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# Initial oxidation and surface stability diagram of Ge(100) as a function of the temperature and oxygen partial pressure through *ab initio* thermodynamics

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## Abstract

Density functional theory calculations in conjunction with thermodynamic modeling were performed to examine the oxygen adsorption on a Ge(100)  $c(4 \times 2)$  surface and the subsequent initial oxidation. For several possible adsorption sites, the adsorption energy of atomic oxygen as well as the atomic configuration and electronic properties of the adsorbed structure were examined. Then the effects of the surface coverage of oxygen from 1/64 to 1/4 monolayers on the adsorption energy were considered. Through the surface Gibbs free energy as a function of the temperature ( $T$ ) and oxygen partial pressure ( $P_{O_2}$ ), the ( $T, P_{O_2}$ ) surface stability diagram was predicted for the O/Ge(100)  $c(4 \times 2)$  surface. The theoretical prediction well reproduced previous experimental observations and provides an insight to control the initial oxidation process of Ge surface with tuned  $T$  and  $P_{O_2}$ .

Supplementary material for this article is available [online](#)

Keywords: oxygen adsorption, Ge(100)  $c(4 \times 2)$  surface, adsorption energy, *ab initio* thermodynamics, surface stability diagram

(Some figures may appear in colour only in the online journal)

## Introduction

As Si-based field effect transistors are reaching their physical limits, Ge has attracted much attention as a potential channel material candidate for metal-oxide-semiconductor field effect transistor (MOSFET) devices due to its enhanced carrier mobility. The most crucial ingredient of the Ge-based MOSFET is to confirm the high-quality interface between the Ge and the gate insulator (GI), as for the Si-based MOSFET. It has been well established that the thermal oxidation of the Si substrate is the best method of assuring a highest-quality Si/GI interface, which must be the case of the Ge-based MOSFET. In contrast to Si/SiO<sub>2</sub>, however, the thermal

oxidation of Ge does not necessarily guarantee a high-quality interface, which may be related to the adverse interaction between the chemically active Ge and GeO<sub>2</sub>. Therefore, the understanding of the interaction of oxygen with the Ge surface, such as surface oxidation, is crucial for improving the performance of the aforementioned devices [1]. Most of the relevant researches, however, focused on the experimental aspects of the subject. As the desired thickness of the GeO<sub>2</sub> GI approaches  $\sim 1$  nm, a more fundamental understanding of the oxidation process, including the oxygen gas adsorption and initial oxidation steps, becomes even more crucial for ensuring high-quality GeO<sub>2</sub> layer growth. Furthermore, the variations in these critical oxidation processes as a function of

the typical process parameters, such as the oxidation temperature ( $T$ ) and oxygen partial pressure ( $P_{O_2}$ ), need to be thoroughly understood.

The oxygen adsorption on the Ge(100) surface has been the subject of numerous studies, and various distinctive configurations of the oxygen adatoms on the (100) reconstructed surfaces have been investigated. These studies attempted to understand adsorbate-substrate bond structures, and similar studies have also been conducted for the other crystallographic surfaces of Ge [2–4]. A number of theoretical studies have been performed for the adsorption of a single O atom, or have focused on the dissociation of  $O_2$  [2, 3, 5–8]. Despite the previous relevant experimental and theoretical works, a thermodynamic understanding of the adsorption and initial oxidation of the Ge(100) surface has yet to be achieved.

In the present study, the coverage-dependent behavior of oxygen adsorption on Ge(100) and the surface stability diagram as a function of temperature and oxygen partial pressure were investigated using *ab initio* thermodynamics. To the authors' knowledge, despite their importance, the relative stability of oxygen-adsorbed Ge(100) in contact with an  $O_2$  environment has not yet been reported, and a direct comparison of the theoretical prediction with the previous experimental reports has yet to be done. The electronic properties of the oxygen-adsorbed Ge surface were also calculated.

## Computational details

All the calculations were performed using the Vienna *ab initio* Simulation Package [9, 10]. For the structural relaxation, the projector-augmented wave method with PBE [11] pseudopotentials was used, with 500 eV cutoff energy. For the electronic structure, on the other hand, the hybrid functional (HSE06) was adopted using the exact exchange coefficient of 0.28, which yielded a 0.73 eV bandgap for Ge [12]. The 4s and 4p orbitals for Ge atoms and the 2s and 2p orbitals for O atoms were treated as valence electrons. Spin-polarized calculations were used.

Only the adsorption of the atomic oxygen was considered. This was based on the previous theoretical study by Shah *et al* [8]. They reported that the dissociation of the  $O_2$  molecule on the Ge(100) dimer sites proceeds through a low energy barrier of  $\sim 0.5$  eV, which can be readily provided by the thermal energy during oxidation. In the calculations on the adsorption of a single oxygen atom, a supercell composed of 80 Ge atoms (10 layers) was used to form a Ge(100) slab. The  $4 \times 4 \times 1$  k-points were adopted. To avoid spurious interactions between the top and bottom surfaces caused by the periodic supercell, a 20 Å vacuum region as well as dipole moment correction were used. The bottom layer of the slab was saturated with H atoms and then fixed while the positions of the top two Ge layers and adsorbate were relaxed until the forces on such atoms were less than  $0.01 \text{ eV \AA}^{-1}$ .

The oxygen adsorption energy ( $E_a^O$ ) was calculated as

$$E_a^O = \frac{1}{N_O} \left( E_{O/Ge}^{\text{slab}} - E_{Ge}^{\text{slab}} - \frac{N_O}{2} E_{O_2} \right), \quad (1)$$

where  $N_O$  is the number of adsorbed oxygen atoms,  $E_{O/Ge}^{\text{slab}}$  is the total energy of the adsorbate-substrate system,  $E_{Ge}^{\text{slab}}$  is the energy of the bare Ge(100)  $c(4 \times 2)$  substrate, and  $E_{O_2}$  is the energy of an isolated oxygen molecule, i.e. the formation energy of  $O_2$  molecule.  $E_{O_2}$  was obtained from the spin-polarized calculations on the triplet-state  $O_2$  molecule [6, 13]. However, the calculated value of 5.56 eV shows a nontrivial overbinding tendency compared the experimental value of 5.12 eV, as has been a well-known problem of the PBE pseudopotential [14–16]. Therefore, the difference of these two values,  $\Delta E_{O_2} = 0.44 \text{ eV}$  was used as a correction term throughout this study, which has been adopted from several previous calculations [17, 18].

The effect of the thermodynamic condition on the relative stability of the surface structures was studied within the framework of *ab initio* thermodynamics. The availability of oxygen from the environment was represented by the oxygen chemical potential change during the desorption process ( $\Delta\mu_O$ ), which is a function of the gas-phase temperature  $T$  and the oxygen partial pressure  $P_{O_2}$ . The dependence of  $\Delta\mu_O$  on  $T$  and  $P_{O_2}$  is given by

$$\Delta\mu_O(T, P_{O_2}) = \Delta E_{ZPE} - \mu_{a,vib}^O + \frac{1}{2}\mu_g^{O_2} + \frac{1}{2}k_B T \ln \left( \frac{P_{O_2}}{P^0} \right), \quad (2)$$

where  $\Delta E_{ZPE}$  is the change in the zero-point energy during the desorption process;  $\mu_{a,vib}^O$  is the vibrational chemical potential of the adsorbed O atom; and  $\mu_g^{O_2}$  is the chemical potential caused by degrees of freedom (translation, rotation, vibration, etc) of  $O_2$  gas, while  $P^0$  is 1 atm. The  $\Delta E_{ZPE} \left( = \frac{1}{2} \sum_{i=1}^{M(g)} \frac{\hbar w_i}{2} - \sum_{i=1}^{M(a)} \frac{\hbar w_i}{2} \right)$ , where  $M(g)$  and  $M(a)$  are the number of the vibrational modes of  $O_2$  molecules and adsorbed O atom, respectively) was obtained by calculating the harmonic vibrational frequencies using the density functional theory (DFT). The  $\mu_{a,vib}^O \left( = \sum_{i=1}^{M(a)} k_B T \ln \left( 1 - e^{-\frac{\hbar w_i}{k_B T}} \right) \right)$  was also calculated based on its vibrational frequencies. On the contrary, for the chemical potential of the free  $O_2$  molecule before the adsorption ( $\mu_g^{O_2}$ ), the experimental value from the NIST database [19] was adopted following previous research [20].

For a given  $\Delta\mu_O(T, P_{O_2})$ , the thermodynamically preferred surface structure is the one with the lowest Gibbs free energy, which was calculated as

$$\Delta\gamma = \left[ G_{O/Ge}^{\text{slab}} - G_{Ge}^{\text{slab}} - \frac{N_O}{2} E_{O_2} - N_O \Delta\mu_O(T, P_{O_2}) \right] / A, \quad (3)$$

where  $\Delta\gamma$  is the relative surface Gibbs free energy per area with respect to the bare Ge(100)  $c(4 \times 2)$  surface. The calculated Gibbs free energies of the oxygenated and oxygen-free slab models are denoted as  $G_{O/Ge}^{\text{slab}}$  and  $G_{Ge}^{\text{slab}}$ , respectively.  $A$  is the in-plane surface area of the slab model. In the

calculations of  $G_{\text{O/Ge}}^{\text{slab}}$  and  $G_{\text{Ge}}^{\text{slab}}$ , the contributions from the vibration of the Ge atoms and the pressure-volume term of the Ge slab were neglected because the surface of interest was fixed as Ge(100)  $c(4 \times 2)$ . On the other hand, the vibrational effect of the adsorbed oxygen were considered, as shown in equation (2). Based on this assumption,  $G_{\text{O/Ge}}^{\text{slab}} - G_{\text{Ge}}^{\text{slab}}$  was replaced by  $E_{\text{O/Ge}}^{\text{slab}} - E_{\text{Ge}}^{\text{slab}}$  obtained from the DFT calculations, as in the previous studies [21, 22]. By combining equations (1), (2), and (3), equation (4) is obtained.

$$\Delta\gamma = [E_{\text{a}}^{\text{O}} - \Delta\mu_{\text{O}}] \cdot N_{\text{O}}/A. \quad (4)$$

## Results and discussion

As surface reconstruction decreases the density of the dangling bonds, it induces a reduction in the surface energy. For the Ge(100) surface, the calculation showed that the  $c(4 \times 2)$  reconstructed surface is energetically more stable than the rest of the reconstructed surfaces, including  $(2 \times 1)$  or  $p(2 \times 2)$ . This result is consistent with the previous calculation results [23, 24] and experimental observations [25, 26]. Therefore, the Ge(100)  $c(4 \times 2)$  reconstructed surface was selected to build a model of oxygen atom adsorption.

Figure 1(a) is the top view of the Ge (100)  $c(4 \times 2)$  surface. The rhombus is the unit cell of this  $c(4 \times 2)$  reconstruction while the dotted rectangle is the calculated cross-sectional area in the slab model whose surface area is twice larger than that of the rhombus. Several potential sites on this surface (dimer-bridge, back bond-down, back bond-up, dangling bond-down, and dangling bond-up sites labeled as A-, B-, C-, D-, and E-sites) were investigated for the adsorption of a single oxygen atom, as the Ge dimer on the top layer of the surface has been reported to be prone to oxygen adsorption [27]. The oxygen coverage 1/32 monolayer (ML). Figure 1(b) shows the relaxed atomic structures of the oxygen-adsorbed surface on these five sites.  $1u$  and  $1d$  denote the dimer-up and dimer-down atoms on the topmost layer of the Ge(100)  $c(4 \times 2)$  surface, respectively.  $R_1$  indicates the bond length between the adsorbed oxygen and the first nearest Ge atom, while  $R_2$  indicates that between the oxygen and the second nearest Ge atom. The vertical height of the oxygen above the topmost Ge layer is indicated as  $d_{\text{O-Ge}}$  in the side view. Table 1 lists the adsorption energy ( $E_{\text{a}}^{\text{O}}$ ) and atomic structures of  $R_1$ ,  $R_2$ , and  $d_{\text{O-Ge}}$ . The negative adsorption energy means that the oxygen adsorption is predicted to be favorable when not considering the  $\Delta\mu_{\text{O}}$  in equation (4).

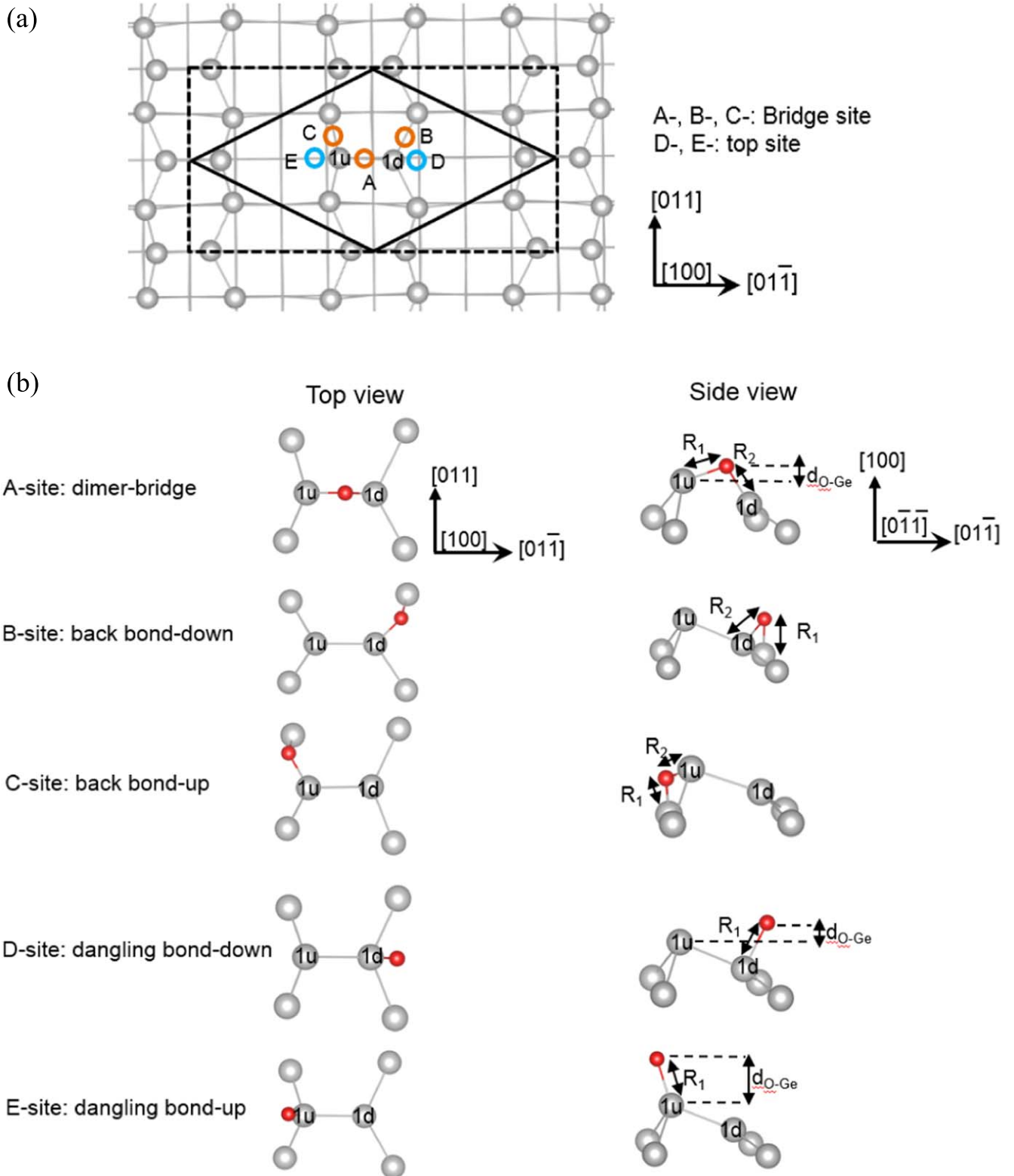
Among the sites that were investigated, the most stable configuration corresponds to the dimer-bridge adsorption with the lowest adsorption energy (A-site). When the oxygen atom was incorporated into the Ge dimer bond, the Ge-Ge dimer bond was broken, and the first and second nearest Ge atoms became  $1u$  and  $1d$  atoms as shown in figure 1(b). The corresponding  $R_1$  and  $R_2$  were found to be 1.80 and 1.88 Å, respectively. These results are in feasible agreement with those of the previous theoretical study of the oxygen

adsorption on Ge(100) by Kirchner *et al* [28], which reported a O-Ge bond length of 1.79 Å. This value is also comparable to the bond length in the rutile-structure  $\text{GeO}_2$ , implying the probable formation of new Ge-O-Ge bonds. The  $d_{\text{O-Ge}}$  in this structure is 0.47 Å, which is consistent with the previous scanning tunneling microscopy (STM) observation [2], showing the typical single-oxygen-atom adsorption onto a Ge-Ge dimer, inducing a broken dimer. Besides the dimer-bridge structure, the back bond-down structure (B-site) also showed relatively low adsorption energy. The O atom on the B-site was bonded between Ge in the second layer and the Ge  $1d$  atom. The  $R_1$  and  $R_2$  were found to be 1.80 and 1.87 Å, respectively. This values are consistent with the previous studies [7, 8]. Grassman *et al* also reported a back-bond insertion site in their STM observation [3].

The electron transfer from Ge to O atoms for the five aforementioned sites was also examined via Bader charge analysis [29, 30], and the results are summarized in table 1. In the dimer-bridge site (A-site), the transferred electron was  $1.20 e^-$ , which is comparable to that of the rutile-structure  $\text{GeO}_2$  ( $1.24 e^-$ ). The electron transfer values for the adsorption at the other four sites (back bond-down, back bond-up, dangled bond-down, and dangling bond-up) were 1.17, 1.12, 0.90, and  $0.96 e^-$ , respectively. It was noted that the lower the adsorption energy was, the higher the electron transfer to the O atom, suggesting that the electron transfer to the surface oxygen atom is related to the adsorption stability as well as the strength of the Ge-O bond.

To study the electronic properties, the layer-resolved density of states (LDOS) was plotted. Figure 2(a) shows the LDOS of the bare Ge(100)  $c(4 \times 2)$  surface showing a 0.53 eV bandgap, which is slightly lower than the calculated bandgap of Ge bulk crystalline (0.73 eV). This may be attributed to the localization of the conduction band minimum (CBM) in several top layers of the Ge slab (see figure S1 in supplementary information which is available online at [stacks.iop.org/PS/95/025701/mmedia](https://stacks.iop.org/PS/95/025701/mmedia)). Figures 2(b) and (c) are the LDOSs for the oxygen-adsorbed surfaces with low adsorption energies; A- and B-sites. Compared with (a), the O adsorption on the A-site in figure 2(b) did not induce any significant change in the LDOS, maintaining the bandgap of Ge at  $\sim 0.53$  eV. In figure 2(c), on the other hand, the LDOS of the O adsorbed on the B-site shows some differences, although the bandgap was maintained at  $\sim 0.53$  eV. It has additional  $\sigma$ -bonding states at 0.6 eV below the Fermi level ( $E_{\text{f}}$ ) and  $\sigma^*$ -antibonding states at 1.2 eV above  $E_{\text{f}}$ , as indicated by the arrows in figure 2(c), which are consistent with the earlier report by Gurlu *et al* [31].

Next, to study the effect of the oxygen coverage on the adsorption behavior for the Ge(100)  $c(4 \times 2)$  surface, the adsorption energy was calculated when the surface coverage of the oxygen atoms varied. For the higher coverage, the various combinations of the adsorption sites were taken and their adsorption energies were calculated. On the other hand, for the lower coverage of 1/64 ML, a slab model with a twice larger cross-sectional area was used (see figure S2 in supplementary information). The k-points along the in-plane directions for the calculations of this larger slab were scaled



**Figure 1.** (a) Surface unit cell of the Ge(100)  $c(4 \times 2)$  reconstructed surface indicated by the rhombus. The calculated cross-sectional area is presented by the dotted rectangle. The potential adsorption sites around the dimer structure are labeled as A-, B-, C-, D-, and E- sites. (b) Top and side views of the relaxed atomic structures of the oxygen-atom-adsorbed surface on the five sites.  $R_1$ ,  $R_2$ , and  $d_{O-Ge}$  indicate the bond length between the oxygen and the first nearest Ge atom, that between the oxygen and the second nearest Ge atom, and the vertical height of the oxygen above the topmost Ge layer, respectively.

**Table 1.** Adsorption energy, atomic structure of  $R_1$ ,  $R_2$ , and  $d_{\text{O-Ge}}$ , and electron transfer of the O-atom-adsorbed Ge(100)  $c(4 \times 2)$  surface, with  $1/32$  ML oxygen coverage. The values of the rutile-structure  $\text{GeO}_2$  are also provided for comparison.

Oxygen adsorption site	Adsorption energy (eV)	$R_1$ (Å)	$R_2$ (Å)	$d_{\text{O-Ge}}$ (Å)	Electron transfer ( $e^-$ )
Dimer-bridge (A-)	-3.14	1.80	1.88	0.47	1.20
Back bond-down (B-)	-3.03	1.80	1.87	—	1.17
Back bond-up (C-)	-2.75	1.83	1.85	—	1.12
Dangling bond-down (D-)	-2.49	1.71	—	0.13	0.90
Dangling bond-up (E-)	-2.35	1.70	—	0.98	0.96
Rutile-structure $\text{GeO}_2$	—	1.90	1.92	—	1.24

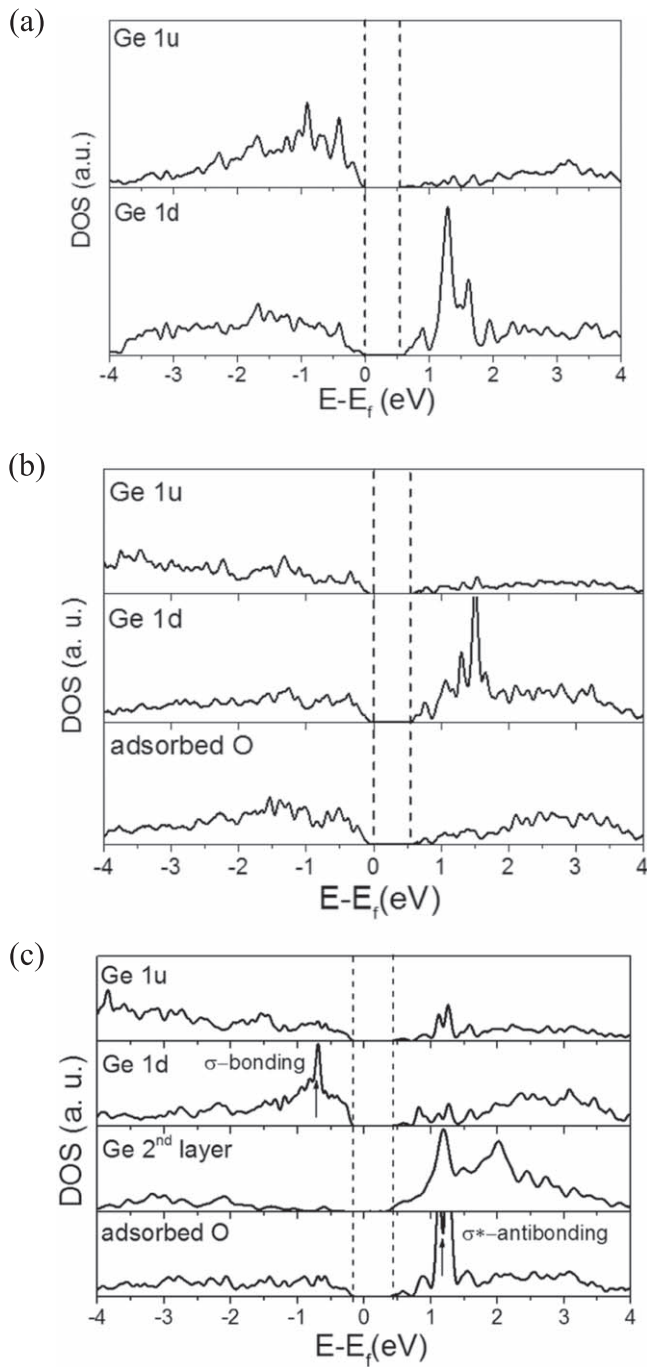
according to the cell size to maintain the k-point density. As shown in table 1, the adsorptions on the A-site and the B-site were notably more favorable than those on the other sites, and thus, only these two sites were considered for the coverage-dependent behavior. For a specific surface coverage with different oxygen adsorption locations, all the possible structures were tested. Figure S3(a) in supplementary information shows an example of various adsorption configurations for  $3/64$  ML oxygen coverage. In figure S3(b), all the calculated adsorption energies of multiple configurations are provided. A minor energy difference of  $\sim 0.1$  eV exists for multiple oxygen adsorptions with different configurations for a given coverage. In the following calculations, only the structure with the lowest adsorption energy was considered.

Figure 3 shows the adsorption energy and electron transfer as a function of the oxygen coverage. The adsorption stability of O on Ge(100)  $c(4 \times 2)$  distinctly decreases with the increase in coverage from  $1/64$  to  $1/4$  ML. The A-site is more favorable for the B-site for the entire range of the coverage, and the difference in adsorption energy between the former and the latter for a given coverage is less than  $0.4$  eV/atom. The electron transfer to the adsorbed O atoms showed a similar tendency to decrease with the coverage. These results coincide with those of a previous theoretical work on oxygen adsorption on the low-index surface of ZrC [32]. It also reported an adsorption stability and electron transfer decrease after successive multiple oxygen adsorptions, and suggested that an increased oxygen coverage contributes to the repulsion between adsorbates, resulting in a decrease in the amount of charge transfer.

From the adsorption energies at various coverages on Ge(100)  $c(4 \times 2)$ , the stability of the adsorbed structures was predicted. Within the framework of *ab initio* thermodynamics, the oxygen atoms on Ge surface is assumed to be in thermodynamic equilibrium with  $\text{O}_2$  gas [33, 34]. The gas phase was represented by the oxygen chemical potential  $\Delta\mu_{\text{O}}$ , as in equation (4), which in turn was given by  $T$  and  $P_{\text{O}_2}$  as in equation (2). The energetically favorable surface is the one with the lowest relative surface Gibbs free energy per area,  $\Delta\gamma$  for a given  $T$  and  $P_{\text{O}_2}$ . Figure 4(a) shows the variation in the  $\Delta\gamma$  of the calculated surface structures as a function of  $\Delta\mu_{\text{O}}$ . These free energies are the relative values compared to the clean surface, as defined in equation (4). The upper limit of  $\Delta\mu_{\text{O}}$  for the oxygen-adsorbed surface was determined to be  $-2.36$  eV, which is the half of the calculated formation energy of bulk  $\text{GeO}_2$ . When  $\Delta\mu_{\text{O}}$  exceeds the upper limit, Ge

itself is no longer stable and the compound  $\text{GeO}_2$  bulk becomes more stable than the oxygen-adsorbed Ge in terms of the chemical potential of one element in compounds [33]. In contrast, at the lower limit of  $\Delta\mu_{\text{O}}$ , corresponding to the lowest  $P_{\text{O}_2}$  or the highest  $T$ ,  $\Delta\gamma$  is above zero. In between these two limits, several oxygenated surface structures appear as straight lines with a  $-N_{\text{O}}/A$  slope (equation (4)). That is, the absolute value of the slope is proportional to the oxygen coverage. The surface structures with the lowest free energy for a given  $\Delta\mu_{\text{O}}$  are represented as bold lines, and the segments are labeled based on the surface structure and the oxygen coverage in ML. The intersection point of the two lowest energy lines corresponds to the transition from one surface structure to another. From the clean Ge(100)  $c(4 \times 2)$  surface, the increase in  $\Delta\mu_{\text{O}}$  to  $-3.01$  eV induces a transition from the  $1/64$  ML dimer-bridge structure to the  $1/32$  ML dimer-bridge structure. A further increase in  $\Delta\mu_{\text{O}}$  at  $-2.75$  eV results in the transition to the  $1/16$  ML dimer-bridge, and that at  $-2.46$  eV results in the transition to the  $3/32$  ML dimer-bridge.

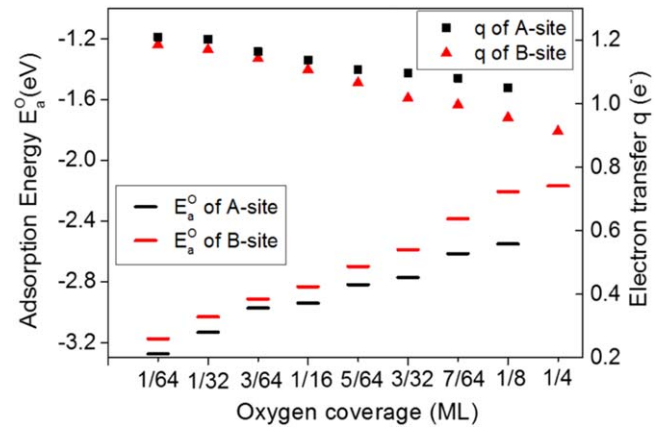
The surface structure with the lowest  $\Delta\gamma$  as a function of  $\Delta\mu_{\text{O}}$  in figure 4(a) was converted to that as a function of  $T$  and  $P_{\text{O}_2}$ , as shown in figure 4(b), using the expression of  $\Delta\mu_{\text{O}}$  as a function of  $T$  and  $P_{\text{O}_2}$  in equation (2). In this surface stability diagram, the stable adsorbed structures between the clean-surface and  $\text{GeO}_2$  regions are shown. The calculated stability diagram can be directly compared with those in previous *in situ* experimental investigations of the oxidation of the Ge(100) substrate. In the work of Molle *et al*, the as-prepared Ge samples were promptly exposed to an atomic O beam at the oxygen partial pressure of  $5 \times 10^{-8}$  bar [35]. Following the oxidation process from room temperature to  $300^\circ\text{C}$ , the transformation of  $\text{GeO}_2$  into suboxides sets at approximately  $400^\circ\text{C}$  ( $673$  K) (marked as a square in figure 4(b)), which is comparable to the calculated result of  $661$  K in this work. On the other hand, Prabhakaran *et al* reported the fabrication of a clean Ge surface by annealing the thin Ge oxide layer formed on the Ge(100) substrate until the peak position of the Ge(100) dimers could be detected via ultraviolet photoelectron spectroscopy [36]. The annealing conditions were  $\sim 500^\circ\text{C}$  and  $\sim 10^{-10}$  bar (marked as a circle in figure 4(b)), which also coincide with the prediction in this work. These observations show that the predicted surface stability diagram for the initial oxidation of Ge(100) is consistent with the experimental reports. Figure S4 in supplementary information without correction term,  $\Delta E_{\text{O}_2}$ , was



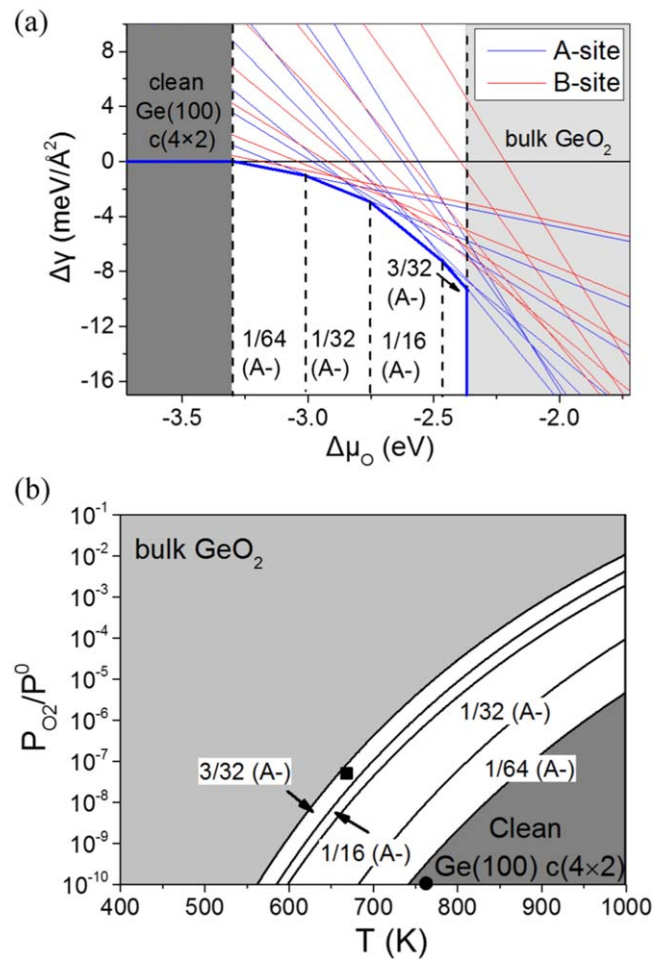
**Figure 2.** Layer-resolved DOS of the (a) bare Ge(100)  $c(4 \times 2)$  surface (b) oxygen-adsorbed on the dimer-bridge (A-site) and (c) oxygen-adsorbed on the back bond-down (B-site) structures. The  $\sigma$ -bonding state below the Fermi level ( $E_f$ ) and  $\sigma^*$ -antibonding states above  $E_f$  are indicated by the arrows.

provided as a comparison. The upper limit of  $\Delta\mu_O$  for the oxygen-adsorbed surface is  $-2.14$  eV in figure S4(a) and the corresponding surface stability ( $T, P_{O_2}$ ) diagram in figure S4(b) shows less agreements with the experimental reports [35, 36].

Practically, the transition between different structures of surface may be continuous due to the configurational entropy [33]. However, the dominant surface structure with more than 0.5 fraction is determined to the structure with the lowest



**Figure 3.** Calculated lowest oxygen adsorption energy and highest electron transfer as a function of the oxygen coverage for the dimer-bridge (A-site) and back bond-down (B-site) structures.



**Figure 4.** (a) Calculated relative surface free energy per area of the oxygen-adsorbed Ge(100)  $c(4 \times 2)$  surface as a function of the oxygen chemical potential; only the dimer-bridge (A-site) and back bond-down (B-site) are considered. (b) Surface stability ( $T, P_{O_2}$ ) diagram showing the most stable structures. The results from the previous experimental reports [35, 36] are also represented by the square and circle symbols.

Gibbs free energy [33]. Therefore, the calculated results provide the direction of the continuous change of the surface stability.

## Conclusion

In summary, the adsorption behavior of atomic oxygen on various adsorption sites of the Ge(100)  $c(4 \times 2)$  reconstructed surface and its oxygen coverage dependency were calculated through density functional theory calculations. The dimer-bridge structure was found to be the most stable for oxygen adsorption, and the back bond-down structure was found to be the second most stable. As the oxygen coverage becomes higher, the adsorption becomes less stable. By combining with thermodynamic modeling, the surface stability diagram as a function of the temperature and oxygen partial pressure was obtained, which enables a direct comparison with the experimental initial oxidation. The computational results obtained in this study are consistent with the previous experimental observations, suggesting that the calculation results can be utilized as a useful guide in determining the appropriate oxidation conditions for high-quality GeO<sub>2</sub> growth.

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## References

- [1] Dimoulas A, Mavrou G, Vellianitis G, Evangelou E, Boukos N, Houssa M and Caymax M 2005 *Appl. Phys. Lett.* **86** 032908
- [2] Fukuda T and Ogino T 1997 *Phys. Rev. B* **56** 13190
- [3] Grassman T, Bishop S and Kummel A 2008 *Surf. Sci.* **602** 2373
- [4] Fleischmann C 2007 *PhD Thesis* Katholieke Universiteit Leuven <https://lirias.kuleuven.be/1761935>
- [5] Soon J, Lim C, Loh K, Ma N and Wu P 2005 *Phys. Rev. B* **72** 115343
- [6] Fan X, Lau W and Liu Z 2009 *J. Phys. Chem. C* **113** 8786
- [7] Fleischmann C, Schouteden K, Merckling C, Sioncke S, Meuris M, Van Haesendonck C, Temst K and Vantomme A 2012 *J. Phys. Chem. C* **116** 9925
- [8] Shah G, Radny M and Smith P 2014 *J. Phys. Chem. C* **118** 15795
- [9] Furthmiller J and Kresse G 1996 *Comput. Mater. Sci.* **6** 15
- [10] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** 558
- [11] Perdew J, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [12] Heyd J, Scuseria G and Ernzerhof M 2003 *J. Chem. Phys.* **118** 219906
- [13] Fan X, Zhang Y, Lau W and Liu Z 2005 *Phys. Rev. Lett.* **94** 016101
- [14] Dorado B, Freyss M and Martin G 2009 *Eur. Phys. J. B* **69** 203
- [15] Morgan B and Watson G 2009 *J. Phys. Chem. C* **113** 7322
- [16] Gryaznov D, Blokhin E, Sorokine A, Kotomin E, Evarestov R, Bussmann-Holder A and Maier J 2013 *J. Phys. Chem. C* **117** 13776
- [17] Dimitrakis D, Tsongidis N I and Konstandopoulos A G 2016 *Phys. Chem. Chem. Phys.* **18** 23587
- [18] Wang L, Maxisch T and Ceder G 2006 *Phys. Rev. B* **73** 195107
- [19] Linstrom P and Mallard W 1997 *NIST Chem. WebBook* (Gaithersburg, MD: National Institute of Standards and Technology) (<https://doi.org/10.18434/T4D303>)
- [20] Ting O, Ye Y, Wu C, Xiao K and Liu Z 2019 *Angew. Chem. Int. Ed. Eng.* **58** 4923
- [21] Zhang H, Xie Y, Yao M, Xu J, Zhang J and Hu L 2018 *Phys. Chem. Chem. Phys.* **20** 14410
- [22] Sosa E and Liu H 2018 *J. Alloys. Compd.* **735** 643
- [23] Stekolnikov A, Furthmüller J and Bechstedt F 2002 *Phys. Rev. B* **65** 115318
- [24] Needels M, Payne M and Joannopoulos J 1987 *Phys. Rev. Lett.* **58** 1765
- [25] Schnell R, Himpfel F, Bogen A, Rieger D and Steinmann W 1985 *Phys. Rev. B* **32** 8052
- [26] Shirasawa T, Mizuno S and Tochihiro H 2006 *Surf. Sci.* **600** 815
- [27] Houssa M, Chagarov E and Kummel A 2009 *MRS Bull.* **34** 504
- [28] Kirchner E and Baerends E 1994 *Surf. Sci.* **311** 126
- [29] Tang W, Sanville E and Henkelman G 2009 *J. Phys.: Condens. Matter* **21** 084204
- [30] Sanville E, Kenny S D, Smith R and Henkelman G 2007 *J. Comput. Chem.* **28** 899
- [31] Gurlu O, Zandvliet H and Poelsema B 2004 *Phys. Rev. Lett.* **93** 066101
- [32] Osei-Agyemang E, Paul J, Lucas R, Foucaud S and Cristol S 2016 *J. Phys. Chem. C* **120** 8759
- [33] Yeu I W, Park J, Han G, Hwang C S and Choi J-H 2017 *Sci. Rep.* **7** 10691
- [34] Yeu I W, Han G, Park J, Hwang C S and Choi J-H 2019 *Sci. Rep.* **9** 1127
- [35] Molle A, Bhuiyan M, Tallarida G and Fanciulli M 2006 *Appl. Phys. Lett.* **89** 083504
- [36] Prabhakaran K and Ogino T 1995 *Surf. Sci.* **325** 263