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Piezoelectric Composites of Fine PZT Rods Realized by LIGA Process

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A ceramic microfabrication process has been developed for a 1–3 piezoelectric composite. This composite material was predicted to be suitable for high-frequency and wideband ultrasonic transducers used in diagnostic medicine and nondestructive testing. However, no process was available to fabricate micro- and high-aspect-ratio lead zirconate titanate (PZT) columnar arrays; therefore, a piezoelectric composite for high-frequency ultrasonic transducers was not realized. We developed a process which employs synchrotron radiation (SR) lithography, electroforming, and micromolding, generally called the "LIGA process." This process produced an array of PZT columns whose cross-sectional area is 25 μm^2 and 250 μm high. As expected from theory, the mechanical quality factor (Q_m) is lower and the electromechanical coupling coefficient in the thick mode (k_t) is higher than conventional materials. Using the composite developed in an ultrasonic endoscope, the ultrasonic pulse-width was improved from 240 ns to 180 ns, and the bandwidth was expanded from 60% to 150%.

1. Introduction

In ultrasonic diagnosis used in medicine, ultrasonic waves are transmitted and received via an ultrasonic probe pressed against the patient's body. A tomographic image is obtained using the time between the transmission and the reception of waves reflected back from the surface of an organ to calculate the distance between the surface and the organ.

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Ultrasonic diagnosis in medicine is more useful than X-ray CT (computerized tomography) or MRI, because it causes little radiation injury to patients, permits the measurement of blood flow and yields real-time image data. However, ultrasonic diagnosis cannot replace X-ray CT or MRI because it has poor resolution and difficult position recognition. It has been reported that changing the transducer material from a piezoelectric ceramic to a composite material composed of piezoelectric ceramic columnar arrays and resin, as shown in Fig. 1, is effective in improving resolution, bandwidth, and sensitivity(1,2) for the following reasons.

(1) Because the resin functions as a damper, the Q_m of the material is low. Therefore, attenuation of the oscillation is rapid, and the ultrasonic pulse becomes shorter. As a result, the resolution in the depth direction is improved.

(2) In addition, because of the low Q_m, the bandwidth increases. The reason for the difficulty in position recognition is that the depth range of piezoelectric ceramics is small, primarily because of the narrow band of the conventional piezoelectric transducer. A wide bandwidth expands the viewable area, and it becomes easier to identify the organ imaged.

(3) Because the aspect ratio (height/width) of PZT columns in the composites is high, the input energy is effectively converted to oscillations in the depth direction; the k_t is higher than that of bulk PZT. This improves the sensitivity of the measurement and results in expanding the viewable area.

(4) Because the resin has a low acoustic impedance, the acoustic impedance of the piezoelectric composite transducer matches that of the human body well. Therefore, ultrasonic transfer loss is small and the sensitivity is high.

Piezoelectric ceramic columns must have a sufficiently small cross section compared with the ultrasonic pulse length. For example, a transducer with a frequency of 10 MHz requires PZT columns having a cross-sectional width below 40 μm wide (1/4 of the wavelength) , because the wavelength in the human body is approximately 150 μm. The aspect ratio of PZT is required to be over 3.(3) The conventional fabrication method for micro-PZT columnar arrays is dicing; however, a limitation exists in decreasing the size of the PZT, because PZT is a fragile ceramic material. In this work, a new micro-fabrication method for PZT columnar arrays was developed and the predicted merits of composites were confirmed.

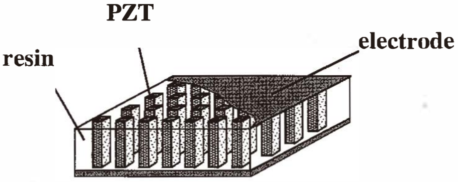


Fig. 1. Schematic view of piezoelectric composites.

2. Production Process

2. 1 *Outline*

We developed a process which employs synchrotron radiation (SR) lithography, electroforming, and a micromolding, generally called the "LIGA process."

Figure 2 shows the developed process. First, SR lithography was performed on a resist structure to form many fine holes with a high aspect ratio on the conductive substrate. The cross-sectional area of the holes was 30 μm^2 and the depth was 300 μm. Then, nickel electroforming, using the substrate as an electrode, was performed to obtain a nickel mold insert as the negative of the resist structure. Using the mold insert, a plastic mold having the same shape as the resist was manufactured. Then a PZT slurry was injected into the plastic mold. After the slurry dried and hardened, the plastic mold was removed by plasma etching. Finally, the PZT columnar array was obtained by removing the binder and 1200°C. The amount of linear shrinkage was 13%; thus an array of PZT columns with a cross-sectional area of 25 μm^2 and a height of 250 μm was realized. In the spaces between the PZT columns, epoxy resin was cast in vacuum, and any superfluous material on the upper and lower surfaces was removed by polishing to a predetermined thickness. Finally, chromium and gold were sputtered to form electrodes. Figure 3 shows scanning electron microscopy (SEM) images of (a) the resist structure, (b) the nickel mold insert, (c) the plastic mold, and (d) the PZT columnar array.

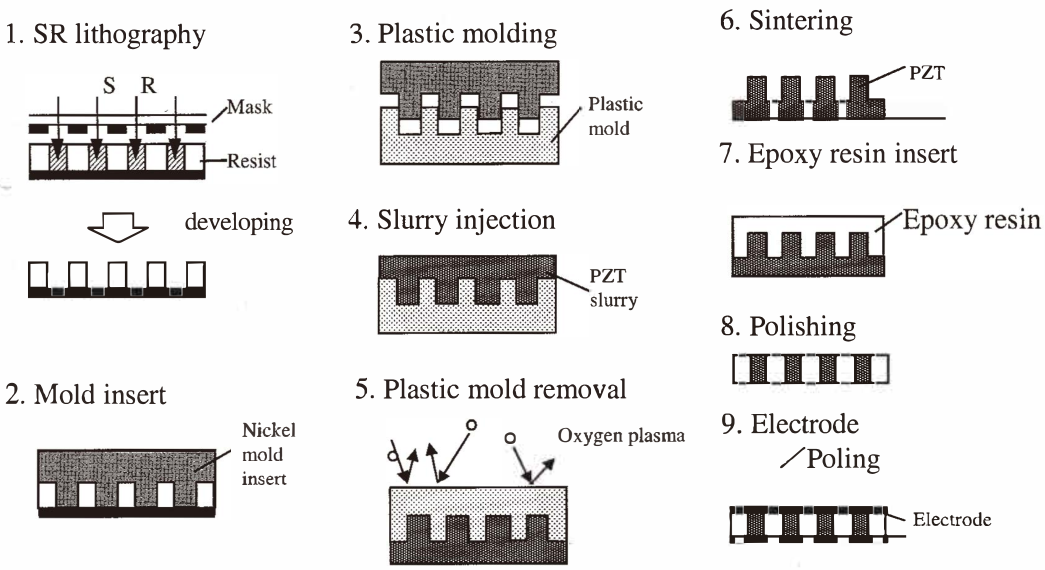
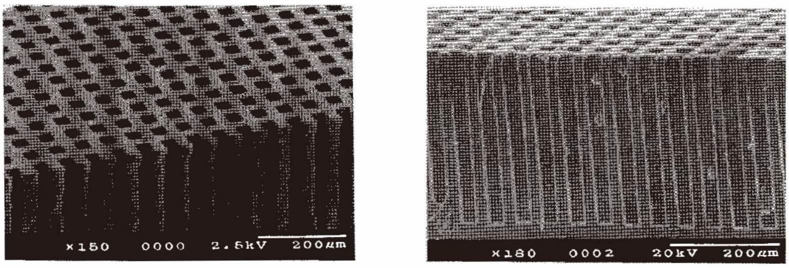
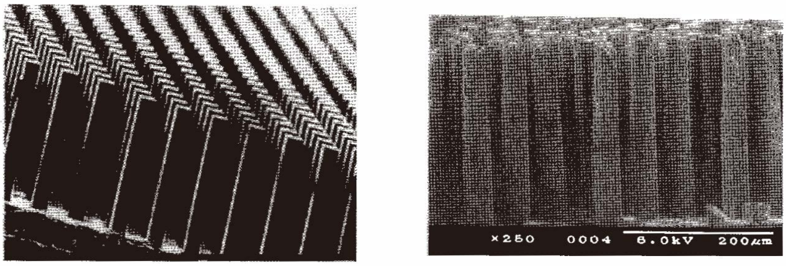


Fig. 2. Fabrication process.



(a) Resist structure (c) Plastic mold



(b) Nickel mold insert (d) PZT columnar array

Fig. 3. SEM images of fabricated composites.

Using this process, the fabrication of PZT columns with cross-sectional dimensions of 25 μm and 250 μm high was realized. In addition, the mass production of PZT columnar arrays using molds is possible, and the production cost of the developed process is lower than that of the conventional dicing process.

The following describes each process in detail.

2.2 *SR lithography*

To shorten the SR irradiation time, a highly sensitive resist was developed. The resist is a copolymer of methyl methyacrylate (MMA) and methacrylic acid (MAA). It is 10 times more sensitive than PMMA, which is usually used for the LIGA process.(4) The precision of the shape is comparable to that of PMMA; a perpendicularity of 0.16 μm or less per 100 μm of height can be realized.

2.3 *Production of the mold insert*

By carrying out nickel electroforming using the resist structure made by SR lithography, a fine-structure metal mold insert was formed. For electroforming into superfine holes with a high aspect ratio, it was necessary to develop ways of allowing the electroforming liquid to permeate, because it is difficult for the liquid to permeate into the holes of the resist structure with high aspect ratios. Step-by-step control of the current density and improvement of liquid circulation resulted in an electroforming process that did not induce internal stress or defects.

The Vickers hardness of the mold insert is 300, and the internal stress is under 30 MPa. The difference between the top and the bottom of a column was 0.8 μm when the height of the column was 300 μm. This taper was sufficient to decrease the demolding force and satisfied the size requirement for composites.

2.4 *Plastic molding*

To enable mass production of plastic molds having the same structure as the resist, a reactive molding technology using the mold insert described above was developed.

This mold insert has micro- and high-aspect-ratio columnar patterns; thus conventional injection molding is not available because the high viscosity of the resin destroys the mold insert. To solve this problem, a resin syrup of low viscosity was injected into the mold insert cavity and polymerized thermally. The syrup contained 15% acrylic polymer, whose molecular weight was 300,000 and viscosity was 700 mPa s.

For molding with the fine and high-aspect-ratio mold insert, reducing demolding stress is important. By optimizing the mold release agent and the temperature profile of polymerization, the demolding stress was suppressed under 10 MPa and a plastic mold with fine holes was realized.

2.5 *Formation of superfine ceramics*

Two problems arise in producing ceramic structures from plastic molds. One is the method of injecting ceramic slurry into the microholes, and the other is the method of removing the resin mold after injection.

For the first, one solution was to reduce the viscosity of the slurry by increasing the content of the solvent. We were able to inject PZT slurry into microholes after vacuuming the holes of the resin mold. For example, the viscosity of the slurry including 56 vol% of solvent was 30 Pa s, and it was able to be injected into holes of 30 μm^2.

However, two problems arose. One was that the handling of PZT slurry after injection was difficult because of its softness and ease of deformation. The other was that the deformation of PZT columns during the sintering was large because the density of the PZT green structure was low. Therefore, the solvent content needed to be reduced.

A new method was developed to inject a slurry of high viscosity (shown in Fig. 4). The solvent in this slurry was 40 vol%. To suppress the entry of the slurry into the gap of the die and facilitate handling, spray-dried PZT powder was placed around the slurry and pressed with the slurry and the plastic mold.

After injecting the PZT slurry into the resin molds, the resin molds must be removed before sintering. When fabricating a ceramic structure using the LIGA process, conventional thermal dissolution is normally used to remove the plastic mold. However, micro-PZT columns with a high aspect ratio topple in the process. This phenomenon occurs because of the following events. The resist melts and moves around the green PZT

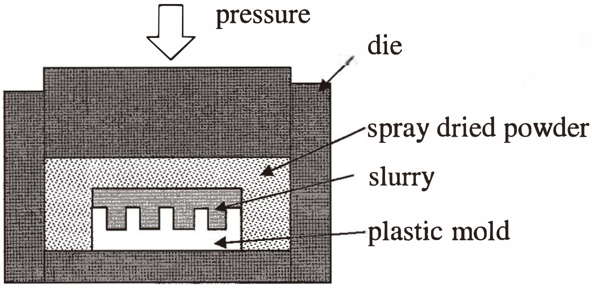


Fig. 4. Injection method developed.

columns. The stress applied to the bottom of the columns increases as the columns' diameter and surrounding space decrease. In addition, binder in the columns is dissolved by the heat; thus the PZT columns topple easily. The resin mold must therefore be removed by a non-thermal process; hence, O_2/CF_4 plasma etching was developed to remove the resin mold.(5) By controlling the RF power and other parameters, removing the plastic mold without the collapse of PZT columns was realized.

We also found that the irradiation of plasma onto PZT columns changes the dielectric constant(6) (Fig. 5). By controlling the radio frequency (RF) power and duration of the plasma etching, the dielectric constant could be controlled between 250 and 400. Although extended plasma etching reduced the dielectric constant , there were no changes in the piezoelectric properties and no defects in the sintered body. Using this technique, it is easy to optimize the dielectric constant for use without changing either the PZT powder or the volume fraction of PZT in the composites. Micro-PZT columns were thus successfully fabricated.

3. Properties of Composites

An example of the impedance curve of the composites developed is shown in Fig. 6. No small peaks are usually observed in the impedance curve of bulk PZT. The Q_m was 7 and k_t was 69%. As expected from theory, the Q_m is lower and k_t higher than those of conventional materials.

Because the volume fraction of PZT and Young's modulus of the resin are important parameters, their effects on the properties were investigated. To determine the properties of piezoelectric materials, the IRE (now IEEE) standard is usually used. However, the Q_m is low and the IRE standard is not applicable for the composites; thus these properties were calculated from impedance measurements and equivalent circuit fitting.

The results are shown in Fig. 7. The specifications of the composites are described in Table 1. Due to the high aspect ratio, the PZT oscillates effectively in the axial direction,

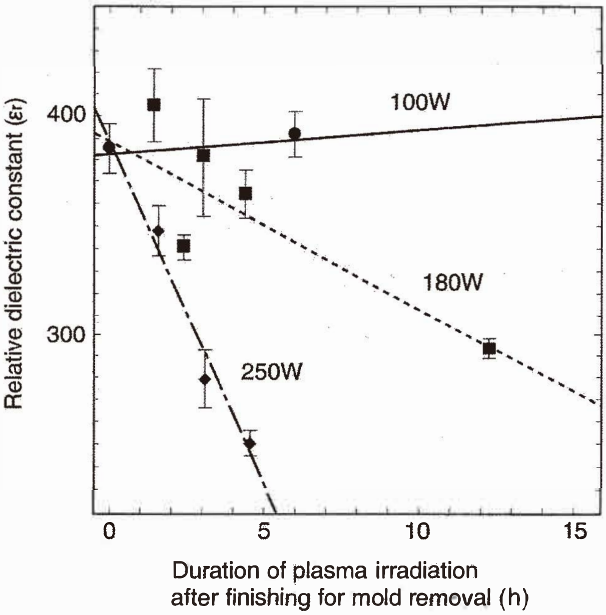


Fig. 5. Relationship between the relative dielectric constant and plasma etching conditions.(6)

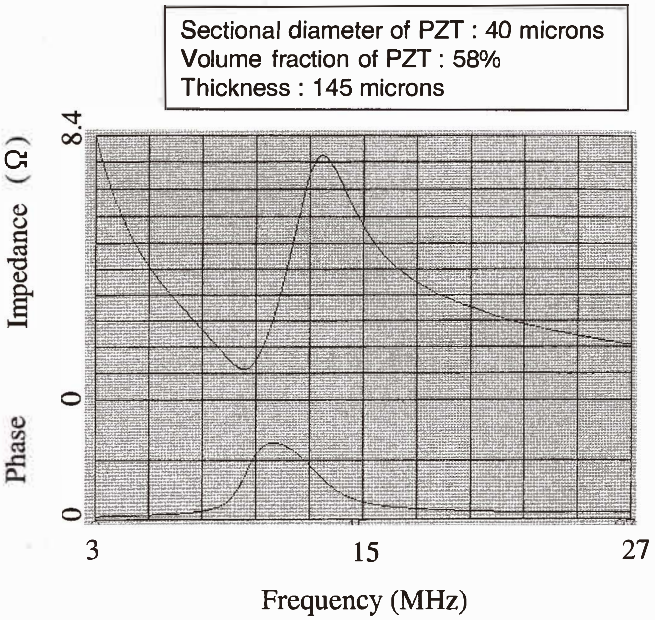
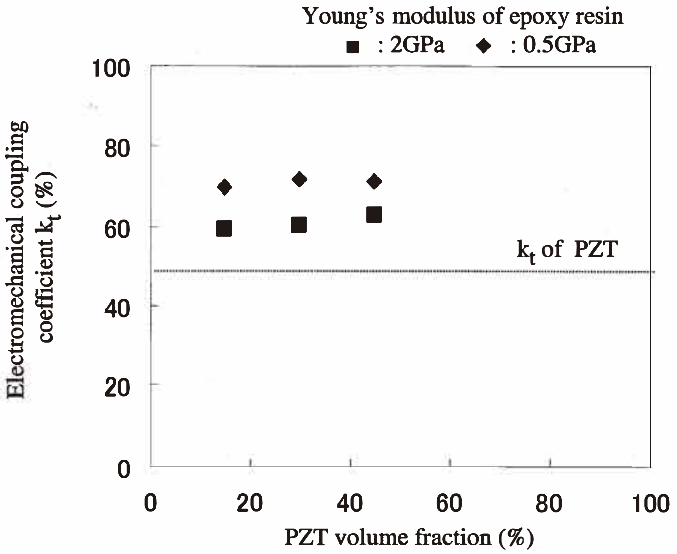
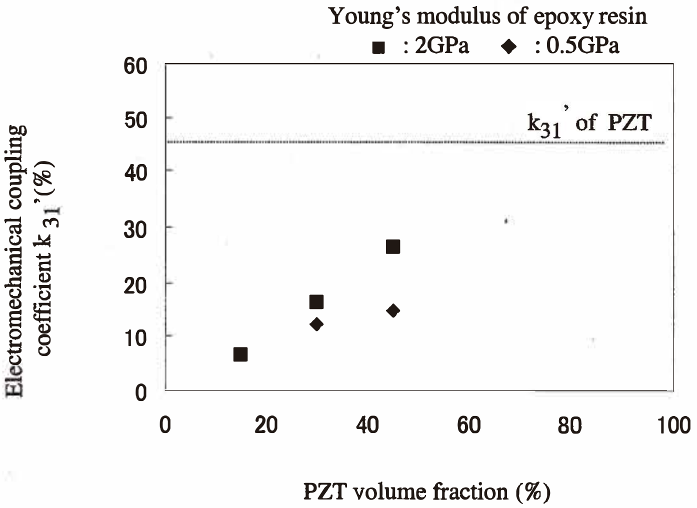


Fig. 6. Example of impedance curve of piezoelectric composites.



(a) k_t



(b) k_{31}'

Fig. 7. Retationship between PZT volume fraction and electromechanical coupling coefficient.

Table 1
Specification of measured composites.

Sectional size of PZT column	25 μm^2
Aspect ratio of PZT column	4
Volume fraction of PZT	15%, 30%, 45%
Young's modulus of epoxy resin	0.5 GPa, 2.0 GPa

and a high value is obtained compared to PZT alone. As shown in Fig. 7(a), differences due to the PZT volume fraction are small, but the value increased to approximately 70% as Young's modulus decreased. These results confirmed that k_t was larger than that of PZT, and could also be effectively increased by reducing Young's modulus of the resin. The electromechanical coupling coefficients in the lateral direction (k_{31}') are shown in Fig. 7(b). These coefficients confirmed that k_{31}' was smaller than PZT and could also be effectively reduced by reducing the volume fraction and Young's modulus of the resin.

Based on these results, the developed piezoelectric composites oscillated sonic waves with good directionality compared with bulk PZT and were expected to suppress cross talk between elements. However, the volume fraction affects the dielectric constant of composites linearly; therefore it must be determined by thinking about some design parameters of the ultrasonic probe. On the other hand, Young's modulus of the resin is determined to be 0.5 GPa. When Young's modulus of resin is under 0.5 GPa, it is difficult to polish the composites to control the thickness.

The frequency constant was also investigated. It does not depend on the volume fraction of PZT and Young's modulus and was 1,400 kHz mm. From that result, acoustic impedance was calculated as 8.7 MRayl when the volume fraction of PZT was 30%. It was one-third of that of PZT and improved the transfer efficiency of acoustic energy into the patient's body.

4. Evaluation

By examining our piezoelectric composite using an ultrasonic endoscope, ENDOECHO, produced by Olympus Corporation, Ltd., we compared the properties of the probe with those of a conventional probe.(7) Figure 8 shows the acoustic pulse shape of each probe.

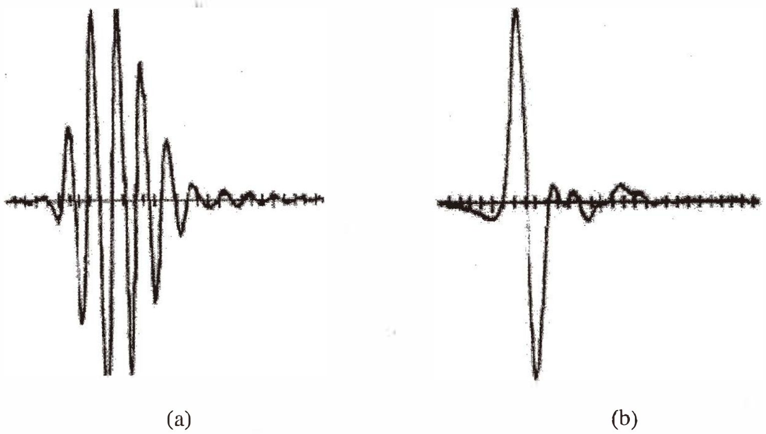

(a) (b)

Fig. 8. Acoustic impulse shape.(7) (a) Conventional transducer (plus width: 240 ns). (b) Piezoelectric composite transducer (pulse width: 180 ns).

The pulse width of the conventional probe is approximately 240 ns and that of the probe with our material is approximately 180 ns. The pulse width of the new probe was approximately 30% shorter and the resolution of the probe was higher than that of the conventional probe.

Figure 9 shows the transfer function of each probe. The relative frequency band (frequency bandwidth (sensitivity –6 dB) /center frequency) of the conventional probe is approximately 60% and that of the new probe is approximately 150%. The frequency bandwidth of the new probe is about 3 times larger than that of the conventional probe. This is useful for doctors because a wide area can be observed at one time.

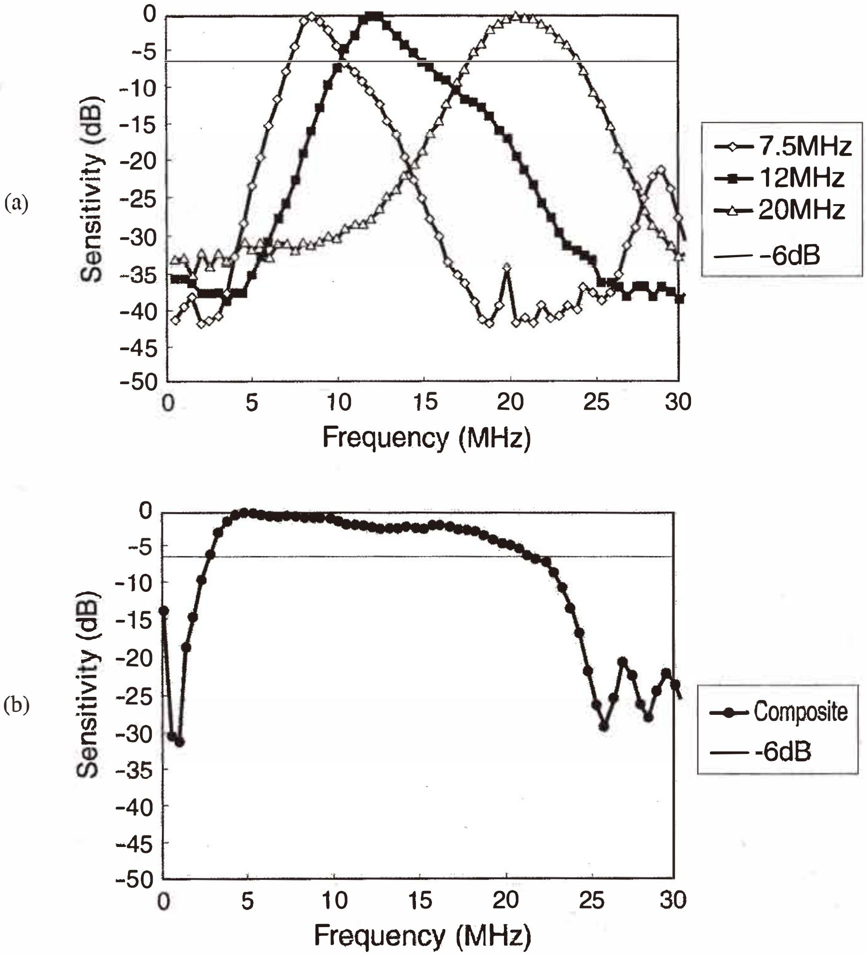


Fig. 9. Transfer function.(7) (a) Conventional transducer. (b) Piezoelectric composite transducer.

The image of an actual human stomach, taken using the new probe, may be compared with that taken using the conventional probe. Figure 10 (whose images are supported by the Internal Medicine Department of the digestion organ, East Hospital at Kitasato University) shows the maximum ultrasonic depth transfer mode for each probe. In the conventional image, only the center part can be clearly discerned, but the other parts of the image cannot be well imaged, as shown in Figure 10(a). Using the new probe, the image is clear in almost all parts, as shown in Figure 10(b), particularly the upper right.

5. Conclusions

Using the LIGA process, a fabrication process for ceramics with a superfine structure was established. The mass production of PZT column arrays with a 25 μm cross-sectional width and 250 μm high was realized. We fabricated a piezoelectric composite transducer using a structure of resin and PZT columns that had a higher resolution (30% higher) and a wider band (2 times wider) than a conventional transducer.

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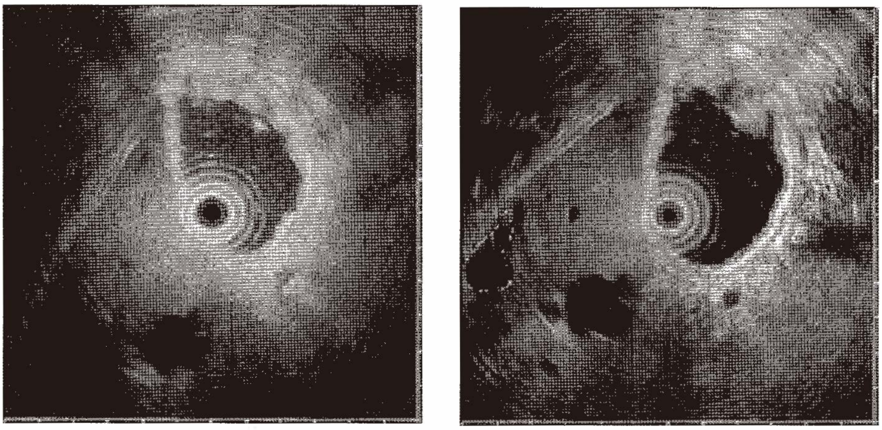
(a) (b)

Fig. 10. Ultrasonic images of actual human stomach.(7) (a) Conventional tranducer 7.5 MHz (12 cm range). (b) Piezoelectric composite transducer C5 mode (12 cm range).

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