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Experimental and Theoretical Investigation of the Surface Electronic Structure of $\text{ZnGa}_2\text{O}_4(100)$ Single-Crystals

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Herein, a detailed experimental and theoretical investigation on the surface electronic structure of $\text{ZnGa}_2\text{O}_4(100)$ bulk single-crystals, with a special emphasis on the surface preparation, is presented. The surface crystallizes in the bulk-derived structure, even at low annealing temperatures. Thermal treatments in ultra-high vacuum have detrimental effects, as they cannot remove the carbon contamination and induce substantial zinc losses, further exacerbated by sputtering. A short sputtering duration and annealing in oxygen atmosphere dramatically reduce the zinc and oxygen losses in the crystal surface, leading to a contamination-free, crystalline surface of nearly stoichiometric composition. The investigation of the valence states along the high symmetry directions of the Brillouin zone compares favorably with *ab initio* pseudopotential calculations, indicating a good surface quality and overall agreement with theory. An in-depth analysis of the measured and simulated valence band peak intensities reveals difficulties associated with the precise description of the metal-oxygen hybridization. This study provides a first fundamental understanding of the electronic structure of ZnGa_2O_4 , while also indicating that the surface thermal instability is a challenging task that should be taken into account for the fabrication of heterostructures based on ZnGa_2O_4 .

1. Introduction

Among the ultra-wide band gap transparent semiconducting oxides (TSOs), $\beta\text{-Ga}_2\text{O}_3$ has attracted a lot of interest because its pseudo-direct band gap of 4.85 eV yields a high breakdown voltage and provides transparency in the UV-range.^[1–5] These properties are accompanied by a good thermal stability, allowing the growth of bulk $\beta\text{-Ga}_2\text{O}_3$ single crystals from the melt.^[6,7] Accordingly, $\beta\text{-Ga}_2\text{O}_3$ is seen as a potential candidate for high-power electronic devices and deep-UV optoelectronic devices.^[8,9] The drawbacks are its mechanical, optical, and thermal anisotropies, due to the monoclinic crystal structure, which make the fabrication of substrates and devices a challenging task.^[10]

For applications, a material with a band gap as wide as that of $\beta\text{-Ga}_2\text{O}_3$, but of higher symmetry, would therefore be highly desirable. Recently, Galazka et al. reported bulk, melt-grown ZnGa_2O_4 (ZGO) single-crystals of high structural quality,

from which differently oriented insulating and semiconducting wafers could be prepared.^[11,12] ZGO crystallizes in a cubic spinel structure (Fd $\bar{3}m$ space group), as illustrated with a ball and stick model in **Figure 1**. Spinel refers to a class of compounds with a chemical formula AB_2X_4 , in which A is a divalent cation like Zn, B is a trivalent cation like Ga, and X is a divalent anion like O. In the normal spinel structure of ZGO, Zn occupies the tetrahedral sites, while Ga occupies the octahedral sites. During growth from the melt, at high temperatures, the occupation of octahedral, and tetrahedral sites is random.^[11] A long cool down stabilizes the normal spinel structure, while antisite defects are introduced by shorter cool down times. Antisite defects lead to n-type conductivity with free electron concentrations in the order of $10^{18}\text{--}10^{19}\text{ cm}^{-3}$. Upon post-growth annealing at 800–1400 °C for 10 h or 700 °C for 40 h in oxidizing atmosphere ZGO crystals can turn into an insulating state.^[11–13] Thanks to its cubic spinel structure, ZGO has isotropic thermal and optical properties. The optical band gap of ZGO was found to be 4.6 eV wide, close to that of $\beta\text{-Ga}_2\text{O}_3$ and no preferred cleavage plane was observed.^[11,12]

These promising characteristics resulted in extensive research activities on the fundamental physical properties of the

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 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/pssb.202100452>.

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DOI: 10.1002/pssb.202100452

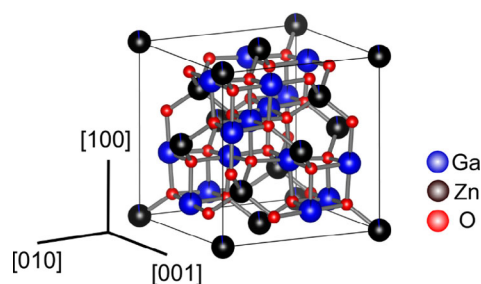


Figure 1. Ball and stick model of the ZnGa_2O_4 unit cell with Ga in blue, Zn in black, and O in red.

material,^[14–16] as well as the fabrication of ZGO based devices such as thin film transistors (TFTs),^[17] metal-oxide field-effect transistors (MOSFETs),^[18] thin-film phototransistors, and self-powered solar-blind UV photodetectors.^[19,20] However, a detailed investigation of the electronic structure of ZGO by photoelectron spectroscopy is still lacking, probably owed to the fact that no bulk crystals were available until recently.

Angle-resolved photoelectron spectroscopy (ARPES) offers a direct way of probing the electronic structure of surfaces and interfaces and was already used to detail the electronic structure of other TSOs such as: ZnO ,^[21,22] CdO ,^[23,24] In_2O_3 ,^[25,26] $\beta\text{-Ga}_2\text{O}_3$,^[27–29] and $\epsilon\text{-Ga}_2\text{O}_3$.^[30] However, ARPES requires a contamination-free surface of single-crystalline quality, which can generally be achieved by in situ growth of thin films or careful in situ surface treatment of substrates. In any case, one needs to evaluate if the measured electronic structure is truly originating from ZGO or from a defective surface. Therefore, we present an investigation of the electronic structure of a ZGO(100) bulk single-crystal prepared by in situ sputtering and annealing, while also delving deep into the effects of the surface preparation.

In the first section, we address the effectiveness of the cleaning procedure and changes to the chemical composition by employing X-ray photoelectron spectroscopy (XPS). In particular, we compare surfaces resulting from annealing in ultra-high vacuum (UHV), annealing in oxygen atmosphere and sputtering. Low-energy sputtering and low temperature annealing in oxygen atmosphere is sufficient to prepare a near stoichiometric surface. We demonstrate, by using low-energy electron diffraction (LEED), that low temperature annealing is sufficient to obtain a crystalline surface, albeit no reconstruction is present.

In the second section, we focus on the electronic structure of the near stoichiometric surface, prepared in oxidizing conditions, utilizing XPS again. We present a detailed analysis of the core-level spectra observing that the surface preparation induces changes to the sample doping, evident by a repositioning of the Fermi-level. Peak fitting of the core-level is used to explain changes in the surface stoichiometry during the surface preparation, while angle-dependent measurements show no signs of a band bending.

In the third section, we show the valence band structure resolved by APRES along the high symmetry directions of the surface Brillouin zone, finding clear dispersion of the O 2p states and the valence band maximum.

In the fourth and fifth sections, ab initio calculations of the band structure are presented. Starting with the calculated bulk

band structure we observe a good agreement with the experiment if we take into account the projection of bulk bands to the surface. However, since the experimental surface is only near stoichiometric, we refine the results by discussing possible surface structures and comparing them to the experimentally obtained data.

2. Results

2.1. Comparison of the Surface Preparation in UHV Versus Oxygen Atmosphere

To evaluate the effectiveness of the surface preparation, we first examine the chemical composition and the removal of adventitious carbon by using XPS. For details on different steps of the surface preparation, see the Experimental Section. **Figure 2** shows the C 1s core-level regions for each applied surface treatment step in a) UHV and b) oxygen atmosphere. In the spectra of the as loaded samples, we observe a small shoulder in the C 1s core-level on the high binding energy side of the main peak (C–H, C–C), whose origin is the C–O binding states of carbon. These C 1s spectra are very similar to those of adventitious carbon, which adsorbed when the samples were in contact with air.^[31,32]

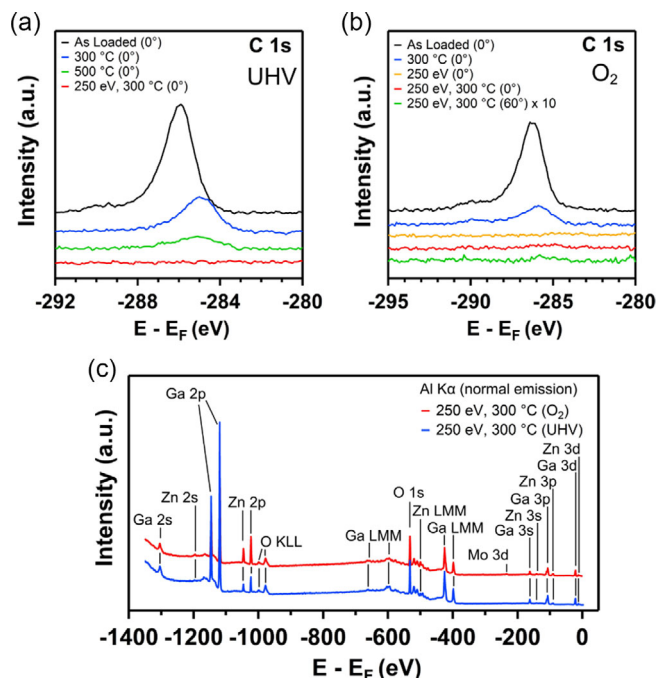


Figure 2. The C 1s core-level region is shown in dependence of the cleaning steps a) in ultra-high vacuum (UHV) conditions and b) when the sample is annealed in oxygen atmosphere (O_2). Spectra were acquired with an excitation energy of 1486.7 eV in normal emission (0°), while in (b) an additional scan in grazing emission (60°) after sputtering and annealing is shown. The intensity was multiplied by a factor of 10 to account for the overall lower intensity in grazing emission. c) Normal emission survey scan after sputtering and annealing, comparing annealing in UHV conditions and oxygen atmosphere. The Mo 3d peak observed is due to the sample holder and has not influenced the chemical analysis.

Annealing the first sample in UHV at 300 °C for 30 min and afterward 500 °C for 30 min reduced the amount of carbon present on the first sample, but was not able to reduce it to below the detection limit (Figure 2a). After a single sputtering step of 250 eV for 10 min and annealing at 300 °C for 15 min it was possible to completely remove the carbon contamination. The normal emission scan in Figure 2c (blue line) shows the absence of any other contamination-related features. For details on the potential impurity species and their expected concentrations see the Supporting Information. However, the chemical composition analysis summarized in **Table 1** reveals changes in the surface stoichiometry. The sensitivity factors of Wagner were used to normalize the fitted peak areas^[33] While absolute values may suffer from inaccuracies, the relative trend is correct within a few percent. The stoichiometric composition of the crystal was checked prior to our experimental investigations.^[11]

With increasing annealing temperature, the amount of Zn in the subsurface was gradually reduced. Annealing at 300 °C decreased the oxygen amount compared to the as loaded sample, but increasing the temperature to 500 °C caused no further reduction. After sputtering and annealing (250 eV, 300 °C (UHV)), around 66 % of the Zn and around 20% of the oxygen was lost. Continued sputtering of the sample with higher energy ions (500 eV, 20 min) revealed an increase of the Zn content and no further change can be observed with increased sputtering duration (500 eV, 40 min). This indicates a preferential sputtering of oxygen and gallium with respect to Zn, leading to a relative increase of Zn. However, annealing the sample again at 300 °C for 15 min (500 eV, 300 °C (UHV)) restores the composition to the previous one before the prolonged sputtering.

We conclude from these observations that the reducing conditions of UHV annealing lead to a significant reduction of Zn in the surface, already at low annealing temperatures. Sputtering was shown to be necessary to remove carbon. While Ga and O are preferentially sputtered with respect to Zn, the necessary follow up annealing (to achieve crystallinity) favors Zn deficiency, leading to a non-stoichiometric surface with about 66% of Zn missing.

To obtain a clean and ordered surface with approximately bulk stoichiometry, we treated a new sample in oxidizing conditions. To avoid excessive Zn loss, the annealing temperature was limited to 300 °C and the sputtering time was reduced to 5 min.

While the initial annealing at 300 °C for 30 min resulted in a reduction of the C 1s intensity (Figure 2b), sputtering was also in

Table 1. Chemical composition analysis by XPS of ZGO(100) prepared in UHV.

	Zn [%]	Ga [%]	O [%]
Nominal ZGO composition	14.3	28.6	57.1
As loaded	15	23.4	61.6
300 °C	12.7	31.3	56
500 °C	6.8	37.9	55.3
250 eV, 300 °C	5	42	53
500 eV, 20 min	9.6	40.6	49.8
500 eV, 40 min	9.6	41.2	49.2
500 eV, 300 °C	5	42.8	52.2

Table 2. Chemical composition analysis by XPS of ZGO(100) prepared in oxygen atmosphere.

	Zn [%]	Ga [%]	O [%]
Nominal ZGO composition	14.3	28.6	57.1
As loaded	15.6	24	60.4
300 °C	15.5	27.8	56.7
250 eV, 300 °C	13	31.5	55.5

this case necessary to achieve a contamination-free surface. After sputtering and a follow up annealing at 300 °C for 15 min, the carbon signal was reduced below the detection limit, even when the surface sensitivity was enhanced by grazing emission. The survey scan after sputtering and oxygen annealing shown in Figure 2c also indicates the absence of other contaminations. The Mo 3d peak associated with the sample holder has no influence on the subsequent analysis.

The annealing in oxygen atmosphere successfully reduced the Zn loss, as shown in **Table 2**. A further beneficial effect of the oxygen annealing is the reduction of the sputtering time necessary to clean the surface, which led to a reduction of the Zn and O amounts lost due to selective sputtering. The follow-up annealing in oxygen atmosphere minimally changed the composition, thus yielding a surface with nearly stoichiometric composition.

To evaluate the surface crystallinity, we show in **Figure 3** the LEED diffraction pattern of the ZGO surface treated in oxygen atmosphere. No diffraction pattern is observable for the as loaded sample in Figure 3a, while annealing at 300 °C for 30 min in oxygen atmosphere results in sharp diffraction spots, shown in Figure 3b. Sputtering and subsequent annealing resulted in no qualitative change of the diffraction pattern in Figure 3c. The diffraction pattern has a fourfold symmetry, with the distances from the (11) to (01) and from the (11) to (10) spots being the same. Yellow arrows in Figure 3d indicate the directions of the reciprocal lattice vectors b_1^* and b_2^* and the arrow length corresponds to the distance between the diffraction spots. By measuring the distance, we obtain a length of $1.1 \text{ \AA}^{-1}$ for b_1^* and b_2^* . Furthermore, the reciprocal vectors are rotated by 45° from the [10 100] directions. The real space vectors b_1 and b_2 in Figure 3e each have a length of $\frac{\sqrt{2} \cdot a}{2}$, hence the reciprocal vectors b_1^* and b_2^* each have a length of $\frac{4\pi}{\sqrt{2}a} = 1.07 \text{ \AA}^{-1}$, using a value of $a = 8.336 \text{ \AA}$ for the lattice parameter.^[11] The magnitude of the reciprocal lattice vectors is in good agreement with the measured value of $1.1 \text{ \AA}^{-1}$ obtained by LEED. Additionally, the absence of any $1/N$ -order spots ($N = 2, 3, 4, \dots$) means that no reconstruction is observed.

While LEED is generally referred to as a surface sensitive technique, it was recently shown on SrTiO₃ surfaces that a (1×1) pattern cannot warrant a pristine surface with a bulk-truncated (1×1) termination.^[34] In fact, LEED also probes the subsurface region about three monolayers deep. While smaller imperfections at the very surface may not necessarily be detected, a (1×1) LEED pattern fitting to ZGO indicates that the low annealing temperatures are sufficient to achieve crystallinity in the same information depth that is probed by ARPES.

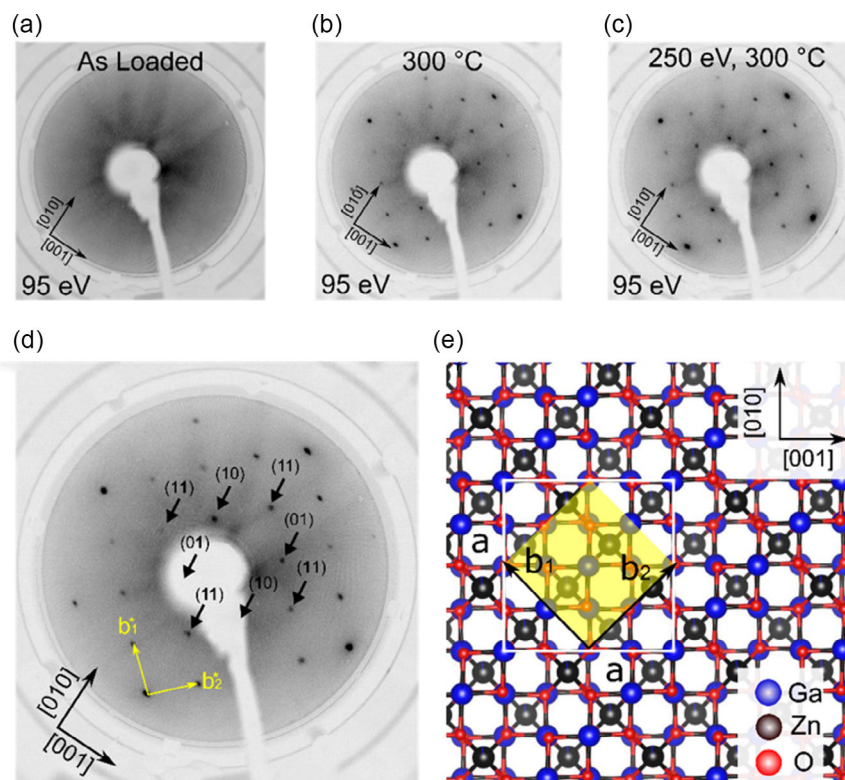


Figure 3. LEED diffraction pattern of the ZGO(100) surface obtained with electron kinetic energies of 95 eV a) for the as loaded sample, b) after annealing in oxygen atmosphere at 300 °C, and c) argon sputtering with 250 eV ion energy followed by annealing in oxygen atmosphere at 300 °C. An enlarged version of (b) is shown in (d), in which the first-order diffraction spots are marked by black arrows and labels. The yellow arrows mark the directions of the reciprocal lattice vectors b_1^* and b_2^* . In panels (a) to (d), the crystallographic directions of the bulk are specified on the left side. The real space surface of ZGO(100) is shown as a ball and stick model in (e) with the in-plane crystallographic directions in the top right corner. The surface of the bulk unit cell is marked by a white square with the side length a , while the surface unit cell is marked by a yellow square with the side length b_1 and b_2 .

2.2. Electronic Structure of the ZGO(100) Surface After Preparation in Oxygen Atmosphere

Since the preparation in oxidizing conditions yielded a nearly stoichiometric composition and sufficient crystalline structure, we focus now on the electronic structure of the surface, starting with a detailed analysis of the core-level measured by XPS. Figure 4a–c shows the Ga 2p_{3/2}, Zn 2p_{3/2} and O 1s core-level after each preparation step in oxygen atmosphere. After the initial annealing to 300 °C, a rigid shift toward lower binding energy by about 0.3 eV of all peaks is observed. Since all core-level shift by the same value, we attribute this observation to a Fermi-level (E_F) shift relative to the valence band maximum and not to a chemical shift induced by the appearance of new chemical species.

After sputtering and annealing, the Ga 2p_{3/2} and O 1s peaks shift by about 0.4 eV to higher binding energy, while the Zn 2p_{3/2} peak only shifts by about 0.1 eV to higher binding energy. At the same time, a broadening of the Zn 2p_{3/2} peak is observed, while the Ga 2p_{3/2} peak has constant line shape, indicating that the cleaning procedure does not change the chemical state of Ga, while it does for Zn. Similarly, the O 1s core-level line shape changes depending on the cleaning step: a high-binding energy tail is present for the as loaded sample, which decreases in

intensity after annealing and vanishes after the sputtering and annealing step. An additional, shoulder on the low-binding energy side appears at about 0.9 eV from the main peak after sputtering and annealing. The peak fitting of the O 1s core-level with pseudo-Voigt model functions after subtraction of a Shirley background is reported in Figure 4d–f. The as loaded O 1s peak features a tail at the high binding energy side due to C–O bonding, which is consistent with previous studies for untreated ZGO and β -Ga₂O₃ surfaces.^[31,32] Fitting the O 1s peak of the as loaded sample with two components, one for the oxygen bond in ZGO and one for C–O, is sufficient. After annealing, the contribution of the carbon-related component is reduced, consistent with the observation on the carbon core-level in Section 2.1. In contrast, sputtering and annealing results in a complete removal of the C–O component and at the same time in the appearance of an additional peak on the low binding energy side of the peak, contributing about 7% to the total intensity. This component is separated by about 0.9 eV from the ZGO main line, a value that is consistent with that of ZnO in the report by Chikoidze et al.^[32] The shoulder occurs together with the broadening a smaller shift of the Zn 2p_{3/2} core-level, which indicates that a new chemical bond is formed between Zn and O. Therefore, we conclude, that sputtering and annealing in oxygen atmosphere induce the formation of ZnO.

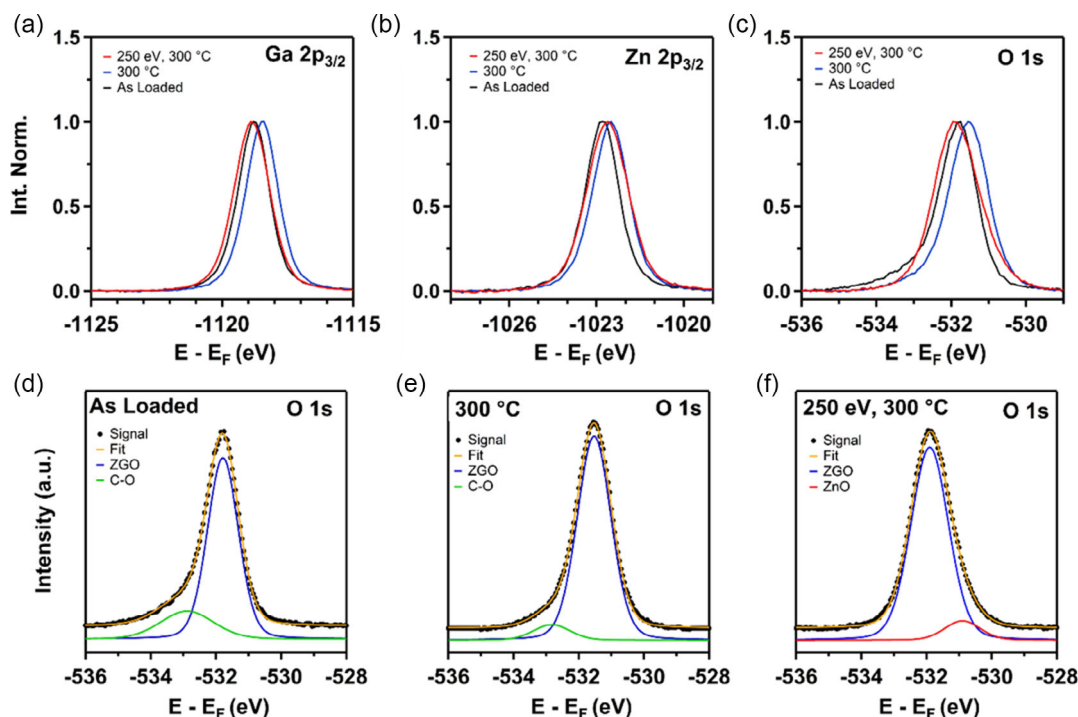


Figure 4. Intensity normalized XPS spectra (1486.7 eV) of a) Ga $2p_{3/2}$, b) Zn $2p_{3/2}$, and c) O $1s$ for the as loaded ZGO(100) surface (“As Loaded”), after annealing in oxygen atmosphere (“300 °C”) and after sputtering and annealing in oxygen atmosphere (“250 eV, 300 °C”). d)–f) Fit of the O $1s$ core-level region after each cleaning step measured at normal emission. Dotted lines indicate the measured signal, while solid lines of different colors indicate the fitted components.

Whether the ZnO is present as an overlayer or phase separated in the subsurface region can be answered by a non-destructive depth-profiling, for example, by angle-dependent XPS measurements, which, at the same time, provide information on the presence of a band bending.^[35] We compare in Figure 5a–d the Ga $2p_{3/2}$, Zn $2p_{3/2}$, O $1s$, and Ga $3d$ core-level spectra taken at normal emission (0°) with spectra taken at grazing emission (60°). Spectra in grazing emission have their information depth reduced by about 50% with respect to normal emission spectra. A band bending would result in a shift of all core-level peaks and/or a narrowing of the peaks upon reduction of the information depth.^[36]

Such changes to the spectra could not be observed, indicating a band bending is either absent or too small to be detected, that is, smaller than 50 meV.

While the Ga $2p_{3/2}$ core-level and the Zn $2p_{3/2}$ core-level are angle-independent, the component related to ZnO in the O $1s$ spectrum broadens. This can be explained by an increase in intensity of the ZnO-related component relative to the ZGO main line and thus, may be associated with an increase of the ZnO component at the surface. In contrast, the angle-independence of the Zn $2p_{3/2}$ hints to uniform depth distribution of the ZnO within the information depth. This apparent contradiction is explained considering the differences in the information depth of O $1s$ and Zn $2p_{3/2}$. If the ZnO is homogeneously distributed in a subsurface region of similar depth as the information depth of Zn $2p_{3/2}$, no angle-dependence will be noticeable. In contrast, since the O $1s$ core-level has a much larger information depth,

it probes deeper below the surface. Halving the information depth with grazing emission (60°) probes the surface in a condition similar to that of the measurement of the Zn core-levels. From this, we conclude that the distribution of ZnO is uniform in the first nanometer of the subsurface region.

In grazing emission, one may also notice a small increase in intensity around the high binding energy side of the O $1s$ peak. As stated earlier, such a shoulder can be associated with C–O bonds. Since we have shown in Figure 2b the absence of carbon after the cleaning, the observation of this shoulder indicates the adsorption of small amounts of C–O from the residual gas of the chamber during the final measurements in grazing emission.

At last, the intensity of the low-binding energy shoulder of the Ga $3d$ core-level under the valence band is reduced in grazing emission with respect to normal emission. Furthermore, the Zn $3d$ semi-core-level intensity is reduced with respect to that of Ga $3d$, indicating that a lower amount of Zn at the surface. As we will outline in the final section of this article, these observations could be related to the intrinsic stabilization of the surface by the termination with gallium oxide.

2.3. Valence Band Structure of the ZGO(100) Surface After Preparation in Oxygen Atmosphere

Our investigation of the surface by ARPES serves two purposes: First, it allows a direct probing of the k -space resolved valence band structure, enabling us to identify electronic states and the position of the valence band maximum of the probed sample.

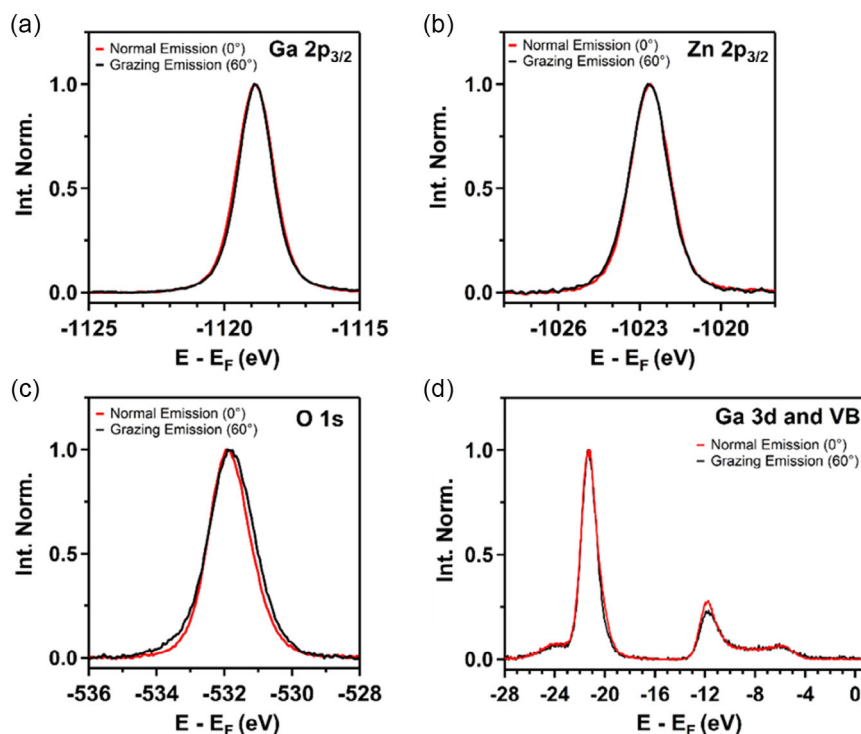


Figure 5. Angle-dependent XPS (1486.7 eV) scans after sputtering and annealing in oxygen atmosphere, shown for the a) Ga $2p_{3/2}$, b) Zn $2p_{3/2}$, c) O $1s$, and d) the Ga $3d$ core-level regions. Two angles are compared with respect to the surface normal: Normal emission (0°) and grazing emission (60°).

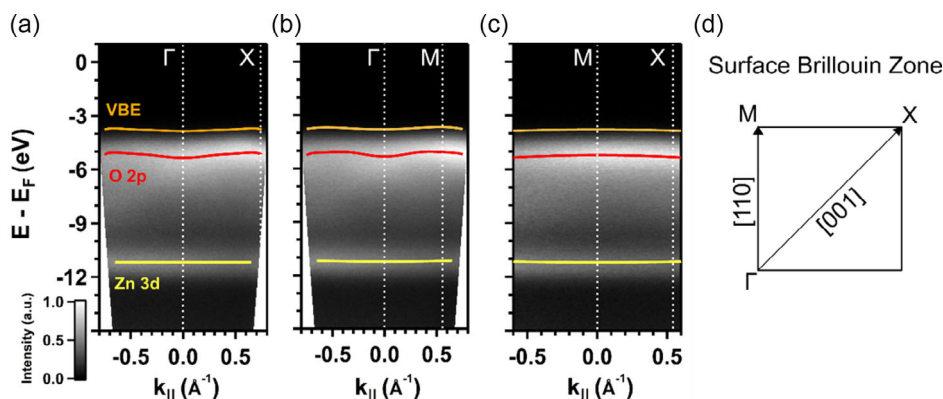


Figure 6. ARPES intensity maps along the a) Γ -X, b) Γ -M, and c) M-X high symmetry directions, measured with an excitation energy of 40.8 eV. Dispersion of the valence band leading edge (VBE) (orange), O $2p$ states (red), and Zn $3d$ semi-core-level (yellow) are indicated by lines. d) A schematic of the surface Brillouin zone, labeled with the in-plane crystallographic directions and the high symmetry points.

Second, the extremely high surface sensitivity will provide further information on the surface quality, especially when compared to calculations in the following sections.

ARPES intensity maps are reported in **Figure 6** for the three high symmetry directions in a-c, as described by the schematic of the surface Brillouin zone of **Figure 6d**. The first notable feature we observe is the Zn $3d$ semi-core-level located at a binding energy of -11.2 eV, indicated by the yellow lines. Due to its core-level character, the feature shows no dispersion in k -space. The most intense feature in the valence band is constituted by the

O $2p$ states and is located between -5 and -6 eV. A sizeable dispersion is present along each of the three high symmetry directions, as indicated by red lines in the graphs. The O $2p$ band reaches its highest binding energy around Γ , while it reaches the lowest binding energies at the M- and X-points. A similar trend is also observable for the valence band leading edge, indicated by orange lines between -3 and -4 eV. Looking at the dispersion along the M-X direction, we find that the electron bands reach a binding energy of -3.65 eV at the M-point, while they lie 100 and 150 meV higher in binding energy at the X- and Γ -point

respectively. This means that the valence band maximum (VBM) is located at the M-point.

A value of $3.65 \text{ eV} \pm 0.05 \text{ eV}$ for $E_F\text{-VBM}$ is significantly smaller than the optical band gap of 4.6 eV . In fact, the intrinsically high n -doping of $6.1 \times 10^{18} \text{ cm}^{-3}$ due to antisite defects should result in a position of E_F at the conduction band minimum, that is, to a larger $E_F\text{-VBM}$ value to be consistent with the optical gap, similar to investigations on other TSOs.^[28] However, annealing in oxygen atmosphere is known to cause the formation of semi-insulating layers (which have the effect of shifting the Fermi-level toward the middle of the bandgap) on TSOs. It appears plausible that we observe a similar effect, as we also observed a shift of all core-level in XPS toward lower binding energy after annealing in oxygen atmosphere.

A flat dispersion of the valence states is expected due to the high effective masses of electrons in the valence band, as shown by our calculations for the ZGO bulk electronic structure in the following section. The presence of dispersion and intensity modulation indicates a good quality of the probed subsurface region, supported by the LEED measurements. However, the observed features in ARPES appear to be broadened, which can be explained by a large number of overlapping bands originating from the large number of atoms in the ZGO unit cell, albeit changes in the stoichiometry cannot be excluded as another possible source for the observed smearing of bands. We are now going to address this matter with the support of first-principles calculations in the following sections.

2.4. Calculated ZGO Bulk Band Structure

In Figure 7a we show the calculated bulk band structure of ZGO, in a) the full band structure and in b) and c) the spectral density in a narrow range around the VBM. Although the details depend to a certain extent on the computational method (see the Supporting Information), this does not affect the discussion in

this paragraph. The theoretical VBM lies slightly above the highest occupied band at Γ and is located close to the M-point on the Brillouin zone edge, which is highlighted in Figure 7b. The location of the VBM around M is in excellent agreement with our experimental results obtained by ARPES. Furthermore, the large number of bands and for oxides usual broadening may explain the small number of resolvable features in the ARPES experiments. A point of disagreement between the calculated and experimental bulk band structures lies in the highest position of bands at X and M, whose energy difference between is too large. This is however not a true discrepancy, as the calculations are for the bulk, while the ARPES measurements show surface-projected bands. In fact, the surface-projected theoretical bulk band structure shown in Figure 7c is in good agreement with our ARPES experiments. Following these results, we are now going to discuss possible surface structures that may have influenced the obtained ARPES data.

2.5. Surface Electronic Structure—Comparison of Theory and Experiment

The influence of the surface is visible in the comparison of experimental and calculated energy distribution curves (EDC) in Figure 8. Major features of the calculated EDC such as the O 2p peak at the VBM and the Zn 3d states together with its hybridized O 2p counterpart are recognizable already for the bulk. However, the O 2p peak is clearly too narrow, and some of its intensity moves to a shoulder that is missing from the experimental EDC. The relative height ratio of both peaks appears to be correct, but this may be due to fortunate cancellation of errors, as explained in Supporting Information.

To infer the surface composition in our calculations, we made use of experimentally acquired information on the periodicity and the electronic states. This way, the discussion of possible surface structures is not solely based on total energies. According to

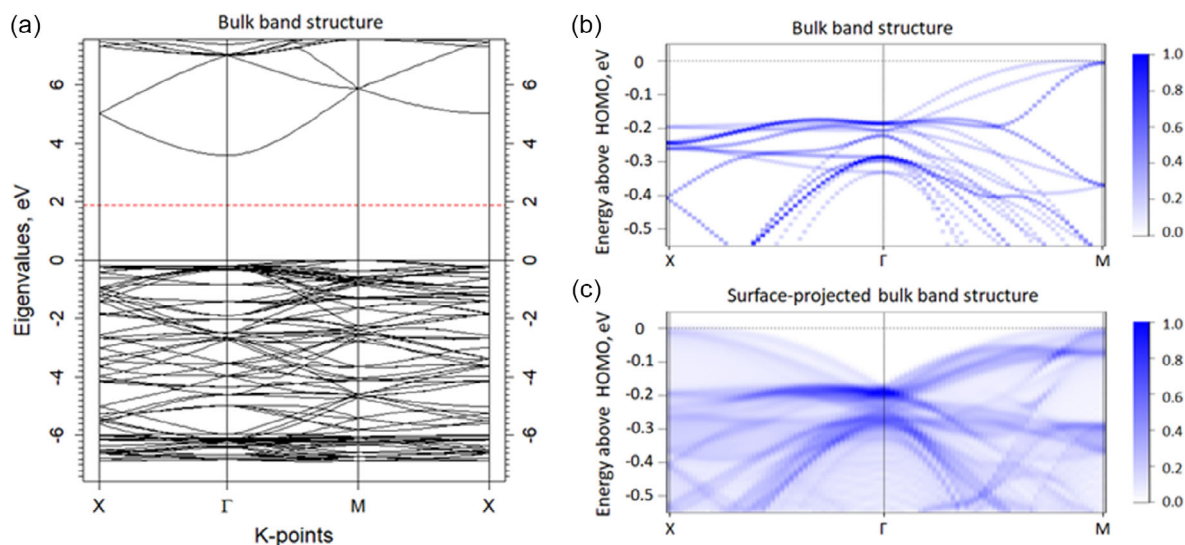


Figure 7. a) Calculated bulk band structure of ZGO (QExa/PBE, see Supporting Information). b) Enlarged valence band structure to highlight the maximum of the valence band around the valence band maximum at the M-point. c) Surface-projected bulk band structure of ZGO. The intensity scale in (b) and (c) reflects the expected photoemission intensity for excitation with He II radiation.

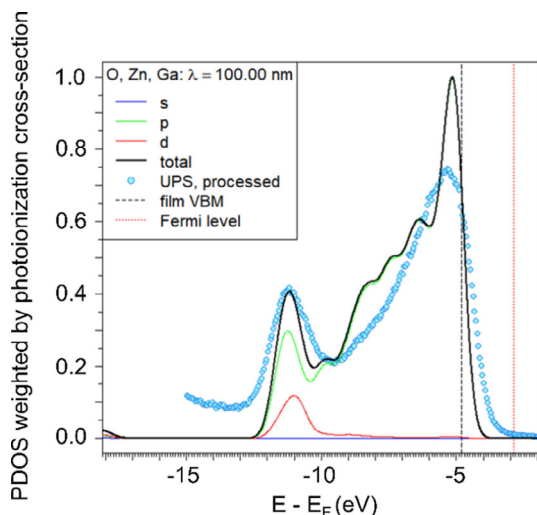


Figure 8. Comparison between the experimental energy distribution curve (EDC) (blue, dotted) and the calculated bulk component EDC, simulated for He II and normal emission (black, solid). The simulated EDC is broadened by 0.4 eV and normalized to the experimental curve area in the range between -3 and -12.5 eV.

LEED, we can sort out surface structures that will not result in a (1×1) diffraction pattern. From the absence of a detectable band bending, we infer that there are no surface states able to trap the Fermi level in n-type samples at energies deeper than about 50 meV below the minimum of the conduction band. Excluded are also structures producing a strong photoemission signal from states within the band-gap and/or near the VBM.

The bulk of ZGO is composed of alternating (100)-oriented, one atom thick layers of two types: positively charged metal layers, Zn, and negatively charged oxide layers, Ga_2O_4 . Because of the bilayer structuring of the bulk, there are two classes of ZGO(100): Zn-terminated and Ga_2O_4 -terminated (see Figure 9a,b). The (1×1) surface unit cell obtained by truncating the bulk at a (100) plane contains either two Zn atoms or two Ga_2O_4 units. Zn-terminated stoichiometric ZGO(100) (1×1) is n-type metallic, which would fit to the experiment. In attempt to account for the surface preparation induced loss of Zn revealed by XPS, we removed half of surface Zn; this renders the surface semiconducting without introducing new photoemission states. The Zn loss suggested by XPS (Table 2) is however higher: given that there are four layers of Zn per ZGO unit cell and an information depth of three-unit cells for the Zn $2p_{3/2}$ core-level, up to two Zn monolayers disappear on sputtering and annealing in oxygen atmosphere. This means that the surface obtained after the sample preparation can only be Zn-terminated, if there was a Zn surplus on the surface of the as loaded sample. If the as loaded sample had a nearly stoichiometric surface, the surface preparation would not result in Zn termination.

Being p-type metallic, unreconstructed Ga_2O_4 -terminated ZGO is incompatible with measurements. Dimerization of two O atoms in each 1×1 cell reduces the energy by 1.5 eV per cell and turns the surface semiconducting. However, for any ZGO(100) surface with marked Zn deficiency, the VBM O 2p peak simulated for He II (40.8 eV) is too strong.

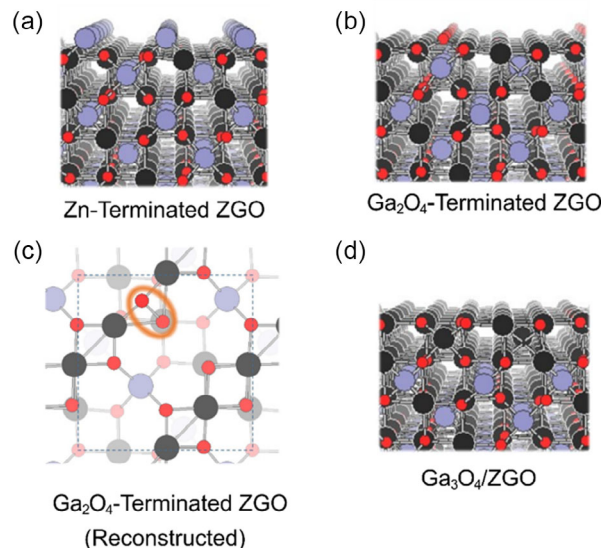


Figure 9. a,b) Side-views of Zn- and Ga_2O_4 -terminated surfaces, respectively. Zn is blue, Ga is black, O is red. c) Ga_2O_4 -terminated, reconstructed ZGO(100) 1×1 (top view). The O dimer is indicated. d) Side-view model of ZGO(100) with a monolayer Ga_3O_4 .

On Ga_2O_4 -terminated ZGO, one O vacancy per (1×1) cell (Figure 9c) reduces the O 2p peak only slightly, though the surface remains semiconducting, with occupied vacancy states within 1 eV to bulk VBM. Additional oxygen vacancies produce surface states, absent from the measured band structure. To explain the experiment, one must a) calibrate the inelastic mean free path (IMFP), b) refer to inaccuracy in the computed degree of Zn–O hybridization (see Supporting Information), or c) allow for a mixture of the two effects.

Further difficulty arises from the relative increase of Ga with respect to Zn at the surface, as detected by XPS. One may explain this increase by assuming that Ga atoms substitute Zn in the topmost bilayer of ZGO, leading to a monolayer of Ga_3O_4 on top of a Ga_2O_4 -terminated ZGO (Figure 9d), or Zn-terminated ZGO with two layers of cubic Ga_2O_3 with O-rich stoichiometry ($\text{Ga}_2\text{O}_{3.2}$, or 7% O surplus). Such a surface remains semiconducting, with an occupied surface band extending over about 1 eV above VBM. However, the simulated photoemission O 2p peak is too high in intensity. Surface oxygen vacancies do not help, as they introduce prominent band gap states. Adjusting the IMFP λ improves the ratios between the peaks, but does not lead to satisfactory spectra, even if an infinite IMFP is assumed. We have therefore considered the possibility that the oxygen peak experiences additional broadening by surface-induced shifts due to atomic configuration dependence of Hubbard U (see Supporting Information). This reduces the relative height of the O 2p VBM peak, broadening its maximum, so that also the troublesome shoulder visible in Figure 8 is less pronounced. Nevertheless, the area of the oxygen peak remains too large and the peak maximum remains too high. The presence of surface defects will contribute to the broadening, but it is not immediately clear that it would significantly improve the relative area under the two peaks. However, the observed discrepancy

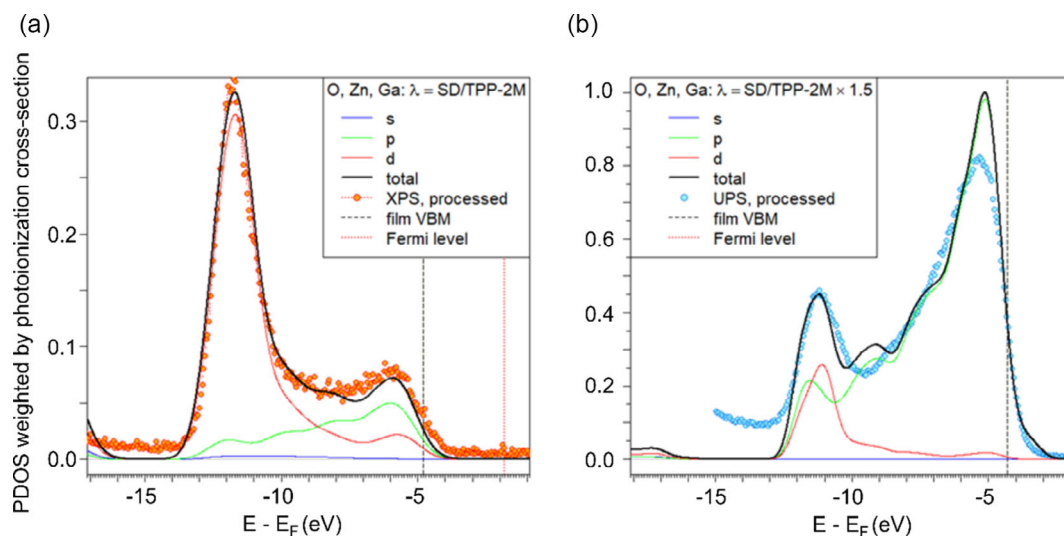


Figure 10. a) QEpaw/PBE calibration of photoemission cross-sections, with broadening by 0.65 eV and area normalization in the range from -3 to -14 eV. b) He II EDC simulated for $\text{Ga}_2\text{O}_4/\text{ZGO}$, with site-dependent Hubbard $U(\text{O})$ and inelastic mean free path increased by 50%. The curve area is normalized to the experimental data in the range from -3 to -12.5 eV, broadening 0.4 eV.

may be associated with the fact that it is not always straightforward to obtain the correct amount of hybridization between oxygen and metal atoms;^[37,38] indeed, even a computed Hubbard U is in practice a constrained quantity and may require renormalization.^[39] For ZGO computed in the GGA + U framework, this amount does indeed depend on the pseudopotentials used (see Supporting Information). Because photoemission cross-sections depend strongly on the photon energy, this inaccuracy limits the transferability of the calibration made at Al $K\alpha$ (1486.7 eV) shown in Figure 10a, to the simulations performed for He II (40.8 eV) shown in Figure 10b. This is not alleviated by a pseudopotential calculation with a hybrid functional (HSE). We obtained the best results with PBE exchange and correlation, with the QEpaw pseudopotential set, with oxygen Hubbard U for ZGO bulk determined by optimization of the ZGO bulk lattice constant, with site-dependent corrections to this bulk value computed self-consistently and with Zn and Ga Hubbard U adjusted to match the positions of the corresponding photoemission peaks. This ambiguity caused by the dependence of the hybridization degree on the pseudopotential might in general be resolved by introducing an intersite V term into the Hubbard functional.^[40,41] However, this solution is unfortunately not practical in this particular case, because it implies the use of computed Hubbard parameters and the values of Hubbard U for the closed-shell atoms (Zn and Ga in ZGO) cannot be obtained in this way.

3. Conclusions

Our comparison of in situ surface preparation methods by sputtering and annealing revealed that annealing in UHV leads to significant Zn loss in the subsurface region, which we were able to suppress by the annealing in oxygen. While a high temperature stability of samples was reported by Galazka et al.,^[11] our results indicate that the surface composition is unstable already

at much lower temperatures. After low temperature annealing, a (1×1) LEED pattern with sharp spots was observed, indicating sufficient crystallinity in the probed subsurface region. This finding was crucial to justify the subsequent analysis by ARPES for comparison with theory. A noncrystalline subsurface region would hold less valuable information due to the lack of band dispersion. A sizeable Zn-loss of at least 17% from the first nanometer indicates stabilization of the surface in a Ga_2O_3 phase. We found this hypothesis to be compatible with ab initio DFT simulations if this oxide is two monolayer thick, although this compatibility requires adjustments to some theoretical parameters (as energy-independent calibration of photoemission cross-sections and 50% increase of the IMFP of photoelectrons).

Reduced sputtering time and annealing in oxidizing conditions are crucial to obtain near-stoichiometric surfaces, albeit measurable quantities of gallium oxide and phase separated ZGO are present in the subsurface region. The optimization of the surface preparation should be investigated in the future by also exploring wet chemical etching in combination with low temperature annealing in oxygen atmosphere.

ARPES revealed dispersion of the O 2p states along the high symmetry directions and the results are compatible with the calculated bulk band structure, both methods finding the VBM located at the M-point. The result obtained by experiment and DFT are mutually supportive, indicating a good quality of the surface after preparation.

Overall, these results present important insights on the fundamental surface electronic structure of ZGO and the thermal instability of the surface, leading to Zn loss. The latter is especially important to consider for heterostructures in devices based on ZGO.

From the analysis of the relative peak height in measured and simulated EDCs we conclude that the Yeh-Lindau photoionization cross-sections need calibration for use with pseudopotential wave functions,^[42] and inaccurate description of metal-oxygen

hybridization by DFT calculations with Hubbard U results in non-negligible calibration errors. This inaccuracy is not alleviated by pseudopotential calculations with Hartree–Fock admixture (hybrid). We also noticed that the site-dependency of Hubbard U has a visible influence on the width of simulated photoemission peaks.

4. Experimental Section

Experimental Details: Two samples were cut from a high-quality melt-grown bulk ZGO single-crystal with one surface aligned parallel to the (100) crystal planes.^[11] For details on the purity of the crystals see the Supporting Information.

The first sample showed n-type conductivity with an electron concentration of $n = 7.49 \times 10^{19} \text{ cm}^{-3}$ and was treated in UHV (reducing) conditions. The intrinsically high doping stems from Ga/Zn antisite defects that have formed during the growth and were not compensated during cool down or by post-growth annealing.^[11–13] The first step of the surface treatment procedure consisted in annealing at 300 °C for 30 min, followed by annealing to 500 °C for 30 min to study the influence of the annealing temperature on the chemical composition and the removal of carbon contamination. The sample temperature was monitored through a thermocouple and the ramping rate was $\approx 0.7 \text{ K s}^{-1}$. Subsequently, sputtering for 10 min by Ar^+ ions with an energy of 250 eV followed by annealing at 300 °C for 15 min was employed to remove the remaining carbon contamination. For sputtering, Ar gas was inserted until a partial pressure of $1 \times 10^{-5} \text{ mbar}$ was reached and the sputter current at the sample was 17 μA . Following the initial sputtering and annealing, the sample was again sputtered by Ar^+ ions, but this time with an energy of 500 eV for 20 min and afterward for an additional 20 min, to alter the composition and detect preferential sputtering. Finally, the sample was annealed at 300 °C for 15 min to investigate the chemical composition after this procedure.

The second sample showed, similar to the first sample, an intrinsic n-type conductivity with an electron concentration of $n = 6.1 \times 10^{18} \text{ cm}^{-3}$ and was annealed in oxidizing conditions with an oxygen partial pressure of 10 mbar. The preparations steps include an initial annealing at 300 °C for 30 min after the sample was loaded into the system. Afterward, the sample was sputtered for 5 min by Ar^+ ions with an energy of 250 eV, followed by annealing at 300 °C for 15 min. For annealing, the temperature was monitored with a thermocouple, the ramping rate was $\approx 0.7 \text{ K s}^{-1}$ and the ramping was also done in an oxygen atmosphere of 10 mbar. Sputtering used an Ar partial pressure of $1 \times 10^{-5} \text{ mbar}$ and the sputter current was 17 μA .

The ARPES measurements were done with a Phoibos 150 analyzer and a monochromated Helium discharge lamp allowing the use of He II (40.8 eV) for the excitation of photoelectrons and delivering a beam of 0.7 mm diameter spot size. For ARPES, the angular resolution was better than 0.2° and the energy resolution was better than 120 meV, dominated by the thermal broadening at room temperature (as measured on the Fermi edge width of a Mo plate in electrical contact with the sample). For XPS, a monochromatized Al K_{α} X-ray source exhibiting a spot size of $3.5 \times 1 \text{ mm}^2$ has been employed, showing an energy resolution better than 600 meV, corresponding to a full-width half maximum of $\approx 700 \text{ meV}$ on the referenced Ag $3d_{5/2}$ peak at $(368.21 \pm 0.02) \text{ eV}$. The angular acceptance of the analyzer was set to be $\pm 2^\circ$, enabling angle-dependent XPS measurements. LEED data was acquired with an ErLEED 150 optics and a CCD camera mounted on the backside of the fluorescent screen.

Theoretical Approach: We applied the ab initio plane wave density functional theory with Hubbard U correction (DFT + U),^[43,44] ultrasoft and norm-conserving scalar-relativistic pseudopotentials of PBE type.^[45] The calculations were conducted on the JUWELS cluster,^[46] using the Quantum Espresso (QE) package.^[47] The valence configuration was 3d 4s 4p for Zn, 3d 4s 4p for Ga, and 2s 2p for O; in tests, we used also 4s 4p for Ga and 3s 3p 3d 4s 4p for Zn. The cutoff energy was 40 Ry for ultrasoft and 80 to 260 Ry for norm-conserving pseudopotentials. The Brillouin zone was sampled with the 2×2 Monkhorst-Pack grid with

offset. The slabs contained about 100 up to 300 atoms (but about 160 atoms for most of the simulations). Because in ZGO(100) the bulk dipole moment cannot be cancelled externally, we used slabs that are symmetric with respect to the middle plane. The slabs were separated by about 1.5 nm of vacuum. The Hubbard U correction was applied to the 3d and 2p states. Because self-consistent calculation of Hubbard U^[44] is challenging for atoms with closed shells,^[48,49] such as Zn and Ga, we first estimated U(O) by fitting the ZGO lattice constant and we adjusted the differences U(Ga)-U(O) and U(Zn)-U(O) to reproduce the positions of the measured XPS peaks. To judge on the site-dependence of Hubbard U, we then obtained self-consistent U(O) for each O atom. We assessed the degree of uncertainty due to the freedom in the pseudopotential construction and in the selection of Hubbard U by adapting various pseudopotential sets and by performing hybrid functional (HSE^[50]) calculations for ZGO bulk and for the surface structures of most interest.

Photoemission was simulated from the projection of single-particle Bloch wave functions onto the atomic states. We adapted the photon energy dependence of photoionization cross-sections σ from the Hartree–Fock calculations by Yeh and Lindau for single atoms,^[42] calibrating their relative magnitude to reproduce the VBM peak area ratio measured with Al K_{α} radiation. The inelastic mean free paths (IMFP) λ_{TPP2M} for XPS and UPS were approximated as $\text{TPP2M}_{\text{[51,52]}}$ roughly corrected at low energies E by a $1/E^2$ term.^[53] For detailed technical information, including accuracy analysis, see Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors gratefully acknowledge the Gauss Centre for Supercomputing e.V. (www.gauss-centre.eu) for funding this project by providing computing time through the John von Neumann Institute for Computing (NIC) on the GCS Supercomputer JUWELS at Jülich Supercomputing Centre (JSC). Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

density functional theory (DFT), photoemission spectroscopy (PES), spinels, surface instabilities, transparent semiconducting oxides (TSOs)

Received: September 3, 2021

Revised: November 29, 2021

Published online:

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