エアロゾル堆積法によるPZT厚膜

Lead Zirconate Titanate Thick Films Fabricated by the Aerosol Deposition Method

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要　旨

音速の加速微粒子を基板に衝突させ，粒子の運動エネルギーを粒子と基板及び粒子間の接合エネルギーに変換する成膜方法であるエアロゾル堆積法(ADM)を用いて，Si基板上にPZT圧電セラミックス厚膜(10μm以上)を作製した．下部電極にPt/Ir/Ta膜を用いて作製した積層アクチュエータ(形状：Siダイアフラム6mm×6mm×65μm，PZT膜：4.5mm×4.5mm×13μm)は，直流50V印加時に1.5μm，共振状態(周波数22.4kHz，振幅8V印加)で22μmなる極めて大きな変位を示す．この時のPZT厚膜の圧電係数(d_{31})は，バルク焼結体の約30%の値に相当する．

ABSTRACT

The lead zirconate titanate (PZT) thick films were fabricated by the aerosol deposition method (ADM), which is based on the impact phenomena of ultrafine particles on the substrate. The actuation properties of PZT on the Si membrane were investigated. For a 6 x 6 mm^2, 65-μm-thick Si membrane driven by a 4.5 x 4.5 mm^2, 13- μm-thick PZT layer, the deflections, which were 1.5 μm upon applying 50 V at non-resonance frequency and 22 μm upon applying 8 V at resonance frequency, were measured. The piezoelectric coefficient (d_{31}) of PZT thick film is approximately 30% of that of the bulk material.

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1. Introduction

For new micro electromechanical systems (MEMS), such as microactuators, micropumps, ink-jet printer heads, flapper-actuators for high density hard disk drive, ultrasonic devices and others, which need large strain and high speed response, it is necessary to produce dense piezoelectric films with thickness in the 1 to 50 µm range structured on a Si substrate.1) There are some reports of the fabrication of PZT (lead zirconate titanate) thick films by the sol-gel,2) sputtering3) or hydrothermal synthesis4) methods. However, PZT thick films produced by these methods usually have cracks, may easily peel from the substrates and fabrication takes a long process time. The etching of thick ceramics films by plasma etching5), inductively coupling plasma etching6), or reactive ion etching7) is also difficult. PZT thick films fabricated by the screen printing method8) have low density and PZT/Pt/Si structures can be damaged because of the long time of firing at temperatures higher than 800°C. Recently, the improvement of the screen printing method with the development of low-temperature sintering and a high-resistance electrode was demonstrated in ref. 9, but the piezoelectric properties of films derived by this method were not reported.

For bulk PZT adhered to the Si membrane, it is difficult to ensure sufficient mechanical and electrical coupling between films, and to avoid the complexity of assembling. Thus, we can conclude that the structuring of thick (over 10 µm) PZT films on Si-based substrates by conventional methods is difficult.

The principle of the aerosol deposition method (ADM)1), which is a variant of the gas deposition method (GDM)10) without vaporization of the material, is based on impact phenomena of ultrafine particles on the substrate. Submicron particles form an aerosol flow by mixing with carrier gas in an aerosol chamber. The aerosol flow is transported through the tube to a nozzle. This flow is accelerated and ejected from the nozzle into a deposition chamber. Ultrafine particles speed up to 300 m/s,11) bombard the substrate and form the film. The structuring12), ferroelectrical13) and piezoelectrical 14) properties, and microstructure15) of PZT thick films deposited by ADM have been previously reported. It is possible to form structures without etching. The density of such PZT thick films is more than 95% of bulk material. The temperature in ADM during deposition and annealing processes does not exceed 600°C. This low process temperature reduces the chemical reaction between PZT film and the substrate material, reducing damages of the structure.

In this paper, we reported on the results of PZT thick film on a Si membrane by AMD. The actuation properties of such a membrane as it relates to micropumps and micromixer fabrication are presented as well.

2. Experimental Procedure

The apparatus and details of our ADM deposition technique have been reported elsewhere.13)

The success of fabrication of a piezo on Si (POS) structure depends on many factors. The construction of a bottom electrode of the Si membrane is very important. This bottom electrode should: 1) have good adhesion force with the Si substrate and PZT during deposition, annealing and post treatment, and 2) function as an effective barrier layer for thermal diffusion between the PZT layer and the Si substrate. During deposition, some Si substrate damage take place.13) Thus, the bottom electrode should: 3) prevent damage to the Si membrane as well.

Taking into account the requirements mentioned above, to fabricate the bottom electrode Pt, Ir and Ta layers were sputtered on 525 µm-thick Si substrate using a DC-magnetron sputtering system. The sputtering conditions were as follows: sputtering gas Ar 100%, gas pressure 3.0 Pa, input power density 1.5 W/cm^2. The Si substrates' temperature during spattering was 460°C.

A square based (5x5 mm^2) PZT layer was deposited by ADM on this Pt/Ir/Ta/SiO_2/Si substrate at substrates temperature 550°C. The experimental parameters in ADM process are listed in Table I. The deposition rate of PZT film was 5-20 µm/min for an area of 5x5 mm^2. Sample was annealed at 600°C for 1 h in air. Next, to obtain a membrane with sufficient thickness, part of the Si layer was etched by the wet-etching process using a potassium hydroxide aqueous solution. The base of the membrane had squared shape and was 7x7 mm^2. The Au electrode was sputtered on the surface of the PZT thick film. The PZT thick film was poled by applying a 60 kV/cm electrical field at 250°C for 30 min. Next, the membrane was fixed at a metal base plate to eliminate any undesired vibrations.

Table I Process parameters

Pressure in deposition chamber	2 Torr
Size of nozzle orifice	5×0.3 mm2
Carrier gas	He
Consumption of carrier gas	2～6 l/min
Average size of PZT particles	0.3 μm
Substrate temperature	550 ℃
Annealing conditions	600℃×1h

The membrane displacements were measured by a laser Doppler interferometer (LV-1610 & LV-0120, Ono-Sokki Co) with resolution 0.01 μm and by a laser displacement sensor (LA-2420, Keyence Co.) with a resolution a 0.02 μm.

3. Results and Discussion

3-1 Formation of PZT layer on substrate

PZT thick films were successfully deposited on the platinum-coated Si substrate. A schematic and view of the POS structure are presented in Fig.1.

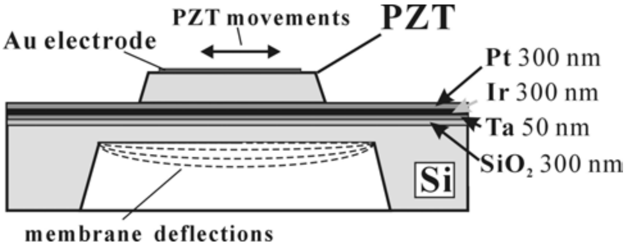

Fig.1 Schematic of the POS structure.

To ensure the good deposition of PZT on the Si substrate coated with Pt, a buffer Ir/Ta layer was introduced between Pt and Si. A 300-nm-thick Pt film was used as a bottom electrode. It provided good adhesion force with PZT thick films. The Ir layer (300 nm thick) was used as a thermal barrier layer during heat treatment to prevent any chemical reaction between PZT and Si. The Ta layer (50nm thick) ensured the adhesion between the Ir and SiO$_2$ layer (1 μm thick) which was brought about by the thermal oxidation of the Si substrate. When the bottom electrode consists of Pt/Ta layers, The PZT thick film has some defects, which result from the chemical reaction of the lead element and the Si substrate. This substrate structure (Pt/Ir/Ta/SiO$_2$/Si) ensures good adhesion during deposition and annealing. A total Pt/Ir/Ta layer thickness of more than 0.6 μm prevents damage to the Si substrate during the ADM deposition.

3-2 Actuation properties of POS structure

The polarization-electrical field (P–E) hysteresis loop for annealed 14-μm-thick PZT film is presented in Fig.2.

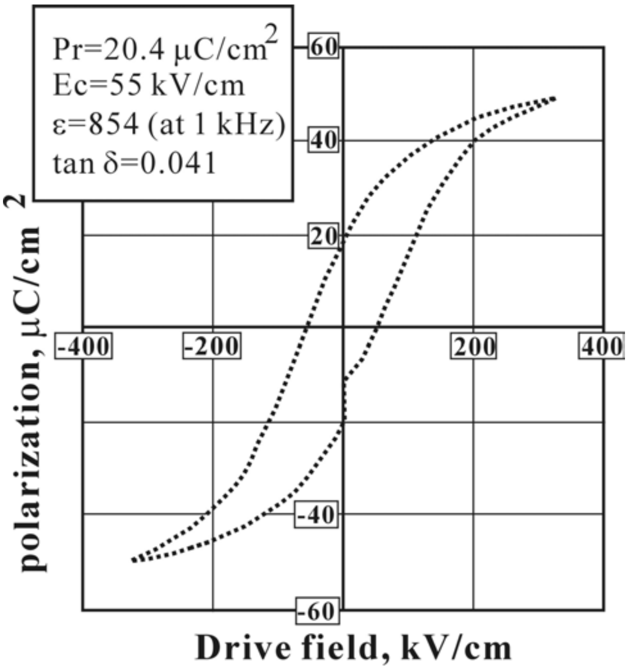

Fig.2 Hysteresis loops of 14-mm-thick PZT thick film on Pt/Ir/Ta/Si substrate after annealing at 600o C for 1 h.

If an electrical field is applied between the top (Au) and bottom (Pt) electrodes of the PZT thick film presented in Fig.1, the PZT will shrink or expend in the horizontal direction. This movement of PZT leads to the deflection of the Si membrane in vertical direction. The responses of central point of the 7x7 mm^2, 170-μm -Si membrane driven by the 5x5 mm^2, 40-μm-PZT layer with unipolar rectangular electric pulses at different driven frequencies are shown in Fig.3. The amplitude of membrane displacement of membrane is 1.6 µm applying 0−+100 V and is constant in the frequency range up to 1 kHz. There is no phase shift between the excitation pulse and the membrane response. The throw rate of the membrane is about 5 µs/µm and the deflection is proportional to the excitation impulse. The damped oscillation shown at the bottom signals in Fig.3 correspond to the resonance frequency of the membrane, 27 kHz. The decay time for the damped oscillation for this membrane is 0.35 ms.

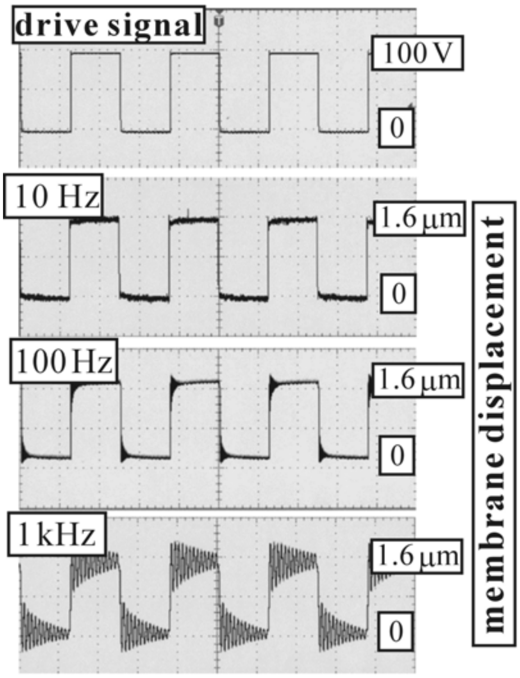

Fig.3 Dynamic response (without liquid) of 7x7 mm^2, 170-mm-thick Si membrane driven by 5x5 mm^2 , 40-mm-thick PZT thick film; displacements were measured at the central point.

To confirm the existence of good electrical and mechanical contacts among the PZT thick film, Pt electrode and Si membrane, measurements of the deflection from the PZT side and the Si side were carried out. If some peeling occurred inside the PZT/Si structure, the PZT thick film and the membrane will not move together in the same direction, and thus the values of the displacements measured from the PZT side and the Si side will be different and recording signals will probably have a phase shift different from 180°. In Fig.4, the deflections of a 7x7 mm^2, 100−µm−thick Si membrane driven by a 5x5 mm^2, 10 µm PZT layer are shown. The excitation signal (indicated as 1 in the Fig.4) was 0 − 50 V, 100 Hz. The recorded displacement signals measured from the PZT side (2) and the Si side (3) have a phase shift of exactly 180°, the shapes of the signals are the same and the amplitudes are 0.7 µm for both. This result shows that the PZT thick film does not peel from the substrate during deflections.

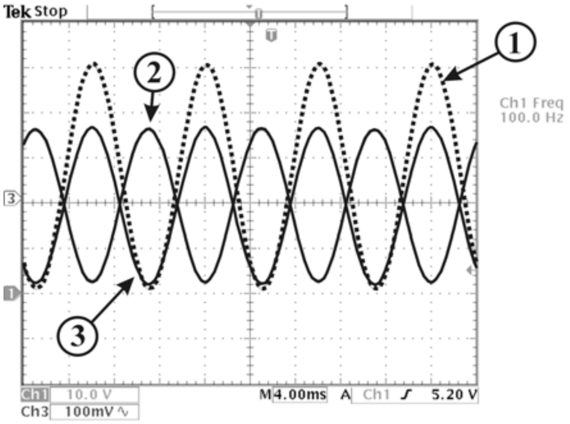

Fig.4 Deflection of 7x7 mm^2 , 100-mm-thick Si membrane driven by 10-mm-thick PZT layer (area 5 x 5 mm^2): 1) Sine wave drive signal 0-50 V, 100 Hz; 2) displacement measurement from PZT side; 3) displacement measurement from Si side.

To evaluate the dynamic response in the wider frequency and excitation voltage ranges, measurements were carried out using sine−wave driving signal. The results of this measurement for a 6.0 x6.0 mm^2, 65−µm −thick Si membrane driven by 4.5 x 4.5 mm^2, 13−µm−thick PZT thick film are presented in Fig.5. The amplitude of the deflection is proportional to applied voltage for the unipolar drive and is 1.5 µm when applying 0−52V at a nonresonance frequency of 1 Hz. The frequency dependence of the displacement for this membrane is presented in Fig.5(a). The phase shift between the excitation signal and the deflection was not observed up to 1 kHz. The decrease of the peak amplitude deflection in the frequency range from 0.01 Hz−10 kHz is less than 10%. The buckling of the membrane before the first resonance mode is shown in Fig.5(b). All membrane points are moving together in the same direction. The buckling shape is symmetrical and can be approximated to a cosine shape.

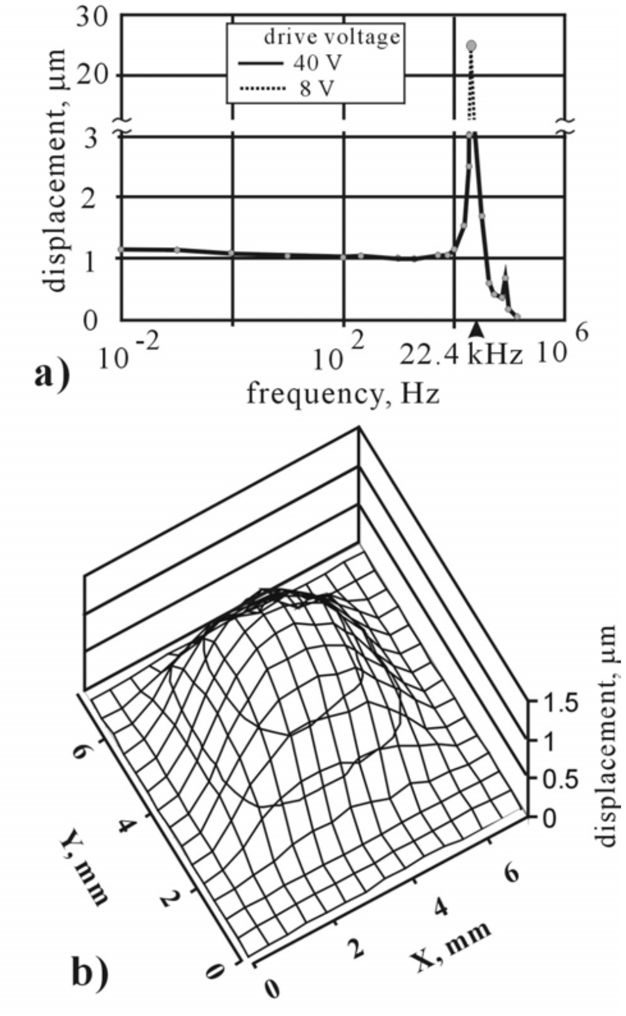

Fig.5 a):Frequency dependence (measured at 40 V) and b) buckling shape (measured at 52 V, 100 Hz) of Si membrane (thickness is 65 mm, area 6.0 x 6.0 mm^2) driven by PZT thick film (thickness is 13 mm, area is 4.5 mm x 4.5 mm^2).

The amplitude of the membranes deflection is about 1–2 μm driven by voltage of 50 V in a wide frequency range and the high response indicate the possibility of using ADM in the fabrication of micropumps and micromixers for liquids. The actuation properties of our membrane are compatible with those of the same scale micropump[16–18] and micromixer[18] based on the bulk PZT material. In refs. 16 and17, the micropump has a deflection at a center point 0.3–0.8μm applying 170 V at nonresonance frequency. In ref. 18, this deflection is 1.3 μm when applying 120 V, 870 Hz. Our membrane has a deflection 1.5 μm at 52 V in the frequency range 0.01 Hz–10 kHz. This deflection value is sufficient to successfully realize micropump and/or micromoxer device driving with low (around 50 V) voltage. The high deflection amplitude of about 20 μm in the membrane at the resonance frequency of 22.4 kHz by applying only 8 V (shown in Fig.5(a) indicates the good possibility of using the membrane for micromixers and other microactuators.

3-3 Comparison with simulation code

A piezoelectric analysis model is fitted for a mechanical analysis model of a finite-element method (FEM) computer simulation using the ANSYSS Rev. 5 code. As the initial input parameters, the geometrical dimensions of the POS structure, the driven electrical field and the piezomechanical coefficients (i.e., piezoelectric coefficients d_{ij}, mechanical compliance S_{ij} and Young's modulus Y_{11}) of the PZT-5A bulk sample were used (Table II).

Table II FEM simulation parameters.

PZT 5A	Symbol	Unit	
Electric permitivity	${}_{33}T/{}_{0}$	–	1700
	${}_{11}T/{}_{0}$	–	1730
Piezoelectric constant	d_{31}	10^{-12}m/V	−171
	d_{33}	10^{-12}m/V	374
	d_{15}	10^{-12}m/V	584
Elastic compliance	$S_{11}E$	10^{-12}m2/N	16.4
	$S_{12}E$	10^{-12}m2/N	−5.74
	$S_{13}E$	10^{-12}m2/N	−7.22
	$S_{33}E$	10^{-12}m2/N	18.8
	$S_{44}E$	10^{-12}m2/N	47.5
	$S_{66}E$	10^{-12}m2/N	44.3
Poisson's ratio	E	–	0.31
density		10^{3}kg/m^3	7.75
Silicon			
Young's modulus	Y	10^{10}N/m^2	19.6
Poisson's ratio		–	0.32
density		10^{3}kg/m^3	2.34

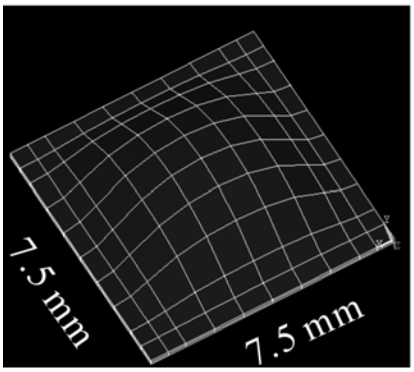

Fig.6 Calculation result by FEM code.

Figure 6 shows the simulation of membrane buckling. The calculated displacement value was higher than the measured value. It appears that the PZT thick film fabricated by ADM has a piezoelectric coefficient d_{31} about 30% of the bulk material and it has mechanical properties closed to that of the bulk material PZT-5A.

4. Conclusions

1) PZT thick film can be directly deposited on the structured Si membrane by ADM. 2) The deposited PZT thick film can drive a thick (over 60 μm) Si membrane with symmetrical buckling. 3) The deflection amplitude is constant over a wide frequency range. The optimization of the structure of the bottom electrode should be studied in the future. The results indicate a possibility of fabricating micropump and micromixers devices using ADM. The aerosol deposition method will become a promising method for the fabrication of ferroelectric-coupled Si microactuators.

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