Increasing vibration power generation energy by increasing the area of BaTiO₃ thick film formed on stainless-steel substrate by aerosol deposition

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In this paper, the results of evaluating vibration power generation by increasing the area of the BaTiO₃ (BT) film formed on a stainless-steel substrate by aerosol deposition (AD) is presented. Fe–Cr–Al-based heat-resistant stainless steel with a thickness of 0.1 mm was used as the substrate. BT films with a thickness of about 10 µm were formed on the substrate of six different shapes with different widths and lengths and BT films were annealed at 1000 °C. Electrodes were formed on the surface of these samples, and the poling process with a voltage of 60 V was applied to prepare samples for evaluation. A weight was attached to the tip of these samples and set up in a cantilever state. A damped vibration under the same stress condition was applied to the BT film by pushing and snapping the tip of samples one time. The generated voltage on the load resistance connected in parallel to the BT film was measured and the generation energy was evaluated. As a result, it was confirmed that the generation energies of the samples with areas of 15 × 3 and 30 × 40 mm² were 0.17 and 39 μJ, respectively. About 230 times as much energy was obtained by increasing the film area about 20 times. This result indicates that increasing the film area using AD method effectively increases the generation energy.

Key-words : Aerosol deposition, Thick film, Pb-free piezoelectric ceramics, Generation energy, Vibration energy harvester

1. Introduction

Vibration energy harvester (VEH) technology is attracting attention as a self-standing power source. VEH technology using the action of pressing a switch has been applied as a remote-control switch.¹,² It has been reported that this VEH technology of pressing a switch generates about 170 μJ.³ In the future, VEH technology is expected to be applied as a self-standing power source for IoT devices. The roadmap of VEH for IoT technology estimates that the energy required to drive IoT devices will be several tens of micro joules due to the development of low power consumption technology for sensors and wireless transmission devices.⁴ Therefore, it is expected that the generation energy by VEH will be required at least several tens of μJ in the future.

Currently, piezoelectric VEH technology has an issue of environmental pollution because piezoelectric ceramics using for VEH contain highly toxic Pb. It is desirable not to use Pb for the self-standing power supply used in IoT technology. In recent years, Pb-free piezoelectric ceramics exhibiting excellent properties have been developed.⁵ Typical Pb-free piezoelectric ceramics are KNbO₃–NaNbO₃ (KNN)-based⁶–⁸ and BaTiO₃-based⁹,¹⁰ materials. KNN-based bulk ceramics will be applied in ultrasonic devices⁰ and piezoelectric actuator devices¹¹ because they exhibit excellent electromechanical coupling coefficients and high Curie temperature. On the other hand, it has been reported that the piezoelectric constant and the dielectric constant of BaTiO₃ ceramics have a maximum value due to the grain size.¹² In particular, BT ceramics with about 2 µm grain size have a larger piezoelectric constant than KNN-based materials and exhibit a piezoelectric constant similar to that of Pb-based materials.¹⁰ We focused on BT material for the above reasons.

Piezoelectric VEH devices are generally applied using a piezoelectric material formed on a substrate with cantilever state. However, there is an issue in mechanical strength since piezoelectric ceramics are brittle.

For a piezoelectric thick film formed on a stainless-steel substrate, it has been confirmed that reliability is improved because it receives compressive stress from the substrate during the manufacturing process.¹³ Further, it has been reported that the VEH device using Pb-based piezoelectric thick film of 30 µm formed on both sides of stainless steel...
can generate about 800 µJ by one damped vibration exited the action of pressing switch. Based on the above technical background, the future, the piezoelectric VEH should consist of a Pb-free piezoelectric thick film formed on a stainless-steel substrate.

We focused on the aerosol deposition (AD) method as technology for forming films with a thickness exceeding 10 µm. The AD method is an innovative particle deposition coating technology that can form a dense thick film at room temperature. The properties and applications of the piezoelectric thick film formed by AD are reported as a review. In AD, the film area can be freely expanded by scanning the nozzle, and the film thickness can be increased by repeatedly laminating the film. The BT film formed by AD requires post-annealing to recover the electrical properties because the particles are crushed and form a film with fine grain size during film formation. When the BT film formed on the stainless-steel substrate is annealed above 1000 °C, there arises an issue of inter-diffusion at the interface between the BT film and the stainless-steel substrate. The issue could be solved by using a Fe–Cr–Al based heat-resistant stainless-steel material containing aluminium. An Al2O3 film layer of thermal oxidation is formed on the surface of Fe–Cr–Al stainless steel by annealing at high temperature in air. It functions as a barrier layer for diffusion between the BT film and stainless-steel during annealing at high temperature. The substrate for forming BT film was prepared by forming Pt/Ti as an electrode layer on a thermal oxide Al2O3 layer. The piezoelectric property of BT film on this substrate was improved by post-annealing. The piezoelectric constant of BT film annealed at 1200 °C exhibits ~54 pm/V for the BT film annealed at 1200 °C.

In this paper, by applying the above technology, the evaluation results on the vibration power generation energy by increasing the area of the BT film formed on the Fe–Cr–Al stainless-steel substrate is presented.

2. Experiment

2.1 Generation energy

In piezoelectric VEH technology, a general method applying stress to the piezoelectric film on a substrate is to apply force to the tip of a cantilever. The energy \( U (J) \) generated by the piezoelectric effect is expressed by Eq. (1),

\[
U = \frac{d_{31}^2}{2\varepsilon_s \varepsilon_0} \cdot T^2 \cdot (A \cdot t_p)
\]

where \( d_{31} \) is the piezoelectric constant, \( \varepsilon_s \) and \( \varepsilon_0 \) are the dielectric constants of piezoelectric material and vacuum, \( T \) is the applied stress, \( t_p \) is the thickness of piezoelectric material, and \( A \) is the electrode area. This equation shows that the generation energy is expressed by three factors: the physical properties of the piezoelectric material \((d_{31}^2/\varepsilon_s)\), the stress \( T \) applied to the piezoelectric film, and the volume \((A \cdot t_p)\) of the piezoelectric film. In this equation, the parameter \( d_{31}^2/\varepsilon_s \) is defined as the figure of merit (FOM).

2.2 Comparison of FOM

Table 1 lists the piezoelectric properties and FOM of typical bulk and thick film piezoelectric ceramics and the reported vibration power generation properties. Bulk BaTiO3, PbTiO3-based 0.4 1030 19 5 AD SS (423) (140 Hz, 1.5 G) 21) The piezoelectric constant \( d_{31} \) of the BT film formed on the stainless-steel substrate by AD has a value close to that of some Pb-based piezoelectric thick films. However, since the dielectric constant of the BT film is large, the FOM is about 1/4 of that of the Pb-based thick film, and it is necessary to increase the generation energy by other methods.

2.3 Conditions for evaluation

To increase the generation energy other than by increasing the FOM, there are two possible methods, increasing the stress and volume as indicated in Eq. (1). We focused on increasing the volume by increasing the area of the piezoelectric film under the same stress condition. The stress \( T \) applied to the piezoelectric material of the unimorph structure under the condition that force is applied to the tip of the cantilever is expressed by the following Eq. (2),

\[
T = \frac{3}{4} Y_p \cdot \frac{t_s + t_p}{1 + B} \cdot \frac{\delta}{L_n^2}
\]

where, \( \delta \) represents the deflection of the tip, \( Y_p \) and \( t_p \) represent the Young’s modulus of the substrate and the piezoelectric material, \( t_s \) and \( t_p \) represent the thickness of...
the substrate and the piezoelectric material, \( L_b \) represents the beam length, and \( B = (Y_p t_p)/(Y_s t_s) \). Equation (2) indicates that in order to evaluate the effect on the generation energy due to the area of the piezoelectric film under the constant stress condition, it is sufficient to evaluate under the condition that the thickness \( t_p \) and \( \delta/L_b^2 \) are constant. In this study, the BT film was formed on the substrate with 6 types of shapes as 2 types of length and 3 types of width, and the generation energy was evaluated. Table 2 shows the specific dimensions and evaluation conditions.

### 2.4 Sample preparation procedure

The powder for AD was prepared as follows. The BaTiO\(_3\) powder was prepared using BT01 (Sakai Chemical Co., Ltd.) as a starting material. It was calcinated at 1100 °C and then milled on 300 rpm for 1 h by a planetary mill in dry. Fe–Cr–Al-based stainless steel with the shape in Table 2 was used as substrates for evaluating piezoelectric properties and generation energy by vibration. These stainless-steel substrates were pre-annealed in air at 1100 °C and then milled on 300 rpm for 1 h by a planetary mill in dry. Fe–Cr–Al-based stainless steel with the shape in Table 2 was used as substrates for evaluating piezoelectric properties and generation energy by vibration. These stainless-steel substrates were pre-annealed in air at 1200 °C for 1 h to form a thermal oxide Al\(_2\)O\(_3\) layer as a diffusion barrier layer on the surface, and the Pt/Ti layer was formed as an electrode on the surface by sputtering.

The BT film with a thickness about 10 \( \mu \)m thick was formed on one side of the substrate by AD using N\(_2\) gas with 41/min at room temperature. The BT film for evaluation was post-annealed at 1000 °C for 1 h, since some substrates were warped during post-annealing above 1000 °C. The top electrode using Au was formed on the surface by sputtering. These samples were polarized by applying 60 V for 1 min at room temperature. The FOM of these BT films was calculated by measured the dielectric constant and the piezoelectric constant. The dielectric constant was obtained from the measured capacitance of the cantilever tip when voltage is applied to the BT film. The generation energy was evaluated by applying one snap vibration as mechanical stress to the piezoelectric film. The sample was set up as a cantilever beam as shown in Fig. 1. In general, the maximum energy of a power source is obtained when the load resistance is equal to the internal resistance of the power source, so the load resistance dependence was evaluated for vibration power generation. Load resistance \( R_L \) was connected in parallel to the samples, and damped vibration was excited by snapping the tip on the condition

\[
\frac{1}{R_L} \int V(t)^2 dt
\]

in Table 2. The time change of generated voltage was measured using an oscilloscope. The generation energy was calculated using the following Eq. (3), with \( t \) (s) as measuring time. The accumulated energy by the damped vibration was evaluated as the generation energy.

### 3. Results and discussion

#### 3.1 Microstructure of BT film

Figure 2 shows the XRD patterns of the as-deposited BT film and the annealed BT film. The result of the broad diffraction peak of the as-deposited film indicated that the as-deposited film is composed of fine polycrystals. The recovery of crystallinity and grain growth of were confirmed in the BT film annealed at 1000 °C since the diffraction peaks of the annealed film are sharpened and the intensity is increased. It was confirmed that the crystallite

### Table 2. Shape dimensions of the sample for the evaluation

| Sample | Substrate | Top electrode | Cantilever |
|--------|-----------|---------------|-----------|
|        | Length, \( L_b \) mm | Width, \( w \) mm | Length, \( L_e \) mm | Width, \( w_e \) mm | Beam length, \( L_a \) mm | Tip deflection, \( \delta \) mm | Weight g |
| A      | 25        | 5             | 18        | 3             | 15       | 3             | 2       |
| B      | 25        | 10            | 18        | 8             | 15       | 3             | 2       |
| C      | 25        | 20            | 18        | 18            | 15       | 3             | 2       |
| D      | 40        | 10            | 35        | 8             | 30       | 12            | 9       |
| E      | 40        | 20            | 35        | 18            | 30       | 12            | 9       |
| F      | 50        | 40            | 35        | 30            | 30       | 12            | 9       |

### Fig. 1. The configuration of a cantilever with a piezoelectric film formed on a substrate for evaluation of generation energy.

### Fig. 2. Comparison of X-ray diffraction patterns of as-deposited BT film and BT film annealed at 1000 °C.
The size of as-deposited film and annealed film obtained from the FWHM at the strongest XRD peak was 11.7 and 40 nm, respectively.

Figure 3 shows the SEM images of the surface and fractured cross section of the BT film annealed at 1000 °C. It can be seen that most of the grains in the film are under 1 μm grain size. The average grain size obtained from the SEM image of surface of the film was 0.4 μm. The grain size obtained from the SEM observation image is larger than the crystallite size obtained from the XRD data. The crystallite size measured by XRD is considered to show the size of the ferroelectric domain structure in the grain.

3.2 FOM of BT film
The dielectric constant $\varepsilon_r$ and the piezoelectric constant $d_{31}$ of BT film annealed at 1000 °C were 1670 and $-16$ pm/V for BT film, respectively. The FOM was obtained 0.2 (pm/V)$^2$ from these values. This FOM is less than that of the BT film annealed at 1200 °C in Table 1. It has been reported that the piezoelectric constant of BT ceramics exhibits a peak value with a particle size of about 2 μm. The cause of the low FOM is considered to be that the grain size with 0.4 μm was smaller than that of BT film annealed at 1200 °C.

3.3 Generation energy
Figure 4 shows the results of generated voltage by piezoelectric effect and a graph of instantaneous power and accumulated generation energy on a load resistance of 10 kΩ measured on sample F with the largest area of 30 × 40 mm$^2$. It could be seen that the maximum instantaneous power is about 80 μW and the accumulated generation energy is 39 μJ.

Table 3 presents the evaluation conditions and results of maximum energy on each appropriate the load resistance. The thickness of the film was measured at three points on the film using a micrometer, and the average value was taken as the film thickness. The maximum energy was obtained 39 μJ on BT film with the area of 30 × 40 mm$^2$. Comparing with sample A (smallest area) and sample F (largest area), it was confirmed that the generation energy increased about 230 times when the area was increased about 20 times. This result indicates that the measured generation energy can yield more generation energy than expected from the relational Eq. (1). In this study, the relationship between the generation energy and the volume of the piezoelectric material was investigated by changing the area of the BT film under the same stress conditions based on Eqs. (1) and (2). Figure 6 summarized the relationship between the volume of the BT films and the generation energy by using beam length on samples A–C and D–F. The volume of the film was calculated using the beam length $L_b$, the electrode width $w_e$, and the film thickness $t_f$ as the volume at which stress is applied to the piezoelectric film. It can be seen that the generation energy...
tends to be almost proportional to the volume of the BT film in the case of the same beam lengths. This result indicates that the relationship between generated energy and volume follows Eq. (1). However, it is found that the proportional coefficient is different on the beam length of 15 and 30 mm. In this experiment, although the same stress condition was assumed according to Eq. (2), it is expected that the actual stress condition on films will be different with the different beam length.

In the future, in order to increase the generation energy with Pb-free piezoelectric materials, it is necessary to apply a Pb-free piezoelectric material with a large FOM and optimize stress condition and the area and thickness of thick film using a device design method.

### Table 3. The measurement conditions and evaluation results for BT films with different film areas

| Sample | Measurement conditions Sample dimensions Evaluation results |
|--------|------------------------------------------------------------|
|        | Beam Length | Tip deflection | Load resistance | Width of substrate | Width of electrode | Thickness of film | Volume of film | Generation Energy |
|        | Lb (mm) mm | δ (mm) | Rl (kΩ) | w (mm) | wo (mm) | tF (μm) | Vol (mm³) | U (µJ) |
| A      | 15 3 50 | | | 5 | 3 | 16 | 0.72 | 0.17 |
| B      | 15 3 50 | | | 10 | 8 | 17 | 2.04 | 0.65 |
| C      | 15 3 5 | | | 20 | 18 | 12 | 3.24 | 2.2 |
| D      | 30 12 10 | | | 10 | 8 | 11 | 2.64 | 4.7 |
| E      | 30 12 10 | | | 20 | 18 | 11 | 5.94 | 13.1 |
| F      | 30 12 10 | | | 40 | 30 | 17 | 15.30 | 39.4 |

Fig. 6. The relationship between the generation energy and the volume of BT films at each beam length Lb.

4. Summary

In order to increase the vibration generation energy using a Pb-free piezoelectric thick film, the FOM of BT film annealed at 1000 °C formed on the stainless-steel substrate and the relationship between the area of the BT thick film and the vibration generation energy were investigated. As the result, it was confirmed that the FOM of BT film was obtained 0.2 (pm/V)^2. The generation energy was increased with increasing the area of the BT film. It was confirmed that the generation energy increased about 230 times when the area was increased about 20 times. The maximum energy was obtained 39 µJ on BT film with the area of 30 × 40 mm². It was confirmed that increasing the film area using the AD method is effective in improving the generation energy.

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