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First-principles study of point defects in β-Ga$_2$O$_3$

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Abstract

Gallium oxide (Ga$_2$O$_3$) has been proposed as a promising candidate for power devices. Under the high electric field and high operating temperatures in such power devices, point defects are expected to form in Ga$_2$O$_3$ that can limit the device performance. We have calculated the thermodynamic stability of intrinsic point defects in stable monoclinic β-Ga$_2$O$_3$, such as V_O, V_{Ga}, O_i, Ga_i, O$_{Ga}$, and Ga$_O$, under various chemical and electron potential using first-principles density functional theory calculations. We find that V_O, Ga_i, and Ga$_O$ exhibit deep donor levels in gallium-rich conditions and do not contribute to n-type doping. Ga$_O$ and Ga_i have high formation energy at low fermi levels in oxygen-rich conditions and can act as electron acceptors.

I.   Introduction

Semiconductor power switching devices are strongly demanded by today's society for their contribution to energy conversion. The power switching devices are used in energy conversion and control systems that consume a tremendous amount of power. Advances in power-electronic converters have made it possible to increase energy efficiency and lower the cost of converting electrical energy to other forms. Semiconductor power devices directly impact the cost and efficiency of connecting electric power to consumers and they have rapidly become an important part of the solution to energy saving. As technology advances, the need for these devices to keep up with the increasing trends in high power density or higher temperature

applications also increases. To catch up with this demand, the device should have low-resistance and fast switching in high-voltage and high-current conditions, and should avoid failure at high temperatures.

Present-day devices are comprised of Si-based technologies that are approaching their performance limits based on the material properties of Si.[1] At temperatures between 150-200°C, silicon power devices undergo failure, indicating its inability to keep up with high-power density trends.[2] Recently, gallium oxide (Ga_2O_3), a compound oxide semiconductor, has emerged as a promising candidate for power devices. Ga_2O_3 exists in five different polytypes with the most stable structure being monoclinic β-Ga_2O_3. Monoclinic β-Ga_2O_3 is an *n*-type semiconductor and has a wide band gap of 4.9 eV.[3] This band gap enables power devices to have a higher breakdown voltage and efficiency. Ga_2O_3 bulk crystals and thin films can have carrier concentrations in a range of 10^{15}-10^{19} cm^{-3} and this carrier concentration is expected to contribute the low electric resistance.[4-7] For the carrier concentration, the intrinsic defects are expected to play a critical role.

Despite the increase in research on this material in recent years, there is a current lack of understanding of the stability of intrinsic and extrinsic point defects in β-Ga_2O_3 and their effect on its electronic properties. Different models report that the *n*-type conductivity is attributed to the presence of dominating oxygen vacancies V_O.[8,9] Calculations have offered insight into the point defects found in Ga_2O_3, however such studies have not considered all the possible intrinsic defects.[10,11] To understand more complex behavior under high temperature and high voltage conditions, the basic understanding of intrinsic defect is necessary. In this study, we report the formation energies of all possible point defects of β-Ga_2O_3 based on first-principles density

functional theory (DFT) calculations. We describe the formation energies of point defects in β-Ga$_2$O$_3$ and their contribution to conductivity of the material.

II.   Methods

DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP).[12] Geometry-optimization calculations were completed using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional until the maximal applied forces were less than 0.01 eV/Å.[13] Core-electron interactions were modeled using the projector-augmented wave method (PAW).[14] The Ga d-electrons were treated as valence electrons. The cutoff energy for the plane-wave basis was set to 400 eV for the PBE calculations. A 160-atom supercell and a $1 \times 4 \times 2$ mesh of Monkhorst-Pack k-points for Ga$_2$O$_3$ was used for all the calculations.

Corrections were included in these calculations to account for the finite-size effects that result from long-range Coulomb interaction of charged defects in a homogenous neutralizing background.[15]

Formation energies (E^f) provide full information about the defect structure and can show the impurity and defect concentrations, the stability of different charge states, and the electronic transition levels. We considered all possible intrinsic point defects of β-Ga$_2$O$_3$: V_O, V_{Ga}, Ga_i, O_i, Ga_O, and O_{Ga}. The formation energy for a point defect (ΔH_f) in Ga$_2$O$_3$ is given by the following:

$$\Delta H_f = E_D - E_{DF}[\text{Ga}_2\text{O}_3] + n\mu_D + q(\epsilon_F + \varepsilon_{VBM}) + E_{corr} \tag{1}$$

where E_D represents the total energy of the supercell containing the point defect and $E_{DF}[\text{Ga}_2\text{O}_3]$ is the total energy of the defect-free supercell, μ_D is the chemical potential of the defect in a reservoir, which is affected by the phase-stability in β-Ga$_2$O$_3$. The O$_2$ molecule (O-rich condition) and the Ga metal (Ga-rich condition) are the standard state of limiting elements in this

case. The chemical potential is defined as (a) Ga-rich limit, where $\mu_{Ga} = \mu_{Ga(\text{bulk})}$ and $\mu_O = E_{\text{Ga2O3}} -$ $\mu_{Ga(\text{bulk})}$ with $\mu_{Ga(\text{bulk})}$ being the energy of a Ga atom within the Ga crystal and E_{Ga2O3} being the energy of one formula unit of ideal Ga_2O_3 without defects, and (b) I-rich limit, where $\mu_O = E_O$ and $\mu_{Ga} = E_{\text{Ga2O3}} - E_O$ with E_O being the energy of one oxygen molecule in its most stable triplet state. The n is the number of species removed from the supercell to create the point defects. q is the charge state of the supercell that is introduced by the point defect. ε_{VBM} is the eigenvalue of the valence band maximum and ϵ_F is the Fermi level defined as zero at ε_{VBM} and varies from 0 to the energy of the optical band gap. E_{corr} is the energy correction which accounts for the finite-size effects which are due to coulomb interactions in charged point defects.

For this study, the defects were modeled using a supercell with period boundary conditions. This supercell approximation creates artificial interactions between charged defects; thus we used a scheme proposed by Freysoldt and Van de Walle based on analysis of the electrostatics in dielectric media to correct such interactions.[15] The correction method can be described by the following equation:

$$E_{corr} = E_{lat} - q\Delta V_{a/b} \tag{2}$$

where E_{lat} is the electrostatic interaction due to image charges and $q\Delta V_{a/b}$ corrects for the offset in the VBM due to the presence of the defect.

The charge distribution modeled in E_{lat} can be described by the following equation:

$$E_{lat} = \int_{\Omega} \left[\frac{1}{2} q \left(\tilde{V}_q^{lr} - V_q^{lr} \right) \right] d^3 \boldsymbol{r} \tag{3}$$

where $\tilde{V}_q^{lr}$ is the long-range potential of the model charge distribution defect and V_q^{lr} is the corresponding quantity in the periodic cell. The $q\Delta V_{a/b}$ is evaluated from the offset in the zero-

4

point reference energy. Because the zero-point reference energy depends on the average charge state of the cell, this should be also considered in long-range potential. This is found using the equation below:

$$\Delta V_{q/b} = \tilde{V}_{q/b} - \tilde{V}_q^{lr} \tag{4}$$

where $\tilde{V}_{q/b}$ is the difference between the potential in the defect-free bulk configuration.

E_{corr} is found using the relaxed bulk neutral defect supercell and the energy of the bulk charged defect supercell. Using the sxdefectalign script written in VASP, the inputs are an ecut of 30, the charge corresponding to the defect, 10 for the dieletric constant for Ga_2O_3, the lattice vector of the defect, and the LOCPOT of the charged and neutral defect supercells.[12] Figure 1, shows an example of the generated vline-eV.dat data file for charged defect Ga_i^{+1}.
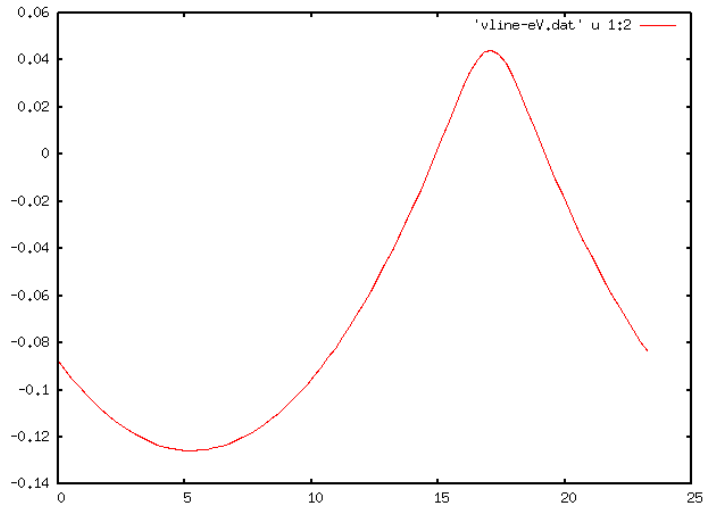

FIG. 1 The vline-eV.dat file depicting the plotted data showing the plateau value for the charged defect at -0.125.

This model shows the plateau value for a Ga_i^{+1} in relation to the neutral defect with a value of -0.125. This value is input into the correction script with the tag –C to generate the correction.

This value can be used in the formation energy calculation using equation 1 for the defect structure.

III. Results and Discussion

A. Type of defects

a   b

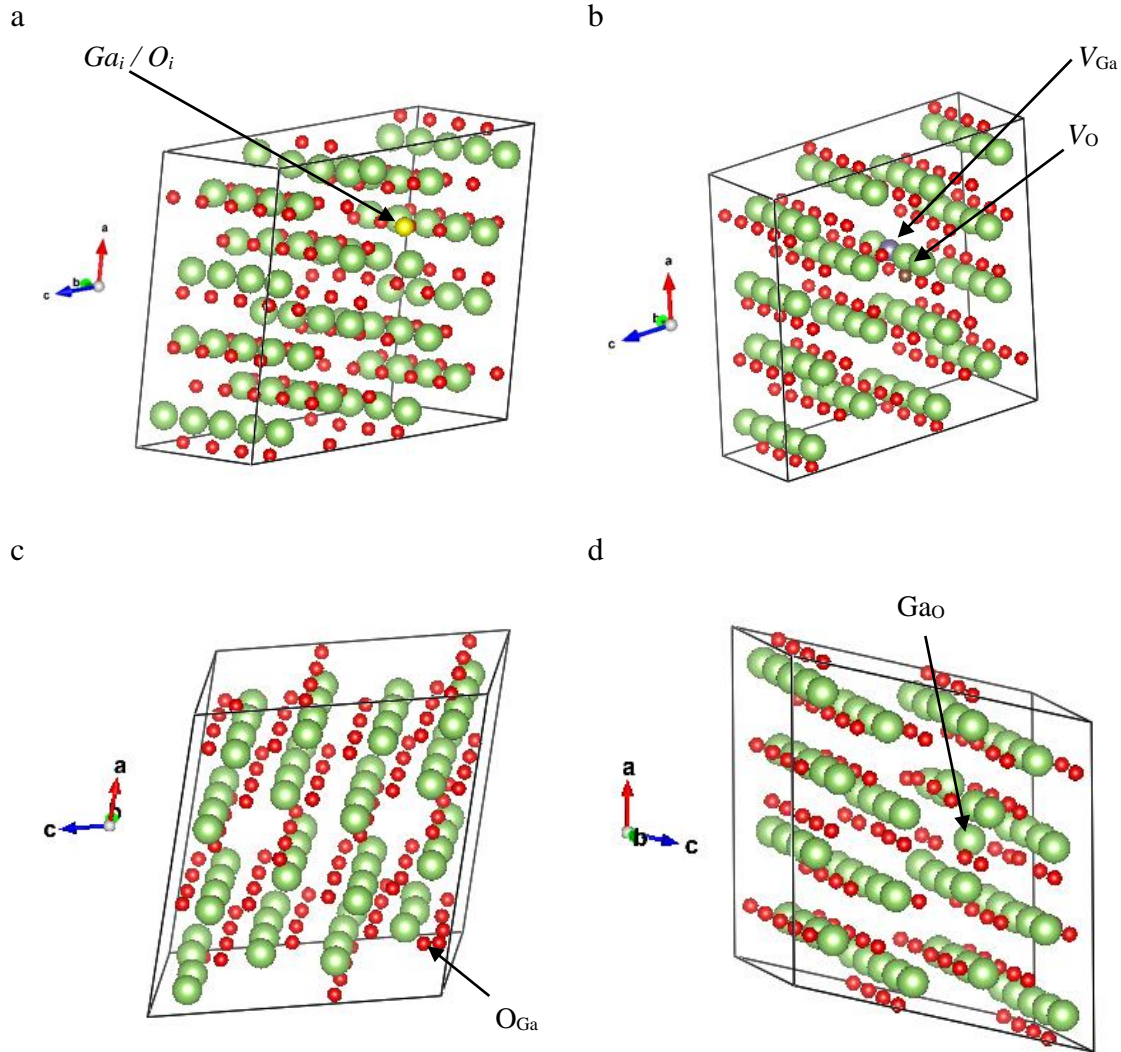c   d

FIG. 2 The positions for point defects in a 160 atom supercell of β-Ga_2O_3. a) Gallium and oxygen are placed at one interstitial site, b) a gallium and oxygen vacancy site is chosen for both atoms, c) an oxygen is placed at a gallium antisite, and d) a gallium is placed at an oxygen antisite.

In Fig. 2, the different gallium and oxygen vacancies, interstitials, and antisites are displayed. For the interstitial point defect calculations, the lowest energy configuration for Ga_i and O_i was identified to one of the 4i sites. For the vacancies, a different location is chosen for the gallium and oxygen. Lastly, antisites were considered in this study of point defects. O_{Ga} and Ga_O point defects are studied along with their corresponding charge defects.

B. Formation Energies of single point defects

The calculated formation energies for V_o, V_{Ga}, Ga_i, O_i, O_{Ga}, and Ga_o are shown in Fig. 3.
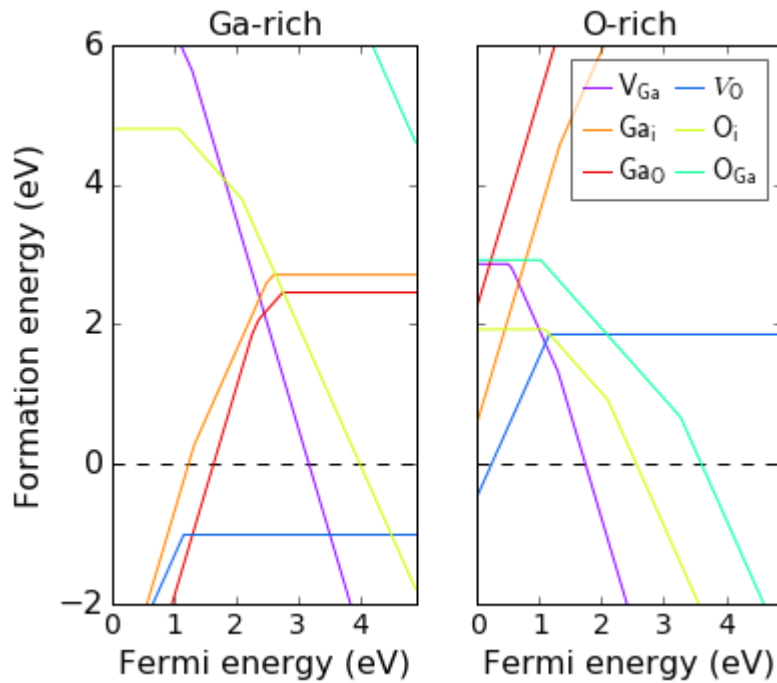

FIG. 3 Formation energy vs. Fermi energy for the point defects in β-Ga_2O_3. Values for Ga-rich and O-rich conditions are shown.

The formation energies are considered as a function of two variables, the chemical potential of elements and the Fermi energy. For the gallium-rich and oxygen-rich conditions, the energies are

plotted against the Fermi-level. From the definition of formation energy in eq. (1), the slope of the formation energy corresponds to the charge state of the defects.

The V_O can be seen to have very low formation energies in Ga-rich conditions and it is expected to be the most dominant defect than any other defect. V_O can play a role as a donor, but its neutral state near the conduction band indicates its 'deep' nature, which cannot contribute to n-type conductivity. These results are in agreement with the previous reported character of V_O.[16-18] V_{Ga} and O_i can be seen to have low formation energies near the conduction band under both of O-rich and Ga-rich conditions for higher Fermi levels. This means, when n-type doping is tried with external dopants, those defects can easily form and generate holes to compensate extra n-type carrier formation. On the other hand, they show neutrality near the valence band, so that it doesn't trigger intrinsic p-type doping. Similarly, two antisite defects, Ga_O and $O_{Ga,}$ and Ga_i are deep level defects and they are expected to act as compensators.

C. Previous study provides comparison for V_O, V_{Ga}, O_i, and Ga_i—not for Ga_O and O_{Ga}

Zacherle's study on intrinsic point defects in the β-Ga_2O_3 structure reviewed oxygen and gallium vacancies and interstitials.[19] Our study shows similar trends compared to their PBE functional even though there is a slight difference. They used a 360-atom supercell and we chose a smaller 160-atom cell. They overestimated the O_2 binding energy by GGA functional (-6.0 eV), but we used the experimental value of -5.12 eV. For the Freysoldt correction, they used a dielectric constant of 12.7 obtained from DFPT calculation, while we used the experimental value of 10. We didn't include the effect of entropy, but they considered configurational and vibrational entropy at different temperatures. Although there is a slight difference, the gallium and oxygen interstitials and vacancies display similar trends in this study compared to our study. Using GGA, V_O has the lowest formation energy in the Ga-rich conditions and V_{Ga} is dominant in the

O-rich condition. One difference is that the formation energy of V_O, their value is -2.25 and ours is -3.13, but it is because of the choice of O_2 binding energy.

Zacherle's study also showed the defect energetics obtained using the HSE06 hybrid functional. The PBE functional has been found to predict a band gap half the size of the experimental value, which is why the result should be validated with HSE06. The HSE06 formation energies show similar trends as the GGA calculations. A large difference between those two studies is that the transitions between different charge states are at higher Fermi levels for the hybrid functional. Another difference is that the V_O has positive formation energy near the CBM region. In future, we plan to use HSE functional for the calculation of formation energies of defects in β -Ga_2O_3.

IV. Conclusion

In this study, the finite-size corrected defect formation energies for several point defects in β-Ga_2O_3 were calculated using the PBE functional. It was found that V_O has low formation energies in Ga-rich conditions and do not contribute to *n*-type conductivity, since they are deep donors. Other favorable antisite and interstitials are also deep level defects. This result indicates that the V_O is the most dominant defect in the high temperature and high voltage operation condition. In future, we plan to calculate the migration barrier of V_O and investigate their tendency to form defect complexes, which will help us understand the defect behavior under operating conditions.

Acknowledgement

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