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Piezoelectric thick films and their application in MEMS

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Abstract

Piezoelectric thick films (up to 10 μm thick) and piezoelectric micromachined ultrasonic transducer (pMUT) have been successfully demonstrated at low temperatures of 650 °C using a composite thick film processing route. Submicron-sized PZT powder was dispersed into sol–gel solution to form homogeneous slurry for spin-coating on silicon substrate. Issues associated with recipe of the slurry, deposition process and sintering of films have been summarized with a view to optimizing the properties of the films and pMUTs. Typical microstructure, ferroelectric and piezoelectric properties of the composite films are given. Thermal stability of bottom electrode, a key issue about device fabrication, has also been investigated. The ultrasound-radiating performance of the pMUT element in response to a continuous alternating current driving voltage has been reported. The generated sound pressure level is 116.8 dB at 76.3 kHz at a measuring distance of 12 mm. The pMUT is suitable for application of airborne object recognition.

Keyword: Composite thick PZT films; Piezoelectric properties; Sol-gel processes

1. Introduction

Piezoelectric thick film integrated on silicon substrate has received considerable attention in recent years for potential applications in Micro Electro Mechanical Systems (MEMS) devices, such as sensors and actuators used in liquid, ultrasonic transducer for high frequency medical imaging, and so on. Since a few years, micromachined ultrasonic transducers (MUT) are investigated for phased arrays in high frequency acoustic imaging to overcome resolution and frequency limits of reticulated bulk $Pb(Zr_xTi_{1-x})O_3$ (PZT) transducers applied today.[1–5] The basic element consists of a micromachined diaphragm that is driven by either capacitive (cMUT)[3] or piezoelectric actuation (pMUT). Simulation result confirms that pMUTs are potentially suited for 10 MHz medical applications. For the Si substrate, to obtain a 3 MHz transducer for imaging in water, the optimal thickness would be 12 μm PZT on 18 μm Si.[4] However, it is a big challenge to prepare such a thick PZT films on silicon wafer. In a previous work, we presented a pMUT made of nanocomposites thick PZT film (up to 20 μm) on silicon.[6] Although, in the nanocomposite thick film process,[7] the use of the nano-sized powder is of great benefit to the uniformity and density of the PZT film, too small a grain size would be detrimental for the ferroelectric properties of the film.[8] We have to compromise between uniformity of the microstructure and the piezoelectric performances of the thick film. Therefore, in this article, the submicron-sized PZT powder was employed to prepare the slurry for spin-coating thick PZT films; properties of the composite thick films have been evaluated; and diaphragm coated with thus made PZT thick films has been studied for pMUT applications.

2. Preparation and characterization of PZT thick films

2.1. Microstructure and single layer thickness

The PZT slurry used for piezoelectric films deposition was fabricated by dispersing submicron-sized (100–300 nm) PZT powder (APC 850) into PZT sol–gel precursor solution (Zr/Ti = 53/47). The experimental details are the same as those of the nanocomposite thick film process described in our previous papers[6–9] except the size of the added PZT powder. It should be noted that the infiltration of powder-free sol into the composite film is increasingly important and efficient to increase the composite film density with increasing size of the added PZT powder. The commercial available PZT powder should be presintered at 1200–1300 °C to improve its crystallinity before

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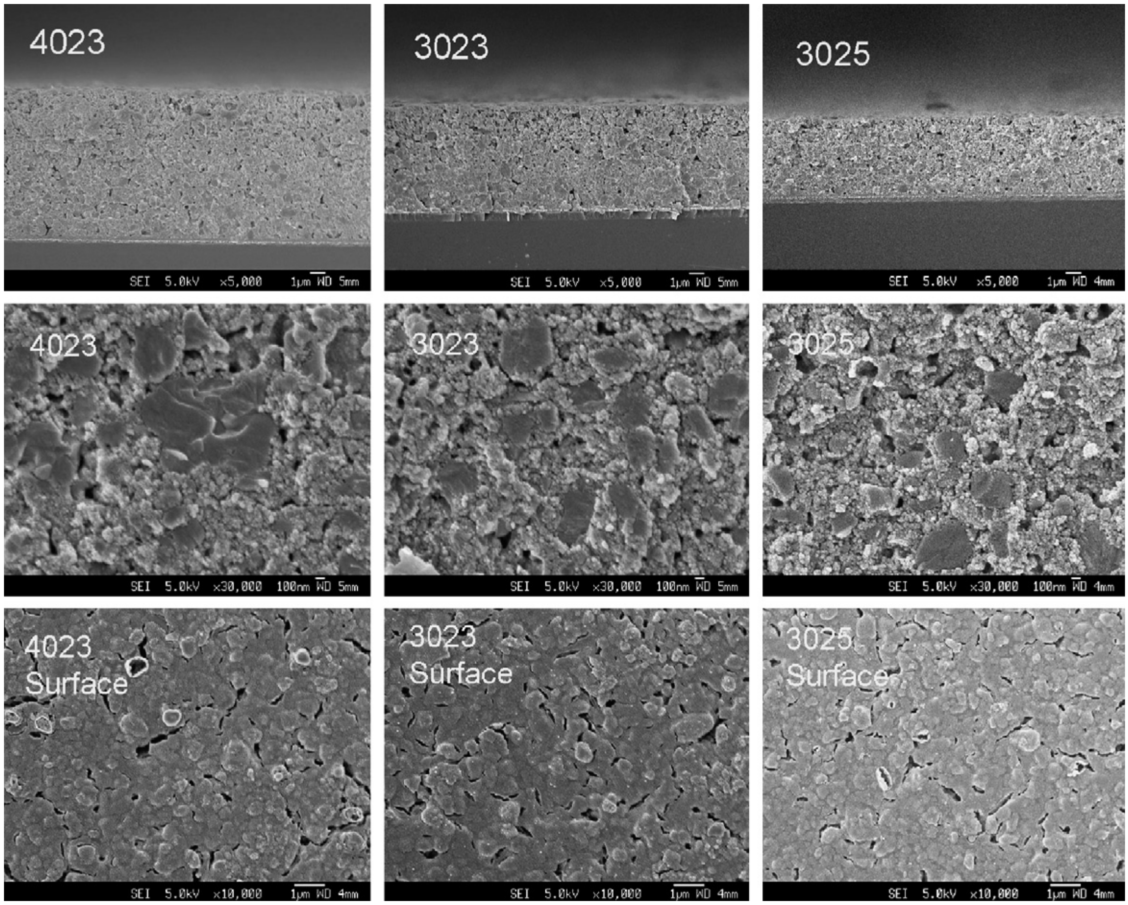

Fig. 1. Cross-section (fracture surface) and as-sintered surface images of the PZT films prepared using different slurry recipes. In micron scale, surfaces are smooth, thicknesses are even and the microstructures are uniform. Thicknesses of the films are 10.0 μm (4023), 7.1 μm (3023) and 5.1 μm (3025), respectively. In sub-micron scale, the added powder is surrounded by sol–gel derived nanograins. Micro-pores in the film and pinholes on the surface do not cause short circuit failure because they do not penetrate through the films.

being mixed with precursor solution to make slurry. This procedure is particularly important, especially when the composite films have to be annealed at temperature lower than 650 °C.

Recipe of the slurry, including the concentration of xerogel solution and powder to solution mass ratio, is a key issue in obtaining uniform, dense and crack-free thick films. Therefore, in this paper, we particularly investigated the effect of the recipe on the final properties of the films, including film thickness, uniformity of the microstructure and the other physical properties. To our convenience, the recipes of the slurry were named after four numbers with regard to above mentioned two important parameters. For example, 3025, the first two numbers represents the concentration of the xerogel solution[9] in weight percent, 30 wt%, and the last two numbers represents the mass ratio of the added PZT powder to xerogel solution, namely two to five. Based on the slurry recipe, we defined "solid phase content" (SPC), to describe the features of the slurry as follows:

$$\mathrm{SPC(wt\%)} = \frac{(p+i)}{(p+s)}$$

where p is the weight of the added PZT powder, s the weight of the precursor solution, and i is the weight of the inorganic component, i.e., the PZT crystalline phase, derived from the precursor solution after annealing, which is 62 wt% of the xerogel.[9] Thus, $i = 0.62cs$, where c is the concentration of the xerogel solution.

A batch of thick films was prepared by using slurry recipes with specially designed SPC. Two concentrations of the xerogel precursor solution (namely 30 and 40 wt%) and three ratios (2:3, 1:2 and 2:5) of the submicron-sized powder to precursor solution were compared. Fig. 1 shows cross section and surface images of three representative films taken by scanning electronic microscope. For all the films, spin-coating steps of the slurry were repeated nine times. A final annealing was carried out in furnace at 650 °C for 30 min. The film thickness can reach 10 μm within nine spin-coating steps with recipe 4023. It can be seen from Fig. 1 that, within the investigated range (from the thickest film 4023 to thinnest film 3025), the recipes of the slurry do not obviously affect the microstructure of the final film but have strong influence on the film thickness. In nanometer scale, typical microstructure of the film is that the added submicron-sized powder is uniformly distributed in the matrix nanograins derived from the sol–gel solution. Only the sol–gel grain is developed during the annealing and it is the developed sol–gel grains that combine the added powder together. Whereas, the shape

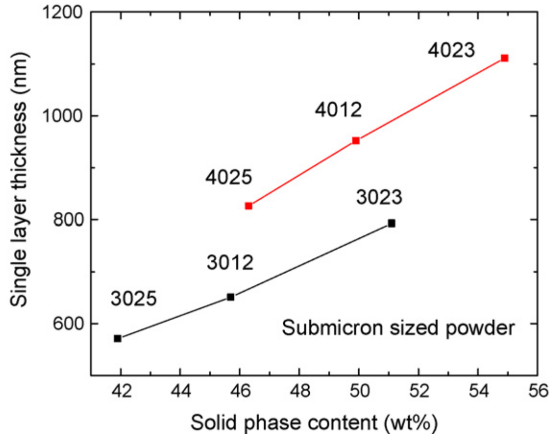

Fig. 2. Single coating thickness of the slurry derived thick composite films. Concentration of the xerogel solution and solid phase content have their respective influence on the thickness.

and size of the added powder does not change after annealing, this implies that neither grain growth nor sintering of the added powder occurs at the annealing temperature as low as 650 °C. Therefore, presintering the added powder at higher temperature is a key procedure to ensure the overall piezoelectric properties of the composite films. In micrometer scale, the films are uniform in spite of some distributed pores and pinholes, indicating that instead of using nano-sized powder in the slurry, mixing submicron-sized powder in the slurry can still obtain relatively dense and crack-free thick films within a relatively broad range of the slurry recipes. This flexibility much benefits the preparation of the slurry and the adjustment of the single layer thickness. Fig. 2 indicates that the single layer thickness is related to concentration of the xerogel solution and the SPC. Firstly, the thickness is mainly determined by the concentration of xerogel solution. The higher the concentration is, the thicker the single layer is. Secondly, while the concentration of the xerogel solution is fixed, the single layer thickness increases with increasing SPC of the slurry. Within the investigation range, the thickness versus SPC exhibits a near linear relation.

2.2. Characterization of film properties

The characterization results of the composite films, including P–E hysteresis curves, effective piezoelectric coefficient and leakage current density were summarized in Fig. 3. The P–E hysteresis loops of the composite films were measured using Precision Pro Ferroelectric Analyzer (Radiant Technology Inc.) with high voltage interface at 1 kHz. It can be seen from Fig. 3(a) that the average remanent polarization $(P_r-(-P_r))/2$ of the films were 20.0, 18.8 and 15.0 $\mu C/cm^2$ for the recipe of 4023, 3023 and 3025, respectively, much higher than that (around 5 $\mu C/cm^2$) of the films prepared with nanocomposite process.[6] This result reveals that using the submicron-sized PZT powder is truly an effective way to improve the remanent polarizations of the composite films. This is reasonable because too small a grain size in nanometer range does not allow the grain to split into domains. That is why the nanocrystalline thick films exhibit lower remanant polarization.

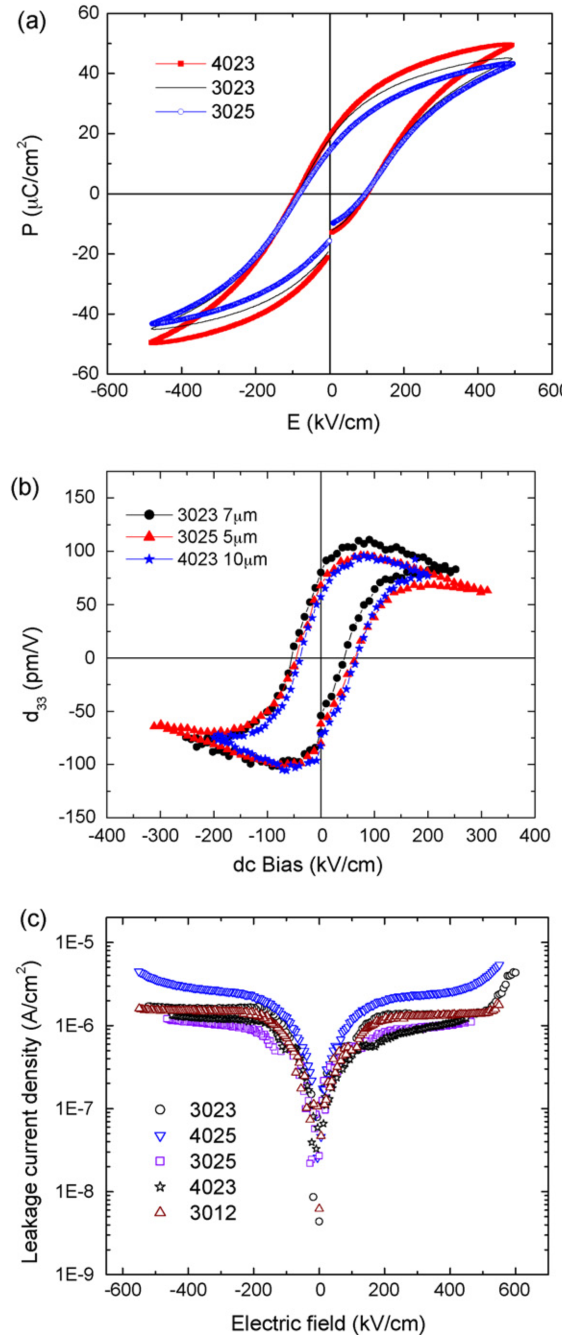

Fig. 3. Typical performances of the composite films with different slurry recipes finally annealed at 650 °C. (a) P–E hysteresis curves. (b) Effective longitudinal piezoelectric coefficient versus DC bias. (c) Leakage current density vs. electric field.

The relations between effective longitudinal piezoelectric coefficients (d_{33}) of the films and applied dc bias were measured with a home-developed scanning modulated interferometer.[10] A 12 V_{p-p} alternating current driving signal was applied on the film during measurement. Fig. 3(b) shows the effective d_{33} of the film at zero bias is around 75 pm/V, and the highest d_{33} values are around 120 pm/V without considering the clamping effect of the substrate. Note that the films were not poled before the measurement, which implies that the saturated d_{33} will be higher if the film is well poled. Again, the piezoelectric performances of these films are quite good compared with those of the nanocomposite films reported in our previous paper.[6] In that case, the d_{33} at 0 bias ranged from 20 to 30 pm/V, and the highest d_{33} at certain bias was around 80 pm/V for films sintered at between 650 and 800 °C. The improved piezoelectric properties of the composite film at lower annealing temperature are also attributed to the use of the presintered powders in the slurry.

The data presented in Fig. 3(c) are dependence of leakage current density on applied field of the films measured with Precision Pro Ferroelectric Analyzer. The mean leakage current density of the films is around 2×10^{-6} A/cm^2 and the breakdown field is higher than 500 kV/cm for all the investigated recipes. The data also indicate that the driving field of 200 kV/cm, i.e., 20 V/μm, is definitely safe for the composite thick film. Besides, the measured relative permittivity of the films ranges from 600 to 1000 at 1 kHz, and the dielectric loss is less than 0.02 within the investigated slurry recipe range. These dielectric properties are also quite acceptable for device application.

3. Buffer layer of bottom electrode

After the multiple coating steps, the PZT film together with its underlayer structure has to be sintered at relatively higher temperature. Pt/Ti/SiO_2/Si is usually adopted as the substrate of PZT films. Initially, we also used Ti as the buffer layer of bottom electrode Pt. However, after pMUT fabrication, we found that Pt/Ti bilayer cannot withstand a high sintering temperature. Blister occurs within the bottom electrode when the sintering temperature exceeds 700 °C. That is why we selected 650 °C as the final annealing temperature of the pMUT. Fig. 4(a and b) show the blisters within the Ti/Pt bottom electrode and a pMUT element. The picture of the pMUT was taken through the transparent SiO_2 and Si_3N_4 layers from the backside. In fact, better piezoelectric properties can be obtained by increasing the final annealing temperature.[6] Fig. 5 also gives evidence by comparing the grain size on the surface of the composite films final annealed at different temperature. Grains derived from the sol–gel phase develop much better at 700 °C than at 650 °C. As such, we tried to improve the heat resistance of the bottom electrode by changing the buffer layer.

TEM observation of the electrode interface, which is not shown here, reveals that the possible cause of the blisters can be attributed to the diffusion of the Ti and oxygen into the Pt layer and the formation of TiO_2 in the Pt grain boundaries during high temperature annealing in oxidizing atmosphere. High compressive stress within the TiO_2 layer results in the occurrence of the blister. Therefore, we attempted incorporating a well reacted TiO_2 layer instead of a pure metallic Ti layer as the adhesion layer to avoid the formation of the blister.

The TiO_2 buffered layer was deposited onto thermal-oxidized silicon wafer at 400 °C using RF magnetron sputtering. The 100 nm-thick TiO_2 layer is reactively sputtered from titanium target at 500 W and 1.8×10^{-3} mbar with an O_2/Ar ratio of 1:9. Pt layer is then sputtered at 200 W and 1.8×10^{-3} mbar in argon. Fig. 4(c and d) show a film cross-section and a square pMUT element with Pt/TiO_2 bottom electrode sintered at high temperature. The result reveals that Pt/TiO_2 combination significantly improves the heat resistance of the bottom electrode. By employing the Pt/TiO_2/SiO_2/Si substrate, the composite thick films can be finally sintered up to 800 °C without the occurrence of the

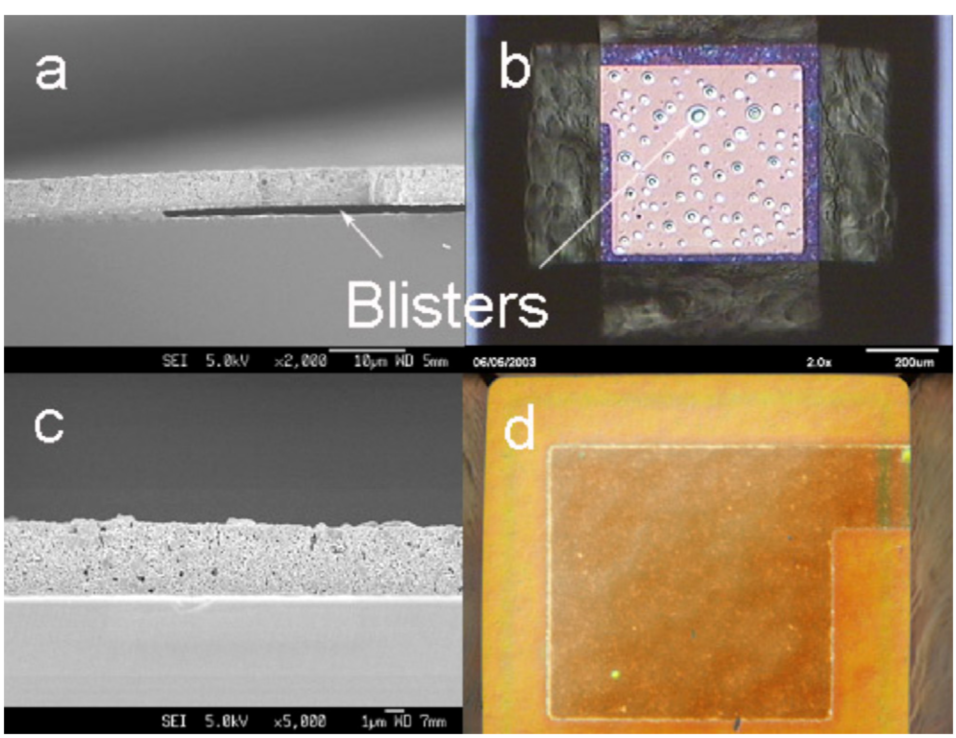

Fig. 4. (a) A blister occurs within Pt/Ti bottom electrode due to high annealing temperature at 700 °C. (b) Backside view of a pMUT element shows blisters within Pt/Ti bottom electrode after annealing at 700 °C. (c) Cross-section of a composite film on Pt/TiO_2 bottom electrode sintered at 800 °C. (d) Backside view of a pMUT element with Pt/TiO_2 bottom electrode. No blister occurs after the final annealing of PZT composite film at 750 °C.

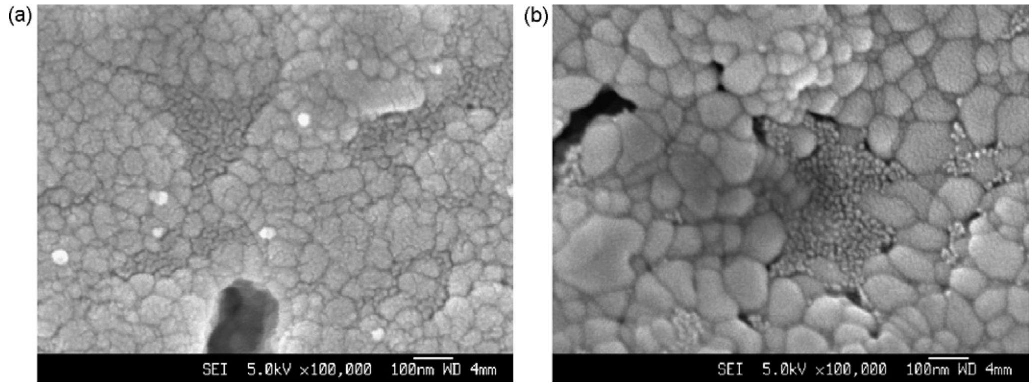

Fig. 5. As-sintered surface of the composite PZT films. (a) 3025 annealed at 650 °C for 30 min. (b) 4023 annealed at 700 °C for 30 min.

blister, which provides us a way to ensure a higher reliability of the device, or alternatively a possible way to improve the performance of the pMUT by increasing the annealing temperature.

4. Performances of pMUT

The individual pMUT element consists of a micromachined diaphragm embedded with a PZT film. The PZT film, sandwiched in between two electrode layers is poled in the thickness direction and the transverse mode of d_{31} is utilized to generate or receive ultrasound. Fig. 6 shows the fabricated pMUT arrays on a 4 in. wafer. The schematic structure and microfabrication issues of the pMUT have been described in our previous papers[6] in details. Therefore, we just report the performances of the newly fabricated pMUT with the improved composite films made of submicron-sized powder. The performances of a 1.5 mm × 1.5 mm pMUT element fabricated with PZT composite film 3025 are summarized in Fig. 7.

The properties of the pMUT as an actuator or micropositioner can be evaluated by quasistatic deflection in response to an applied AC driving voltage at very low frequency. As such, a 500 Hz, 30 V_{p-p} ac driving voltage superimposed on 20 V dc bias was applied to the pMUT, while the defection response of the pMUT diaphragm was measured with laser Doppler Vibrometer (Polytec). The 20 V dc bias is applied instead of poling of the film since the film was not poled before measurement. Fig. 7(a) shows a clear time dependence of the piezoelectric deflection responses at the centre of the diaphragm. The displacement response is 180° out of phase with respect to the driving voltage due to the positive dc bias. The peak to peak displacement amplitudes is 170 nm at 30 V_{p-p} driving voltage, i.e., 5.7 nm/V, indicating the piezoelectric property of film is not bad.

The properties of the pMUT as an ultrasound transmitter can be evaluated by output sound pressure level (SPL) at resonant frequency. The continuous ultrasound wave emitted by the

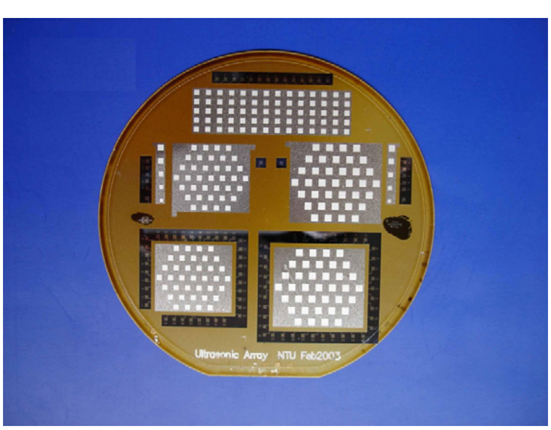

Fig. 6. PMUT arrays fabricated on a 4 in. silicon wafer.

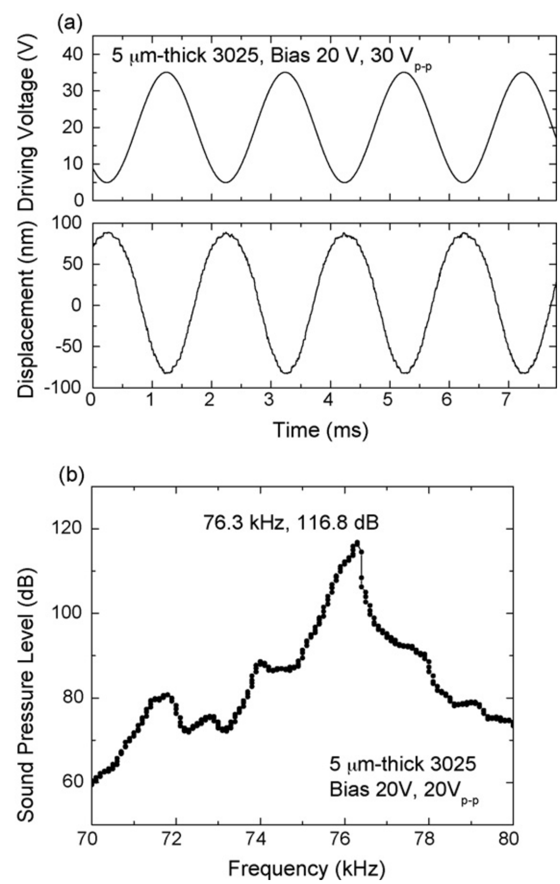

Fig. 7. Performances of a 1.5 mm × 1.5 mm pMUT element fabricated with PZT composite film 3025. Final annealing temperature is 650 °C. PZT layer is 5 μm-thick. (a) Quasistatic deflection at the centre of the diaphragm in response to an ac driving voltage at 500 Hz. (b) Frequency dependence of output sound pressure level.

pMUT is measured in air with Brüel and Kjær 2825 test system, including a 7521 signal analyzer interface module, 3016 input module, and 2670 microphone. The highest frequency of the system can reach 100 kHz. Fig. 7(b) shows the measured results on frequency dependence of the SPL. The distance between the transmitter and the microphone is 12 mm. The maximum SPL is 116.8 dB at 76.3 kHz. This SPL data is among the best results obtained from pMUT. The developed pMUT can be used as transducer for airborne object recognition and distance measurement.

5. Conclusion

Thick piezoelectric film pMUT has been demonstrated by combining silicon micromachining and the composite thick PZT film deposition technology. Preparing the slurry with submicron-sized PZT powder is an effective way to improve the remanent polarizations thus the piezoelectric coefficient of the composite film at the expense of the film density. The leakage current density and breakdown field of the film, however, are quite acceptable for MEMS device application in spite of relatively higher porosity of the film in comparison with nanocomposite film. The success of the fabrication of the pMUT mainly owes to the thick, crack-free and homogeneous composite thick film. Using a well reacted TiO_2 layer instead of a pure metallic Ti layer as the adhesion layer of the bottom electrode is an effective way to avoid the formation of the blister. The developed pMUT array has potential applications in ultrasound beam forming and beam steering, either at low ultrasonic frequency in air or high frequency in liquid medium or human body.

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