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Thermal induced depletion of cationic vacancies in conducting NiO thin films studied by X-ray absorption spectroscopy at the O 1s threshold

The electrical properties of oxide materials are strongly influenced by the presence of vacancies and other point defects. Whereas purely stoichiometric oxides are usually poor conductors, vacancies can significantly increase their electrical conductivity, being of n-type in the case of oxygen vacancies, like in ZnO, [1], or p-type in the case of cationic vacancies, like in NiO [2]. Many applications of these materials depends to a high extent on their electrical conductivity, like those related to chemical sensors, solar cells, or electrochemical capacitors.

In previous works we have investigated NiO thin films grown by magnetron sputtering from a NiO target with variable oxygen content in the plasma [3-5]. We found that the electrical conductivity of the films depends on the concentration of Ni vacancies, and we found this concentration to be dependent on the oxygen content in the plasma [3]. Among other techniques, we used X-ray absorption spectroscopy (XAS) at the O 1s threshold as a reliable technique to get a direct measure of the density of vacancies in our samples [4]. In this work we show, using XAS at the O 1s threshold, that a thermal annealing of NiO thin films with a certain vacancy concentration decreases this concentration and can even lead to stoichiometric NiO. Changing the probing depth of XAS we were able to see that the transition towards stoichiometric NiO starts at the surface. Two different types of experiments were carried out. A first set of samples was annealed at different temperatures during growth, and a second set was grown at room temperature and annealed subsequently, during the XAS measurements. In both cases the observed effect was very similar.

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