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Material Characterization techniques for zinc oxide thin films

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Characterization of Materials
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Abstract

Zinc oxide is a piezoelectric ceramic material with a promising future in the design of biosensors, ZnO is composed of tetrahedral linked zinc and oxygen atoms. Thin films of ZnO gained special attention for de design of biosensors due to their biocompatibility, high piezoelectric response and low production cost. To take full advantage of the multiple ZnO properties is important to characterize through various techniques such spectroscopies and microscopies that will be analyzed on this paper.

Introduction

Several characterization techniques can be used to determine the viability of the thin films for their implementation on the design of biosensors. A first approach for thin films is to characterize its surface by atomic force microscope (AFM) and scanning electron microscopy (SEM). To understand the chemical composition and structure of the ZnO films several spectroscopies must be used, Uv-Vis can be used to determine the photoluminescence spectra, infrared (IR) and X-ray photoelectron spectroscopies are commonly used to determine composition and can be supported by energy dispersive x ray spectroscopy.

For this proposal, samples are zinc oxide thin films that were prepared via reactive magnetron sputtering [1] using a 99.99% pure zinc target and an atmosphere of Argon and Oxygen. Samples are typically deposited over a 1 inch diameter disk of 304L stainless steel with a zinc adhesion layer. Thin films had a thickness of around 1.2 micrometers. Zinc oxide thin film can also be obtained with Spin coating [2] or Dip-Coating [3] The final objective of such samples is to be a part of a biosensor system being the zinc oxide the piezoelectric signal transducer.

Characterization proposal

With SEM we would be looking to analyze three important points for thin films: the surface morphology of the samples, the composition that can be obtained through SEM coupled Energy dispersive X ray Spectroscopy (EDS) and the thickness of the thin film. The first two aspects can be analyzed directly on the sample without further preparation. To analyze the thickness the surface must be scratched before the analysis. In figure 1-a surface of a sputtered ZnO thin film can be observed, thickness of the film is showed on 2-b, 2c is the graphic corresponding to the EDS Analysis with its corresponding atomic percentages.

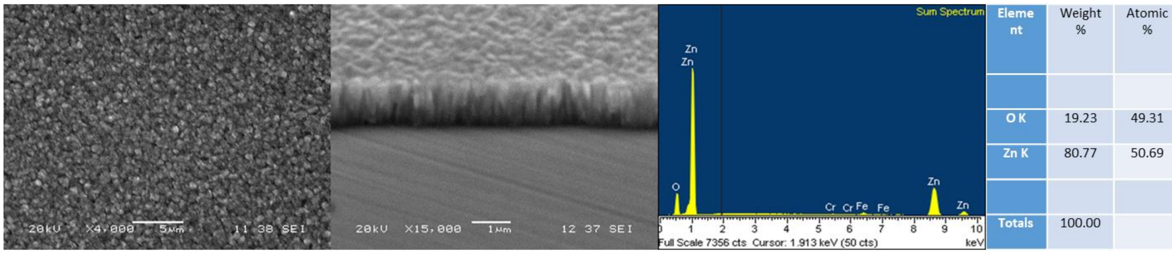

Figure 1: from left to right (a) surface morphology of the zinc oxide thin films, (b) cross section of the same film and (c) EDS analysis graphic and table.

Atomic Force microscopy can be used to quantitatively analyze the surface roughness of samples. In thin films used for biosensors this can be important since the alignment of biological components on the surface can be affected with a change in surface roughness [4]. For this analysis no further preparation would be needed. In figure 2 AFM micrographs are shown. It is easy to see that sputtered zinc oxide, presents a granular surface [5], this is mostly conserved on doped depositions (2-b)[6]**.**

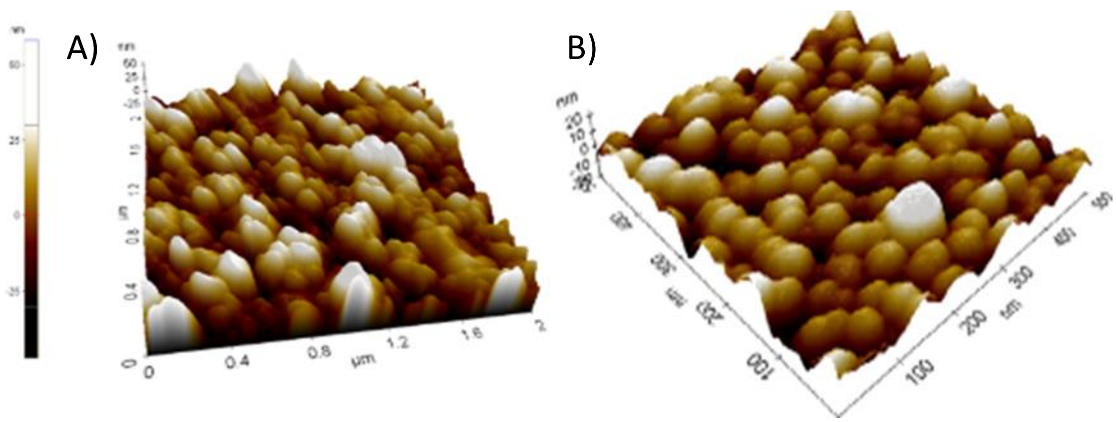

Figure 2: AFM 3D images of sputtered ZnO thin film(a)[5] and Ni Doped ZnO (b) [6].

To analyze composition multiple techniques can be used, mainly, attenuated total reflectance-FTIR (ATR-FTIR) and X Ray photoelectron spectroscopy (XPS) can be used to determine sample composition. ATR-FTIR can be used to analyze the vibrations of the Zn-O bond that has two peaks between 550 cm^{-1} and 450cm^{-1} [7]. Since ATR can analyze films no further preparation of the sample is necessary. Figure 3 shows the Infrared spectra of pure zinc oxide [8] aside the two main bands a broad band can be observed around the 3500 cm^{-1} this broad band is related to the vibration of -OH groups and is interpreted as adsorbed water on the sample for this case but can also be used to monitor Hydrogen doping in the case of using ZnO as a catalytic material [9].

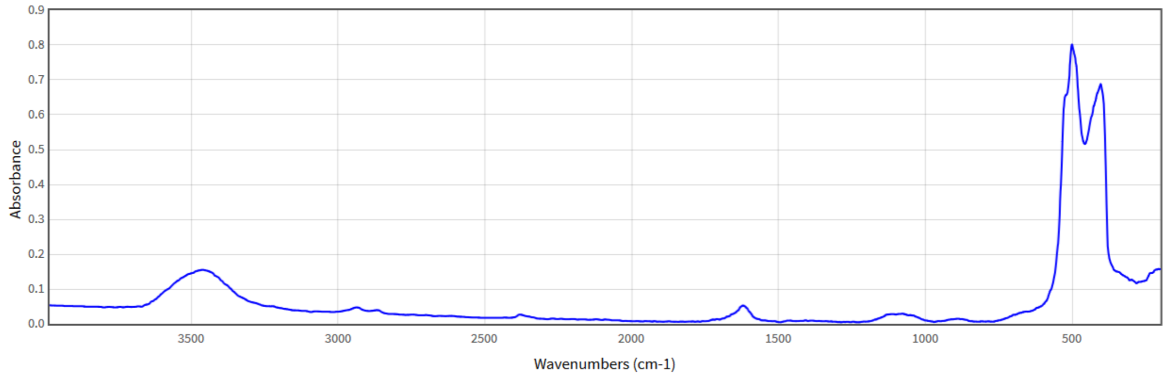

Figure 3: Infrared Spectrum of pristine zinc oxide nanoparticles [8]

XPS is used to analyze the energy of the bonds of compounds and to determine if true bonding is being formed. For this analysis the samples must be laser ablated to reach the center of the sample [10], this can be done inside most XPS equipment. XPS is complementary to X-ray diffraction (XRD) since the last gives the crystalline arrangement of the sample.

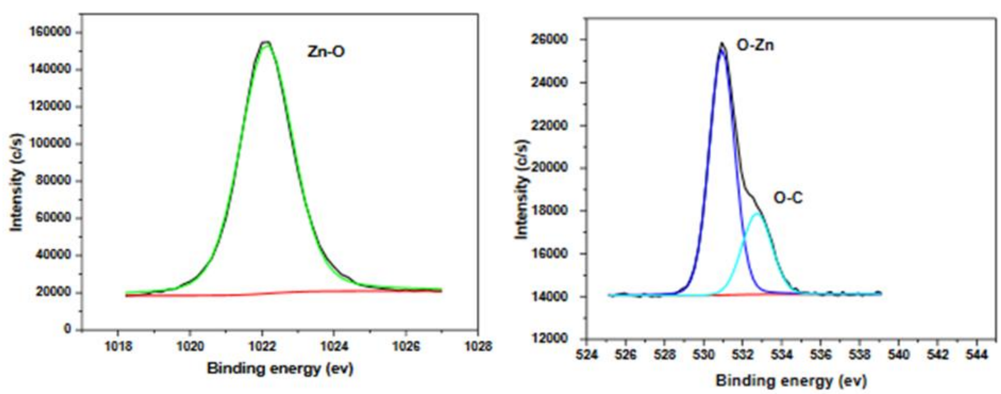

Figure 4: XPS spectra of a ZnO material Doped with Cu [12]

On a typical XPS spectra of ZnO only the Zn-O bond should be observed on the oxygen and zinc bands and no deconvolution would be necessary. XPS is useful to determine if there are impurities on the structure such as the formation of metal hydroxides or for the detection of Dopants[11], on figure 3 we can se a Copper doped ZnO structure, since Cu can be bonded directly with oxygen, it appears as a broadening of the Oxygen spectra, with proper deconvolution contribution of each bond can be assigned to its band[12].

Zinc oxide can be obtained with two main crystal structures, the most common is the hexagonal wurzite and a cubic zincblende [13], being the hexagonal form the most relevant to this study since it can present piezoelectricity [14]. Different methodologies can be implemented to improve the orientation on ZnO films, the obtention method has an important role in the crystallographic orientation [15]. Radiofrequency magnetron sputtering usually is reported as on of the best ways to obtain a (002) oriented growth but it requires High purity pre-oriented ZnO targets [16]. Another approach to obtain an oriented film is by thermal treatments, it has been proved that heating ZnO over 500°C recrystallizes the material giving preference to the (002) plane [17].

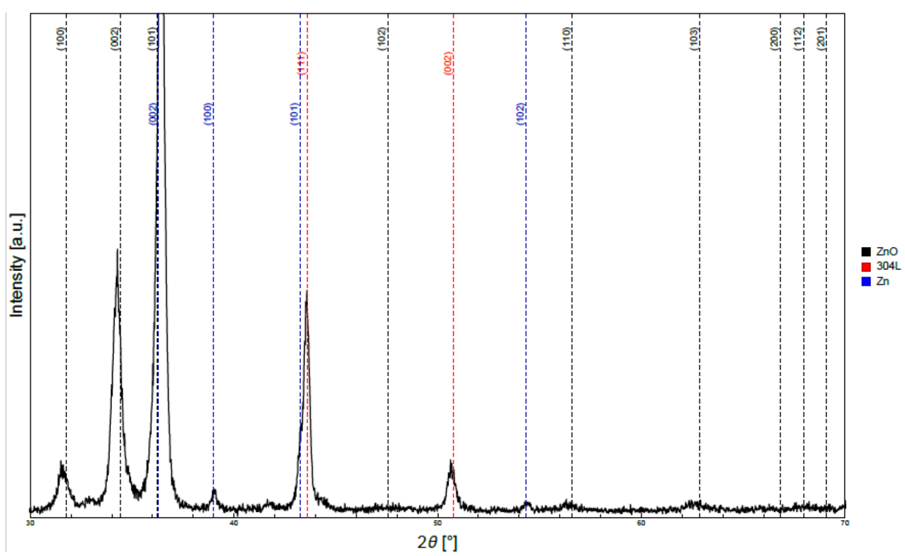

Figure 5: XRD spectra of ZnO obtained from 20° to 80° with indexed card for ZnO (black).

Additional techniques can be used to analyze different properties of zinc oxide such as Photoluminescence (PL), this characteristic can be analyzed using a Fluorimeter, the PE spectra can change according to interactions between the ZnO thin film and different materials added upon functionalization for the biosensing application [18]. PL spectra can also be modified with dopants to induce a red shift or a blue shift depending on the desired emission wavelength [19]. Using the PE property of ZnO for the desing of biosensors sensitivity of up to ng/ml can be achieved [20]

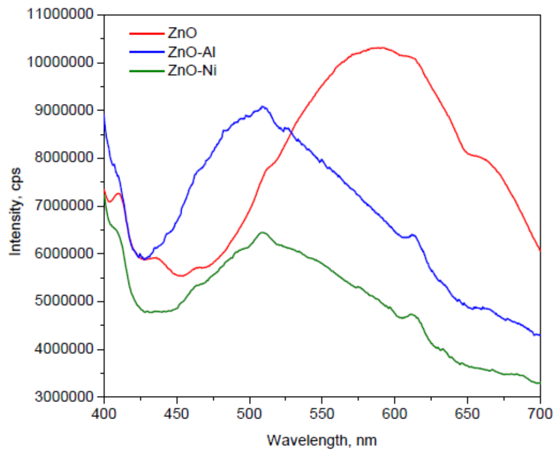

Figure 6: PE spectra of ZnO (red), Al doped ZnO (blue) and Ni doped ZnO (green) [19].

Conclusion and overview for this project

For the purpose of this project and the future design of a biosensor, three techniques outstand the rest. The first being Atomic force microscopy for its overall analysis of properties such as surface morphology and defects that could affect the biofunctionalization process. SEM is useful to analyze Cross section and surface morphology. To implement the ZnO as a piezoelectric transducer on a biosensor a dense and compact cross section is desired. This would allow the piezoelectric effect to spread on the material and generate a readable signal between electrodes. Since ZnO only presents a piezoelectric effect when the structure grows aligned with the (002) plane X-Ray diffraction is mandatory and should be, if not the first, the second Characterization technique implemented for ZnO thin films.

Many characterization techniques can be implemented to analyze a material, in the specific case of ZnO the spectroscopies and microscopies are very useful specially when complemented with X ray diffraction. With the researched references it has been shown that the design of biosensor using zinc oxide is viable under the right conditions such as a preferential growth on the (002) plane that can be obtained through modification of the processing parameters during sample elaboration or post annealing as suggested on literature

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