Characterization proposal for Zn/ZnO sputtered thin films

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Abstract

This document describes the process to obtain bilayer thin films and its desired characteristics. The suitable characterization techniques for the measurement or identification of the desired characteristics are discussed and discriminated based on its complexity and the information that can be obtained from them.

Introduction

ZnO thin films can be obtained via reactive magnetron sputtering[1–3], these films are of interest because of its piezoelectric properties and its potential to be used as substrate on surface acoustic wave (SAW) sensors[4]. The piezoelectric response of ZnO depends heavily on the orientation of the film, increasing with the amount of (002) orientation[5]; other important characteristic are the homogeneity of the film, its chemical composition and, in a lesser degree, the roughness of the film surface.

To obtain a film with the desired characteristics via reactive magnetron sputtering is important to know the effects that the process parameters have on the obtained film. The temperature of the substrate on which the film is deposited, as well as the process power and the pressure play important roles to define the orientation of the obtained film[3], however, these three parameters interact with each other in a non-linear way[2,6–8], which makes difficult the prediction of the characteristic of a film given either the process parameters or the change in its values with respect to another experiment.

The chemical composition of the films, as well as the roughness, depend mainly on the same parameters than the crystallographic orientation, which means that trying to achieve the best value of all three characteristics at the same time can be complicated and time consuming. Obtaining the adequate parameters for sputtered films is a complex topic that

exceeds the scope of this document, there are different approaches to this problem like the use of the Taguchi method and experimental optimization[9–12].

Preparation of the films

The films are deposited on 304L steel discs that need prior preparation before being used in the sputtering process. The discs have a 1-inch diameter and an average thickness of 3mm. The disc is grinded with increasingly fine silicon carbide (SiC) sand paper and finally polished until a mirror finish is obtained.

The polished disc is then placed inside the chamber of the sputtering device and fixed in place using binder clips. The chamber of the device is then evacuated using a mechanical and a turbomolecular pump until a vacuum pressure of around 5.5*10^-5 Torr has been reached. The chamber is then filled with argon (Ar) gas with a flow rate of 20 sccm and the pumping speed is adjusted in order to reach a stable pressure of around 4 Pa. Once the pressure has been reached and stabilized, the sputtering process is started applying a 50W power to a Zinc (Zn) target with a diameter of 2 inches, the process is let to run for about 2 minutes to ensure proper cleaning of the target and the pressure is set to 2 Pa.

The sample is placed over the target and inside the confinement region of the plasma for 1 minute to be coated with a pure Zn film and then is moved away from this location. Oxygen (O_2) is introduced in the chamber at different rates depending on the experiment planning, the flow rate can be between 5 to 20 sccm, once O_2 has been introduced to the chamber the pressure must be set again to 2 Pa. The sample is placed again inside the confinement region of the plasma for 10 minutes now to be coated with a ZnO film, once the process is complete, the sputtering process is stopped, the Ar and O_2 flow rates are set to zero and the sample is allowed to cool until it reaches room temperature, then the pumping process is stopped and the chamber is vented to take the sample out of the chamber.

Ideal characteristic of the films

The needed characteristic for the use of the ZnO films to be used in SAW biosensors is a strong (002) orientation, a stoichiometric ZnO composition, and a smooth surface.

Characterization techniques

The techniques that can be used to find the composition of the films can be X-ray methods such as energy dispersive X-Ray spectroscopy (EDS) or X-Ray photoelectron spectroscopy (XPS), any of these methods should be able to determine the elements present in the sample, however, EDS can only detect the presence of the elements but not if they are bonded together, XPS can detect the bonding of elements trough chemical shifts in the spectra, which would confirm the presence of the compound trough the adequate deconvolution and interpretation of the results.

In Fig. 1, SEM imaging and composition maps of a Zn/ZnO composite are presented, in the image we can appreciate that the Zn mapping, in green, covers almost every place in the field of view, while the oxygen mapping, in red, is not as homogeneous as the Zn mapping. Because EDS cannot identify compounds but only its components, we have no guarantee that there is ZnO, but its presence can be inferred in the zones in which the two mappings overlap.

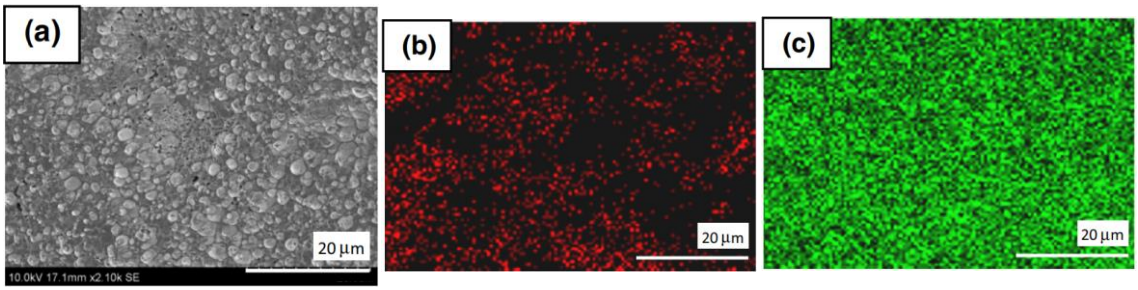

Fig. 1 EDS composition maps of a Zn: ZnO composite. (a) SEM image, (b) Mapping of oxygen and (c) mapping of Zn[13].

In Fig. 2 the XPS spectrum of a ZnO layer can be observed, we can appreciate that the peaks correspond to those of oxygen and Zn, It is important to mention that a film with oxygen bonding uniquely to Zn and one where there is bonding with Zn and hydrogen (H)

would look identical under EDS examination, this because H cannot be detected using EDS.

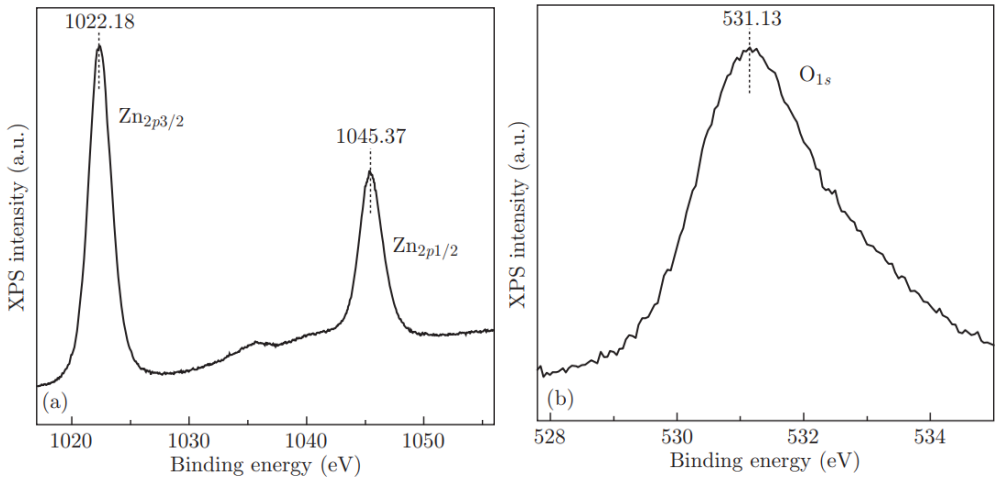

Fig. 2 XPS spectra of a ZnO layer[14] trimmed to only show Zn and oxygen peaks..

There is, however, a way in which this could be inferred, because in zinc hydroxide ($Zn(OH)_2$) there is twice the amount of oxygen than in ZnO, a non-stoichiometric composition of the film could be exposed trough EDS analysis, unfortunately, in samples such as the ones described in the introduction, this non-stoichiometry could be disguised because of the pure Zn layer, which could make the identification of $Zn(OH)_2$ harder, because of this, the use of XPS is preferred.

In Fig. 3, we can see a similar spectrum than the one in Fig. 2 and the superimposed deconvolution. As we can see, the peak corresponding to oxygen is the one that shows the more components. The red curve corresponds to vacancies, the blue curve corresponds to oxygen bonded to Zn, forming ZnO, the green curve corresponds to oxygen bonding to H, forming a hydroxyl group, finally, the purple curve corresponds to oxygen bonding to adsorbed water and organic contaminants.

Additional advantages of using XPS is the increased accuracy and the fact that XPS can analyse thin films more easily without too much interference from the substrate, combined with its ability to obtain depth profiles, it would be an adequate technique to determine the films composition.

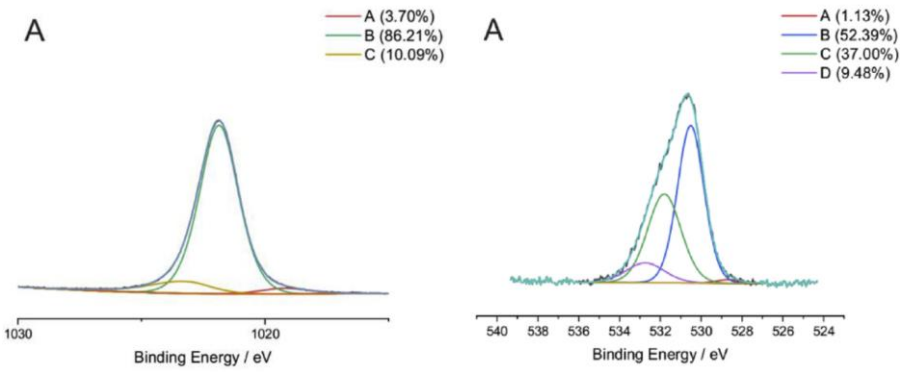

Fig. 3 Deconvoluted spectrum of ZnO nanoparticles trimmed to only show Zn and oxygen peaks[15].

To determine the crystallographic orientation of the films, X-Ray diffraction (XRD) can analyse the structure of the film and the orientation can be easily determined, it can also give information about the residual stress present in the film. In Fig. 4, the diffraction pattern of ZnO layers obtained by different method can be observed, these films have an almost absolute preferred (002) orientation, however, this is not always the case.

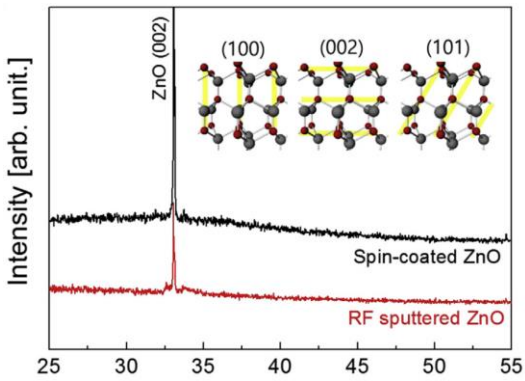

Fig. 4 XRD diffraction patterns of ZnO buffer layers deposited on glass substrates. Inset shows the lattice structure of ZnO (wurtzite)[16].

In Fig. 5 we can see a more common diffraction pattern of a ZnO film, in which there is more than one peak corresponding to different crystal orientations, the pattern of a modified ZnO film is also shown and it also exhibits more than one orientation. The crystal orientation can be improved trough thermal treatments or using sapphire substrates[17,18].

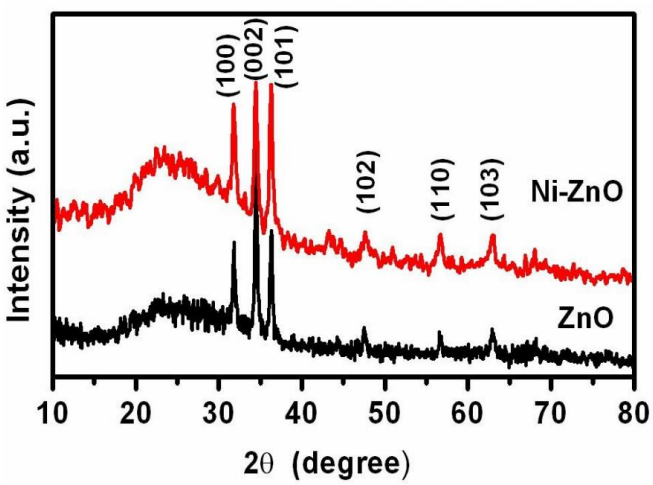

Fig. 5 Diffraction pattern of ZnO films obtained through spin-coating[19].

The limitation of the use of XRD to find the orientation of the samples is the presence of crystallographic texture in films texture. A single round of analysis will not be able to find or even infer the existence of texture, this is because the results of a textured sample will be undistinguishable from a textured one if only one analysis is made, to be able to find the texture at least two rounds of XRD per sample, each one at different rotation angle, if the sample has texture, the diffraction patters will be different from one another. Another way to know if there is texture in the sample is using two dimensional XRD[20].

The limitation of using XRD to find texture is that it can be time consuming and it would require several analysis per sample to approximate the texture, because of this other techniques would be preferred in this case, also, films similar to the ones described in the introduction have being found to have texture, this sets a precedent and considering this possibility from the start may save valuable time.

Electron backscattering diffraction (EBSD) can also be used to obtain the orientation of the films and can also generate a map of the different crystal orientations in a region, which would be useful to determine if the film orientation is homogeneous or if it depends on the location within the sample. Another advantage of the use of EBSD is the fact that it allows to superimpose the orientation mapping on a SEM image, this means that it is possible to identify regions or individual structures that present certain orientation. In Fig. 6 orientation mappings superimposed to SEM images are presented, this figure also

shows that the technique can be used in cross section images, this is particularly useful if the orientation is suspected to be depth dependent.

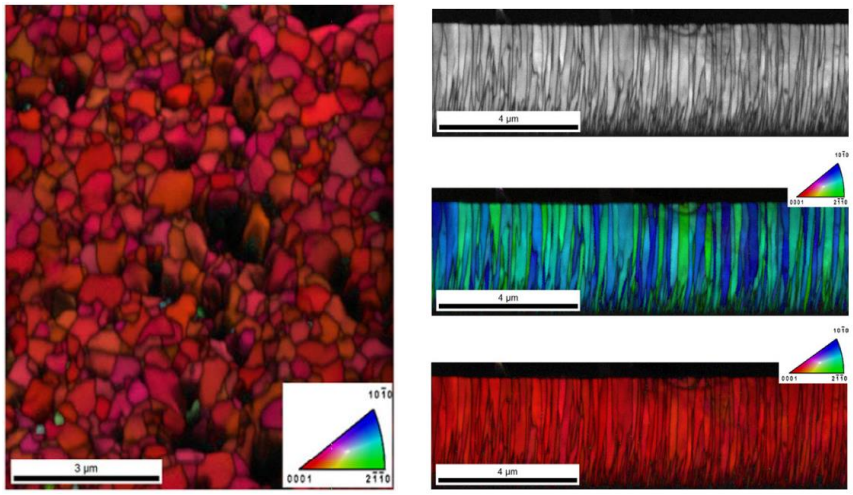

Fig. 6 EBSD mapping superimposed on a SEM image (left). Cross section SEM image (top right), EBSD mapping superimposed (middle right) and a 90° rotation on the colour of the EBSD mapping (bottom right) [21].

To analyse the surface profile, scanning electron microscopy will suffice, there is no need for the surface profile to be quantitatively known, which means that scanning probe microscopy (SPM) is not necessary.

In summary, the use of SEM, XPS and EBSD are enough to characterize the described samples and avoid the possible conflicts of interpretation that can arise using only XRD and EDS.

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