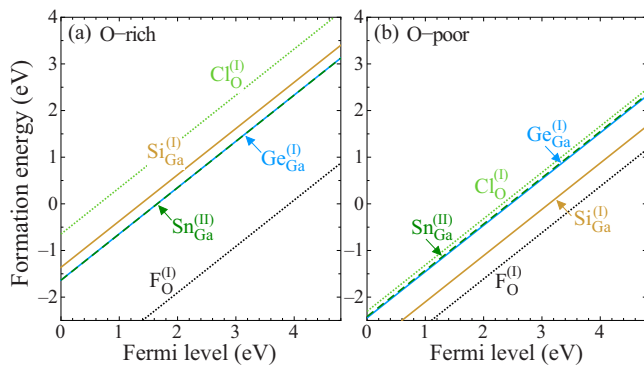


FIG. 3. (Color online) Formation energy vs Fermi level for several shallow donor impurities in β -Ga₂O₃ under (a) O-rich and (b) O-poor conditions. The labels (I) and (II) refer to the inequivalent Ga or O sites; only the results for the lowest-energy site are shown.

In addition to hydrogen, we find that other impurities may also contribute to the observed *n*-type behavior. In Fig. 3, we show the formation energies of Si, Ge, and Sn substituting on the Ga site,²³ as well as F and Cl on the O site,²⁴ all of which are shallow donors that may contribute to the *n*-type conductivity of Ga₂O₃. Si and Ge prefer the tetrahedral coordination of the Ga(I) site, while Sn prefers the octahedral coordination of the Ga(II) site. F and Cl both prefer the threefold coordination of the O(I) site. The formation energies suggest that Si, Ge, Sn, F, and Cl are readily incorporated. Indeed, it has been observed that Si is a dominant background impurity in both high-purity powders (6N) and single crystals,²⁵ with the increase in Si content of the single crystals possibly due to the presence of quartz in the various growth techniques.^{25,26} When intentionally incorporated, both Si (Ref. 27) and Sn (Ref. 2) have been shown to notably enhance the conductivity. Our results suggest that F and potentially Cl will also be effective *n*-type dopants.

In summary, we have presented hybrid functional calculations for oxygen vacancies and several candidate donor impurities in β -Ga₂O₃. We find that oxygen vacancies cannot explain the observed unintentional *n*-type conductivity, since they are deep donors with an ionization energy of more than 1 eV. Our results suggest that unintentionally incorporated impurities are likely to be responsible for the observed *n*-type conductivity. Hydrogen, Si, Ge, Sn, F, and Cl are all calculated to be shallow donors in β -Ga₂O₃.

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