Development of Deposition and Etching Technologies for Piezoelectric Elements for Ferroelectric MEMS

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1. Introduction

Recently, MEMS (Micro Electro Mechanical Systems) technology has been increasingly evolving and its applications have spread to inkjet printer heads, acceleration sensors, HDD head micro-actuators and other fields. A material with an excellent piezoelectric property, $Pb(Zr,Ti)O_3$(PZT), is actively studied for its application to MEMS as the material acting as a bridge between the mechanical and electrical actions. A piezoelectric element has a ferroelectric materials of several micrometers to several tens of micrometers, sandwiched by rare metal electrodes. Conventionally, these ferroelectric materials were formed by sintering and mechanical, chemical[1] and other types of processing. As the piezoelectric elements have become finer and more precise with the miniaturization of MEMS, the limits of applications of the technology have been pointed out. As a technique that replaces this conventional fabrication method, the adaptation of semiconductor processes using the thin-film PZT is actively being studied[2]. To fabricate high-quality piezoelectric elements, the improvement of the deposition and processing technologies for PZT, electrodes and other parts is essential.

We have studied and developed the manufacturing technologies for nonvolatile memories (FeRAM) using ferroelectric thin films for many years. Like piezoelectric elements, FeRAM has a thin-film ferroelectric thin films sandwiched by rare metal electrodes. The deposition methods for ferroelectric thin films for FeRAM and piezoelectric elements include the solution coating (sol-gel and MOD: Metal-Organic Decomposition) methods[3-5], the MOCVD (Metal-Organic Chemical Vapor Deposition) method and the Aero-sol Deposition method. There are reports that excellent PZT thin films have been fabricated using such methods. In contrast, we selected the sputtering method[6-9] due to its superiority in many points, and have developed the mass production technologies. Anticipating the future demands for finer piezoelectric elements, we have developed the dry etching technology as a processing technology that provides excellent shape controllability[10]. This paper introduces the results of our development of sputtering and etching mass production technologies demanded in fabrication of piezoelectric elements.

2. Issues of sputtering technologies for ferroelectric thin films

For the mass production of piezoelectric elements, the following are important issues for development of ferroelectric PZT sputtering technologies:

① Throughput - Realization of high deposition rate

Ferroelectric sputtering has a substantially lower deposition rate than other processes, such as electrode film deposition, and limits the throughput. There are two methods for improving the throughput; higher deposition rate and thinner films. The latter often degrades the film characteristics, so higher deposition rate is more likely to improve the throughput.

② Control of film composition

The film composition determines other film qualities (composition, crystal structure and electric properties). PZT contains the volatile constituent (Pb) and is sensitive to the temperature and the plasma conditions, and is easy to fluctuate. The control of film composition is the basis of the process.

③ Uniformity on large-diameter substrates

The use of large substrates of 6 to 8 inches in diameter is essential for mass production. Needless to say, the uniformity of film thickness and film quality holds the key to mass production.

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④ Process stability and reliability

For the insulation sputtering using ceramic targets, there are more concerns about the stability and reliability of the process, compared to Al, Ti and other metallic materials. There are possibilities that the film composition deteriorates with time.

⑤ Measures against particles

The characteristics of ceramic targets and insulation thin films increase the mechanical factors that cause particles (such as adhesion and heat expansion) as well as the electric factors (such as dielectric breakdown due to charge-up), making it more difficult to take countermeasures against particles.

3. Ferroelectric sputtering systems and processes for mass production

3.1 Sputtering systems for mass production

As a deposition system for PZT piezoelectric films for MEMS, we use the SME-200 (Electronics Equipment Division), which is a multi-chamber mass production sputtering system equipped with a special module for ferroelectric sputtering that supports high-temperature deposition. This system features excellent basic performance, including easy maintenance, short exhausting time and short downtime, and also has the following features:

(1) ϕ300 mm targets can be loaded and ϕ200 mm large-diameter substrates can be processed in the process chambers. The single ceramic target is used for deposition of the PZT films.

(2) The process chambers, including the heating chamber, have a modular structure to make the processes flexible. The system currently supports the sputtering deposition of base electrodes (for example, Ti, Pt and Ir), the sputtering deposition of ferroelectric materials and the in-situ processing of top electrodes (for example, Pt and Ir) as the standard processes.

(3) The temperature can be controlled accurately and quickly in a wide range from low to high temperatures by using the electrostatic chuck type hot plate or the high uniform SiC hot plate as the substrate heating mechanism.

(4) Measures against noise due to RF leakage are taken for the RF magnetron sputtering chamber for ferroelectric film deposition.

3.2 Ferroelectric film sputtering technique

In the PZT sputtering for MEMS, the PZT film can be as thick as 10 μm. Therefore, it is necessary to control the crystallization and the warpage of the substrate, and thus it is necessary to control the film stress. We adopt the high-temperature deposition method in which the substrate temperature is heated to about 500 to 600℃ during the deposition. The high-temperature deposition method features high-rate deposition, film composition control and higher stability of the sputtering process as described below.

3.2.1 Relationship between the sputtering target and the deposition rate

As shown in Figure 1, when the target density increases from 70% to 95%, the sputtering rate at 1.5 kW increases from 35 nm/min to 48 nm/min. The target with a density of 95% has cleared the problem of damage to the target due to the high power input that occurred on the target with a density of 70%. In addition, by using a backing plate that has an enhanced cooling effect, the increased sputtering efficiency and high-power input realized even higher deposition rate.

3.2.2 Film composition control and measures against deterioration with time

The important thing in PZT deposition is the control of the amount of Pb in the film. There are many factors that affect the amount of Pb in the film. We conducted research on the influences of typical sputtering condi-

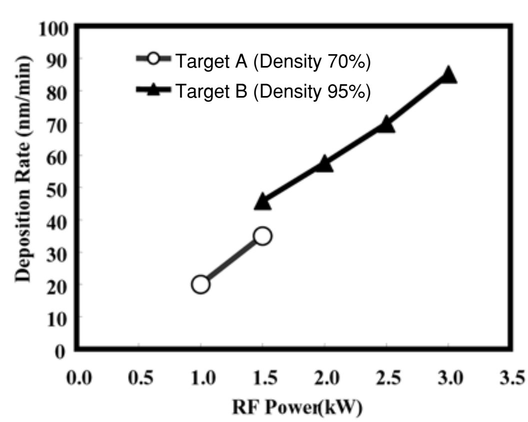

Figure 1 Relationship between the target density and the deposition rate

tions (the power and the Ar gas pressure) and the substrate potential, and found that the amount of Pb in the film is affected by the RF power and the Ar gas pressure as shown in Figure 2, and the amount of Pb can be controlled dynamically and precisely by combining these conditions. As shown in Figures 3 and 4, the control of substrate potential is also effective for the control of the amount of Pb. If it is impossible to largely change the sputtering conditions, this method can be used for the film composition control, and this is very meaningful in terms of process margin.

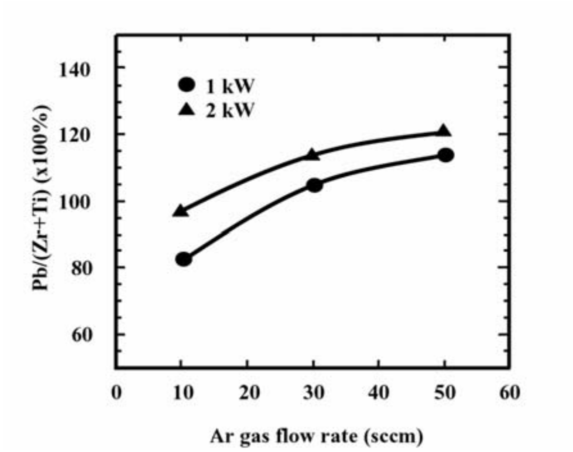

Figure 2 Dependency of the lead composition ratio on the argon flow rate and the sputtering power

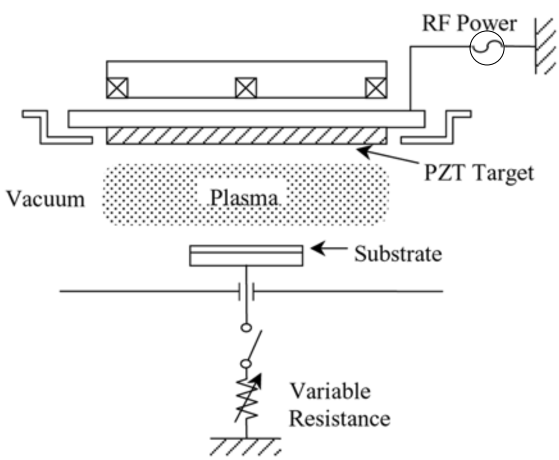

Figure 3 Substrate impedance variable mechanism

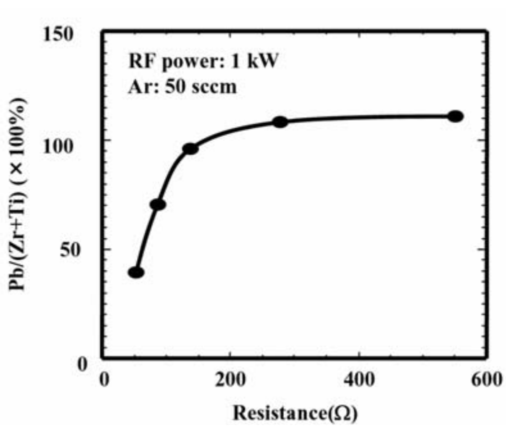

Figure 4 Relationship between the lead composition ratio in the film and the substrate impedance

3.3 Fabrication of the PZT films for MEMS and their properties

This section describes the properties of the PZT films deposited by using the high-temperature deposition method. We used ϕ 6-inch silicon substrates (100) with a thickness of 625 μm and with a 100-nm thermally-oxidized layer, and used Ti for the adhesion layer and Pt for the bottom electrode. Pt was preferentially crystallized to (111) orientation. The PZT film was deposited over it for evaluation of the film properties. Figures 5 and 6

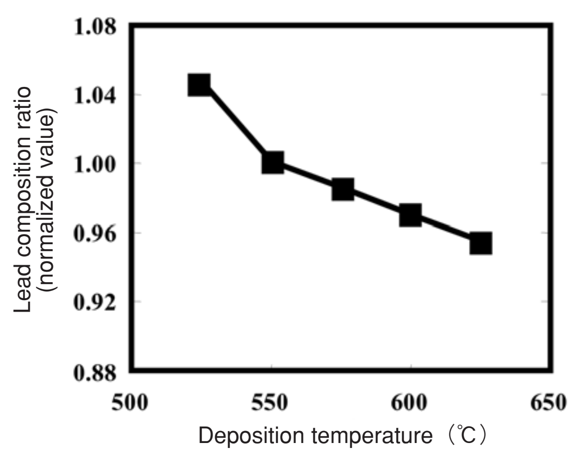

Figure 5 Dependency of the lead composition ratio on the deposition temperature

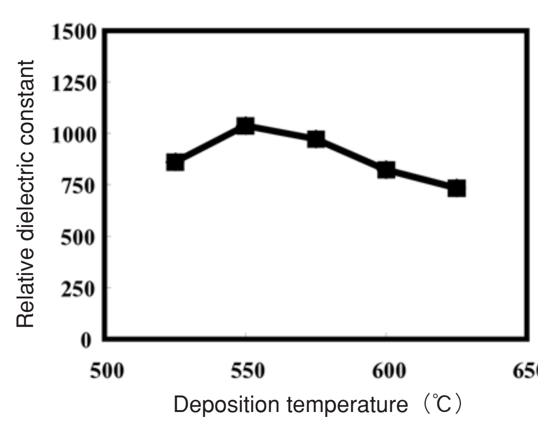

Figure 6 Dependency of the relative dielectric constant on the deposition temperature

show the values of the lead composition ratio in the film and the relative dielectric constant when the deposition temperature was changed from 525 to 625℃. The lead composition ratio in the film decreases sharply as the film deposition temperature rises. The relative dielectric constant reaches the maximum value at the deposition temperature of 550℃, and tends to decrease at 575℃ or higher. This is probably because the temperature of 525℃ was insufficient for crystal growth and the highly volatile material, lead, vaporized without being taken into the PZT crystal at 575℃ or higher. It is considered that the relative dielectric constant decreased because the metastable pyrochlore phase was formed due to the decrease of the lead composition ratio in the film. This way, the film quality of the PZT film greatly depends on the deposition temperature. Therefore, the deposition temperature must be controlled strictly in the high-temperature PZT deposition. Figure 7 shows the X-ray diffraction pattern of the PZT film deposited at 550℃ at which the relative dielectric constant reached the peak. It is shown that the PZT film is preferentially crystallized to (001)/(100) orientation on Pt(111) and there is no pyrochlore phase in PZT film.

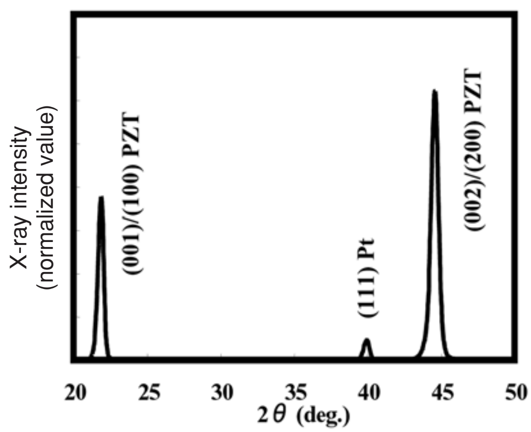

Figure 7　X-ray diffraction pattern of the PZT film

To evaluate the piezoelectric properties, we made a cantilever with a length of 28 mm and a width of 4 mm and measured the displacement with a laser Doppler vibrometer when the AC voltage was applied across the top and bottom electrodes. As a piezoelectric property, Figure 8 shows the displacement at the end of the cantilever when a voltage of 30 V (peak-to-peak) with a frequency of 250 Hz was applied. A negative bias voltage was applied at the same time for measurement. Figure 9 is a graphic representation of the displacement at the end of the cantilever when the applied voltage was changed from 0 V to 30 V. As the applied voltage increased, the displacement at the end of the cantilever increased linearly, and a large displacement of 7.8 μm was obtained when 30 V was applied. From this displacement, we estimated the piezoelectric constant $e_{31} = -7.8$ C/m^2 (the piezoelectric constant d_{31} is about -130 pm/V assuming that Young's modulus of the PZT film is 60 GPa). This indicates that the sputtered PZT film functions as a satisfactory piezoelectric film.

These results indicate that the PZT film is very sensitive to the process conditions and the stability of the

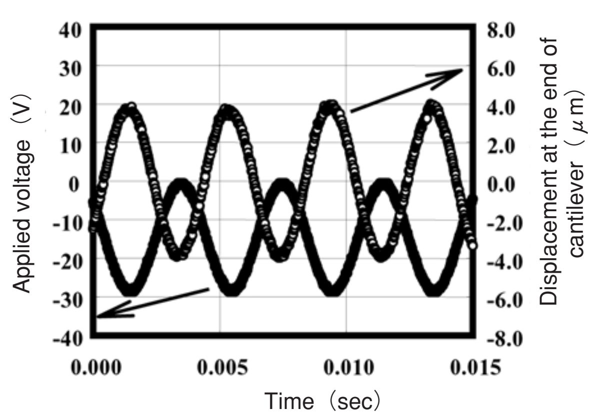

Figure 8　Cantilever piezoelectric vibration property (when 250 Hz is applied.)

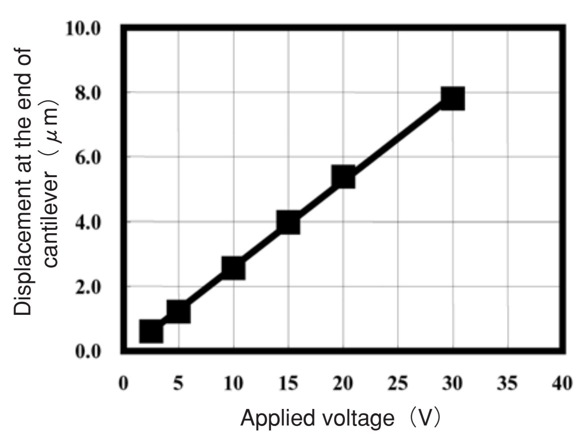

Figure 9　Dependency of the displacement at the end of cantilever on the applied voltage

process is very important. Figure 10 shows the changes in the deposition rate, the lead composition ratio and the relative dielectric constant when 35 layers of PZT film with a thickness of 3 μm were continuously deposited (the accumulated film thickness is 105 μm). It is shown that the deposition rate remains almost the same in the continuous processing and the fluctuation of the lead composition ratio in the film sensitive to the heating process is within ±1%, indicating that the PZT film can be formed stably. In addition to the deposition rate and the lead composition ratio in the film, the relative dielectric constant of the PZT film is very stable. These results proved that this system provides a high reproducibility as the mass production equipment.

4. Issues of ferroelectric etching technology

Conventionally, piezoelectric elements have been

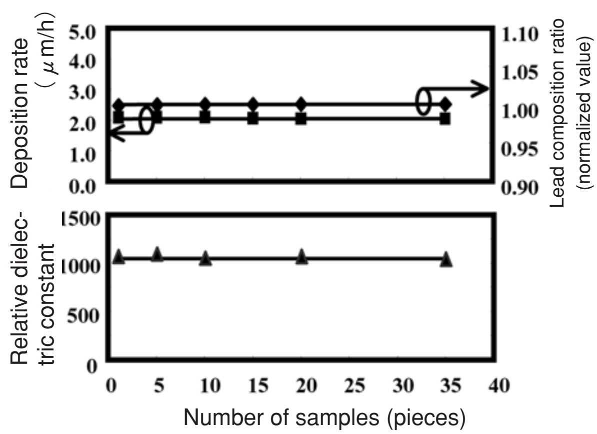

Figure 10 Stability of properties in the continuous deposition (The deposition temperature is 550℃ and the PZT film thickness is 3 mm.)

processed mainly by chemical wet etching or argon milling. With the miniaturization of MEMS, there have been increasing demands for dry etching with the excellent shape controllability. The Pt, Ir and other rare metal electrodes and the PZT ferroelectric thin films that compose piezoelectric elements react poorly with halogen gases and their halides have low vapor pressures. For these reasons, these materials are called hard-to-etch materials. The following technical issues are important for dry etching of the PZT ferroelectric thin films:

① Etching selectivity to resist mask and the bottom rare metal electrode

A piezoelectric element film consists of PZT with a thickness of several micrometers and the rare metal electrodes with a thickness of about 100 nm. Generally, the bottom electrode is left after the PZT etching. Therefore, a low etching rate for the bottom electrode, the so-called high etching selectivity, is important as a PZT etching condition.

② Adhesion of conductive deposit to the pattern sidewalls and damage to PZT

The materials are hard to etch, and their etching products easily adhere to the pattern sidewalls, and result in leaks between the top and bottom electrodes. What is worse, the pattern sidewalls are exposed to reactive gas plasma during etching, and tend to suffer lead and oxygen coming out and other damages.

③ Plasma stability during continuous processing

Adhesion of etching products to chamber walls, especially the RF introduction window that generates plasma, causes alteration of plasma and deteriorates the etching rate and the shape reproducibility. Avoiding of adhesion of etching products to chamber walls is impor-

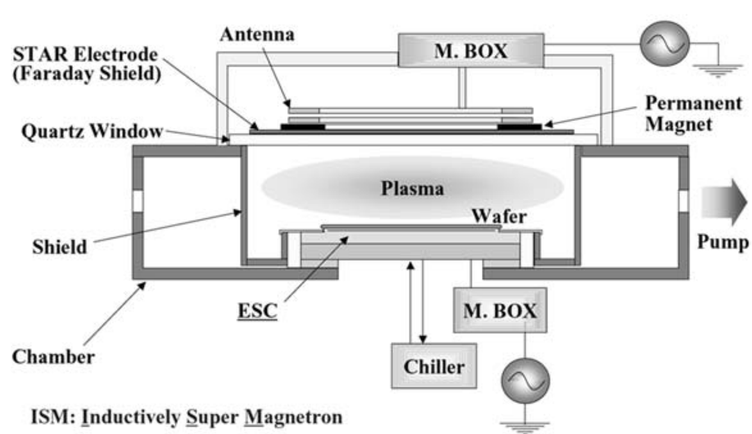

Figure 11 Ferroelectric etching system equipped with ISM plasma source

tant for mass production.

④ Uniformity of etching rate within wafer

As in the case of ①, to stop the thick PZT at the thin bottom electrode after etching, the uniformity of etching rate within wafer is important.

5. Ferroelectric etching systems and process for mass production

5.1 Ferroelectric etching systems

As the piezoelectric PZT etching systems, we use the etching systems (NE series) made by the Semiconductor Equipment Division 2. We meet diversified user needs, with a lineup of NE series products, ranging from the NE-550 for R&D to the NE-7800 of multi-chamber type for mass production. The etching module is equipped with the ISM (Inductively Super Magnetron) plasma source that can generate low-pressure and high-density plasma. Figure 11 shows a drawing of the etching module. Table 1 shows the comparison between the normal ICP type plasma source and the ISM plasma source. The RF antenna is mounted in the upper part of the etching chamber, so that RF is introduced through the quartz window into the etching chamber to generate plasma. The uniformity of the etching rate within wafer can be easily optimized by positioning permanent magnets under the antenna. A STAR electrode is provided between the antenna and the quartz window to control adhesion of etching products to the quartz window by applying RF to the STAR electrode. The substrate is held on the electrostatic chuck. The substrate temperature is controlled by introducing He to the back side of the substrate. The ion energy is controlled by applying RF power to the substrate. The materials to be etched are nonvolatile, and the etching products adhere to the shield located in the chamber. The temperature of the shield is kept constant by heater, so process is high stability.

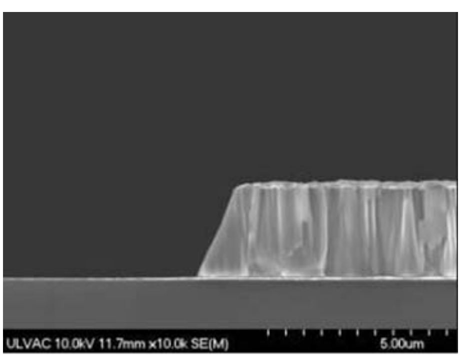

Figure 12 SEM image of the piezoelectric element after etching and resist removal

5.2 Ferroelectric etching process

Figure 12 shows a SEM image after the piezoelectric element was etched and the resist mask was removed. The film composition is Pt/PZT/Pt=100 nm/3 μm/100 nm, and the top Pt electrode and PZT were continuously etched by using a 5-μm photo resist as a mask. We used chlorine and fluorine mixed gases for PZT etching. The etching shape (taper angle) is about 65°, and nothing adhered to the pattern sidewalls. Despite 20% of over etching, the bottom Pt electrode was hardly etched. This indicates that a high etchig selectivity to Pt was achieved. Figure 13 shows the dependency of the etching rate and the taper angle on the bias power. As the bias power increases, the etching rate increases linearly. When 400 W was applied, the PZT etching rate of 190 nm/min was achieved. The taper angle also increased gradually as the bias power increased.

Table 1 Comparison of plasma properties between ISM and ICP

	ISM	ICP
Plasma Density (cm^{-3})	$1\times10^{10}\sim1\times10^{11}$	$5\times10^{9}\sim5\times10^{10}$
Operating Pressure (Pa)	$0.07<P<7$	$0.5<P<50$
Uniformity	Optimized Magnetic Layout	Determined by Chamber Structure
Damage	Plasma Density and Substrate Bias can be Controlled independently.	
Repeatability, Stability	Low Pressure Etching formulates less re-deposition→Better Repeatability.	High process pressure causes re-deposition.
Maintenance	Chamber Structure is Simple for easy maintenance.	

6. Piezoelectric element fabrication technology

By using the aforementioned deposition and etching technologies, we made a prototype piezoelectric element and evaluated its properties[11]. Figure 14 shows the flowchart of prototyping of the piezoelectric element. We used φ6-inch silicon substrates (100) with a thickness of 625 μm and with a 100 nm thermally-oxidized layer, and used Ti for the adhesion layer and Pt for the bottom electrode. Pt was preferentially oriented in the direction of the (111) plane. A 3 μm PZT film was deposited over it, and then Pt was deposited as the top electrode. After making a photo resist pattern on the top Pt electrode, we etched the top Pt electrode and the PZT film. We processed the element to the minimum size of φ30 μm in diameter, and evaluated the ferroelectric properties and the piezoelectric properties by using a combination of an atomic force microscope (AFM) and a ferroelectric evaluation system[12]. Figure 15 shows an SEM image of the dry-etched φ50 μm diameter piezoelectric element array. For each element, nothing adhered to the pattern sidewalls and a good etching profile was obtained. Figure 16 shows the dependency of the remanent polarization property and the coercive electric field property of φ30 to φ500 μm diameter elements on the size. The remanent polarization value is 41 μC/cm^2 and the coercive electric field is 46 kV/cm, indicating that satisfactory properties were obtained with no dependency on size. Figure 17 shows the piezoelectric displacement property of φ50 μm diameter elements. The ratio of displacement to the electric field is 0.23% for the PZT film thickness of 3.0 μm, indicating a satisfactory piezoelectric displacement property.

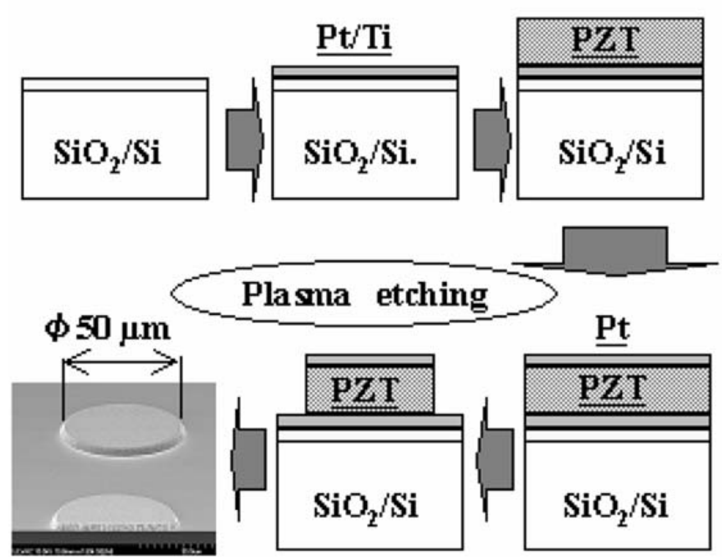

Figure 14 Flow of fabrication of piezoelectric elements using the PZT film

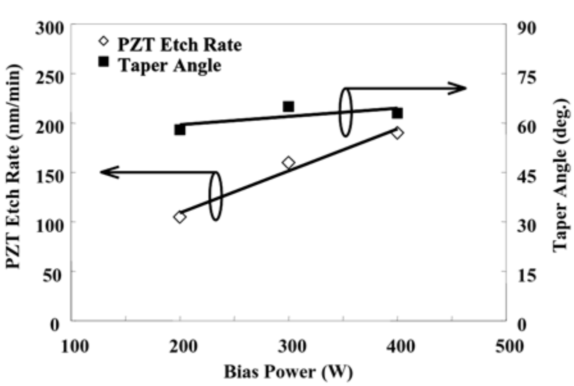

Figure 13 Dependency of the PZT etching rate and the taper angle on the bias power

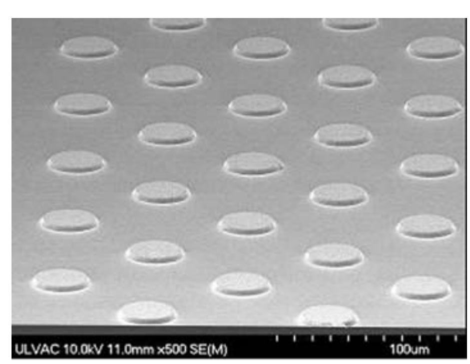

Figure 15 Dry-etched 50-mm diameter piezoelectric element array

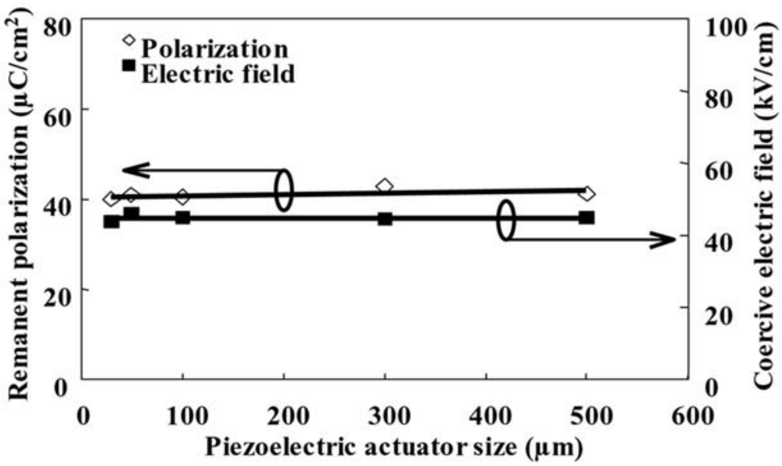

Figure 16　Dependency of the remanent polarization and the coercive electric field on the element size

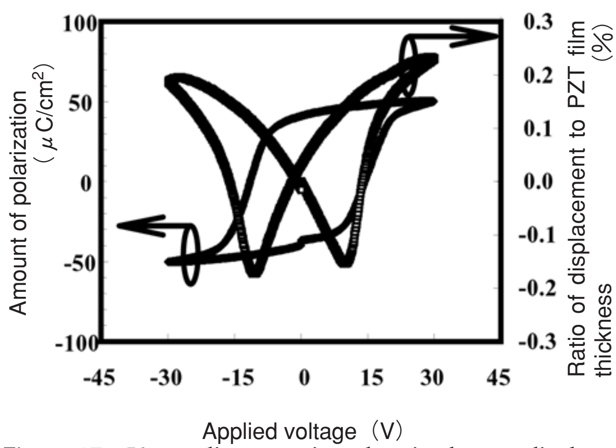

Figure 17　50-mm diameter piezoelectric element displacement property

7. Conclusion

For the MEMS devices expected to be further miniaturized in the future, piezoelectric elements using PZT are considered as a material to bridge mechanical and electric actions. As a technology that replaces the conventional bulk PZT fabrication technology, this paper has introduced thin-film PZT fabrication technology with sputtering and piezoelectric element processing technology with dry etching. For both technologies, we have been developing systems and processes, bringing the MEMS mass production into view, and we have established elemental technologies applicable to mass production systems. We have uniquely prototyped piezoelectric elements and obtained excellent properties. These technologies are very promising for MEMS mass production in the near future. We will continue development for further technical improvement and positively transmit information to enter the MEMS-related fields.

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