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The O_{As} defect in GaAs: A hybrid density functional study

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ABSTRACT

The O center substitutional to As (O_{As}) is addressed through hybrid functional calculations as a candidate defect to explain the Fermi-level pinning in oxygen-doped GaAs. The defect center shows amphoteric behavior which could lead to Fermi-level pinning. However, the calculated charge transition levels only moderately agree with the experimental pinning level. Furthermore, the first-neighbor shell of the O atom and the absence of negative-U behavior clearly contrast with the experimental characterization. Thus, the present results do not support the O_{As} center as origin of the observed Fermi-level pinning in oxygen-doped GaAs.

1. Introduction

Oxygen is the most common unintentional impurity in bulk GaAs. When it is present in high concentrations (between 10^{14} and 10^{15} cm^{-3}), Fermi-level pinning is observed at 0.4 eV below the conduction-band minimum (CBM) [1]. A rich experimental characterization of oxygen defects in GaAs has been achieved, but a theoretical description which captures all the observed features has so far remained elusive.

The Fermi-level pinning behavior has experimentally been assigned to an oxygen-related defect showing a local vibrational mode (LVM) absorption spectrum consisting of three bands, *A*, *B*′, and *B* at 730.7 cm^{-1}, 714.9 cm^{-1}, and 714.2 cm^{-1}, respectively [1–3]. Each of these bands shows a triple fine structure due to the natural isotopic abundance of Ga atoms, thereby indicating that the oxygen atoms have two Ga atoms in their first-neighbor shell (Ga—O—Ga) [4]. The three bands correspond to three different charge states of this defect [5]. In particular, it could be shown through optical excitation and optically detected electron-nuclear double resonance experiments that the defect state associated to the *B*′ band is neutral, paramagnetic, and metastable [6–9].

To account for the Ga—O—Ga configuration, an O atom substitutional to As (O_{As}) has been proposed [4]. In this defect center, the O atom is off-center within an As vacancy in analogy to the *A* center in silicon [10]. Local density functional (DF) calculations supported this O_{As} defect model showing that such an O atom indeed goes off-center and binds to two Ga atoms [11]. Furthermore, the doubly negative charge state was found to be metastable in accord with the properties of the *B*′ band [11]. These results were confirmed in subsequent studies [12,13]. Under the assumption that the calculated valence band edge could be aligned to the experimental one, these calculations give −1/−3 charge transition levels at 0.5 eV below the CBM [12,13], in fair agreement with the measured Fermi-level pinning position. This model thus accounts for the experimental characterization except for the fact that the metastable state is found in the −2 charge state rather than in the neutral one. Taguchi and Kageshima did not find metastability for the −2 charge state and proposed a defect structure in which the O atom bridges between two regularly bonded Ga atom of the GaAs lattice [14]. However, this model was unable to reproduce the experimental Fermi pinning level [14]. Finally, Pesola et al. proposed a defect model in which the oxygen atom binds to a defect complex combining two intrinsic defects of GaAs [15]. This model favorably accounts for the Ga—O—Ga first-neighbor configuration and the occurrence of three charge states [3], but yields an unsatisfactory Fermi-level pinning position at mid-gap.

In this work, we study the O_{As} defect within a hybrid density functional scheme which reproduces the experimental band gap. Particular care is devoted to the correction of the finite-size effect, through the use of the scheme proposed by Freysoldt, Neugebauer, and Van de Walle (FNV) [16,17]. The resulting description of the atomic and electronic structure of the O_{As} defect differs considerably from the generally accepted picture in the literature [11–13]. On the basis of the present state-of-the-art methods for defect description, the O_{As} defect is no longer tenable in comparison with the available experimental characterization.

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2. Computational methods

Local and semilocal approximations to density functional theory often reproduce geometrical, energetic, and magnetic properties of defects in solids [18], but are not equally successful in determining charge transition levels because of the well known band gap underestimation problem [19,20]. This problem can be corrected by applying a posteriori a scissor operator, which consists in rigidly shifting the CBM to higher energy until the experimental band gap is recovered. However, the band gap is underestimated in the calculation and the defect state could hybridize with the host bands resulting in a delocalized state [21]. Hybrid functionals can reproduce experimental band gaps and recover the localized nature of the defect states [21,22]. A benchmark calculation involving the As_{Ga} antisite shows that charge transition levels calculated with hybrid functionals can be expected to agree with their experimental counterparts within ~0.2 eV [23]. Furthermore, it has been shown that for atomically localized defect states a suitable alignment procedure provides a connection between defect levels obtained with semilocal and hybrid density functionals [20,24–26].

The defect study is approached through the calculation of formation energies and charge transition levels, which correspond to Fermi energies at which formation energies of different charge states coincide. The formation energy $E_f[X^q]$ of the defect X in its charge state q can be expressed as a function of the Fermi energy ϵ_F given with respect to the valence band maximum (VBM) [18]:

$$E_f[X^0] = E_{tot}[X^q] - E_{tot}[\text{bulk}] - \sum_i n_i\mu_i + q(\epsilon_F + \epsilon_v + \Delta v_{0/b}) + E^q_{corr}, \quad (1)$$

where $E_{tot}[X^q]$ is the total energy of the defect structure and E_{tot}[bulk] the total energy of the pristine bulk supercell. Different growth conditions can be described by varying the chemical potential μ_i of the species i. In the case of a Ga-rich environment, μ_{Ga} corresponds to bulk Ga in its solid orthorhombic phase, whereas μ_{As} is obtained from the equilibrium condition of GaAs: $\mu_{As} = \mu_{GaAs} - \mu_{Ga}$. At variance, As-rich environments are described with μ_{As} corresponding to the As_4 molecule and $\mu_{Ga} = \mu_{GaAs} - \mu_{As}$. For μ_O, the O_2 molecule is taken as reference. ϵ_v is the VBM of GaAs as obtained from a separate bulk calculation. $\Delta v_{0/b}$ is a potential alignment (PA) term which accounts for the potential shift between the bulk and the neutral defect calculation [21].

E^q_{corr} corrects for the finite-size error due to the long-range nature of the Coulomb interaction and the use of periodic boundary conditions. In the present work, E^q_{corr} is evaluated through the FNV scheme [16,17], which has been found to be robust and widely applicable [27]. The FNV scheme also allows one to control the defect charge localization. This property can be examined by studying the planar average of the electrostatic potential far from the defect and checking whether it tends to a constant value. In Fig. 1(a), we compare the potentials as found in the DF calculation and as obtained when modeling the defect charge with a Gaussian model charge distribution. The difference between these potentials corresponds to a short range potential and gives a constant value far away from the defect site [16]. This behavior is characteristic of well localized defect charge distributions. For illustration, we show in Fig. 1(b) a case in which the defect charge is not well localized. The difference between the DF and model potentials is no longer short ranged and does not converge to a constant value, indicating that the DF potential does not reproduce the expected long-range behavior for the nominal charge state of the defect.

For each defect structure, we perform full structural relaxation with the semilocal PBE functional. We use 64-atom supercells at the experimental lattice constant of 5.65 Å [28]. The final electronic properties are obtained with the hybrid functional proposed by Heyd, Scuseria, and Ernzerhof (HSE) [29,30]. The fraction of nonlocal Fock exchange is set to $\alpha = 0.35$ in order to reproduce the experimental band gap ($E_g = 1.52$ eV [28]) following the approach defined in [23]. We use plane-wave basis sets in conjunction with normconserving pseudopotentials. A kinetic energy cutoff of 70 Ry is used. The Brillouin zone is sampled with a $2 \times 2 \times 2$ mesh which does not contain the Γ point. The exchange potential is treated as described in Ref. [31]. We use the Quantum-ESPRESSO suite of programs [32], with the HSE implementation described in Ref. [26].

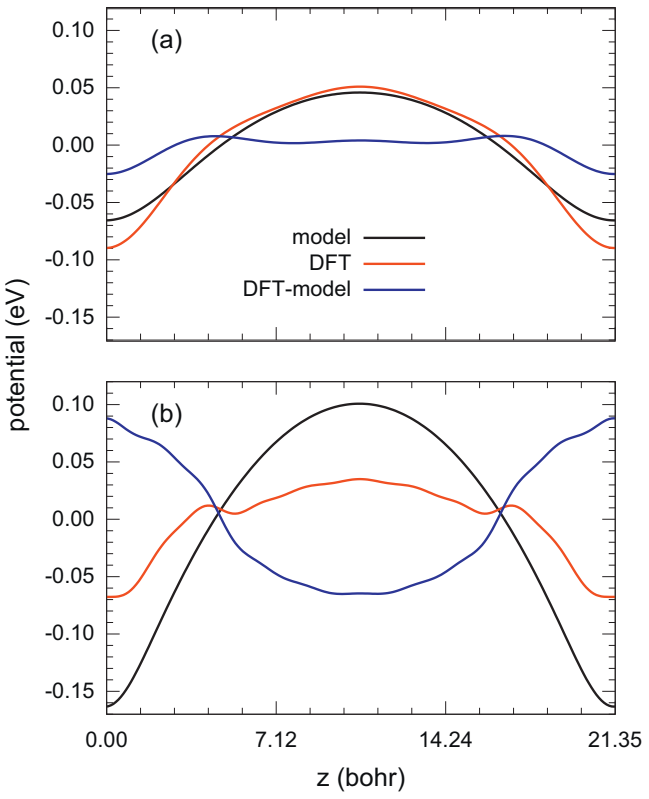

Fig. 1. Planar averages of the electrostatic potential of the O_{As} defect located at the origin, (a) in charge state −1 at the hybrid density functional level and (b) in charge state −2 at the semilocal density functional level. Black lines correspond to the potential obtained when the defect is modeled by a Gaussian charge distribution with a width of 1 bohr. Red lines correspond to the potential in the density-functional defect calculation. Blue lines represent the short-range defect potential and are obtained from the difference between the red and the black lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3. Results

We first perform PBE relaxations of the various charge states of the defect. In the positive charge state, the O atom occupies the highly symmetric T_d position, as shown in Fig. 2(a). The four Ga atoms relax towards the central O atom by 0.58 Å, forming Ga—O bonds of 2.17 Å. Detailed structural properties such as bond lengths and bond angles are given in Table 1. The charge density of the highest occupied state is found to correspond to a delocalized state of the valence band [Fig. 2(a)]. This structure is consistent with electron counting arguments. In fact, every Ga dangling bond pointing towards the As vacancy may be thought as contributing $\frac{3}{4}$ electrons while the O atom in the charge state +1 brings 5 electrons. This results precisely in 8 electrons which account for the four Ga—O bonds.

In the neutral charge state, the O atom still occupies a position of T_d symmetry [Fig. 2(b)]. The Ga—O bond lengths do not vary in an appreciable manner (Table 1). Inspection of the charge density