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A total current spectroscopy study of metal oxide surfaces: II. Unoccupied electronic states on TiO₂(110) and SrTiO₃(100) surfaces

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Abstract. Unoccupied densities of states (DOS) for the ordered and atomically clean TiO₂(110) and SrTiO₃(100) surfaces were studied using the total current spectroscopy (TCS) technique. Obtained TC spectra reveal the Ti-derived (Ti 3d(e_g))—5.2 eV, Ti 4s—23.5 eV) and Sr-derived (Sr 3d—triplet: 7.3, 9.0 and 10.5 eV; Sr 5p/O 2p—15 eV) maxima of unoccupied DOS. Main oxygen-derived maxima are located at 11.2 and 15.0 eV for TiO₂ and at 11.8, 18.0 and 19.6 eV for SrTiO₃. The results are discussed in comparison with the previously reported data on DOS of these materials and they provide additional detailed information on the energy structure of unoccupied DOS on TiO₂(110) and SrTiO₃(100) surfaces in the 4–25 eV range above the Fermi level.

1. Introduction

Metal oxides are characterized by a variety of unique physical and chemical properties which are related to their applications as advanced materials, as catalysts and as chemical sensors [1, 2]. For a thorough understanding of the physical and chemical properties and their modification for a special purpose a knowledge of the electronic energy structures of valence and conduction bands is important. Investigations of the conduction band structure (unoccupied density of states (DOS)) are most promising in the case of transition metal oxides as these unoccupied states originate from anti-bonding combinations of metal and oxygen orbitals, are characterized by a pronounced DOS structure due to p–d hybridization and are very sensitive to chemical reactions occurring at the surface. It should be mentioned that experimental studies of unoccupied DOS are usually performed using near-edge x-ray absorption fine structure (NEXAFS), inner shell electron energy-loss spectroscopy (ISEELS) and inverse photoemission spectroscopy (IPES) [3–8].

Titanium dioxide samples have been carefully studied both theoretically and experimentally. The main unoccupied DOS maxima in the energy range 0–10 eV above Fermi level have been revealed by IPES [7, 8], NEXAFS and ISEELS [3–6, 9–12] and have been identified as the t_{2g} and e_g components of the Ti 3d band hybridized with the O 2p band by means of calculations of unoccupied DOS [5, 7]. The best agreement between the experimental and the theoretical data in terms of both peak position and relative intensities

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was achieved in [12] using the p-projected DOS of TiO_2 , which was obtained from an augmented spherical wave calculation. Experimental studies of unoccupied states utilizing NEXAFS and ISEELS are uncertain because of preliminary high-energy excitation, because of dipole selection rules and because the electronic structure of solids may be influenced by core-hole effects [3–6]. These problems may be avoided by using a low-energy electron reflection technique—total current spectroscopy (TCS)—which does not involve preliminary electronic excitation of the surface and may be considered as a gentle alternative tool for an unoccupied DOS study in the energy range above the vacuum level [13–17]. The TCS experiment possesses the following advantages: (1) simplicity of experimental realization—it may be performed by using a conventional low-energy electron diffraction (LEED) system; (2) a beam of slow electrons (0–30 eV) of low intensity (10^{-6} – 10^{-5} A cm^{-2}) provides a nondestructive surface characterization (very important in the case of non-stable metal oxide surfaces); (3) extremely high surface sensitivity (the TCS signal originates due to modulation of elastic electron reflection by unoccupied DOS: the reflectivity from the energy gap is equal to unity [14, 15]).

Results from TCS studies of unoccupied electronic states for some metal oxides (Fe_2O_3 , CuO , ZnO , MgO) surfaces and for C_{60} layers have been published recently [16–19]. In this communication we present data from comparative studies of unoccupied DOS for $\text{TiO}_2(110)$ and $\text{SrTiO}_3(100)$ surfaces.

2. Experiment

All data discussed below were obtained under UHV conditions (base pressure 10^{-8} Pa). Surface characterization was performed by Auger electron spectroscopy (AES), low-energy electron diffraction (LEED) and by TCS. The experimental setup that combines the above mentioned techniques has previously been described in more detail [13, 18, 20]. In the TCS equipment a beam of slow electrons is directed onto the surface under study, and total current $J(E)$ transmitted through the sample is monitored as a function of incident-electron energy in the range 0–30 eV. The TCS signal $S(E) = dJ/dE$ is measured using the lock-in amplification technique. The maxima in $S(E)$ are associated with the energy location of the unoccupied band edges [14, 15, 18], and the negative derivative of $S(E)$ will correspond to the energy location of DOS maxima. Thus the negative derivative of the TCS signal ($-dS/dE$) is more suitable for the characterization of DOS features.

In the present study, surfaces of $\text{TiO}_2(110)$ and $\text{SrTiO}_3(100)$ single crystals (MaTeck, Germany) were investigated. The samples were in the form of thin ($1 \times 10 \times 10$) mm^3 plates oriented to within 0.3° of the selected orientation. Well polished and methanol-rinsed samples were cleaned in the experimental chamber by repeating cycles of (1) prolonged (about 5 hours) etching in oxygen, $P(\text{O}_2) = 10^{-4}$ Pa, under the action of a focused beam from an external xenon lamp (300 W); and (2) surface annealing under the action of the same lamp in UHV conditions. The sample temperature during the process of sample cleaning did not exceed 900 K. After three to five cycles of cleaning, both samples exhibited good surface ordering and atomic cleanliness. During the cleaning procedure the colour of the samples changed to blue (for TiO_2) and to light grey (for SrTiO_3) corresponding to oxygen vacancy creation on the surface under study. Both surfaces were characterized by sharp LEED patterns. The $\text{TiO}_2(110)$ surface exhibited a predominant (1×1) diffraction pattern with a very weak (1×2) superstructure. The structure observed is characteristic for a slightly oxygen deficient $\text{TiO}_2(110)$ surface [21]. The obtained LEED picture of the $\text{SrTiO}_3(100)$ surface was characterized by a (2×2) reconstruction. The (2×2) surface arrangement of strontium titanate is one of the previously observed reconstructions of oxygen deficient $\text{SrTiO}_3(100)$ surfaces

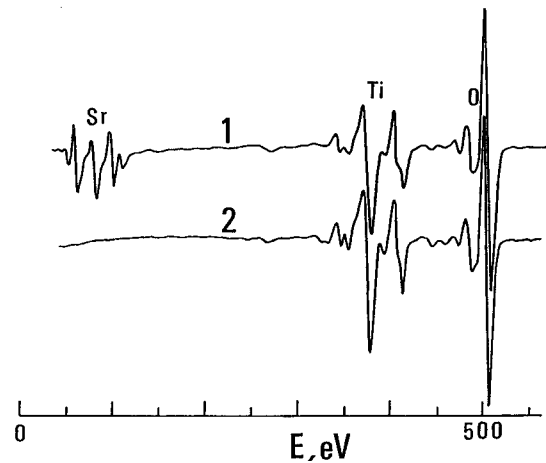


Figure 1. Auger electron spectra from (1) the SrTiO₃(100) and (2) TiO₂(110) surfaces. The spectra are normalized to the oxygen peak-to-peak height.

depending on annealing conditions [22, 23]. Atomic compositions of the surfaces under study are presented by the Auger spectra shown in figure 1, curves 1 and 2 for SrTiO₃ and TiO₂, respectively.

The spectra presented are normalized to the oxygen peak-to-peak height. The main lines of the spectra are as follows: Sr (68, 86 and 104 eV), Ti (382 and 416 eV) and O (510 eV). Their energy positions correspond well to those previously reported [24, 25]. Intensity relations (taking into account sensitivity factors [26]) of $I_{Ti}/I_{Sr} = 1.1$ testify that we are dealing with an oxygen deficient SrTiO₃(100) surface which consists of nearly equal areas of TiO₂ and SrO planes. The intensity ratio for TiO₂, $I_{Ti}/I_{O} = 0.61$, corresponds to a slightly oxygen-deficient TiO₂(110) surface. The values obtained for the work functions (3.6 ± 0.1 eV for TiO₂ and 4.0 ± 0.1 eV for SrTiO₃) correspond to a surface Fermi level location close to the bottom of the conduction band of the materials under study, in accordance with the high surface concentration of oxygen vacancies.

3. Results and discussion

3.1. Comparison of TC spectra from TiO₂(110) and SrTiO₃(100) surfaces

Comparative investigations of the TC spectra from TiO₂ and SrTiO₃ surfaces seem to be very promising as the additional features corresponding to the Sr-derived states will be observed in the SrTiO₃ spectrum. TC spectra for both materials are presented in figure 2 by curves 1 and 2 for TiO₂ and SrTiO₃, respectively. In figure 2 an incident electron energy E is measured with respect to the Fermi level E_F . The arrows 1 and 2 mark the position of vacuum levels for TiO₂(110) and SrTiO₃(100) surfaces, respectively. The TC spectrum from the TiO₂ surface contains a set of maxima: A (5.2 eV), C (10.4 eV), C₁ (15 eV) and D (23 eV). It should be mentioned that the TC maximum location corresponds to the bottom edge of the band of unoccupied DOS. The TC spectrum from the SrTiO₃ surface is characterized by the following additional features of the fine structure: (1) appearance of the three narrow maxima: B (6.9 eV), B₁ (8.7 eV) and B₂ (10.2 eV); (2) appearance of the maxima B₃ (14 eV), which overlaps the maximum C₁ in TiO₂; (3) a shift to higher energy of maximum C (11.5 eV) and the appearance of a new maximum C₂ (17.5 eV), and broadening and a small shift to lower energy

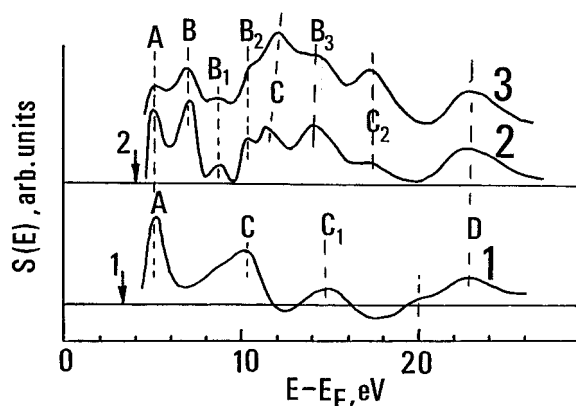


Figure 2. TC spectra $S(E)$ from (1) the $\text{TiO}_2(110)$ and (2) the $\text{SrTiO}_3(100)$ surfaces. (3) spectrum 2 after oxygen adsorption. Arrows 1 and 2 mark the vacuum level position for TiO_2 and SrTiO_3 , respectively. Horizontal lines show zero levels for the spectra 1 and 2.

of maximum D. Curve 3 in figure 2 presents a variation of the SrTiO_3 TC spectrum induced by oxygen adsorption (exposure of the SrTiO_3 sample to 10^{-4} Pa oxygen atmosphere for 10 min). Oxygen adsorption was followed by an attenuation of maxima A, B, B_1 , B_2 and B_3 and by a strong increase of maxima C (and its shift to a higher energy: 2.2 eV) and C_2 . The observed variation in the oxygen-induced spectrum allows us to reach the conclusion that the C group of maxima may be considered as an oxygen-derived one, and maxima A, B and B_3 as metal-derived ones. Moreover, maximum A is related to Ti states and the B group of maxima are related to Sr states. It is worthwhile to mention that the main oxygen-derived maximum C is located in the vicinity of 10 eV (both for SrTiO_3 and for TiO_2). A similar contribution of oxygen-derived states has been observed in our previous TCS studies of other metal oxides: ZnO, CuO and MgO [18, 19].

3.2. Unoccupied electronic states of the $\text{TiO}_2(110)$ surface

In order to reveal precisely the energy location of unoccupied DOS maxima we will consider the negative derivative of the TCS signal ($-dS/dE$). In figure 3, a plot of ($-dS/dE$) for TiO_2 (curve 3) is presented in comparison with data on unoccupied DOS in TiO_2 derived from NEXAFS (curve 1 [10]) and from ISEELS (curve 2 [11]) measurements. Data derived from inverse photoemission (IPES) are not presented in figure 3 because the energy range of IPES measurements is 0–16 eV above the Fermi level and a comparison can be made only in the beginning part of our spectrum. Peaks A' and C' (figure 3) are in accordance with IPES data [7]. The calculated DOS for TiO_2 was derived also in the 0–10 eV range and the peak A' may be related to a Ti $3d(e_g)$ band [5].

We will now carry out a comparative analysis of the spectra presented in figure 3 following the scheme of DOS classification for TiO_2 and SrTiO_3 in the energy range of interest [12]. In this article [12], data on partial DOS of metal (Ti, Sr) and oxygen have been presented together with the total p-projected DOS. In order to compare with our experimental spectra the total calculated DOS is shown by dotted lines in figures 3 and 4 for TiO_2 and SrTiO_3 , respectively. The first Ti $3d(t_{2g})$ maximum is located below the vacuum level (marked by an arrow in figure 3) and it is not observed in the TC spectrum. Peak A' corresponds well to the second Ti $3d(e_g)$ maximum and it is observed in all spectra presented. The maxima C' and

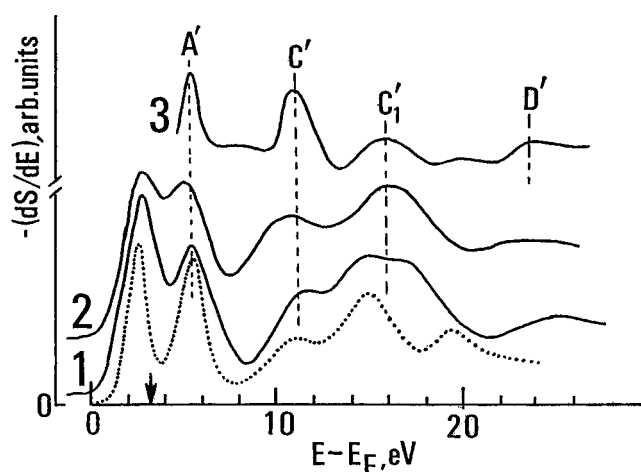


Figure 3. $-(dS(E)/dE)$ curves (3) in comparison with (1) NEXAFS data [10], (2) ISEELS data [11] and (dotted line) with the calculated p-projected DOS [12] for TiO_2 . The arrow marks the vacuum level position.

C'_1 may be directly related to the oxygen 2p bands, which were assigned to an anti-bonding combination of direct oxygen–oxygen interaction [21]. Maximum C' is more pronounced in the TC spectrum while the maximum C'_1 dominates in the NEXAFS and ISEELS spectra. Moreover, this maximum has split in the NEXAFS spectrum (curve 1, figure 3). In the energy range 22–25 eV we observe a broadened maximum D' which may originate from the Ti 4s band. A sensitivity of the C' -group maxima to oxygen adsorption, as shown in the previous section, supports a conclusion (made in [12]) on the oxygen-derived character of these states. Similarity between the TC spectrum and the NEXAFS and ISEELS ones for TiO_2 justifies that all states in the energy range 0–20 eV may be considered as Ti–O hybridization and O orbitals exhibiting a presence of p character, in accordance with the theoretical consideration [5]. The latter conclusion is based on the fact that the data obtained by low-energy TCS are not influenced by the dipole selection rule and that ISEELS and NEXAFS involve the electron transitions from a core state (1s) to unoccupied electron states which are allowed if the final states have a contribution from p-type orbitals. The similarity of spectra observed in figure 3 also supports an assumption that core–hole action does not significantly change the energy structure of unoccupied DOS in TiO_2 since the TC spectrum is not influenced by core–hole effects. The experimental spectra considered in figure 3 are generally in accordance with the calculated one (dotted line in figure 3) [12].

3.3. Unoccupied electronic states of $\text{SrTiO}_3(100)$ surface

The structure of the unoccupied DOS of such a complete oxide as SrTiO_3 is determined by the contribution of different empty states: 4d and 5sp of strontium, 3d and 4sp of titanium and 2p of oxygen. Chemical interactions result in the hybridization between metal and oxygen orbitals. Fingerprints of unoccupied DOS in TCS measurements are presented in figure 4 by the $-(dS/dE)$ curve (2) in comparison with the NEXAFS (curve 1, [12, 27]) and calculation (dotted line, [12]) data.

As discussed in the previous section, the maximum A' corresponds to the Ti 3d/O 2p hybridized state. The triplet structure B' , B'_1 and B'_2 which may be directly attributed to the

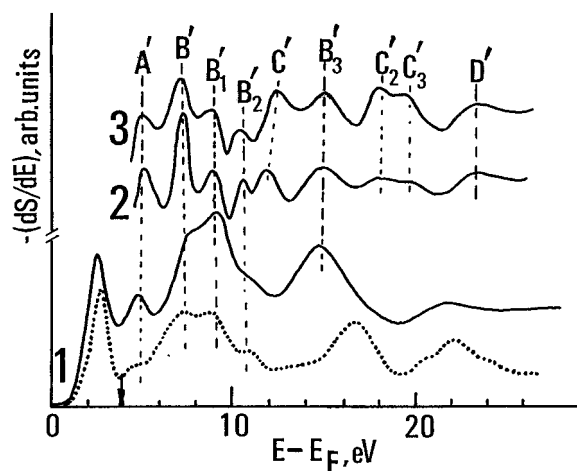


Figure 4. $-(dS(E)/dE)$ curves (2) in comparison with (1) NEXAFS data [12] and with the calculated p-projected DOS (dotted line) [12] for SrTiO_3 . (3) Variation of curve 2 after oxygen adsorption. The arrow marks the vacuum level position.

Sr 4d/O 2p states is observed in both the TCS and NEXAFS spectra, and its appearance was predicted in the calculated DOS [12, 28]. Maximum B, most probably, may be connected with the DOS contribution of Sr 5p/O 2p hybridized states in accordance with the NEXAFS results and with the data of the calculation [12].

A broad maximum D' originates, obviously, from the mixed contributions of Ti 4s and Sr 5p states [12]. The maxima C' , C'_2 and C'_3 are closely connected with the adsorbed oxygen on the SrTiO_3 surface and they are not presented in the NEXAFS data (curve 1, figure 4). The appearance of these DOS features may be influenced by the distortion of the interatomic coordination in the surface layers of SrTiO_3 in comparison with the coordination in the bulk, but the additional DOS features observed in the TC spectrum can—as discussed above—be explained by taking into account the higher surface sensitivity of the TCS technique.

4. Conclusions

Total current spectroscopy was used to study the energy structure of unoccupied DOS on well ordered and atomically clean $\text{TiO}_2(110)$ and $\text{SrTiO}_3(100)$ surfaces, as characterized by LEED and AES. A comparative analysis of the TC spectra for TiO_2 and SrTiO_3 surfaces has provided information on energy locations (above the Fermi level) of Ti-derived (Ti 3d(e_g) at 5.2 eV and Ti 4s at 23.5 eV) and Sr-derived (Sr 3d triplet at 7.3, 9.0 and 10.5 eV, and Sr 5p/O 2p at 15 eV) maxima of unoccupied DOS.

Oxygen-derived states were identified in the course of an oxygen adsorption experiment. Here, the main oxygen-derived maxima of unoccupied DOS were found to be located: (1) at 11.2 and 15.9 eV for the $\text{TiO}_2(110)$ surface and (2) at 11.8, 18.0 and 19.6 eV for the SrTiO_3 surface. The TCS data attained are discussed in comparison with results of NEXAFS and ISEELS measurements and with DOS calculations. Additional DOS features observed in TC spectra are found to be connected with the higher surface sensitivity of the TCS technique in the energy range 5–30 eV above the Fermi level.

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