The effects of post-growth thermal annealing on the structural and electrical properties of RF-magnetron sputtered ZnO

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Abstract: The effects of two thermal annealing steps on the crystallographic orientation, film stress and crystal domain size in RF-magnetron sputtered ZnO thin films for ultrasonic transducers were investigated. As-grown films contained high levels of compressive stress introduced by the sputtering process, as well as low (002) crystal orientation selectivity. It was shown that residual stress could be eliminated by post-growth annealing at temperatures of 400°C or higher, however, that annealing process also lead to a reduction in the desired (002) crystal orientation selectivity. The use of the relatively low temperature (250°C) in-situ anneal in the sputtering chamber in an oxygen-rich environment was found essential for prompting grain growth and recrystallisation, resulting in (002) textured ZnO films that have high electrical resistivity.

Keywords: piezoelectricity; thin-films; zinc-oxide; thermal annealing; RF-magnetron sputtering; crystal properties; stress; orientation selectivity.


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1 Introduction

Acoustic microscopy allows the imaging of the internal structure of materials by utilising the contrast produced by high frequency ultrasonic waves owing to the spatial variation in elastic properties in the material [1]. Such acoustic waves are generated and detected by piezoelectric transducers that are typically integrated with buffer rod and lens systems. To increase the imaging resolution, higher frequency ultrasonic waves are required, while ensuring minimal acoustic losses in the imaging system, a task which becomes too expensive and difficult at frequencies exceeding 100 MHz [1].

We aim to fabricate ultrasound transducers that can operate in the 300 MHz–1 GHz frequency range, to be used for the development of a novel scanning acoustic microscope (SAM). Owing to its versatile and suitable properties [2], zinc oxide was selected as the piezoelectric material of choice for our thin film transducer films. To produce an ultrasound transducer that operates at 1 GHz, a ZnO thin film should theoretically have a thickness of ~3µm, with a high electrical resistivity. To maximise the piezoelectric activity in thickness mode, a wurtzite ZnO crystal should have its c-axis oriented perpendicular to the substrate [3–5]. Therefore, columnar growth of ZnO films with an (002) crystal orientation is the first but not only requirement for piezoelectric response. In addition, the average crystallite domain size (CDS) along the (002) orientation which textures the surface should be as large and uniform as possible to maximise the vector sum of the generated mechanical response (inverse piezoelectric effect) owing to an applied electric field, while the films should not suffer from inherent stress that may degrade their piezoelectric activity [3].

To ensure reasonable fabrication time and cost, RF-magnetron sputtering was used to grow our ZnO films [2]; however, sputtered films tend to suffer from inherent compressive stresses [6] resulting not only in a deterioration of the piezoelectric response, but also in film cracking and peeling from the substrate [7]. An established process for relieving stress in thin films is thermal annealing, which may also prompt grain growth and improve the electrical, electromechanical, and structural properties of piezoelectric films [8–10].

For this study, our ZnO films were subject to both an in-situ annealing step where the Ar/O2 gas composition could be adjusted, as well as a post-growth anneal where temperature could be raised further than was possible in the sputtering chamber. The effects of both thermal annealing steps on the crystal orientation and mean domain size, stress, and electrical resistance of our sputtered ZnO films were evaluated; thereby, the effects of the anneal parameters on the film properties critical for piezoelectric response were determined.
2 Fabrication

An Auto500 RF magnetron sputtering system from HHV was used to deposit the ZnO films, while metal electrodes were deposited using an Angstrom Engineering thermal evaporation system. When considering crystalline substrates, lattice mismatches between the deposited films and the substrate play a major role in defining the films’ residual stress levels and dislocation density [2]. In addition, Fons et al. [11] and Chen et al. [12] reported an epitaxial relation between the c-plane normal of grown ZnO films and sapphire wafers, as well as between the m-plane normal of a ZnO film and the a-plane normal of a sapphire wafer; such epitaxial alignment can be helpful for achieving a better selectivity for ZnO film growth along the c-axis orientation. Hence, for comparison both amorphous borosilicate glass and double sided polished c-plane oriented sapphire were used as substrate materials. The transducer fabrication process was started by depositing a Cr (2 nm)/Au (50 nm)/Cr (2 nm) bottom electrode on the substrate, after which a 500 nm thick ZnO buffer layer was sputtered at a relatively low RF power in Ar gas at a pressure of ~1.5 × 10⁻² mbar. This step was found necessary to produce the desired (002) orientation in the ZnO films [13]. After this deposition, the films were subjected to an in-situ anneal inside the sputtering chamber using a substrate quartz lamp heater. This step was done at 250°C in an Ar:O₂ gas mixture for 1 h. Adding more oxygen to the annealing gas mixture is expected to improve the ZnO stoichiometry by reducing any oxygen deficiency. To test this theory, four different in-situ annealing gas-mixture compositions were used in this study, while a reference sample was prepared without the in-situ annealing step:

- Sample-1 (S-1): annealing gas mixture was 100% Ar.
- Sample-2 (S-2): annealing gas mixture was 70% Ar, 30% O₂.
- Sample-3 (S-3): annealing gas mixture was 30% Ar, 70% O₂.
- Sample-4 (S-4): annealing gas mixture was 100% O₂.
- Reference (Ref): no in-situ annealing step.

Next, a second ZnO layer was deposited to achieve the final device thickness of 3 µm. This was done using the same conditions as the buffer layer, except for the RF-power which was increased to 250°C. Finally, to anneal at higher temperatures than could be achieved in the sputtering system, samples were removed from the sputter chamber and a final post-growth (external) anneal was performed in a tube furnace for two hours under a 95%Ar : 5%O₂ gas flow. The temperature during these anneals was set from 400°C to 800°C, in steps of 200°C. Following this anneal, the top electrode structure of Cr (2 nm)/Au (50 nm) was deposited as needed for electrical measurements.

3 Characterisation

The structural properties of the samples were evaluated using (∈−2∈) scans of an X’Pert Pro PANalytical X-ray diffraction (XRD) system. Dislocations, grain-boundaries, and strains (lattice deformations) contribute to stresses embedded in a crystalline specimen, and such deviations from the ideal crystal structure have important consequences on
diffraction measurements [14]. By measuring any deviations in the (002) peak position ($\theta_{002}$), we can directly calculate the associated residual stress $\sigma$ within a film using Hooke’s law:

$$\sigma = \frac{1}{S} \times \frac{c - c_0}{c_0}$$

where $c_0$ is the unstrained unit cell distance, and $c$ is the measured unit cell distance. The constant of proportionality $S$ is the corresponding elastic compliance, which for zinc oxide’s hexagonal structure is given by Hong et al. [15] and Chen et al. [16]. Substituting into equation (1):

$$\sigma(\text{GPa}) = -232.812 \times \frac{c - c_0}{c_0}$$

Careful visual inspection was carried out to ensure proper sample mounting on the diffractometer’s circle, to minimise the dominant sample-displacement error. According to Cullity and Stock [17], and by substituting the $\theta$ value for ZnO’s (002) peak, the stress measurement uncertainty due to this error is ~0.11 GPa per 100 µm of displacement. For sapphire samples, further diffractogram calibration with respect to sapphire’s (006) theoretical peak position was done, effectively minimising this error. Therefore, stress measurement uncertainties are assumed to be larger for borosilicate samples.

The crystal orientation selectivity was judged by comparing the preferred ZnO (002) peak maxima to the strongest detected unwanted ZnO crystal orientation (101) in the diffractograms. Having a finite CDS causes peak broadening, as complete destructive interference will not result when Bragg’s Law is not satisfied. The relation between peak broadening and the CDS is given by Scherrer’s formula [18]:

$$\text{CDS} = \frac{K \lambda}{\text{FWHM} \times \cos \theta}$$

where CDS is measured along a direction perpendicular to the Bragg planes; $K$ is a dimensionless shape factor with a typical value of 0.9 [19]; $\lambda$ is the X-ray’s wavelength; $\theta$ is the corresponding Bragg angle; and FWHM is the full-width at half-maximum of the peak (rad). For our ZnO films, it is desirable to have large crystalline domains along the $c$-axis, to yield a stronger and more coherent piezoelectric response across the top and bottom electrodes; hence, we want our measured (002) peaks to be as narrow as possible. Before and after each post-growth annealing step, the electrical resistance of each ZnO film was measured using a precision semiconductor parameter analyser (Agilent 04156C).

4 Results and discussion

When examining the reference samples – with no in-situ anneal – of both substrate materials (Figure 1), they were found to suffer from high compressive stresses (2–4 GPa), and had a (002) : (101) selectivity ratio of less than 2, indicating that the required (002) orientation was competing with other unwanted orientations. The (002) peaks showed a
FWHM around 0.8° (CDS of ~10 nm). Both reference samples had electrical resistances exceeding 80 Ω/µm across the ZnO layer.

Figure 1  The change in stress (a) and orientation selectivity (b) as a function of the Ar : O₂ ratio during the in-situ anneal step for ZnO films on both sapphire and borosilicate substrates

The results are similar to those reported in various sources [10,20,21], particularly in terms of stress and selectivity.

The in-situ annealing step had significant effects on the properties of the ZnO films. First, the residual stress was not only reduced, but also changed from compressive to tensile, predominantly for borosilicate samples. This can be attributed to thermal mismatches between our thin films and the substrates [2,13]. The exception occurred when the in-situ anneal was performed in a 100% O₂ atmosphere; in this case a relatively modest reduction in the compressive stress was observed for ZnO films deposited on both substrate materials. At the same time, the in-situ anneal was found to favour the growth and recrystallisation of the (002) orientation, where this desired (002) orientation became more dominant as the O₂ gas content increased during annealing. The trend indicated an exponentially better selectivity when increasing the oxygen content. This improvement can be attributed to the combination of two effects: when ZnO is sputtered in pure argon, the resulting films tend to be Zn-rich with poor c-axis alignment [22,23]. On the other hand, the ZnO (002) orientation is the most closely packed with the lowest free surface energy. Thus in a thin wurtzite ZnO film, the (002) orientation is preferred [20], unless oxygen vacancies are introduced during the process. We therefore suggest that such oxygen vacancies are reduced during annealing in an oxygen-rich gas mixture. These results were reproducible when using both substrate materials, with sapphire substrates consistently yielding more dominant (002) textured films.

These ZnO films were then subjected to a post-growth anneal at temperatures from 400°C to 800°C for sapphire substrates, and at 400°C for borosilicate substrates. The borosilicate substrates deformed when annealed at higher temperatures, hence the XRD results provided no further insight. As can be seen in Figure 2, the higher temperature anneal further reduced the stress left after the in-situ anneal step, leading to very small values of stress observed for all anneal temperatures, even to Sample 4 that contained significant compressive stresses prior to this post-growth anneal step.

FWHM values of the (002) peak extracted from the X-ray diffractograms showed that as the annealing temperature increased, the FWHM values decreased in a nearly linear fashion, indicating an increase in the average CDS at higher annealing temperatures (Figure 2).
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Figure 2  (a) Stress evolution for films deposited on sapphire substrates with respect to the post-growth annealing temperature; (b) The estimated CDS of the ZnO (002) peaks as a function of the annealing temperature across both the in-situ and post-growth annealing steps.

Increasing the temperature of the post-growth anneal resulted in a decreased (002) to (101) selectivity ratio, indicating a preferential growth of the (101) crystallites at the expense of the desired (002) orientation in all samples apart from Sample 4 (Figure 3). For Sample 4, which had a pure oxygen atmosphere during the in-situ anneal, the (002) orientation became dominant at the higher post-growth anneal temperatures. This difference between Sample 4 and the other samples was observed for both sapphire and borosilicate substrates, but was particularly significant for sapphire.

Figure 3  The measured (002) : (101) ZnO orientation selectivity as a function of the annealing temperature across both annealing steps.

Electrical measurements indicated that an oxygen rich environment during the in-situ annealing step was critical to ensure having reproducible resistance values (over 100 $\Omega/\mu m$) across the buffer ZnO layer. External thermal annealing at elevated temperatures did not have a significant effect on the electrical resistance of the films.

5 Conclusion

The results showed the importance of having an oxygen-rich environment during the in-situ anneal step of sputtered ZnO films to achieve the requirements of low stress, large crystallite domain size, (002) texture and high electrical resistance. A lowering of the relative oxygen concentration during this step caused the undesired crystal orientations to dominate, which leads to deterioration in the films piezoelectric performance. Compressive stress inherent in as-grown films could be eliminated by
annealing at a temperature of 400°C, however anneal temperatures as high as 800°C are needed to ensure a dominant (002) textured film. It is suggested that the in-situ anneal in an oxygen atmosphere aids the elimination of oxygen vacancies which are formed during the sputtering process. The elimination of these vacancies is essential to ensure favouring the desired (002) texture during recrystallisation.

References

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