Surface relaxation and rumpling of Sn-doped β -Ga₂O₃(010)

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We have studied the surface structure of single-crystal, wide-gap semiconductor β -Ga₂O₃(010) using x-ray photoelectron diffraction (XPD), low-energy electron diffraction (LEED), and x-ray photoelectron spectroscopy (XPS). The XPS measurements show typical spectra for stoichiometric Ga₂O₃(010). Annealing in vacuum produced a sharp (1 × 1) LEED pattern, characteristic of the monoclinic structure. The XPD angular anisotropies were collected for the Ga $2p_{3/2}$ and O 1s core levels. Surface interlayer relaxation up to 8% of the bulk interplanar distance and 0.11–0.14 Å rumpling are observed at the β -Ga₂O₃(010) surface. At the surface, the oxygen atoms shift toward the vacuum with respect to the gallium atoms. The rumpling decreases to zero and and the interplanar distance reaches the bulk value of 1.52 Å by the sixth atomic layer. The surface structure agrees with that predicted by first-principles density functional theory calculations which, in addition, suggest a significant band gap narrowing of \approx 1 eV in the surface layer, due to surface states spatially localized on surface oxygen atoms of O_{II} type.

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I. INTRODUCTION

Gallium oxide (Ga₂O₃) is an important wide-band-gap semiconductor with a range of potential high-power applications from semiconducting lasers [1] and field-effect devices [2] to high-temperature gas sensors [3,4]. β -Ga₂O₃ is the most stable bulk phase at room temperature [5] and, compared with SiC and GaN, β -Ga₂O₃ has higher breakdown field of 8 MV/cm and faster electron drift mobility of 300 cm² V⁻¹ s⁻¹ [6], making it suitable for the drift layers of vertical power transistors and diodes. β -Ga₂O₃ has a 4.8to 4.9-eV band gap, responsible for the very high breakdown field.

Recently, most research and technological developments have focused on the β -Ga₂O₃ phase because of its suitability for large-area single-crystal epitaxy. Bulk β -Ga₂O₃ phase can be obtained by conventional methods such as floating zone, edge-defined film-fed growth and Czochralski preparation processes [7] and can be manufactured at low cost with high volume. The crystal structure is base centered monoclinic (space group C2/m) with lattice parameters a = 12.23 Å, b = 3.04 Å, c = 5.80 Å, and $\beta = 103.7^{\circ}$ [8]. For the Ga₂O₃ (010) surface orientation, the surface termination maintains the Ga₂O₃ stoichiometry, as shown in Fig. 1. Figures 1(a) and 1(b) show the unit cell of β -Ga₂O₃. There are two crystallographically inequivalent Ga positions, Ga_I with tetrahedral oxygen coordination and Ga_{II} with octahedral coordination. The arrangement of oxygen ions is in a "distorted cubic" closely packed array. There are three crystallographically distinct sites, O_I , O_{II} , and O_{III} . One is a tetrahedral while the two others are trigonal [9].

The two principle applications for Ga_2O_3 in power electronics are Schottky barrier diodes and field-effect transistors (FET) with an *n*-doped Ga_2O_3 channel. In the case of a FET, the top electrode and a gate insulator must be grown on the surface of an β -Ga₂O₃ channel. The channel is *n* doped. For molecular beam epitaxy growth, the favored dopants are Si [10], Sn, and Ge [6,11]. The heterojunction interfaces can play a crucial role in device operation, for example, in determining the barrier heights for electron and hole transport. To elucidate the properties of such interfaces, the surface electronic structure of the Ga₂O₃ must be determined. Knowledge of the surface atomic positions and structure is therefore important in optimizing applications of Ga₂O₃.

The surface of β -Ga₂O₃ (100) has been studied with atomic force microscopy (AFM) [12], showing a uniform step height of half the unit cell. The wide terraces suggest step flow growth of homoepitaxial Ga₂O₃ films but the (100) orientation is also a cleavage plane making them mechanically unstable and subject to fracturing. The (010) orientation is not an easy cleavage plane and furthermore offers the possibility of rapid growth on small facets. With *n*-doped Si or Ge, and given suitable growth conditions, it may be possible to form a

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FIG. 1. (a) *a-b* and (b) *a-c* views of the β -Ga₂O₃ unit cell. There are two inequivalent Ga sites (Ga_I and Ga_{II}) and three O-sites (O_I, O_{II}, and O_{III}). Oxygen atoms are large red circles, and gallium atoms are small blue circles.

two-dimensional (2D) electron system on a high-k dielectric [13]. The substrate surface roughness can play a crucial role in the structural quality of the homoepitaxial film and the resulting dielectric properties, including the high breakdown voltage which characterizes Ga_2O_3 . Surface atomic relaxation will modify the local electronic structure, which may be of importance in the band lineup of a Schottky diode or at the interface with a transistor channel.

Meyer and Vanderbilt [14] define the relaxation by the average atomic displacement $\beta = [\delta(M) + \delta(O)]/2$, where $\delta(M)$ and $\delta(O)$ are the displacements perpendicular to the surface plane of the metal cations and anions, usually oxygens, respectively, from the bulk positions. The change Δ_{ij} in the interlayer spacing d_{ij} is the difference in the average atomic displacements for two adjacent layers *i* and *j*. The intralayer corrugation, buckling or rumpling is defined as $\eta = [\delta(M) - \delta(O)]/2$, i.e., the vertical displacement of anions and cations away from in-plane positions. The surface plane is indexed i = 1. Thus, if an atom moves up toward the surface then $\delta < 0$, whereas if it moves into the bulk then $\delta > 0$. Measuring the surface rumpling and relaxation requires surface sensitive experimental tools capable of revealing the local atomic displacements with chemical sensitivity.

X-ray photoelectron diffraction (XPD) is a powerful technique which combines information on local chemistry and atomic structure [15]. By measuring the angular anisotropy of core level intensity, one can, by comparison with simulations, deduce the local atomic and chemical environment around each type or species of emitting atom.

In this work, we will use XPD to determine the interplanar relaxation and atomic rumpling in the first five atomic layers of single crystal, Sn-doped Ga₂O₃ (010). Sn-doped Ga₂O₃ has been chosen to increase conductivity and to avoid significant charging during photoemission. Annealing at 823 K yielded a well-ordered surface with (1×1) low energy electron diffraction (LEED) pattern. The comparison between experimental and theoretical XPD results indicates surface rumpling, with O atoms systematically higher, i.e., closer to the surface, than Ga, nominally in the same (010) plane. By the sixth atomic layer, the rumpling tends to zero, and the interplanar distance is that of the bulk structure. The atomic relaxation and rumpling as determined from XPD agrees well with density functional theory (DFT) calculations of the surface and subsurface structure and suggests an $\approx 1 \text{ eV}$ band gap narrowing at the surface. The observed rumpling and relaxation may have important consequences for the surface electronic structure and hence device performance.

II. METHODS

A. Experiment

A commercial, Sn-doped Ga₂O₃ (010) substrate (3.0×10^{18} /cm³) was used. X-ray photoelectron spectroscopy (XPS) and XPD measurements were carried out using a five-axis sample manipulator with sample heating up to 900 K (UHV Design); a focused, monochromatic x-ray source (Al K α = 1486.6 eV); and an ARGUS-128 hemispherical energy analyzer (both ScientaOmicron). In addition, the chamber was equipped with an ion gun for *in situ* sample cleaning and an LEED system. The acceptance angle of the analyzer was 1.0° . The base pressure was kept below 5.0×10^{-8} Pa during the experiments.

The substrate was cleaned by annealing at 823 K for 30 min in vacuum (UHV) to minimize the surface C contamination. The C 1s line at 284.6 eV from the residual contamination was used to calibrate the binding energy (BE) scale. The XPS spectra were measured at 0° (normal emission with respect to the surface). The surface order was verified by LEED. The polar angle is defined as the angle between the analyzer axis and the surface normal. The experimental XPD measurements were performed by varying the azimuthal angle ϕ from 25° to 195° (25° to 180°) in steps of 1° (2°) and the polar angle θ from 10° to 70° (10° to 52°) in steps of 1° (2°) for O 1s (Ga $2p_{3/2}$), exploiting the twofold symmetry. At each angular position, the spectra were acquired in the detector snapshot mode with pass energy of 70 eV, corresponding to an energy window of 10 eV with 128 points. All the measurements were done at room temperature. We have used WINSPEC software to analyze the core level results. A Shirley background was subtracted from Ga $2p_{3/2}$ and O 1s core levels spectra.

B. Simulations

The XPD patterns were simulated by the multiple scattering calculation for diffraction (MSCD) code [16] implemented using a genetic algorithm for surface structure optimization [17,18]. The degree of agreement between the theoretical simulations and the experimental data was evaluated using the well-established reliability factor (*R*-factor) analysis [19,20],



FIG. 2. Proposed cluster model used in the multiple scattering simulations of Ga $2p_{3/2}$ and O 1s emitters. The interlayer spacings are indicated on the right of the figure.

given by

$$R = \sum_{i} \frac{\left[\chi_{c}^{i}(\theta, \phi) - \chi_{e}^{i}(\theta, \phi)\right]^{2}}{\chi_{c}^{i}(\theta, \phi)^{2} + \chi_{e}^{i}(\theta, \phi)^{2}}$$

The quantities χ_c and χ_e are the calculated and experimental XPD anisotropies, respectively, with χ defined as $(I - I_0)/I_0$. Smaller *R*-factors are correlated with better agreement with the experiment. The uncertainty associated with the numerical value of the *R*-factor can be estimated by $R_{\min}\sqrt{2/N}$, where R_{\min} is the minimum *R*-factor and *N* is the number of experimental polar curves. A good *R*-factor for an oxide surface is ≈ 0.30 [18,21].

The phase shifts were obtained using the muffin-tin potential for the Ga and O in the bulk Ga₂O₃ phase. We have used 24 electrons in the valence band: $4s^24p^1$ and $2s^22p^4$ for Ga and O in the XPD simulations, respectively and a band gap of 4.9 eV [6]. The cluster models had a paraboloid shape with 12 Å surface radius and 19 Å depth (nine atomic layers), containing approximately 530 atoms. The schematic in Fig. 2 shows the cluster used for the Ga_2O_3 (010) surface in the XPD simulations. Up to eight scattering events were considered using fourth-order Rehr-Albert approximation [16]. Initial guess for the Debye temperature was obtained from x-ray diffraction results for a bulk Ga₂O₃ [22]. Using bulk interatomic distances, the optimized Debye temperature and inner potential were 730 K and 6.0 eV, respectively. These values are then fixed for the structural optimization. The surface structure was optimized by allowing rumpling and interplanar relaxation parameters over the first six atomic layers.

C. First-principles calculations

The surface was also studied by the means of DFT calculations, with the ABINIT code [23]. The projector augmented wave (PAW) method [24,25] was employed, with PAW atomic data taken from the Jollet, Torrent, and Holzwarth table [26]. The calculations were performed in the framework of the generalized gradient approximation (GGA-PBE) [27]. We used a plane-wave cutoff of 25 hartrees (and 35 hartrees for the double grid). First, we simulated the bulk of β -Ga₂O₃. We performed a full structural optimization of the 20-atom conventional unit cell (space group *C*2/*m*), using a criterion of 1.0×10^{-5} Hartree/Bohr for the maximal component of the atomic forces and 1.0×10^{-7} Hartree/Bohr³ for the maximal component of the stress tensor. The first Brillouin zone was





FIG. 3. The supercell used for the DFT calculation of the 16layer slab. The supercell (periodically repeated along the three directions by the code) is here replicated for a better view of the β -Ga₂O₃ (010) surface. The thin light gray lines are the limits of the supercell (and of the periodic images represented). The thicknesses are those obtained after optimization of the atomic positions.

sampled by a *k*-point mesh of $4 \times 16 \times 8$. The equilibrium lattice constants and angles were a = 12.465 Å, b = 3.088 Å, c = 5.884 Å, and $\beta = 103.69^{\circ}$. The lattice constants are slightly overestimated by 1.5–2.0% with respect to experiment (a = 12.23 Å, b = 3.04 Å, c = 5.80 Å, $\beta = 103.7^{\circ}$ from Ref. [8]; a = 12.214 Å, b = 3.037 Å, c = 5.798 Å, $\beta = 103.83^{\circ}$ from Ref. [22]), which is typical from the GGA approximation. Convergence with respect to the *k*-point mesh was checked. This preliminary bulk calculation is used to validate the numerical scheme and serves as a reference for the calculation of the surface relaxation, the rumpling, and the surface energy.

Then, starting from the theoretical bulk geometry, three slabs of β -Ga₂O₃ (010) are constructed, having 8, 12 and 16 layers, with the surface perpendicular to the *y* direction (Fig. 3). The corresponding supercells contain thus 80, 120, and 160 atoms, respectively, with periodic boundary conditions applied in the three directions. In each case, a large amount of vacuum (equivalent to the slab thickness) is introduced to separate the slabs from their periodic images along *y*. The supercells are then structurally optimized, with their size and shape maintained fixed. In particular, the lattice parameters and angles of the surface unit cell are fixed to their theoretical bulk values (*a*, *c*, β), while the atomic positions are optimized, minimizing the total energy as a function of atomic positions. The optimization of the slabs is stopped when the components of the atomic forces are all below 2.0×10^{-4}



FIG. 4. XPS survey scan of clean β -Ga₂O₃ (010) single crystal measured as received and after annealing at 823 K.

hartree/bohr ($\approx 0.01 \text{ eV/Å}$). The Brillouin zone associated with the supercells are sampled with a 4 × 2 × 8 *k*-point mesh. Convergence with respect to the vacuum thickness was checked on the eight-layer slab: a difference of only 0.3 meV on the total energy of the slab was obtained between vacuum thicknesses equivalent to 8 and 16 layers. The surface energy of the (010) surface is very well converged with the slab thicknesses used (eight-layer slab: 1.40 J/m², 16-layer slab: 1.41 J/m²).

All the first-principles calculations are performed using pure β -Ga₂O₃ (no Sn impurity): all the systems studied by DFT are thus electronic insulators.

Finally, the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06) [28] has been used on the bulk of β -Ga₂O₃ and on the eight-layer slab in order to get a better estimation of the band gap. This calculation has been performed using the Vienna *ab initio* simulation package VASP 5.4 [29,30] in the PAW formalism [24], with a plane-wave cutoff of 450 eV. The densities of states obtained with VASP, as well as the *k*-point meshes used in those calculations, are presented in the Supplemental Material [31].

III. RESULTS AND DISCUSSION

A. XPS

XPS was used to check the surface stoichiometry and chemistry. Figure 4 shows survey spectra for the β -Ga₂O₃ (010) single-crystal surface measured as received and after annealing at 823 K. There is evidence for surface C, approximately half the number of Ga atoms. This decreases to 0.3 after annealing at 823 K. The temperature dependence of the C 1s to Ga 2p intensity ratio is plotted in the Supplemental Material [31], Fig. S1. The detailed XPS scans shows a stoichiometry consistent with the Ga₂O₃. Minimal C contamination was observed after annealing as can be seen from Fig. 4.

The Ga $2p_{3/2}$ and O 1s XPS spectra for the (1×1) surface measured at normal emission are shown in Fig. 5 for the sample as received and after annealing at 823 K. Each core



FIG. 5. Shows Ga $2p_{3/2}$ and O 1s spectra obtained from the single-crystal Ga₂O₃ (010) [(a), (b)] as received and [(c), (d)] after annealing at 823 K in vacuum.

level, i.e., Ga $2p_{3/2}$ (BE = 1119 eV), O 1s (BE = 531 eV), and C 1s (BE = 284.6 eV), was analyzed using Voigt functions and a Shirley background subtraction. The Ga $2p_{3/2}$ spectra [Figs. 5(a) and 5(c)] can be fitted by a single component corresponding to Ga_2O_3 . The background at low binding energy for the Ga spectra is due to the proximity of the O KLL Auger emission. The Ga $2p_{3/2}$ peak shifts as a function of annealing temperature. In the as-received sample, BE is 1118.43 eV, shifting to 1118.18 at 823 K. Annealing can create oxygen vacancies (V_{Ω}) . Positively charged oxygen vacancies $(V_{\Omega}^{..})$ free two electrons which, if localized on neighboring Ga atoms, should give rise to a second, low-binding-energy (LBE) component in the Ga 2p spectrum similar to Ti reduction in SrTiO₃ [32,33]. Ramana *et al.* [34] reported two Ga $2p_{3/2}$ components at 1117.5 and 1118.5 eV for a sample following ion beam sputtering and annealing at 500 °C, and they ascribed them to metallic, i.e., reduced, Ga and Ga₂O₃, respectively. Here we observe only a single component, suggesting that the annealing process has not significantly reduced the surface which may therefore be considered stoichiometric. On the other hand, straightforward *n*-type doping would shift the energy levels to higher BE, whereas we measure a shift of 0.25 eV to lower BE. We suggest that the improved conductivity after annealing results in a reduction of slight residual charging due to the photoemission process.

The core level spectra of O 1s also reveals information about the surface chemistry of Ga₂O₃. The O 1s peak is asymmetric, while the main peak is centered at a BE of 531.12 eV, and there is a small shoulder at a BE of 532.43 eV as shown in Figs. 5(b) and 5(d). The main peak is associated with Ga-O bonding in the highest oxidation state of Ga (Ga³⁺). The less intense contribution at higher BE is associated to either carbonyl or hydroxyl groups [34], which are adsorbed onto the surface. They are assumed not to affect the XPD pattern and are not further considered here. A similar shift in BE to that of the Ga 2p is observed. The BE of the main (shoulder) 1s peak at normal emission was 531.24 eV (532.43 eV) and 531.04 eV (532.23 eV), for as received and after annealing



FIG. 6. LEED patterns for $Ga_2O_3(010)$ annealed at 823 K for 30 min, measured at an electron primary energy of (a) 100 and (b) 200 eV.

at 823 K, respectively. Thus, the core-level shifts were 0.20 and 0.38 eV, follow closely those observed on Ga $2p_{3/2}$ peak, confirming that the shift is not due to local chemistry but can be explained by an overall electrical shift which we ascribe to residual charging.

B. LEED

No LEED pattern was observed on the as-received sample, presumably due to the surface contamination, evidenced by the stronger C 1s XPS intensity in Fig. 4. Figures 6(a) and 6(b) show the LEED patterns measured at 100- and 200-eV electron primary energy after annealing at 823 K for 30 min. The LEED spots are sharp and the diffuse background is weak. The patterns shows a $p(1 \times 1)$ surface. Both are the signature of a high degree of surface ordering. The pattern has twofold symmetry and low background, indicating a well-ordered surface of monoclinic Ga₂O₃ (010) surface, suitable for XPD analysis [35].

C. XPD

Using Al K α excitation, the kinetic energies (KE) of the Ga $2p_{3/2}$ and O 1*s* electrons are 368 and 956 eV, respectively. As forward scattering dominates diffraction patterns for photoelectrons with high KE, the main XPD peaks can be directly related to the nearest-neighbor scattering directions, although, as we will see, the information contained in the XPD patterns is much richer, probing the atomic positions in space up to five layers below the surface.

In Figs. 7(b) and 7(c), we present the raw experimental Ga $2p_{3/2}$ and O 1s XPD patterns. The data are presented in the form of a projection shown in Fig. 7(a) or diffractogram in which the angular coordinates (θ, ϕ) have been transformed into a (r, α) plot. The (θ, ϕ) scale is annotated in the experimental plots with normal emission at the center and more grazing angle emission at the edge of the diffractogram. Based on the twofold symmetry expected for a (010) orientation, the XPD data have been symmetrized to provide the full 2π diffractograms shown in Figs. 7(b) and 7(c). In order to maintain the same angular resolution over the whole scan, the polar angle starts at 10° off normal. The anisotropy, as defined by $\chi = (I - I_0)/I_0$ is given in the bottom left of each panel. The values are consistent with typical XPD anisotropies reported in the literature [15,18]. Bright spots are visible, typical of forward focusing along dense crystal axes, together with weaker intensity structures.



FIG. 7. (a) Experimental XPD for Ga₂O₃(010) obtained with 1486.7 eV photon energy for raw data and symmetrized data of the (b) Ga $2p_{3/2}$ and (c) O 1*s* emission. The XPD anisotropy, defined by $\chi = (I - I_0)/I_0$, is 0.2 for Ga $2p_{3/2}$ and 0.4 for O 1*s*, respectively. Polar (θ) and azimuthal (ϕ) angles are indicated in degrees.

D. Simulations

The XPD simulations first require us to determine two nonstructural parameters: The Debye temperature and the inner potential. We note that in contrast to LEED I-V simulations, for XPD the simulation uses only an average Debye temperature for the Ga and O atoms [36]. These have been refined against experiment using the bulk structure. The optimized Debye temperature and inner potential were 730 K and 6.0 eV, with *R*-factors 0.34 ± 0.09 , and 0.44 ± 0.08 , for the Ga $2p_{3/2}$ and O 1*s*, respectively.

Each (010) atomic layer contains five inequivalent atomic sites, two Ga atoms, and three oxygen atoms (Ga_I, Ga_{II}, O_I, O_{II}, and O_{III}). Each Ga_I is fourfold coordinated (tetrahedral environment) while each Ga_{II} is sixfold coordinated (octahedral environment). Each OI is threefold coordinated to Ga atoms, with these three Ga being at the centers of two oxygen octahedra and one oxygen tetrahedron. Each O_{II} is threefold coordinated to Ga atoms, with these three Ga being at the centers of one oxygen octahedron and two oxygen tetrahedra. Each O_{III} is fourfold coordinated to Ga atoms, with these four Ga being at the centers of three oxygen octahedra and one oxygen tetrahedron [37]. The planar relaxation can be written as the weighted average of the individual atomic displacements making up the (010) layer, $\beta = [\delta(Ga_I) + \delta(Ga_{II}) +$ $\delta(O_I) + \delta(O_{II}) + \delta(O_{III})]/5$ and the interplanar relaxation as $\Delta_{ij} = \beta_j - \beta_i$. The rumpling is calculated as the difference of the average Ga and O displacements, $\eta = [\overline{\delta}(Ga) - \overline{\delta}(O)]/2$. Thus, for a given atomic plane, if the Ga atoms are shifted above the O atoms then $\eta_i < 0$, whereas if the O atoms are nearer to the surface than the Ga atoms then $\eta_i > 0$.



FIG. 8. Comparison of symmetrized experimental (a) Ga $2p_{3/2}$ and (b) O 1s XPD patterns with the best multiple scattering simulations after optimization of Debye temperature, inner potential, interplanar distances, gap, and rumpling for (c) Ga 2p and (d) O 1s emitters.

Considering the first six atomic layers gives 30 distinct, vertical atomic positions to be determined. Given the surface sensitivity of XPD, it is the structure of the first two layers which dominates the expected XPD signal; nevertheless, this is a large parameter space. Note also that each atom type (e.g., Ga_I or O_{II}) must have the same vertical position everywhere in a given layer in order to calculate the diffraction pattern. To reduce the chances of finding a false minimum, we have used a genetic algorithm approach [17,18]. Figure 8 compares the optimized XPD simulations with the symmetrized experimental data. The atomic displacements with respect to the bulk positions in successive (010) planes are given in Tables I and II.

The atomic displacements, interplanar relaxation, and rumplings are also calculated from the optimized atomic positions



FIG. 9. Interplanar relaxation Δ_{ij} and rumplings η_i obtained by DFT, as a function of slab thickness. Only the data relative to layers that do not exceed the middle of the slab are displayed.

obtained by DFT for the three slabs. Figure 9 shows how these quantities converge with the slab thickness. The atomic displacements are given in parentheses in Tables I and II. The agreement between experiment and DFT is rather good with the exception of the fourth layer, in which the displacements as measured by XPD are very large. We think that this is most likely due to the extreme surface sensitivity of the XPD measurements. The optimized vertical atomic positions in deeper layers contribute less to the quantitative *R*-factor than the first few layers and can therefore vary more than expected. Here, the fourth layer shifts forming the bulk positions are larger than expected.

As can be seen from Tables I and II, the quantitative atomic displacements determined by the Ga 2p and O 1s XPD are qualitatively the same and quantitatively similar. The differences can be attributed, at least partially, to the relative depth sensitivity of Ga 2p and O 1s photoelectrons. The latter, with higher KE, are more sensitive to layers deeper in the bulk, whereas the Ga 2p photoelectrons are more sensitive to the top most layers. From Fig. 8, all of the the main anisotropies in the experimental data are well reproduced by the optimized simulations, reflected by the good *R*-factors 0.29 and 0.40 for Ga 2p and O 1s emission. The sign of Δ and η alternates over the first few atomic layers. The relaxation and rumpling of the

TABLE I. Changes in the atomic positions of the Ga_I , Ga_{II} , O_I , O_I , and O_{III} atoms in the first six atomic layers as determined by the Ga 2*p* XPD simulations. Negative values indicate a shift up toward vacuum, and positive values indicate a displacement down into the bulk. The surface is layer 1. All displacements are in Å. DFT values are in parentheses (16-layer slab).

	Layer					
	1	2	3	4	5	6
$\delta(Ga_I)$	0.14 (0.23)	-0.26 (-0.13)	0.01 (0.00)	-0.18 (-0.04)	-0.00 (0.00)	-0.01 (-0.02)
$\delta(Ga_{II})$	0.15 (0.29)	-0.37 (-0.12)	0.12 (0.07)	-0.06(-0.03)	0.02 (0.02)	-0.01 (-0.01)
$\delta(O_I)$	-0.08(-0.10)	0.49 (0.09)	-0.01(-0.05)	0.04 (0.03)	-0.03 (-0.01)	0.02 (0.01)
$\delta(O_{II})$	-0.00(-0.10)	-0.11 (-0.09)	-0.01 (-0.03)	0.01 (0.01)	-0.01(-0.02)	0.01 (0.00)
$\delta(O_{III})$	-0.15 (-0.11)	0.11 (0.05)	-0.01 (-0.04)	-0.01 (-0.01)	-0.00(0.00)	-0.00 (0.00)

displacements are in A. DFT values are in parentneses (10-layer slab).						
	Layer					
	1	2	3	4	5	6
$\delta(Ga_I)$	0.10 (0.23)	-0.13 (-0.13)	0.02 (0.00)	-0.31 (-0.04)	-0.00 (0.00)	-0.01 (-0.02)
$\delta(Ga_{II})$	0.26 (0.29)	-0.18 (-0.12)	0.04 (0.07)	-0.18(-0.03)	0.02 (0.02)	-0.01(-0.01)
$\delta(O_I)$	-0.14(-0.10)	0.12 (0.09)	-0.04(-0.05)	0.08 (0.03)	-0.03 (-0.01)	0.02 (0.01)
$\delta(O_{II})$	-0.00(-0.10)	-0.09(-0.09)	-0.03(-0.03)	0.06 (0.01)	-0.01(-0.02)	0.01 (0.00)
$\delta(O_{\rm III})$	-0.17 (-0.11)	0.09 (0.05)	-0.03 (-0.04)	-0.06 (-0.01)	-0.00(0.00)	-0.00(0.00)

TABLE II. Changes in the atomic positions of the Ga_I, Ga_{II}, O_I, O_{II}, and O_{III} atoms in the first six atomic layers as determined by the O 1*s* XPD simulations. Negative values indicate a shift up toward vacuum, whereas positive values indicate a displacement down into the bulk. All displacements are in Å. DFT values are in parentheses (16-layer slab).

deeper layers can only be calculated for the thicker 12- and 16-layer slabs because of mirror symmetry.

Using the atomic displacements reported in Tables I and II, we have calculated the rumpling η_i of the first six atomic layers and the interlayer relaxation Δ_{ij} . The rumpling and relaxation values are given in Tables III and IV, respectively, and compared to the DFT values.

The rumpling magnitude is large in the first two layers (0.11-0.14 and 0.10-0.18 Å, respectively), which agrees quite well with the DFT magnitudes of 0.18 and 0.07 Å, but decreases to almost zero by the sixth layer. This is in good agreement with the calculations of Bermudez [37]. The XPD simulations show significant interlayer relaxation between the first few atomic layers but by the fifth atomic layer, the relaxation is small, giving an interlayer distance similar to that of bulk Ga₂O₃. Thus, the maximum interlayer relaxation is 8% of the bulk interlayer distance. The bulk structure is attained by the sixth layer. Figure 10 shows a sectional view of the surface layers.

As can be seen from Table IV, the interplanar relaxation deduced from the O 1s XPD analysis is lower at the surface than for the Ga 2p results although the qualitative trend is the same. We suggest that this may be due to the higher surface sensitivity of the Ga 2p (KE = 368 eV) compared to the O 1s (KE = 956 eV). The inelastic mean free paths, as calculated using TPP-2M algorithm [38], are 1.94 and 0.99 nm, respectively.

The atomic arrangement at the surface of $Ga_2O_3(010)$ therefore undergoes significant relaxation compared to the bulk over the first five or six layers. This is quite extensive and is fully compatible with typical 2D structures capable

TABLE III. Layer rumpling η_i determined by the atomic displacements obtained from the Ga 2*p* and O 1*s* XPD and from DFT (16-layer slab). For a given atomic plane, if the Ga atoms are shifted above the O atoms then $\eta_i < 0$; if the O atoms are nearer to the surface than the Ga atoms then $\eta_i > 0$. All values in Å.

	Ga $2p_{3/2}$	O 1 <i>s</i>	DFT
$\overline{\eta_1}$	0.11	0.14	0.18
η_2	-0.18	-0.10	-0.07
η_3	0.04	0.03	0.03
η_4	-0.07	-0.14	-0.02
η_5	0.01	0.01	0.01
η_6	-0.01	-0.01	-0.01

of supporting, for example, surface currents. As a result, the surface electronic structure cannot be predicted on the basis of simple bulk termination. Instead surface order via relaxation and rumpling (or buckling) may induce significant electronic reconstruction and play an important role in, for example, channel conductivity in highly doped Ga_2O_3 .

E. Electronic surface states

The band gap in bulk Ga₂O₃ has been measured between 4.54 and 4.90 eV [39–42]. Calculations based on the HSE06 hybrid functional by Peelaers and Van de Walle (direct gap: 4.88 eV; indirect gap: 4.84 eV) [39] reproduce well these experimental values (these authors use for that a mixing parameter of 35% between the Hartree-Fock exchange energy and the GGA-PBE). Here, within the GGA-PBE functional, we find for the bulk of Ga₂O₃ a band gap of \approx 2.0 eV. This value is strongly underestimated with respect to experiment, typical when using the GGA functional. However, despite such underestimation, we expect that the GGA provides a correct tendency concerning the possibility of surface states, and thus the reduction of the band gap $E_g(E_g^{slab} < E_g^{bulk})$.

Figure 11 displays the GGA-PBE electronic density of states (e-DOS) of the eight-layer slab, compared to that of the bulk. We observe that, from the bulk to the slab, this band gap E_g is reduced by about 1 eV (bulk: $E_g^{\text{bulk}} = 2.1$ eV; slab: $E_g^{\text{slab}} = 1.1$ eV), due to the appearance of a band of occupied states above the valence band maximum (VBM) of the bulk. An additional calculation of this eight-layer slab using the HSE06 functional (in the geometry obtained from the GGA-PBE structural optimization) is presented in the Supplemental Material, Fig. S2 [31]: The e-DOS obtained with HSE06 is very similar to that obtained with the PBE functional (same shape and width of the valence band, same

TABLE IV. Interlayer relaxation Δ_{ij} up to the sixth atomic layer from the surface. All values are given in Å. The DFT values are taken from the 16-layer slab.

	Ga $2p_{3/2}$	O 1 <i>s</i>	DFT
Δ_{12}	-0.11	-0.05	-0.08
Δ_{23}	+0.12	0.03	0.03
Δ_{34}	-0.06	-0.07	0.00
Δ_{45}	0.04	0.08	0.00
Δ_{56}	0.00	0.00	0.00



FIG. 10. Relaxation and rumpling for the first five atomic layers in β -Ga₂O₃ unit cell obtained from the Ga $2p_{3/2}$ XPD. The relaxed atomic layer positions are indicated by dotted lines.

band of occupied states above the bulk VBM), except that the band gap is enhanced to $E_g^{\text{slab}} = 2.7 \text{ eV}$ (for a mixing parameter between Hartree-Fock exchange and PBE exchange of 0.25) and 3.5 eV (for a mixing parameter of 0.35). This mixing parameter of 0.35 is the one used by Peelaers and Van de Walle [39] in their calculation of bulk β -Ga₂O₃. We have also performed a HSE06 calculation on the bulk of β -Ga₂O₃ (using also the geometry obtained from the GGA-PBE structural optimization): it provides a band gap $E_c^{\text{bulk}} =$ 3.8 eV (with a mixing parameter of 0.25) and 4.5 eV (with a mixing parameter of 0.35); see Fig. S3 and Table S1 in the Supplemental Material. We see that the band-gap reduction from the bulk to the slab is the same with HSE06 than with the GGA-PBE (\approx 1 eV). These additional calculations with the HSE06 functional further suggest that the GGA-PBE is suitable to describe the atomic and electronic structures of the surface, at the exception of the band gap that the GGA-PBE underestimates by about 2.8 eV.



FIG. 11. Electronic density of states (GGA-PBE) of the eightlayer slab (top), compared to that of the bulk (bottom), calculated using the tetrahedron method. The zero of the energies corresponds to the energy of the highest occupied state of the slab. The valence band maximum of the bulk has been aligned on the valence band maximum of the slab. Inset: Enlargement of the band of surface states.



FIG. 12. Electronic band structure (GGA-PBE) of the eight-layer slab (along a path in the surface Brillouin zone of the monoclinic supercell). The surface states are in red.

The band of occupied states above the bulk VBM is rather broad ($\approx 0.8 \text{ eV}$) and probably consists of surface states made of some 2p orbitals of surface oxygen atoms, in relation with the charge-transfer nature of the gap in Ga_2O_3 . Figure 12 shows the GGA-PBE electronic band structure obtained on the eight-layer slab: We see that these occupied gap states (in red on Fig. 12) originate from one band (in fact twice degenerate in the calculation due to the presence of surface states on both surfaces of the slab), which appears as being separated from the rest of the valence band by a very small gap ($\approx 0.1 \text{ eV}$). Note that the associated e-DOS exhibits two peaks, at the energy minimum and at the energy maximum of this band (see inset of Fig. 11), like the density of states of a one-dimensional system of electrons. This suggests that the electrons occupying this band may be spatially confined along a linear chain at the surface.

The situation is made clear by inspecting the layer-by-layer orbital projected e-DOS, displayed on Fig. 13: We observe that the band of occupied states lying above the bulk VBM is spatially confined to the surface layers of the slab (and a little bit on the subsurface layers): this is a band of surface states. It consists of 2p orbitals on oxygen atoms, which may have been destabilized by the reduction of the Madelung potential at the surface. The band gap narrowing predicted as a result of the surface structure should therefore modify the barrier heights for both electron and hole conduction in a Ga₂O₃-based heterostructure, for example, in a field effect transistor or power diode, which may have important consequences for electrical performance. Following Higashiwaki *et al.*, the 1-eV narrowing of the band gap at the surface corresponds to a 5-MV/cm breakdown field [43].

Finally, we scrutinize the spatial localization of the surface states. First, O_I and O_{III} surface oxygens do not contribute to the band of surface states: The surface states are only present on the orbital-projected e-DOS associated with surface oxygen atoms of type O_{II} . To confirm this spatial localization, we extract from the DFT calculation the Kohn-Sham wave function, at the Γ point, associated with the band of surface states $[\Psi_{\Gamma}^{surf}(\vec{r})]$, and plot on Fig. 14 an isosurface of $|\Psi_{\Gamma}^{surf}(\vec{r})|^2$: We observe that indeed $|\Psi_{\Gamma}^{surf}(\vec{r})|^2$ is spatially



FIG. 13. Orbital-projected electronic density of states (GGA-PBE) of the eight-layer slab, plotted for each layer of the slab, calculated using the tetrahedron method. Layers 1 and 8 are surface layers.

confined on the surface oxygens of type O_{II} and consists of 2p orbitals lying in plane and oriented along the *c* direction. Since the surface O_{II} atoms are also aligned along c, we have a linear chain of 2p orbitals, probably slightly hybridized with each other (in relation with the fact that the band exhibits a dispersion of $\approx 0.8 \text{ eV}$). Note that, however, the O_{II} oxygens are rather distant from each other (≈ 2.91 and 2.98 Å). The confinement of the surface states along this linear chain of O_{II} surface oxygens (quasi-one-dimensional system of electrons) gives an explanation to the shape of the e-DOS, as pointed above (Fig. 11, inset). Note that the surface states are also present and spatially localized on the same atoms (surface O_{II}) even in the absence of relaxation and rumpling, i.e., when the atoms are placed in their ideal bulk positions. However, in that case, their energy lies higher in the gap. The rumpling and relaxation in the surface layers therefore modify the electronic structure at the surface but do not induce qualitative changes with respect to the bulk.



FIG. 14. Two views of the optimized eight-layer slab, with an isosurface (yellow) of the surface state $(|\Psi_{\Gamma}^{surf}(\vec{r})|^2)$ associated with the top surface (the isovalue is chosen as the tenth of the maximal value).

The slab has been relaxed by the DFT calculations, but, from these calculations, it is not possible to say whether a more stable reconstructed configuration exists for this surface. Since the appearance of the 1D chain of states on the $O_{\rm II}$ atoms is associated to the present geometry, a different surface reconstruction, due to, for example, epitaxial strain, could accentuate or attenuate the 1D electronic state. One obvious experiment would be angle-resolved photoemission to map out the band structure.

IV. CONCLUSION

A detailed XPD investigation of the surface structure of Ga_2O_3 (010) is presented. After annealing in vacuum at 823 K, a sharp (1 × 1) LEED pattern with twofold symmetry of the monoclinic structure is observed, indicating a clean, ordered surface. The stoichiometric surface state is confirmed by XPS analysis. The angular anisotropy of the Ga 2p and O 1s core levels are recorded in the same ultrahigh vacuum system. Maximum anisotropy of 0.2 and 0.4, respectively, is observed. Multiple scattering calculations implemented using a genetic algorithm are used to refine a structural model of the large parameter space with lowest *R*-factor. A good agreement (*R*-factor 0.29 for the Ga 2p XPD) is found for a structural model presenting both rumpling and interlayer relaxation. At the surface, the magnitude of the atomic rumpling or buckling

is 0.11–0.14 Å and the interlayer relaxation can reach 8% of the bulk interlayer separation (1.52 Å). Both rumpling and interplanar relaxation tend to zero going into the bulk. Within the XPD uncertainty, the bulk structure is reached by the sixth atomic layer. DFT calculations confirm the experimental result of surface rumpling and relaxation, and give evidence for significant reduction of the band gap at the surface, due to oxygen 2*p*-type surface states destabilized with respect to the valence band maximum of the bulk. These surface states originate from one single band and are spatially localized on surface oxygen atoms of type O_{II}. From the band gap narrowing, we estimate a surface breakdown field of the order of \approx 5 MV/cm.

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