Contents lists available at ScienceDirect

Surface Science



journal homepage: www.elsevier.com/locate/susc

Core-level binding energy shifts between interior, terrace and edge atoms in MnO(001) thin films *



Jade Barreto^a, Rubem Caetano^a, Maria I. Ramos^b, Astrid Alí^a, Guilherme Félix^a, Emilia Annese^a, Niklas Nilius^c, Hans-Joachim Freund^d, Braulio S. Archanjo^b, Carlos A. Achete^b, Paul S. Bagus^{e,*}, Fernando Stavale^{a,*}

^a Brazilian Center for Research in Physics, Rua Dr. Xavier Sigaud 150, Rio de Janeiro, RJ 22290-180, Brazil

^b National Institute of Metrology, Quality and Technology, Duque de Caxias 25250-020, Brazil

^c Institut für Physik, Carl von Ossietzky Universität, Oldenburg D-26111, Germany

^d Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, Berlin D-14195, Germany

^e Department of Chemistry, University of North Texas, Denton, TX 76203-5017, USA

ARTICLE INFO

SEVIER

Keywords: X-ray photoelectron spectroscopy Transition-metal oxides Surface & interfacial phenomena Electronic structure

ABSTRACT

Understanding the physical origin of core-level photoemission line shapes can offer valuable information about the chemical and physical properties of surfaces. For instance, in a large number of transition metals oxides, changes in the line shape allow the accurate determination of their oxidation states and cation site symmetry. Yet, despite this importance, experimental investigations on core-level shifts have been much neglected in recent years. In order to provide further evidence of the physical relevance, we have, in this contribution, introduced a new aspect of interior-, terrace- and edge- atom core-level binding energy shifts to describe monolayers of MnO (001) films grown on an Au(111) substrate. By this means we were able to distinguish the line shape contributions related to different types of atomic sites. We show that their relative intensities and energy shifts are able to provide information about the relative amount of under coordinated atoms on the surface and, thus give insights into their catalytic properties. Our findings reveal the importance of a detailed surface science characterization to provide the correct interpretation of distinct photoemission line shapes when considering thin film samples as well as nanostructures in general.

1. Introduction

In the present work, we describe a new aspect of the shifts of corelevel binding energies, BEs, that can provide new insights into the structure of supported oxide overlayers. The fact that the BEs of surface and bulk atoms of metals are shifted, described as Surface Core Level Shifts (SCLS), has been known for some time; see, for example, the review by Egelhoff [1]. Remarkably, there has been much less studies of SCLS for oxides [2,3] despite the possible importance for the chemical and physical properties of their surfaces [4–6]. The original analysis of the nature of the SCLS was based on a Born Haber cycle of the energetics of moving an impurity atom between bulk and surface [4,7]. While this was useful, it did not provide a direct connection between the SCLS and the electronic structure differences between bulk and surface. A different analysis developed by Bagus and collaborators [8] showed that the SCLS could be directly related to the electronic structure of bulk and surface atoms and further that the shift was largely dependent on the initial state since the relaxation in response to the core-hole was very similar for ionized bulk and surface atoms. More recently, the SCLS of the surfaces of oxides, MgO [2] and CaO [3,9] thin films have been measured. It was found that the unexpected difference between the SCLS of the cations and the anions gave significant insight into the surface properties, and hence into the chemical activity of the surface atoms.

The extension that we have made is to study BE shifts between the interior, terrace and edge atoms for monolayers of MnO(001) grown on an Au(111) substrate; whereby we concentrate on the Mn 2p XPS spectra. Specifically, we examined distinct forms of MnO(001) films, characterized by thick and thin films as well as islands exhibiting a c(2)

* Corresponding authors.

https://doi.org/10.1016/j.susc.2022.122159

Received 20 January 2022; Received in revised form 17 June 2022; Accepted 8 July 2022 Available online 16 July 2022 0039-6028/© 2022 Elsevier B.V. All rights reserved.

^{*} This article is part of the "Young Investigator Special Issue 2022". The CV of the first author can be found under link - https://ars.els-cdn.com/content/image/ 1-s2.0-S0039602822001443-mmc2.pdf.

E-mail addresses: paul.bagus@unt.edu (P.S. Bagus), stavale@cbpf.br (F. Stavale).

 \times 2) surface structure. The (1 \times 1)-terminated oxide was observed for thick, bulk type films as well as for few-layer films, while the $c(2 \times 2)$ terminated overlayer mostly occurs in the form of fairly small islands. Our well-defined films on Au(111) have been thoroughly characterized by low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and scanning transmission electron microscopy (STEM). For these films, we could identify shifts of the BEs related to interior, terrace and edge atoms that we describe with the acronym CLS for Core Level Shifts and unambiguously relate to the specific positions of the different oxide atoms. As for the SCLS, the CLS leads to a superposition of peaks, or since there is a considerable multiplet splitting for the Mn $2p_{3/2}$ XPS in MnO, to a superposition of multiplet features [10,11]. The CLS, in particular the relative intensities of the shifted features, is able to provide information about the relative amount of low-coordinated atoms on the surface and. hence, to improve our understanding of their possible catalytic properties. Additionally, we expect that our analysis might be extended to understand XPS core-level line shapes of other oxide thin films and nanomaterials.

2. Experimental details

The experiments have been performed in two distinct ultrahigh-vacuum (UHV) systems with base pressure better than 1×10^{-9} mbar. Manganese oxide films were prepared as described in a recently published report from Möller et al. [12]. In short, the films were deposited by electron-beam evaporation of metallic Mn pellets at 1×10^{-7} mbar O₂ partial pressure onto a clean Au(111) single crystal. Subsequently, the deposited films were annealed in either 5×10^{-8} mbar or 1×10^{-7} mbar O₂ partial pressure as indicated in the text. The oxide film deposition rate of ~ 0.15–0.2 nm/min was determined using a quartz-micro balance and later, confirmed using transmission electron microscopy images. The MnO film thicknesses, investigated in the following, were found to be ~2 nm for MnO (1 × 1) thick films and ~1 nm for MnO (1 × 1) thin films, later identified in the text.

The STM measurements were performed in a STM-UHV setup contained an Aarhus-150 (SPECS) operated at room-temperature and standard facilities for sample preparation. STM images were obtained in the constant current mode using a chemically etched tungsten-tip employing 1–2 V sample bias. STEM images were obtained using a probe-corrected (spherical aberration (Cs)) Titan (FEI Company) instrument working at 300 kV. The cross-section specimens were prepared using a dual beam microscope – Helios Nanolab 650 (FEI Company). A gold protection layer of about 2–5 nm was evaporated *in-situ* on the entire film surface, so that the samples could be transported in air, without further modifications of the MnO(001)/Au(111) interface, to a dual beam for the STEM sample preparation. The thin slices used for STEM have been cut perpendicular to the Au($1\overline{10}$). These samples were subsequently plasma cleaned and then transferred to the STEM instrument.

The XPS UHV setup comprised a Phoibos150 spectrometer (SPECS) equipped with a monochromatic Al-K_{α} source, an ErLEED system and standard facilities for sample preparation. XPS spectra were analyzed using CasaXPS software [13]. All photoemission spectra were taken at normal emission and sample charging was found to be less than 0.5 eV and 0.1 eV for thick and thin films, respectively. Binding energies calibration (84 eV Au 4f_{7/2}) and spectral resolution (0.65 eV FWHM) were determinate based on the fitting analysis of the Au 4f_{7/2} peak of a clean Au(111) substrate using a Gaussian (10%) – Lorentzian (90%) sum function (GL(90)) multiplied by a line shape asymmetry parameter given by T(2.4). Mn 2p_{3/2} core-level region spectral analysis was carried out after Shirley-type background subtraction by fitting the peak envelope using a Gaussian (70%) – Lorentzian (30%) sum function ascribed as GL(30). Please see the Supplemental Material (SM) for further experimental and analysis details.



Fig. 1. (a) LEED pattern of ~2 nm thick (1×1) and (b) of $\lesssim 1$ nm thick c(2 × 2) films at 45 eV together with corresponding LEEDpat simulations. The expected positions of the film and substrate spots and the three-fold domains structure of the film (dashed coloured squares) are indicated in the simulation. The red arrow in (b) indicates concentric ring-spots connected to the c(2 × 2) fingerprint. STEM survey image in (c); (d) high-resolution images of ~2 nm thick film. STM images (V_s = 2–3 V; I_t = 1.0 nA) of (e) ~1 nm thick and (f) < 1 nm thick films. Inset image show the atomic structure of the islands top-surface with scalebar given by 2 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

The MnO film structure was characterized by LEED. Fig. 1a displays the typical diffraction patterns obtained for ~ 2 nm thick (1 × 1) MnO (001) films using 5×10^{-8} mbar partial pressure of oxygen followed by

post-annealing at 750 K. The MnO(001) square lattice is observed with a lattice parameter of 0.3 nm compared to the literature value of 0.315 nm [14]. The LEEDpat simulation [15], on the right side, identifies the film structure as well as the formation of several domains with respect to the substrate pattern. In the simulations, one can note empty circles related to the expected positions for Au(111) diffraction maxima and filled circles representing the film pattern. The film is characterized by the formation of three domains rotated by 60° (indicated by three colored squares), reflecting the mismatch between the film's square symmetry and the hexagonal symmetry of the substrate. The first ring of twelve spots inside the gold spots of the simulation match very well the LEED diffraction pattern; the gold spots are not observed since the film is thick and covers all the substrate surface. Next, we analyze ≤ 1 nm thick MnO films obtained through annealing at 650 K in 1×10^{-7} mbar oxygen partial pressure. Fig. 1b shows that the typical MnO(001) LEED pattern, revealing a clear $c(2 \times 2)$ reconstruction. The relatively diffuse diffraction maxima of the film are related to the formation of a discontinuous layer (i.e., dispersed islands on the surface), as will be discussed later. In this low thickness regime, the fine adjustment of temperature and oxygen partial pressure may convert the MnO(001) $c(2 \times 2)$ into a (1×1) termination at elevated temperatures and lower oxygen pressure. Further analysis of the MnO films, displayed in Fig. 1b, reveal the gold spots (with hexagonal symmetry) and two inner rings with twelve spots, divided into three square pattern due to the threefold domain structure of the $c(2 \times 2)$ islands. The corresponding substrate diffraction pattern is now visible due to the finite film thickness. In Fig. 1b right side, the corresponding LEED pattern simulation is displayed to facilitate the identification of the diffraction maxima from the substrate and the c (2×2) MnO(001) films. In both, experimental data and simulation, one can identify the inner ring connected to the doubled unit cell size of the reconstructed MnO islands with respect to the initial (1 \times 1) pattern. (In SM Figure S4, LEED patterns obtained for the (1 \times 1) and c(2 \times 2) film structures are displayed for a wider range of beam energies).

Further characterization of the film structure was performed by STEM and STM; due to the insulating nature of the \sim 2 nm thick MnO films, their atomic level structure is explored only by STEM. In the panel Fig. 1c one can observe a cross-sectional STEM image of the (1×1) MnO (001) film grown on the Au(111) substrate. The film-substrate interface was sliced and their corresponding crystallographic directions are indicated in the image where the MnO(100) and Au($1\overline{1}0$) planes are exhibited. In Fig. 1d, the image contrast of the MnO film portion is connected to atomic columns related to an equal amount of intercalated Mn-O atoms in the [100] film direction. The oxide quality can be directly visualized based on the highly ordered atomic column structure and sharp film-substrate interface. Indeed, the homogeneous phase largely corresponds to MnO domains in [100] direction, oriented parallel to the Au substrate $[11\overline{2}]$ crystallographic direction. This film atomic row alignment is in close agreement with our previous study, where the [100] film crystallographic direction follows a row-matching behavior and runs parallel to the $Au[11\overline{2}]$ crystallographic direction as well [12].

An STM image obtained for thin (1×1) MnO films is presented in Fig. 1e. At this film thickness and preparation conditions, relatively compact films could be obtained which were generally characterized by a MnO(001) (1×1) LEED pattern. Unfortunately, attempts to obtain atomic resolved images are not successful possibly related to the film's poor conductivity. Nevertheless, a typical film height of either ~0.2 nm or ~0.4 nm was found based on the images line profile analysis shown in SM Figure S5, a measure compatible to a few layers thick MnO film. Fig. 1f shows an STM image of films prepared with a nominal thickness \leq 1 nm at the conditions of the LEED patterns in Fig. 1b. These films are typically discontinuous and characterized by crystalline islands exposing top facets with a (2×2) MnO(001) reconstruction. The island height is characterized by ~0.4 nm and their density on the surface depends strongly on the annealing conditions (STM line profile analyses

are displayed in SM Figure S4). In Fig. 1f, clean patches of the substrate show the unique Au(111) herringbone reconstruction co-exists with the MnO crystallites on the $c(2 \times 2)$ surface. In the inset of Fig. 1f, we show the islands surface atomic structure characterized by a square symmetry with ~0.58 nm lattice periodicity. These findings are in agreement with our previous report on MnO film growth on Au(111) as well as with the LEED pattern discussed above [12].

Thus, MnO films grown on Au(111) result in either (1 \times 1) or c(2 \times 2) surface structures depending primarily on film thickness and oxidizing conditions. In both cases, the surface is characterized by a square-symmetry with periodicity of either \sim 0.32 nm for (1 \times 1) or ${\sim}0.58$ nm for c(2 ${\times}$ 2). The (1 ${\times}$ 1) films are continuous with about ${\sim}2$ nm thickness, and characterized by large terraces and bulk-like structures in the film interior. As the film thickness decreases down to ~ 1 nm, relatively discontinuous films are obtained characterized by a large portion of terrace atoms and relatively few atoms in bulk-like, edge or kink positions of the layer. In the latter regime, MnO(001) bulk-like thermodynamic stability is still achieved and no surface reconstruction is observed [16]. In contrast, a further decreases in film thickness leads to the formation of a discontinuous film, characterized by crystalline islands in MnO(001) c(2 \times 2) configuration [17–19]. Based on this detailed information on the MnO film morphology, we will explore their photoemission spectra in the following.

Fig. 2 shows the Mn 2p spectra for the thick, thin and island films. The spectral fingerprint of MnO is generally related to its line shape characterized by two satellite structures located at \sim 6 eV higher BE with respect to each main spin-orbit component [20-24]. We note that the main Mn $2p_{3/2}$ -line at ~640 eV is distinctly modified by the surface structure of the MnO films. This becomes particularly evident in the fine-structure close to the peak maximum (The overall peak line shape, including the XPS before background subtraction and Au 4p1/2 peak removal are shown in SM Figure S2). In order to rationalize these features, we have followed the general theoretical assumptions presented by Bagus et al. [11] In this procedure, we have analysed Mn 2p_{3/2} envelope using four multiplets, considering that the relative energy (Erel) and intensity-area (Irel) of each multiplet are given approximately by 0, 1.4, 2.5 and 3.2 eV and 1, 0.7, 0.4 and 0.2, respectively. Additionally, to consider core-level shifts related to changes in the Mn coordination site between interior (bulk-like), terrace- and edge-atoms in each film preparation, we have employed 3 sets of four multiplet components and one single satellite in the fitting analysis. These sets are identified by different colours in Fig. 2. The multiplet contributions to the $2p_{3/2}$ XPS region arise from the angular momentum coupling of the open $2p_{3/2}$ shell with the open valence 3d shell of the Mn²⁺ coupled to high spin ⁶S [10,11]. Indeed, the energy separation of these multiplets and their relative XPS intensities provide a good fit to the Mn 2p_{3/2} XPS [11]. On the other hand, the multiplet contributions to the $2p_{1/2}$ line shape are more complex, because of the angular momentum coupling of the $2p_{1/2}$ shell with the $3d^{5}(^{6}S)$ that is different from that of the $2p_{3/2}$ [10,11], and because of shake up satellites make contributions to the intensity in this region [25]. For this reason, we have limited our analysis to the $2p_{3/2}$ only. It worth mentioning that the satellite component is known to depend on the Mn cation chemical environment, too. Nevertheless, we have kept its fitting as a single component constrained into BE energy interval of 646-649.8 eV, to avoid complicating our analysis of the CLS of the main Mn 2p_{3/2} peak. The fitting results displayed in the Fig. 2 indicate that indeed the satellite intensity contributes slightly to both $2p_{3/2} \mbox{ and } 2p_{1/2} \mbox{ regions.}$ Nevertheless in all films investigated here, the satellite BE, FWHM and relative intensity contribution to the 2p3/2 energy region was found to be essentially the same. More important, we emphasize that attempts to describe the 2p3/2 line shape using a smaller set than three spectral contributions from interior, terrace, and edge atoms have failed. The three contributions considered in our fitting procedures were found to be necessary, assuming the theoretical description of the Mn 2p_{3/2} line shape nature presented by Bagus et al. [11] and considering that each multiplet relative energy (E_{rel}) and



Fig. 2. Mn 2p photoemission spectral analysis after background removal described in the SM for (a) thick; (b) thin; and (c) island-rich films. Black circles display the experimental data after background subtraction; Pink curves correspond to the total fitted intensity with contributions from interior atoms (in blue), terrace atoms (in red), edge atoms (in green) and the Mn^{2+} satellite (in gray). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

relative intensity-area (I $_{rel}$) could vary within $\pm 0.1\,$ eV and 10%, respectively.

Before we discuss the fitting parameters, we consider the origins and magnitudes of the BE shifts between interior, terrace, and edge atoms. An important contribution to these BE shifts is the change of the electrostatic potential for atoms in different environments. For the interior, bulk atoms, this is simply the Madelung potential [26]. If we assume that the (001) surface of the oxide is unrelaxed and unreconstructed, then the electrostatic potential is simply the Madelung potential for the surface of a truncated perfect crystal which can be obtained with a suitable Ewald Sum. The magnitude of the difference between surface and bulk Madelung potentials is ~1 eV for cubic crystal structures with lattice constants of $\sim 0.4-0.5$ nm; see Refs. [2,3] and references therein. For the MnO lattice constant, the difference would be 0.8 eV. The electrostatics is such that the O BEs are reduced for surface O anions with respect to those of interior O anions and the BEs of surface cations are larger than the BEs of interior cations [2,3]; although the magnitude of the BE shift is the same for anions and cations. However, there are factors that may modify the shift due to the electrostatics. This will include the fact that the surface cations and anions have a different distribution of charge than the bulk- and interior-atoms connected to their surface relaxation and corrugation; as discussed in detail for MgO [2] and CaO [3]. In the present case of MnO films, the CLS for O BEs has been examined as well, but were not exceptionally large, as expected (see SM Figure S2 and discussion therein, why is it expected). Thus, we will use our fits to determine the BE shifts for low-coordinated Mn cations.

Now, we focus on the physical meanings of the changes in our fitting analysis of the Mn 2p3/2. In the present analysis, we have taken advantage of the varying morphologies of our MnO films to further explore the CLS phenomenon and to provide relevant insights into the catalytic activity of oxide surfaces. Hereby, we have considered the interior-, terrace- and edge-core level shifts in our line shape analysis. This is in full agreement with the underlying nature of the SCLS which, for the cations, are dominated by the differences in electrostatic potentials (i.e.: Madelung potentials) experienced by low-coordinated cations in terrace and edge compared to interior, bulk sites. The magnitude of the electrostatic potential, which lowers the cations BE, decreases from its MnO bulk value with 6 nearest oxygen neighbours, to 5 neighbours in the MnO surface and finally to 3–4 neighbours along the edges of the island structures. These changes in Madelung potential and its consequences on the SCLS were previously theoretically and experimentally confirmed by Nelin and co-workers for MgO films [2] where the SCLS for the Mg 2p XPS was predicted by theory to be 0.9 eV. In Fig. 2, one can compare the $2p_{3/2}$ core-levels for MnO films obtained for thick and thin continuous films (in Fig. 2a and 2b) as well as the discontinued films (in Fig. 2c) that exhibit core level shifts between interior- and terrace-atoms of +0.4 eV and between terrace- and edge-atoms of +0.8 eV. It is worth comparing the Mn $2p_{3/2}$ BE shift from interior to terrace atoms of 0.4 eV to the somewhat larger shifts of 0.60 and 0.65 found for MgO [2] and CaO [3], respectively. The reduction could arise from a stronger surface reconstruction of the MnO films than for MgO and CaO or it could arise from uncertainties in the more complex fitting procedure for MnO with respect to the closed shell oxides. However, the MnO BE shifts are of the same order of magnitude as in the closed shell oxides, discussed earlier. In this analysis, we observe a consistent trend in which the relative multiplet intensities associated with certain atom positions in the oxide correlate with the structural characteristics of the MnO films. Evidently, in the thick (1 \times 1) film (Fig. 2a), interior and terrace-atoms components are predominant. As the film thickness decreases (Fig. 2b) the contributions from the terrace-atoms increase at the expenses of the interior-atoms. In the analysis of the $c(2 \times 2)$ island phase, CLS contributions from terrace and edge atoms become predominant for the line shape features and their intensity behavior can directly be correlated with the number of low-coordinated sites.

The fitting analysis results are found in Table 1 (see details in SM Table S1). We note that for each of the different films and for each of the different types of Mn atoms, edge, terrace, and interior, the fitted E_{rel} and I_{rel} within one multiplet are nearly the same. For the E_{rel} , the differences are normally less than 0.05 eV and the variation of the I_{rel} is less than 5%. This strong similarity follows because the origin of the four

Table 1

 $Mn 2p_{3/2}$ region fitting results: Binding energy (BE) and full-width-half-maximum (FWHM) are given in electron-volts (eV); Relative contribution of a certain multitplet component to the total area (A) in%; CLS values obtained for interior relative to terrace and interior relative to edge atoms are represented by superscript * and #, respectively. C_{rel} values related to interior, terrace and edge atoms are indicated by superscript I, T and E, respectively.

Spectral contributions	Thick film				Thin film				Island film			
	BE (FWHM)	Erel	А	I _{rel}	BE (FWHM)	Erel	Α	I _{rel}	BE(FWHM)	E_{rel}	А	I _{rel}
Interior-atoms multiplets	639.78 (1.23)	0.00	25.75	1.00	639.68 (1.30)	0.00	3.74	1.00	639.65 (1.30)	0.00	0.69	1.00
	641.00 (1.23)	1.22	18.60	0.72	640.93 (1.30)	1.25	2.22	0.71	641.00 (1.30)	1.35	0.41	0.69
	642.08 (1.23)	2.30	10.47	0.41	641.95 (1.30)	2.27	1.52	0.40	641.96 (1.30)	2.31	0.28	0.41
	642.99 (1.23)	3.21	4.54	0.18	643.05 (1.30)	3.37	0.55	0.15	642.95 (1.30)	3.30	0.14	0.14
Terrace-atoms multiplets	640.16 (1.25)	0.00	10.05	1.00	640.14 (1.25)	0.00	33.24	1.00	640.12 (1.30)	0.00	25.69	1.00
	641.41 (1.25)	1.25	6.61	0.66	641.40 (1.25)	1.26	22.02	0.70	641.41 (1.30)	1.29	18.51	0.72
	642.48 (1.25)	2.32	3.17	0.32	642.45 (1.25)	2.31	12.05	0.39	642.47 (1.30)	2.35	10.50	0.41
	643.30 (1.25)	3.14	1.65	0.16	643.30 (1.25)	3.16	6.09	0.21	643.24 (1.30)	3.12	4.55	0.18
Edge-atoms multiplets	640.98 (1.25)	0.00	8.13	1.00	640.96 (1.30)	0.00	7.34	1.00	641.00 (1.30)	0.00	17.13	1.00
	642.16 (1.25)	1.18	5.37	0.67	642.15 (1.30)	1.19	5.67	0.68	642.21 (1.30)	1.21	11.74	0.68
	643.56 (1.25)	2.58	3.58	0.45	643.60 (1.30)	2.64	3.60	0.45	643.51 (1.30)	2.51	6.21	0.36
	644.26 (1.25)	3.28	2.07	0.25	644.31 (1.30)	3.35	1.94	0.25	644.30 (1.30)	3.30	4.14	0.24
CLS & C _{rel}	0.4^* and $1.2^{\#}$ & 59.4 ^I ; 21.5^{T} & 19.1^{E}				0.4* and $1.2^{\#}$ & 8.0 ^I , 73.4 ^T and 18.5^{E}				0.4* and $1.2^{\#}$ & 1.5^{I} , 59.2^{T} and 39.2^{E}			

multiplet components is dominated by the angular momentum coupling of the localized open $2p_{3/2}$ shell with the localized $3d^5$ shell which in the initial state is coupled to ⁶S. Of course, there will be variations in the E_{rel} and I_{rel} because the 3d shell has a covalent mixing with the O 2p and a ligand field splitting which modifies the atomic character [27]. There may also be variations because of uncertainties in the fitting procedure. To assess the reliability of our fits, we give theoretical relative intensities obtained for the four multiplet peaks of bulk MnO (1.00, 0.72, 0.42 and 0.20), remarkably close to the values in Table 1 [11]. We have also introduced in Table 1 the percentage (Crel) of interior-, terrace- and edge-atoms to the total intensity of 2p_{3/2} line, not considering the satellite contribution since it is almost constant for all film preparations. The calculated values for the ~ 2 nm thick MnO films reveal relative spectral contributions for interior-, terrace- and edge atoms of 59.4%, 21.5% and 19.1%, respectively. Remarkably, this finding agrees with our CLS analysis since it matches with the expected spectral weight of each component, as revealed from the structural characteristics of the \sim 2 nm thick films. For instance, the thick MnO film displayed in the Fig. 1c (\sim 7–8 monolayers thick) is characterized by at least 2 monolayers of terrace-atoms located either at the film/substrate or film/vacuum interface, whereas the remaining ~5 layers are formed by the interior-atoms, which indeed contribute around 60% to the total spectral response.

4. Conclusions

In conclusion, we have performed a detailed Mn $2p_{3/2}$ line shape analysis on well-defined MnO (001) thin films in which robust evidence for the defining role of the BE shifts of different atomic coordinations, namely interior-, terrace-, and edge- Mn cations is presented. Our findings reveal the importance of a detailed surface science characterization to provide the correct interpretation of distinct photoemission line shapes when considering thin film samples as well as nanostructures in general.

Credit author statement

J.B and F. S have conceived the experiments, analyzed the results and written the manuscript text. P. B have conceived the theoretical analysis. J. B and R.C have performed XPS/LEED and STM experiments, respectively. M. I. R, B. S. A and C. A. A have performed STEM experiments. A. A, G. F, E. A, H-J. F and N. N have reviewed the manuscript text.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors acknowledge the Brazilian financial support from CAPES, CNPq and FAPERJ. F. Stavale thanks the Surface and Nanostructures Multiuser Lab at CBPF. PSB's efforts were supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences (CSGB) Division through its Geosciences program at Pacific Northwest National Laboratory (PNNL). PNNL is a multi-program national laboratory operated for the DOE by Battelle Memorial Institute under contract no. DE-AC05–76RL01830.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.susc.2022.122159.

References

- W. Egelhoff, Core-level binding-energy shifts at surfaces and in solids, Surf. Sci. Rep. 6 (6–8) (1987) 253–415.
- [2] C.J. Nelin, F. Uhl, V. Staemmler, P.S. Bagus, Y. Fujimori, M. Sterrer, H. Kuhlenbeck, H.J. Freund, Surface core-level binding energy shifts for MgO(100), Phys. Chem. Chem. Phys. 16 (40) (2014) 21953–21956.
- [3] P.S. Bagus, C.J. Nelin, S.V. Levchenko, X. Zhao, E.M. Davis, H. Kuhlenbeck, H. J. Freund, Surface core level BE shifts for CaO(100): insights into physical origins, Phys. Chem. Chem. Phys. 21 (45) (2019) 25431–25438.
- [4] B. Johansson, N. Mårtensson, Core-level binding-energy shifts for the metallic elements, Phys. Rev. B 21 (10) (1980) 4427–4457.
- [5] C.Q. Sun, Y. Nie, J. Pan, X. Zhang, S.Z. Ma, Y. Wang, W. Zheng, Zone-selective photoelectronic measurements of the local bonding and electronic dynamics associated with the monolayer skin and point defects of graphite, RSC Adv. 2 (6) (2012) 2377.
- [6] C.Q. Sun, Surface and nanosolid core-level shift: impact of atomic coordinationnumber imperfection, Phys. Rev. B Condens. Matter Mater. Phys. 69 (4) (2004) 1–8.
- [7] A. Rosengren, B. Johansson, Surface heat of segregation from surface core-level binding-energy shifts, Phys. Rev. B 23 (8) (1981) 3852–3858.
- [8] P.S. Bagus, F. Illas, G. Pacchioni, F. Parmigiani, Mechanisms responsible for chemical shifts of core-level binding energies and their relationship to chemical bonding, J. Electron Spectrosc. Relat. Phenom. 100 (1–3) (1999) 215–236.
- [9] P.S. Bagus, C.J. Nelin, X. Zhao, S.V. Levchenko, E. Davis, X. Weng, F. Späth, C. Papp, H. Kuhlenbeck, H.J. Freund, Revisiting surface core-level shifts for ionic compounds, Phys. Rev. B 100 (11) (2019), 115419.
- [10] P.S. Bagus, R. Broer, W.A. d. Jong, W.C. Nieuwpoort, F. Parmigiani, L. Sangaletti, Atomic many-body effects for the p-shell photoelectron spectra of transition metals, Phys. Rev. Lett. 86 (16) (2000) 3692–3693.
- [11] P.S. Bagus, E.S. Ilton, Effects of covalency on the p-shell photoemission of transition metals: mnO, Phys. Rev. B Condens. Matter Mater. Phys. 73 (15) (2006) 1–14.
- [12] C. Möller, J. Barreto, F. Stavale, N. Nilius, Manganese oxide thin films on Au(111): growth competition between MnO and Mn₃O₄, J. Phys. Chem. C 123 (13) (2019) 7665–7672.

J. Barreto et al.

- [13] N. Fairley, "CasaXPS: processing software for XPS Version 2.3.24," Casa Software copyright, see www.casaxps.com, (2021).
- [14] W.B. Pearson, G.H. Vineyard, A handbook of lattice spacings and structures of metals and alloys, Phys. Today 11 (9) (1958) 36.
- [15] K. Hermann (FHI) and M. Van Hove (HKBU), "LEEDpat, Version 4.2," Berlin /Hong Kong, 2014. [Online]. Available: http://www.fhi-berlin.mpg.de/KHsoftware/ LEEDpat/index.html.
- [16] E.A. Soares, R. Paniago, V.E. De Carvalho, E.L. Lopes, G.J.P. Abreu, H.D. Pfannes, Quantitative low-energy electron diffraction analysis of MnO(100) films grown on Ag(100), Phys. Rev. B Condens. Matter Mater. Phys. 73 (3) (2006) 1–7.
- [17] J. Schoiswohl, S. Agnoli, B. Xu, S. Surnev, M. Sambi, M.G. Ramsey, G. Granozzi, F. P. Netzer, Growth and thermal behaviour of NiO nanolayers on Pd(1 0 0), Surf. Sci. 599 (1–3) (2005) 1–13.
- [18] K. Heinz, L. Hammer, Epitaxial cobalt oxide films on Ir(100) The importance of crystallographic analyses, J. Phys. Condens. Matter 25 (17) (2013), 173001.
- [19] C. Franchini, R. Podloucky, F. Allegretti, F. Li, G. Parteder, S. Surnev, F.P. Netzer, Structural and vibrational properties of two-dimensional Mnx Oy layers on Pd (100): experiments and density functional theory calculations, Phys. Rev. B Condens. Matter Mater. Phys. 79 (3) (2009) 1–12.
- [20] A.K. Kundu, K.S. Menon, Growth and characterization of ultrathin epitaxial MnO film on Ag(001), J. Cryst. Growth 446 (2016) 85–91.

- [21] F. Allegretti, C. Franchini, V. Bayer, M. Leitner, G. Parteder, B. Xu, A. Fleming, M. G. Ramsey, R. Podloucky, S. Surnev, F.P. Netzer, Epitaxial stabilization of MnO (111) overlayers on a Pd(100) surface, Phys. Rev. B Condens. Matter Mater. Phys. 75 (22) (2007).
- [22] G. Rizzi, M. Petukhov, M. Sambi, R. Zanoni, L. Perriello, G. Granozzi, An X-ray photoelectron diffraction structural characterization of an epitaxial MnO ultrathin film on Pt(111), Surf. Sci. 482-485 (2001) 1474–1480.
- [23] L. Zhang, Z. Tang, S. Wang, D. Ding, M. Chen, H. Wan, Growth and vibrational properties of MnOxthin films on Rh(111), Surf. Sci. 606 (19–20) (2012) 1507–1511.
- [24] F. Müller, R. de Masi, D. Reinicke, P. Steiner, S. Hüfner, K. Stöwe, Epitaxial growth of MnO/Ag(001) films, Surf. Sci. 520 (3) (2002) 158–172.
- [25] P.S. Bagus, C.J. Nelin, C.R. Brundle, B.V. Crist, N. Lahiri, K.M. Rosso, Origin of the complex main and satellite features in Fe 2p XPS of Fe₂O₃, Phys. Chem. Chem. Phys. (2022) (Submitted).
- [26] N.W. Ashcroft, N.D. Mermin, Solid State Physics, New York, Rinehart and Winston, London, 1976.
- [27] P.S. Bagus, E. Ilton, C.J. Nelin, Extracting chemical information from XPS spectra: a perspective, Catal. Lett. 148 (7) (2018) 1785–1802.