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Processing of PZT Microstructures

Shinan Wang, Jing-Feng Li[1], Xinghua Li[2] and Masayoshi Esashi[3]

Venture Business Laboratory, Tohoku University
[1]Department of Materials Processing, Graduate School of Engineering, Tohoku University
[2]Faculty of Engineering, Tohoku University
[3]New Industry Creation Hatchery Center, Tohoku University
Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

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Lead zirconate titanate (PZT) ceramic microstructures have been obtained by two reciprocal approaches, both of which are batch-fabrication-oriented. One approach starts from PZT powders using a lost Si mold technique, where a Si mold is prepared by deep reactive ion etching (RIE) and sintering of PZT after slurry casting is performed by glass-encapsulated hot isostatic pressing (HIP). The Si mold is finally etched away selectively by XeF_2. The resulting PZT structures are of high density and accurately reflect the complementary shapes of the Si molds. The highest aspect ratio is over 15. Fine PZT rod arrays for ultrasonic microtransducers and parallel plates for stacked piezoelectric microactuators have been achieved. The finest rods are 7 μm square in cross section, 90 μm in height and 12 μm in period; the 25-μm-pitch PZT plates are 18 μm thick and 130 μm high. The other approach is to fabricate bulk PZT substrates into microstructures by deep RIE using SF_6 gas with electroplated Ni films as protective masks. The etch depth is 70 μm and the etch rate is 0.3 μm/min.

1. Introduction

Due to its superior piezoelectric and ferroelectric properties, lead zirconate titanate (PZT) ceramic has been widely applied in sensors, actuators and electronic components. To meet device performance requirements, fabrication techniques of fine PZT structures are strongly desired.

In the case of high-resolution ultrasonic transducers for medical diagnosis and nondestructive testing, PZT/polymer 1-3 composites have been employed to realize good performance and acoustic impedance matching. As illustrated in Fig. 1, such a 1-3 composite generally consists of a PZT rod array embedded in a piezoelectrically inactive polymer matrix. It has been shown that among existing fabrication techniques, the lost mold process is the most suitable for 1-3 composites in the frequency range higher than 20 MHz, where fine-scale and high-aspect-ratio PZT features are essential.(1) However, significant structure deformation seems unavoidable in the conventional lost mold process when the feature sizes are smaller than 20 μm due to the necessity of removing the plastic mold before PZT sintering,(2) which therefore limits the forming of finer-scale PZT structures.

In the case of actuators, stacked PZT structures have been used to lower the driving voltage. Figure 2 shows the concept of a stacked piezoelectric actuator consisting of PZT plates intercalated by electrodes. The driving voltage is proportional to the PZT plate thickness. Such structures have been conventionally fabricated by tape casting(3) or paste printing(4) methods where the driving voltage can be lowered to 40 V with the PZT sheet thickness of about 40 μm. However, these methods have reached their limitations in lowering the actuator driving voltage because of the difficulty of forming thinner PZT sheets.

In order to achieve a breakthrough, we have developed a lost Si mold process,(5) by which finer PZT structures have been achieved with high design flexibility, which will meet the device requirements mentioned above.

On the other hand, it is desirable to carve bulk PZT into fine structures without degrading its original material properties. For this purpose, methods such as diamond saw dicing,(6) ultrasonic cutting(7) and laser-assisted etching(8) have been developed. Besides the cost and yield limitations of dicing and cutting methods, it is also difficult to fabricate PZT structures finer than 20 μm by these methods. RIE techniques using halogen plasma have been used for fine structure patterning on PZT thin films due to their high degree of anisotropy.(9–11) However, there are no reports on deep RIE of PZT so far due to low etch rates, an issue which this paper will address.

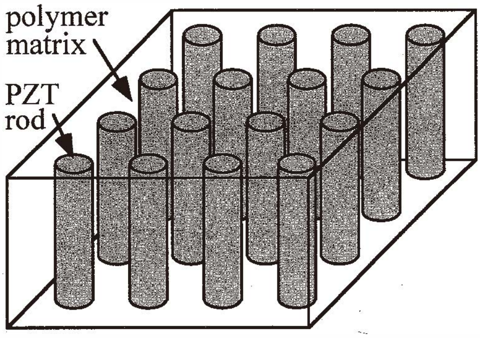

Fig. 1. Schematic of PZT/polymer 1-3 composite.

2. Lost Si Mold Technique

The lost Si mold process, depicted in Fig. 3, is a combination of Si micromachining and ceramic sintering techniques. First, deep RIE is used to fabricate the Si mold of designed PZT 1-3 structures. The protection mask used is a patterned photoresist (PR) layer. Second, PZT slurry is cast into the Si mold. The slurry is made of 0.3 μm PZT powder ($Pb(Zr_{0.52}Ti_{0.48})O_3$, Sakai Chemical Corp.) with 10% polyvinyl alcohol (PVA) used as a binder. After natural solidification, calcination is performed at 500°C to burn out the

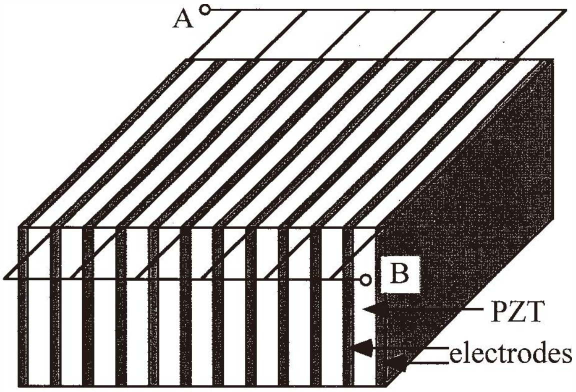

Fig. 2. Concept of stacked piezoelectric actuator.

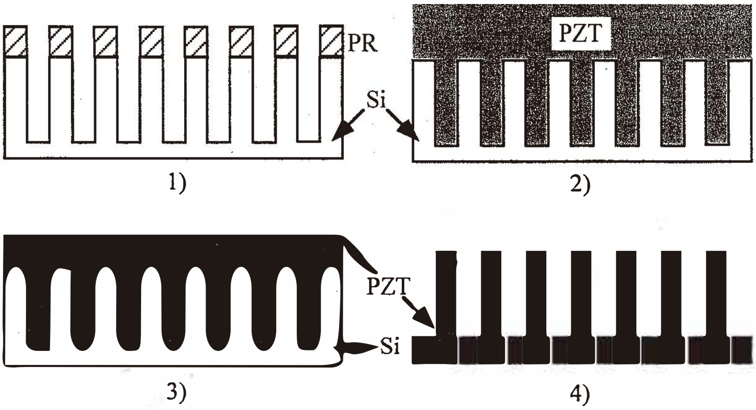

Fig. 3. Lost Si mold process: 1) fabrication of a Si mold by deep RIE, 2) PZT slurry casting, solidification and calcination, 3) PZT sintering by HIP, 4) removal of the Si mold.

binder completely. Third, glass-encapsulated hot isostatic pressing (HIP) is performed at 1100°C under 70 MPa for two hours to sinter the PZT powders in the Si mold. Lastly, the Si mold is selectively removed by XeF_2 etching.(12) Details of the above process have been described in ref. (5).

A scanning electron microscope (SEM) image of the obtained PZT rod array is shown in Fig. 4. The 12-μm-period rods are 7 μm square (rounded corners) in cross section and 90 μm in height, meaning an aspect ratio of over 12. Figure 5 shows another example where rod cross sections gradually decrease from 12.5 μm square at the bottom to 9 μm square at the top. The aspect ratio is higher than 15. In view of acoustic impedance matching, the structure shown in Fig. 5 may be superior to that in Fig. 4 because its composite acoustic impedance varies successively in the thickness direction, and therefore the matching will be better. Its transducer resonant frequencies, determined mainly by the PZT rod height, will be almost the same as that of a composite using rods of the same height but with uniform cross sections.

In Fig. 6, a parallel PZT plate structure is shown with plates 18 μm thick, 130 μm high and 25 μm in period. The stacked piezoelectric microactuator shown in Fig. 2 can be obtained by filling the plate spaces with a conductive material as electrodes. The material may be a metal formed afterwards by, for example, electroplating; it may also just be Si. In this work, a high-conductivity Si substrate is used as the mold. After PZT sintering, unnecessary parts of the Si mold can be selectively removed by RIE while Si between the PZT plates will remain as the actuator electrodes. Since the PZT plates shown in Fig. 6 are 18 μm thick, the driving voltage of such a piezoelectric actuator is expected to be as low as

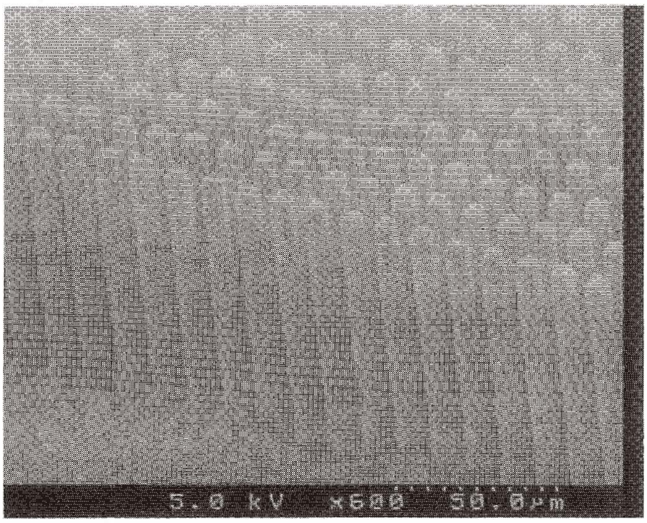

Fig. 4. PZT 1-3 structure for use in a high-resolution ultrasonic transducer with the 12-μm-period rods 7 μm square (round corners) in cross section and 90 μm in height.

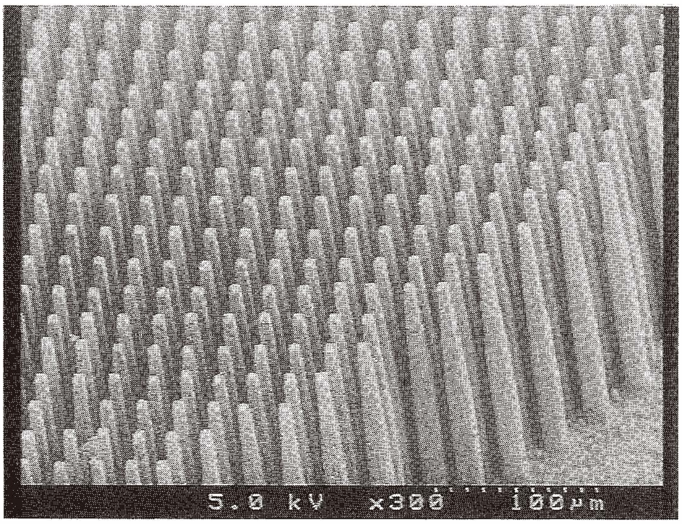

Fig. 5. PZT rod array with the square rod cross sections thinning gradually from 12.5 µm at the bottom to 9 µm at the top. The rod height is 190 µm.

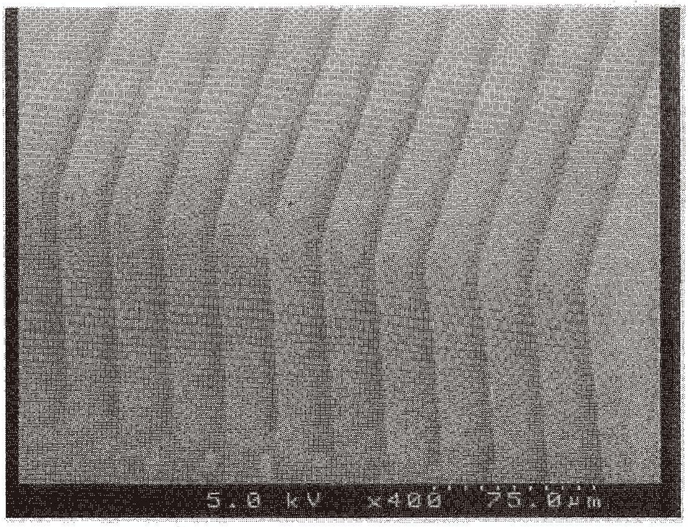

Fig. 6. Parallel PZT plates for stacked piezoelectric microactuator with PZT plates 130 µm high, 18 µm thick and 25 µm in period.

18 V. Thinner PZT plates are also formable by the above process.

As seen in Figs. 4, 5 and 6, PZT structures obtained by the lost Si mold technique are fine with high aspect ratios and designable shapes; their density is also very high. X-ray diffraction (XRD) analyses indicate that these structures are mainly in the perovskite phase, which is essential for piezoelectric and ferroelectric applications.

3. Deep RIE of PZT

The PZT deep RIE process is illustrated in Fig. 7. In the first three steps, a Ni mask pattern is formed on the PZT substrate: a thin Au/Cr film (0.1/0.1 μm) is first deposited on the PZT surface, onto which a 6-μm-thick photoresist (PR) film is coated and patterned by photolithography; using the exposed parts of the Au/Cr film as electrodes, Ni is then selectively electroplated onto the PZT substrate. After removing the photoresist with acetone, PZT fine structures are formed by deep RIE using SF_6 plasma with the Ni pattern as a mask.

In order to achieve a high etch rate and vertical profiles, a high-density inductively coupled plasma (ICP) RIE system(13) is used. Two 13.56 MHz RF sources are used: one supplied to a single-turn coil which is fixed on top of the quartz chamber lid to create the inductively coupled plasma, and the other to the sample stage (the cathode) to create the self-bias. A permanent magnet is located at the center of the coil to densify the plasma at the chamber center. The etch rate and profiles are found to depend on the RF powers, the process pressure and the stage temperature.

Typical PZT structures defined by the deep RIE process are shown in Fig. 8, and a close-up is shown in Fig. 9; the etch depth is 70 μm. In this experiment, the coil RF power is 150 W while the stage RF power is adjusted for the RF self-bias to be −390 V; the stage

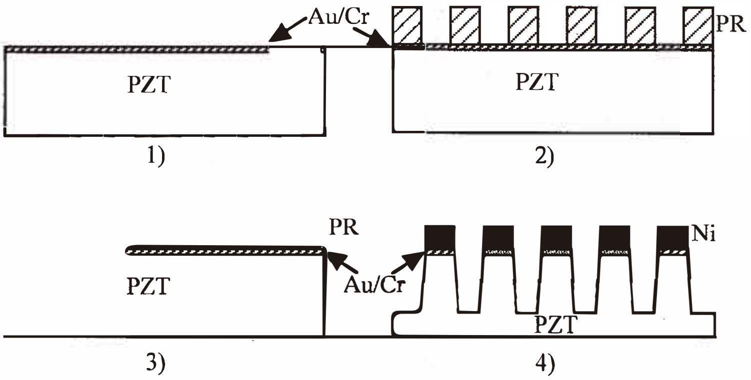

Fig. 7. Deep RIE process: 1) Au/Cr deposition on a PZT substrate, 2) photoresist (PR) coating and patterning, 3) Ni electroplating, 4) deep RIE of PZT with Ni as a mask.

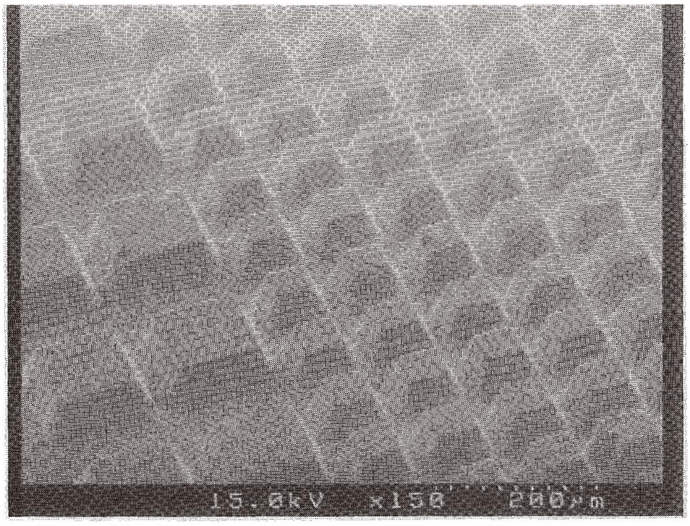

Fig. 8. SEM image of PZT structures defined by deep RIE. The etch depth is 70 μm.

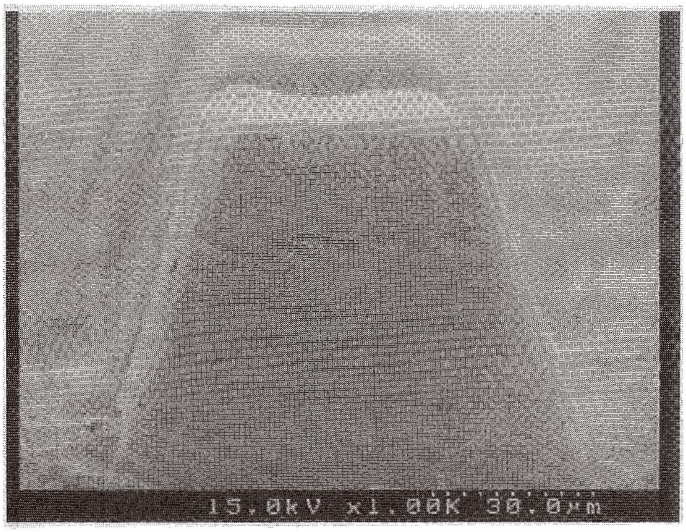

Fig. 9. Close-up of the PZT structures in Fig. 8. The white top layer is the Ni mask.

temperature is held at 20°C, and the process pressure is kept at 6 mTorr. Under these conditions, the etch rate is 0.3 μm/min, and the selectivity of PZT to the Ni mask is more than 35. In Fig. 9, the white top layer is the remaining Ni mask which can be selectively removed or retained as an electrode if necessary. The etched PZT profiles are very smooth, although the average grain size of the original PZT substrate (N-10, Tokin Corp.) is larger than 2 μm. The sidewalls, however, are positively sloped with the base angles being about 75°, which may be a result of the etching protection of reaction products deposited on the sidewalls. A conventional evaluation has confirmed that the PZT material properties are almost unaffected by the deep RIE process.

4. Discussion

In the lost Si mold process, by taking advantage of the high melting point and high strength of Si, PZT sintering under high pressures (HIP) within the Si mold becomes possible. As a result, PZT structures have high density and reflect the Si mold features exactly. Additionally, the present Si deep RIE techniques have enabled the control of the sizes and profiles of Si molds.(14,15) Therefore, the lost Si mold process has given rise to a new way of realizing fine PZT structures (less than 10 μm) with high aspect ratios (over 10) and three-dimensional design flexibility. Great improvements in performance can be expected for devices using thus-obtained PZT structures. The lost Si mold process is also applicable to fine structure formation of other ceramic materials.

In the PZT deep RIE process, the high etch rate and high selectivity have made it possible to pattern bulk PZT into fine structures directly without degrading the material properties. At present, the sidewalls of the structures are still not satisfactorily vertical. This may be improved by adjusting the RIE conditions and mixing other gases with the main gas, SF_6. The improved PZT deep RIE technique will be very practical for PZT fine structure definition due to the retention of material properties and the simple batch-fabrication-oriented process.

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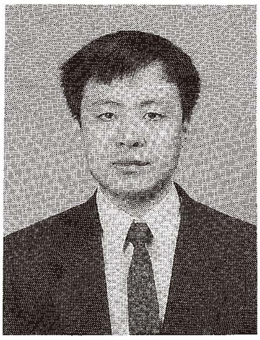
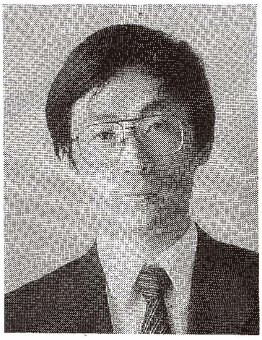
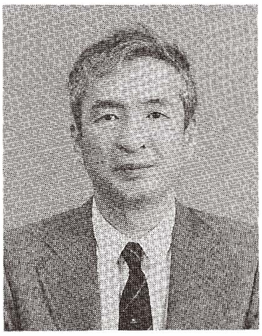


Shinan Wang, born in Heilongjing, China, in 1964, is currently a lecturer at the Venture Business Laboratory at Tohoku University and is devoted to micromachining, including ceramic micro-processing. He received a B.S. degree in Semiconductor Physics and Devices from Jilin University, China, in 1987. He received a M.S. and Ph.D. degree in Electronic Engineering from the University of Tokyo, Japan, in 1992 and 1996. His research interest includes quantum electronic devices. He will soon take a position at the Institute of Electrical Engineering, Chinese Academy of Sciences, Beijing, China.



Jing-Feng Li was born in Hubei Province, China, in 1963. After graduating in 1984 from Huazhong University of Science and Technology, Wuhan, China, he earned his M.S. and Ph.D. in materials science and engineering from Tohoku University in Japan in 1988 and 1991. Prior to joining Tohoku University in 1992, he was with Nihon Ceratec Corporation, Japan. At present Dr. Li is an Associate Professor in the Department of Materials Processing, Tohoku University. His main research interests include ceramic processing, phase transformation, and microstructure-process-property relationships in ceramic materials.

Xinghua Li was born in Shenyang, China, in 1971. She received her B.S. from Shenyang University of Technology, China, in 1994. She is presently pursuing an M.S. in Mechatronics and Precision Engineering at Tohoku University in Japan. Her research interests include micromachining and related applications.



Masayoshi Esashi was born in Sendai, Japan, on January 30, 1949. He received a B.E. degree in electronic engineering in 1971 and a Doctor of Engineering degree in 1976 from Tohoku University. From 1976 to 1981, he served as a research associate at the Department of Electronic Engineering, Tohoku University and was an associate professor from 1981 to 1990. He has been a professor at the Department of Mechatronics and Precision Engineering from 1990 to 1998. Since 1998, he has been a professor at the New Industry Creation Hatchery Center at Tohoku University. He is a director of the Venture Business Laboratory in Tohoku University and an associate director of the Semiconductor Research Institute. He has been studying microsensors and integrated microsystems fabricated with micromachining. His current research topic is a microtechnology for saving energy and natural resources. He is a member of the IEEE and the IEE of Japan.