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Stability of valence alternation pairs across the substoichiometric region at Ge/GeO_2 interfaces

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ABSTRACT

Through hybrid density functional calculations, we compare the Ge–Ge bond energy with the formation energy of a valence alternation pair as the O concentration varies across the Ge/GeO_2 interface. First, hole trapping energies are calculated for three atomistic models with different O concentrations: bulk Ge with isolated O atoms, amorphous GeO, and amorphous GeO_2 with an O vacancy. The reaction is then broken down in three steps involving the breaking of a Ge–Ge bond, charge transfer processes involving dangling bonds, and the formation of a threefold coordinated O atom. The energy of each elemental reaction is estimated through suitable model calculations. The charge transition levels resulting from this analysis agree with those obtained for the atomistic models. Our estimates indicate that hole trapping at low O concentrations occurs at no energy cost for p-type germanium owing to the formation of threefold-coordinated O atoms. Applied to n-type Ge, our analysis indicates that electron trapping in dangling bonds obtained from the breaking of Ge–Ge bonds is unfavorable. The formation energy of a valence alternation pair is evaluated and discussed in relation to previous results.

1. Introduction

Germanium is presently being investigated as a promising material for future electronic devices [1]. The successful implementation of Ge-based devices relies to a large extent on our capability of controlling and passivating the high defect density presently found at germanium/oxide interfaces. In molecular dynamics simulations, the structure of substoichiometric GeO_x has been found to be composed of a significant fraction of valence alternation pairs, involving negatively charged Ge dangling bonds and positively charged threefold coordinated O atoms [2]. The creation of such pairs results from the breaking of Ge–Ge bonds followed by charge transfer processes between the Ge dangling bonds and by the formation of threefold coordinated O atoms, which stabilize the unoccupied Ge dangling bonds [3].

In this work, we study the energetics of the Ge–Ge bond breaking process as the oxygen concentration varies across the substoichiometric transition region at the Ge/GeO_x interface. We calculate reaction energies and charge transition levels associated to this process for three models showing different O concentrations: (i) bulk Ge with isolated O atoms, (ii) amorphous GeO, and (iii) amorphous GeO_2 with an O vacancy. The achieved results are supported by an analysis in which the reaction is decomposed in elemental steps.

2. Methods

The calculations were performed with hybrid density functionals within a scheme based on plane-wave basis sets and pseudopotentials [4]. For calculations in Ge, we used the screened hybrid functional proposed by Heyd, Scuseria, and Ernzerhof (HSE) [5,6]. For calculations in GeO_2, we used the hybrid functional proposed by Perdew, Burke, and Ernzerhof (PBE) [7], known as PBE0. The use of different hybrid functionals is motivated by our aim of correctly reproducing the band gap of the involved materials. Indeed, HSE gives a band gap of 1.1 eV for Ge, whereas PBE0 gives a band gap of 5.6 eV for GeO_2, both in good agreement with the respective experimental band gaps of 0.7 eV [8] and 5.6 eV [9]. Both the HSE and the PBE0 functionals are based on the same semilocal functional [10] and give total energy differences of similar accuracy [5,11,12]. When the band alignments are performed through the average electrostatic potential [13–15], the resulting charge transition levels are fully compatible [12]. An energy cutoff of 70 Ry was used throughout this work.

3. Hole trapping through atomistic models

Using various atomistic models showing different O concentrations, we investigate the energetics of the hole trapping reaction:

$$\mathrm{Ge{-}Ge} + 2h^{+} + 2\Delta E^{h} \rightarrow 2\mathrm{O}_{\mathrm{III}}^{+}, \tag{1}$$

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where h^+ indicates a positively charged hole, O_{III}^+ a threefold coordinated O atom, and ΔE^h the reaction energy cost per involved Ge atom. In writing Eq. (1), we adopt the convention that non-explicitly mentioned species on either side of the equation assume regular bonding configurations, viz. O atoms are twofold coordinated with Ge atoms and Ge atoms are fourfold coordinated with O atoms.

The case of low O concentration is addressed through a 64-atom model of crystalline germanium, in which two interstitial O atoms have one Ge atom as common nearest neighbor [Fig. 1(a)]. Upon hole trapping, a nearby Ge–Ge bond breaks and two new Ge–O bonds are formed, giving rise to two O_{III}^+ [Fig. 1(b)]. For a Fermi level fixed at the valence band edge (p-type Ge), our calculations indicate that this reaction proceeds without any energy cost, resulting in a charge transition level that coincides with the valence band edge (Fig. 2). For high O concentration, we used a previously generated model of amorphous GeO_2 model [16], in which we created an O vacancy by omitting one O atom. In the neutral charge state, the formation of a Ge–Ge bond is observed. The removal of two electrons generally causes the system to relax into a structure with two O_{III}^+. The resulting charge transition level occurs at 2.5 eV above the valence band edge of GeO_2. The energy window in Fig. 2 results from a statistical study at the semilocal level [10] involving 80 different O vacancies. We also added in Fig. 2 the charge transition level corresponding to the intermediate O concentration of GeO, as obtained previously [3].

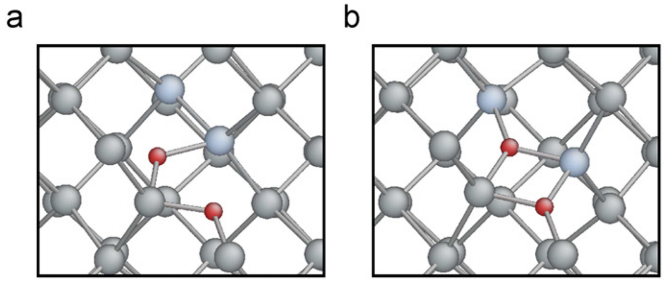

Fig. 1. Atomic structure (a) before and (b) after reaction (1) in bulk Ge containing two O atoms. Red and grey balls correspond to O and Ge atoms, respectively. Blue balls indicate Ge atoms which undergo a coordination change in the reaction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

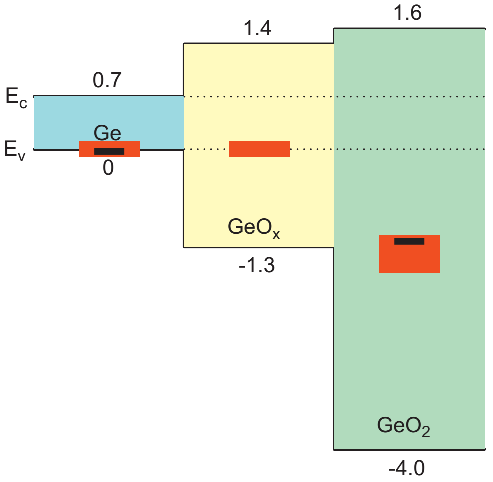

Fig. 2. Band diagram of the Ge/GeO_2 interface. Charge transition levels as calculated through atomistic models (red) and as estimated through the analysis in elemental steps (black) are indicated. The band structure of GeO is aligned to that of GeO_2 through the O 2*s* level [17]. The experimental value of 4 eV [18] is used for the valence band offset between Ge and GeO_2. Energies are given in eV. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Hole trapping through a sequence of elemental steps

In this section, we break down the hole trapping reaction in elemental steps. First, we consider the breaking of a Ge–Ge bond into two singly occupied Ge dangling bonds (DB_{Ge}^0):

$$Ge{-}Ge + 2\Delta E_1 \rightarrow 2DB_{Ge}^0. \qquad (2)$$

To estimate the strength of a Ge–Ge bond, we used molecular models as in Ref. [19]. We found that the breaking of a Ge–Ge bond costs 2.50 eV, i.e. $\Delta E_1 = 1.25$ eV. This result is consistent with the experimental value of 3.85 eV for the cohesive energy of germanium [20], from which we infer $\Delta E_1 \sim 1$ eV. Using the molecular models, we also investigated the dependence on the Ge oxidation state finding variations of ΔE_1 of at most ~ 0.1 eV. We therefore assume in the following that ΔE_1 does not depend on O concentration.

The second elemental step concerns the hole trapping in dangling bonds, resulting in unoccupied dangling bonds (DB_{Ge}^+) that are positively charged:

$$2DB_{Ge}^0 + 2h^+ + 2\Delta E_2 \rightarrow 2DB_{Ge}^+. \qquad (3)$$

Charge transition levels for Ge dangling bonds in Ge were studied previously [21] and can be used to estimate the energy of reaction (3) for low O concentrations. For convenience, these results are reproduced in Fig. 3(a), where they are compared to the formation

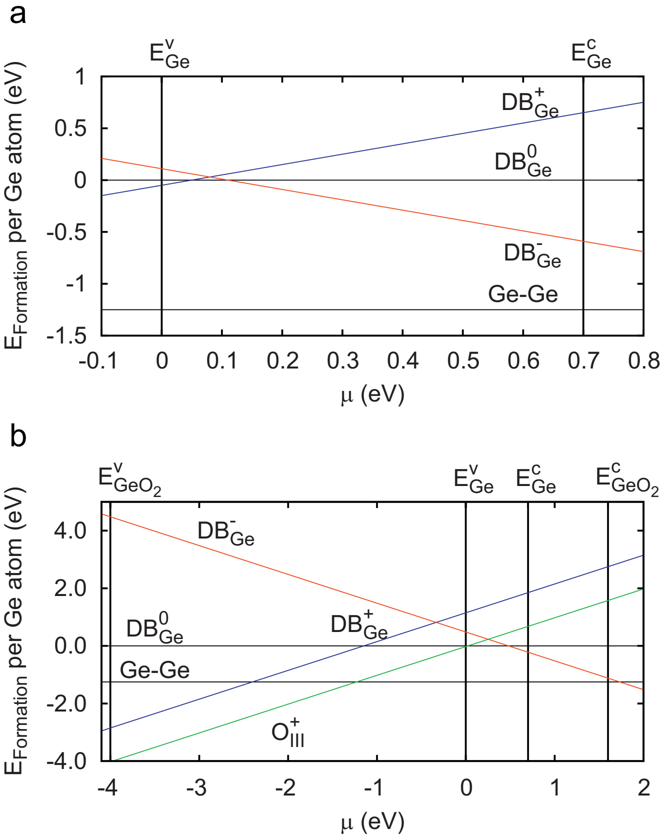

Fig. 3. Formation energies vs. electron chemical potential for the Ge dangling bond in (a) bulk Ge (taken from Ref. [21]) and (b) in α-quartz GeO_2. The formation energies are referred to the respective singly occupied dangling bonds. The horizontal line labeled Ge–Ge corresponds to the formation energy of a Ge–Ge bond. The formation energy of O_{III}^+ is also shown in (b). The electron chemical potentials are given with respect to the valence band edge in Ge through the band alignment given in Fig. 2. The band edges of Ge and GeO_2 are indicated by vertical lines.