Characterization of Nanostructures by Electron Spectroscopies

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In regard of the chemical composition, bonding and electronic structure of nanostructures, the most relevant and detailed information is still given by electron spectroscopies like PES, AES, etc. However, a proper spectral information may be made difficult by interfacial and size effects, as well as by final state effects and even charging effects. In fact many efforts have been made to interpret large energy shifts of core level photoemission or AES peaks and Auger parameters as well as valence band intensities and lineshape changes. In this contribution, the capabilities to obtain significant information on the chemical characterization and electronic structure of transition metal oxide nanostructures and ultrathin films, from conventional and synchrotron based electron spectroscopies, are presented with the help of some selected examples. In particular I will present recent results on the growth of ultrathin films of TiO_2 on different substrates (i.e. SiO_2, Al_2O_3, Au) and on the growth of NiO on MgO (100).

1. Introduction

Nanostructures are nanometer sized objects, at least for one of their dimensions, whose preparation and characterization are topics of great interest in basic and applied research. The definition includes ultrathin films, nanowires, clusters and nanoparticles and even punctual defects or adsorbates. In this necessarily short contribution we focus on the characterization of oxide nanostructures supported on oxides and oxide/oxide interfaces using electron spectroscopies. We present some general results and some recent case studies.

2. Characterization problem

Due to their reduced dimensionality the characterization of nanostructures, require techniques with adequate lateral/depth resolutions, which are not always available. Furthermore, as the properties of supported nanostructures are strongly related to the specific characteristics of the interface, a complete characterization, (i.e. structure, morphology, composition, bonding and electronic structure) should include the interfacial interactions with the substrate. Apparently much more is known about the morphology and structure than on the composition and electronic structure, probably due to the development of techniques like Transmission Electron Microscopy (TEM) [1] and scaning probes (e.g. STM, AFM, etc.) [2], which enable atomic resolution. On the contrary, although Scanning Tunneling Spectroscopy, STS, is capable to determine the local electronic structure with atomic resolution, the technique is still developping and combined STM/STS studies have been reported rarely [2,3]. In fact, the electron spectroscopies (e.g. XPS, AES, EELS, etc.) still give the most relevant information about the electronic structure [4,5]. Their major drawback is however that most of these techniques probe extended areas and the information is averaged at the corresponding scale. Increasing the lateral resolution with which compositional and electronic structure information can be obtained is in fact the objective of recent developments. Scanning Auger Microscopy (SAM) and other ion beam based techniques reveals the chemical composition with high accuracy and lateral resolution approaching the nanometer scale (10-50 nm). However, specimen charging, damage and modification are serious handicaps for its application in compounds and insulators. In fact, the analysis of nanostructures by SAM is rather limited to metals on metals and semiconductors, where the damage effect is less determinant. The strategies and limitations can be found in the recent review by Cazaux [6].

In regard of the electronic structure and chemical characterization of oxide nanostructures, the most widely used technique is photoemission electron

spectroscopy (PES) [4,7-10]. Nevertheless, its limited lateral resolution (mm^2-μm^2) hinders the characterization of individual nanostructures, except if they are homodispersed, i.e. the same size and shape. The usual experiments are carried out on supported nanostructures grown by vapor nucleation, so that the nanostructures are present in a broad size distribution, whose average size grows with the deposition time. The characterization is then performed as a function of the coverage or film thickness. In fact, the electron spectroscopy itself (XPS, AES,...) is also used to characterize the growth mode and kinetics. Quantitative information on the overlayer growth mechanism is obtained through the analysis of adsorbate to substrate intensities ratio [11] or in terms of the formalism developped by Tougaard [12] for the analysis of core level spectra including a broad energy ($\approx$50 eV) region below the peak; however, a definite conclusion about the degree of dispersion, the shape and size distribution of the growing nanostructures, requires additional information provided by other techniques, e.g. STM, AFM, LEIS, etc.

3. General results and case studies

Although, over the last decade a lot of supported small particles have been characterized by AES and PES, most of them were metals on metals and on semiconductors. In fact, metals on oxides have been much less studied [7,8], and the characterization of oxides on oxides is rare [9,10]. In general, the studies try to relate intensity changes, lineshape changes and energy shifts in core level and valence band photoemission lines as well as in X-ray absorption edges, Auger lines or Auger parameters, with the size and/or shape of the nanostructure [7]. However, many times, those effects appear masked by strong interactions with the substrate, and many other subtle effects. In fact, it has been experimentally evidenced in several oxide/oxide systems that the observed changes are mainly determined by the nanostructure/support interface and their interactions and not only by quantum size effects [13-19]. All these complexities make difficult the interpretation of the experimental data and lead to long standing controversies.

Core level shifts:

In Fig.1 a) and b), we have depicted the changes in the binding energy of the Ti2p and in the Auger parameter α' respectively, for TiO_2 deposited on Al_2O_3 and on Au as a function of the XPS Ti/Al(Au) intensities ratio. The binding energy reference was taken at 84 and 74 eV for Au 4f and Al 2p repectively. In both cases we observe significant variations at low coverages until the value for bulk TiO2 is reached.

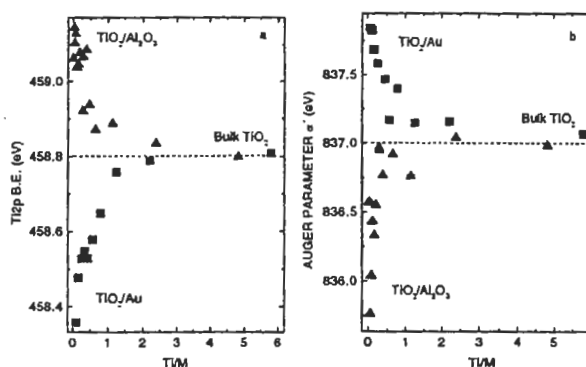Figure 1. Plots of the Ti2p binding energy and Auger parameter of Ti as a function of the Ti/ M intensities ratio for TiO_2 on Au and Al_2O_3.

Furthermore, the figure shows rather clearly that the substrate modifies significantly the tendency of such changes. The variation of the Ti2p binding energy and α' values follows opposite patterns when TiO_2 is deposited on Au or on Al_2O_3 (cf. Fig.1) It seems that the metallic/insulator character of the substrate influences significantly the photoemission process of the TiO_2 deposited at the interface, leading to shifts of different sign when the coverage decreases. Similar results were observed previously by the group of Gonzalez-Elipe [16-18] studying the growth of TiO_2 on SiO_2, MgO and Ag. Basically those shifts are interpreted in terms of initial and final state effects, where the former are related to the actual evolution of the electronic structure of the nanostructure, and the latter to the screening and relaxation mechanisms of the core hole, which depends not only on the cluster size and shape but also on the substrate and their interactions. In a first approximation the initial state effects can be estimated by $\Delta\varepsilon=\Delta\alpha'/2+\Delta BE$, where $\Delta\alpha'$ and ΔBE are the observed variations in the Auger parameter and core level binding energy respectively, but

usually is only important for very small clusters. Initial state effects have been nicely observed in the case of metal clusters deposited on metals or inert substrates [19-21], where the other effects can be neglected. However, in many other cases it has been shown that the measured energy shifts could be due to final state effects, i.e. changes in the extraatomic relaxation energy (i.e. $\Delta\alpha'/2$), and accounted for by the different responses of the interfaces. In a recent PES study of the TiO_2/SiO_2 interface [17,18] the measured variations in both the Auger parameter and core level binding energies were explained in terms of strong bonding interactions at the interface due to the formation of cross-linking oxygen bonds, i.e. Si-O-Ti, at the interface. Furthermore, molecular orbital calculations with clusters simulating the TiO_2/SiO_2 and TiO_2/Ag interfaces also concluded that the differences in the screening mechanism at the interface could be the cause for the different behavior of the core level binding energy and Auger parameter as a function of coverage, depending on whether the substrate is a metal or an oxide [18].

Core level lineshape:
The sensitivity of the cation to the type of interface and local coordination through the corresponding screening mechanism has been very nicely shown in a recent study of the NiO/MgO (100) interface by XPS [22-24]. The shape of core level photoemission peaks and not only their energy locations may provide important information about the electronic interactions of the nanostructure with the support. The interpretation of the Ni2p core level XPS of NiO has been controversial for many years. In fact, a proper interpretation of the satellite peak at around 1.6 eV higher binding energy than the main $Ni2p_{3/2}$ and $Ni2p_{1/2}$ lines has been given only very recently by Veenendaal and Sawatzky [24,25]. These authors explain the satellite in terms of the so called non-local screening mechanism, and conclude that the shoulder is inherent to NiO although its relative intensity can depend on the local coordination, i.e. defects, nearest and next nearest neighbours, etc.
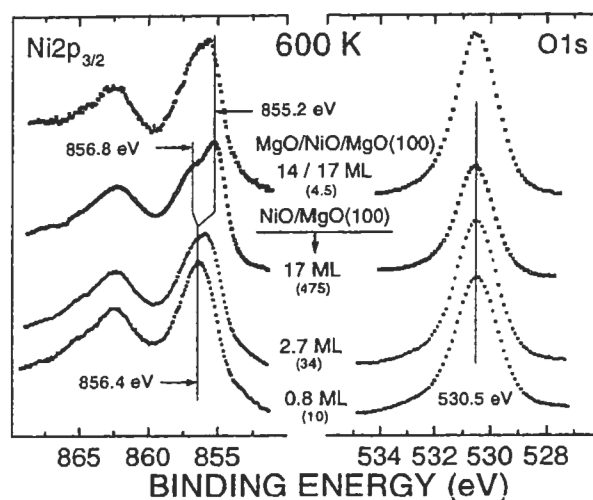

Figure 2. Ni $2p_{3/2}$ and O1s XPS spectra for NiO films of different thickness grown on MgO (100). Spectra for 14ML of MgO on top of 17 ML of NiO are also included.

Fig.2 shows the layer thickness dependence of both the Ni2p and O1s XPS spectra of NiO grown on MgO (100) at 600K. Fig.2 includes in parenthesis the corresponding Ni2p/Mg2p intensities ratio. The binding energies have been calibrated by locating the Mg2p peak at 49.5 eV as a reference. Under these conditions we observe only one O1s symmetric peak at 530.5 eV independent on the neighbour cation (i.e. Mg^{2+} or Ni^{2+}) and without any shoulder caused by adsorbed species (e.g. OH⁻, H_2O, etc.). On the contrary, Fig.2 also shows that the $Ni2p_{3/2}$ XPS line depends significantly on the oxide thickness. The effect can also be observed in the $Ni2p_{1/2}$ counterpart. For coverages below 1ML the Ni2p main line consists in just one peak that shifts from 856.7 eV up to 856.4 when the coverage increases from 0.15 ML up to 1.5 ML, but when the film thickness increases the spectrum evolves towards the characteristic spectrum for bulk NiO with a sharp peak at 855.2 eV and the shoulder at 856.8 eV. Considering that NiO grows on MgO(100) in a layer by layer mode, the observed changes in the Ni2p photoemission spectrum can be associated to the formation of the NiO/MgO interface. According to that, during the growth of the first monolayer, the presence of Mg^{2+} ions as next nearest neighbors of the growing Ni^{2+} ions, influences significantly the Ni2p lineshape. Further support for this picture can be found in experiments with buried NiO

layers (i.e. MgO/NiO/MgO) as that included on the top of Fig.2. The spectrum corresponding to 14 equivalent monolayers of MgO grown on top of 17 ML of NiO clearly indicates a transfer of intensity from the lower (855.2 eV) to the higher binding energy (856.8 eV) feature, which is in the inverse direction of that observed during the growth of NiO on MgO. Apparently the presence of Mg^{2+} at the interface prevent the non-local screening mechanism that leads to the characteristic shoulder in the spectrum of NiO. We would like to mention that a single $Ni2p_{3/2}$ main line peak is also observed for Ni^{2+} ions well dispersed in MgO. An example is shown in Fig.3. for a 5at% NiO well dispersed in a 25 ML thick film of MgO, prepared by simultaneous evaporation of Ni and Mg in an oxygen atmosphere on a SiO_2 substrate at room temperature. For comparison we have included the spectrum for the 0.15 ML of NiO grown on MgO(100). The similarity is very clear except for the small energy shift ($\cong 1$ eV) probably due to differences in the bulk and surface Madelung potentials.
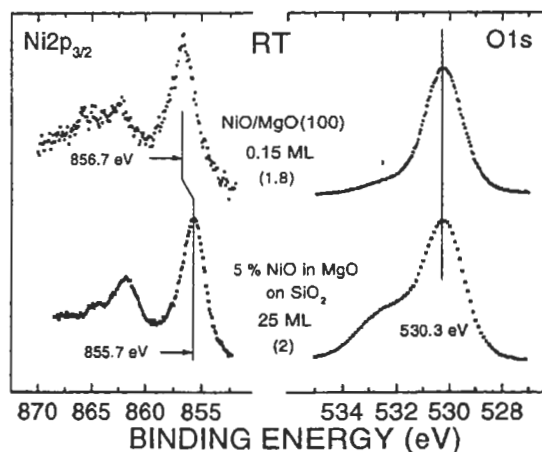
Figure 3. Ni $2p_{3/2}$ and O1s XPS spectra for 0.15 ML NiO/MgO(100) and 5%NiO in MgO on SiO_2.

Valence band and X-ray Absorption edge:
Fig.4 shows the valence band spectra of TiO_2 deposited on SiO_2 corresponding to different coverages, as labelled, measured at a photon energy of 45 eV (i.e. at the $Ti3p \rightarrow 3d$ resonance). These bands have been obtained after subtracting the SiO2 contribution from the substrate.
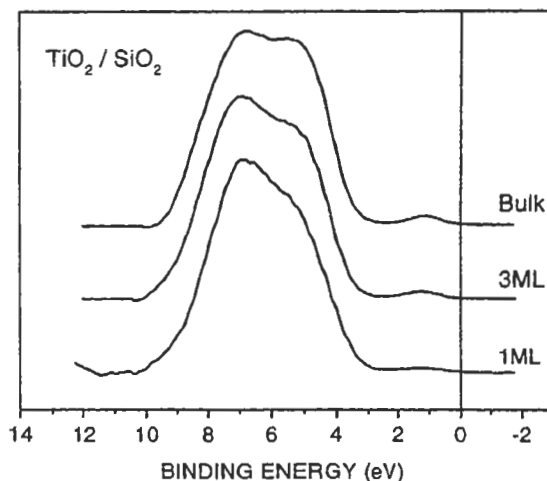

Figure 4. Valence band spectra of bulk TiO_2 and 1 and 3 ML of TiO_2 on SiO_2 at hv=45 eV.

Fig.4 clearly reveals that the valence band structure is sensitive to the TiO_2 coverage. The valence band is clearly narrower at lower coverages. The full width at half maximum increases from 3.7eV for 1ML TiO_2 up to 4.1 eV for bulk TiO_2. In addition, the bonding region of the valence appears much more enhanced for the thinner films. Although these effects could be associated, at least partially, to quantum size effects, it is clear from the previous discussion that they are mainly due to the the influence of the interface. In fact a more detailed analysis of the results obtained by Resonant Photoemission is beeing performed, in order to draw more clear conclusions.

The influence of the substrate (i.e. SiO_2 or Au) on the electronic structure of the growing TiO_2 could also be observed by XAS. This technique is sensitive to the symmetry of the initial state, i.e. local coordination, chemical state, etc. and therefore, can be used to characterize the interface. Fig.5 a) and b) show the Ti2p XAS spectra of TiO_2 deposited on SiO_2 and on Au respectively, as a function of the thickness. As the growth mechanism is different for both substrates, the labelled thickness corresponds just to equivalent monolayers as determined by the usual formalism for homogeneous overlayers [4]. The spectra have been aligned at the threshold according to the spectrum of a reference sample of TiO_2, therefore any information

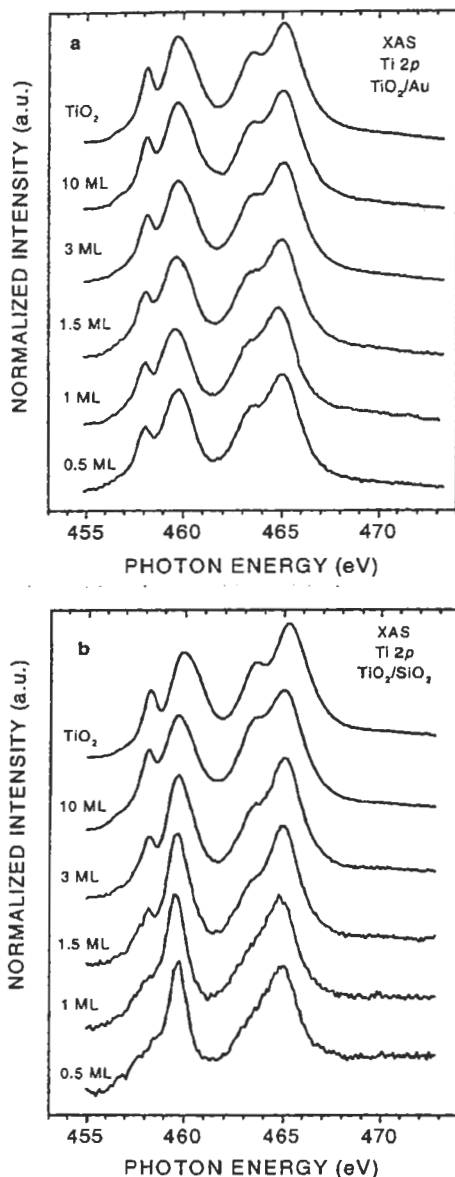about energy shifts is lost. Nevertheless a comparison between both figures indicates

Figure 5. Ti 2p XAS spectra of TiO_2 on a) Au and b) SiO_2 as a function of coverage.

clear differences between both systems. A detailed interpretation of the spectrum in terms of atomic multiplets in the presence of a crystal field can be found in the literature[26]. It is interesting to observe that in the case of TiO_2 on Au the growing islands develop from the beginning the complete multiplet structure of the bulk material. On the contrary, in the case of TiO_2 on SiO_2, it is observed that for low coverages (first monolayer) the spectrum shows only two asymmetric narrow peaks, which evolve (i.e. progressively split into four peaks and change the relative energies)

towards the spectrum corresponding to bulk TiO_2 when the coverage is increased above 3ML. In order to elucidate an explanation, we can consider the dependence on crystal field of the Ti^{4+} multiplet as calculated by De Groot et al. [26]. A comparison of these calculations with our spectra in Fig. 5a) indicate that the observed changes in the XAS spectrua correspond to a significant variation in the crystal field (i.e. 10Dq) of the Ti^{4+} ions from almost zero (i.e. spherical symmetry) at the interface up to 1.8 eV for bulk TiO_2. All that supports the existence of strong interactions at the TiO_2/SiO_2 interface which affect the crystal field and the local coordination of the Ti^{4+} ions. On the contrary, the data corresponding to the growth of TiO_2 on Au are consistent with the formation of large islands of TiO_2 which resemble the bulk material in respect to the XAS spectrum.

4. Conclusions

Whereas in the case of metallic nanostructures a characterization at an atomic scale seems now possible due to the development of new techniques that enable a direct visualization and spectroscopic analysis of individual nanostructures, the characterization of oxides and insulating nanostructures relies on the use of large area spectroscopies (mainly PES) which only give average information at the corresponding scale. Moreover, a proper interpretation of the observed effects in order to obtain useful information seems necessary. We have presented some case studies of oxides supported on different substrates where it was shown that not only quantum size effects but the nature of the support and the existence of interfacial interactions can lead to significant changes in the photoemission process (e.g. binding energy and auger parameter shifts, core level and valence band lineshape changes, etc.). The interpretation of these changes can be rather controversial due to the complexity and large variety of possible effects .

5.References

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