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Fabrication of PZT Composite Thick Films for High Frequency Membrane Resonators

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Abstract. High frequency, thickness mode resonators were fabricated using a 7 μm PZT thick film which was produced using a modified composite ceramic sol-gel process. Initial studies dealt with the integration of the PZT thick film onto the substrate. Two different diffusion barrier layers were tested, titanium oxide and zirconium oxide, in conjunction with the use of 2 types of silicon substrate (differing in the etch stop layer employed, either silicon nitride or silicon oxide). Zirconium oxide gave good results in conjunction with silicon oxide. Using these conditions, devices were produced and the acoustic properties measured for different electrode sizes ranging from $45 * 45$ to $250 * 250$ μm^2. The best electrode size, which maximised the acoustic response and minimised the insertion loss, was found to have an area of $110 * 110$ μm^2. This device showed a resonant frequency of about 200 MHz, an effective electro-mechanical coupling coefficient of 0.29 and a Q factor of 22.

Keywords: PZT, thick film, resonator

Introduction

Lead zirconate titanate (PZT) materials have received considerable attention in the area of micromachined ultrasonic transducers (MUT) for their ability to generate and sense vibrations due to their high electromechanical coupling coefficient [1, 2]. MUT are of particular interest in medical imaging systems as they emit no ionising radiation, are capable of 2D imaging in real time and are portable. PZ26 (Ferroperm, DK) PZT ceramic was selected for its high coupling properties that make it particularly suitable for underwater ultrasonic applications [3]. Assuming similar properties to those of bulk ceramics, the use of a PZT composite film, 9 μm thick, in thickness mode, will have a much higher resonant frequency (about 250 MHz using Eq. (1) than that of a typical micromachined ultrasonic transducer operating in flexural mode (a few MHz) [1, 2]. High frequencies translate to small wavelengths improving the spatial resolution and allowing finer details to be resolved, albeit at the cost of higher attenuation.

$$f_r = \frac{1}{2t}\sqrt{\frac{C}{\rho}} \tag{1}$$

where f_r is the resonant frequency, t the thickness of the bulk PZT, C its stiffness and ρ its density.

The resonator is based on a thin film FBAR (thin Film Bulk Acoustic Resonator) structure [4]. The PZT film is sandwiched between 2 electrodes to form a vibrating membrane once released by bulk micromachining of the silicon (Fig. 1).

Initial devices were fabricated using the process employed for the production of a thin film FBAR and showed very poor acoustic properties. This was believed to be the consequence of PZT compositional fluctuations resulting in delamination of the back electrode as shown in Fig. 2. At 710°C, the PZT thick film sintering temperature, lead can diffuse into the silicon (Si) substrate to form lead silicates, which can themselves form a liquid phase responsible for the formation of the voids observed. The lead diffusion also may cause degradation of the piezoelectric properties. In order to address this issue, a diffusion barrier layer (DBL) was employed to help in minimising lead diffusion and hence delamination.

The work reported here first examines the fabrication of the as-described resonant structures, then discusses their acoustic properties.

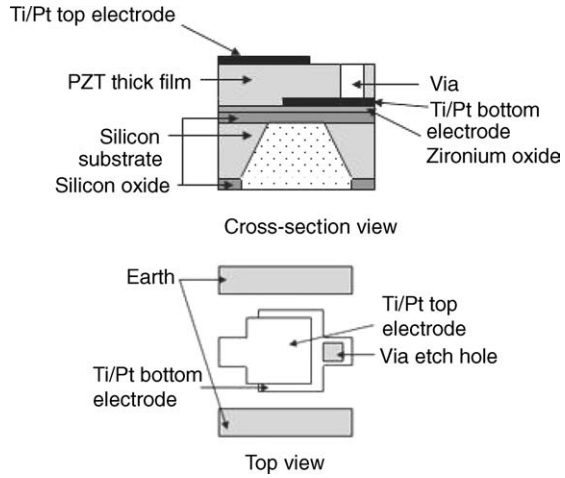

Fig. 1. Top and cross section view of the resonant structure developed.

Experimental Procedure

The integration issue was addressed using pieces of silicon nitride (SiN_x 200 nm) or oxide (SiO_2 400 nm) coated Si wafers. Titanium oxide (TiO_2 350 nm) was prepared by thermal oxidation of the metal Ti in air at about 700°C in a furnace in air. The Ti film was prepared by RF magnetron sputtering [5]. Zirconium oxide, ZrO_2 was prepared by a sol-gel method. In a 200 ml flask, 4.344 g of zirconium *n*-propoxide (Aldrich, 75 wt% solution in 1-propanol) was mixed with 3 ml of acetic acid (Aldrich 99.7%). Then, 47 ml of ethanol (Aldrich, anhydrous) was added and the resulting solution was stirred for 10 min at room temperature. Three layers of ZrO_2 were deposited giving a final thickness of approximately 60 nm. Each layer was deposited at 3000 rpm for 30 s, followed by a drying at 350°C for 60 s. The film was sintered at 700°C in air in a furnace.

The final devices were prepared on 4-inch double-sided polished silicon wafers. The silicon wafers supplied were coated on both sides with a layer of silicon oxide (SiO_2, 500 nm). The back face layer was patterned in a RIE (Reactive Ion Etching, Plasmatech 80) machine in a gas mixture of trifluoromethane, oxygen and argon. The back electrode, Ti (8 nm)/Pt (200 nm) layer was deposited by sputtering onto the DBL [5].

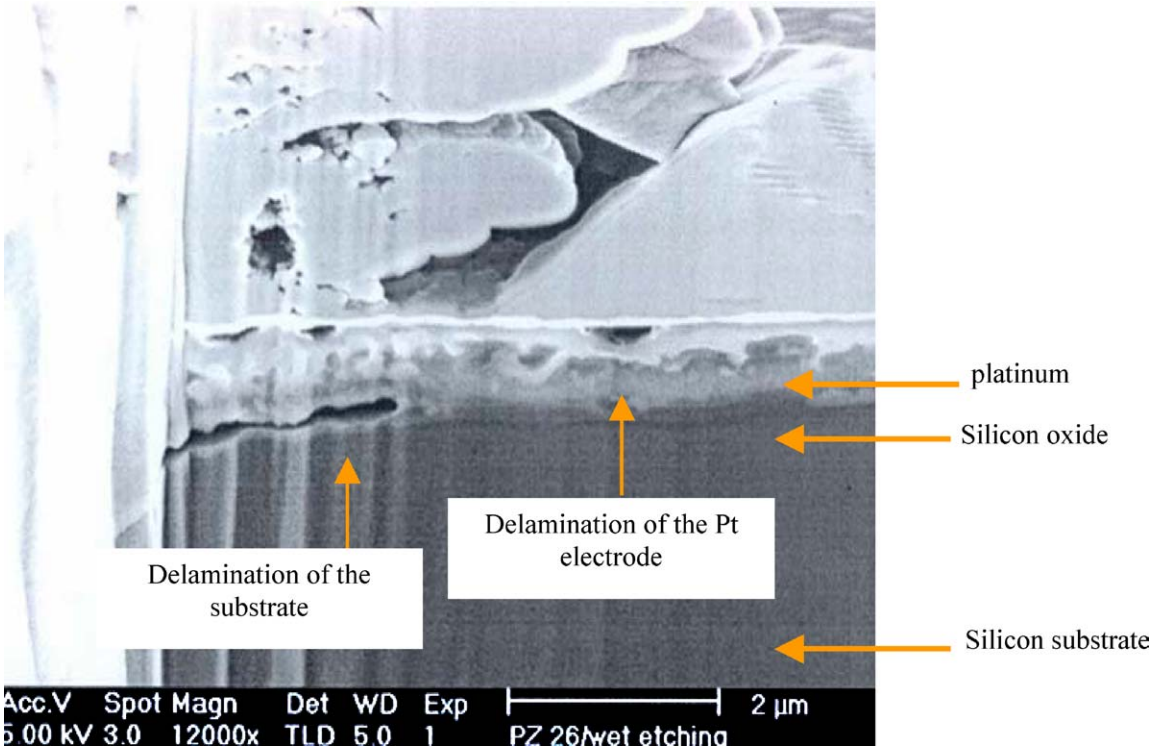

Fig. 2. SEM photomicrograph of a FIB cross section of a 10 μm PZT film deposited on Si/SiO_2 400 nm / Ti 8 nm / Pt 100 nm.

The PZT thick film was deposited by spin-coating a composite slurry made of PZT powder and PZT sol [6]. The PZT layer was patterned by wet etching carried out in a very dilute solution of hydrochloric and hydrofluoric acid at 50°C for 4 min [5]. The top electrode (Ti 8 nm/Pt 100 nm) was deposited in the same way as that of the back electrode. The silicon etching was carried out in an aqueous solution of TMAH (Tetramethyl ammonium hydroxide) (12.5 wt.%). The sample was mounted face down on a glass plate using commercial wax to protect the PZT film from the etchant. Every 2 hours, the sample was removed from the etch bath and the wax sealing was reapplied. The temperature was fixed at 70°C giving a Si etch rate of about 25 μm/hr. A Dektak® Surface Profiler was used to evaluate the thickness of the films by measuring the step height in the etch hole. The thickness was found to be about 7 μm. In order to exhibit piezoelectric properties, the PZT thick films were corona poled by applying the voltage to a needle fixed at 4 cm from the copper base on which the sample was placed and earthed. The devices were poled at 10 kV for 10 min at about 130°C. The resonators were probed using a Summit 9000 analytical probe station equipped with ACP40 (GSG200) probes which have a ground-signal-ground configuration. A 8753D Hewlett Packard VNA (Vector Network Analyser) analyses the signals using 48" flexible K-connector cables. The VNA can measure S-parameters from 30 kHz to 3 GHz.

Results

As reported earlier [5], a delamination free interface was obtained when using 350 nm of TiO_2, deposited on SiN_x substrates, in the presence of a Pt back electrode. Since the back electrode is patterned in the final device (Fig. 1), a robust interface is also required between the DBL and the PZT film. Unfortunately, after the final sintering at 710°C for 30 min in air, the PZT did bubble where it was in direct contact with TiO_2. It is believed that an excessive formation of $PbTiO_3$, at the Ti-rich interface TiO_2/PZT, occurred which does not have a good lattice match with PZT. Using ZrO_2 as an alternative DBL, chemically related delamination still occurred at the interface structure SiN_x/ZrO_2/PZT. Delamination free interfaces were obtained both with (Fig. 3) and without (Fig. 4) the electrode structure present when changing the etch stop layer to SiO_2. This enhanced protection may be due to the formation of a zirconium silicate compound (zircon, $SiZrO_4$) at the SiO_2/ZrO_2 interface [7].

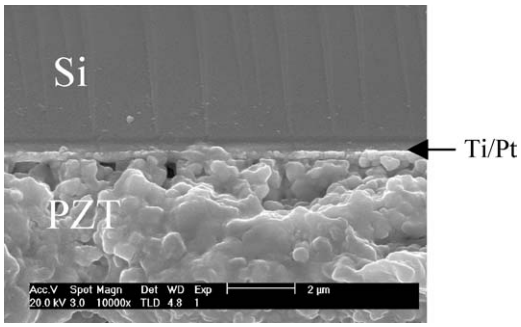

Fig. 3. SEM cross section of a PZT thick film deposited on Si/SiO_2 400 nm /ZrO_2.

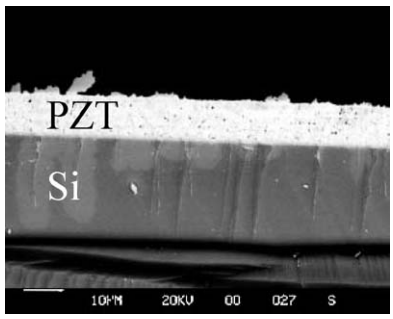

Fig. 4. SEM cross section of a PZT thick film deposited on Si/SiO_2 400 nm/ZrO_2.

The resonators were characterised by measuring the S_{11} and S_{21} parameters as a function of the electrode size (from $45*45$ μm^2 to 110 $\mu m*110$ μm^2) over the frequency range 100–500 MHz (Fig. 5). The derived parameters, k_{eff} (Eq. (2)) and Q (Eq. (3)) can be considered as figures of merit for the device. They are of interest as they give a measure of the acoustic loss within the resonator.

$$k_{\text{eff}} = \sqrt{\frac{\left(f_a^2 - f_r^2\right)}{f_a^2}} \tag{2}$$

where f_a and f_r are the resonant and anti-resonant frequencies respectively.

$$Q = \frac{f_a}{\Delta f} \tag{3}$$

where Δf represents the bandwidth measured at 3 dB from the S_{21} minimum.

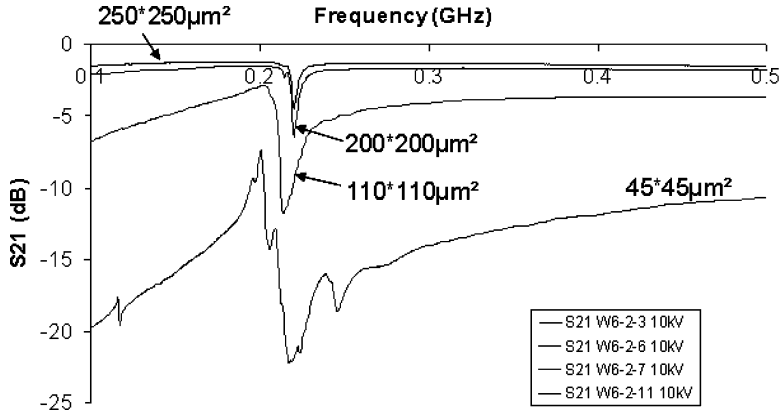

Fig. 5. S_{21} parameters for different electrode sizes (poling @ 10 kV).

The area of the electrode will determine the clamped capacitance and hence the final properties of the device. The resonant frequency was found to be about 200 MHz and smaller than that estimated from Eq. (1). This was reasonably expected since the non-piezoelectric layers affect the final resonant frequency of the whole structure. The anti-resonant frequency was between 215 and 220 MHz. The notch was rather broad due to the high electro-mechanical coupling coefficient of PZT. Spurious resonances were observed for an electrode size of $45 * 45\ \mu\text{m}^2$. They could be reduced by an increase of the electrode size. The resonant and anti-resonant frequencies were affected by the change in electrode size such that the separation between f_r and f_a increased when the electrode size was reduced. This resulted in an apparent increase of the effective electromechanical coupling coefficient from 0.15 up to 0.38 (Eq. (2)).

The other figure of merit to be measured was the quality factor Q, which represents the loss in the resonator [12]. Q was found to increase from 8 to 45 when increasing the electrode size. This was expected since the insertion loss is minimised with large areas.

Conclusion

High frequency resonators were successfully fabricated using sol-gel derived PZT thick films. It was found that sol-gel derived zirconium oxide was required as a diffusion barrier layer when using silicon oxide as the etch stop layer.

The best global response, which minimised the insertion loss but maximised the acoustic response, was achieved with an electrode size of $110 * 110\ \mu\text{m}^2$. This area led to an electro-mechanical coupling coefficient of 0.3 and a maximum Q factor of 22.

This structure may hold some promise for thickness-mode UHF (Ultra High Frequency) pMUT (piezoelectric Micromachined Ultrasonic Transducer).

Acknowledgment

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