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Lead Zirconium Titanate Surface Acoustic Wave Biosensors with Sub-micron Inter-digital Transducer Electrodes for Biomolecules

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1. Introduction

By depositing inter-digital transducer (IDT) electrodes on piezoelectric crystals, White and Voltmer [1] successfully generated surface acoustic waves (SAW) on the surface of these piezoelectric crystals and produced the first SAW device in 1965, which resulted in the extensive applications of SAW devices in the past forty years. Among numerous piezoelectric materials, lead zirconium titanate (PZT) has great potentials for SAW device applications due to its superior properties of high surface phase velocity, excellent dielectric and ferroelectric properties, high piezoelectric coefficients, and high electromechanical coupling coefficient. It is widely applied in passive devices including pressure sensors, accelerometers, micro-actuators, biochips, surface acoustic wave devices [2,3]. Due to their high sensitivity, PZT SAW devices have been utilized in communication devices as well as all kinds of sensors including biosensors [3,4].

In this paper, the fabrication of PZT thick films and PZT SAW devices with sub-micron IDT electrodes by the micro-powder-sol-gel method is reported. The results of utilizing these PZT SAW devices as biosensors for the detection of human IgG biomolecules are also reported, with the bio-sensing performance of these PZT SAW biosensors being compared with that of quartz crystal microbalance (QCM) biosensors under the same immobilization and sensing conditions.

2. Experimental

PZT ($PbZr_{0.53}TiO_{0.47}O_3$) precursor solutions were made by separately dissolving lead acetate tri-hydrate, zirconium n-propoxide, titanium isopropoxide in 2-methoxy ethanol and mixing the resulting three solutions rigorously in an ice-bath until the mixing solutions became clear. PZT mircro-powders were then produced by calcining the xerogels obtained from the precursor solution at 550°C for 90 minutes s. These PZT micor-powders along with dispersant (Nopcosperse) were added to the original PZT precursor solutions and ball milled for 15 hours to produce the coating slurry. PZT thick films were deposited on $Pt/Ti/SiO_2/Si$ substrates by repeated coatings of a single thin buffer layer using the PZT precursor solution and three consecutive thick layers using the costing slurry until desired thickness of PZT thick films was obtained. The buffer layer was soft-baked at 250°C for 10 minutes while the thick layers were annealed at several different conditions. PZT SAW devices were then prepared by depositing Al IDT electrodes of 0.5 μm width on the PZT thick films through lithography and wet etching. The detailed design of the IDT electrodes can be found in a previous article [5]. The PZT SAW biosensors were then prepared by the following procedure: (1) coating the sensing area between the IDTs with tetraethoxysilane (TEOS) to form silane groups (-Si-OH); (2) generating surface amine groups ($-NH_2$) by modifying the silane groups with 3-Amimopropyltriethoxysilane (APTES); (3) creating aldehyde groups (-C=O) by reacting the surface amine groups with the di-aldehyde cross linker, Glutaraldehyde; (4) immobilizing protein A within the sensing area of the PZT SAW biosensors with the surface aldehyde groups. These PZT SAW biosensors with sub-micron IDT electrodes were finally used to detect human IgG biomolecules and their bio-sensing performance was compared with that of the quartz crystal microbalance (QCM) biosensors under the same immobilization and sensing conditions.

3. Results and Discussion

Fig. 1 shows the XRD patterns of PZT thick films annealed at different conditions. All the PZT thick films possess perovskite structure with some showing traces pyrochlore ($2\theta=29°$) impurities. From electrical property measurement (Fig. Table 2), PZT thick films annealed at 600°C for 1 hour possessed best dielectric, ferroelectric, and piezoelectric properties (ε_r=1889.4, Pr=29.3 μC/cm^2, Ec=32.4 kV/cm, d_{31}=-418.6 pC/N, d_{33}=916.7 pC/N at 1kHz). Due to their best overall electrical properties, PZT thick films annealed at 600°C for 1 hour were used to fabricate PZT SAW devices. By using thermal evaporation, lithography, and wet etching, Al IDT electrodes of 0.5 μm width (Fig. 2(A))and PZT SAW devices (Fig. 2(B))were

successfully fabricated. Table 2 shows the performance of these PZT SAW devices measured by Agilent PNA E8364A network analyzer. The measured center frequency of the PZT SAW devices and the surface phase velocity of PZT were 2.30 GHz and 4589 m/s, respectively. These values are slightly less than the theoretical values of 2.4 GHZ and 4800 m/s. In addition, the insertion loss of the PZT SAW devices is 16.14 dB, which is relatively high for practical applications. Degraded performance of these PZT SAW devices in practical applications may be expected, which can be attributed to the inadequate design of IDT electrodes and the defects created during the PZT thick film deposition and IDT electrode deposition.

Table 1 The electrical properties of PZT thick films annealed at different conditions

Sample	ε_r	d_{31}	d_{33}
550°C/30 min	508.9	-59.6	130.6
550°C/1 hr	1601.9	-345.2	756.0
550°C/2 hr	904.9	-126.6	277.2
600°C/1 hr	1889.4	-418.6	916.7

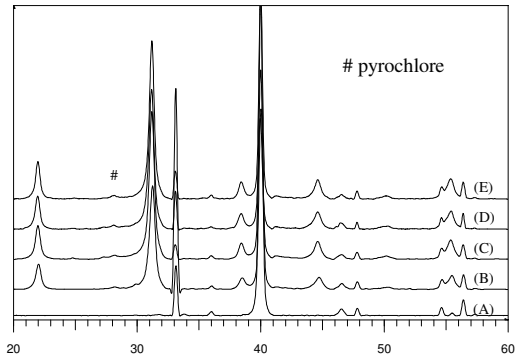
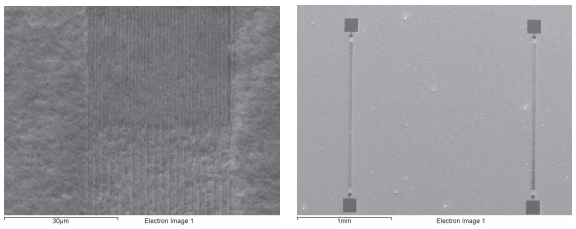


Fig. 1 The XRD patterns of PZT films annealed at different conditions: (A) Pt/Ti/SiO_2/Si substrate, (B)550°C/30 min, (C)550°C/1 hr, (D) 550°C/2 hr (E) 600°C/1 hr



(A) (B)

Fig. 2 SEM micrographs of (A) IDT electrodes (2000X) and (B) PZT SAW devices (50X)

Table 2 Performance of PZT SAW devices

Item	unit	value
Measured Center Frequency	GHz	2.30
Insertion Loss	dB	16.14
Measured Phase Velocity	m/s	4598

Fig. 3 shows the results applying these protein A-immobilized PZT SAW biosensors to the detection of human IgG biomolecules. It is clear from Fig. 3 that the human IgG detection limit for PZT SAW biosensors is 10^{-9} g/ml, which is two orders of magnitude more sensitive than that of QCM (10^{-7} g/ml) under the same immobilization and sensing conditions.

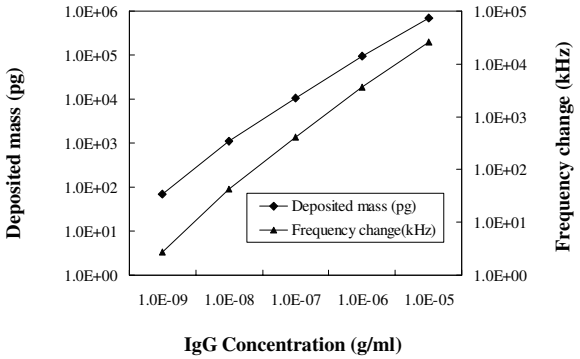


Fig. 3 Human IgG detection results of PZT SAW biosensors

4. Conclusion

PZT thick films and PZT SAW devices with sub-micron IDT electrodes were successfully fabricated by the micro-powder-sol-gel method. PZT thick films prepared from the precursor coating slurry solutions made from PZT micro-powders calcined at 550°C for 90 minutes have best electrical properties (ε_r=1889.355, Pr=29.3 μC/cm^2, Ec=32.4 kV/cm, d_{31}=-418.580 pC/N, d_{33}=916.681 pC/N at 1kHz) after being annealed at 600°C for 1 hour. The central frequency and the insertion loss of PZT SAW devices prepared from PZT films mentioned above are 2.30 GHz and 16.14 dB, respectively. When used for the actual detection of human IgG biomolecules, the detection of limit of PZT SAW biosensors is 10^{-9} g / ml and is better than that of the QCM (10^{-7} g/ml) under the same immobilization and sensing conditions.

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