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The influence of defects on the Ni 2p and O 1s XPS of NiO

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Abstract. The Ni 2p and O 1s XPS of NiO single crystals were measured using monochromatic Al K α radiation. Different treatments of the crystals allow us to give a description of the influence of defects on these spectra.

The Ni 2p_{3/2} spectrum of *in-situ*-cleaved NiO exhibits clearly visible features at 854.1 eV, 855.6 eV and 861 eV. The intensity ratio changes after ion bombardment and an additional peak at 852.2 eV appears. Apart from a slight increase in linewidth the O 1s spectrum remains unchanged. The O 1s spectrum from an *in-situ*-cleaved NiO single crystal exhibits only a single peak at 529.4 eV which can be fitted by a Gaussian line profile. Further measurements allow us to attribute the well known O 1s satellite at 531.2 eV to emission from oxygen-containing species adsorbed at defects.

1. Introduction

NiO has been the subject of many experiments and discussions over the last decade. The Ni 2p and O 1s spectra, particularly, are of great interest. It is well accepted that the Ni 2p photoelectron spectrum of NiO exhibits a very strong satellite structure. In particular the satellite at 1.5 eV above the lowest binding energy line has been interpreted by several authors [1-7].

However, in connection with the discussion and identification of defect structures on NiO surfaces, this feature has been assigned to the Ni³⁺ species existing on the surface. Recently, Tomellini [5] correlated the feature assigned to Ni³⁺ with an additional feature in the O 1s spectrum. He concluded that the energy shift between the main peak and the satellite in both the O 1s and Ni 2p XPS is due to a change in the ionic charge and in the oxygen coordination induced by cation vacancies. This conclusion has important consequences for the understanding of catalytic processes.

We will show in the present paper that the situation is slightly more involved. Primarily, on the clean, well ordered surface, satellite structure on the Ni 2p emission is clearly identified. Secondly, in the case where the surface contains defects, the satellite structure is superimposed with the emission resulting from Ni³⁺ centres. However, the Ni³⁺ emission is not directly interrelated with the extra feature in the O 1s spectra, as suggested by Tomellini, but rather the latter is due to the emission from adsorbed oxygen-containing species.

2. Experiment

The experiments were performed in a PHI 5500 Multitechnique System (NiO single crystals) and a modified Leybold multitechnique system (epitaxially grown film). All XPS for the single crystals were obtained with monochromatized Al $K\alpha$ radiation. We used a double focusing monochromator with a spot diameter of 0.8 mm. The photoemitted electrons were analysed by a hemispherical 11 inch analyser and detected with a multichannel detector. All spectra were analysed with a spot diameter of 0.4 mm and an energy resolution of 1.5% of the pass energy. The NiO single crystals (1.5 × 4 mm) were cleaved *in vacuo* at a base pressure of 5×10^{-10} Torr. A differentially pumped ion gun with a beam diameter of 0.5 mm, ion currents up to 5 μ A and a sputter area of 5 × 5 mm was used for sputtering. The spectra were calibrated by a comparison with UPS data [8–10] and the Ni 2p spectra have been corrected by subtracting the inelastically scattered electrons according to the Tougaard formalism [11]. For the O 1s spectra a background subtraction was not necessary. The spectra on the thin NiO films were also obtained with monochromatized Al $K\alpha$ radiation. The monochromator is of 0.4 m Rowland type. The photoemitted electrons are analysed with a hemispherical analyser of 127 mm mean radius and counted with a multichannel device. The ultimate overall resolution as measured at the Fermi edge of a Ag sample was 0.4 eV at a pass energy of 6 eV. The NiO(100) films were prepared as described earlier [8]. They were characterized using LEED and a Kelvin probe within a preparation chamber from which the sample can be transferred to the analysing position in a separate chamber by means of a horizontally mounted sample manipulator. The base pressure in the vacuum system was 5×10^{-11} Torr. The spectra were recorded at two exit angles of the photoemitted electrons, namely at normal and at grazing (70°) emission.

3. Results and discussion

In figure 1, XPS of an *in-situ*-cleaved NiO(100) surface which has been successively sputtered are shown. The sputter conditions are indicated in the figure. In order to compare the spectra, the binding energies of the main peak have been aligned to the binding energy which has been found for the freshly cleaved surface. During sputtering all features shift to higher binding energies by about 1 eV as discussed earlier [8]. In figure 1(a) the Ni 2p_{3/2} and Ni 2p_{1/2} spectra are shown. Clearly, additional features develop with sputter time. The feature which develops at the low binding energy side ($E_B = 852.2$ eV) can be attributed to metallic Ni [12–13], whereas a structure which develops at 855.6 eV can be attributed to Ni³⁺ states. On the freshly cleaved perfect surface (figure 1(a), spectrum a), the shoulder at 855.6 eV already exists due to correlation effects. This feature shows no intensity variations with emission angle on the perfect surface (cf figure 2(a)), whereas the sputter induced feature at the same binding energy clearly shows intensity variations with angle (cf figure 2(b)). This leads us to the conclusion that the intensity of the shoulder at 855.6 eV of the sputtered surface originates from a superposition of a bulk effect and Ni³⁺ species localized close to the surface. In the corresponding O 1s spectra shown in figure 1(c) no extra features are observed. This is not consistent with [5]. The situation is more clearly revealed in the intensity plot (cf figure 1(b)) of the Ni⁰ and Ni³⁺ intensities of figure 1(a). As the origin of all features in the

Ni 2p spectrum is still unclear we did not try a detailed peak separation for Ni²⁺ and Ni³⁺ as in [7], but monitored in figure 1(b) only the increasing intensity of the feature at 855.6 eV relative to figure 1(a), spectrum a. During sputtering both the Ni⁰ and the Ni³⁺ features increase significantly in intensity, whereas there is obviously no change in the O 1s spectra. Accordingly, the formation of the Ni³⁺ species in the sputtering process is not connected with the formation of additional features in the O 1s spectra. It is near at hand that the formation of metallic nickel results from a loss of oxygen at the surface in the sputtering process. This assumption is corroborated by the observation that these nickel states are significantly attenuated by reoxidation of the sample. On the other hand the Ni³⁺ features are not affected by this procedure (not shown).

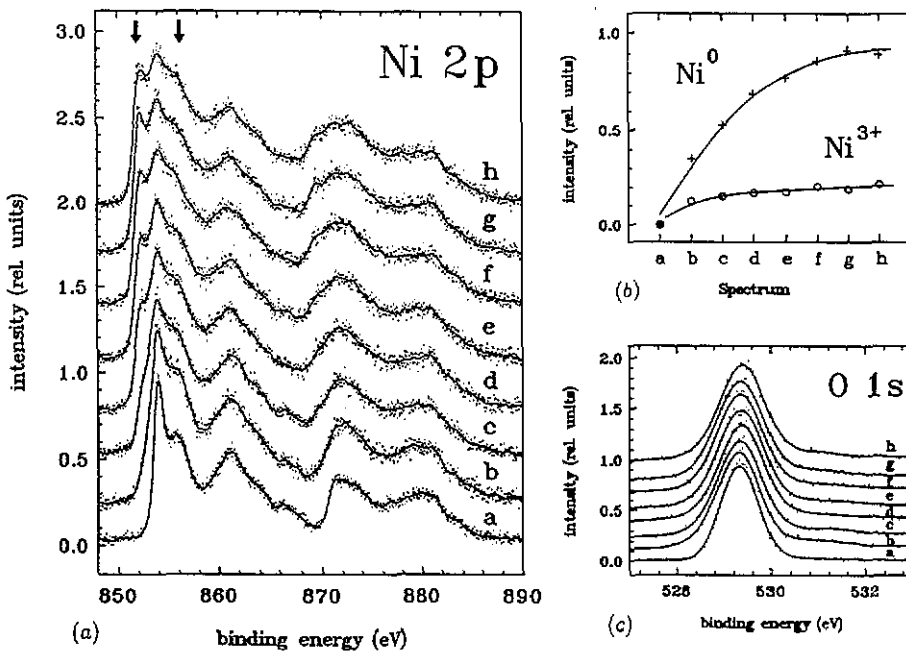


Figure 1. (a) Ni 2p XPS of a NiO(100) single crystal after successive sputter cycles. Sputter conditions: a, freshly cleaved *in vacuo*; b, 1 min/0.5 kV; c, 1 min/0.5 kV; d, 5 min/0.5 kV; e, 5 min/1 kV; f, 5 min/1.5 kV; g, 5 min/2 kV; h, 10 min/4.5 kV. (b) Intensity plot of the Ni⁰ and Ni³⁺ intensities from the Ni 2p_{3/2} spectra of panel (a). (c) O 1s XPS corresponding to the Ni 2p XPS of panel (a).

In the following we will show that the formation of extra features in the O 1s spectra can be related to the adsorption of oxygen-containing species on the surface of the NiO sample. This will be demonstrated by a sequence of arguments. The lowest trace in figure 3(a) shows the O 1s spectrum of a perfect NiO(100) surface after cleavage in vacuum. Note that the line-shape can be well described by a single symmetric Gaussian line profile as shown in the inset of figure 3(a). We already noted that sputtering under controlled conditions as far as the cleanliness of the sputter gas is concerned leads to no extra features in the O 1s spectra except for a slight increase in the linewidth. Although all experiments were performed under UHV conditions with a base pressure of 5×10^{-10} Torr, as early as a few hours after

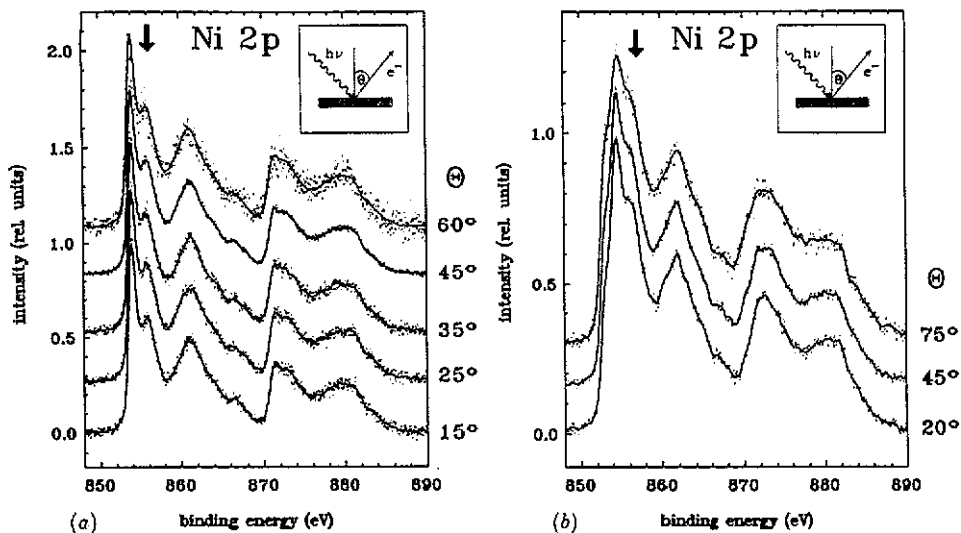


Figure 2. (a) Ni 2p XPS of a freshly cleaved NiO(100) single crystal at different polar angles as indicated. (b) Ni 2p XPS of a softly sputtered NiO(100) single crystal at different polar angles as indicated.

cleaving an extra feature at 2.0 eV lower binding energy begins to develop. This behaviour is intensified when the crystal is sputtered. Figure 3(a), trace b, shows the O 1s spectrum after exposure for 24 h to the residual gas in the vacuum chamber after the crystal was softly sputtered. If we expose a perfect surface, as represented in trace a, to atmospheric conditions containing mainly water, the extra feature is clearly visible as shown in trace c. We may in passing note that the Ni 2p_{3/2} spectra remain unchanged (i.e. no indication for the formation of extra Ni³⁺ features). If we treat an intensively sputtered surface under conditions comparable to those used to record trace c then trace d is registered. An increase of the high binding energy extra feature is observed. The relative intensity of the extra feature at 531.2 eV is strongly angle dependent as seen in figure 3(b). In this figure a series of spectra at different polar angles is plotted. At grazing incidence where the highest surface sensitivity is achieved the extra feature exhibits the highest intensity. The O 1s spectra of the perfect surface without this high binding energy feature do not show an angle-dependent increase of an extra feature (not shown). From this we must conclude that there is an oxygen-containing species localized at the surface. A very similar situation is found for an epitaxially grown film. The chemical nature of these species is further elucidated by investigating the adsorption of water on a NiO(100) film. These results are presented in figure 4(a). Upon adsorption of 5 L of H₂O at 115 K the upper spectrum was obtained at grazing electron incidence. A strong emission of an ice layer at a binding energy 4.0 eV below the O 1s signal of the NiO film is observed. Accompanied by a slight shift in binding energy there is a strong attenuation of the intensity of the peak as the temperature of the sample is increased. Concomitantly a second feature at a binding energy 2 eV below the NiO O 1s line appears. This peak also decreases in intensity as the temperature is increased. Above 240 K no further variation in intensity is observed. The remaining species may be attributed either to OH⁻ or to an O⁻ species. Further energy loss experiments will allow us

to decide between these possibilities. Due to the temperature dependence, adsorbed H_2O , however, can be ruled out.

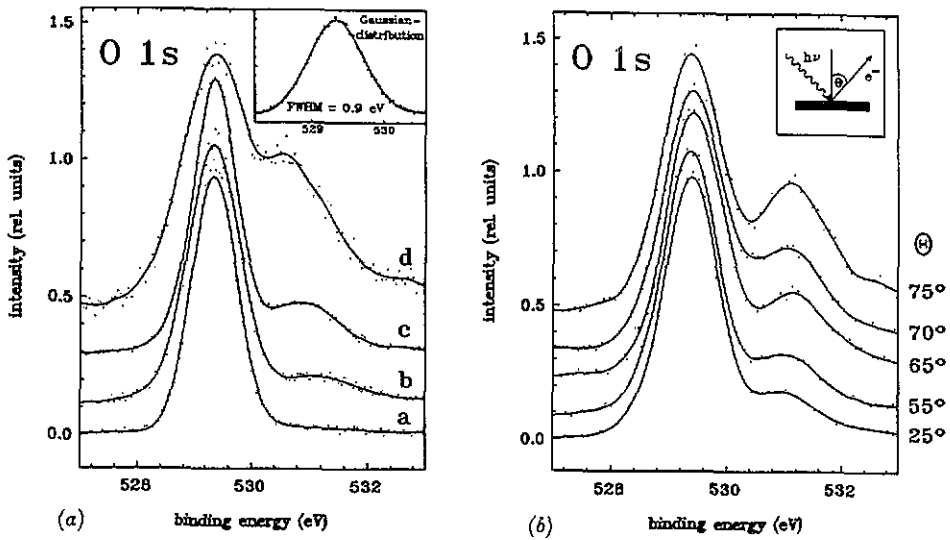


Figure 3. (a) O 1s XPS of a NiO(100) single crystal after different preparations; (inset: spectrum a, fitted by a single Gaussian line profile). Preparations: a, freshly cleaved in vacuo; b, after sputtering of 1 min/0.5 kV and 24 hours in UHV; c, cleaved *in vacuo* and 3 min under atmospheric conditions; d, cleaved *in vacuo*, sputtering of 10 min/4.5 kV and 3 min under atmospheric conditions. (b) O 1s XPS of a NiO(100) single crystal with the extra high binding energy feature at different polar angles as indicated.

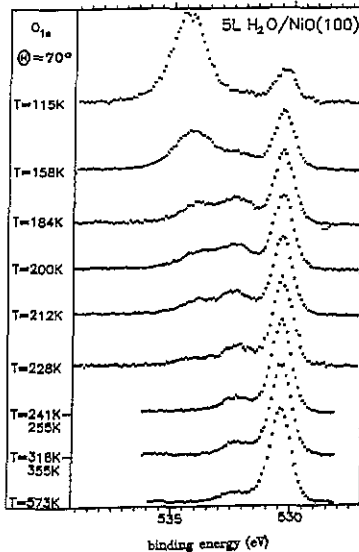


Figure 4. O 1s XPS after adsorption of 5 L H_2O on NiO(100) at $T = 115$ K and successive heating to temperatures as indicated.

The comparison of the data obtained on the film and the cleaved single-crystal surfaces allows us to draw the following conclusions. First of all there are no Ni^{3+} defects either on the freshly cleaved or on the epitaxially grown surfaces [8] they can only be produced by sputtering. Nevertheless we observe the formation of the same adsorbed species on both surfaces within the limits of our experiment. This means that the defects leading to adsorption found on the chemically prepared film and on the sputtered single-crystal surface are similar and not directly connected to the formation of Ni^{3+} . Coadsorption experiments [15] of H_2O and NO on the surface reveal that NO , which we know from previous work [8] to adsorb preferentially on the $\text{NiO}(100)$ terraces, may still be adsorbed on a water saturated surface of a film. This indicates again that, at room temperature, H_2O adsorbs at defect sites and not at the terraces.

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