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Lift-off PMN-PT Thick Film for High Frequency Ultrasonic Biomicroscopy

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Abstract

Piezoelectric 0.65Pb(Mg_{1/3}Nb_{2/3})O₃-0.35PbTiO₃ (PMN-35PT) thick film with a thickness of approximately 12 μm has been deposited on the platinum buffered Si substrate via a sol-gel composite method. The separation of the film from the substrate was achieved using a wet chemical method. The lifted-off PMN-35PT thick film exhibited good dielectric and ferroelectric properties. At 1 kHz, the dielectric constant and the dielectric loss were 3,326 and 0.037, respectively, while the remnant polarization was 30.0 μC/cm². A high frequency single element acoustic transducer fabricated with this film showed a bandwidth at −6 dB of 63.6% at 110 MHz.

Keywords

lift-off; PMN-PT; thick film; high frequency transducer

1 Introduction

The desire to employ ultrasonic biomicroscopy (UBM) as clinical tool to examine the anterior segment of the eye, skin, and intravascular structures has driven the ultrasound frequency higher and higher, because the potential resolution of the ultrasound transducer increases with the operation frequency¹. It is quite a challenge to develop ultrasound transducers at operating frequencies greater than 100MHz due to the difficulty in the preparation of a reliable, low-cost, and sensitive piezoelectric layer with a thickness on order of only a few micrometers. Lapping down and mechanically machining traditional piezoelectric ceramics or piezoelectric crystals to the desired thickness are complicated and time-consuming. Additionally, the deterioration of piezoelectric ceramics at frequency (> 60MHz) and the brittle nature of the piezoelectric single crystals are also the obstacles in preventing these two kinds of materials being applied to the fabrication of high frequency (>100MHz) transducers. 1 Therefore, piezoelectric thick film technology is a viable

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alternative to solving this problem and simplifying the high frequency transducer fabrication process.

In our previous work, lead zirconate titanate (PZT) 2 and zinc oxide (ZnO) 3·4 thick films have been investigated for high frequency (>100MHz) ultrasound transducer applications. Compared to ZnO and PZT, lead magnesium niobium titanate (PMN-PT) has higher piezoelectric mechanical coupling coefficient and more desirable dielectric constant. Hence, PMN-PT thick films may be meritorious in building small aperture high frequency ultrasound transducers and arrays. The piezoelectric electromechanical coupling coefficient of the film is the most important parameter for the transducer design. In general, the higher the piezoelectric coefficient is, the higher the sensitivity of the transducer will be. The relative permittivity of the piezoelectric thick film, another crucial parameter, plays an important role in the electrical impedance matching of transducer to the electronic system because the electrical impedance of the piezoelectric element is inversely proportional to the relative permittivity of the piezoelectric material. With the miniaturization of the transducer, there has been a greater demand for piezoelectric thick films with high relative permittivity, especially for high frequency array applications.

Recently, Pyrochlore-free PMN-PT thick films have been successfully fabricated via a variety of methods, such as screen printing,^{5,6} electrophoretic deposition⁷ and tape casting.⁸ However, there has been no report on the application of PMN-PT thick films to high frequency ultrasound transducers. Therefore, an investigation on PMN-PT thick film high frequency ultrasound transducers was undertaken. The biggest problem to overcome in doing so is the removal of the substrate on which PMN-PT film is deposited, because the substrate which has low attenuation is in general not a suitable backing medium. During the fabrication process of PZT thick film high frequency ultrasound transducer, XeF₂ etching⁹ and rapid heating and cooling technology¹⁰, two effective routes, have been utilized to eliminate the effect of substrate. The former is suitable for the removal of silicon substrate but too expensive; the latter can be exploited to lift off piezoelectric thick film from the Ti substrate because of the very different coefficients of thermal expansion (CTE) between piezoelectric thick film and Ti substrate. Although, Luo et. al.⁸ has suggested a novel way to obtain free standing PMN-PT thick film with the thickness more than 20 μm, the technology is so complicated that it is difficult to prepare 10 μm free standing PMN-PT thick film which is needed for high frequency (>100MHz) ultrasound transducer application. Hence, in order to build high frequency (>100MHz) ultrasound transducers and arrays, it is necessary to find a simpler and more economical method to separate PMN-PT film of approximate 10 μm thickness from the substrate.

In this work, the deposition of approximately 12μm 0.65Pb(Mg_{1/3}Nb_{2/3})O₃-0.35PbTiO₃ (PMN-35PT) thick film on Pt/Ti/SiO₂/Si substrate using sol-gel composite method by spin-coating is reported. A wet chemical technology (alkali solution) which is much cheaper than XeF₂ etching will be introduced to remove the PMN-35PT thick films from Pt/Ti/SiO₂/Si substrate without any cracks in a larger area.

2 Experimental Procedure

The PMN-35PT precursor solution¹¹ was synthesized using lead acetate trihydrate (Pb(C₂H₃O₂)₃·3H₂O, Aldrich Chemical Co., Milwaukee, WI), magnesium ethoxide (Mg(OC₂H₅)₂, Aldrich Chemical Co.), niobium ethoxide (Nb(OC₂H₅)₅, Chemat Technology, Northridge, CA), titanium isopropoxide (Ti(OC₃H₇)₄, Aldrich Chemical Co.) and 2-methoxyethanol was used as the solvent. The PMN-35PT composite solution was prepared by ball milling of a mixture of PMN-35PT powder and sol-gel solution for 24 hours. The mass ratio of powder to solution was 1: 4. After deposition on Pt(111)/Ti/SiO₂/

Si(100) substrate at 3000 rpm for 30 s, each layer was subjected to a two-stage pyrolysis sequence to drive out the solvent and decompose organic compounds. A 1-min heat treatment at 250°C was followed by another at 400°C for 1 min. Each layer was then annealed at 650°C for 60s using rapid thermal annealing (RTA). This step was repeated to obtain the desired thickness. Finally, the PMN-35PT thick film thus obtained was sintered at 750°C for 1h at air atmosphere. After sputtering the gold as electrode and depositing E-solder 2022 as a backing material for transducer on top of the PMN-35PT film, the film was placed in the alkali solution with the mass concentration of 20% and the temperature of 80°C. Around 5 minutes later, PMN-35PT thick film with a backing material would separate from the platinum buffered Si substrate.

The particle size distribution in the PMN-35PT slurry was measured with a particle size distribution (PSD) analyzer (Particle Sizing Systems Inc., Santa Barbara, CA). The crystalline structure of the PMN-35PT film was examined using an x-ray diffractometer (D8 Advanced XRD, Bruker AXS, Germany) with Ni filtered Cu K α radiation. The morphology of the film was monitored by a scanning microscope (SEM; Hitachi, S-3500N, Tokyo, Japan). To characterize the electrical properties of the film, 1.5mm diameter circular Au-top electrodes were sputtered onto the film through a shadow mask. The dielectric and ferroelectric properties were measured using an impedance analyzer (HP4194A, Hewlett-Packard) and an RT6000 (Radiant Technology, Albuquerque, NM) ferroelectric test system, respectively. The transducer pulse-echo response was measured in de-ionized water bath at room temperature by reflecting the transmitted signal off a polished x-cut quartz target. A monocyclus function generator (AVB2-TC-C, Avtech Electrosystems Ltd., Canada) was used as the transmitter by applying a 100 MHz, 90 Vp.p., single-cycle sine wave. The reflected waveform received by the transducer was digitized by a 200 MHz oscilloscope (LC534, Lecroy Corp., Chestnut Ridge, NY).

3 Results and Discussions

As shown in Figure 1 (A), the average particle size of the PMN-35PT slurry after 24h milling was 150 nm. The photograph of separated PMN-35PT thick film and the Si substrate is shown in Figure 1(B), indicating that the removal of PMN-35PT thick film without any cracks in a large area from the Si substrate could be achieved.

Figure 2 shows an x-ray diffraction (XRD) pattern of the PZT thick film deposited on a Pt buffered silicon wafer. The film appeared to be in a well crystallized perovskite phase. No pyrochlore was detected by XRD analysis. A scanning electron microscope (SEM) cross-sectional micrograph of the film is shown in the inset. It can be seen that the PMN-PT thick film is highly dense and crack-free. The thickness is around 12 μ m.

The dielectric property of PMN-35PT thick film after removing the substrate is shown in Fig. 3. The relative permittivity (ϵ_r) and the dielectric loss ($\tan\delta$) vary slightly in the frequency range from 1 kHz to 1 MHz. The values of ϵ_r and $\tan\delta$ of the film at 1 kHz are 3,326 and 0.037, respectively. The relative permittivity of PMN-35PT films is similar to those results reported in other publications.⁵⁻⁸ It is worth noting that the relative permittivity of PMN-35PT thick film is much higher than that of PZT thick films,^{2,10} indicating that PMN-35PT thick films are promising candidates for high frequency array applications. The inset depicts the relative permittivity as a function of temperature for PMN-35PT thick film on the substrate at 1kHz. It is clear from the curve that the phase transition temperature is 170°C, in agreement with the T_c value in the literatures,^{5, 6} which has no impact on the performance of the device made of this PMN-35PT thick film at room temperature.

Figure 4 displays the polarization field dependence of PMN-35PT thick film after removing the substrate. It can be seen that the polarization (P_r) and the coercive field of the PMN-35PT thick film are $30.0 \mu\text{C}/\text{cm}^2$ and $100 \text{ kV}/\text{cm}$, respectively. The saturation polarization (P_s) is around $55.0 \mu\text{C}/\text{cm}^2$. The polarization of the film is comparable to those of the films reported in the literature,^{5–8} proving that the wet chemical method used to remove the platinum buffered Si substrate does not impair the polarization of the film.

PMN-35PT thick film single element transducer was built in a manner similar to that used for conventional ceramic and single-crystal materials¹² since the film had a backing layer. The transducer was finished after poling at 100°C for 5 min at 100V. A polymer parylene with acoustic impedance of 2.6 MRayl was evaporated on the transducer to cover the surface as the acoustic matching layer. A pulse echo waveform and the normalized frequency spectrum of the PMN-35PT thick film single element transducer are depicted in Fig. 5. With 30dB gain, the output voltage is 1.1V, while the central frequency is 110 MHz and bandwidth is 63.6% at -6dB .

4 Conclusions

In summary, via a sol-gel composite method, we have successfully fabricated high relative permittivity PMN-35PT thick films with a thickness of approximately $12 \mu\text{m}$ in a well-crystallized pyrochlore-free perovskite phase. A wet chemical method was introduced to remove the silicon substrate. The separated film exhibited good dielectric and ferroelectric properties. At 1 kHz, the relative permittivity and the dielectric loss were 3326 and 0.037, respectively. The remnant polarization was $30.0 \mu\text{C}/\text{cm}^2$ at room temperature. Using this PMN-35PT thick film, a high frequency single element transducer (110 MHz) with 63.6% bandwidth was fabricated. The result demonstrated that this type of PMN-PT thick film transducer (over 100 MHz) may be suitable for ultrasonic biomicroscopy application.

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Figure 1.
(A) Particle size distribution measured by PSD; (B) Photograph of separated PMN-35PT thick film.

Figure 2.
X-ray diffraction (XRD) pattern of the PMN-PT film. The inset: A scanning electron microscope (SEM) cross-sectional micrograph of the film

Figure 3. The dielectric properties of PMN-35PT thick film after removing the substrate. The inset: the temperature dependence of relative permittivity for PMN-35PT thick film on the substrate.

Figure 4.
The P-E loop of PMN-35PT thick film after removing the substrate

Figure 5.

A pulse echo waveform and the normalized frequency spectrum of the PMN-35PT thick film single element transducer