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AB-INITIO CALCULATIONS OF OXYGEN VACANCY IN Ga_2O_3 CRYSTALS

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Gallium oxide β-Ga_2O_3 is an important wide-band gap semiconductor. In this study, we have calculated the formation energy and transition levels of oxygen vacancies in β-Ga_2O_3 crystal using the B3LYP hybrid exchange-correlation functional within the LCAO-DFT approach. The obtained electronic charge redistribution in perfect Ga_2O_3 shows notable covalency of the Ga-O bonds. The formation of the neutral oxygen vacancy in β-Ga_2O_3 leads to the presence of deep donor defects with quite low concentration. This is a clear reason why oxygen vacancies can be hardly responsible for n-type conductivity in β-Ga_2O_3.

Keywords: *β-Ga_2O_3, ab-initio calculations, band structure, DFT, oxygen vacancy.*

1. INTRODUCTION

Performance optimization of the functional properties of many advanced oxide materials depends on the control of point structural defects and also on a deep knowledge and understanding of their various properties and characteristics [1]–[9]. Special attention has recently been paid to gallium oxide β-Ga_2O_3 as a very promising candidate for optoelectronic devices operating at short wavelengths. Due to its wide band gap and possible modulation of optical properties by synthesis methods and doping impurities, it is a very attractive material for use in different optoelectronic devices, as well as in photocatalysis, optical fibres and scintillators [10]–[17].

One of the most important areas of both research and application is the control of electrical conductivity through doping of the material. Traditionally, in many oxygen-containing materials, oxygen vacancies (V_O) are considered a source of electrical conductivity [1], [2], [10], [18], [19]. However, recent density functional theory (DFT) calculations of Ga_2O_3 have shown that oxygen vacancies do not play a key role in conductivity [20]. At the same time, already small amounts of unintentional donors, like hydrogen, completely change the electronic structure and explain the observed activation energy of conductivity (1.7 eV) [20]. In this regard, DFT calculations play an exceptional role in understanding this fundamental issue through the study of the electronic structure and defects energetics.

In this paper, we present the results of *ab-initio* calculations of a pure and defective (with one oxygen vacancy) β-Ga_2O_3 crystal using the hybrid B3LYP exchange-correlation functional and the LCAO approximation. To describe the effect of oxygen vacancy onto electronic and conductivity properties, the charge transition levels as function of the Fermi energy have been calculated.

2. COMPUTATIONAL SET AND Ga_2O_3 CRYSTAL STRUCTURE

Large-scale *ab initio* calculations have been performed using a linear combination of atomic orbital method within the density functional theory (LCAO-DFT) approach. The hybrid B3LYP [21] functional has been used, allowing us to perform very accurate calculations of the band gap, unlike the standard LDA or GGA-type functionals. The basic sets for Ga and O atoms have been taken from Ref. [22], [23], respectively. The integration over the Brillouin zone in the reciprocal space has been performed within a 4×4×4 Pack-Monkhorst grid [24]. Effective atomic charges have been estimated using the Mulliken population analysis [25].

The β-Ga_2O_3 unit cell is shown in Fig. 1, where a⊥c, b⊥c, and the angle between *a* and *c* axes is 104°. The lattice parameters are *a* = 12.19 Å, *b* = 3.05 Å, and *c* = 5.82 Å. By symmetry, there are two distinct Ga sites, labelled Ga(1) and Ga(2) (Fig. 1). The Ga(1) atoms are bonded to four neighbouring O atoms in a (roughly) tetrahedral arrangement. The Ga(2) atoms are in an octahedral environment and bind to six neighbouring O atoms. The O atoms have three distinct sites: O(1) and O(2) bind to three Ga atoms, while O(3) binds to four Ga atoms. The Ga–O bond lengths range from

1.8 to 2.1 Å.

To simulate an oxygen vacancy, a periodic model of the extended unit cell of the crystal – a supercell – with an expansion matrix of 2×2×2 and containing 80 atoms has been used.

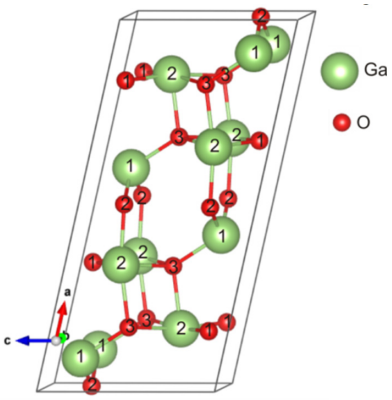

Fig. 1. Schematic representation of crystal structure of monoclinic β-Ga_2O_3. Unique positions of Ga/O atoms in the lattice are designated.

Further, we have calculated the bulk properties of pure Ga_2O_3 obtaining good agreement with the experimental data (Table 1). The optimized lattice parameters *a* and *c* slightly overestimate those obtained in experiments. The error in the estimate of band gap energies obtained using hybrid calculations has been found to be much smaller than the error in standard GGA-PBE or Hartree-Fock calculations (resulted in a huge underestimate/overestimate of the band gap). Proper estimate of band gap is an important point, since the correct description of formation energy depends on it. Mulliken's analysis showed a slight difference in the ionic charge on atoms with different positions in the crystal, which was associated with the anisotropy of the electronic properties [q(Ga1) +1.48e, q(Ga2) +1.58e, q(O1) = - 0.994e, q(O2) = - 0.997e, q(O3) = - 0.079e], as well as a considerable covalency of the Ga-O bonding (~ 0.2e).

Table 1. Bulk Properties of Pure β-Ga_2O_3 as Calculated by Means of DFT-LCAO Method

	HF	GGA-PBE	B3LYP	Exp [10]
a, Å	12.19	12.34	12.34	12.12÷12.34
b, Å	3.05	3.11	3.09	3.03÷3.04
c, Å	5.82	5.90	5.87	5.80÷5.87
E_g, eV (direct/indirect)	13.8	2.36/2.3	4.49/4.45	4.4÷5

3. FORMATION ENERGIES AND TRANSITION LEVELS

As it is known, formation energy of defect D with charge q in system X is defined as:

$$E_f = E_{tot}(D) - E_{tot}(X) + \sum_i n_i\mu_i + q(E_F + E_V) + E_{corr}, \quad (1)$$

where $E_{tot}(D)$ and $E_{tot}(X)$ are the total energies of the system with and without a defect, n_i represents the number of atoms of the element i that are removed from the system when a defect is formed (a negative value for n_i means the addition of atoms), μ_i is the chemical potential of element i, it is the energy of atoms that are removed

(or added) into the system when a defect is formed. The study is performed for dopant-rich condition, using molecular O_2 as a dopant source in the gas phase. The fourth term $q(E_F+E_V)$ is a change in the electron energy due to the exchange of electrons and holes with the carrier reservoirs. E_F+E_V is the Fermi energy relative to the maximum of the valence band of a defect-free system. E_{corr} term includes energy offset correction [26] and first-order Makov-Payne correction [27].

To calculate chemical potentials included in Eq. (1), we take the O_2 molecule (oxygen-rich conditions) and the Ga metal (oxygen-poor conditions) as limiting phases. Combining the expressions $\mu_O < 1/2\mu(O_2) = 1/2E_{tot}(O_2)$; $\mu_{Ga} < \mu_{Ga-metal} = E_{tot}(Ga)$; $2\mu_{Ga}+3\mu_O=\mu(Ga_2O_3)=E_{tot}(Ga_2O_3)$ and the formation energy of the compound $E_f(Ga_2O_3) = E_{tot}(Ga_2O_3)-2\mu_{Ga-metal}-3/2\mu(O_2)$, one gets the range of μ_O, the chemical potential of oxygen in gallium oxide:

$$1/2\mu(O_2) + 1/3\ E_f(Ga_2O_3) < \mu_O < 1/2\mu(O_2).$$

To determine the charge state transition levels for various defects, we used the approximation described by Lany and Zunger [28], based on previous studies by Scherz and Scheffler [29], stating that the transition level is the Fermi energy, at which the formation energy of a charged defect is equal to that of a neutral defect:

$$E_{tot}(D,q) - E_{tot}(X) + \sum_i n_i\mu_i + q\left(\varepsilon\left(\frac{q}{q'}\right) + E_V\right)$$
$$= E_{tot}(D,q') - E_{tot}(X) + \sum_i n_i\mu_i + q'\left(\varepsilon\left(\frac{q}{q'}\right) + E_V\right),$$

thus

$$\varepsilon(q/q') = \frac{E(D,q')-E(D,q)}{q-q'} - E_V. \quad (2)$$

The zero energy reference is set at the top of the valence band, E_V=0.We have considered cases in which an electronic charge is added to the system, i.e., the state q' corresponds to a state with an extra electron, q+1e: this corresponds to a transition from a neutral state to a negatively charged state, ε(0/-1).

4. RESULTS AND DISCUSSION

The formation energy for oxygen vacancies in three different crystallographic positions (see Fig.1) is shown in Fig. 2. Neutral V_O has the lowest energy on the O(3) site. The bend of the curve corresponds to the transition of the defect charge state. As formation energies for all types of V_O in 1+ charge state are around 2.5 eV, the oxygen vacancy is an example of a negative-U defect, where the 1+ charge state is unsta-

ble. At low Fermi energies, the 2+ charge state becomes more preferable, whereas when Fermi level is high, the neutral state becomes the most stable. For an oxygen-poor conditions, we obtain ε(2+/0)=4 eV for O(1), ε(2+/0)=3.8 eV for O(2), ε(2+/0)=3.1 eV for O(3). Under an oxygen-rich condition, formation energy increases by ~2.76 eV. Transition levels are equal or more than 1eV below CB. The amount of thermal energy required to promote an electron from the defect level to the CB is much greater than the room temperature; therefore, oxygen vacancies are *deep donors* and cannot serve as the effective source of the electron charge. Hence, oxygen vacancies cannot be responsible for n-type conductivity in Ga_2O_3. However, they can compensate acceptors by donating their electrons. As acceptor doping increases, the Fermi level is pushed down toward the VB. This reduces the formation energy for oxygen vacancies. At some point, the formation energy gets small such that the Fermi level is prevented from going any lower.

On the other hand, as shown earlier, hydrogen can be easily accumulated in a crystal due to a small migration barrier of 0.34 eV [30]. After penetrating into a crystal, hydrogen can occupy many interstitial sites (H_i) nearby to oxygen atoms with creating of O-H bounds, and also penetrate into oxygen vacancies (H_O). In all cases, hydrogen acts as a *shallow donor*. It is important to note that similar behaviour of hydrogen as a donor impurity appears in other oxide materials (ZnO, SnO_2, In_2O_3) and thus has some generality in these properties [10], [30]. There is some experimental support to the fact that hydrogen may be a shallow donor in β-Ga_2O_3 from experiments on its muonium counterpart and from electron paramagnetic resonance of single-crystal samples [31], [32]. Therefore, we believe that hydrogen is more preferable as a source of unintentional background n-type conductivity.

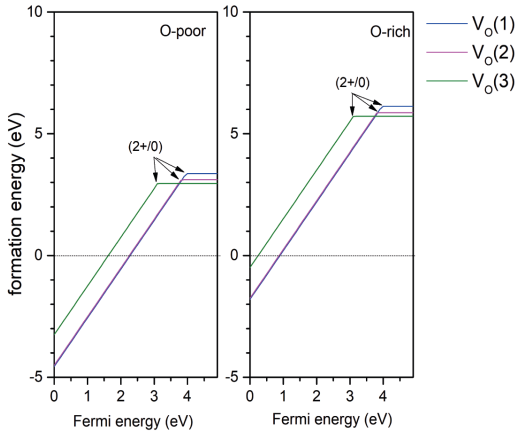

Fig. 2. Formation energies of V_O in *β*-Ga_2O_3 plotted against the Fermi energy for (a) oxygen-poor and (b) oxygen-rich conditions. For V_O, the three different vacancies are denoted $V_O(1)$, $V_O(2)$ and $V_O(3)$ as shown in Fig. 1.

5. CONCLUSIONS

In this study, we have calculated the formation energy and transition levels of oxygen vacancies in Ga_2O_3 crystal using the B3LYP hybrid exchange-correlation functional within the LCAO-DFT approach. The electronic charge redistribution in perfect Ga_2O_3 shows notable covalency of the Ga-O bonds. Formation of the oxygen vacancy in β-Ga_2O_3 leads to the presence of deep donor defects. That is why neutral oxygen vacancies can be hardly responsible for n-type conductivity in β-Ga_2O_3 accompanied by their quite high formation energy. In this respect, In this regard, we assume that the observed n-type conductivity in gallium oxide is due to the presence of interstitial and substituting hydrogen impurities in the crystal lattice.

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