Analysis of empty states in p-type conducting nanostructured NiO thin films with tailored physical properties

Domínguez-Cañizares G.[1], Gutiérrez A. [1], Krause S. [2], Ovsyannikov R. [2], Abbate M.[3], Díaz-Fernández D. [1], Soriano L.[1]

1. GRIN, Departamento de Física Aplicada and Instituto de Ciencia de Materiales Nicolás Cabrera, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain.
2. BESSY II, Helmholtz-Zentrum Berlin für Energie und Materialien GmbH, Albert-Einstein-Strasse 15, 12489 Berlin, Germany
3. Departamento de Física, Universidade Federal do Paraná, Caixa Postal 19044, 81531-990 Curitiba, PR, Brazil

guillermo.dominguez@uam.es

Abstract

Nickel oxide is an important material for several technological applications such as catalysis or gas sensing. The interaction with the surrounding environment in such devices plays an important role and the use of nanostructured materials increases the effective surface. We are able to prepare nanostructured NiO films with tailored electrical and optical properties by controlling the amount of Ni vacancies in the NiO lattice.

In this work we have grown nanostructured NiO films by magnetron RF sputtering with mixed oxygen-argon plasma onto alumina membranes, as well as onto several flat substrates for comparison. The NiO films grow in columns on the alumina substrates, maintaining the ordered porous structure (Fig. 1). The properties of these nanoporous NiO membranes are modulated by the oxygen content in the plasma during deposition. The electrical conductivity and the refraction index both increase by increasing the oxygen content of the plasma (Fig. 2). These changes in physical properties open new possibilities for using NiO membranes in advanced applications. In order to understand the mechanisms that lead to modify the NiO properties upon oxygen addition, it is essential to get insight into the electronic properties of the films.

With this aim, we performed a near-edge x-ray absorption fine structure spectroscopy study (NEXAFS) at the oxygen K-edge of several samples grown under different experimental conditions. The measurements were carried out at the BESSY II Facility in Berlin, Germany, using the PM4-Optics and the UE52-PGM beamlines. The near edge structure at the oxygen K-edge shows the density of empty Ni d-states hybridized with oxygen p-states above the Fermi level, and it is very sensitive to chemical and structural changes [1, 2].

The presence of oxygen in the plasma during NiO growth induces an oxygen enrichment in the films, which produces Ni vacancies and, consequently, hole states of O2p character above the Fermi level [3]. The concentration of these vacancies relates to the observed change in properties. For instance, the electrical conductivity increases with the oxygen content of the films, i.e., with the density of Ni vacancies, leading to p-type conduction. The corresponding hole states must appear below the bottom of the first empty states of the conduction band, and, therefore, they should be visible at the pre-edge of the oxygen K-edge the x-ray absorption spectra. Fig. 3 shows the presence of a pre-edge feature in the O K-edge spectra of several samples with increasing oxygen content in the plasma during deposition. This pre-edge peak is absent in the stoichiometric NiO reference sample, and can only be associated with hole states produced by nickel vacancies, as suggested by its increasing trend with the oxygen content of the plasma. The thermal stability of the density of vacancies was probed by annealing the different samples in vacuum simultaneously to the x-ray absorption data acquisition. The results are shown in Fig. 4. As it can be seen, the intensity of the pre-peak decreases with temperature and time, which suggests that there is a reorganization of the NiO lattice with a consequent decrease in the density of vacancies.

References

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Figures

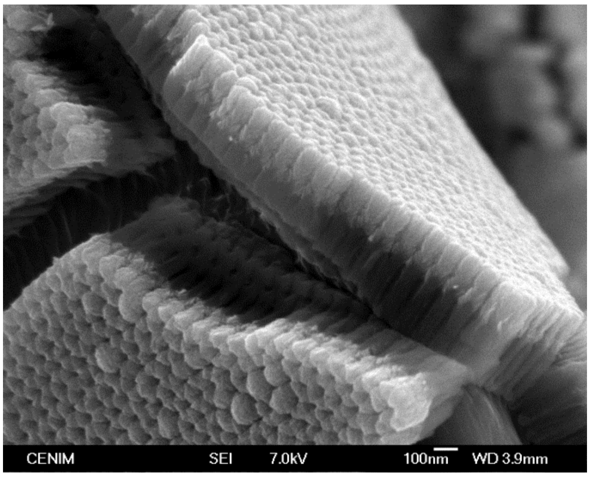

Figure 1: SEM micrograph of NiO thin film growth on nanoporous alumina membrane

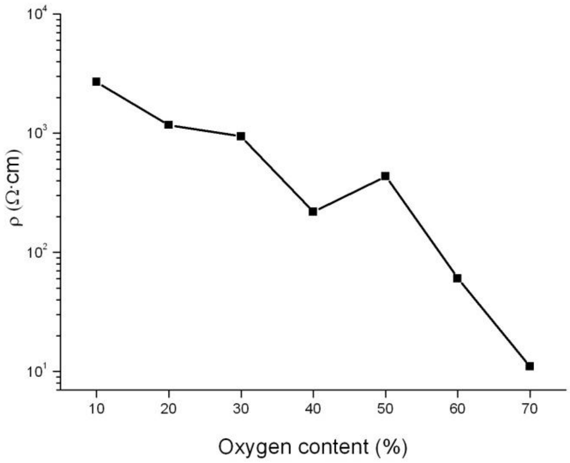

Figure 2: Resistivity of the NiO thin films with the Oxygen content in the reactive plasma

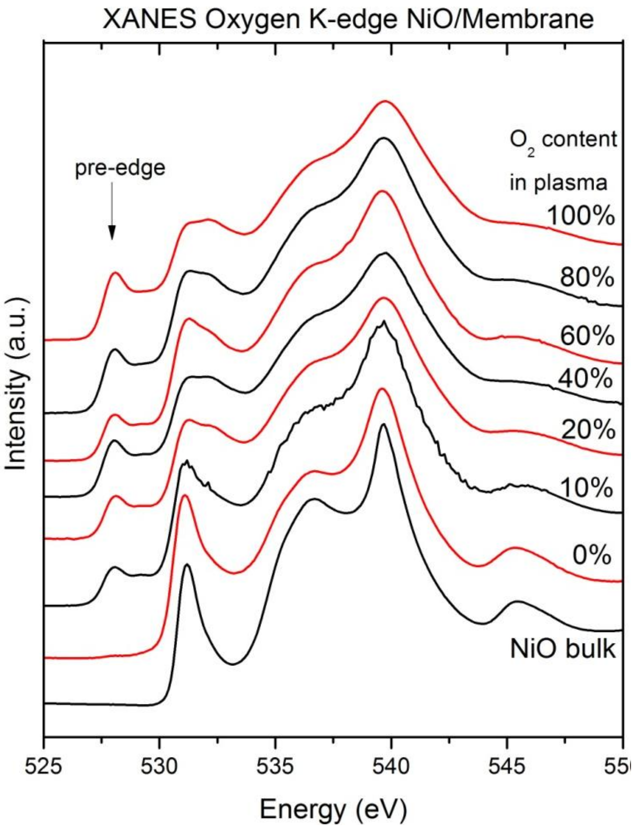

Figure 3: XANES spectra of Oxygen K-edge

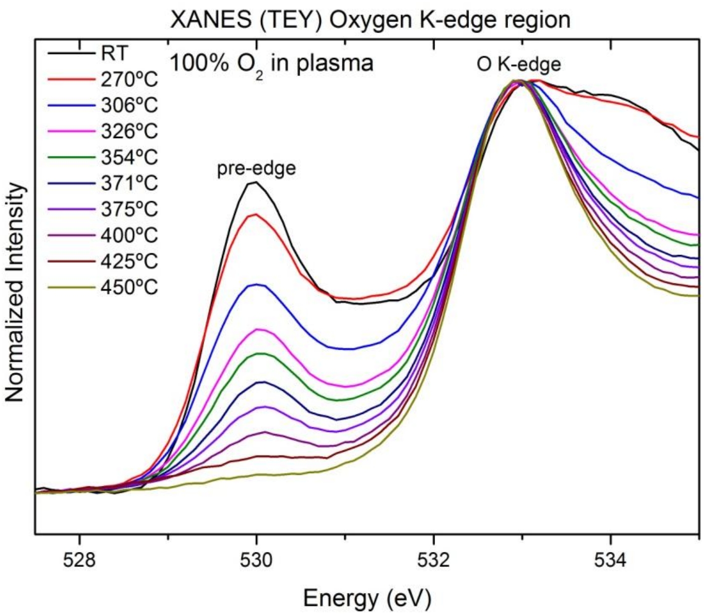

Figure 4: XANES pre-edge region of Oxygen K-edge