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Low Temperature Fabrication of $Bi_4Ti_3O_{12}/TiO_2$

$Bi_4Ti_3O_{12}/TiO_2$ の低温作製に関する研究

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1. Introduction

In recent years, non-destructive testing (NDT) in operation has been demanded for industrial fields because of safety assurance and economical reason. Sol-gel composite materials could be suitable because of no couplant/backing material requirement.[1)] $Bi_4Ti_3O_{12}$(BiT)-based sol-gel composite is used as a material that can be used in high temperature such as thermal power plants. In previous study, BiT/Pb(Zr,Ti)O_3(PZT), BiT/BiT, BiT/$BaTiO_3$(BT), BiT/$Ba_{0.7}Sr_{0.3}TiO_3$(BST) and BiT/$SrTiO_3$(ST) have been developed.[2-4)] However, in the process of fabricating these sol-gel composite materials, it is necessary to fire at about 650°C. Depending on the fabrication condition, there is concern that the temperature cannot be raised such a high temperature because BiT-based sol-gel composite is assumed to be used at around 500°C. Therefore, sol-gel composite material that can be fired below 500°C is desired. In addition, firing at lower temperature can contribute lower fabrication cost. In this study, in order to realize fabrication at low temperature firing, TiO_2 was used as a sol-gel solution. According to our experiment, amorphous TiO_2 was synthesized around 400°C, so firing at low temperature can be achieved. Also, poling at room temperature could be possible because amorphous TiO_2 has high resistivity. Therefore, in this study, Ultrasonic performance of BiT/TiO_2 with 400°C firing was investigated at various temperatures.

2. Sample Fabrication

BiT/TiO_2 sol-gel composite film was fabricated by sol-gel spray technique. BiT powders and TiO_2 sol-gel solution were mixed, and ball milled for 24 hours or more because of achieve a suitable viscosity for splay coating and homogeneous mixing.[5)] BiT/TiO_2 sol-gel composite film was fabricated on a titanium substrate with dimensions of ~3cm length, ~3cm width, and ~3mm thickness. Then, drying at 150°C and firing at 400°C for 5min each were performed after spray coating process. These spray coating processes and thermal processes were repeated until the target thickness was achieved to avoid the cracking of films owing to internal stress. In this study, the target film thickness was 50µm. The film thickness was measured by a micrometer after each firing process. After these processes, poling was performed to achieve the piezoelectricity of sol-gel composite films. DC corona poling with a DC high-voltage source is the conventional poling method for sol-gel composite materials because a high electrical field could be applied without dielectric breakdown by positive ion discharge onto the sol-gel composite film. Poling process was carried out at room temperature for 5min. The output voltage of power supply was 23kV. After poling process, high temperature silver paste was coated on the film as a top electrode. The top electrode diameter was ~1cm. For drying silver paste, thermal process at 93°C were carried out for 2 hours. After these processes, piezoelectric constant d_{33} value was measured by piezo d33 meter. The d_{33} value of sample was ~5.4pC/N. Optical image of BiT/TiO_2 film fabricated onto titanium substrate is shown in **Fig.1**.

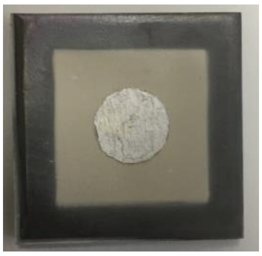

Fig.1 50µm thick BiT/TiO_2 film with silver top electrode on 3mm thick titanium substrate.

3. Experimental Results

The thermal cycle test was performed between room temperature and 500°C for BiT/TiO_2 sol-gel composite film on titanium substrate. The sample was set onto a hot plate and platinum wires were used as electrical cables and electrical connection between electrodes and wires were established by a ceramic weight. Hot plate temperature was changed every 100°C up to 500°C. After 5min holding time at each temperature, ultrasonic waveform in pulse-echo mode was recorded by a digital oscilloscope. This thermal cycle test was conducted for 3 cycles. Ultrasonic response of this cycle test for 3rd cycle at 500°C is shown in **Fig.2**. From Fig.2, clear multiple echoes were still observed at 500°C. Also, high signal to noise ratio (SNR) were obtained even at high temperature. Fast fourier transform (FFT) result of third reflected echo at 500°C is shown in **Fig.3**. The center frequency at 500°C was 17.0MHz and the 6dB bandwidth was about 14.8MHz. From Fig.3, BiT/TiO_2 sample has relatively high frequency and broadband characteristic.

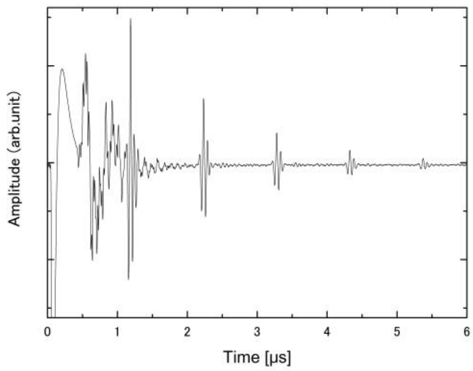

Fig.2 Ultrasonic response at 500°C in the 3rd cycle of BiT/TiO_2 sample fired at 400°C.

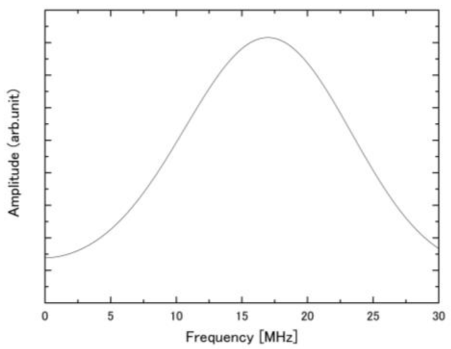

Fig.3 Result of FFT at 500°C of BiT/TiO_2 sample.

Then, the sensitivity was calculated for the quantitative evaluation purpose. The sensitivity was calculated as following equation;

$$\text{Sensitivity} = -(20\log V_1/V_2 + \text{P/R Gain})\ [\text{dB}] \quad (1)$$

where V_1 is the reference amplitude ($0.1V_{p\text{-}p}$[V] in this study), and V_2 is the signal amplitude [V] of third echo. The sensitivity of BiT/TiO_2 ultrasonic transducer at various temperatures is shown in **Fig.4**. In all the cycles, the transition of the sensitivity between room temperature and 500°C is within 10dB. In 1st cycle, the sensitivity was improved from room temperature to 300°C. This phenomenon is caused by the silver paste used in this study. This silver paste has high conductivity as the temperature rises. In the 2nd cycle and 3rd cycle, the electrode of the silver paste was cured, so this phenomenon was not noticeable. The sensitivity transition at the 3rd cycle compared with the 1st cycle and 2nd cycle is found to decrease. This decrease in sensitivity is affected by deterioration of adhesive strength of the silver paste. At the end of the 2nd cycle of the thermal test, the silver electrode was slightly peeled off. Therefore, the resistivity of the silver electrode in the 3rd cycle increased from the 1st cycle and 2nd cycle.

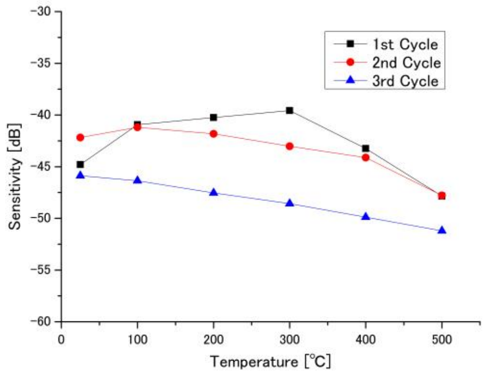

Fig.4 Sensitivity of BiT/TiO_2 sample at various temperatures during thermal cycle test.

4. Conclusions

BiT/TiO_2 sol-gel composite film fired at 400°C was fabricated onto titanium substrate by sol-gel splay technique. High temperature thermal cycle test was carried out from RT to 500°C for 3 cycles. In all cycles, clear ultrasonic response and reasonable SNR were obtained. Therefore, BiT/TiO_2 was found to be able to pole at room temperature and obtain sufficient high temperature durability. These results indicated that BiT/TiO_2 ultrasonic transducer fired 400°C have good potential for practical application.

References

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