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# Deposition Rate Influence in $O_3$ Sensing Response of Sputtered ZnO Thin Films †

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**Abstract:** The study of semiconductor materials applied as chemical gas sensing devices is currently focused on the production of new sensing materials with the best possible properties in terms of detection limits, selectivity, work temperature and response time. Although theoretical models show the great importance of film morphology on gas detection, a direct relation between structure size/morphology and the gas sensing properties has not been experimentally established. In this work, RF-sputtering deposition technique was used for the synthesis of zinc oxide thin films, and deposition conditions are variated to achieve a remarkable difference in nanostructure size of the material. The electrical resistance variation of the air-exposed films in presence of different ozone concentrations show a strong dependence on the feature size and film morphology, demonstrating the effectiveness of use the parameters of RF sputtering deposition as tunable factors to improve the ZnO sensing properties.

**Keywords:** metal oxide gas sensor; zinc oxide; RF-sputtering synthesis; gas sensing effects

## 1. Introduction

In the past few years, metal oxide semiconductor films used as gas sensing devices has become an important subject in material science [1]. Numerous experimental studies conclude that the sensing properties, sensitivity and selectivity of the film depend upon the type of semiconductor material, the presence of doping elements and the synthesis method [2]. Moreover theoretical models for conduction in metal oxide gas sensors predict that the thin film morphology play a major role in the material's sensitivity and work temperature [3]. On this theoretical approach, morphology controls surface area available for adsorption, number of adsorption sites and conductivity between the grains, which are the most important aspects for the gas detection.

Despite the irrefutable importance of morphology in controlling operating characteristics of solid-state gas sensor, reported studies of zinc oxide materials synthesis picture the complexity of finely controlling microstructural features in thin film growth [4], hindering the study of ZnO morphology influence in the gas sensing properties. In this work, we study the Zinc Oxide (ZnO) thin film morphology and its relationship with gas sensing properties towards ozone detection. Radio Frequency (RF) sputtering is used to deposit Zinc films; this technique is one of the best-known physical deposition methods, allowing a highly controllable and stable deposition process for the formation of porous and uniform films [5], with great reproducibility and specific gas sensing properties.

## 2. Materials and Methods

Zinc oxide films were obtained by sputtering of metallic zinc and subsequent thermal oxidation. The films were deposited on silicon substrates in a RF-magnetron sputtering system with a working pressure of $2 \times 10^{-3}$ mbar of argon and radio frequency at 13.5 MHz. To understand the influence of the argon atoms energy, depositions were made using powers between 30 and 250 W. Thermal oxidation was achieved by treatment of zinc films into a furnace at 530 °C during one hour in air atmosphere. Oxidized films thickness was determined by Atomic Force microscopy around 550 nm.

Crystal structure was determinate with grazing incidence X-ray diffraction (GIXRD) using a Multi purpose Rigaku Ultima IV system with a source wavelength of 1.54 Å (CuK$\alpha$) and incidence angle of 1.5°. To study the surface morphology, Scanning Electron Microscopy (SEM) images were acquired using an INSPECT F50 Electron Microscope (FEI, The Netherlands). Image J software was used in image processing. Finally, film composition was studied by X-ray photoelectron spectroscopy in a Scienta Omicron ESCA spectrometer with monochromated X-ray source Al K$\alpha$ (1486.7 eV).

For gas sensing measurements films about 110 nm thick were deposited onto platinum interdigitated electrode ($SiO_2$/Si substrates). Deposition powers of 30, 120 and 250 W were used and oxidation treatments at 530 °C during 12 h was performed. The sensing properties were measured placing the film onto a plate with controlled temperature inside a chamber. On electrode extremes is applied a voltage (1V) and the electrical resistance of the film was measured using a Keithley electrometer. While the temperature is controlled, a mixture of dry air and ozone is injected right above the sample at a constant flux of 500 mL/min. The ozone is obtained with a pen-ray UV lamp that generates ozone concentrations between 0.05 and 0.89 ppm. The base line is acquired in 0 ppm of $O_3$. The sensor response is defined as the ratio between the electrical resistance in the presence of ozone and the base line resistance. The response time is defined as the time required for the sensor to reach the 90% of the final electric resistance after gas exposure, while recovery time is the time the sensor takes to return to 10% above the resistance before exposure.

## 3. Results and Discussion

Regardless deposition powers, XRD patterns of zinc films are in good correspondence with zinc hexagonal structure. Thermal treated samples reveal in XRD fully oxidation of Zn into ZnO (wurtzite crystal structure)

Scanning electron microscopy images exhibit distinctively porous films for all deposition powers with meaningful differences in the structure sizes. The tendency becomes more noticeable for oxidized films where the feature size increases with respect to metallic films and bigger structures result from higher deposition powers (Figure 1). This can be explained considering that rising the deposition power increase the potential for argon atoms ionization, what implies higher ions density and higher kinetic energy of ions impinging the target material. In another words when ions velocity is high, the sputter yield increases allowing the removal of bigger Zn clusters and yielding the formation of bigger structures on the way to the substrate. This variation in film growth dynamics is cleary observed in Figure 1; final ZnO structures variate in size from 120 nm (films deposited with 30 W) to 260 nm (deposition of 250 W).

Prior to gas sensing measurements, electrodes were chemically characterized by the XPS technique. Survey spectra of films before and after thermal oxidation show the absence of contaminants elements.

The sensor working temperature was determined between 200 and 350 °C in 0.13 ppm of ozone during 30 s. Lower temperatures were not considered due to the unstable and low response presented. All sensors demonstrated the highest response next to 300 °C.

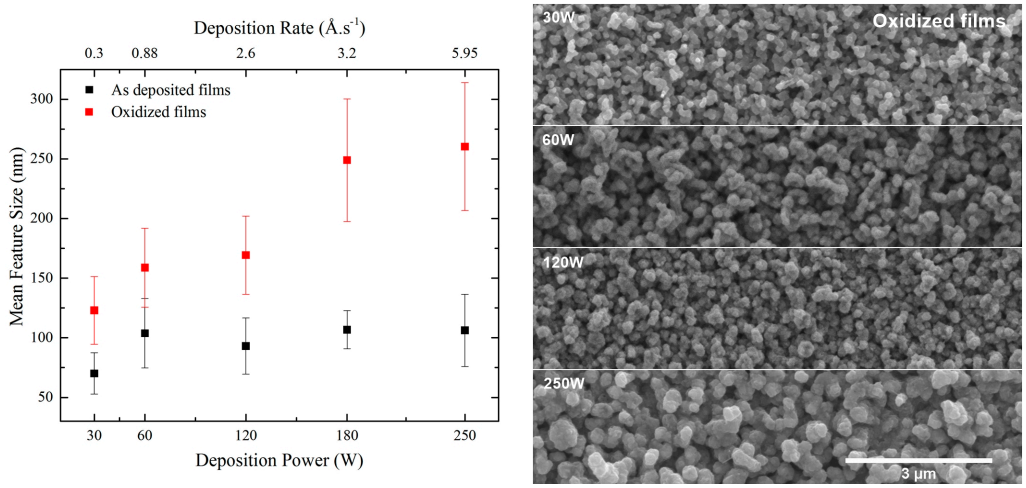


**Figure 1.** Mean feature size in function of power and rate deposition for metallic and oxidized films (**left**). Top view SEM images of films synthetized with different deposition powers (**right**).

As shown in Figure 2 there is a remarkable difference in the films response, as the film deposited with 30 W exhibits almost twice the response from the 250 W one. This behavior can be associated to ZnO morphology considering the differences in features size for the different depositions power (SEM images from Figure 2). According to the inset in Figure 2, the response shows that the smaller the feature size the higher is the sensor response. Smaller structures relates to an increase in the number of adsorption sites, due to the increment in the surface area available for interaction with the gaseous phase. From the conduction model perspective [3], smaller structures also indicate greater contributions from depletion layer to film conductivity; hence it is possible to neglect the bulk contribution to the inter-grain conductivity and minimize the quantity of material unaffected for gas interaction.

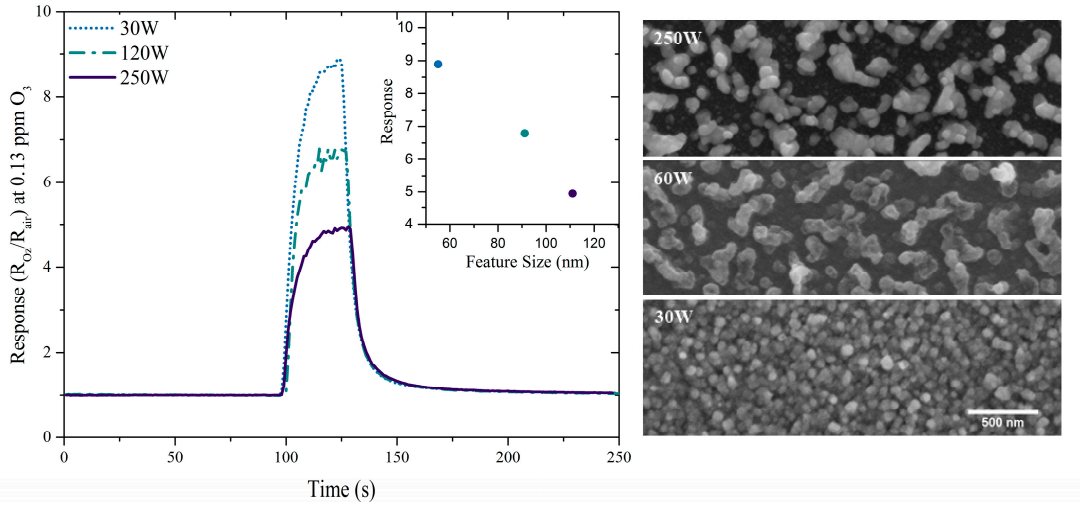


**Figure 2.** ZnO sputtered films sensing response at 300 °C and gas response in function of the grain size (**left**). SEM images for ZnO films in sensor electrodes (**right**).

The response of zinc oxide sensor deposited with 30 W (structures ~55 nm) is studied in crescent ozone concentration (Figure 3). It is noticeable that the sensor response is quite linear below 0.31 ppm of ozone, above 0.31 ppm the increment rate in the response is lower. This tendency support the idea that there is a detection limit for higher ozone concentration, above which the sensor would saturate. For all sensors, the response and recovery times for an ozone concentration of 0.13 ppm at 300 °C are about 20 and 18 s respectively.

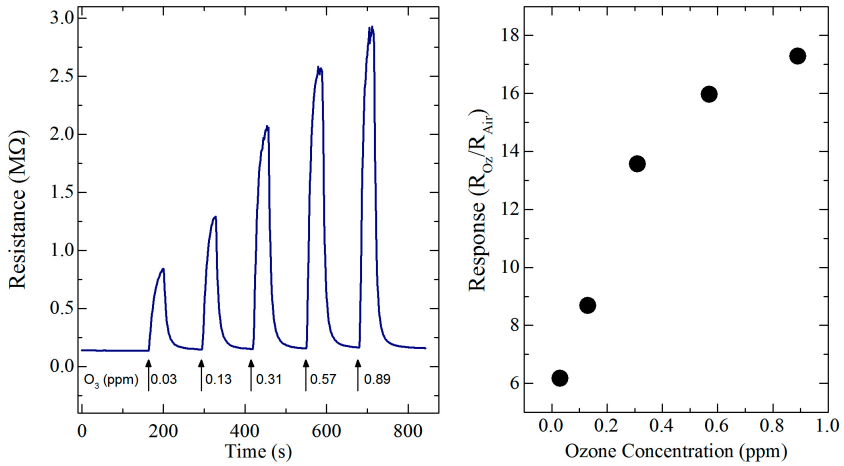


**Figure 3.** Change in resistance of the ZnO material deposited with30 W and exposed at different $O_3$ concentrations during 30 s (**left**). Response of the sensor in function of ozone concentration (**right**).

## 4. Conclusions

Our experiments demonstrates that in RF-sputtering deposition, the energy of the argon atoms, controlled by the deposition power, can be used as a tuning factor to achieve desirably structure size, where higher deposition powers create bigger structures. The experiments performed in this study show that the feature size and, therefore, surface area are major factors on which a sensor response can be modified. By decreasing the sputtering rate we can improve the conductivity contribution of the regions interacting with the gaseous phase (surface and particle boundaries).

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**Conflicts of Interest:** The authors declare no conflict of interest.

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