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# Barium and oxygen interaction on the Ni(110) surface at low coverages studied by soft x-ray photoemission spectroscopy: Ba negative binding energy shifts and their correlation with Auger electron spectroscopy shifts

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Received 2 May 2006, in final form 6 June 2006

Published 14 July 2006

Online at [stacks.iop.org/JPhysCM/18/6997](http://stacks.iop.org/JPhysCM/18/6997)

## Abstract

In this work, barium and oxygen interaction on the Ni(110) surface is investigated, by means of soft x-ray photoemission spectroscopy (SXPS), mainly at submonolayer and monolayer coverages. The results show that oxygen interacts with barium and the substrate as well forming BaO and NiO respectively. The formation of both oxides is consistent with previous Auger electron spectroscopy (AES) results. The oxidation of barium on the surface induces negative binding energy shifts of the Ba low core atomic levels 4d, 5s and 5p. Both initial and final state effects are shown to be necessary in order to explain these peculiar energy shifts. This interpretation is based on correlating the core level binding energy shifts with previously recorded AES transition line shifts, also taking into account the changes of the work function of the surface. The analysis shows that the extra-atomic relaxation energy decreases on going from metallic Ba to BaO. This implies that the reduction of the free electron screening more than counteracts the increase in relaxation energy due to the polarizable O<sup>2-</sup> anions.

## 1. Introduction

The alkaline earth metal oxides (AEMOs) are generally very important materials, from the technological point of view, mainly because of their electron emitting properties. Specifically, these materials present considerable applications in thermionic energy conversion [1] and in the manufacturing of modern dispenser cathodes [2–5]. Also, AEMOs show

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catalytic properties [6], and play an important role in a rich variety of physical properties in magnetism, ferroelectricity, structural transformations, metal–insulator transitions and superconductivity [7, 8]. Concerning the latter, the presence of highly ionic cations like Sr and Ba is a necessary requirement for superconductivity in the high- $T_c$  superconducting oxides [9].

Among AEMOs, barium oxide, BaO, presents particular interest because of the low work function, electron emissivity and catalytic properties. More specifically, BaO has had widespread use as a cathode material in the fabrication of impregnated dispenser cathodes [2, 10–13]. Moreover, BaO thin films on surfaces have shown storage capabilities of  $\text{NO}_x$  components, establishing an efficient storage component in the design of a model catalyst [14, 15].

In order to gain knowledge on the structural, electronic and catalytic properties of AEMO thin films, the atomic and electronic structure should be investigated. Although, over the last decades, a number of studies have been performed related to BaO overlayers on several surfaces, both from the experimental [16–22] and the theoretical viewpoint [23–25], there are still obscure and controversial points concerning how the oxidation of the alkaline earth metal starts and develops on the surface. Among these points are the unusual negative binding energy shifts (NBESs) of some low core atomic levels (Ba 4d and 5p) after barium oxidation. In particular, van Doveren and Verhoeven [26], in a very detailed study, by performing x-ray photoemission measurements on the alkaline earth metals and their oxides, documented NBESs for all the studied Ba core levels. In addition, Lampert *et al* [27], by measuring the Ba 3d levels, also recorded NBESs on going from metal to oxide. Several explanations have been proposed for these rather unexpected energy shifts which are not what one would expect in metal oxidation [28]. To interpret the NBESs, Lampert *et al* [27] based their argument on relaxation effects. A different explanation for the NBESs of the Ba core levels in BaO with respect to those in the metal was given by Wertheim [29], who pointed to an electron redistribution in the outer orbitals with flow of charge into orbitals with smaller spatial extent. Actually, he claimed that for the transition from Ba metal to BaO, a change in the electronic configuration from  $6s^25d^0$  into  $6s^{2-x}5d^x$  takes place. On the other hand, Jacobi *et al* [30] did not observe any filled Ba 5d states in BaO. On the contrary, they observed partially filled 5d states in the metal and attributed the NBESs to the  $\text{O}^{2-}$  species and to the highly polarizable O states. Trying to resolve this dispute, Hill *et al* [31] demonstrated that the previously reported NBESs are due to changes in the position of the Fermi level ( $E_F$ ) in the energy gap of the oxide. From the above discussion, it is concluded that despite the effort and the extended arguments on the issue of the NBESs of the atomic Ba levels, no clear explanation has been given so far.

In the present work an attempt is made to clarify the above controversy, by investigating Ba–O interaction through recording of the low core levels and the valence band region, by soft x-ray photoelectron spectroscopy (SXPS). The study takes place at the monolayer and the submonolayer regime, in order to obtain information on the early stages of Ba oxidation. To the best of our knowledge the Ba submonolayer coverages are studied for the first time. The processes we follow are (a) the oxidation of a bariated nickel surface and (b) barium deposition on an oxygenated nickel surface. The present work is a continuation of our previous works [32, 33].

## 2. Experimental details

The experiments were performed at the beam line 41 at the Swedish National laboratory Maxlab. The analyser chamber was at a base pressure  $2 \times 10^{-10}$  mbar and was equipped with low energy electron diffraction (LEED) optics, an ion sputtering gun and a goniometer mounted spherical electron energy analyser (VSW HA50) for photoemission measurements. A

toroidal grating monochromator (TGM) with four gratings was used for selecting the photon energy of the primary beam, which was fixed at 130 eV for all of the measurements. By using the fourth grating with  $1200 \text{ l mm}^{-1}$ , the achieved energy resolution was at about 0.25 eV. The sample was a single Ni(110) crystal cleaned by repeated cycles of  $\text{Ar}^+$  ion bombardment at 2 keV and followed by annealing at about 1000 K. The temperature was measured by a thermocouple attached to the sample case and calibrated by an infrared pyrometer. When it was necessary, the substrate was exposed to spectroscopically clean  $\text{O}_2$  via a leak valve (the purity was 99.998 vol%). The dosage was given in Langmuirs ( $1 \text{ L} = 10^{-6} \text{ Torr s}$ ) determined by the uncorrected pressure rise in the analyser chamber. Barium was deposited from a resistively heated SAES getter source at constant heating current 6.5 A. The coverage was estimated by work function (WF) measurements taken at the secondary emission cut off by applying a bias voltage on the sample equal to  $-9 \text{ V}$ . This was done in order to separate the secondaries from the sample from those produced in the spectrometer itself. Based on the WF change of the surface versus Ba deposition time and on a previous source calibration [34], we estimated that a dosage of 2 min deposition time corresponds to 0.13 ML of Ba within an uncertainty of  $\pm 0.05 \text{ ML}$ . Barium dosing on the nickel surface was done in steps of 2 min deposition time.

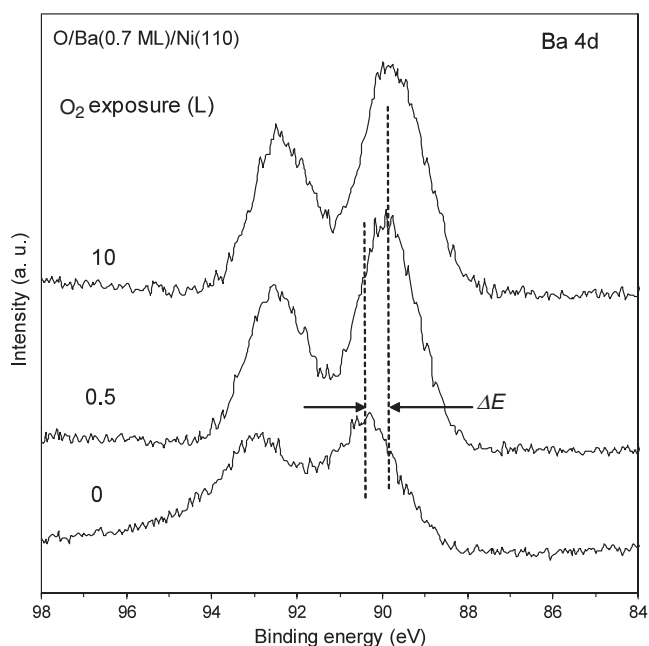
### 3. Results and discussion

#### 3.1. Ba adsorption on Ni(110)

Our first step was to investigate Ba adsorption on the Ni(110) surface, carrying out low core level and valence band measurements. In addition, we recorded the WF change,  $\Delta\Phi$ , of the surface as a function of Ba coverage. These measurements are reported in detail in a separate work [33]. We summarize here the main findings. At low Ba coverage ( $< 0.5 \text{ ML}$ ), the Ba 4d spin-orbit doublet ( $d_1$ ) appears quite symmetric at binding energies (BEs) 93.2 and 90.6 eV. Further coverage increase induces an asymmetry on the high energy sides of the doublet, with the final appearance of a new doublet ( $d_2$ ) at higher BEs, 93.9 and 91.4 eV. The two doublets seem to coexist within a range of Ba coverage of about 0.5–1.1 ML. However, the  $d_2$  doublet progressively dominates as the coverage increases, while the intensity of the  $d_1$  doublet decreases almost down to zero. The  $d_1$  doublet has been attributed to the strongly chemisorbed and polarized adatoms, whereas the  $d_2$  doublet can be assigned to the Ba–Ba interaction and hence to the metallic state of the adsorbate. The metallization of the Ba overlayer, near 1 ML, was verified by the WF as well as the valence band measurements, where metallic Ba 5d, 6s and 6p states were recorded. These results are consistent with previous independent Auger electron spectroscopy (AES), low energy electron diffraction (LEED), thermal desorption spectroscopy (TDS) and WF measurements, which have been presented in a detailed study of Ba deposition on the Ni(110) surface [34]. According to these measurements Ba grows in successive layers in two adsorption states: (1) chemisorption at very low coverages and (2) metallization at higher coverages (above 0.75 ML).

#### 3.2. Oxygen adsorption on Ba/Ni(110)

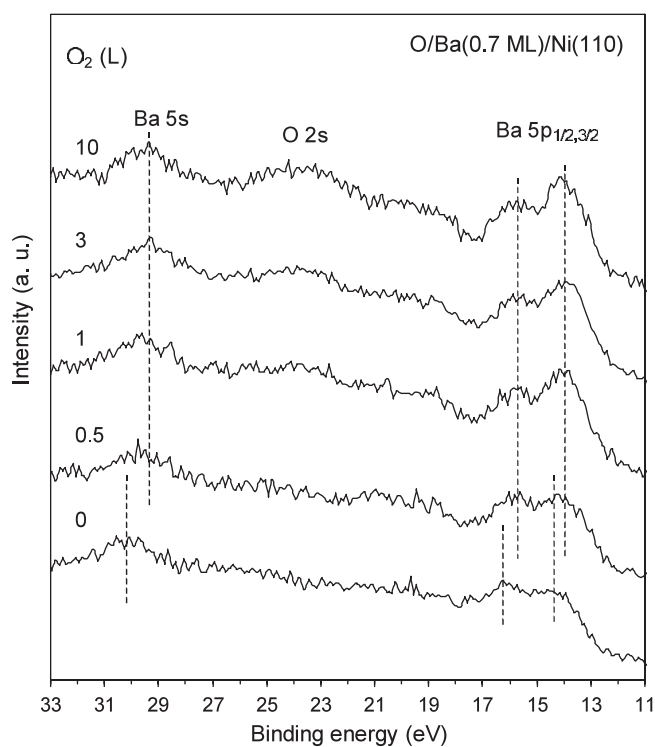
Our next step was to expose the barium covered Ni(110) surface to oxygen gas ( $\text{O}_2$ ). Figure 1 shows the Ba 4d core levels for the Ba (0.7 ML)/Ni(110) surface with subsequent oxygen exposure. At this coverage, the Ba overlayer starts to become metallic and the Ba 4d doublet is asymmetric with a long tail on the high BE side. This tail is due to losses associated with free electrons from the metallic overlayer [35]. Oxygen exposure of 0.5 L shifts the doublet to lower BE ( $\sim 0.5 \text{ eV}$ ), making it symmetrical by eliminating the tail. These changes have been



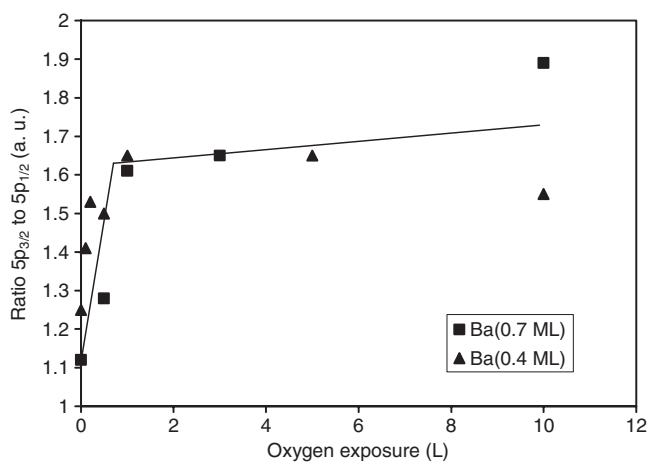
**Figure 1.** The SXPS spectrum of Ba 4d core levels of the Ba(0.7 ML)/Ni(110) surface, before and after oxygen exposure. Note the energy shift defined by the dashed lines.

previously reported for oxidation of bulk Ba by Jacobi *et al* [30], and attributed to the Ba–O interaction. This interaction leads to the transformation of the metallic Ba overlayer into a rather insulating one, probably to barium oxide (BaO), followed by a reduction of the free electron density. Thus, the loss region of the 4d doublet vanishes, intensifying the emission by  $\sim 30\%$ . The Ba 4d levels showed similar NBESs for oxygen exposure at different Ba coverages (0.2 and 1.3 ML, not shown) suggesting that Ba–O interaction takes place on the surface, regardless of the Ba adsorption stage (chemisorbed atoms or metallic layer) on the nickel surface. The NBES of the Ba 4d levels after oxidation is observed at submonolayer Ba coverage for the first time to the best of our knowledge. As will be shown below, other Ba atomic levels also present NBESs after oxygen adsorption.

In figure 2 the SXPS spectra of Ba  $5p_{1/2,3/2}$ , Ba 5s and O 2s are shown as a function of oxygen exposure onto Ba(0.7 ML)/Ni(110). In the region of the Ba 5p level there is an obvious total peak shape change from 0 to 10 L exposure, which consists in the apparent relative intensities of the Ba  $5p_{3/2}$  and Ba  $5p_{1/2}$  changing in favour of the former. These spectral changes correlate with those of the Ba 4d spectra (figure 1), which we argued signify the transformation from Ba to BaO. The changes of the Ba 5p doublet are probably due to a combination of background, individual peak lineshape and real intensity changes. Without resorting to a detailed peak analysis, we may use the peak shape of the Ba 5p doublet as a fingerprint of the two end states: metallic Ba and BaO. In order to be the least biased in assessing a particular fingerprint, we take the ratio of the recorded Ba  $5p_{3/2}$  to Ba  $5p_{1/2}$  peak heights, after subtracting a linear background, as a measure of the fingerprint. The results are shown in figure 3 for two different bariated surfaces, 0.4 and 0.7 ML. It seems that the ratio increases with oxygen exposure as BaO forms on the surface. Besides the peak shape changes in figure 2, we observe an NBES for the Ba 5s ( $\sim 0.8$  eV) and a smaller one for the Ba 5p ( $\sim 0.5$  eV), better seen in the background subtracted spectrum (not shown). In the following,



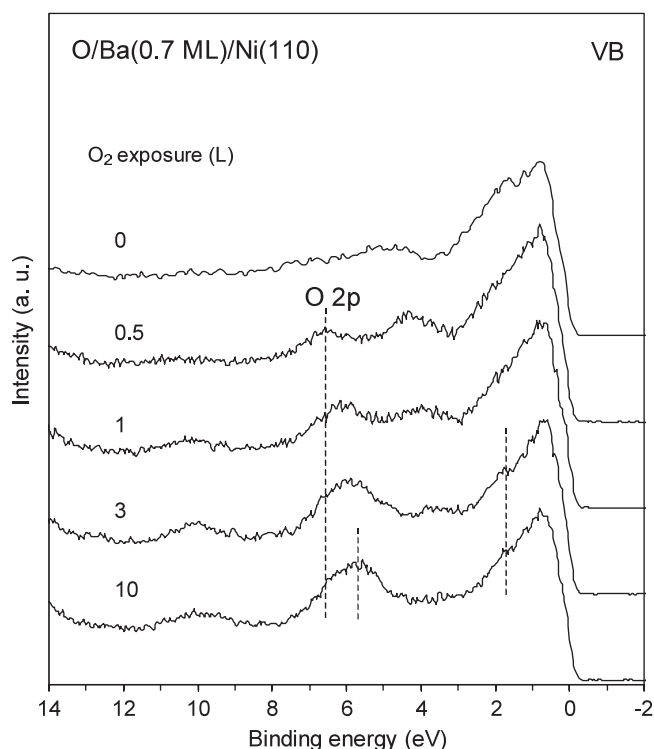
**Figure 2.** The SXPS spectrum of Ba 5s, 5p and O 2s low core levels of the Ba(0.7 ML)/Ni(110) surface before and after oxygen exposure.



**Figure 3.** The ratio of Ba 5p<sub>3/2</sub> to 5p<sub>1/2</sub> peak heights as a function of oxygen exposure.

we consider the lineshape of the Ba 5p doublet, along with its NBES from that of the metallic Ba, as a BaO fingerprint.

The valence band (VB) spectra of the Ba(0.7 ML)/Ni(110) before and after oxygen exposure is shown in figure 4. For the non-oxidized Ba(0.7 ML)/Ni(110) surface, a peak



**Figure 4.** The valence band photoemission spectrum of the Ba(0.7 ML)/Ni(110) surface before and after oxygen exposure.

appears at about 4.6 eV, which decays and at the same time drifts to lower BE with the oxygen exposure. It is noteworthy that this peak was absent in the VB spectrum of 0.4 ML of Ba (not shown), where it is considered that the metallization has not started yet [33]. Therefore, it is plausible to relate this peak to the metallization of the Ba overlayer. Although its origin is not quite evident, the explanation for that can be based on the very early VB photoemission measurements carried out by Kress and Lapeyre [36], who assigned the emission up to  $\sim 4$  eV from  $E_F$  to the  $s$ - $p$  hybridization bands of metallic Ba. Thus, we consider that this peak is probably due to the  $6sp$  hybridized band. For Ba(0.7 ML)/Ni(110) too, a weak shoulder appears at about 1.5 eV from  $E_F$ . This might be due to the Ba 5d states, in accordance with the results of Kress and Lapeyre [36] and Jacobi *et al* [30].

The oxygen exposure on the bariated nickel surface causes the appearance of a new peak at about 6.4 eV below  $E_F$ . This peak should at least partly be due to the O 2p atomic level which participates in BaO bonding. It is clearly increasing with oxygen dosing, while at the same time the 4.6 eV peak is being reduced. This reduction is reasonable, since as BaO develops on the surface, the metallic character of the barium overlayer vanishes, so the  $6sp$  band becomes weaker. In addition to the decrease of the O 2p intensity, there is a gradual energy shift towards lower BE by  $\sim 1$  eV.

Figure 4 also shows two extra features developing with oxygen exposure: (1) a broad peak at about 10 eV and (2) a weak shoulder (pointed out by a dashed line) next to the Ni 3d emission at about 1.7 eV. Both of these features have been observed in a separate experiment of the oxidation of the clean Ni(110) surface (shown later) and are taken to be characteristic of NiO.

Indeed, previous works have reported similar features as those two described above in the VB of NiO single crystal [37], oxidized Ni(100) [38] and Ni(110) surface [39]. The 10 eV emission has been characterized as a NiO valence band satellite feature due to the Ni 3d<sup>7</sup> final state, caused by the strong on-site Coulomb interaction [40]. On the other hand, the 1.7 eV feature is due to the hybridization of the non-dispersive Ni 3d with the strongly dispersive bandlike O 2p states [37, 41, 42]. Fujimori and Minami performed cluster calculations [43], showing that Ni–O interaction takes place via hybridization to some extent. The authors assigned the low BE valence band feature near to 2 eV to the oxygen screened 3d<sup>8</sup> L<sup>-1</sup> configuration (L indicates a hole in the O atom), while the higher BE valence band feature between 7 and 10 eV was attributed to the nickel unscreened 3d<sup>7</sup> states. In conclusion, it seems that apart from Ba–O interaction on the surface, Ni–O interaction takes place as well, leading to NiO formation. This is also borne out by our recent AES and WF results of oxygen adsorption on a bariated nickel surface [32]. More specifically, low energy AES spectra show simultaneous development of NiO and BaO on a bariated nickel surface. The same behaviour has been observed for the oxidation of lead-precovered Ni(100) surface, where oxygen interacts not only with the Pb deposit but with the substrate too [44].

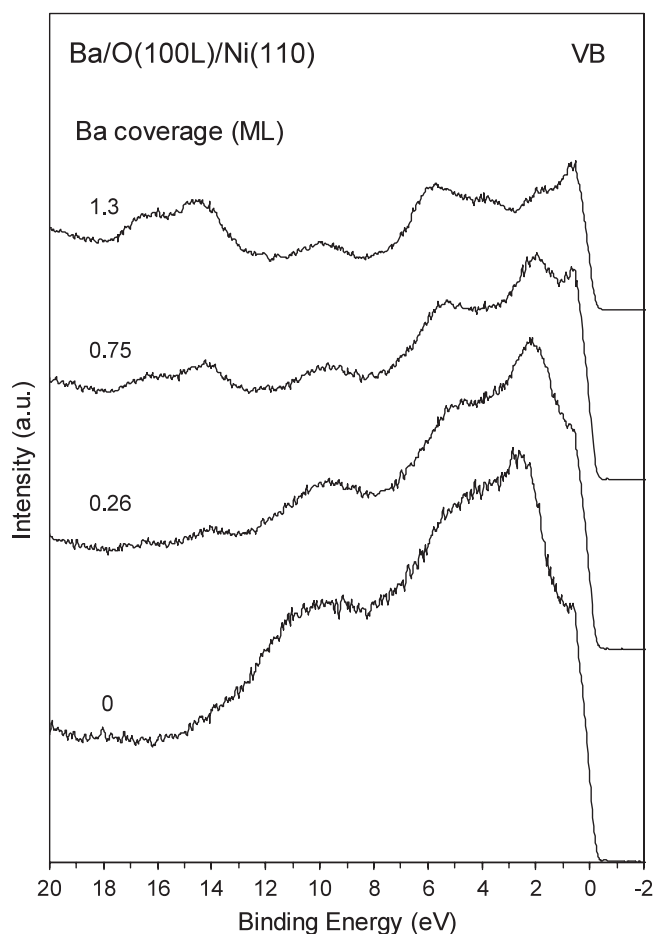
Regarding the structure of the Ba adlayer on Ni(110), no ordering was observed at room temperature by LEED measurements [32]. Oxygen adsorption on various bariated nickel surfaces ranging from 0.15 to 1.8 ML also did not produce any ordered structures. This indicates that the BaO overlayer should be amorphous. In addition, AES measurements did not show any Ba agglomeration after oxygen adsorption, which suggests that BaO remains layer-like as Ba on Ni(110) [32].

### 3.3. Ba adsorption on oxygenated Ni(110)

Following a different sequence of adsorption, we deposited Ba on the oxygenated nickel Ni(110) surface. Figure 5 shows the VB measurements including the Ba 5p levels for the development of barium on the 100 L oxygenated Ni(110) surface. At this oxygen exposure, we expect the formation of a nickel oxide thin film on the surface. Indeed, the spectrum of the O(100 L)/Ni(110) surface is very similar with that of the nickel oxide after oxidation of a single Ni(100) crystal [45]. As the barium coverage increases, the Ba 5p levels develop, showing the fingerprint which is characteristic of BaO (figure 3, Ba 5p<sub>3/2</sub> to 5p<sub>1/2</sub> peak heights ratio  $\geq 1.6$ ). Regarding the valence transitions we observe that the peak at  $\sim 2.5$  eV diminishes with a shift to smaller BE. This peak is related to the Ni<sup>2+</sup> 3d states, which participate in NiO formation. At the same time the peak at about 5 eV shows a tendency to move to higher BE, while the peak near 10 eV, which characterizes NiO, is present in all the spectra. The 5 eV peak can be attributed to O 2p of the oxygen atoms taking part in NiO and being hybridized with the metallic Ni 3d states [38]. The O 2p level seems to become more bound with barium deposition due to the Ba–O interaction. More specifically, the O 2p shifts to higher BE reaching the energy of  $\sim 5.6$  eV, which is about the same energy as that measured for the same peak in figure 4. This energy shift indicates that part of the O atoms probably interacts with the deposited Ba, forming BaO, i.e. at least a partial transformation of NiO into BaO is occurring. This is also indicated by the decrease of the ratio of the NiO feature due to the Ni<sup>2+</sup> 3d to that of the metallic Ni 3d level (near the  $E_F$ ) with Ba coverage.

The Ba 4d levels for the barium deposition on the O(100 L)/Ni(110) surface are shown in figure 6. Note that the lineshape of the Ba 4d levels markedly differs than those of the metallic Ba overlayer (lowest curve in figure 1). In fact, it resembles that recorded for the oxidation of the barium on the surface (top curve in figure 1). This resemblance further supports that Ba adatoms interact with part of the preadsorbed oxygen atoms forming BaO and

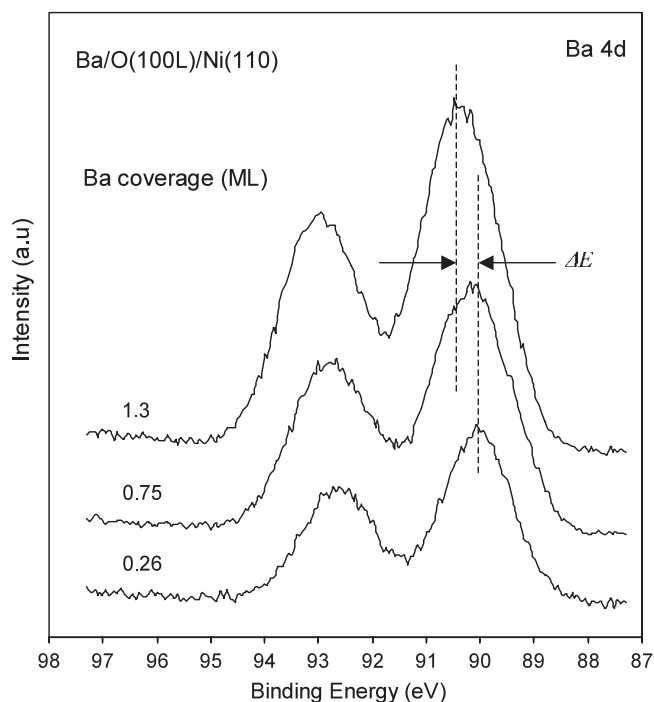




**Figure 5.** The valence band photoemission spectra including Ba 5p levels for barium deposition on the oxygenated O(100 L)/Ni(110) surface.

probably reducing the already formed NiO. This reduction seems to be reasonable, because if we ignore the similar entropy changes, we can compare the formation enthalpy of BaO, equal to  $-548 \text{ kJ mol}^{-1}$  [46], to the much lower value for NiO,  $-241 \text{ kJ mol}^{-1}$  [47]. Further, in figure 6, it is noteworthy that as the Ba coverage increases, the Ba 4d doublet drifts to higher BE showing a positive binding energy shift (PBES) of  $\sim 0.4 \text{ eV}$ . This observation will be discussed later.

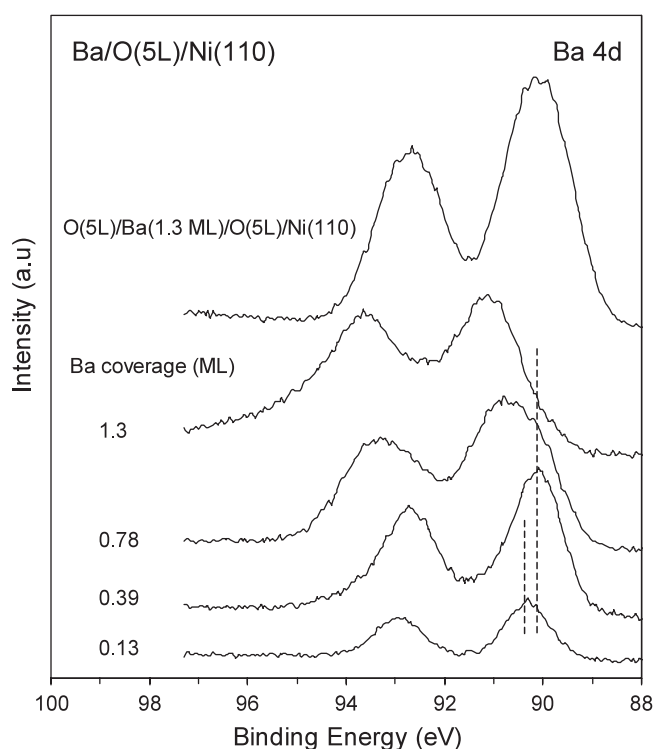
Except of Ba deposition on a nickel oxide thin film, we also deposited Ba on the O(5 L)/Ni(110) surface. At this exposure, the oxygen atoms are chemisorbed on nickel according to our WF measurements in comparison to the Benndorf *et al* results [48]. The Ba 4d levels for this experiment are shown in figure 7. The Ba 4d lineshape at 1.3 ML is quite similar to that of the metallic Ba overlayer (the lowest curve in figure 1). At 0.39 ML, the Ba 4d levels appear at lower BE (90 eV for the  $4d_{5/2}$ ) than that of the metallic phase at 1.3 ML (91 eV for the  $4d_{5/2}$ ) and equal to the BE at 0.26 ML (the lowest curve in figure 6). This implies that Ba–O interaction also takes place at the oxygen chemisorption stage when Ba deposition starts. This finding was confirmed by recent AES measurements in our laboratory (not shown), where the characteristic BaO low energy Auger line at  $\sim 68 \text{ eV}$  [32] clearly developed. Further, if we provide 5 L of oxygen on the Ba(1.3 ML)/O(5 L)/Ni(110) surface, the Ba 4d becomes sharper



**Figure 6.** The SXPS spectra of Ba 4d levels for barium deposition on the oxygenated O(100 L)/Ni(110) surface.

with NBES, showing the same behaviour as that observed in the case of BaO formation on the surface (figure 1). Thereby, we conclude that the adsorbed oxygen reacts with the metallic Ba forming BaO, without excluding that some of the O atoms may penetrate the metallic overlayer and react with the substrate forming NiO as well.

The above interpretation is verified by the VB measurements shown in figure 8. We note that the Ba 5p doublet having BE and fingerprint characteristic of BaO (figures 2, 3 and 5) develops at 0.39 ML. This observation is in agreement with the results of figure 7 where Ba–O interaction takes place in the oxygen chemisorption stage. As Ba coverage increases up to 1.3 ML the characteristic Ba 5p doublet of metallic Ba appears. Also the 4.6 eV peak and the Ba 5d states near  $E_F$  are present. All these features are characteristics of the barium overlayer metallization. Following exposure of 5 L of oxygen on the Ba(1.3 ML) overlayer, the VB structure changes drastically, with the 10 eV peak, which is considered as a NiO feature, also appearing. In addition, the Ba 5d states disappear and the BaO Ba 5p fingerprint reappears. Another indication of BaO development is the shift towards lower BE of the O 2p and Ba sp states. The same changes in VB spectra have been observed for the oxidation of the barium-precovered nickel surface (figure 4). It is noteworthy that the O(5 L) exposure on the bariated nickel surface (lowest curve in figure 8) causes the appearance of the characteristic 10 eV peak of NiO. Given that this exposure to oxygen is rather low to form a surface nickel oxide, this is an indication that the Ba overlayer promotes the Ni–O interaction as previous AES measurements have shown [32]. In conclusion, the development of BaO and NiO occurs simultaneously at the Ba–Ni interface, proving that part of the O atoms reacts with the adsorbate and part with the substrate after oxygen penetration through the Ba overlayer.

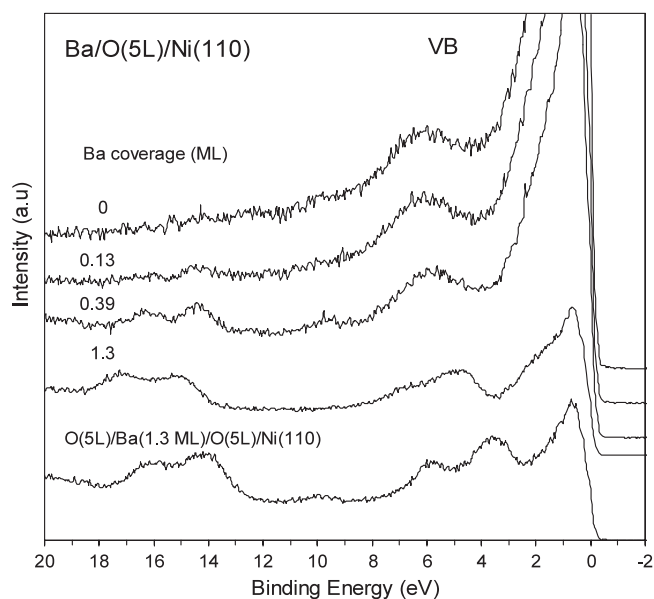


**Figure 7.** The SXPS spectra of Ba 4d levels for barium deposition on the oxygen chemisorbed O(5 L)/Ni(110) surface.

### 3.4. Correlation of the negative binding energy shifts with published AES lines shifts

In the present work, in all the cases where an interaction between Ba and O to form BaO was argued for, the Ba core levels 4d, 5p, 5s shifted to lower BEs by 0.5–1 eV. It has long been known that BE shift arguments based only on the change in the electrostatic potential at the core of the photoelectron emitting atom are not always adequate [49]. This potential change is caused by bonding, which gives rise to valence charge density variations in the ground state. Instead, in many cases, contributions from both initial (ground) and final (ion) state effects have to be taken into account. However, in the case of Ba metal being oxidized, Wertheim [29] and Jacobi *et al* [30] remarked that considering the simplest initial and final state effects, i.e. charge transfer in the initial state and the absence of metallic screening in the final state, the BE shifts of the Ba core levels are in the wrong direction (NBESs). This fact led Wertheim to suggest partial covalency in the Ba–O bond resulting in an initial state shift towards lower BE. In contrast, Jacobi *et al* [30] focused on the final state, attributing the NBESs to the large polarization energy of the O<sup>2-</sup> anions.

The NBESs, in most of the cases studied so far, concerns the comparison between bulk Ba (or Ba films several layers thick) and bulk BaO (or BaO films). The observation of the *in situ* interaction of adsorbed Ba with O, in the near monolayer regime, has only been made in a few cases [17, 27, 30]. This situation may differ in several aspects from the bulk Ba to BaO state of affairs. The most important difference is that Ba and BaO are directly adsorbed on a substrate, which is naturally expected to play an active role in the surface interactions. *Ab initio* calculations, performed by Almanstötter *et al* [23], for an ordered layer of BaO on



**Figure 8.** The valence band photoemission spectra for barium deposition on the oxygen chemisorbed O(5 L)/Ni(110) surface.

W(100), showed significant W–O and W–Ba bonding with strong mixing of the Ba 5d orbitals (unoccupied in the free atom), in addition to the W 5d and O 2p ones. We do not know of any similar calculations for BaO on Ni, but XPS shifts from Ba to BaO on polycrystalline W [27] agree very well with our work down to the monolayer coverage, which was the minimum coverage studied in that work. In contrast, we disagree with Jacobi *et al* [30], in two aspects: (1) they did not see metallization of Ba monolayer and (2) the BE shift on oxidation of a monolayer was positive. If these discrepancies are not due to differing coverage calibrations in the two works, then it may be significant that the substrates are different. Specifically, in [30] the substrate was Al, a free electron-like metal with very different chemisorption properties from transition metals like W [27] and Ni (our case). We stress here that we observed NBESs even at submonolayer Ba quantities (subsection 3.2), definitely below the WF minimum [33]. This indicates that regardless of the absolute coverage in the two works, before the Ba metallization sets in, there are opposite shifts on Ba oxidation, thus calling attention to the effect of widely different adsorbents. The possible influence of the particular substrate on which BaO grows does not seem to have been pointed out before, except in the context of AES line energy shifts reported by Haas and Shih [17].

As a general rule, energy shifts are also observed in AES when the environment of an atom changes. Several AES line shifts were recorded for the Ba + O system in our previous work [32], but their interpretation was rather tentative, due to the many unknown contributing changes involved in the Auger transition energies. A combination of AES and XPS energies has been used for several years in the form of the Auger parameter (AP), in order to characterize chemical states. For the AP to be meaningful, Auger kinetic energies (KEs) and XPS binding energies have to be measured in the same experimental system or even better in the same spectrum, so that referencing problems will be eliminated. However, when only energy shifts are of interest, we will show below that photoemission and AES results can be reliably compared, even if they have been recorded on two different systems. In the

following, by combining the SXPS shifts observed in this study with AES peak shifts, which we have measured before [32], we draw conclusions concerning initial and final state effects. In particular, in the present paper, we deal only with the Ba(MNN) Auger line shift, which is of direct relevance to the NBES controversy and in a subsequent work we will analyse the rest of the measured AES lines.

Considering first the measured shift of the Auger KE,  $\Delta E_K^{\text{AES}}$ , of the core–core–core Ba(3d, 4d, 4d) transition at about 590 eV, when adsorbed Ba changes between two chemical states, we may write:

$$\Delta E_K^{\text{AES}} = \Delta E(3d) - 2\Delta E(4d) + \Delta R(4d, 4d) + a\Delta\Phi_S(\theta) \quad (1)$$

where  $\Delta E(3d)$  and  $\Delta E(4d)$  are the experimentally determined BE shifts of the respective levels and  $\Delta R(4d, 4d)$  is the change of the extra-atomic relaxation energy around the 4d–4d double hole. Here we have assumed the changes of the interaction of the two 4d holes, of the intra-atomic relaxation and of the analyser work function to be zero. However, we have allowed for the fact that a Ba adatom may be sitting somewhere inside the varying part of the surface dipole it creates when it adsorbs [49], which is a function of coverage  $\theta$ . The possible influence of the changing WF of the specimen was recently observed for Ba adsorption on nickel [33]. The parameter  $a$  varies from zero, if the Ba adatom is on the surface side of the induced dipole, to one if it is on the vacuum side. Thus, if the change of the WF of the sample is  $\Delta\Phi_S$ , some fraction  $a$  of  $\Delta\Phi_S$  will be included in the measured  $\Delta E_K^{\text{AES}}$ . We may assume that  $\Delta E(3d) \approx \Delta E(4d)$  but the following argument is not affected by this assumption, as long as  $\Delta E(3d)$  has the same sign (negative) as  $\Delta(4d)$  which surely cannot be in doubt. Hence, we have

$$\Delta E_K^{\text{AES}} = -\Delta E(4d) + \Delta R(4d, 4d) + a\Delta\Phi_S(\theta). \quad (2)$$

We note that in equation (2),  $\Delta E(4d)$  is the BE shift that *would be measured without the effect of the varying surface dipole*. However, the measured BEs are derived from the KEs of the photoelectrons for which we also have (as with the measured Auger KE)

$$\Delta E_K^{\text{XPS}}(\text{measured}) = \Delta E_K^{\text{XPS}} + a\Delta\Phi_S(\theta) \quad (3)$$

where  $\Delta E_K^{\text{XPS}}(\text{measured}) = -\Delta E_B^{\text{XPS}}(\text{measured})$ , i.e. minus the measured BE shift of a given core level in the presence of the adsorbate induced work function, and  $\Delta E_K^{\text{XPS}} = -\Delta E_B^{\text{XPS}}$ , i.e. minus the BE shift of a given core level without the effect of the changing surface dipole. Substituting into (3) we obtain

$$\Delta E_B^{\text{XPS}} = \Delta E_B^{\text{XPS}}(\text{measured}) + a\Delta\Phi_S(\theta). \quad (4)$$

Applying equation (4) to the Ba 4d level, and substituting into equation (2) we finally obtain

$$\Delta E_K^{\text{AES}} = -\Delta E_B^{\text{XPS}}(\text{measured})(4d) + \Delta R(4d, 4d) \quad (5)$$

where the two  $a\Delta\Phi_S(\theta)$  terms, the one in equation (4) and the other in equation (2), have been mutually cancelled. This is because the two shifts, i.e.  $\Delta E_K^{\text{AES}}$  and  $\Delta E_B^{\text{XPS}}(\text{measured})$ , although recorded at two different experimental systems, were taken at the same coverage ( $0.70 \pm 0.05$  ML) and hence they corresponded to the same  $a\Delta\Phi_S(\theta)$ . The common reference between the two systems as far as coverage is concerned is assured via (1) the WF variation with its characteristic minimum at  $0.40 \pm 0.05$  ML, (2) the use of the same nickel sample and (3) the same type of Ba evaporation source with the same dosing calibration. Equation (5) shows that for studies focused on the adsorbate and carried out at different places, the Auger peak shifts can be related to the XPS ones, as long as the two shifts are measured at the same coverage.

Using in equation (5)  $\Delta E_B^{\text{XPS}}(\text{measured})(4d) = -0.5$  eV and  $\Delta E_K^{\text{AES}} = -1.5$  eV [32], we find  $\Delta R(4d, 4d) = -2$  eV. Put into words, this means that on going from a rather metallic

Ba to BaO the extra-atomic relaxation around the 4d–4d double hole decreases considerably. The BE shift  $\Delta E(4d)$  appearing in equation (2) is given by

$$\Delta E(4d) = \Delta E_c(4d) - \Delta R(4d) \quad (6)$$

where  $\Delta E_c(4d)$  is the ‘chemical shift’ which includes all the initial state effects, i.e. the electrostatic potential changes in the ground state, and  $\Delta R(4d)$  is the change of the extra-atomic relaxation in the final state of the photoelectron emitting atom. Naturally,  $\Delta R(4d)$  will also be negative, although reduced in size compared to  $\Delta R(4d, 4d)$  due to the single hole, thus  $-2 \text{ eV} < \Delta R(4d) < 0$ . It may have contributions from several factors possibly acting in opposite directions. For instance, on going from a metallic to a rather ionic state, we expect a decrease of  $R(4d)$  due to the reduction of the free electron density, but an increase due to the formation of highly polarizable  $\text{O}^{2-}$  anions. The present inference is that the net effect of these two relaxation mechanisms (plus any other that one can think of) on  $\Delta R(4d)$  is negative.

From equation (4), it is found that  $-1.25 \text{ eV} \leq \Delta E(4d) \leq -0.5 \text{ eV}$ , because  $\Delta\Phi_S(\theta)$  upon oxidation of Ba(0.7 ML) was  $-0.75 \text{ eV}$  and  $0 \leq a \leq 1$  depending on the position of the Ba adatoms on the surface, which is not known *a priori*. From the above estimations of  $\Delta R(4d)$  and  $\Delta E(4d)$ , equation (6) shows that  $\Delta E_c(4d)$  should also be negative. Consequently, this is an experimental proof that the NBES of Ba core levels on oxidation is unlikely to be due to final state effects only, such as for example the polarization energy of the  $\text{O}^{2-}$  anions advocated by Jacobi *et al* [30]. The conclusion is then that a significant decrease in the initial state energy is required to explain the NBES. The importance of initial state effects has been confirmed very recently by van der Heide [50]. This author studied a series of bulk oxides and found a linear dependence between BE shifts and  $1/d$  ( $d$  is the interionic distance), concluding that there is a strong initial effect due to the Madelung potential. However, the author assumed that final state effects (relaxation and polarization) are either negligible or constant thus minimizing their contribution. This result is also not consistent with our conclusion above, where a significant extra-atomic relaxation shift  $\Delta R(4d)$  was estimated. Thus, according to the above discussion, we conclude that both initial and final state effects should be taken into account when interpreting BE shifts for the Ba to BaO transformation. In addition, there is an added complication in the present situation compared to the bulk Ba-to-BaO studies. The initial state shift is not simply due to the transition from metallic Ba to an ionic oxide, or to a partially ionic one (predominantly ionic [51] or almost covalent [29]). Instead, the transition is (a) from Ba metallic-strongly bonded to Ni (probably covalently) to chemisorbed BaO for  $\theta \geq 0.7 \text{ ML}$  and (b) from Ba chemisorbed on Ni to chemisorbed BaO for  $\theta \leq 0.7 \text{ ML}$  (subsections 3.1 and 3.2). Consequently, the initial state effects apart from the Madelung potential contribution should also involve changes in the covalent bonding of the barium adsorbate.

There remains to discuss the positive energy shift of Ba 4d ( $\sim 0.4 \text{ eV}$ ) shown in figure 6. This PBES can be attributed to a combination of two factors: (a) a decrease of the Madelung potential around the Ba cations as more BaO is formed at the expense of NiO and (b) a WF reduction of  $\sim 0.3 \text{ eV}$  from 0.26 to 1.3 ML of Ba (not shown). The first effect is related to the considerably larger lattice constant of BaO (2.80 Å) compared to that of NiO (2.10 Å), assuming that the ionicities of the two oxides are similar.

#### 4. Conclusions

Summarizing, in this work we studied the interaction of barium and oxygen on the Ni(110) surface, by soft x-ray photoelectron spectroscopy. The study took place mainly at submonolayer and monolayer Ba coverage. Oxygen adsorption on the barium covered nickel surface shows BaO formation from the very early stages of gas exposure. Part of the adsorbed

oxygen atoms penetrate underneath the Ba overlayer and interact with the substrate of nickel forming NiO as well. The formation of both oxides is in agreement with previous Auger electron spectroscopy results. When barium adsorption takes place on oxidized nickel (NiO thin film), Ba atoms react with the O ones reducing the substrate by transforming part of the NiO into BaO. This transformation is favoured thermodynamically. However, it appears that the pre-deposited Ba promotes NiO formation, which presumably is a kinetic effect.

The oxidation of the pre-deposited barium on nickel causes negative binding energy shifts of the Ba 4d, 5s, 5p core levels. By correlating the energy shifts of the previously recorded Ba(MNN) Auger transition line with the Ba 4d binding energy shifts, the extra-atomic relaxation energy of the Ba core levels is shown to decrease on going from metallic Ba to BaO. Concurrently, there has to be an initial state shift to lower binding energies, probably through a combination of the Madelung potential of BaO and changes in the hybridization of the Ba orbitals, when going from chemisorbed or metallic Ba to adsorbed BaO. Thus, it seems that both initial and final state effects are responsible for these peculiar negative binding energy shifts of barium atomic levels.

### Acknowledgments

This work was financially supported by the European Community—Access to Research Infrastructure action of the Improving Human Potential Programme (ARI). The authors thank Stefan Wiklund (Max-lab, Lund University) and the Max-lab National Swedish Institute for providing the facilities to perform the experiments.

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