"XPS and XANES study of $Ti_{1-x}Nb_xO2$ nanopowders for gas sensing applications"

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Nb-doping of TiO_2 powders has been shown to modify the sensing response of this material to several gases. The modification of sensitivity is due to structural, microstructural and electronic effects induced by Nb introduction into the titania lattice. In a previous article [1, 2] we put into evidence the influence of niobium on structural and microstructural properties. We showed that Nb-doping allows retarding the anatase-to-rutile transformation and the grain growth. Both effects could, at least partially, explain the different response of doped material compared to pure TiO_2. In the present work, we were interested in determining how Nb doping would affect the electronic properties of the base material.

We thus performed an XPS and XANES (beamline BM29 at the ESRF) study in order to determine the valence state of both Nb and Ti species. These two techniques are complementary since XPS is more sensitive to surface states while XANES gives an information about both bulk and surface states. We focussed on samples with composition $Ti_{1-x}Nb_xO_2$ (x = 0, 2,4, 6, 8, 10%) heat-treated at 600ºC and 900ºC.

In figure 1, we present the XANES spectra at the Nb-K edge of samples synthesized at 900ºC. These spectra are compared to NbO_2 and Nb_2O_5 reference compounds spectra. All Nb-doped TiO_2 samples present a first shoulder in the edge, similar to that observed for Nb_2O_5 compound. The values of absorption edge energy as a function of Nb content and calcinations temperature are reported in figure 2. We observe that Nb oxidation state mainly depends on Nb content and only slightly on synthesis temperature. For Nb ratios between 0% and 6%, the oxidation state of niobium lays between +4 and +5, getting closer to +5 when the niobium content increases. Similarly, XPS results (fig.3) indicate that Nb is not in a purely +5 oxidation state. The results of both XPS and XANES analyses indicate that Niobium may present both +4 and +5 oxidation states. While Nb^{+4} species will not create new electronic states in the band gap, Nb^{+5} species will present a donor-type behavior. Due to the charge transfer the number of electrons increases in the conduction band of the host material, therefore, the work function of the host material decreases. In these materials chemical sensitization mechanism is suggested because oxygen molecules get adsorbed at the TiO_2 sites, where the excess of electrons are available in the conduction band of Ti due to Nb doping. These adsorbed oxygen species will favor the CO gas detection, since they react readily with CO to form CO_2. when this reaction occurs, it liberates several electrons, which further increases the conductivity of the base material, allowing the gas detection.

In the present work, we showed that a special care for determining oxidation states is necessary to identify the mechanisms involved in gas sensing. We demonstrated that not only the introduction of niobium into TiO2 allows to modify the structural and microstructural properties of $Ti_{1-x}Nb_xO_2$, but also introduces new electronic states which oxidation of CO gas, leading to an enhancement of the sensitivity.

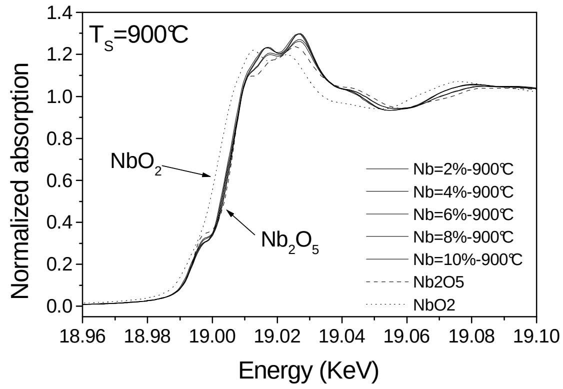

Figure 1 : Nb-K absorption edge of $Ti_{1-x}Nb_xO_2$ samples synthesized at T_S=900ºC compared to reference standards NbO_2 and Nb_2O_5

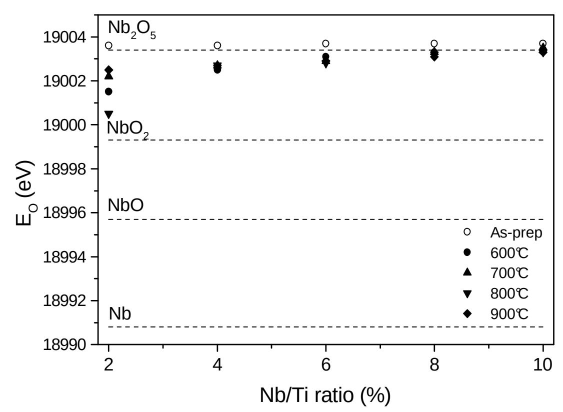

Figure 2 : Absorption Edge energy at the Nb-K edge for $Ti_{1-x}Nb_xO_2$ samples compared to absorption edges energies of Nb, NbO, NbO_2, Nb_2O_5 standards compounds

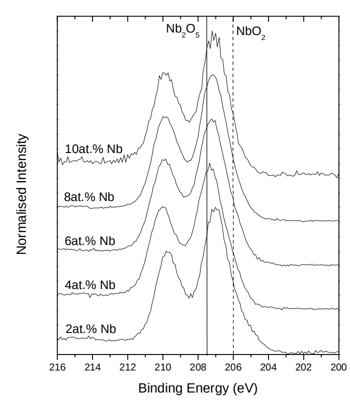

Fig. 3. XPS spectra in the Nb3d region for the samples calcined at 900ºC. The binding energies of Nb_2O_5 and NbO_2, indicated by vertical lines, were taken from [1,2].

[1]A. Ruiz, G.Dezanneau,J.Arbiol,A.Cornet, J.R. Morante Gas sensing properties of Nb-doped TiO_2 based sensors III[rd] International Seminar on Semiconductor Gas Sensors, 18-22 Septembre 2002, Ulstron, Poland
Thin Solid Films, submitted

[2] J. Arbiol, J. Cerdà, G. Dezanneau, A. Cirera, F. Peiró, A. Cornet, and J. R. Morante, Effects of Nb doping on the TiO_2 anatase-to-rutile phase transition J. Appl. Phys. **92**, 853 (2002)