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A total current spectroscopy study of metal oxide surfaces: I. Unoccupied electronic states of ZnO and MgO

P J Møller[†]§, S A Komolov[‡] and E F Lazneva[‡]

[†] Department of Chemistry, University of Copenhagen, Universitetsparken 5,
DK-2100 Copenhagen, Denmark

[‡] Research Institute of Physics, St Petersburg University, Uljanovskaja street 1,
St Petersburg 198904, Russia

E-mail: pjm@kiku.dk

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Abstract. Unoccupied density of states (DOS) for the polar (0001) Zn, (000 $\bar{1}$) O and non-polar (10 $\bar{1}$ 0) ZnO surfaces and for a MgO(001)-c(2 × 2) thin film were studied using total current spectroscopy (TCS). TC spectra of the ZnO surfaces reveal the Zn 4s–O 2p band (6.2 eV) and two DOS maxima in the Zn 4p–O 2p band which exhibited different energy positions on the Zn-terminated (8.1 eV) and O-terminated (11.0 eV) surfaces. In the TC spectra of the MgO thin film, the energy location of Mg-derived (8.0, 14.8 and 21.0 eV) and O-derived (11.6, 14.2 and 18.5 eV) maxima of DOS were determined. Previously reported data on DOS of these materials is discussed, and it is shown that additional detailed information on the energy structure of unoccupied DOS in ZnO and MgO in the 5–25 eV range above E_F has been found.

1. Introduction

The electronic band structure concept is of great importance for understanding of physical and chemical properties of solids. A knowledge of the energy structure of unoccupied electronic states is of particular interest as these states are very sensitive to the local bonding environment, such as the number of valence electrons, their spin configuration and the symmetry and coordination number of the structural unit cell. Experimental studies of unoccupied states are usually performed by using near-edge x-ray absorption fine structure (NEXAFS), inner-shell electron energy-loss spectroscopy (ISEELS), appearance potential spectroscopy (APS), inverse photoemission spectroscopy (IPES), bremsstrahlung isochromat spectroscopy (BIS) [1, 2] and total current spectroscopy (TCS) [3–5]. The excitation process in NEXAFS, ISEELS and APS involves electronic transitions from a core state to an unoccupied state above the Fermi level, and they are governed by the dipole selection rule. In addition, an unoccupied DOS may be affected by core-hole effects. In IPES and BIS, electron transitions occur from higher to lower states which both are located above the Fermi level, and the final DOS determination requires a knowledge of the higher (initial) states from which de-excitation of the electrons occur. These problems may be avoided by using a low-energy electron reflection technique which does not involve preliminary electronic excitation in the solid surface under study and in which only one electronic state is involved (electron transition from vacuum into the solid). An accurate study of the energy dependence of the electron reflection may be performed by

§ Corresponding author.

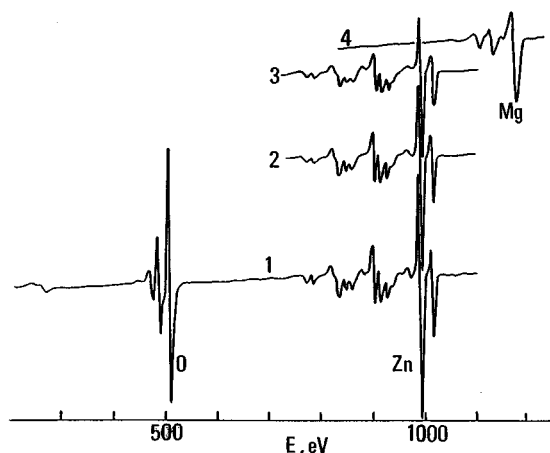


Figure 1. Auger electron spectra from polar ZnO(0001) Zn (1) and ZnO(000 $\bar{1}$) O (3) and from non-polar ZnO(10 $\bar{1}$ 0) (2) surfaces, and from an MgO ultrathin film. All spectra are normalized to the intensity of the oxygen peak-to-peak height.

a TCS technique in which the energy dependence of current transmitted through a sample is analysed over the 0–30 eV range [3–6].

Metal oxides possess unique physical and chemical properties, resulting in their application as advanced materials, as catalysts and as chemical sensors [7, 8]. Our results in applying in studies of unoccupied states in α -Fe₂O₃ and CuO have been published recently [9, 10]. In the present communication we analyse the structure of unoccupied DOS for different crystal surfaces of ZnO and for a MgO thin film using TCS.

2. Experiment

The investigations were carried out in a UHV system (base pressure 10^{-8} Pa) that combines different surface analytical techniques. A four-grid low-energy electron diffraction (LEED) system can be switched between the LEED mode and an operational mode in which TC spectra are measured. Auger electron spectroscopy (AES) characterization of the surface under study was performed using a double-pass cylindrical mirror analyser. The experimental setup has previously been described in more detail [11]. In the TCS experiment a well collimated beam of slow electrons is directed onto the surface under study, and the total current $J(E)$ in the sample circuit is monitored as a function of incident-electron energy E in the range 0–30 eV [3, 12, 13]. In order to reveal the fine structure present in the total current, the first derivative of the current, $S(E) = dJ/dE$, is measured using the lock-in amplification technique. $S(E)$ is referred to as the TCS signal. In our equipment an electron beam current of 1–10 nA (beam energy was modulated at 800 Hz, 0.1 eV peak to peak) was incident normal to the surface, focused into a 0.2–0.4 mm diameter spot. Such gentle probing of the sample by TCS provided a nondestructive surface characterization. The ‘primary’ peak in TCS indicates the vacuum-level E_{vac} of the surface under study. Its shift along the retarding-voltage scale corresponds to the work-function variation due to surface treatment. In order to obtain the absolute values of the work functions, the Fermi level E_F was calibrated with respect both to the tungsten cathode and to a freshly deposited gold film.

The fine structure of the TC spectrum is determined by the energy dependence of the electron reflection coefficient. The latter is represented as the sum of two components,

one being the elastic reflection and the other the inelastic one. At low primary energies ($E < 20\text{--}25$ eV) the elastic reflection component may be considered as predominant [3–5]. An energy dependence of the elastic reflection is closely related to the energy band structure of the solid in the energy range corresponding to the primary electron energy [3–6]. We are dealing with the electronic states of solids located above the vacuum level (unoccupied states). If in the energy range under consideration there is an energy gap, then the electrons are totally reflected. When reaching the allowed band, the elastic reflection decreases abruptly and transmission electron current increases. The energy dependence of the transmitted current $J(E)$ will be determined by the density of unoccupied states (DOS). Therefore the $(S(E) = dJ/dE)$ maxima will be associated with the energy location of the unoccupied band edges, and the maxima of $(-dS(E)/dE)$ will be associated to the energy location of DOS maxima. Thus the negative derivative of the TCS signal is more suitable for comparison of the theoretically and experimentally derived DOS (using other techniques for unoccupied DOS studies). Further details of TCS experiments and of TC spectra interpretations in relation to the surface electronic structure have been discussed elsewhere [3–6, 12, 13].

2.1. ZnO

A transparent colourless zinc oxide crystal was used for our study. The samples were cut from a bulk crystal in the form of thin ($0.5 \times 8 \times 8$ mm³) plates oriented to within 0.3° of the selected orientation. We used the polar (0001) Zn and (000 $\bar{1}$) O and the non-polar (10 $\bar{1}$ 0) surfaces of ZnO. After short series of flash annealing to 770 K in the UHV conditions, all three surfaces under study exhibited sharp (1×1) LEED patterns with the usual pure singlets of sixfold (for both polar surfaces) and rectangular (for the non-polar surface) symmetries [14–16]. Surface atomic composition was characterized by the Auger-electron spectra which are shown in figure 1 (curves 1, 2 and 3 correspond to the Zn-terminated, non-polar and O-terminated surfaces, respectively). We note that the relative intensity of the Zn LMM Auger signal decreases in the considered set of the spectra, in accordance with the decrease of the AES-determined average Zn concentration in the surface layer (the escape depth of electrons is equal to about 1.9 nm at the energy corresponding to the Zn Auger line [17]). Zinc oxide surfaces under study were characterized by the different values of the work functions: $\phi = 3.6 \pm 0.1$ eV (for the Zn-terminated surface), $\phi = 4.5 \pm 0.1$ eV (for the non-polar surface) and $\phi = 4.8 \pm 0.1$ eV (for the O-terminated surface). These work function data are in accordance with the results of previous studies [10, 18, 19]. All three ZnO surfaces under study exhibited stability in the full range of the experiments as demonstrated by the unchanged LEED, work function and TCS characteristics.

2.2. MgO

It was not possible to measure TC spectra from the MgO crystal samples due to a strong effect of charging. In order to eliminate the charging, ultrathin deposited MgO films were used in our study. SrTiO₃(001) surfaces were used as substrate. The films were prepared *in situ* both by electron beam evaporation from a compressed powder pellet of metal oxide and by thermal evaporation of Mg metal followed by oxidation. In both cases, ultrathin films (of thickness of about 5–6 monolayers (ML)) were characterized by the LEED picture corresponding to an MgO(001)-c(2×2) superstructure [20], by the electron energy-loss spectra well known for MgO [20–22] and by the Auger spectrum which is presented in figure 1, curve 4. It should be mentioned that during Mg deposition the substrate SrTiO₃(001)-(2×2) LEED picture was gradually attenuated, and the work function was characterized by the curve with the minimum

at monolayer coverage (2.2 ± 0.1) eV and by the saturation value of (2.6 ± 0.1) eV at 5–6 ML. Oxidation of the Mg film was performed *in situ* in oxygen atmosphere ($P_{O_2} = 10^{-5}$ Pa) and a sample temperature of about 500 K for 5 hours. After oxidation the work function became equal to 3.4 ± 0.1 eV and new diffraction spots corresponding to MgO(001)-c(2×2) superstructure appeared. The observed values of the work function for the thin film Mg–MgO system are in agreement with previously reported data [23, 24].

3. Results and discussion

3.1. TC spectra from MgO and ZnO surfaces

TC spectra were monitored through the process of deposition of the Mg film and its subsequent oxidation. Curve 1 in figure 2 presents the spectrum from the freshly deposited Mg film. A coverage of 5–6 ML of Mg is enough for a complete attenuation of the TC spectrum from the substrate, and the presented spectrum is characteristic for the Mg film. In figure 2 the incident electron energy E is measured with respect to the E_F . Arrows 1–5 mark the positions of vacuum levels E_{vac} for all corresponding spectra presented in figure 2. The difference between the vacuum and Fermi levels gives the value of the work function $\phi = E_{vac} - E_F$ for each presented spectrum. The TC spectrum from the MgO surface (curve 2) is characterized by additional maxima c and c'' in comparison with the spectrum from the Mg surface (curve 1). One can conclude that the maxima a, b and d are connected with Mg-derived band edges of unoccupied electronic states and that the maxima c and c'' are oxygen derived.

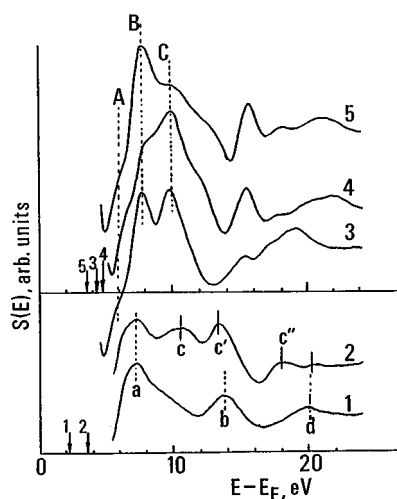


Figure 2. TC spectra from (1) freshly deposited Mg film, from (2) MgO film and from (3) a non-polar ZnO(10 $\bar{1}$ 0) surface, and from (4) a polar ZnO(000 $\bar{1}$) O and (5) ZnO(0001) Zn surfaces. Arrows 1–5 mark the vacuum level position for corresponding curves.

Curves 3–5 (figure 2) present the TC spectra from different ZnO surfaces: the non-polar (10 $\bar{1}$ 0) surface (curve 3), the (000 $\bar{1}$)-O-terminated surface (curve 4) and the (0001)-Zn-terminated surface (curve 5). The main maxima in the spectra are marked by the letters A, B and C. A fine structure in the energy range slightly above 14 eV might be derived by the intensity variation of diffraction beams as previously discussed [14]. A remarkable property of the spectra under consideration consists in an intensity variation of the maximum B in

comparison with maximum C. In curve 3, these two maxima are equal. In this case we are dealing with the non-polar surface ZnO(10 $\bar{1}$ 0) which consists of equal amounts of Zn and O atoms. Maximum C becomes the most pronounced one for the O-terminated surface (curve 4) and it is well attenuated for the Zn-terminated one (curve 5). A possible explanation of such behaviour consists in the assumption that maximum C is connected with the band edge of O-derived electronic states which are localized in the vicinity of oxygen layers in the ZnO crystal.

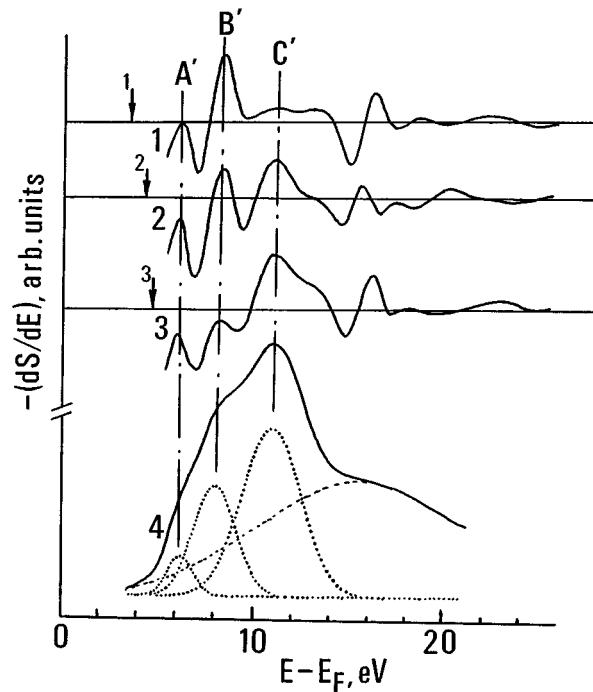


Figure 3. $-(dS(E)/dE)$ from ZnO surfaces: (1) ZnO(0001); (2) ZnO(10 $\bar{1}$ 0); (3) ZnO(000 $\bar{1}$), in comparison with (4) an O 1s x-ray absorption spectrum (from [25]). Arrows 1–3 mark the vacuum level position for corresponding curves.

When comparing the TC spectra of MgO and ZnO (curves 2–5, figure 2) one can conclude that for both oxides, the O-derived maximum in the spectra is located at the energy $E = (10\text{--}11)$ eV.

3.2. Unoccupied DOS difference between Zn- and O-terminated surfaces of ZnO

The electron energy structure of metal oxides (in contrast to metals) is characterized by an alternation of pronounced bands and gaps of unoccupied DOS. On the other hand, a maximum location in the TC spectrum corresponds to the boundary between gap and band at which an electron reflectivity decreases. In order to reveal the DOS maximum location inside the unoccupied bands we will consider the negative derivative of TCS ($-dS(E)/dE$). A set of $-(dS(E)/dE)$ spectra is presented in figure 3 for Zn-terminated (curve 1), non-polar (curve 2) and O-terminated (curve 3) surfaces. Here the $-(dS(E)/dE)$ curves are considered in comparison with the data from empty DOS in ZnO (curve 4) derived from NEXAFS measurements [25]. The obtained structure of the O 1s absorption edge was assigned to the

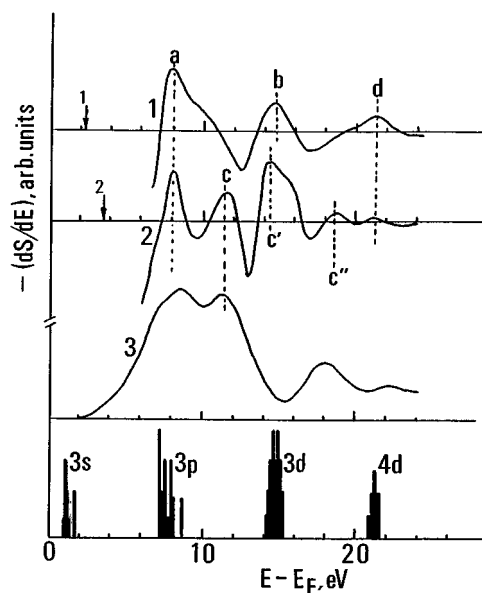


Figure 4. $(-dS(E)/dE)$ curves from (1) an Mg film and (2) an MgO film in comparison with (3) an O 1s X-ray absorption spectrum (from [27]). At the bottom of the figure, a histogram of Mg^{2+} excited states is presented (from [26]). Arrows 1 and 2 mark the vacuum level position for corresponding curves.

transition of O 1s electrons to the empty hybridized orbitals of O 2p and Zn 4sp [25]. Curve 4 in figure 3 is fitted by three Gaussian functions with maximum locations at 6.2, 8.1 and 11 eV, respectively, above the Fermi level. These three maxima correspond well to the maxima A', B' and C' which are observed in the $(-dS(E)/dE)$ curves. Maximum B' dominates on the Zn-terminated surface (curve 1) and its intensity has decreased on the O-terminated one (curve 3). In contrast, maximum C' decreases on the O-terminated relative to the Zn-terminated surface. Thus the maximum C' may be directly connected to the O-derived DOS contribution, and the maximum B' to the Zn-derived one. A possible explanation of this behaviour consists in the assumption that a hybridized Zn 4p–O 2p π band is characterized by the two DOS maxima which exhibit different energy positions on the Zn- and O-terminated surfaces. On the Zn-terminated surface the DOS maximum is located at about 8.1 eV and on the O-terminated at about 11.0 eV above E_F . The intensity of maximum A' (6.2 eV) is practically the same for different crystal surfaces. This DOS maximum may be related to the hybridized Zn 4s–O 2p σ orbital which corresponds to σ -type interaction between Zn and O planes in the ZnO crystal.

3.3. Unoccupied electronic states of MgO

In order to trace an empty DOS evolution through the process of a thin Mg film oxidation we will consider the negative derivatives of TCS $(-dS(E)/dE)$ for the freshly deposited Mg film (figure 4, curve 1). In case of the Mg film, the maxima in $(-dS(E)/dE)$ will reflect energy locations of empty bands, which, in the first approximation, may be considered as a result of summation of the excited electronic states of individual Mg^{2+} ions. In the bottom part of figure 4, a histogram of the optical excitation spectra for Mg^{2+} ions is presented. This histogram was used successfully by Henrich *et al* [26] for explanation of an Mg 2p electron

energy-loss spectrum. The presented histogram predicts the energy locations of the 3s, 3p, 3d and 4d bands of empty states. One can see that the energy locations of maxima a (8.0 eV), b (14.8 eV) and d (21.0 eV), figure 4, curve 1 correspond well to the location of 3p, 3d and 4d empty bands presented in the histogram. An evolution of the $(-dS(E)/dE)$ spectrum during oxidation consists in a weak attenuation of maxima a and b and in an appearance of the new maxima c, c' and c'' which are located at the energies 11.6, 14.2 and 18.5 eV above E_F , respectively (figure 4, curve 2). The main O-derived maximum c is placed between Mg 3p (a) and Mg 3d (b) bands, and maximum c' overlaps with the Mg 3d band. Observed MgO empty DOS may be compared with the empty DOS derived from the NEXAFS data for MgO [27] which is presented by curve 3 in figure 4. One can see that both spectra are characterized by the presence of the Mg 3p–O 2p band (with two maxima of DOS, a and c) and of the c'' band. The latter band may be associated with the DOS of the mixed 3d and 4sp states at the Mg site and the 2p states at the oxygen site. It should be noted that the Mg 3d–O 2p band (overlapping maxima c' and b) is not observed in the O 1s x-ray absorption spectrum (curve 3). This fact can be explained taking into account the possibility of relatively weak interaction between empty O 2p and Mg 3d orbitals (weak hybridization). In the absence of any p–d hybridization, the probability of the O 1s to 3d transition should be zero because the s–d transition is forbidden by the dipole selection rule [2]. In the TCS measurements there is no such limitation on electron passage from the vacuum into the empty band of the solid, and the Mg 3d–O 2p band is observed in the TC spectrum (curve 2, band c' + b in figure 4).

4. Conclusions

Total current spectroscopy was used to study an energy structure of unoccupied DOS for the polar (0001)Zn, (000 $\bar{1}$)O and non-polar (10 $\bar{1}$ 0)ZnO crystal surfaces and for MgO(001)-c(2×2) ultrathin films. The surfaces under study were monitored by LEED, AES and EELS. Comparative analysis of the TC spectra for Mg and MgO thin films provided information on the energy location of Mg-derived (8.0, 14.8 and 21.0 eV) and O-derived (11.6, 14.2 and 18.5 eV) maxima of unoccupied DOS. TC spectra from the polar and neutral surfaces of ZnO crystal revealed a Zn 4s–O 2p band (6.2 eV) and two empty DOS maxima in a Zn 4p–O 2p band which exhibited different energy positions at the Zn-terminated (8.1 eV) and O-terminated (11 eV) surfaces. It was demonstrated that the TCS technique provides more comprehensive and additional information on the spectra of empty DOS in comparison with NEXAFS, ISEELS and APS techniques as long as TCS does not involve preliminary electronic excitation of the solid and is not limited by the dipole selection rules.

Acknowledgments

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