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Improvement electrical properties of sol–gel derived lead zirconate titanate thick films for ultrasonic transducer application

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Abstract In this work, a fabrication process of piezoelectric PZT [$Pb(Zr_{0.52}Ti_{0.48})O_3$] thick films up to 60 μm deposited on silicon and aluminum substrates is reported. Crystalline spherical modified PZT powder about 300 nm in diameter was used as filler. PZT polymeric precursor produced by Chemat Inc. was used as the matrix material. Spinning films were annealed at 700 °C for one hour in the furnace in air. The thickness of the thick films was measured using a scanning electron microscope (SEM). Compared with previous piezoelectric PZT composite films, the modified piezoelectric thick films exhibit better dielectric properties. The dielectric constant is over 780 and dielectric loss is 0.04 at 1 KHz. Using a PiezoCAD model, the high frequency transducer was designed and fabricated. It showed a bandwidth of 75% at 40 MHz.

Introduction

High frequency ultrasound imaging has many clinical applications because of its improved image resolution. It is gaining acceptance as a clinical tool for the examination of the anterior segment of the eye, skin and intravascular imaging [1, 2]. Its development has pushed the limits of ultrasonic imaging technology, giving diagnostic quality information about microscopic structures in living tissue. One of the technical challenges for high frequency imaging is the fabrication of transducers with piezoelectric elements of a thickness of only a few tens of micrometers. It is very difficult and time consuming to lap down the ceramic to very thin elements and to dice very small elements in the fabrication of high frequency single element transducers and arrays. Piezoelectric thick film technology is an alternative solution with a low manufacture cost.

To data, there are a number of groups that have successfully fabricated PZT films using different technology. Tsuzuki et al. [3] prepared PLZT thick films by a multiple electrophoretic deposition and sintering process. Sayer et al. [4] have reported thick PZT ceramic coatings using acetic acid based sol–gel porous 0–3 composites. Cross et al. [5] prepared PZT thick films by a modified sol–gel process involving an acetic acid route. Milne et al. [6] also fabricated PZT thick films using titanium di-isopropoxide bi-acetylacetonate as a precursor material. In this work, fabrication of PZT composite thick films using a Chemat PZT polymer solution was investigated. The improvement dielectric properties of PZT thick films up to 60 μm are achieved. A single element high frequency transducer with backing and matching layers was fabricated.

Experimental procedure

Sol–gel precursor

The basic principle of the sol–gel process is that a metal organic solution contains the components of the

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oxide compound in an organic solvent. This solution was coated onto various substrates by spinning, dipping or spray coating. During the process, the solution is hydrolyzed to polymerize the solution and to form a metallorganic gel. Then the crystalline oxide films can be obtained by annealing at temperatures over 600 °C. For a conventional sol–gel process, the thickness of an individual layer is less than 200 nm. It is difficult to obtain thicker films using a conventional sol–gel process because residual stress within the multilayer leads to cracking [7].

The fabrication process of thick films in this work is based on a ceramic power/sol–gel solution composite method [8–12]. In this process, PZT polymeric precursor (PZT 9103, Chemat Technology Inc.) was used as the matrix instead of pure alkoxide PZT precursor derived from 2-methoxyethanol or acetic acid. The composition of precursor is $Pb(Zr_{0.52}Ti_{0.48})O_3$ near the morphotropic phase boundary, which has a high piezoelectric properties.

Fabrication of submicron PZT powder via mechanochemical milling process

The micron PZT powder was purchased from EDO Electro-Ceramic Products (EC-64 PZT). The average particle size is about 5 μm, the dielectric constant and piezoelectric coupling coefficient (k_t) are 1,300 and 0.50, respectively. EC-64 PZT powder (50 g) was milled with zirconia media (ZrO_2 beads, ϕ = 0.33 mm, 50 g) in the presence of IPA (isopropanol) solution (IPA 230 mL and dH_2O 20 mL), using a stainless steel twin-shell blender at room temperature for 24 h. A mixture of PZT powder with ZrO_2 beads was then washed by distilled water (dH_2O), the solution of PZT powder was dried in an oven at 100 °C overnight. The particle size of the grinded PZT powder is in the range of 220–430 nm. The average size is about 314 nm obtained by high-energy milling process (Fig. 1). It was seen that the particle size distribution is very uniform.

Processing of thick PZT films

Sol–gel PZT polymeric precursor was purchased from Chemat Technology Inc. with concentration of 0.8 M/L. The PZT composite solution was prepared by PZT ultrafine powder and previous PZT polymeric precursor, followed by ultrasonic dispersion for 30 min before depositing films. In order to prepare the homogeneity and crack-free films, the ratio of PZT powder with solution is very important [10]. For different ratios comparison of films, it was found that quantity of films is good with ratio of 15 g PZT ultrafine power and 100 mL PZT polymeric precursor. In this work, we fixed concentration of PZT solution purchased from Chemat Technology Inc., then try to choose 100 mL solution, and add different amounts of PZT powder to prepare the films. It is shown that the film's quality is good when PZT ultrafine powder is 15 g. The film is easy crack and more pores if concentration is higher. However, each layer of films is so thinner if concentration is slower.

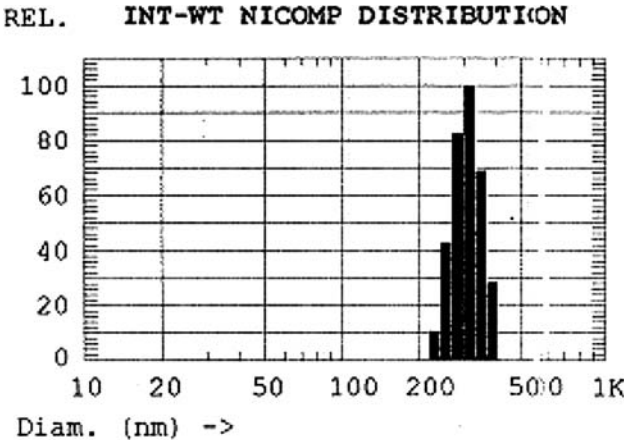

Fig. 1 Sub-micron PZT powder by high-energy milling

Preparation of films

Platinum coated silicon wafer (Pt/Si) purchased from Ramtron International Corporation was used as substrate. The PZT composite solution was deposited on Pt/Si substrate by spin-coating at 2,000 rpm for 30 s. After deposition, each layer was subjected to a two-stage pyrolysis sequence to drive out the solvent and decompose the organic compounds. This sequence consisted of a 2 min heat treatment at 150 °C followed by another at 400 °C (2 min). The amorphous layer was then crystallized to phase-pure perovskite at 700 °C for 1 h in a conventional box furnace. Each layer may grow to 2–5 μm in thickness. The spin-coating procedure was repeated in order to produce samples of desired thickness up to 60 μm. The process of sol–gel derived PZT composite films is shown in Fig. 2.

Characterization of films and devices

The structure of the films was examined using a Rigaku X-ray diffractometer (XRD) with Ni filtered CuK_{α} radiation. Patterns were recorded at a rate of 4°/min in

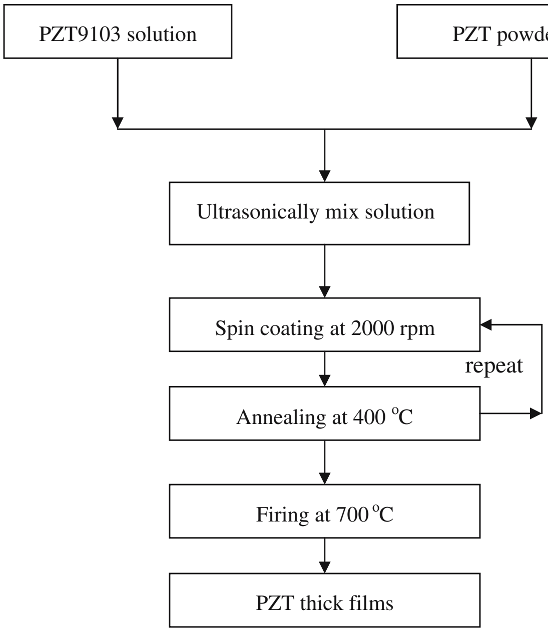

Fig. 2 Flow diagram for preparing a sol–gel derived composite films

the 2θ range of 20–60°. Film thickness and the morphology of the films were monitored using a scanning electron microscope (SEM; Hitachi, S-3500N, Tokyo, Japan). The particle size of the grinded PZT powder was examined using Nicomp Particle Size System. The dielectric permittivity and loss were measured using an impedance analyzer (HP4194A, Hewlett-Packard) with an oscillation amplitude of 30 mV. High field hysteresis properties were characterized using an RT6000 (Radiant Technology, Albuquerque, NM) ferroelectric test system with a voltage amplifier. The transducers were tested in a deionized water bath in pulse/echo mode by reflecting the signal off an X-cut quartz target placed at the focal point. For pulse/echo measurements, transducer excitation was achieved with a Panametrics (Waltham, MA) model 5900 PR pulser/receiver. The reflected waveforms were received and digitized by a 500-MHz LC534 Lecroy (Chestnut Ridge, NY) oscilloscope.

Results and discussions

Figure 3 shows an XRD pattern of a 3 μm PZT thick film deposited on Pt/silicon wafer. The film appears to be well-crystallized and one strong peak along (111) was observed. It was found to be the pure perovskite phase of the PZT film with some (111) orientation. It was likely that the crystallization and growth of the PZT thick film was significantly influenced by Pt (111) structure due to the close matching of lattice parameters. However, the film was more randomly oriented with increasing thicknesses. From the sintering test, there is not evidently difference to be observed for crystalline temperature after adding PZT ultrafine powder into the solution.

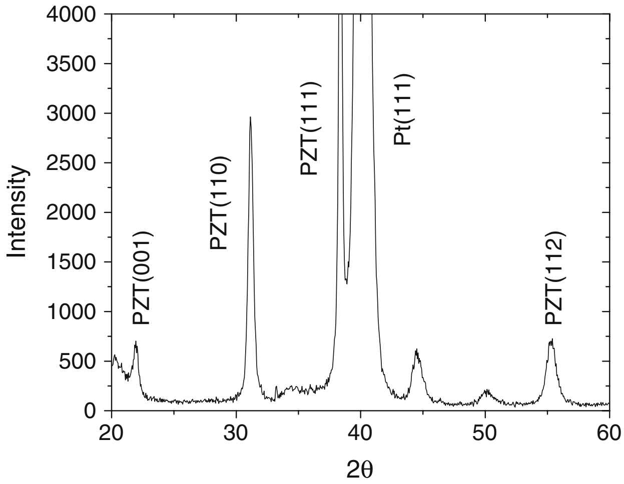

Fig. 3 The XRD pattern of a 3 μm PZT thick films deposited on Pt/silicon wafer

Figure 4a and b show SEM cross-sectional pictures of PZT thick films deposited on silicon and aluminum, respectively. The thickness was over 16 μm on the silicon substrate (Fig. 4a) and the grains consist of different particles, which come from the original PZT powder and the crystallization particles derived from the sol–gel solution. The agglomerated size is in the range of 200 nm to 0.5 μm. Figure 4b shows that thickness of the PZT thick film was about 60 μm on the aluminum substrate. In our previous work [10], we used PZT nano powder less than 100 nm to prepare films, but it is hard to get more thick films up to 20 μm. Comparing to this work, using a large particle such as 300 nm is benefit to obtain thicker films.

The dielectric permittivity (ε_r) and the dielectric loss (tanδ) were evaluated using an HP4192A impedance analyzer, shown in Fig. 5. It can be seen that ε_r and tanδ vary slightly with frequency from 1 kHz to 1 MHz. The values of ε_r and tanδ of the film at 1 kHz are 780 and 0.04, respectively. The value of ε_r for thick film was lower than that of 7 μm PZT thick films derived from a sol–gel process [7]. For pure sol–gel derived thick films, the films has high density, the dielectric constant is about 1,000, however, it is much higher than that of PZT composite films (300) derived from acetic acid because there are many holes in this films [8].

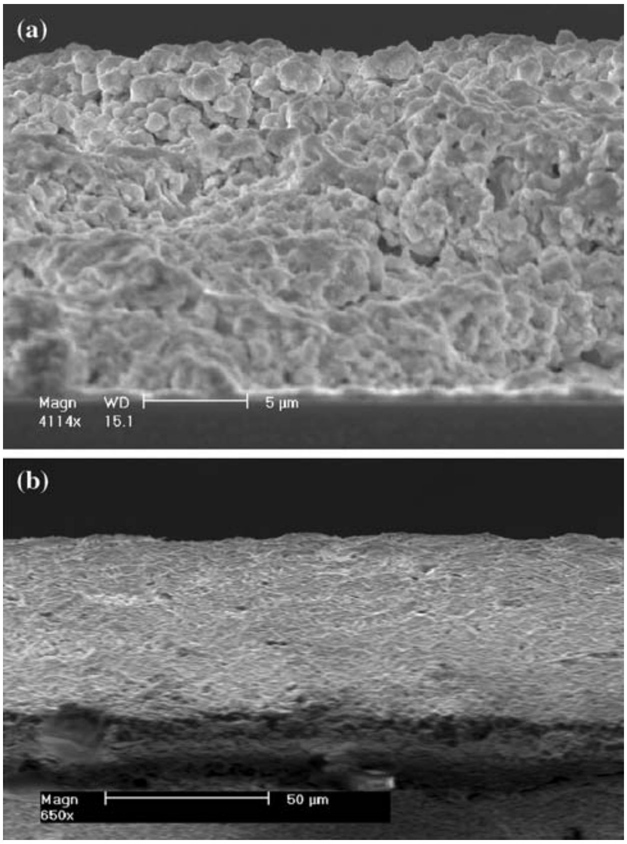

Fig. 4 SEM cross-sectional pictures of PZT thick films deposited on (**a**) silicon and (**b**) aluminum

The ferroelectric hysteresis loops of a 16 µm PZT thick film deposited on a Pt substrate are shown in Fig. 6. The remnant polarization (P_r) in the PZT thick film was about 11.5 μC/cm^2 for E_{max} = 130 kV/cm, the saturation polarization (P_s) was over 20 μC/cm^2 and the coercive field was about 30 kV/cm. The value of polarization is lower than that of pure PZT thick film, caused by some pores in the thick film. As we knew, for PZT bulk materials, the density is very high because it sintered at high temperature. The remnant polarization is about 35 μC/cm^2. For density PZT films with thickness of 7 µm, the remnant polarization is about 30 μC/cm^2. Comparing to values of polarization, it is lower than that of pure PZT thick film, caused by some pores in the thick film. However, it is better than derived from acetic acid [8]. For this kind of thick films, there may be one advantage, which is that only matching layer is needed to fabricate the transducer because of its lower acoustic impedance. Two match layers may be needed for fabricating the transducer with bulk PZT ceramics due to its high acoustic impedance.

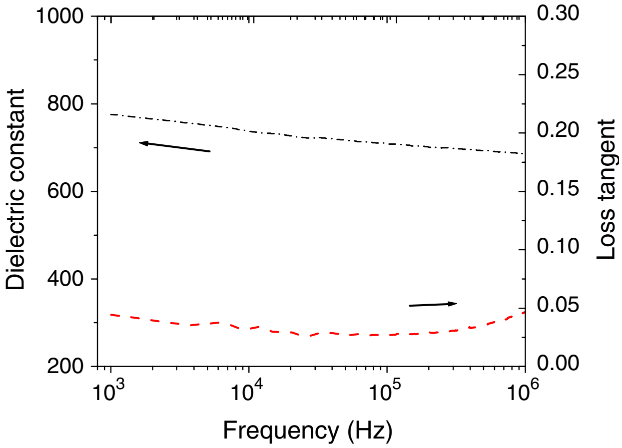

Fig. 5 Frequency dependence of the dielectric permittivity and loss of PZT thick films

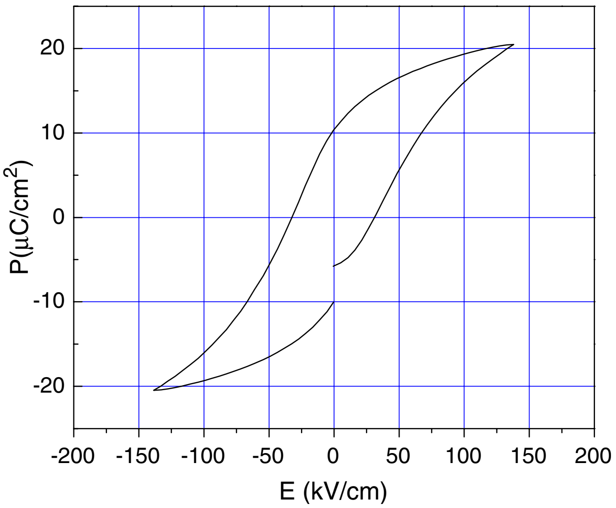

Fig. 6 Polarization–electric field hysteresis loop of PZT thick films

PZT thick film transducers were built using conventional technology and silicon etching. Firstly, a conductive epoxy (E-SOLDER 3022, Von Roll Isola Inc., New Haven, CT) was cast onto the housing as the backing material (5.92 Mrayl) and cured overnight. A lathe was used to turn down the backing layers to the desired diameter of 1.5 mm, matching the PZT electrode area. The electrical wire was inserted into the backing layer and fixed by a conductive epoxy. The acoustic stack was placed inside brass housing, and an insulating epoxy (301) was poured into the gap between the housing and the device. Then the film was glued to the backing layer, and the silicon was etched using a XeF_2 etching system. A thin layer of chrome/gold was then sputtered across the transducer as front face. The transducer was finished once parylene with acoustic impedance of 2.6 MRayl was

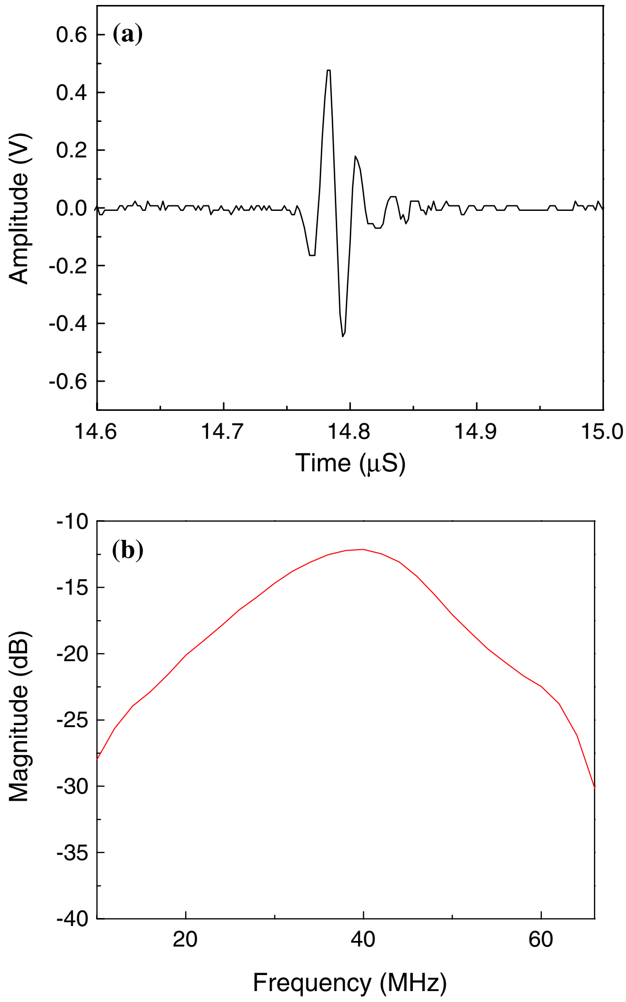

Fig. 7 Pulse echo response (**a**) and spectrum (**b**) of PZT thick film transducer

evaporated to cover the surface of the transducer as the acoustic matching layer. Figure 7 shows a pulse echo waveform (a) and the normalized frequency spectrum (b) of the PZT thick film transducer. The center frequency of the transducer was 40 MHz, the bandwidth at –6 dB was around 75%. These results suggest that this approach has the potential to fabricate broadband high frequency medical ultrasonic transducer.

Conclusions

PZT thick films up to 60 μm deposited on silicon and aluminum substrates have been successfully prepared using PZT ultrafine powders dispersed into Chemat PZT9103 Polymer. The dielectric constant is about 780 and dielectric loss is 0.04 at 1 KHz. The remanent polarization (P_r) in PZT thick films was about 11.5 μC/cm^2 for E_{max} = 130 kV/cm, the saturation polarization (P_s) was over 20 μC/cm^2 and the coercive field was about 30 kV/cm. Using one matching layer, a high frequency transducer (40 MHz) was fabricated with 75% broad bandwidth.

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