EFFECTIVE PIEZOELECTRIC ACTIVITY OF ZINC OXIDE FILMS GROWN BY RF PLANAR MAGNETRON SPUTTERING

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Abstract:

We present a study of the effective piezoelectric activity of thin ZnO films produced by RF planar magnetron sputtering. The energetic plasma particles which bombard the substrate in the above deposition system increase the substrate temperature, thus causing a gradual variation in film structure during the beginning of the film growth. As a result, a precursor layer is formed which consists of small randomly oriented crystallites, and exhibits poor piezoelectric activity. Hence, the film thickness responsible for piezoelectric activity is generally less than the physical thickness of the film. This leads to an increase in the resonant frequency of the film. For example, a film designed to have a half-wave resonance at 288 MHz, was found to be resonant at 332 MHz. The poorly structured initial layer meant in this typical case that only 87 % of this film volume exhibited piezoelectric activity. Investigations based on the deposition conditions (substrate temperature, and deposition rate), the optical losses, SEM imaging and RF electrical behaviour are presented in this letter.

Highly oriented polycrystalline piezoelectric zinc oxide films are of great interest for many acoustooptic components, such as high performance acoustooptic modulators which are used in optical switching, Q-switching and mode locking of lasers [1]. Zinc oxide is considered an attractive piezoelectric material due to its large electromechanical coupling constant [2]. To obtain films of high piezoelectric activity capable of launching bulk longitudinal acoustic waves into a substrate, it is important that the crystallite c axes are normal to the substrate surface with a common orientation. RF planar magnetron sputtering of ZnO is known as an efficient process for the deposition of highly oriented zinc oxide films and has been widely described in literature [3-6]. However, film reproducibility remains a problem despite considerable research into ZnO deposition. The problem of reproducibility is excasibated by the large number of interdependent sputtering parameters; the input RF power, the sputtering gas pressures and the substrate temperature can all be tuned to vary the film's structure. Film thickness is the single most important parameter as it determines the resonant frequency of the transducer. However, it is often observed that the actual resonant frequency of RF sputtered piezoelectric ZnO films is higher than that predicted from knowledge of the physical thickness of the film. In this letter, we show that the discrepancy between the measured and the expected resonant frequency is due to a poorly structured, non-piezoelectric layer which is formed at the beginning of the film growth. This initial layer results in the film thickness exhibiting piezoelectric activity being smaller than the total film thickness, and thus leads to a higher resonant frequency. An experimental investigation of the above observation is presented in this letter. Although a specific sputtering apparatus has been used (a Nordiko RFG 1250 sputterer), the results are of general validity.

It is well known that the structure of RF sputtered ZnO thin films depends strongly on the deposition parameters. In particular, raising substrate temperature gives the deposited atoms extra

surface mobility, allowing them to reach the lowest thermodynamically favoured lattice positions, and therefore has a significant effect on the film structure. The substrate temperature is usually monitored by a thermocouple in contact with the substrate holder. Since the thermocouple is not in direct contact with the substrate on which the film is deposited, the measured temperature does not correspond to the *actual* substrate temperature. We monitor the *actual* substrate temperature using a second RF filtered thermocouple located inside the vacuum chamber, in contact with the substrate. Time dependent temperature measurements have been carried out with increasing input RF power. Figure 1 shows the evolution of the substrate temperature with time for different values of input RF power. During this measurement, the initial substrate temperature was 100 °C and the argon and oxygen pressures were 8 mTor and 1.5 mTor respectively. It can be seen that the glow discharge, initiated in the chamber to grow the ZnO film, increases the substrate temperature. An input RF power of 100 W increases the substrate temperature by about 23 °C, while the increase in temperature is 41 °C for 300 W and 56 °C for 500 W. An important observation is that it takes approximately 50 mn for the substrate temperature to stabilise. As a consequence, the film structure must vary during this initial period.

The deposition parameters, *i.e.* the argon and oxygen pressures and the input RF power, are held constant during the film deposition. Consequently, the deposition rate is expected to remain constant throughout the process, provided that the film density also remains constant. On measuring the deposition rate during the beginning of the film growth, we find that this is not so. Figure 2 shows the evolution of the film growth rate (measured with the Crystal thickness monitor provided with the sputterer) over an initial period of 100 mn under the following typical conditions; argon and oxygen pressures 8 mTor and 1.5 mTor respectively, substrate temperature 100 °C and RF power 500 W. It can be seen that the rate increases during the first 50 mn of the process, before stabilising

to a constant value. Assuming that the quantity of incoming zinc and oxygen atoms remains constant, this variation in the deposition rate can be attributed to a variation in the film density. The density variation can be related to the variation in the deposition rate as follows:

$$\frac{dR}{d\rho} = - \frac{r_{Zn/O}\, h\, V}{(\rho V + M)^2} \quad (1)$$

where R is the deposition rate, ρ is the film density, $r_{Zn/O}$ is the quantity of incoming zinc and oxygen atoms per unit time, d, V, and M are the film thickness, volume and mass respectively. The right hand side of the above expression is constant and negative. Therefore, an increase in the measured deposition rate corresponds to a decrease in the film density. From figure 2, we can thus say that the density is initially high but decreases continuously as the temperature stabilises during these first 50 mn. At first, we attributed the higher density to the deposition of an amorphous layer at the beginning of the process, but we will illustrate that it is more a randomly oriented polycrystalline phase, than an amorphous layer.

We have recently developed an *in situ* interferometric method for measurement of both film thickness and depth resolved optical losses during the deposition. Figure 3 shows the evolution of the optical losses of a ZnO film as a function of the film thickness. This real time optical loss measurement was recorded while growing a 9270 nm thick ZnO film with a deposition rate of about 11.2 nm/mn. It appears that the optical losses are very high during the deposition of the first 600 nm of the ZnO film. According to a deposition rate of 11.2 nm/mn, the time required for the optical losses to reach a lower and more stable value is about 54 mn (*i.e.* when the film thickness is greater than 600 nm). After that period, the film quality stabilises, and the optical losses are effectively constant. Since the initial optical losses are high, the first layer is not amorphous, as it is well known that amorphous materials exhibit low optical scattering losses. Hence, we conclude that the

first layers of a sputtered ZnO film consist of small, randomly oriented crystallites. Figure 4 shows an SEM picture of a 9000 nm thick ZnO film deposited on an optical fibre where the varying structure is clearly visible.

This depth resolved variation in the structure of sputtered ZnO films is an important problem as it implies that only a part of the films grown by RF planar magnetron sputtering contributes to piezoelectric activity. Therefore, we can define two different thicknesses: the physical thickness d_0 and the piezoelectric thickness d_1 which effectively induces piezoelectric activity. Let f_0 be the expected, and f_1 be the measured resonant frequency. The thickness of the randomly oriented layer can then be expressed as:

$$\Delta = d_0 - d_1 = \frac{v}{2} (1/f_0 - 1/f_1) \quad (2)$$

where v is the sound velocity in the transducer material (v = 5300 m/s for sputtered ZnO). Figure 5 shows the S_{11} reflection coefficient obtained by testing a 9205 nm thick ZnO film with a HP 8753B network analyzer. This film was sputtered on a Cr/Au coated fused quartz disk with a deposition rate of 29 nm/mn. The device was electrically matched and a plot of S_{11} vs frequency is shown in figure 5. The closely spaced dips are caused by acoustic resonances in the 1 mm thick fused quartz disk (the average frequency spacing between two consecutive dips is equal to the free spectral range (FSR) of the acoustic cavity defined by the disk thickness, FSR = 2.9 MHz). The expected resonant frequency was f_0 = 288 MHz, while the measured resonant frequency was f_1 = 332.5 MHz. Therefore, (from equation (2)) the thickness of the non-piezoelectric layer is Δ = 1231 nm. The deposition rate, used to grow the film in question, was equal to 29 nm/mn, implying that the initial randomly oriented 1231 nm was grown in the first 43 minutes. This period is shorter than the 50 mn required to stabilize the substrate temperature, but the discrepancy arises because the film

structure evolves continuously from a poorly piezoelectric state to a highly oriented state, which is not accounted for by equation (2).

In conclusion, we have shown that the increase in substrate temperature due to the plasma energy in sputtering systems, leads to a continuous variation in the structure of ZnO films. At the beginning of deposition, the film is randomly oriented and poorly piezoelectric, but evolves to a highly oriented and piezoelectric state when the substrate temperature has stabilised. Therefore, the effective piezoelectric thickness of the film is less than its physical thickness, leading to a higher resonant frequency. Real time measurements of the substrate temperature, the deposition rate, and the optical losses of ZnO films during deposition all indicate that the film structure evolves over the first 50 mn. SEM images of the initial layer corroborated our prediction, and network analyzer measurements of the resonant frequency provided further confirmation. The initial evolution of the structure of sputtered thin films, caused by plasma heating, is an inherent problem of RF sputtering deposition. We conclude that in order to obtain films of high electromechanical coupling efficiency and predictable resonance frequency it is important to consider carefully the design of the substrate holder and its associated temperature servo in order to maintain the temperature as constant as possible throughout deposition, and that in-situ optical monitoring techniques for loss and thickness are of great value in understanding and controlling the growth of such films.

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Figure captions:

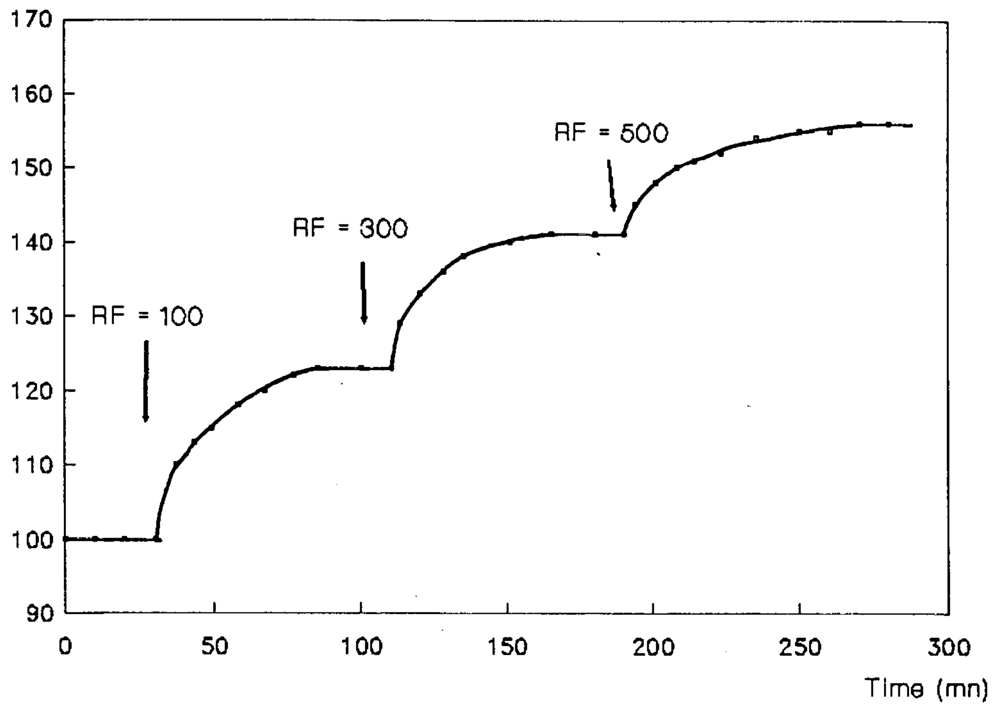
Figure 1: Evolution of the substrate temperature with time for different values of the input RF power. The initial temperature was 100 °C. The temperature increases due to plasma heating are 23 °C for 100 W, 41 °C for 300 W, and 56 °C for 500 W. The temperature stabilization time is about 50 mn.

Figure 2: Evolution of the deposition rate over the first 100 minutes of the process. The initial substrate temperature was 100 °C, and the RF power was 500 W. The deposition rate stabilises after about 50 mn.

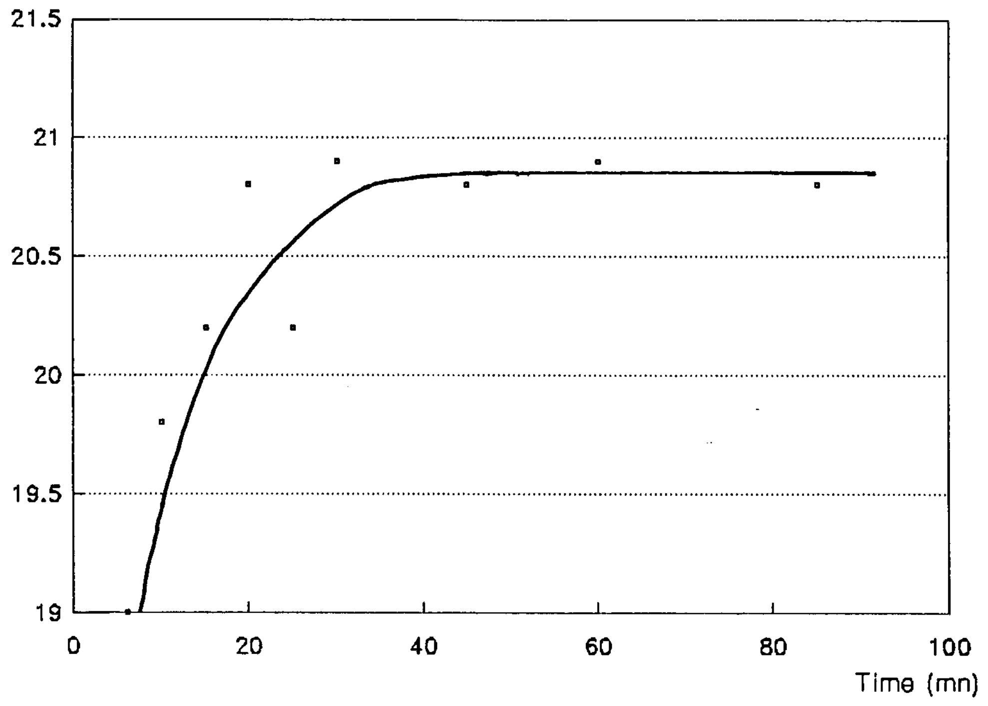
Figure 3: Interferometrically measured depth resolved optical losses as a function of film thickness. The losses are high at the beginning of the film growth, but decrease during the deposition of the first 600 nm. The deposition rate was 11.2 nm/mn, implying a stabilization time of 54 minutes.

Figure 4: Scanning Electron Microscope image of a 9000 nm thick ZnO film deposited on an optical fibre (x 8000 magnification). The varying film structure is clearly visible.

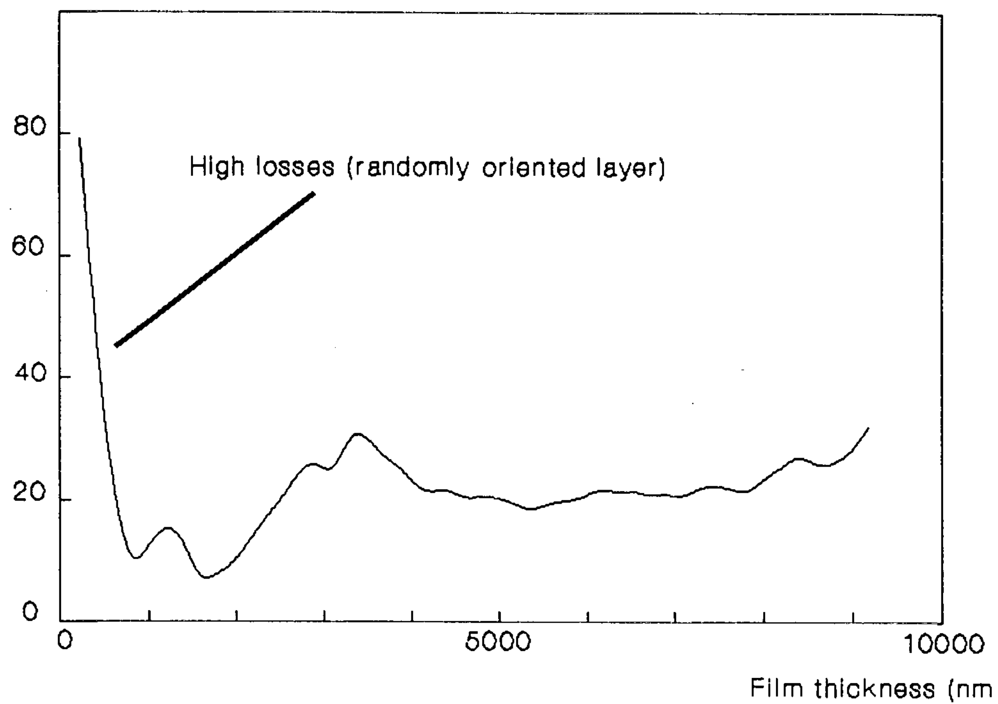
Figure 5: S_{11} reflection coefficient obtained by testing a 9205 nm thick ZnO film with a HP 8753B network analyzer. The - 39 dB dip locates the resonant frequency, which occurs at 332.5 MHz instead of 288 MHz as expected. The closely spaced dips define the FSR of the fused quartz disk to be 2.9 MHz.

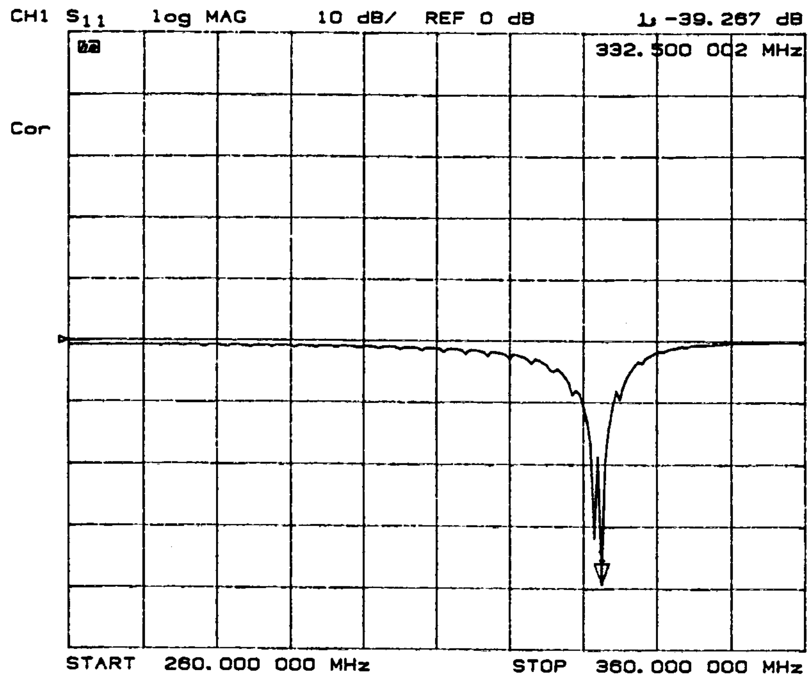


Substrate temperature (ºC)
170
160
150
140
130
120
110
100
90
0
50
100
150
200
250
300
Time (mn)
RF = 100
RF = 300
RF = 500



Deposition rate (nm/mn)
21.5
21
20.5
20
19.5
19
0
20
40
60
80
100
Time (mn)


Optical losses (mm⁻¹)
80
60
40
20
0
High losses (randomly oriented layer)
0
5000
10000
Film thickness (nm


CH1 S11 log MAG 10 dB/ REF 0 dB 1: -39.267 dB
332.500 002 MHz
Cor
START 260.000 000 MHz
STOP 360.000 000 MHz