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Glancing Angle Deposition of Nanostructured ZnO Films for Ultrasonics

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Abstract— **Ultrasonic sensors have demonstrated great potential for non-destructive testing (NDT) of materials, being widely applicable in health care/monitoring (e.g. biomedical, muscle recovery, cancer early detection), industry, and defence (e.g. proximity sensors used in unnamed aerial vehicles – UAV; detection of submarines). Most conventional ultrasonic sensors are based on monolithic piezoelectric ceramic materials (e.g. PZT, $PbTiO_3$ or PMN-PT) which are too bulky and non-conforming to enable their integration on flexible substrates. To address these drawbacks, ZnO thin films have emerged as an alternative piezoelectric material for low profile and high-frequency ultrasonic transducers due to properties such as high piezoelectric coefficient, great tuneability of working frequency, large bandwidth, low-cost of materials and manufacturing, compatibility with flexible substrates, and biocompatibility. This work analyses glancing angle deposition (GLAD) of ZnO thin films at different reactive sputtering conditions optimised to meet dual requirements of highly crystalline c-axis orientation while controlling the inclined angle of resulting nanostructured films for their application as piezoelectric material in ultrasonic sensors. Characteristics of ZnO nanostructured films, including morphology, crystallinity, and composition, are analysed as a function of GLAD conditions (gas flux angle with respect the substrate surface (α) and plasma conditions (plasma power, substrate position, substrate temperature, total gas-flow, and processing/reactive gas ratio). The obtained piezoelectric values for β angles of $\alpha=88^\circ$ present d_{33} values of 33.1±1.7 pm/V, surpassing the piezoelectric coefficient found in ZnO bulk 12.4 pm/V. The influence of film titled angle (β) on piezoelectric performance for ultrasound sensing applications will be studied.**

Keywords—glancing angle deposition, reactive sputtering, zinc oxide, piezoelectric sensor, ultrasounds

I. INTRODUCTION

Ultrasonic sensors have demonstrated an enormous utility in evaluating materials in health care (e.g. measurement of flow rates with automatic fluid intake, monitor of fluid levels in human body, detection of smallest amounts of blood in dialysates, etc.), as well as in other industries such as material science, food industry, defence, transportation/navigation and Internet of Things [1–3]. For the past years, most conventional ultrasonic sensors are based on monolithic piezoelectric ceramic materials which are bulky and non-conforming to enable their integration on non-conventional substrates - essential for wearable and flexible electronics applications [4]. Despite their large piezoelectric coefficients provide highly efficient transducers, it is difficult to produce transducers for high resolution ultrasonic imaging, the spatial resolution is limited to hundreds of microns in soft tissue [5].

To address this drawback, ZnO thin films have emerged as an alternative piezoelectric material for low profile ultrasonic transducers, providing properties such as piezoelectricity, compatibility with flexible substrates, high crystallinity, non-toxicity, abundance in nature and its easy deposition through standard techniques. Moreover, ZnO thin films can be fabricated at the micron scale without the use of lapping techniques that result in delicate and fragile ceramics, allowing then resulting ultrasonic sensors to reach stable frequencies up to 1 GHz [6]. These high frequencies are required, for example for its use as acoustical tweezers for non-contact manipulation of microparticles or biological cells [7], to increase spatial resolution under the 100 micron limit or for ultrasound use in therapeutic purposes [5].

The existing procedures to deposit ZnO thin films, controlling the crystalline structure, composition, and morphology of the resulting piezoelectric material, have been further enhanced by the use of techniques such as glancing angle deposition (GLAD), allowing the deposition of inclined nanostructured films, or also called tilted films (Figure 1) which has opened a whole new research around ultrasonics [8]. However, the crystal structure and piezoelectricity of the resulting GLAD deposited ZnO layers have not been discussed in detail in literature. GLAD is a technique that uses the well-known physical vapor deposition mechanism under conditions of an oblique angle incident flux and limited adatom diffusion that results in a columnar nanostructure (Figure 1).

As deposition occurs, the columnar structures are influenced by the so-called shadowing effect (Figure 1). This effect causes the nanostructures to grow tilted with a certain angle β that depends on the relative angle between the incident gas and the surface of the substrate, the so-called α angle. Understanding the correlation between the incident flux angle (α) and the resulting columnar tilting angle (β) has been a matter of intensive investigations, comprising from basic geometrical models [9-10] to more advanced growth kinetics models based on Monte Carlo simulations [11]. On one hand, the so-called geometrical models consists of tangent [10] and cosine rules [9]. The former provides a reasonable estimation specifically for $\alpha < 60^\circ$, while above that range the accuracy decreases significantly. The latter is based on a ballistic model, considering a mean free path larger than the sample-to-target distance. This equation has led some research to good and accurate results, but it fails for some sputtered materials. The main issue of these two formulas is the

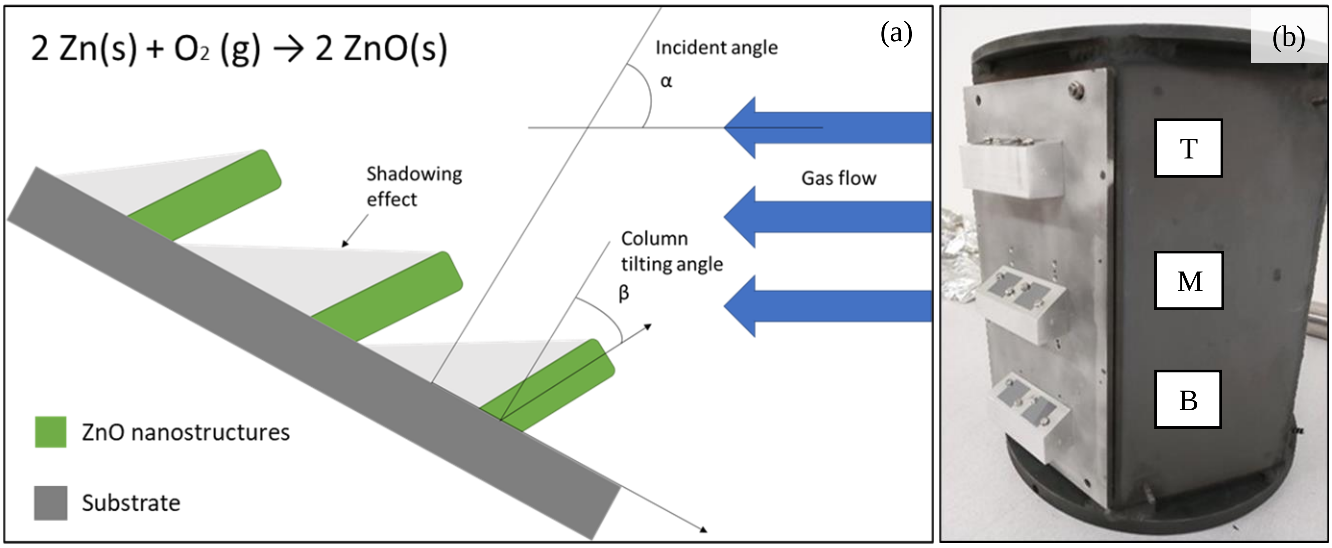

Figure 1. **(a)** Schematic of Glancing Angle Deposition (GLAD) technique. The diagram shows the characteristic angles belonging to GLAD. On the one hand, the incident angle (α) is defined as the angle between the incident molecular flow and the normal vector of the substrate. On the other hand, β represents the resulting column tilting angle. This angle is affected by the so-called shadowing effect. The front structures which gas reaches first act as a mask for the substrate behind, making the layer to grow in a tilted nanostructured manner. **(b)** Photograph of the drum utilised to support the substrate holders at different heights (top: T, middle: M and bottom: B). Each block is 70mm distant from each other.

assumption of the deposition being entirely geometrical, without any influence from the physical or chemical nature of the deposited elements. This fact causes these rules not to be universal for every scenario, therefore one must be careful when using them.

On the other hand, there are MC simulations showing great match the relation β vs. α obtained experimental and through the simulations in between titanium oxide thin films [11]. More investigations are still needed to study other metal oxides, including ZnO.

As such GLAD is promising for the deposition of ZnO along c-axis or (002) orientation, as well as c-axis inclined ZnO films. In particular, it has been shown that at certain β, the partial or even total extinction of S (shear) and L (longitudinal) acoustic modes could be observed [12]. This feature has a huge impact on ultrasonic applications in different mediums, where one acoustic mode (L or S) couples into the medium, creating excessive damping (e.g. L-mode in liquids). Therefore, a device where different modes can be suppressed at certain deposition angles is possible.

Piezoelectricity of the deposited film is essential for the final objective, the utilisation of ZnO to create an ultrasonic device. Previous research suggested that changes to the inclination of the films would significantly reduce the d_{33} piezoelectric coefficient as a decrease in the crystallinity was observed [12].

This work presents GLAD nanostructured ZnO thin films deposited at different angles with respect to the incident gas flow, and the characterisation of resulting film properties (piezoelectric coefficient, morphology, composition, columnar tilting angle and crystal structure) for application in ultrasonic sensors.

II. EXPERIMENTAL DETAILS

Prior to the deposition, all substrates (Si(100) from University Wafers) were cleaned in a staged ultrasound bath, first in acetone for 3 min, in IPA for 3min and dried under N_2 flow. After the cleaning, the substrates were mounted on substrates holders titled at different angles (α) and loaded to the sputtering system to prevent their contamination. ZnO thin films were deposited by DC-magnetron sputtering system from a 100×300 mm^2 Zn (99.99% purity) target using O_2 and Ar as reactive gases. The sputtering system comprised an industrial chamber that can allocate up to 56 samples of $20x20mm^2$, using a dual DC magnetron system (left and right). Each substrate holder consists of three locations for blocks with different angles (Figure 1). For the sake of comparability, only the middle position was studied. The sputtering conditions were as follows: plasma power 200 W, chamber pressure 0.3 Pa, Ar/O_2 flow ratio 5/7 sccm, and target to substrate distance 70mm. The deposition rate was 0.6μm/h (as measured in samples mounted at $\alpha = 0$). No intentional substrate heating was implemented, and temperature stayed below 80 °C.

The morphology, structure, composition, and piezoelectric properties of resulting nanostructured ZnO titled films were characterised by scanning electron microscopy (SEM characterisation was carried out and the resulting columnar tilting angles were estimated using ImageJ Software [13]); energy dispersion X-ray diffraction (EDX), X-ray diffraction (XRD) and piezoelectric coefficient (d_{33}) measurements. Moreover, the resonance mode used in the d_{33} measurements was extracted using finite elements analysis (FEA).

To investigate the correlation between α and β, set of blocks was fabricated to hold two samples at a designated angle. For this study, we evaluated the columnar tilting angle for samples oriented at 60º, 70º, 80º, 82º, 84º, 86º and 88º. The minimum angle selected was 60º as previous work suggests that angles below this do not produce films with significant β values [12].

The utilised set-up for measuring the piezoelectric coefficient consisted of a single point laser vibrometer (Mach–Zehnder interferometer, from Polytech). The set-up was calibrated using PZT material with different thicknesses at different resonance frequencies. The sample measurement was

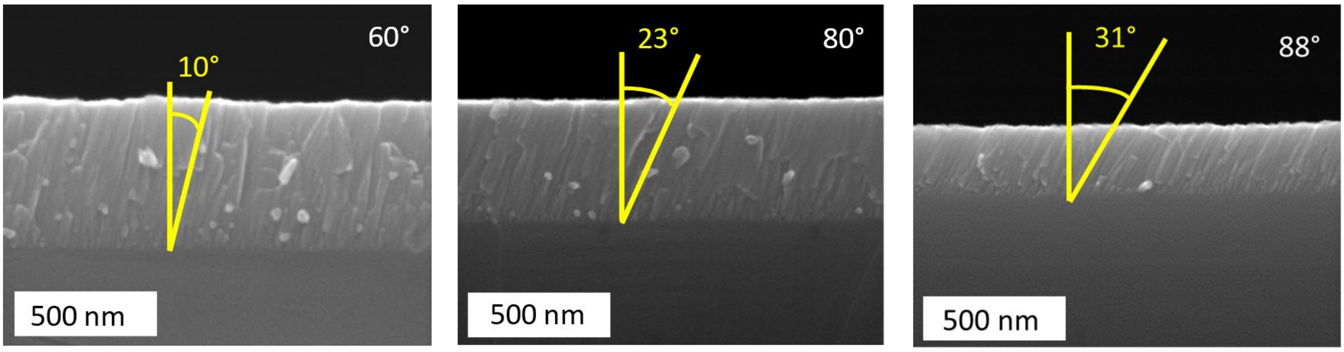

Figure 2. Cross-section SEM images, taken at 70kX, of the ZnO films deposited at different α angles. Yellow solid lines show the utilized measurement to estimate the columnar tilting angle β. The obtained value is shown in yellow. The white value shown in the top-right corner of each image represents the incident flux angle α at which the film was deposited.

repeated tens of times and the background thermal noise was subtracted to ensure the accuracy of the calculation.

The thickness is a key parameter when discussing the piezoelectricity of a material, therefore, the chosen samples for the study were the grown at α=0º, 60º and 80º because they exhibit larger differences in β (0, 10º and 23º, respectively). The samples were excited at a frequency of 56.6 kHz, corresponding to one of the resonant modes for the ZnO (estimated using FEA). The applied voltage ranged from 0 to 20 V peak-to-peak, with a 0.5 V step. To prevent the bending of the substrate and other external effects, the samples were bonded with epoxy onto a heavy piece of metal.

III. RESULTS AND DISCUSSION

A. Incident flux angle (α) vs. columnar tilting angle (β)

SEM images demonstrate the successful deposition of tilted ZnO nanostructured films (Figure 2), exhibiting relationship between α and β. The stoichiometric nanostructured films - demonstrated by EDX - present an increase of β from 10º up to 31º as α increases from 60º up to 88º. This result was obtained at fixed sputtering conditions described above, however, further studies will be needed in order to find the effects of parameters such as pressure, gas flow, and substrate temperature on this trend. This control over the magnitude β by changing α allows to fabricate different nanostructured films which could be very interesting for ultrasonic applications. In fact, the observed values of β close to the limits reported in the literature for ZnO films (β = 34.2±1.0º), are highly demanded for the development of pure mode ultrasonic sensors [12]. This dependence between the β and α is possible due to the well-known shadowing effect characteristic in GLAD [14], which also produces a drastic effect on the thickness of the resulting films with respect to the standard growth conditions.

For the sake of comparison, β extracted from cosine and tangent rule, we confirmed the non-adjustment of the expressions to the experimental values. Therefore, following what previous works suggested, the correlation between β and α is something to be estimated for each material individually when dealing with angles close to glancing (α>60º). The derivation of the expression governing this correlation must be estimated by Monte Carlo simulations as has been done previously for materials such as TiO_2, SiO_2 or Ta_2O_5 [9-10]. Additionally, the utilised source of atoms is far from being a point source, causing the observed variability for a given set of samples (Figure 3). Further studies to confirm this correlation β vs α will consist of transforming the distributed target into a point source, equalising the deposition rates and reducing the atomic collisions that prevent the system to maximise the angular increase

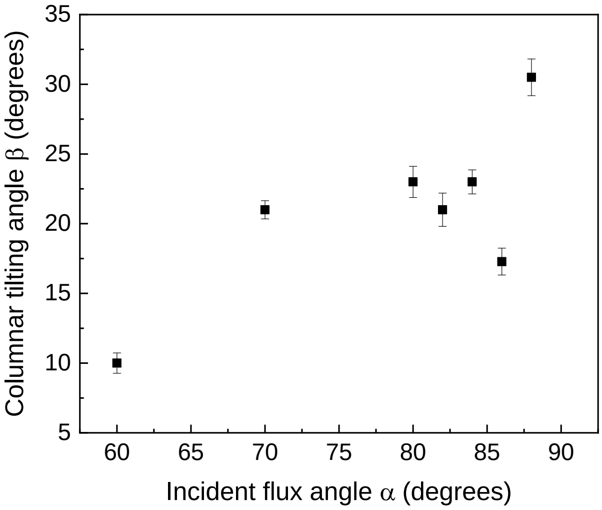

Figure 3. Experimental results for the correlation β vs. α on ZnO tilted nanostructures. There is a trend suggesting the higher the deposited angle (α), the bigger the resulting columnar tilting angle (β).

B. Structure of inclined ZnO thin films

XRD analysis demonstrates that all films are highly crystalline, with (002) peaks predominant over the rest, and independently on α. It is worth noting that (002) peak does not shift significantly by means of α, compared to the resulting film angles β, as observed in Figure 4. This result may suggest the c-axis of ZnO wurtzite structure is still parallel to the normal vector of the substrate, independently on resulting β (angle of the column) in agreement with previous research found in literature [15]. However, it will be validated on another work by performing χ-scan studies. From Figure 4, it could also be observed how increasing the tilting of the ZnO films produces a decrease in the deviation from the ZnO powder peak at 34.2º. This effect could be attributed to the geometrical dispositions of the tilted grain boundaries within the crystal structure, resulting in a more relaxed layer and reducing the stress of the film.

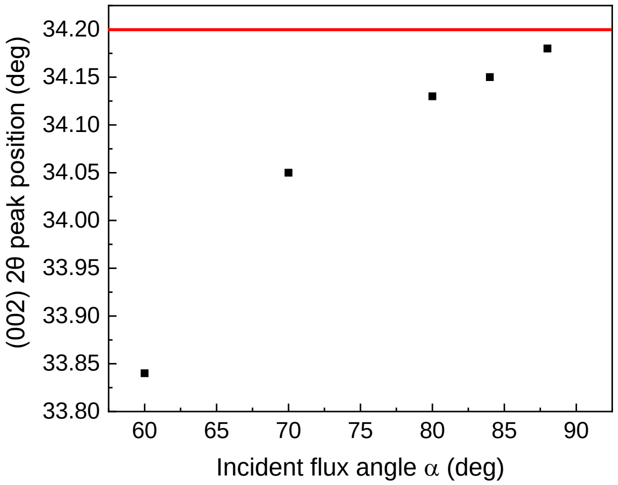

Figure 4. (002) peak 2θ position as a function of the incident flux angle α. The little variation of the peak with respect of the bulk position can be attributed to a compressive stress caused by the tilting of the film. The more tilted the layer, the closer the (002) peak to the powder peak (marked with a red line), suggesting higher angles produce a more relaxed film.

C. Piezoelectricity of inclined ZnO thin films

The piezoelectric coefficient (d_{33}) was measured in ZnO thin films titled at different β angles, exhibiting values ranged between 15±2.7 pm/V and 33.1±1.7 pm/V. The lower β angles, close to the planar thin films show averaged values around 15±2.7 pm/V, whereas higher β angles of $\alpha=88^{\circ}$ present d_{33} values of 33.1±1.7 pm/V, the latter surpassing the piezoelectric coefficient obtained in ZnO bulk 12.4 pm/V.

From this preliminary d_{33} measurements, one could conclude that an increase in the columnar tilting angle β causes higher displacements in piezoelectric films for a given voltage. While this could be explained by an increase in the film porosity allowing the ZnO to flex more freely, this increase in porosity has not been observed in the SEM micrographs in Figure 2. Another possible cause may be a change in the stress state of the film, which could alter the measured d_{33}. This could also explain the shift in the location of the (002) peak in the XRD data shown in Figure 4. However, as the obtained piezoelectric coefficient about three times larger than the bulk value, further study will be performed to validate that there is not a contribution of other vibrational modes or substrate bending causing an overestimation of the calculated d_{33}.

IV. CONCLUSION

In this paper, we have discussed how ultrasound can revolutionise the sensing industry with more accurate, precise, and non-toxic devices. In many cases, new materials have been developed to fulfil these requirements. ZnO, as we have examined within this work, is a highly prospective material for the explained purpose. Specifically, tilted nanostructured ZnO thin films have been demonstrated to be great candidates for their use as a new ultrasonic transducer, as they could be tuned by means of deposition angle.

We have demonstrated the successful growth of titled ZnO films by means of GLAD, and the correlation between the incident flux angle α and the resulting columnar tilting angle β.

Additionally, we have observed how this relationship cannot be expressed by a simple geometrical equation, but a comprehensive model is required.

From the crystallographic point of view, we have shown how the ZnO wurtzite internal structure is highly crystalline, and the films show a predominant (002) peak XRD spectra. Further study will confirm the orientation of the c-axis when tilting the structure.

Finally, regarding the use of these tilted films as transducers, we have proved how tilting the structure can produce piezoelectric coefficient (33.1±1.7 pm/V) larger than its counterpart the bulk material (12.4 pm/V). That suggests ZnO tilted nanostructures could potentially be the next material for efficient and flexible ultrasonic sensing platforms. Future studies will be the investigation of the performance of these GLAD ZnO thin films in an ultrasonic device.

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