# Oxidation of the GaAs(001) surface: Insights from first-principles calculations

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We performed a detailed investigation of the oxidation of the technologically relevant GaAs(001)-$\beta 2(2 \times 4)$ surface via density functional calculations. The purpose is to gain insights on the atomistic mechanisms and local bondings that underlie the degradation of the surface properties once exposed to oxygen. The study comprises the adsorption of single O atoms, through the sampling of several adsorption sites, and the subsequent formation of the O adsorbate at increasing coverage by taking into account multiple-atom adsorption. Based on the evaluation of the energetics and the structural properties of the atomistic models generated, the results here reported delineate a consistent picture of the initial stage of the surface oxidation: (i) at low coverage, in the limit of single O insertions, oxygen is incorporated on the surface forming a twofold-bridging Ga-O-As bond; (ii) at increasing coverage, as multiple O atoms are involved, this is accompanied by the formation of a threefold-coordinated bond (with two Ga and one As atoms); (iii) the latter has important implications regarding the electronic properties of the adsorbate since this O bonding may result in the formation of As dangling bonds. Moreover, a clear trend of increased energy gain for the incorporation of neighboring O atoms compared to single O insertions indicates that the formation of oxide clusters is favored over a regime of uniform oxidation. Our findings provide a detailed description of the O bonding and stress the importance of modeling the adsorption of multiple O atoms for an accurate description of the surface oxidation.

## I. INTRODUCTION

GaAs and other III-V compounds, such as InGaAs and InP, with their high intrinsic electron mobility, have been the subject of intensive studies as alternative channel materials for high-performance complementary metal-oxide-semiconductor devices.[1–4] However, in spite of the significant effort invested by the scientific community, some major issues remain that hamper the path toward their successful implementation for the microelectronic industry. The most critical problem arises from the poor quality of the interfaces between the III-V's and the dielectric that leads to the degradation of the electronic properties of the device and is bound to the so-called phenomenon of *Fermi-level pinning*[5,6] that occurs at the III-V/oxide interface (the origin of which is not fully understood and quantified[2]). In order to solve this issue and identify an interface with the optimal properties, it is crucial to gain basic insights on the atomistic processes involved upon oxide growth on the III-V substrate and on the resulting structure of the interface at the atomic scale.

Among the III-V compounds, we have chosen to investigate GaAs as it has been the object of thorough experimental investigations[1,6] and numerous technological applications.[7] We have employed density functional theory based methods to investigate the reaction of oxidation of the GaAs(001) surface and the ensuing formation of the oxide film. In a previous work,[8] we were able to provide an atomistic model of the GaAs(001) surface oxidation in its early stages. Particularly, we identified a key mechanism of stress release upon atom ejection into the amorphous oxide, which naturally leads to the formation and accumulation of native defects at the interface between the crystalline substrate and the oxide layer. That work, based on first-principles molecular dynamics (MD) simulations, aimed both at providing a dynamical picture of the oxidation and a realistic description of the atomistic mechanisms that occur during the reaction by taking explicitly into account the role of temperature. This approach, however, due to the coupling of the system with the thermal bath, does not provide an accurate energetic description of the single microscopic processes.

Here, we present a complementary study, based on the evaluation of the energetics of the key atomistic processes involved in the reaction, to describe the progressive surface oxidation. The investigation of the adsorption of single O atoms first, and then multiple atoms at increasing O coverage, is pursued through a series of structural optimizations based on oxygen atoms insertion in Ga-As bonds, at submonolayer coverage. The analysis of the energetics of the resulting structural models allows us to quantify the adsorption and the oxidation energies at increasing O coverage and to gain insight on the structural properties and local bonding of O with the III-V.

## II. METHODOLOGY

Among the different surface reconstructions that GaAs exhibits depending on the experimental growth conditions, we considered the arsenic-terminated GaAs(001)-$\beta 2(2 \times 4)$ (Refs. 9 and 10) since it is the most commonly one obtained experimentally by molecular beam epitaxy (MBE). The density functional theory (DFT) calculations were performed using the SIESTA software package.[11,12] The exchange and correlation energy was accounted for through the local density approximation (LDA) in the parametrized form of Ceperley and Alder.[13] Core-valence interactions were described by adopting norm-conserving pseudopotentials in the form of

Troullier-Martins[14] with the following electronic configuration of the elements: H $1s^1$, O $[1s^2]2s^22p^4$, Ga [Ar] $3d^{10}4s^24p^1$, and As [Ar, $3d^{10}$] $4s^24p^3$ (the square brackets denoting the core configurations). A DZP-type (double zeta with polarization orbitals) basis set was employed to describe the valence electrons, and a SZ (single zeta) basis was considered for the semicore Ga $3d$ states.

We used a periodically repeated slab to model the GaAs(001)-$\beta$2(2 × 4) surface, consisting of 9 layers of GaAs terminated by a layer of hydrogen atoms, for a total amount of 78 atoms, with the slabs being separated by a vacuum region of ≈14 Å. The termination layer of H atoms adopted a specific topology that provides the right amount of charge to fully passivate the dangling bonds and therefore ensures a correct electron counting.[15] An energy cutoff of 250 Ry and a 4 × 2 × 1 Monkhorst-Pack grid[16] for the sampling of the Brillouin zone were adopted, which ensure that the total energy is well converged. Full structural relaxation of the top seven layers of the surface and of the adsorbate configurations were performed using the conjugate gradient algorithm,[17] while the bottom two layers as well as the hydrogen atoms were kept fixed, until forces converged to 20 meV/Å. Moreover, the self-consistent dipole correction implemented in the code is used in order to cancel the effects of spurious electric fields that may be induced by the periodic boundary conditions.[18]

A top view of the optimized structure of the reconstructed GaAs(001)-$\beta$2(2 × 4) surface is shown in Fig. 1(a). This surface is characterized by two present and two missing As dimers on the top layer. In the second layer, Ga atoms that lie beneath the two missing As dimers are absent, which leads to an exposed third layer of As atoms that dimerize themselves. Thus, the surface exhibits parallel rows of trenches separated by dimer blocks,[19] as illustrated in Fig. 1(b). The computed bond lengths of the As dimers of the top and third layers are 2.49 and 2.52 Å, respectively, in agreement with previous theoretical studies.[9,10]

The study has been carried out through the following steps: (a) First, a single O atom is absorbed on the GaAs(001) surface. Several adsorption sites were considered in order to establish a proper sampling of the surface potential, and in each case the adsorption energies and the bonding geometries of the resulting adsorbates were computed; the results are reviewed in Sec. III A. (b) Next, a study of the adsorption at increasing O coverage was performed. In particular, the mutual influence of the adsorption of neighboring O atoms was investigated by sampling several adsorption configurations at increasing O coverage and the resulting O-bonding geometries were evaluated, reported in Sec. III B.

## III. RESULTS AND DISCUSSION

### A. Energetics of atomic O adsorption on the GaAs(001) surface

We model the adsorption of one O atom on the reconstructed GaAs(001)-$\beta$2(2 × 4) surface by considering eight sampling configurations, as schematically illustrated in Fig. 1(a). The O atom is placed on top of specific bonds at the surface, roughly midway in a guessed bridgelike configuration. The sampled sites include on top of the As-As bonds of the dimers in the upper layer 1 and in trenches 2; at the back bonds of the As
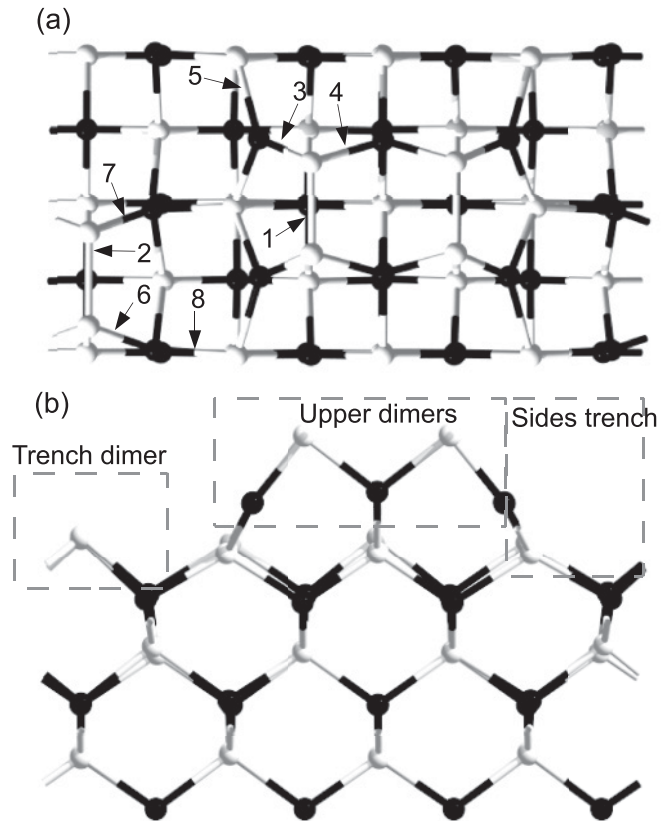


FIG. 1. (a) Top view of the reconstructed GaAs(001)-$\beta$2(2 × 4) surface with the eight adsorption sites considered for the O atom indicated by an arrow. The Ga and As atoms are depicted with black and white balls, respectively. (b) Side view of the reconstructed GaAs(001)-$\beta$2(2 × 4) surface, subdivided in three regions for the sampling of multiple-O-atom adsorbates: the upper dimers (UD), the trench dimer (TD), and the sides of the trench (ST) regions.

dimers of the upper layer, where we may distinguish external bonds 3 and internal ones 4; on a Ga-As bond on the side of the trench 5; on the two back bonds of an As dimer in the trench, 6 and 7; and finally, on another inner Ga-As bond on the side of the trench 8.

Structural optimizations of these adsorbate configurations were performed and the adsorption energy, referenced with respect to the clean surface and a free oxygen molecule, is calculated as

$$\Delta E_{ads} = -\left(E_{ads} - E_{surf} - \tfrac{1}{2}E_{O_2}\right), \qquad (1)$$

where $E_{ads}$ and $E_{surf}$ are the total energies of the final adsorbate system and the clean reconstructed GaAs(001) surface, respectively, and $E_{O_2}$ is the total energy of a free $O_2$ molecule in its ground state, the spin triplet,[20] computed in a box of side 20 Å. With this sign convention, a positive value of the adsorption energy corresponds to the energetic gain of an exothermic reaction. Note that these calculations were performed within the framework of the non-spin-polarized scheme of the DFT-LDA.

The properties of the O-GaAs(100) adsorbate configurations sampled are reported in Table I, and almost all the final bonding configurations are bridging As-O-Ga ones, except the first two: configuration 1 forms a bridge As-O-As bond on a

TABLE I. Computed properties of the structurally optimized O-GaAs(001) adsorbates corresponding to the eight sampling configurations shown in Fig. 1(a): the adsorption energies, bonding geometries, adsorption sites, and bond lengths are given.

| Config. | Ads. energy (eV) | Bonding | Ads. site | As-O (Å) | Ga-O (Å) |
|---|---|---|---|---|---|
| 1 | 1.59 | As-O-As | Up dimer | 1.83 | |
| 2 | 1.29 | As=O | Trench dimer | 1.67 | |
| 3 | 1.73 | As-O-Ga | Back bond up dimer | 1.82 | 1.85 |
| 4 | 1.65 | As-O-Ga | Back bond up dimer | 1.77 | 1.92 |
| 5 | 1.79 | As-O-Ga | Side trench | 1.80 | 1.86 |
| 6 | 1.84 | As-O-Ga | Back bond trench dimer | 1.78 | 1.90 |
| 7 | 1.75 | As-O-Ga | Back bond trench dimer | 1.79 | 1.90 |
| 8 | 1.58 | As-O-Ga | Side trench | 1.75 | 1.93 |

dimer on the top layer, with energetic gain of 1.59 eV [see Fig. 2(a)], while the configuration 2 leads to the formation of a double bond As=O [O attached to As of the dimer in the trench, Fig. 2(b)], and corresponds to the O bonding with the lowest adsorption energy (1.29 eV) among those examined. The most favorable bonding configurations are those with O atoms inserted in a back bond of the As dimers, forming As-O-Ga bridge bonds, such as 3 in the top layer dimer, 6 and 7 in the trench dimer [Fig. 2(c)]. Bridging As-O-Ga bonds are also formed in configurations 5 and 8, with O inserted on the sides on the trench.

It is interesting here to observe that, due to the complex morphology of the reconstructed surface, similar bonding geometries can have remarkable variations in adsorption energies, depending on the adsorption sites on the surface; for example, back bonds are formed both in configurations 3 and 4, but in the first case the O is inserted in the external bond of the dimer block, while an internal bond is formed in the latter. The external back bond allows a better bonding geometry optimization compared to the internal one, as reflected by the higher adsorption energy (cf. Table I). Similarly, both configurations 5 and 8 have bridging bonds on the sides of the trench, but different adsorption sites.

In summary, regarding the adsorption of a single O atom on the GaAs(001)-$\beta 2(2 \times 4)$ surface, the most representative type of bonding turns out to be the O inserted as back bond of the As surface dimers as shown in Fig. 2(c), with an energy gain of 1.84 eV (with respect to the clean surface and a free $O_2$ molecule) for the most favorable adsorption site on the single dimer in the trench, and with computed bond lengths of 1.78 and 1.90 Å for As-O and Ga-O, respectively.

### B. Energetics of multiple-O-atom adsorption on the GaAs(001) surface

In a second stage, the adsorption of multiple O atoms on the surface was considered in order to evaluate the effects of mutual interaction of O atoms and eventually model the adsorbate at increasing O coverage. The following procedure was adopted: the reconstructed GaAs(001)-$\beta 2(2 \times 4)$ surface was subdivided into three smaller regions, as shown in Fig. 1(b). These include, at the top layer, the region of the upper dimers (henceforth denoted as UD); at the bottom surface layer, the region of the trench dimer (TD); and in-between, the sides of the trench (ST). Each region was sampled by inserting progressively O atoms into the available neighboring surface bonds of the lowest energy adsorbate configurations.

For the case of two O atoms, through this approach, we generated a sampling of totally 15 configurations, 5 per region. Based on the results listed in Table I for the single O adsorption, the adsorbate models chosen as starting configurations are the 3, 6, and 5 for the upper dimers, the trench dimer, and the sides trench, respectively. An extra O is then inserted in neighboring surface bonds. The adsorption energy is computed using the following expression:

$$\Delta E_{ads}(n) = -\left[ E_{ads}(n) - E_{surf} - \frac{n}{2} E_{O_2} \right], \quad (2)$$

a straightforward generalization of Eq. (1) to the adsorption of $n$ oxygen atoms on the surface, where $E_{ads}(n)$ is the total energy of the adsorbate containing $n$ O atoms.

This quantity, however, provides information only on the overall energetic balance relative to the same initial state,
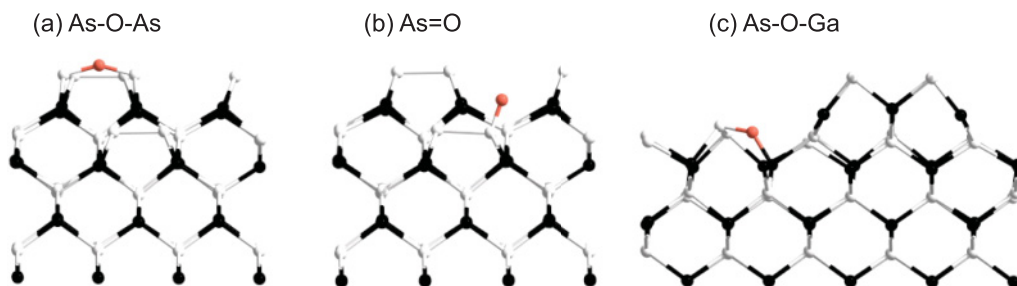


(a) As-O-As          (b) As=O          (c) As-O-Ga

FIG. 2. (Color online) Representative bonding geometries of the O-GaAs(001) adsorbate, obtained for single O insertion: (a) O bridging an As surface dimer, (b) O forming a double bond As=O, (c) twofold bond with O inserted as As-O-Ga (the most favorable bonding configuration). The O, Ga, and As atoms are depicted with grey (red), black, and white balls, respectively.

TABLE II. Computed properties of the structurally optimized O-GaAs(001) adsorbates containing two O atoms. Adsorption and binding energies, bonding geometries, and adsorption sites relative to the second O atom inserted are given.

| Config. | Ads. energy (eV) | Bin. energy (eV) | Bonding | Ads. site |
|---|---|---|---|---|
| Two O: Region UD | | | | |
| 1 | 3.37 | 1.64 | As-O-Ga | Back bond up dimer |
| 2 | 3.49 | 1.76 | As-O-Ga | Back bond up dimer |
| 3 | 3.37 | 1.64 | As=O | Up dimer |
| 4 | 3.33 | 1.60 | As-O-Ga | Back bond up dimer |
| 5 | 3.49 | 1.76 | As-O-Ga | Back bond up dimer |
| Two O: Region TD | | | | |
| 1 | 4.68 | 2.84 | Threefold-O | Trench dimer |
| 2 | 3.58 | 1.74 | As-O-Ga | Back bond trench dimer |
| 3 | 3.29 | 1.45 | Threefold-O | Trench dimer |
| 4 | 3.61 | 1.77 | As-O-Ga | Inner bond |
| 5 | 3.10 | 1.26 | As-O-Ga | Inner bond |
| Two O: Region ST | | | | |
| 1 | 3.35 | 1.56 | As-O-Ga | Back bond up dimer |
| 2 | 3.28 | 1.49 | As-O-Ga | Side trench |
| 3 | 2.84 | 1.05 | As-O-Ga | Trench |
| 4 | 3.87 | 2.08 | As-O-Ga | Side trench |
| 5 | 3.74 | 1.95 | As-O-Ga | Trench |

represented by the clean surface and the free oxygen molecule. In order to access information on the energetics relative to a specific O bonding formed via the incorporation of an extra oxygen in a adsorbate containing $(n-1)$ O atoms, the following expression for the binding energy is used:

$$\Delta E_b(n) = -\left[ E_{\text{ads}}(n) - E_{\text{ads}}(n-1) - \tfrac{1}{2} E_{\text{O}_2} \right], \quad (3)$$

which expresses the energetic gain for the adsorption of the $n$th O atom in terms of the total energies of the final adsorbate structure with $n$ O atoms, the starting adsorbate structure considered with $(n-1)$ O atoms, and the free oxygen molecule, respectively. Note, however, that this criterion is purely indicative and it should be considered merely for guiding purposes, as the differences in the adsorption energy between the different configurations are not so considerable and variations in the energy ordering could be found if the calculations were performed with different approximations of the exchange-correlation functional, such as the generalized gradient approximation.

The results obtained for the adsorption of two O atoms are listed in Table II. For the sampling of the upper As dimers region, we found that the extra O mostly inserts in the back bonds of the dimers, with an associated energy gain varying between 1.60–1.76 eV. The most favorable configuration was found to be with oxygens inserted on the two dimers on the same side (configurations 2 and 5, cf. Table II), as shown in Fig. 3(a). Regarding the trench dimer region, configuration 1 shows a remarkably high binding energy relative to the incorporation of the second O atom (2.84 eV), which may be ascribed to the specific O bonding adopted; namely, a threefold-coordinated bonding formed through a mechanism in which the O displaces the As atom from the site, and binds itself with the two neighboring Ga and the displaced As atoms above, as shown in Fig. 3(b). In the following, we will refer to this bonding configuration as being *displacive*.

Interestingly, this threefold-coordinated bonding is very much similar to the bonding geometry identified by Stroscio *et al.*[21] for oxygen adsorbate on the GaAs(110) surface through scanning tunneling microscopy measurements. As a matter of fact, from high-resolution measurements, the authors deduce a bonding configuration with O in an interchain bridging position bonded to a single As and two Ga atoms. From this experimental confirmation, we can deduce that, independently from the surface orientation of GaAs, the local chemical environment favors this peculiar threefold-coordinated bonding geometry for oxygen.

It is worth to note here that also configuration 3 displays a similar threefold-O bonding, but with a much lower binding energy (only 1.45 eV). This remarkable difference in the binding energy between the two similar bondings can be explained in terms of local strain relief: in configuration 1, the two O atoms are attached to the same As of the dimer as can be seen in Fig. 3(b), this allows a cooperative O rotation that reduces locally the surface strain induced by the oxidation, maintaining in this way bond angles for the As atom involved comparable to the As surface ones (the computed O-As-O bond angle is 86.1° and well matches with the surface Ga-As-Ga bond angle of 93.4°); on the contrary, a measured O-As-O bond angle of 49.8° in configuration 3 is a clear indication of a strongly compressed bond. In a similar way, configurations 4 and 5 show a similar O insertion in an inner (bulklike) bond, but with a difference in the binding energy of ~0.5 eV, which can be explained in terms of favorable bonding that allows surface local strain relief in the first case.

To conclude with the side trench region, both configurations 2 and 4 have two bridging bonds on the sides of the trench, the latter with a high binding energy (2.08 eV) due to the oxygens bridging the same As atom [configuration shown in Fig. 3(c)], and therefore perturbing less the local bonding (as a consequence of the cooperative O arrangements), compared to 2, in which the oxygens form single insertions. A similar
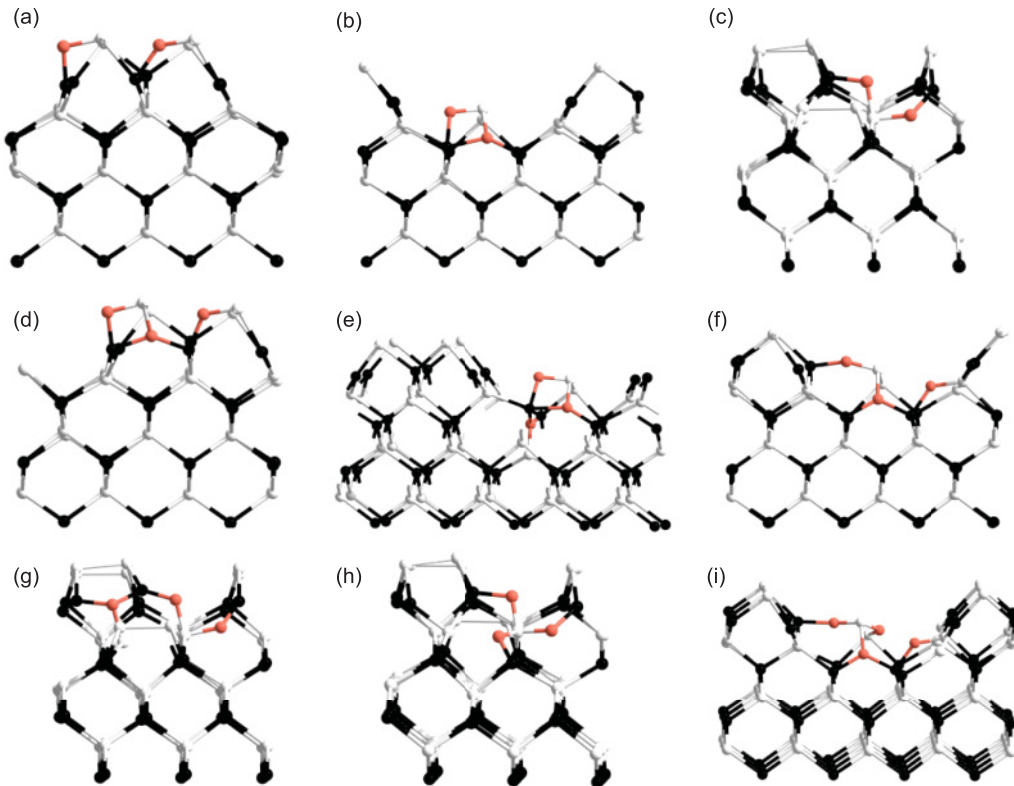
FIG. 3. (Color online) Representative bonding geometries obtained for the O-GaAs(001) adsorbate at increasing O coverage. For $n = 2$ O atoms: in (a) two bridging As-O-Ga bonds on the upper layer As dimers, (b) threefold-coordinated displacive O-bonding with two Ga and a single As atom, on the trench dimer, (c) two bridging bonds with O atoms attached to the same As, a favorable bonding arrangement as compared to separated As-O-Ga bonds. For $n = 3$ O atoms: (d) threefold-coordinated O bonding on the upper layer As dimers, (e) threefold-coordinated O at the trench dimer forming a defective bonding, as being the neighboring As atoms underneath with unsaturated bonds, (f) bridging and threefold-O bonding arrangements on the trench dimer, (g) another defective bonding represented by a threefold-O bonding on the side trench, (h) favorable bonding arrangement comprised of three bridging bonds with O atoms attached to the same As. For $n = 4$ O atoms: (i) another favorable bonding arrangement, due to clustering of O atoms, describing the oxidized trench dimer region.

difference can be observed in configurations 3 and 5, in which the extra O is bridging in the trench region, but while in 5 the two O atoms are linked to an As, this is not the case for 3, displacing separated insertions and a lower energy gain of 0.9 eV compared to 5.

Using the same approach for the adsorption of three neighboring O atoms on surface, the sampling of the UD region was performed through the insertion of an additional O atom to the lowest energy adsorbate with two O atoms. In total, 10 configurations were sampled and the corresponding energies are reported in Table III. Configuration 1 shows the formation of a displacive threefold O bonding on the top As dimer [Fig. 3(d)] with an associated high binding energy (3.52 eV). Regarding the other configurations of this sampling, they have almost all the same bonding geometry, i.e., bridging O inserted in Ga-As bonds, with binding energy of the same order of what is found for single O adsorption (cf. Table I), except for two configurations with higher energetic gain, the 2 and 8. In both cases, differently from the other configurations, oxygens are linked to the same Ga or As atoms, thus providing a more efficient way of local strain relief due to the O-cooperative bonding optimization.

Similarly, the other two surface regions (TD and ST) were sampled with eight configurations each. Concerning the trench

region, configurations 3 and 4 form inner bridge bonds, with lower binding energy as compared to the other surface bonds (only 1.31 eV). An interesting configuration is the 6, where the O atom, inserted in an inner (bulklike) Ga-As bond, forms a threefold bond with two Ga and an As underneath, leaving the two neighboring As with two dangling bonds, as shown in Fig. 3(e). Here, clearly, a *defective bonding* is formed and despite the low binding energy (0.72 eV), it elucidates this point: the formation of a threefold-coordinated O bonding in a local bulklike environment, differently from surface bonds, leaves necessarily the neighboring As with dangling bonds because of the coordination mismatch, as being As and Ga fourfold coordinated. Another interesting configuration is the 8, with a high energy gain (2.25 eV): it displays a local bonding arrangement with resulting formation of bridge bond on the side trench and a threefold-O bond on the trench [Fig. 3(f)].

Finally, the side of the trench region was sampled. Interestingly, configuration 2 forms a threefold O on the side trench [shown in Fig. 3(g)], with two Ga and an As, leaving the latter with an unsaturated bond (defective bonding). The same mechanism occurs for configuration 3, resulting in a threefold O and associated defective As (not shown). In configuration 4, another bridging bond is formed via O incorporation; here, however, the three oxygens are attached to the same As atom

TABLE III. Computed properties of the structurally optimized O-GaAs(001) adsorbates containing three O atoms. Adsorption and binding energies, bonding geometries, and adsorption sites relative to the third O atom inserted are given.

| Three O: Region UD | | | | |
|---|---|---|---|---|
| Config. | Ads. energy (eV) | Bin. energy (eV) | Bonding | Ads. site |
| 1 | 7.01 | 3.52 | Threefold-O | Up dimer |
| 2 | 6.01 | 2.52 | As-O-Ga | Up dimer |
| 3 | 5.00 | 1.51 | As=O | Up dimer |
| 4 | 5.16 | 1.67 | As-O-Ga | Up dimer |
| 5 | 5.16 | 1.67 | As-O-Ga | Up dimer |
| 6 | 5.13 | 1.63 | As-O-Ga | Up dimer |
| 7 | 5.20 | 1.71 | As-O-Ga | Side trench |
| 8 | 5.49 | 2.00 | As-O-Ga | Up dimer |
| 9 | 5.36 | 1.87 | As-O-Ga | Up dimer |
| 10 | 5.15 | 1.66 | As-O-Ga | Up dimer |
| Three O: Region TD | | | | |
| 1 | 6.14 | 1.46 | As-O-Ga | Trench dimer |
| 2 | 6.27 | 1.59 | As-O-Ga | Trench dimer |
| 3 | 5.99 | 1.31 | As-O-Ga | Inner bond |
| 4 | 5.99 | 1.31 | As-O-Ga | Inner bond |
| 5 | 6.32 | 1.64 | As-O-Ga | Side trench |
| 6 | 5.40 | 0.72 | Threefold-O | Inner bond |
| 7 | 6.58 | 1.90 | As-O-Ga | Trench dimer |
| 8 | 6.93 | 2.25 | As-O-Ga | Side trench |
| Three O: Region ST | | | | |
| 1 | 5.48 | 1.61 | As-O-Ga | Back bond up dimer |
| 2 | 5.88 | 2.00 | Threefold-O | Side trench |
| 3 | 5.31 | 1.44 | Threefold-O | Side trench |
| 4 | 6.01 | 2.13 | As-O-Ga | Side trench |
| 5 | 5.00 | 1.13 | As-O-Ga | Inner bond |
| 6 | 5.51 | 1.64 | As-O-Ga | Trench dimer |
| 7 | 5.88 | 2.00 | Threefold-O | Side trench |
| 8 | 5.45 | 1.58 | As-O-Ga | Back bond up dimer |

TABLE IV. Computed properties of the structurally optimized O-GaAs(001) adsorbates containing four O atoms. Adsorption and binding energies, bonding geometries, and adsorption sites relative to the fourth O atom inserted are given.

| Four O: Region UD | | | | |
|---|---|---|---|---|
| Config. | Ads. energy (eV) | Bin. energy (eV) | Bonding | Ads. site |
| 1 | 8.62 | 1.61 | As-O-Ga | Up dimer |
| 2 | 8.66 | 1.64 | As-O-Ga | Up dimer |
| 3 | 9.62 | 2.61 | As-O-Ga | Up dimer |
| 4 | 8.95 | 1.93 | As-O-Ga | Side trench |
| 5 | 8.97 | 1.96 | As-O-Ga | Side trench |
| 6 | 8.79 | 1.78 | Threefold-O | Inner bond |
| 7 | 8.87 | 1.85 | As-O-Ga | Side trench |
| 8 | 8.45 | 1.43 | As-O-Ga | Side trench |
| 9 | 8.87 | 1.86 | As-O-Ga | Side trench |
| 10 | 9.08 | 2.07 | As-O-As | Up dimer |
| Four O: Region TD | | | | |
| 1 | 8.50 | 1.57 | As-O-Ga | Trench dimer |
| 2 | 8.11 | 1.17 | As-O-Ga | Side trench |
| 3 | 8.10 | 1.17 | As-O-Ga | Inner bond |
| 4 | 8.45 | 1.52 | As-O-Ga | Inner bond |
| 5 | 8.63 | 1.70 | As-O-Ga | Trench dimer |
| 6 | 9.43 | 2.50 | As-O-As | Trench dimer |
| 7 | 8.51 | 1.58 | As-O-Ga | Side trench |
| 8 | 8.65 | 1.71 | As-O-Ga | Trench dimer |
| 9 | 8.60 | 1.67 | As-O-Ga | Trench dimer |
| 10 | 9.09 | 2.15 | As-O-Ga | Side trench |

[Fig. 3(h)], and this allows a bonding geometry optimization as indicated by the resulting high energetic gain (2.13 eV).

Next, the adsorption of four O atoms was performed, yet by only for two areas of the surface unit cell, the UD and the TD regions, since the O coverage in this case is such that these two regions are extended and overlap with the sides of the trenches; the results are reported in Table IV. Similarly to the previous cases, the lowest energy structures with three O adsorbed in these two regions are chosen as starting points and an extra atom is then inserted in a neighboring bond, for a total sampling of 20 configurations, 10 per region. Regarding the UD region, we observe that both configurations 1 and 3 have the same extra O bonding: a bridge O at the external up dimer, but in 3 the two oxygens are attached to same As of the dimer, and this brings a much higher binding energy ($\sim$1 eV) as compared to 1. In an analogous way, the high binding energy found for configurations 4, 5, and 9 (1.86 $\sim$ 1.96 eV) is associated to bridge O bonds in cluster, i.e., attached to the same atoms, while single O insertions show a lower energy gain, such as in configuration 8 of only 1.43 eV.

To conclude with the trench dimer region, it is worthy to mention that configuration 6 forms an As-O-As bond on the oxidized trench dimer [see Fig. 3(i)], here with a remarkable high binding energy (2.50 eV), which can be explained by the favorable bonding configuration, with three O atoms linked to the As of the dimer, and with bond angles close to the surface As dimer ones (the computed O-As-O bond angles are 103.69°, 92.96°, and 96.88°).

In conclusion of this section, it is worthy to focus the attention on the atomistic mechanisms underlying the formation of the displacive threefold-O bonding and its implications. The analysis of the energetics of the O adsorption on the GaAs(001) surface performed at increasing O coverage, together with the description of the mutual effects of neighboring O atoms, suggest the following mechanisms for the surface oxidation, as schematically illustrated in Fig. 4: The O atoms are first adsorbed on the surface by breaking of the Ga-As bonds and forming bridge bonds. The most favorable adsorption sites are the available back bonds of the As surface dimers [Fig. 4(a)]. The further adsorption of O atoms in this configuration (in the available back bonds) lifts up the As dimers block according to a peeling mechanism, which has also been suggested to occur for the silicon oxidation case (see Ref. 22). At higher O coverage, the surface is increasingly disordered and the influence of the neighboring O atoms starts playing a role: the O atoms in the bridge bonds rearrange locally toward lower energy configurations in order to reduce the strain [Fig. 4(b)]. In the latter configuration, the distance between the O and the neighboring Ga of the layer underneath is reduced, and the O atom easily forms an extra bond and is accommodated in the favorable displacive threefold configuration [Fig. 4(c)] with an associated remarkably higher binding energy (2.84 eV) as compared to the twofold bridging bond ($\sim$1.70–1.80 eV).

This is regarding the formation of surface threefold-O bonds, i.e. relative to O atoms that bind to As surface dimers. On the other hand, the formation of the same bonding on the subsurface layer, as schematically shown in Fig. 4(d), may have detrimental effects for the electronic properties of the O adsorbate. As a matter of fact, the O binds to two Ga and one
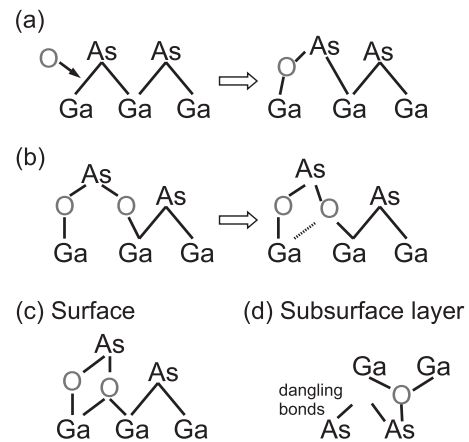


FIG. 4. Schematic illustration of a qualitative model for the adsorption of atomic O and the further oxidation of the GaAs(001) surface at increasing O coverage: (a) atomic O insertion on the back bonds of the As dimers in the bridgelike Ga-O-As bonding geometry; (b) at increasing O coverage, the O atoms rearrange locally toward a strain-reduced lower-energy bonding geometry, which finally leads to the threefold-coordinated O bonding, the most favorable bonding geometry (c). However, the formation of the latter at the subsurface layer may lead to a defective bonding with As dangling bonds (d).

As atom, leading in this way to the formation of As dangling bonds.

## IV. SUMMARY AND CONCLUSIONS

We have carried out a theoretical investigation of the reaction of oxidation of the GaAs(001)-$\beta 2(2 \times 4)$ surface via density functional total energy calculations. The study covered the adsorption of single and multiple O atoms, at increasing coverage and for an extensive sampling of configurations. For single O atoms adsorption, the favorite bonding geometry is a twofold-bridging As-O-Ga, in which O inserts in the back bonds of the surface As dimers. The adsorption energy in this case is estimated in the range 1.65–1.84 eV, depending on the adsorption site. Lower values of adsorption energies were found for the twofold As-O-As bridging bond (1.59 eV) and for the double bond As=O (1.29 eV).

Regarding the multiple-atom adsorption, the following conclusions can be drawn from this study. (i) There is no evidence of a regular pattern or ordered geometry for the adsorbate at increasing O coverage; on the contrary, the growth of an amorphous layer takes place. (ii) The adsorption of neighboring O atoms is energetically favored over noninteracting single-O-atom insertions. By analyzing the adsorption energies and structural properties of the several adsorbate models generated, this clear trend occurring at every O coverage has been explained by a higher flexibility in the local bonding optimization for adsorbate models including nearest-neighboring O atoms. As a result of this aspect, a clustering of oxide is energetically favored over a uniform growth mode of the oxide, at monolayer regime. (iii) Two main O-bonding geometries were identified, the above-discussed bridging Ga-O-As is the most frequent one, and a threefold-coordinated O bonding with two Ga and one As atoms, that takes place at an increasing O coverage of the surface. The

latter is highly favorable from an energetic point of view, with an adsorption energy that exceeds the O bridge one by more than 1 eV. Its formation, however, is bound to the presence of neighboring O atoms, therefore it is expected to occur at increasing O coverage. Interestingly, a similar bonding geometry with O bonded to two Ga and a single As atoms has been deduced from scanning tunneling microscopy measurements of oxygen adsorbate on the GaAs(110) surface.[21]

Finally, one important conclusive aspect concerns the impact that this threefold-O bonding, differently from the twofold bridging, may have on the degradation of the electronic properties of the O-GaAs(001) adsorbate. As a matter of fact,

our calculations show that its presence may induce locally the formation of As dangling bonds, especially at the subsurface layer. This can be understood with the following simple argument. In the twofold bonding, O is simply inserted in a Ga-As bond and it does not affect the neighboring bonds, whereas a bonding mismatch results from the threefold-coordinated O with two Ga and one As atoms, namely, involving three atoms which are fourfold coordinated in the bulk GaAs. The oxidation of the GaAs(001)-$\beta 2(2 \times 4)$ surface is a complex reaction involving many atomistic processes, and we attempted with this work to elucidate some aspects of this reaction and to gain new insights that can be fruitfully employed for a clarification of the whole picture.

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