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Piezoelectric Vibration Energy Harvester Using Polyvinylidene Difluoride Film Formed by Bar-Coating Method and Its Spray-Coating Method on a Three Dimensional Surface

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Additional information is available at the end of the chapter

Abstract

A cantilever-type vibration energy harvester (VEH) made of polyvinylidene difluoride (PVDF) was fabricated and characterized. PVDF is one of the polymer piezoelectric materials, which is more flexible than ceramic-based piezoelectric materials such as lead zirconate titanate (PZT). The fabrication process of VEH is as follows: a PVDF film was coated on a phosphor bronze plate by bar-coating method, followed by polarization by corona discharge method. Aluminum top electrode was deposited on the PVDF film by sputtering. One end of the plate was clamped by a fixture to form a cantilever, the length of which is 25 mm. Output power P at the resonance frequency (=55 Hz) was measured as a function of load resistance R with the acceleration set at 17 m/s^2. Maximum output reached 4.3 μW at R = 2.1 MΩ. This result is not inferior compared with other reported VEHs using ceramic piezoelectric material. Spray coating was carried out to form PVDF film on a 3D surface. This method is suitable for fabricating a uniform thin film on a three-dimensional (3D) surface, even if it is complicatedly curved. In this study, PVDF film was formed on a 3D helical compressing spring, and the deposition on it was successfully achieved.

Keywords: piezoelectric polymer, PVDF, thin film, vibration energy harvester, bar coating, spray coating

1. Introduction

Recently, energy harvesting technologies have been actively studied as an energy source for wireless sensor's battery [1, 2]. There are various energy sources for energy harvesting such as solar power, thermal energy, wind power, and vibration. Among these power generation methods, a vibration energy harvester (VEH) is necessary in environments where solar cells cannot be used, for example, bridges, cars, underground places, buildings, and other environments. There are three main types of VEH generation methods: electromagnetic, electrostatic, and piezoelectric. Piezoelectric VEH has high electromechanical coupling coefficient. In addition, its structure is simple and suitable for miniaturization [3]. In many cases, the structure of piezoelectric VEH is like this: piezoelectric thin film is deposited on the surface of leaf spring made of metal or single crystal silicon. Weight is set on the tip of the spring [4–13]. By matching the design of leaf spring to the vibration condition, it can generate electric power under low frequency vibration and low acceleration.

In previous study, Refs. [6–10] fabricated piezoelectric VEHs using ceramic piezoelectric material. They fabricated cantilever-type piezoelectric VEHs. These piezoelectric VEHs were composed of metal cantilever and PZT film having high piezoelectricity on it. The output power of 1–17 μW was reported in the vibration frequency range of several hundred hertz. Although PZT has high piezoelectricity, it contains poisonous lead and it is a typical brittle material. Destruction of the VEH devices under large vibration or impact is a practical problem. In place of PZT, lead-based piezoelectric materials other than PZT and lead-free ones are being studied for VEHs, but piezoelectricity still remains lower than PZT [11, 12].

We adopted polyvinylidene difluoride (PVDF) which is a piezoelectric polymer material. PVDF has greater flexibility compared to ceramic PZT, so it can withstand large deformation. PVDF can be dissolved in an organic solvent such as methyl ethyl ketone (MEK), which forms PVDF solution. It can be coated on substrates or parts by several coating methods, making it compatible with micro electro mechanical systems (MEMS) technology. By using PVDF, therefore, it is possible to fabricate small devices. Toprak et al. fabricated a small piezoelectric VEH device in which a cantilever was made of single crystal silicon coated with a PVDF thin film [13]. However, its vibration frequency was 1074 Hz, and the output power was very small pW order. A VEH, which is coated with PVDF thin film and suitable for low frequency of 100 Hz or lower, has not been reported yet.

At the beginning of this chapter, we aimed to fabricate VEH coated with bar-coated PVDF film on leaf springs which can generate electric power even at low frequency. First, a PVDF thin film was prepared by bar-coating method, and then, it was polarized by corona discharge method. Mechanical and electrical properties of bar-coated films, such as surface roughness, residual stress, Young's modulus, XRD pattern, piezoelectric constant, were characterized. Then, a cantilever-type VEH using a bar-coated PVDF film was fabricated, and its power generating ability was evaluated.

Bar-coating methods enable PVDF film to coat on a completely flat substrate; however, it is not suitable for coating thin film on a three-dimensional (3D) surface (e.g., curved surface, uneven surface) caused by its coating principles.

In contrast, spray-coating method is suitable for coating a thin film on 3D surface. Spray coating was well researched by Sasaki et al. [14]. They have developed spray-coating technique

of photoresist onto 3D microstructures for the purpose of photolithography. In the case of PVDF, a pyroelectric image sensor was fabricated using its thin film formed by electrospray coating [15]; however, the film was deposited on only flat substrate. Coating PVDF thin film on completely 3D microstructure has not been reported yet. Recent years, ultramicro 3D fabrication technique such as 3D printing is progressing. A technology to form PVDF thin film on the surface of fine 3D structure is expected. In this chapter, we tried to apply the spray-coating method to PVDF coating on 3D structure.

In the latter part of this study, spray coating was carried out to form PVDF thin film on the surface of 3D helical spring. A state of a spray-coated film was observed by a scanning electron microscope (SEM). The SEM image showed that the spray-coated PVDF thin film deposition was successfully achieved.

2. Preparation of PVDF film by bar-coating method

2.1. Formation of PVDF film

Spin-coating method is typically employed in MEMS process. However, it was found that the thickness of PVDF film can be controlled only in the range of 5–10 μm by this method. Perhaps because of cracks, spin-coated films with a thickness of 5–10 μm were easily discharged in the polarization process. In order to prevent cracks, it was necessary to obtain a thicker film. As a method for obtaining a thick film, bar-coating method was used.

Figure 1 shows a schematic diagram of the bar-coating method. First, drop the PVDF solution onto substrate and slide the bar coater on spacer to expand the PVDF solution. On the surface of the bar-coater, grooves are provided to obtain a uniform film thickness.

PVDF solution was prepared by dissolving PVDF in methyl ethyl ketone (MEK). A bar coater (Model: 065-2-40 μm, Allgood Corp.) having diameters, lengths, and groove depths of 9 mm,
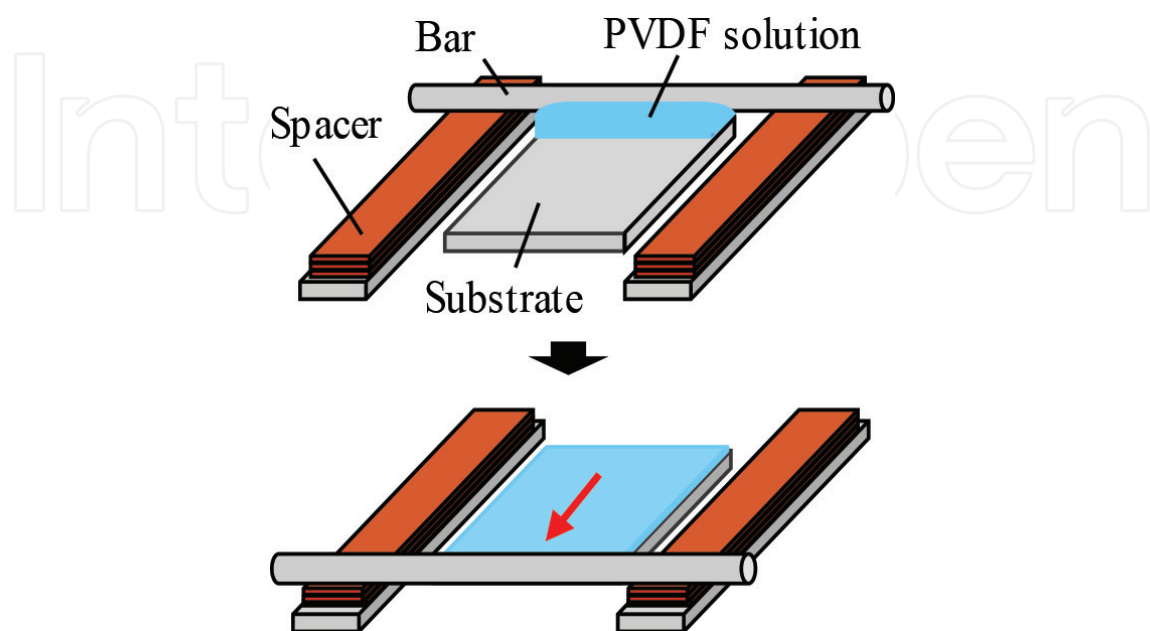

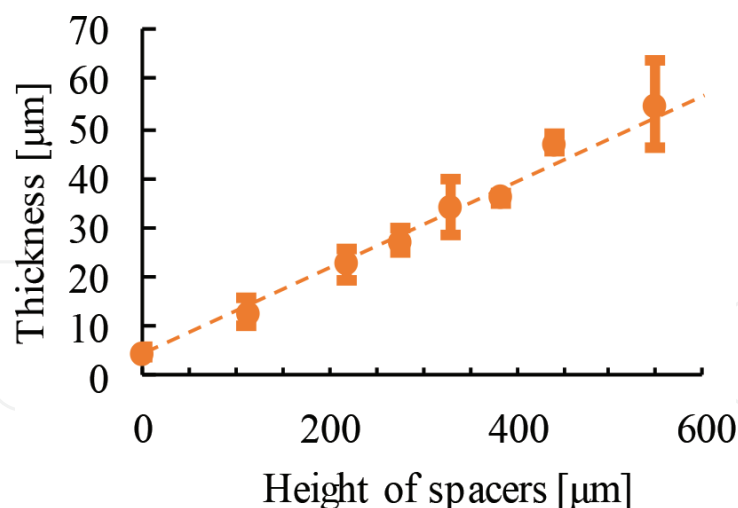**Figure 1.** Schematic illustration of bar-coating method.

Figure 2. Relationship between obtained thickness of bar-coating PVDF film and spacer height.

320 mm, and 40 μm was used in this study. After coating, the substrate was heated on a hot plate at 90°C for 10 min to evaporate the MEK.

In this method, it was possible to control the film thickness to 50 μm by changing the height of spacer while sliding the bar coater. As a result of the measurement, it was found that the thickness of the bar-coated PVDF film linearly increases in proportion to the height of spacer (see **Figure 2**). However, the surface irregularities increased in the case of the film thickness exceeded 30 μm. Considering this, the thickness was decided to set to 30 μm. Namely, the reason for determining the thickness largely depends on the constraints of the film-forming process. In this chapter, bar-coated films with thicknesses of 30 and 12 μm are prepared and used.

2.2. Characterization of properties of bar-coated PVDF film

Figure 3 shows the surface morphology and roughness of obtained PVDF film measured by a stylus-type step profiler (DekTakXT, Bruker Daltonics K.K). The surface waviness was within ±1.5 μm along 25 mm line (see **Figure 3(a)**). The surface roughness (Ra) was estimated as
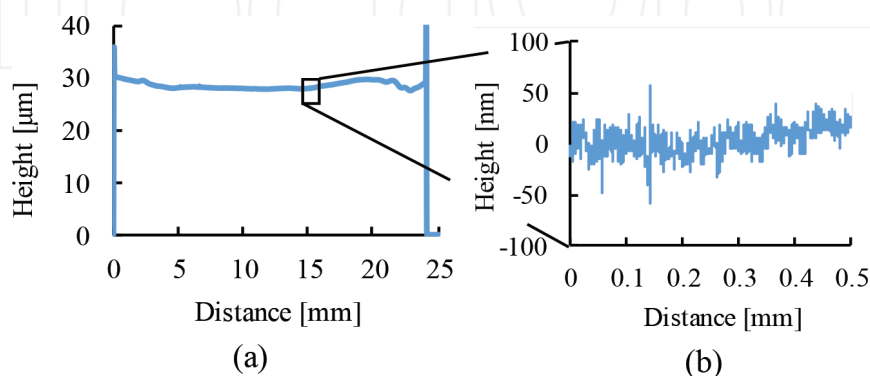

Figure 3. Measurement result by a stylus-type step profiler; (a) surface morphology and (b) surface roughness of PVDF film obtained by bar-coating method.

11 nm using the data shown in **Figure 3(b)**. Observation of the film surface using a scanning electron microscope (SEM) showed no cracks or pinholes of several micrometers.

Residual stress of the PVDF film was measured using a thin-film stress measurement apparatus (FLX—2320—S, Toho technology Corp.). The curvature radius before and after PVDF film formation on a 4-in silicon wafer was measured. A laser beam was scanned along a straight line on the wafer surface; the reflected light was detected to yield a profile of the surface. Using the difference between these radii, the residual stress was calculated as 5 MPa, which is quite low stress compared with usual polymer films [16].
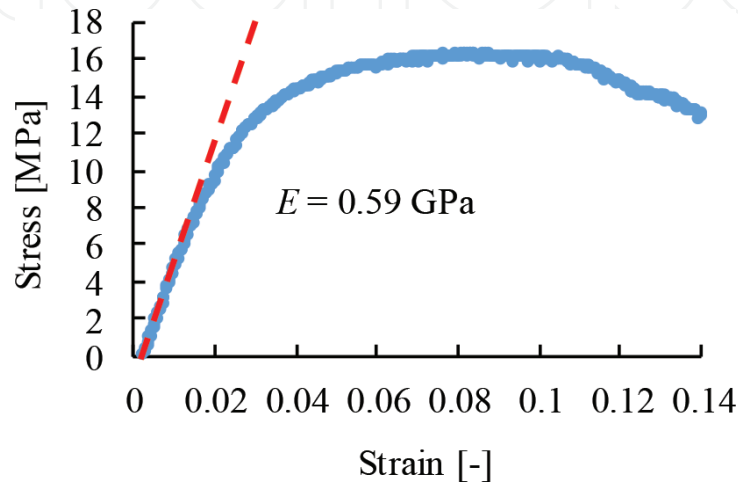

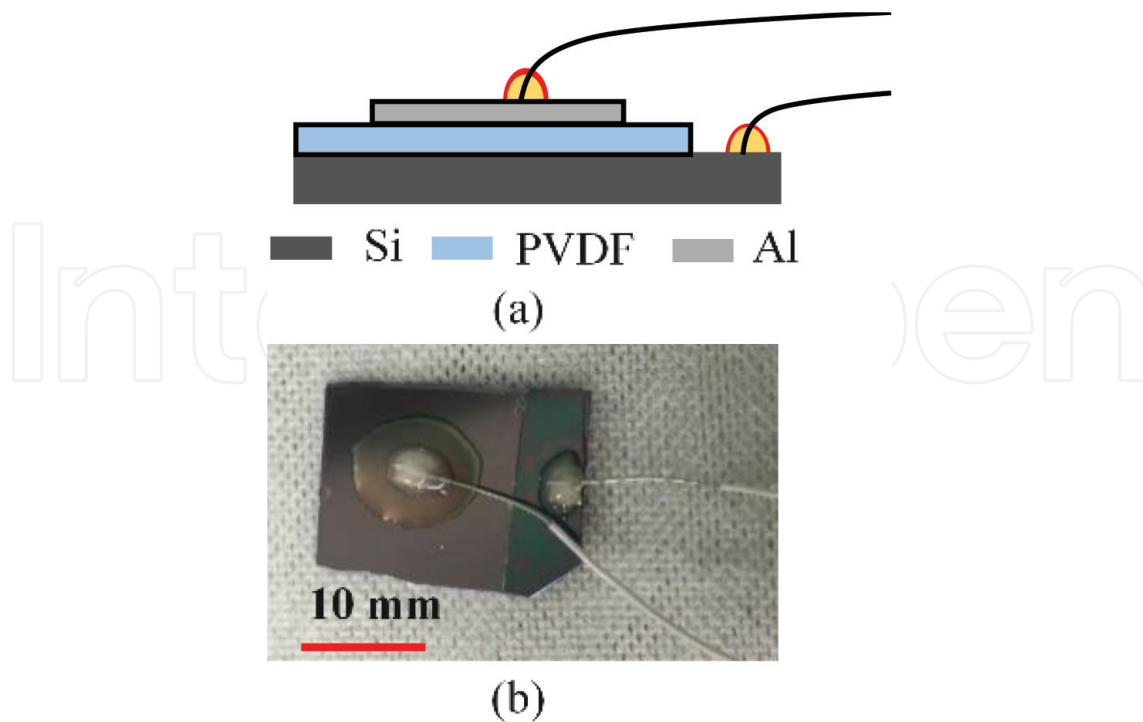**Figure 4.** Stress-strain curve of bar-coated PVDF film.

Figure 5. (a) Schematic illustration and (b) photograph of the test sample to measure *P-E* hysteresis loops.
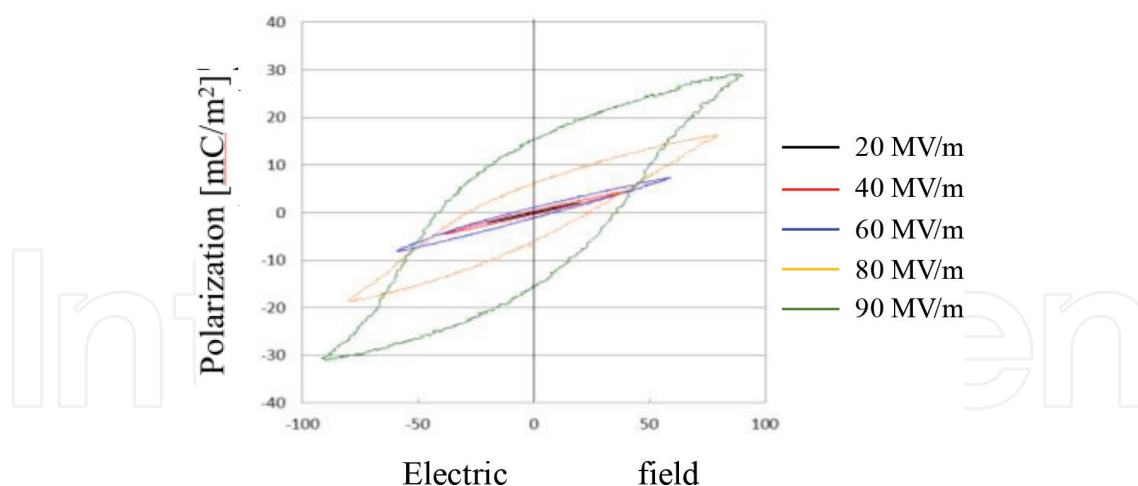
Figure 6. Obtained *P-E* hysteresis loops.

Young's modulus was measured by pulling it physically. The resulting stress-strain curve is shown in **Figure 4**. It has been reported that Young's modulus of bulk PVDF is 1–3 GPa, and that of thin PVDF film is about 0.5 GPa [17, 18]. Therefore, the result of 0.6 GPa calculated by the initial inclination of the curve is considered to be a reasonable value.

Polarization vs. electric field (*P-E*) hysteresis loops for the PVDF film was measured using a Sawyer-Tower circuit. A fabricated test sample was shown in **Figure 5**. PVDF film was formed on a low-resistance silicon substrate (resistivity: 0.2 Ωcm or less) by bar-coating method. Then, aluminum electrode was deposited on PVDF by sputtering, and a lead wire was connected to the electrodes. Electric field was applied by changing it from 20 to 90 MV/m. Obtained *P-E* hysteresis loops were shown in **Figure 6**, which shows good ferroelectricity.

3. Polarization of PVDF film

3.1. Corona polarization method

Following coating a PVDF film, it was polarized by applying high voltage. In early stage of this study, top and bottom electrodes were deposited on PVDF film, then high DC voltage was applied between them for polarizing the film; however, high electric field could not be applied, since discharge often occurred. In almost all cases, the discharge was creeping one, i.e., the route of discharge is on the substrate surface, followed by the route along its side wall to the electrical ground. It indicates that the film itself endures the applied high voltage, i.e., the discharge across the film thickness due to cracks or pinholes does not occur.

In order to solve the discharge problem, charge injection was performed into the PVDF film surface using corona discharge method. In this method, PVDF film was applied high electric field before depositing the top electrode. We call this method as corona polarization. **Figure 7** shows schematic diagram of corona polarization setup. The procedure of this polarization method is as follows: a needle electrode was placed over the center of PVDF film, followed by applying a voltage of −10.0 kV. Distance between the electrode and the test sample was set at 20 mm. Applying time was set for 10 min. In corona polarization, no discharge or any other problems occurred.
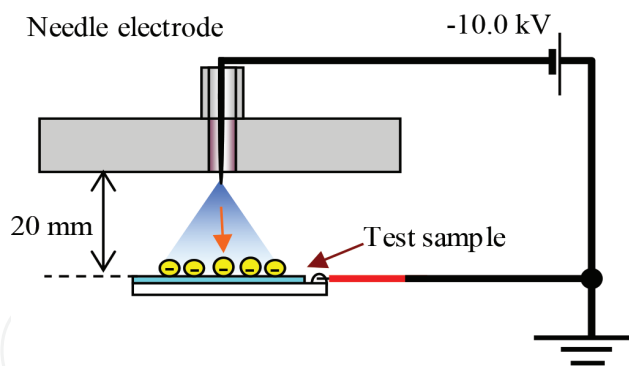
Figure 7. Schematic of corona polarization.

3.2. Characterization of piezoelectric properties

To obtain the information of crystal structure of PVDF film, X-ray diffraction (XRD) analysis was performed. Result of XRD pattern is shown in **Figure 8**. The sharp and narrow peak at 20° indicates the dominant β-phase in PVDF thin film, which is beneficial for the piezoelectric effect. The measured XRD pattern matched well with that of a typical β-phase PVDF film discussed in previous studies [19, 20]. This result shows that bar-coated film had a good crystalline structure.

In order to confirm whether or not the polarized PVDF film has piezoelectricity, the piezoelectric constant d_{33} was measured. The process of fabricating test sample for measuring d_{33} is as follows: As already described in Section 2.1, a PVDF film was prepared on a low-resistance silicon substrate (size: 40 × 30 mm) by bar-coating method. One end of PVDF film was cut, and the lead wire was connected to the exposed low-resistance silicon substrate by a conductive adhesive. The effective area of PVDF film after cutting was 30 mm².

Piezoelectric constant d_{33} of PVDF was measured by an apparatus (product name; d_{33} meter, PIEOTEST Corp.). The center of PVDF film right under the needle electrode is a region where charge injection is easy. On the other hand, the amount of charge decreases as going away from the center of film. In other words, the internal electric field generated in PVDF film depends on the location, and there is a possibility that the PVDF film cannot polarize away from the electrode. In order to investigate the success range of one corona polarization, we
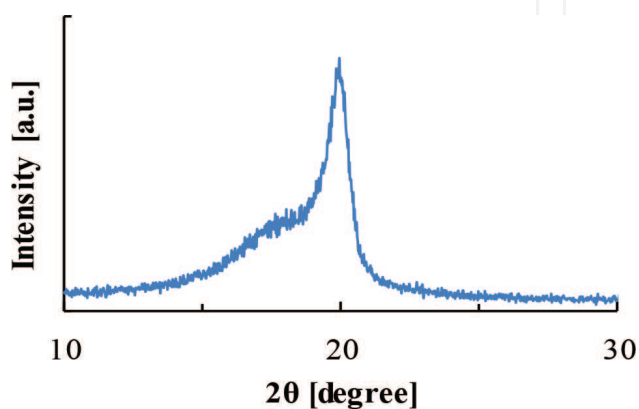

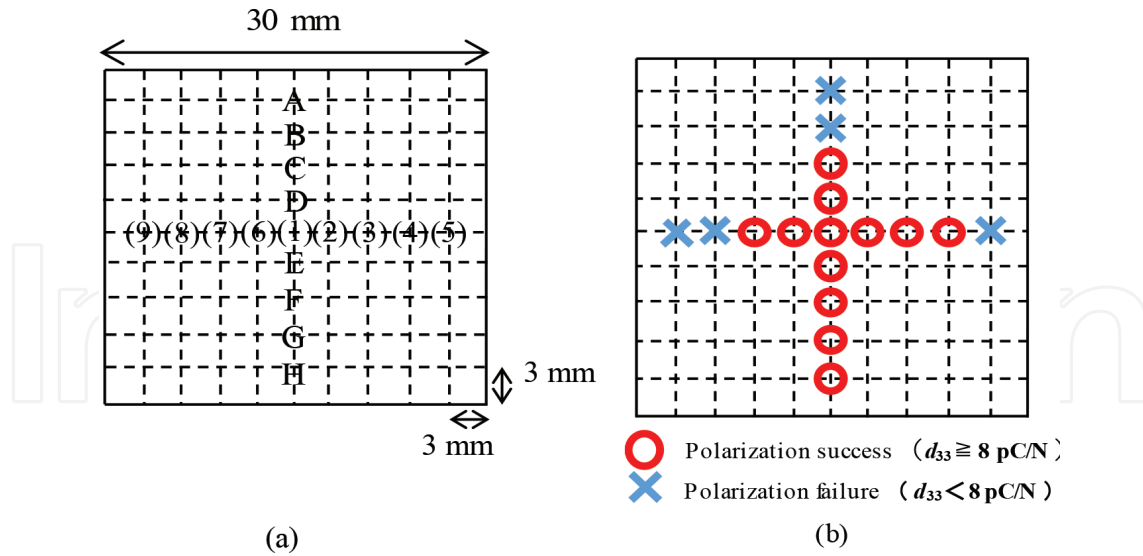**Figure 8.** Result of XRD analysis of bar-coated PVDF.

Figure 9. (a) Measurement points of piezoelectric constant d_{33} and (b) result of success or failure of polarization.

	d_{33} [pC/N]		d_{33} [pC/N]
(1)	-9.93	A	-5.59
(2)	-8.86	B	-7.72
(3)	-10.7	C	-8.01
(4)	-9.81	D	-9.46
(5)	-6.89	E	-10.6
(6)	-10.0	F	-11.2
(7)	-8.85	G	-11.1
(8)	-3.40	H	-8.02
(9)	-3.43		

Table 1. Results of piezoelectric constant d_{33} of the PVDF after corona polarization.

measured d_{33} at 17 points at 3 mm intervals. **Figure 9(a)** shows the distribution of measurement points on PVDF film. About 17 points ((1)–(9) and A–H) were adopted as measuring points. **Table 1** shows measurement result of d_{33}. The maximum value of d_{33} was −11.2 pC/N (see **Table 1**). **Figure 9(b)** shows success or failure of corona polarization at each point. When the value of d_{33} was greater than or equals to 8 pC/N, we considered that polarization was successful, otherwise, we considered that polarization was failed. Success range of one corona polarization was within the circle, of which diameter was approximately 15 mm. In the outside area, sufficient piezoelectricity was not achieved.

The resistivity of low-resistance silicon is higher than typical metals, and it may affect the piezoelectricity of PVDF films. We verified the effects of material difference in bottom electrode on piezoelectricity. The d_{33} of PVDF film of 30 and 12 μm in thickness coated on phosphor bronze ($2–6 × 10^{-6}$ Ωcm [21]) was −8.5 pC/N and −10.1 pC/N (see Section 4.1 below), while that was approximately −10 pC/N (distributing among sampling points) on a low-resistance single crystal Si (0.2 Ωcm or less).

Considering these results, although the data is limited, the material of substrate, e.g., the resistivity of substrate, does not affect so much on the piezoelectricity of PVDF film.

4. Fabrication of piezoelectric cantilever-type VEHs

4.1. Preparation of PVDF film for VEHs

PVDF film was formed on a rectangular phosphor bronze plate by bar-coating method. The size of phosphor bronze plate was 35 mm in length, 15 mm in width, and 0.1 mm in thickness. Phosphorus bronze was adopted due to its good spring characteristics. We fabricated two VEHs with different PVDF thicknesses; one is 30 μm (called sample 1) and the other is 12 μm (called sample 2). The dimensions of these samples are shown in **Table 2**.

After forming PVDF film, a lead wire was connected to phosphor bronze plate to perform corona polarization. The conditions of corona polarization were same as described in Section 3.1. In order to securely polarize the entire surface of the PVDF film, corona discharges were performed at six points at intervals of 5 mm (see **Figure 10**).

PVDF thickness sample1	30 μm
PVDF thickness sample2	12 μm
Phosphor bronze thickness	100 μm
Cantilever length	25 mm
Cantilever width	15 mm
Electrode length	22 mm
Electrode width	10 mm

Table 2. Dimensions of cantilever VEH device.

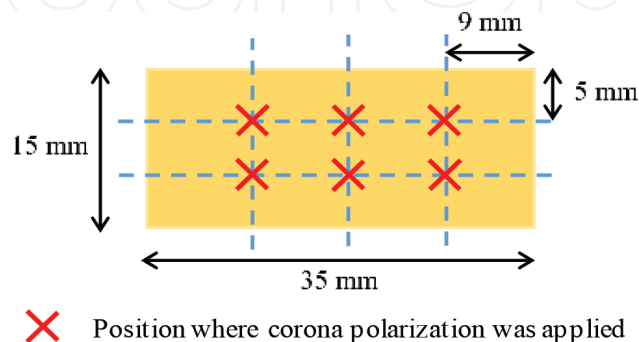✗ Position where corona polarization was applied

Figure 10. Schematic of points where corona polarization was applied.

After polarization, d_{33} of these PVDF films was measured. The average measured values of d_{33} of polarized PVDF thin films were −8.5 pC/N (sample 1) and −10.1 pC/N (sample 2), respectively. For comparison, d_{33} of PVDF, which was not treated with polarization, was −0.87 pC/N. These values (−8.5 pC/N and −10.1 pC/N) are not bad compared with the typically reported values (−10 to −20 pC/N) [22]. The difference of d_{33} between −8.5 and −10.1 pC/N may be caused by the thickness difference. However, considering only the difference in electric field due to thickness, the difference would be large. It is difficult to identify the reason at present.

In this study, PVDF film operates in d_{31} mode. It is reported that d_{31} of PVDF film is approximately 70% of its d_{33} [23, 24]. Considering that d_{33} of our PVDF film is approximately 10 and it is the same order as other reported values, d_{31} is not bad.

An aluminum upper electrode was deposited on PVDF film by sputtering. The size of electrode was 30 mm in length, 10 mm in width, 0.3 μm in thickness. A capacitance of the prepared VEHs was measured with an LCR meter (E4980A, Agilent Technology). The capacitance and loss tangent were measured at frequencies from 1 kHz to 2 MHz. The measurement results are shown in **Figure 11**. The electrostatic capacity of VEHs were 1.6 nF (sample 1) and 1.8 nF (sample 2) at 1 kHz, respectively. The calculated dielectric constants were approximately 16 and 10, respectively. These dielectric constants are in the same order as the reported values such as 13 at 1 kHz [25]. Loss tangents were 0.013 (sample 1) and 0.021 (sample 2) at 1 kHz, respectively. These values are equivalent to the previous reported PVDF film properties [26].

4.2. Vibration test and power generating result

One end of the plate was clamped by a fixture to form a cantilever. A proof mass (m = 0.2 g) was attached to the other end. Effective length of clamped cantilever was 25 mm. **Figure 12** shows a schematic illustration and photograph of fabricated cantilever VEH.

Figure 13 shows measurement setup of vibration test. Fabricated VEH was mounted on a vibration generator (PET-05, IMV Corp.). Lead lines between top and bottom electrodes were connected to the external load resistance R, which is composed of a fixed resistance (100 kΩ) and a variable resistance (from 0 to 9 MΩ) in series. A laser displacement meter was used
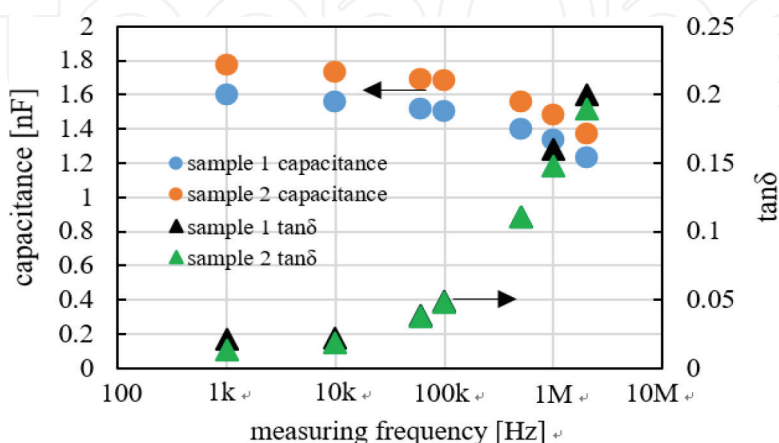

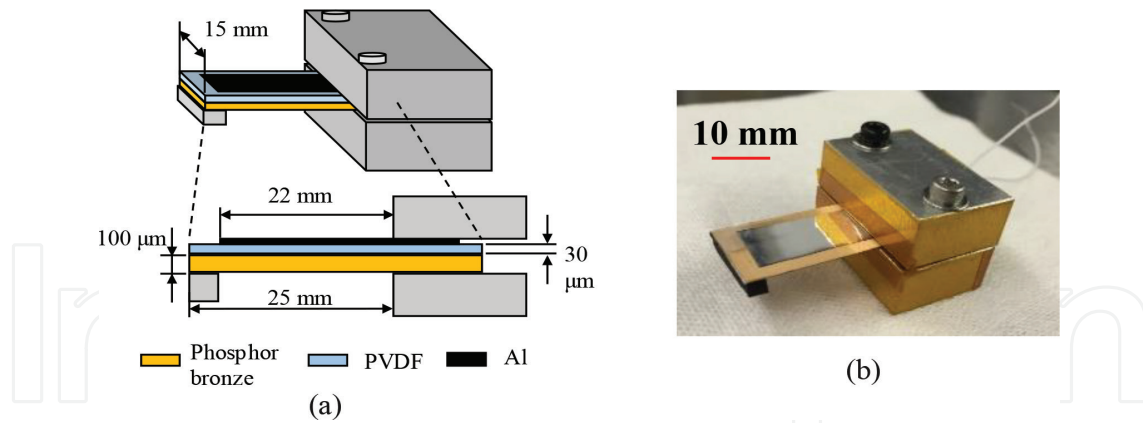**Figure 11.** Capacitance and loss tangent of the VEH device.

Figure 12. (a) Schematic illustration and (b) photograph of VEH using bar-coated PVDF film on phosphor bronze cantilever.
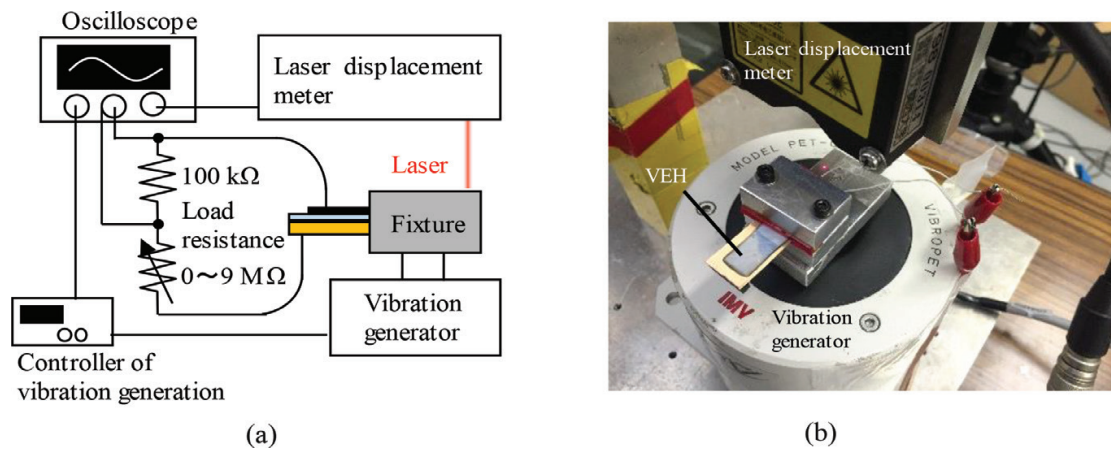

Figure 13. (a) Schematic illustration and (b) photograph of experimental setup for verifying power generation for free vibration.

for determining the acceleration. Output voltage $V(t)$ generated at the load resistance was measured by an oscilloscope. Output power P was calculated by Eq. (1).

$$P = \frac{\int p(t)\,dt}{T},$$ (1)

where $p(t) = V(t)^2/R$, T is the period. By changing R from 0.1 to 9.1 MΩ at intervals of 1 MΩ, the optimal value was searched.

Acceleration and frequency of vibration were set to 17 m/s^2 and 55 Hz (it is the resonant frequency of the cantilever), respectively. At the same time, state of vibrations was taken using a high-speed camera (Memrecam fx-k5, Nac Corp.). In this vibration conditions, half amplitude of the free end of cantilever was approximately 6 mm, as shown in **Figure 14**.

Measurement result of the vibration test is shown in **Figure 15**. Maximum output of 4.3 μW was achieved at $R = 2.1$ MΩ in case of sample 1. Looking at this result, the thicker PVDF film is, the higher output power is obtained. The reason is considered as follows: in the thicker
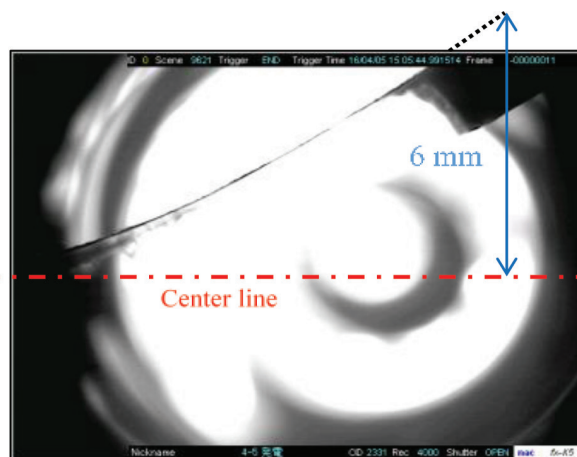
Figure 14. Image of the vibration of the VEH taken by high-speed camera.
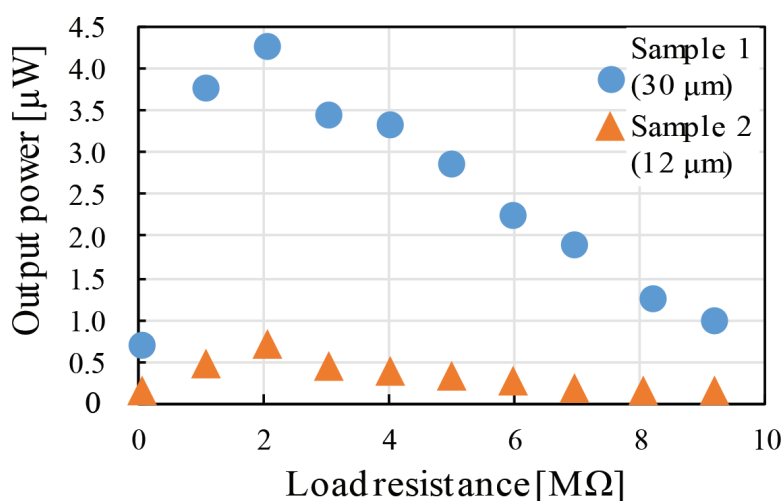

Figure 15. Output power vs. load resistance for free oscillation at 17 m/s², 55 Hz.

PVDF film of VEH (sample 1), the distance between neutral axis and PVDF film is greater than that in the thinner PVDF film of VEH (sample 2). Therefore, stress and strain induced on the PVDF film of sample 1 are higher than those of sample 2. In simple and approximately calculation, the 30/12 = 2.5 times larger strain would lead to 2.5² = 6.25 times larger output power. Looking at **Figure 15**, the peak power of sample 1 is 4.3 μW and the peak power of sample 2 is 0.7 μW; the former is 6.1 times larger than the latter, which agrees with the calculation.

Table 3 shows the performance of our VEH and comparison with other cantilever-type piezoelectric VEHs. According to the reports by Kanno et al., the output of their VEHs composed of ceramic PZT film achieved 1–17 μW [6–10]. However, the vibration frequency of power generating test was 108–890 Hz. This value is higher than our VEH. Considering that the theoretical output power is proportional to the square of frequency, our VEH composed of piezoelectric polymer PVDF film shows performance equivalent to that of other VEHs using ceramic PZT.

Although piezoelectric constant of PVDF is lower than PZT [27], we could obtain equivalent power. This is caused by large deformation due to flexible polymer PVDF, which increases power generation [28].

	Piezoelectric material	Effective volume [mm³]	Frequency [Hz]	Acceralation [m/s²]	Out put power [μW]	Power density [μW/mm³]
I. Kanno[8]	PZT	0.2	344	25	2.5	12.5
Sung Sik Won [11]	KNN	2	132	9.8	3.62	1.8
G. Tang [12]	PMN-PT	0.6	237	19.6	5.93	9.83
Z.Cao [28]	AlN	1.7	69	15.7	8.7	5.18
Q.Wang [29]	PZT	4.3	89	9.8	15.4	3.62
This study	PVDF	6.6	55	17	4.3	0.65

Table 3. Comparison of VEHs performance.

5. Spray-coating method

5.1. Spray-coating equipment

To coat PVDF thin film onto the 3D surface, spray-coating method was carried out. **Figure 16** shows the setup of spray-coating equipment (Ushio Mechatronics, Inc.: USC-2114SM-ANG) used for this study. The spray nozzle was set in the chamber facing down toward a work stage. A sample was placed on the stage, which was computationally controlled to move at a constant speed of 60 mm/s. The sample was fixed on the stage by a vacuum chucking. The stage moves under the spray nozzle so as to draw a zigzag course repeatedly (240 times), allowing uniform PVDF coating on the sample. The PVDF solution and N_2 gas (pressure: 0.4 MPa) were supplied to the nozzle through individual tubes, and these fluids were physically mixed in it, followed by sprayed in the form of circular cone having tip angle of 24° (see **Figure 16**). Flow rate was controlled at 60 g/h using a mass flow controller. The distance between the nozzle and the work stage was set to be 45 mm. The total time of spray-coating process was 20 min.

There are several parameters to be set for spray-coating method [29]. These parameters have a complex effect on film properties to each other. Among the parameters, in this study, the kind
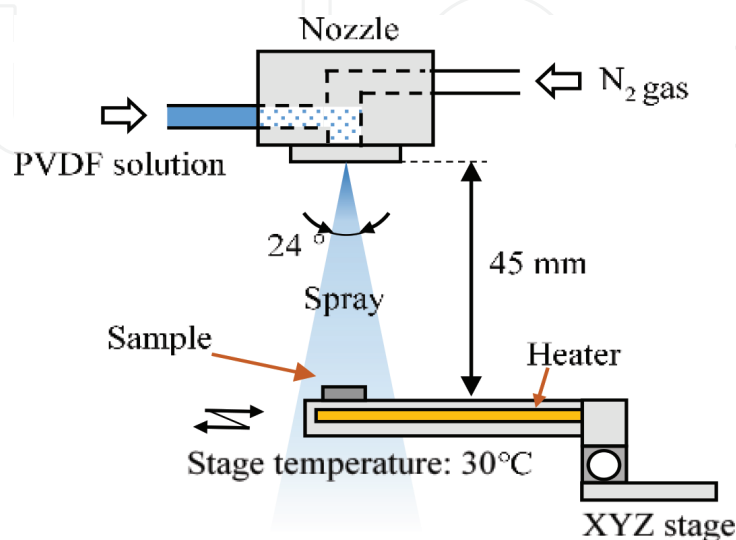

Figure 16. Schematic illustration of the setup of spray-coating equipment.

of organic solvent of diluting PVDF and its dilution rate were changed and examined. The other parameters such as flow rate were set at default values as mentioned above.

5.2. PVDF thin-film formation by spray-coating method

PVDF solution which is already dissolved by vendor in 24 wt% with methyl ethyl ketone (MEK) was used. However, this solution cannot be used for spray coating because of its high viscosity. To adjust the concentration of PVDF, the original PVDF solution was further diluted with organic solvent in addition [30].

At first, PVDF solution was diluted with additional MEK and spray-coated on flat surface of a silicon substrate. The concentration of PVDF after additional dilution was as follows: (a) 1.2 wt%, (b) 1.8 wt%, (c) 2.4 wt%, and (d) 3.0 wt%. After spray coating, PVDF thin film was baked at 90° on a hot plate for 10 min to evaporate the organic solvent (MEK) completely.

The thickness and surface morphology were measured using a contact-type stylus step profiler. To measure the thickness, a part of PVDF thin film on a silicon substrate was cut and a level difference was provided.

Figure 17 shows results of measuring surface morphology with surface roughness (R_a) on each condition. Surface roughness R_a was calculated from the following equation:

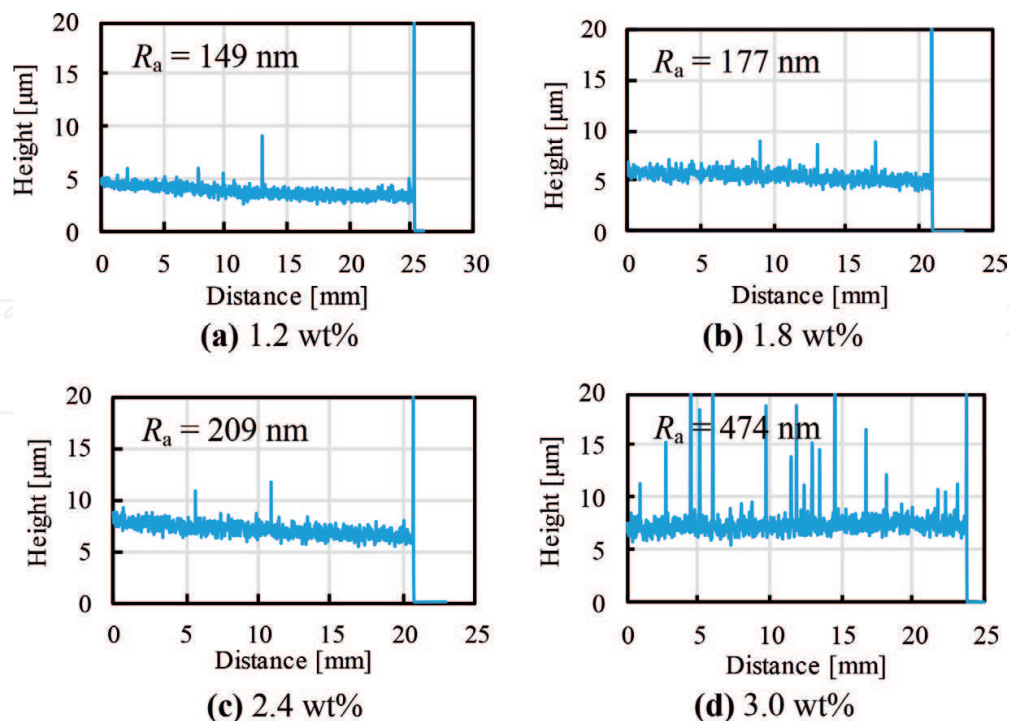$$R_a = \frac{1}{L} \int_0^L |y(x)|dx \qquad (2)$$

Figure 17. Surface morphology and roughness of spray-coated PVDF thin films measured by a stylus step profiler. Weight ratio of PVDF to total weight varies for each sample.

where L is the evaluation length and $y(x)$ is the height along x direction. These measurement results showed that the higher concentration of PVDF, the thicker PVDF film was obtained. However, as the concentration of PVDF increases, surface roughness R_a increases. In case of condition (d) 3.0 wt%, many particles of which size is approximately 10 μm were observed. Several particles were also observed under other conditions. **Figure 18** shows a SEM image in case of condition (c) 2.4 wt%, in which many particles are observed. They may be PVDF particles generated by the spray-coating process. The drying speed of solvent of diluting PVDF may affect generating particles. In case of only using MEK as diluting solvent, PVDF is sprayed to the sample in a solid state. It is because the boiling point of MEK is low, which promotes its evaporation before arriving at the sample. These particles of generating several micron surface roughness may produce bad effects on the electrode formed on PVDF film. Since the electrode thickness is usually less than 1 μm, the particles may cause the crack of electrode, which leads to the reduction of effective electrode area. Improving the surface condition of spray-coated film is future study.

5.3. Spray-coating PVDF on 3D surface

PVDF solution was spray-coated on a helical compression spring. A helical spring was adopted because it can be largely deformed. Since PVDF can easily follow the deformation of helical spring due to its flexibility, high output power is expected. The material of spring was stainless (SUS304), and its size is as follows: free length: 4.3 mm; coil diameter: 2.16 mm; and wire diameter: 0.16 mm.

Figure 19(a) shows the schematic of the setup of spray coating for 3D helical spring. **Figure 19(b)** shows a SEM image of spray-coated PVDF thin film coated on it. The SEM image shows that the PVDF film was formed even on the bottom side of helical spring, showing that the PVDF solution was spray-coated omnidirectionally in this case. Eventually, PVDF thin
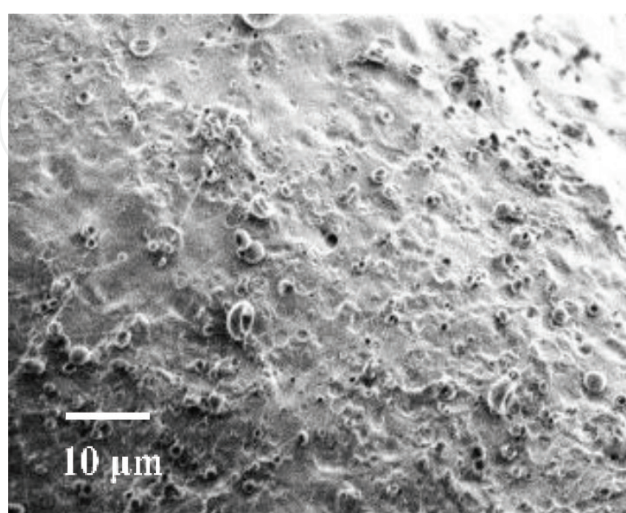

Figure 18. A SEM image of the surface of spray-coated PVDF thin film formed by the condition (c).
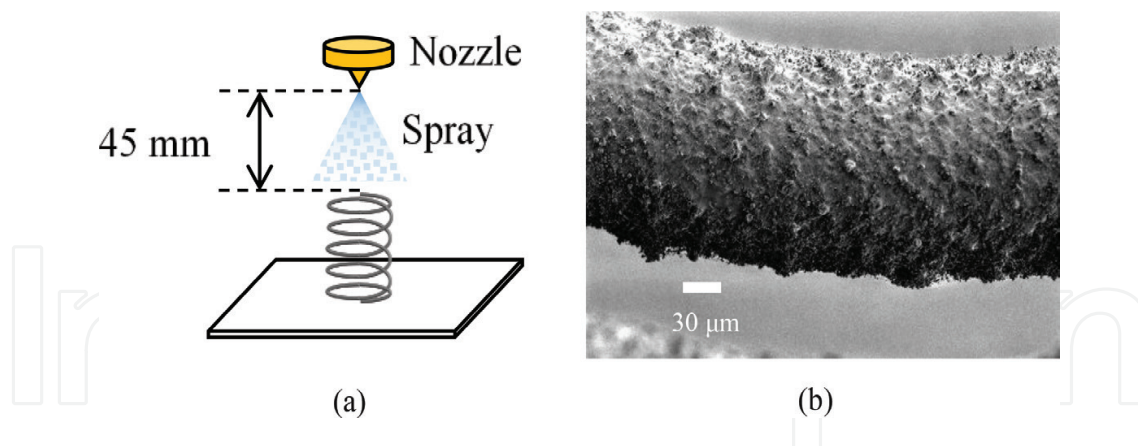
Figure 19. (a) Setup of spray coating for helical spring and (b) a SEM image of the surface of PVDF thin film.

film deposition to the helical spring was successfully achieved. Energy harvesters composed of PVDF-coated 3D spring such as helical spring will be fabricated in the future.

6. Conclusion

PVDF film was formed by bar-coating method and characterized its mechanical and piezo-electric properties. A cantilever-type vibration energy harvester (VEH) made of a PVDF film was fabricated on a phosphor bronze rectangular plate. The dimensions of the cantilever were 25 mm in length and 15 mm in width. After corona polarization, the piezoelectric constant d_{33} of PVDF was calculated to be −8.5 pC/N and −10.1 pC/N at 30 and 12 μm thickness, respectively. As a result of the vibration test, the maximum output at $R = 2.1$ MΩ was 4.3 μW in case of the device with a thickness of 30 μm, which was the same performance as other cantilever-type VEH using ceramic piezoelectric PZT. PVDF is a flexible material and it was able to generate large strain due to flexibility of the device.

The thickness of PVDF film and corona polarization condition should be optimized for improving piezoelectric constant of PVDF film. Optimizing the structure of VEH should be done using MEMS technology in the future.

PVDF thin film was formed by spray-coating method. PVDF thin film was deposited on a 3D surface by spray coating. A helical compressing spring was adopted. The deposition on it was successfully achieved. However, surface conditions of it are currently not good. Improving the surface conditions of PVDF film and its application to a power-generating device are ongoing works.

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References

[1] Beeby SP, Tudor MJ, White NM. Energy harvesting vibration sources for microsystems applications. Measurement Science and Technology. 2006;**17**(12):175-195

[2] Matsumoto K, Saruwatari K, Suzuki Y. Vibration-powered battery-less sensor node using MEMS electret generator. Digest Tech. Power MEMS'11. 2011:134-137

[3] Hosokawa S, Hara M, Oguchi H, Kuwano H. Vibration based energy harvester employing ZnO film on the stainless steel substrate. IEEJ Transactions on Sensors and Micromachines. 2013;**133**(4):126-127

[4] Liu JQ et al. A MEMS-based piezoelectric power generator array for vibration energy harvesting. Microelectronics Journal. 2008;**39**(5):802-806

[5] Roundy S, Wright PK. A piezoelectric vibration based generator for wireless electronics. Smart Materials and Structures. 2004;**13**(5):1131-1142

[6] Tsujiura Y, Adachi K, Kanno I. Piezoelectric MEMS energy harvesters of PZT thin films on stainless steel cantilevers. PowerMEMS'12. 2012:500-503

[7] Kanno I, Morimoto K, Wasa K, Kotera H. Energy harvester of c-axis oriented epitaxial PZT films on stainless steel sheets. IEEJ Sensors and Micromachines. 2009:594-597

[8] Kanno I, Sagawa K, Oka R, Kotera H, Ogawa J, Yamauchi N, Aizawa K, Matsushima T. Piezoelectric energy harvesters of PZT films deposited on titanium cantilevers. Power MEMS'10. 2010:379-382

[9] Kanno I, Kotera H, Shibata K, Mishima T. Characterization of vibration energy harvesters composed of piezoelectric thin films. The Japan Society of Mechanical Engineers Micro-Nano Science & Technology Division. 2011:26-27

[10] Tsujiura Y, Suwa E, Kurokawa F, Hida H, Kanno I. Reliability of vibration energy harvesters of metal-based PZT thin films. Power MEMS'14. 2014:557

[11] Won SS et al. Lead-free Mn-doped $(K_{0.5}Na_{0.5})NbO_3$ piezoelectric thin films for MEMS-based vibration energy harvester applications. Applied Physics Letters. 2016;**108**:232908

[12] Tang G et al. Piezoelectric MEMS low-level vibration energy harvester with PMN-PT single crystal cantilever. IET Electronics Letters. 2012;**48**(13):784-786

[13] Toprak A, Tigli O. MEMS scale PVDF-TrFE-based piezoelectric energy harvesters. Journal of Microelectromechanical Systems. 2015;**24**(6):1989-1997

[14] Sasaki M et al. Heating effect on photoresist in spray coating technique for three-dimensional lithography. Japanese Journal of Applied Physics. 2003;**42**(Part 1, No. 6B): 4027-4030

[15] Fujitsuka N et al. Monolithic pyroelectric infrared image sensor using PVDF thin film. Sensors and Actuators A. 1998;**66**:237-243

[16] Oh SR et al. Residual stress in piezoelectric poly(vinylidene-fluoride-co-trifluoroethylene) thin films deposited on silicon substrates. Thin Solid Films. 2010;**519**(4):1441-1444

[17] Choi M et al. Mechanical and electrical characterization of PVDF-ZnO hybrid structure for application to nanogenerator. Nano Energy. 2017;**33**:462-468

[18] Porter DA et al. Effects of in-situ poling and process parameters on fused filament fabrication printed PVDF sheet mechanical and electrical properties. Additive Manufacturing. 2017;**13**:81-92

[19] Liu W, et al. Fabrication of Spiral-Shaped PVDF Cantilever Based Vibration Energy Harvester. In: Proc. IEEE, Nano/Micro Engineered and Molecular Systems; 2014. pp. 458-461

[20] Choi SB et al. Measurement of flexoelectric response in polyvinylidene fluoride films for piezoelectric vibration energy harvesters. Journal of Physics D: Applied Physics. 2017;**50**:075502

[21] Hakko co., Ltd. Available from: http://www.hakko.co.jp/qa/qakit/html/h01100.htm

[22] Furukawa T, Goho T, Date M, Takamatsu T, Fukada E. Piezoelectricity of corona-poled poly (vinylidene fluoride). Kobunshi Ronbunshu. 1979;**36**(10):685-688

[23] Measurement Specialties Inc. Piezo Film Sensors, Technical Manual. Online Available. Available from: http://www.meas-spec.com

[24] Dargahi J. A piezoelectric tactile sensor with three sensing elements for robotic, endoscopic and prosthetic applications. Sensors and Actuators. 2000;**80**:23-30

[25] Sasaki Y et al. Correlation between different crystal structures and physical properties of PVDF films fabricated by solvent casting from a single solvent. Kobunshi Ronbunshu. 2013;**70**:489-495

[26] Jain A et al. Dielectric behaviour of PVDF thin films. Indian Journal of Advances in Chemical Science. 2014;**2**(3):212-216

[27] Tanaka T, Murakami S, Uno M, Yamashita K. Development of MEMS ultrasonic sensor using P(VDF/TrFE) thin films. IEEJ Transactions on Sensors and Micromachines. 2015;**135**(5):145-151

[28] Cao Z, Zhang J, Kuwano H. Design and characterization of miniature piezoelectric generators with low resonant frequency. Sensors and Actuators A: Physical. 2012;**179**:178-184

[29] Wang Q, Cao ZP, Kuwano H. Metal-based piezoelectric energy harvesters by direct deposition of PZT thick films on stainless steel. Micro & Nano Letters. 2012;**7**(12):1158-1161

[30] Sasaki M et al. Spray coating of photoresist for three dimentional micromachining. IEEJ Transactions on Sensor and Micromachines. 2002;**122**(5):235-243