Energetics and electronic structure of native point defects in \(\alpha\)-Ga\(_2\)O\(_3\)

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We report first-principles calculations that clarify the formation energies and charge transition levels of native point defects (Ga and O vacancies, interstitials, and a Ga vacancy-O vacancy pair) in corundum structured \(\alpha\)-Ga\(_2\)O\(_3\). Either under a Ga- or O-rich growth condition, the negatively-charged Ga vacancy and the positively-charged Ga interstitial on a site surrounded by six O atoms are dominant when the Fermi level approaches the conduction and valence band edges, respectively. These defects would compensate carrier electrons and holes, respectively. Ga-rich conditions relatively suppress the formation of the Ga vacancy and, therefore, are suited for extrinsic \(n\)-type doping of \(\alpha\)-Ga\(_2\)O\(_3\).

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Gallium oxide (Ga\(_2\)O\(_3\)) has emerged as an attracting material for a wide range of applications\(^{1–5}\), such as power electronics\(^{6,7}\) and deep-ultraviolet photodetectors\(^{8,9}\). Among the five common polymorphs in Ga\(_2\)O\(_3\) (i.e. \(\alpha\), \(\beta\), \(\gamma\), \(\delta\), and \(\varepsilon\))\(^{8}\), the monoclinic structured \(\beta\)-Ga\(_2\)O\(_3\) has been intensively studied and a number of devices were demonstrated in the past decades. For instance, Schottky barrier diodes (SBDs)\(^{9}\) and metal–semiconductor field effect transistors (MESFETs)\(^{10}\) and depletion-mode metal–oxide-semiconductor field effect transistors\(^{11}\) were reported. Many of theoretical studies have also been focusing on the fundamental and defect properties of \(\beta\)-Ga\(_2\)O\(_3\) so far.\(^{12–19}\)

For instance, formation energies and charge transition levels were reported for its native point defects including vacancies of Ga and O (\(V\)\(_{\text{Ga}}\) and \(V\)\(_{\text{O}}\)),\(^{13,18}\) and interstitials (\(\text{Ga}\)\(_i\) and \(\text{O}\)\(_i\)),\(^{15–17}\) and donor\(^{18}\) and acceptor-type impurities.\(^{19}\) It was shown that \(V\)\(_{\text{O}}\) behaves as a deep donor,\(^{15–17}\) while impurities such as Sn, Si, Ge, F, and Cl act as shallow donors.\(^{18}\)

In recent years, corundum structured \(\alpha\)-Ga\(_2\)O\(_3\) has also been attractive as well. Starting with the heteroeptaxy of \(\alpha\)-Ga\(_2\)O\(_3\) thin films on \(\alpha\)-Al\(_2\)O\(_3\) substrates by ultrasonic mist chemical vapor deposition,\(^{20}\) fabrication and operation of devices, such as SBDs\(^{21}\) and MESFETs\(^{22}\) were reported. Its band structure,\(^{23,24}\) interfacial band alignment,\(^{25}\) thermodynamic properties,\(^{12}\) and hole polarons\(^{26}\) have also been investigated using first-principles calculations. However, only few theoretical reports on point defect properties are available for \(\alpha\)-Ga\(_2\)O\(_3\); although there is a study concerning impurity properties (Si, Sn, and Mg),\(^{20}\) systematic investigation into the properties of native defects such as vacancies and interstitials is still lacking and thus are highly demanded.

In this study, we investigated defect properties of \(\alpha\)-Ga\(_2\)O\(_3\) by first-principles calculations using a hybrid functional. We calculated the formation energies and charge transition levels under Ga- or O-rich crystal growth conditions, focusing on the native point defects.

All calculations in this study were performed based on projector augmented wave method\(^{27}\) as implemented in the Vienna Ab-initio Simulation Package code.\(^{28,29}\) We applied the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional\(^{30–32}\) with Fock-exchange mixing and screening parameters of 0.35 and 0.208 Å\(^{-1}\), respectively. The parameters were determined so as to reproduce the experimental bandgap of \(\beta\)-Ga\(_2\)O\(_3\)\(^{13,18}\) as described in detail later. The cutoff energies in the plane wave basis set were set to 520 and 400 eV for the

\[ E_F[D^q] = E[D^q] + E_C[D^q] - E_F - \sum_i n_i \mu_i + q(e_{\text{VBM}} + \Delta\varepsilon_F). \]

Here, \(E[D^q]\), \(E_F\), \(e_{\text{VBM}}\), and \(\Delta\varepsilon_F\) are the total energy of the supercell with \(D^q\), that of the perfect crystal supercell, the energy level of the valence band maximum (VBM), and the Fermi level with respect to the VBM, respectively. \(n_i\) and \(\mu_i\) are the number of added (\(n_i > 0\)) or removed (\(n_i < 0\)) \(t\)-type atom and its chemical potential, respectively. \(E_C[D^q]\) is a correction term for removing the spurious long-range Coulomb interactions between \(D^q\), its periodic images, and the background charge under three-dimensional periodic boundary conditions. We applied the extended Freysoldt–Neugebauer–Van de Walle (FNV) scheme\(^{33,36}\) for the correction, which can correct energies of charged defects accurately in various systems.\(^{33,36–38}\) The correction requires a dielectric tensor, of which ionic part was calculated with density functional perturbation theory\(^{39,40}\) with the Perdew–Burke–Ernzerhof (PBE) functional.\(^{41,42}\) The ion-clamped electronic part of the dielectric tensor was calculated with a finite-electric-field approach\(^{43}\) with the HSE0(0.35, 0.21) functional. We checked with the PBE functional that, together with the extended FNV corrections,\(^{33,36}\) the difference in the formation energy of \(V\)\(_{\text{O}}^{2+}\) in \(\alpha\)-Ga\(_2\)O\(_3\) between 120-atom (\(2 \times 2 \times 1\)) and 480-atom (\(4 \times 4 \times 1\)) supercells is less than 0.2 eV, indicating that the present cell-size corrections together with the 120-atom supercell are quite sufficient to obtain a well-converged defect formation energy. We considered two extreme crystal growth conditions, where the chemical potentials of the atomic species are given as
parts of dielectric tensors were $\varepsilon_{11}^{\text{ion}} = \varepsilon_{22}^{\text{ion}} = 6.08$, $\varepsilon_{33}^{\text{ion}} = 9.32$ and $\varepsilon_{11}^{\text{ele}} = \varepsilon_{22}^{\text{ele}} = 3.54$, $\varepsilon_{33}^{\text{ele}} = 3.44$, respectively, resulting in a total dielectric tensor of $\varepsilon_{11} = \varepsilon_{22} = 9.62$, $\varepsilon_{33} = 12.76$. All the Ga and O atoms in $\alpha$-Ga$_2$O$_3$ are symmetrically equivalent, respectively, so we investigated the vacancies ($V_{\text{Ga}}$ and $V_{\text{O}}$) on these sites. For a Ga vacancy-O vacancy pair ($V_{\text{Ga}}$–$V_{\text{O}}$), we only considered the nearest neighbor case. For the interstitials (Ga, and O), we investigated three inequivalent high-symmetry interstitial sites as depicted in Fig. 1(b): a site surrounded by two Ga and three O atoms (site 1), six O atoms (site 2), and two Ga and two O atoms (site 3).

The calculated band structure of $\alpha$-Ga$_2$O$_3$ is depicted in Fig. 2. Since the experimental bandgap of $\alpha$-Ga$_2$O$_3$ varies in the literature ($4.9$–$5.6$ eV$^{20,46–49}$), we determined the Fock-exchange mixing parameter in the HSE functional to be $0.35$ with the screening parameter kept fixed at a standard value of $0.208$ Å$^{-1}$ so that the calculated bandgap of $\beta$-Ga$_2$O$_3$ ($4.89$ eV) agrees well with the experimental one ($4.9$ eV$^{51}$). We also checked that the deviation from the generalized Koopmans’ theorem (gKT) condition$^{52}$ (i.e. $E[V_{\text{Ga}}] - E[V_{\text{Ga}}] - E[V_{\text{O}}])$ is $0.11$ eV for the gallium vacancy in $\alpha$-Ga$_2$O$_3$, using this functional. This approach has been shown to reproduce the experimental ionization potential well and nearly satisfies gKT for a self-trapped hole in $\beta$-Ga$_2$O$_3$. The direct bandgap at the $\Gamma$ point and indirect bandgap of $\alpha$-Ga$_2$O$_3$ obtained using this functional are $5.73$ and $5.49$ eV, respectively. This calculated indirect bandgap is close to a previously reported value of $5.39$ eV from a G$_0$W$_0$@HSE03 calculation.$^{25}$

Figure 3 shows the formation energies of the investigated defects under either Ga- or O-rich condition. Either under Ga- or O-rich condition, negatively-charged $V_{\text{Ga}}$ and positively-charged Ga$_i$ are energetically favorable when the Fermi level approaches the CBM and VBM, respectively. The formation energy of $V_{\text{Ga}}$ takes a negative value under either Ga- or O-rich conditions when the Fermi level is low. This implies that the realization of a p-type material is difficult because of the carrier compensation by Ga$_i$, as well as the small hole polaron formation and related deep, polaronic nature of dopant-induced acceptor states.$^{24}$ At the Ga-rich limit,
neutral and positively-charged \( V_0 \) have a low formation energy in a wide range of the Fermi level position from intrinsic to \( n \)-type conditions. However, the \( O \) vacancy is a deep donor with a transition level far below the CBM, and unlikely to be a source of native \( n \)-type conductivity, as in the case of \( \beta-Ga_2O_3 \).\(^{15-17}\) At the O-rich limit, positively-charged \( V_0 \), as well as \( Ga_i \), is rather favorable for lower Fermi level values, which is also a similar trend to \( \beta-Ga_2O_3 \).\(^{5,10}\) We also see that the formation energy of \( V_{Ga} \) takes a negative value when the Fermi level is near CBM at the O-rich limit, indicating that even \( n \)-type doping would be difficult for the extreme O-rich condition. Thus, crystal growth under a condition close to the Ga-rich limit is preferred in realizing \( n \)-type material.

We found that \( V_{Ga} \) takes \(-3\) to \(+3\) charge states depending on the position of the Fermi level. In \( \alpha-Ga_2O_3 \), \( V_{Ga} \) is surrounded by six \( O \) atoms. In the neutral charge state, three holes localize onto 2p orbitals of three different \( O \) atoms around \( V_{Ga} \), exhibiting polaronic charge localization, and the remaining three \( O \) atoms can capture three more holes. Thus, \( V_{Ga} \) acts as a triple hole trap as well as a triple acceptor depending on the Fermi level. Similar hole localization is reported in other oxide semiconductors such as ZnO.\(^{54}\) We found that \( V_O \) acts as a deep donor showing small negative-\( U \) behavior: \( U = E_F[V_0^0] + E_F[V_0^{+2}] - 2E_F[V_0^{+1}] = -0.16 \) eV. The \((\pm 2/0)\) transition level of \( V_O \) is located at \( E_C - 1.72 \) eV, close to the value of about \( E_C - 2.1 \) eV calculated by Lyons.\(^{55}\) The energy gain for the formation of a Ga vacancy-\( O \) vacancy pair (i.e. \( V_{Ga} + V_O \rightarrow V_{Ga} - V_O \)) is about 0.9 eV at the \( n \)-type limit, indicating the vacancy pair formation in \( n \)-type materials, in particular at low temperatures where entropic energy gain is small for isolated defects.

The optimized structures of the stable \( Ga \) and \( O \) interstitials are shown in Fig. 4. The most favorable form of \( Ga_i \) is \( Ga_{i,3} \), in which the interstitial \( Ga \) atom is surrounded by six \( O \) atoms. Note that the \( Ga_{i,3} \) eventually converged to the same structure as \( Ga_{i,2} \), and thus shows similar formation energy as \( Ga_{i,2} \) (Fig. 3). In Fig. 3, we see that \( Ga_{i,3} \) is always in \(+3\) charge state regardless of the position of the Fermi level, indicating that the defect supplies electrons to the conduction band if they are not compensated by acceptor-type defects and thus operates as a shallow donor.

Among the oxygen interstitials, we found that the split interstitials, \( O_{i,1} \) and \( O_{i,3} \), are favorable when the Fermi level is located at the lower half of the bandgap, whereas the negatively-charged interstitial without splitting, \( O_{i,2} \), becomes favorable under \( n \)-type conditions. The reason why the split interstitials (\( O_{i,1} \) and \( O_{i,3} \)) are not stabilized in negatively-charged states can be understood by considering the molecular orbital of an \( O_2 \) molecule; In the ground state of an isolated, neutral \( O_2 \) molecule, two up-spin electrons are in the antibonding \( \pi^* \) states, realizing a triplet state. In \( Ga_2O_3 \), each \( O \) atom formally receives two electrons from \( Ga \) atoms because of the difference of electronegativity of \( Ga \) and \( O \) atoms, and thus the split interstitials (\( O_{i,1} \) and \( O_{i,3} \)) together with a host \( O \) atom accommodates two more electrons than a neutral \( O_2 \) molecule. Then, the \( \pi^* \) states are fully occupied with 4 electrons in the neutral condition. To add an additional electron into this system, the electron should go into \( \sigma^* \) states with high energy loss. Thus, the split interstitials do not take negatively-charged states. Indeed, we confirmed that 2 up- and 2 down-spin electrons fully occupy the states with similar energy levels (\( E_V + 0.55 \) eV and \( E_V + 0.58 \) eV) in the neutral charge state of \( O_{i,3} \). The fact that the bond-length of two oxygen atoms (1.372 Å) in the neutral split-interstitial is longer than that of the calculated value for an \( O_2 \) molecule (1.207 Å) also suggests that electrons get into the antibonding \( \pi^* \) states in the case of the split-interstitial in the neutral charge state.

In summary, we report the formation energies and charge transition levels of the native point defects in corundum structured \( \alpha-Ga_2O_3 \). We found that negatively-charged \( V_{Ga} \) and positively-charged \( Ga_i \) are favorable when the Fermi level is near the CBM and VBM, respectively, regardless of crystal growth conditions (Ga-rich or O-rich). Either under
Ga- or O-rich condition, the formation energy of Ga$_n$ takes a negative value when the Fermi level approaches the VBM, implying that the realization of a $p$-type material is difficult because of a strong carrier compensation. At the Ga-rich limit, neutral and positively-charged $V_O$ are favorable within a wide range of the Fermi level from an intrinsic to $n$-type condition. However, the O vacancy is a deep donor and unlikely to be a source of native $n$-type conductivity. At the O-rich limit, positively-charged $V_O$ becomes comparable in energy to Ga$_n$ at lower Fermi levels. We also found that the formation energy of Ga$_n$ takes a negative value when the Fermi level approaches the CBM at the O-rich limit, indicating that even extrinsic $n$-type doping is difficult in thermal equilibrium state for such O-rich conditions. Thus, crystal growth under a Ga-rich condition is preferred in $n$-type doping.

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