Synthesis of nano-structured cobalt oxide thin films for gas sensing by RF-magnetron sputtering

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I. INTRODUCTION

Cobalt oxides, CoO and Co₃O₄[1], have recently found many applications in scientific and technological research. In particular, Co₃O₄ shows a spinel structure, where Co²⁺ and Co³⁺ are situated in different reticular sites, which makes it a versatile material for many different applications.

In the atmosphere, Co₃O₄ presents on its surface a chemisorbed oxygen layer, that catalyses the oxidation of reducing gases as hydrocarbons and carbon oxide. These well known catalytical properties, through the reduction of activation energy for chemisorption of gas molecules, can be suitable for building gas sensors with high sensitivity and low operating temperature.

Since the interactions taking place during the sensing process are localized on the oxide surface, these sensors are actually produced as thin films or porous bulk materials.

The RF-magnetron sputtering technique shows many advantages in the field of thin films deposition respect to chemical deposition techniques, as the absence of organic impurities and solvents, a better film homogeneity control and the tunability of plasma parameters affecting film microstructure.

II. EXPERIMENTAL

The cobalt oxide films were deposited via RF-magnetron sputtering in an Ar/O₂ reactive atmosphere starting from metal Co target on silicon and silica. During sputtering the total pressure was maintained at 0.8 Pa. The composition of Ar/O₂ reactive gas controlled, in order to obtain films with different O content.

Moreover, the substrates were heated during the deposition up to a temperature of 350°C in order to promote the nucleation of cobalt oxide crystals.

The composition of the samples was determined via Rutherford backscattering (RBS) using a 2.2 MeV 4He⁺ beam. The morphology was investigated by AFM microscopy and the chemical bonding by FT-IR and Raman spectroscopy. The microstructure of the films was characterized by XRD.

III. RESULTS

All the deposited samples are nearly homogeneous and have a thickness of the order of 100 nm.

From RBS analysis, the samples show a Co/O ratio near to 0.7, in agreement with the expected value for Co₃O₄ equal to 0.75.

Beyond a threshold (oxygen flow ≥ 1.5 sccm), oxygen flow variation doesn’t influence in any way film composition.

The IR spectra, in a range between 500 and 800 cm⁻¹, show two absorption bands corresponding to those of Co₃O₄[2,3] with spinel structure. Moreover, the spectra of the samples deposited at different substrate temperature (fig.1) exhibit a specific trend: increasing the substrate temperature, each peak became sharper and more intense. This behavior can be ascribed to crystallization phenomena that lead to an increase of the crystal dimensions in the film.

The same effect was highlighted in Raman spectra, where the peaks corresponding to Raman-active modes of Co₃O₄ [4] become for increasing deposition temperatures narrower and narrower (fig. 2).

Therefore, substrate temperature is a fundamental parameter to control film microstructure. In this case, deposition rate is really low (of the order of 4·10⁻³ nm/s),
so that surface residence time of atoms coming from the
target is really high and allows a spatial rearrangement of
the atoms on the substrate.

Crystal formation can take place only if atoms have
enough nucleation energy: this energy is provided by
heating the substrate. In this way, the higher the deposition
temperature, the higher the crystallization degree.

Raman spectroscopy also allows to verify surface
homogeneity of the samples: the spectra collected in
different regions of the same sample are perfectly
reproducible.

FIG. 2: Raman spectra of cobalt oxide thin films deposited at
different substrate temperature.

In the XRD spectra (fig.3) all the main peaks
corresponding to the spinel cubic $\text{Co}_3\text{O}_4$ structure are found
and, in particular, the samples grown at high substrate
temperature have a preferred orientation in the (111)
direction.

The crystallite dimensions calculated utilizing the
Scherrer formula are of the order of 5-10 nm, increasing
with increasing substrate temperature.

The AFM images contain some further information: on
10x10 µm scale, grains are visible, with a diameter less
than 1 µm and height of the order of 10 nm; at higher
magnification, the regions without grains appear smooth
and free of any kind of structure. The sample deposited at
room temperature presents smooth surface.

IV. CONCLUSION

The films synthesized via RF-magnetron sputtering are
constituted of cobalt oxide in the crystalline phase $\text{Co}_3\text{O}_4$,
which is suitable for the production of gas sensors. The
samples are homogeneous in composition and show a
thickness of the order of 100 nm.

Substrate temperature is a fundamental parameter to
control film microstructure: the higher the deposition
temperature, the higher the crystallization degree.

Beyond a threshold (oxygen flow $\geq 1.5$ sccm), oxygen
flow variation doesn’t influence in any way film structure
and composition.

FIG. 3: XRD spectrum of a cobalt oxide thin film
deposited at 250°C with an oxygen flow of 1.5 sccm.

FIG. 4: AFM image of a cobalt oxide thin film deposited at
250°C with an oxygen flow of 1.5 sccm.

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