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Abstract. Total current spectroscopy (TCS) was used to study an evolution of unoccupied states through the process of thin-layer copper deposition and its oxidation on polar ZnO(0001) and (000$\bar{1}$) surfaces. Zn-derived and O-derived unoccupied bands were identified in the TC spectrum at 7.7 and 9.8 eV, respectively, from the clean and well ordered polar ZnO faces, while the spectra from a thin CuO layer reveal an intensive fine structure in the 6–25 eV energy range above the Fermi level, which is discussed in comparison with previously reported results of experimental and theoretical investigations. The obtained data provide additional information on the energy location of the edges of unoccupied bands in CuO in the 6–25 eV range relative to E_F.

1. Introduction

A knowledge of the band structure of an unoccupied electronic state above the vacuum level is useful for both a correct interpretation of the data of electron spectroscopy techniques and for testing and correction of theoretical band structure and density of states (DOS) computational schemes. Experimental studies of unoccupied states utilizing inverse photoemission (IP), secondary electron spectroscopy (SES), bremsstrahlung isochromat spectroscopy (BIS) and x-ray absorption (XAS) are uncertain in many cases because of two states being inherently involved and since the electronic structure of solids under high-energy excitation may be influenced by core-hole effects [1–4]. These problems may be avoided using a low-energy electron reflection technique which does not involve preliminary electronic excitation. An accurate study of the energy dependence of electron reflection may be performed by a total current spectroscopy (TCS) technique in which the energy dependence of current transmitted through a sample is analysed over 0–30 eV [5–9].

In the present work we have analysed an evolution of the empty electronic state structure during the process of thin CuO layer formation on the polar faces of a ZnO crystal using the TCS technique. The CuO/ZnO system under study is of present particular interest in heterogeneous catalysis and sensor applications [10, 11].

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2. Experimental set-up and sample preparation

Experiments were performed in a UHV system (base pressure 10^{-8} Pa) that combines different surface analytical techniques. Surface characterization by Auger electron spectroscopy (AES) was performed using a double-pass cylindrical mirror analyser. A four-grid low-energy electron diffraction (LEED) system can be switched between the LEED mode and a operational mode in which TC spectra are measured. The experimental set-up has previously been described in more detail [8]. In the TCS experiment a well collimated beam of slow electrons is directed at normal incidence onto the surface under study, and the total current $J(E)$ in the sample circuit is monitored as a function of the incident-electron energy E in the range 0–25 eV. In order to reveal the fine structure present in the total current, the first derivative of the current, $S(E) = dJ(E)/dE$, is measured using a lock-in amplification technique. $S(E)$ is referred to as the TCS signal. In our equipment an electron beam current of 10 nA was incident normal to the surface, focused into a spot of 0.5 mm in diameter. Such gentle probing of the sample by the TCS provided a nondestructive surface characterization [7]. The 'primary' peak in TCS indicates the vacuum-level position of the sample surface under study. Its shift along the retarding-voltage scale corresponds to the workfunction variation due to surface treatment. In order to obtain the absolute values of the workfunction, the values of the Fermi-level position were calibrated with respect both to the tungsten cathode and to a freshly deposited gold film. Further details of TCS experiments and of TC spectra interpretations in relation to the surface electronic structure have been discussed elsewhere [5–9]. The incident-electron beam energy was modulated at 800 Hz, 0.1 eV peak to peak.

A transparent colourless zinc oxide crystal was used for our study. The samples were cut from a bulk crystal in the form of thin (0.3 mm × 6 mm × 6 mm) discs, oriented within 0.3° of the (0001) orientation. Both surfaces (zinc terminated and oxygen terminated) were mechanically diamond-paste polished, rinsed in methanol and thermally annealed in UHV. A sharp 1 × 1 LEED pattern with the usual pure singlets of sixfold symmetry was observed in the electron energy range 20–150 eV after short series of flash anneals to 770 K. It is worthwhile to emphasize that an oxygen-terminated surface turned out to be more stable (in comparison with a zinc-terminated one) under prolonged thermal annealing. It has been shown [12] that prolonged annealing of the zinc-terminated surface was followed by a subsextet structure formation in the LEED picture. Both ZnO surfaces exhibited stability in the full experiment, as demonstrated by the unchanged LEED, workfunction and TCS characteristics.

Copper deposition was performed *in situ* at room temperature (RT) onto both polar surfaces, which were initially characterized by the pure singlet 1 × 1 LEED picture. Copper was deposited *in situ* from an electron beam evaporator, and the average thickness of the deposits was monitored by a quartz crystal microbalance [8]. During copper deposition the LEED intensities were gradually attenuated and were practically eliminated at an average copper layer thickness of 2 nm without appearance of any new LEED spots from this unannealed Cu layer. The latter observation testified no ordered superstructure formation at RT during copper deposition. Subsequently the deposited copper particles were oxidized at 15 Pa and a temperature of 600 K up to an exposure of about 10^9 L [13].

The above steps of sample treatment are illustrated by a series of Auger electron spectra in figure 1 where curves 1 and 2 correspond to the Zn-terminated and O-terminated surfaces, respectively. We note that the Zn LMM Auger signal is well attenuated on the O-terminated surface. Spectra 1 and 2 are normalized to the oxygen peak-to-peak height. After copper deposition (figure 1, curve 3), the attenuated oxygen KLL and zinc LMM signals are still
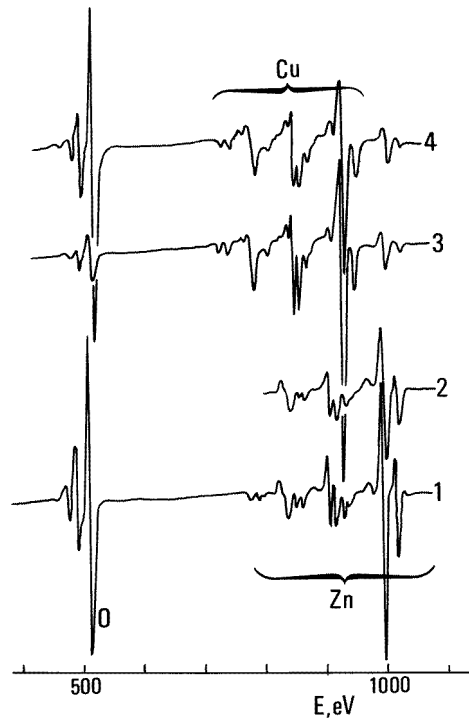
Figure 1. Auger electron spectra from clean well ordered surfaces: 1, ZnO(0001); 2, ZnO(000$\bar{1}$) surfaces; 3, after 30 Å Cu-layer deposition; 4, after oxidation of the latter.

seen in the Auger spectrum. Probably we are dealing with an inhomogeneous Cu coverage containing small patches of open ZnO substrate. This situation occurs for both surfaces under study.

Sample oxidation is followed by a strong increase of the oxygen Auger signal (figure 1, curve 4). The relatively intense Zn LMM signal (about 16% of the Cu LMM signal) may be explained not only by the inhomogeneous structure of the Cu film but also by the possibility of thermally activated interdiffusion of Zn and Cu atoms through the ZnO/Cu interface [14]. Taking into consideration a higher AES sensitivity to oxygen [15] it is possible to determine the copper oxide composition as CuO.

3. Results and discussion

3.1. Comparison of TC spectra from Zn- and O-terminated surfaces

TC spectra from the clean well ordered zinc oxide surfaces are presented in figure 2 for a ZnO(000$\bar{1}$) O-terminated surface (curve 1) and for a ZnO(0001) Zn-terminated surface (curve 2). The incident electron energy E is measured with respect to the Fermi level E_F. Arrows 1 and 2 mark the corresponding energy positions of the vacuum levels E_V for both surfaces which coincide with the position of the first peak in the TC spectra (first peaks are not shown in figure 2). The difference between the vacuum and Fermi levels gives a value of the work function, $\phi = E_V - E_F$. In our case we observe different work functions for Zn-terminated ($\phi = 3.6 \pm 0.1$ eV) and for O-terminated ($\phi = 4.8 \pm 0.1$ eV) surfaces. These
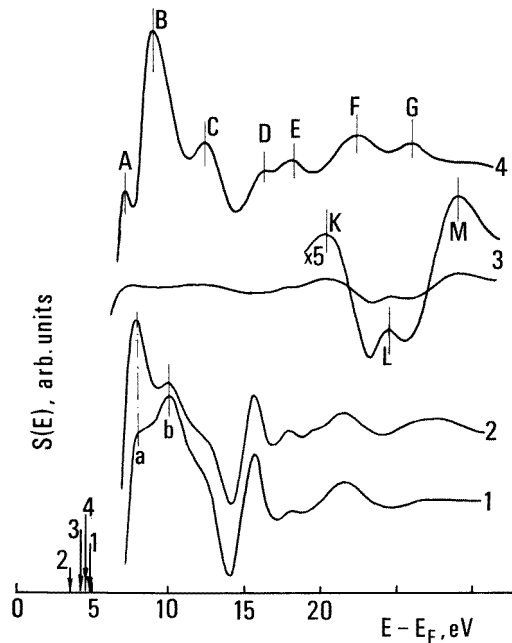
Figure 2. TC spectra from clean well ordered surfaces: 1, ZnO(000$\bar{1}$); 2, ZnO(0001); 3, after 30 Å Cu-layer deposition; 4, after oxidation of the latter. Arrows 1–4 mark the vacuum level positions for corresponding spectra.

work-function data were reproducible in the ZnO-surface treatment in ultrahigh vacuum used (thermal annealing followed by a prolonged relaxation at room temperature) as reported in previous publications [8, 12, 16, 17]. A connection of the observed fine structure in the spectrum to the energy distribution of the density of unoccupied electron states located above E_V has been discussed previously [8, 12, 17] for the Zn-terminated surface.

The main difference between spectra 1 and 2 in figure 2 is an intensity variation of maxima a ($E = 7.7$ eV) and b ($E = 9.8$ eV). Maximum a is most pronounced for the Zn-terminated surface and maximum b for the O-terminated one. A possible explanation of such behaviour consists in the assumption that the band of empty states located in the range 6 eV $< E <$ 14 eV is constructed from the Zn and O orbitals, and that the lower part of this band is mainly Zn derived (maximum a) while the upper part is O derived (maximum b). Similar contributions of Zn- and O-derived states in the lower part of the conduction band (energy range 1 eV $< E <$ 5 eV) have been discussed previously [18].

3.2. Unoccupied electronic states of CuO

Copper deposition was followed by a strong attenuation of the TC spectrum fine structure from zinc oxide. At an average Cu-layer thickness of about 3 nm a very different spectrum was obtained (curve 3, figure 2). It is emphasized that the Cu deposition was followed by a workfunction increase on the Zn-terminated substrate (from 3.6 to 4.4 eV) and by a decrease on the O-terminated one (from 4.8 to 4.4 eV). In both cases the values of the workfunction were equal to $\phi = 4.4 \pm 0.1$ eV (arrow 3), which is in accordance with the previously published data for deposited Cu layers [17]. Such behaviour of the workfunction in comparison with the data on AES discussed above allows us to reach a conclusion on the

nearly complete 3 nm Cu coverage on polar ZnO surfaces. The Cu-layer fine structure is easily observed by additional multiplication of the spectrum as three maxima, K, L and M. These peaks are related to the electron reflectivity variations at the band edges of the copper band structure in the (111) direction. More precisely, the local maximum L locates the Cu deposition at 24.3 eV with respect to the Cu Fermi level [19] or 19.7 eV with respect to the vacuum level [9]. The relatively weak intensity of these peaks testifies [9] to formation of a polycrystalline Cu film containing a small fraction of (111)-oriented Cu clusters [17].

During Cu-layer oxidation the TC spectrum suffered a strong reconstruction with appearance of an intensive structure characterized by peaks A (6.8 eV), B (8.8 eV), C (12.2 eV), D (15.9 eV), E (17.8 eV), F (22.2 eV) and G (26 eV). The workfunction after oxidation increases to 4.6 ± 0.1 eV. Such an intensive TCS structure for polycrystalline materials may occur if the material under study is characterized by a pronounced structure of density of unoccupied states in the energy range of interest.

The structure of unoccupied electronic states of CuO has been studied both theoretically and experimentally [1–4], and their presence in the calculated and measured spectra of pronounced bands and gaps was observed. A peculiarity of the TCS technique is the following. If the primary electron energy corresponds to the energy gap, the electrons do not enter the sample and the electron reflectivity is high. At the boundary between a gap and a band, a strong electron-reflectivity decrease followed by a TCS maximum appearance occurs. Therefore the TCS maxima may be associated to the energy location of the unoccupied band edges [7, 9]. In the case of the CuO surface a set of maxima (A–G, figure 2, curve 4) reflects the locations of the bottom edges of unoccupied bands. In figure 3 the observed TC spectrum of CuO is presented in comparison with the data from an experimental observation of the density of empty states of CuO derived from the structure of the O 1s absorption edge [3]. Figure 3, curve 1 shows the CuO TC spectrum and curve 2 shows an XA spectrum from the O 1s edge which reflects the empty DOS in CuO [3] while curve 3 shows the first derivative of curve 2. It should be mentioned that the first derivative of the DOS is more suitable for comparison to the TC spectrum. Good agreement is obtained between the maximum locations in the TC spectrum (curve 1) and in the derivative of the DOS (curve 3).

Moreover, a more detailed fine structure is observed in the TC spectrum in comparison with the SE spectrum [2], the BI spectrum [1] and the XA spectrum [3, 4]. Data obtained by low-energy TCS are not influenced by core-hole effects or by selection rules. Following the scheme of partial DOS classification for CuO [4] we may identify the maxima observed in the TC spectrum. Maxima A–C (6 eV$< E < 14$ eV) would be assigned to the unoccupied electronic states which have mixed 4s, 4p and 3d character at the Cu site, and mixed p and d character at the oxygen site. Maximum A reflects a shoulder that was observed by O 1s XAS [3], and maximum C corresponds most probably to an increase of mixed O(p–d) DOS. Maxima D and E (14 eV$< E < 20$ eV) reflect a structure of DOS derived from O(p–d) and Cu(p) states. Maximum F (at about 22 eV) may be associated with the increase of DOS derived from O(d) and Cu(f) unoccupied states.

4. Conclusions

Total current spectroscopy was used to study an evolution of empty DOS during thin-copper-layer deposition onto polar ZnO(0001) and (000$\bar{1}$) surfaces and its successive oxidation. Processes of copper deposition and oxidation were monitored by low-energy electron diffraction and Auger electron spectroscopy. Comparative analysis of the TC spectra for the clean well ordered polar faces of ZnO leads to the conclusion of different energy locations
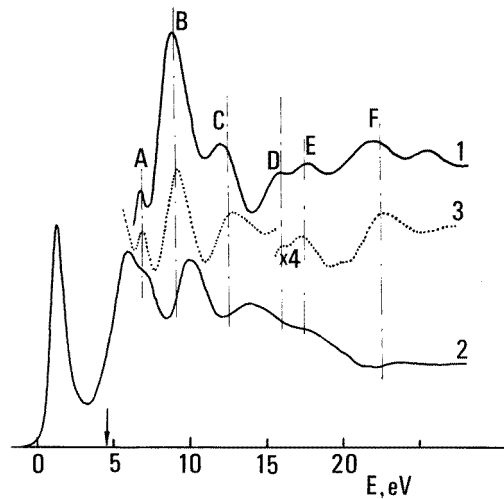
Figure 3. The TC spectrum from an ultrathin CuO layer (1), the O 1s XA absorption spectrum (from [3]) (2) and the derivative of the latter (3).

of Zn-derived (7.7 eV) and O-derived (9.8 eV) bands of empty DOS. The TC spectrum of an ultrathin CuO surface reveals a set of intensive maxima in the energy range 6–25 eV above the Fermi level. These maxima are identified as the band edges of empty electronic states of different orbital character derived by copper and oxygen contributions.

The data obtained correspond in general to the previous theoretical and experimental studies of empty DOS in CuO [1–4] but they are characterized by more detailed information on the energy location of the band edges.

Acknowledgments

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