THE PIEZOELECTRIC PZT THIN FILMS DEPOSITED ON METAL SUBSTRATES

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Abstract. In this study, we deposited PZT thin films directly on various kinds of metal substrates by rf-magnetron sputtering, and measured their crystal structure, and ferroelectric and piezoelectric properties. We used metal substrates of austenitic stainless steel (ASS), ferritic stainless steel (FSS), Ti, Ni, Zr and W for the PZT deposition. From the x-ray diffraction (XRD) measurements, we confirmed the PZT thin film was directly grown on each substrate with a perovskite phase. The dielectric constant of the PZT thin films showed obvious dependence on the coefficient of thermal expansion (CTE) of substrates. This result suggests that the dielectric constant, which is one of the important parameters for the piezoelectric vibration energy harvesters (PVEHs), can be controlled by the CTE of the substrates. The PZT film deposited on the FSS showed the best piezoelectric coefficient $e_{31,f}$ of -2.4 [C/m²], which was comparable to that of the PZT film formed on the platinum-coated metal substrates.

1. Introduction
Recently, many researches have reported piezoelectric thin-film devices to realize new functional micro-devices beyond the limitation of conventional MEMS. The PZT thin films have been the most popular piezoelectric thin films among piezoelectric MEMS including piezoelectric vibration energy harvesters (PVEHs). The PZT thin films are generally deposited on Pt-coated Si mainly because of the compatibility with MEMS fabrication process. On the other hand, from the viewpoint of the application to PVEHs, metal substrates are much more preferable than Si because of not only higher toughness for the large and long-term vibration, but also low cost. However, the deposition of Pt bottom electrodes on metal substrates causes the longer deposition process as well as increase the device cost. Therefore, direct deposition of the PZT thin films on metal substrates are preferable for the practical application of PVEHs. However, systematic study on the dependence of kinds of substrates has not been reported so far. In this study, we prepared the PZT thin films directly on a variety of metal substrates by rf-magnetron sputtering and evaluated their piezoelectric properties for the applications to PVEHs.

2. Deposition of PZT thin films
We prepared 2.5 μm-thick PZT thin films on the both sides of 50 μm-thick metal foils. We selected six different metal substrates; austenitic stainless steel (ASS), ferritic stainless steel (FSS), Ti, Ni, Zr and W for PZT depositions. The PZT thin films were deposited at the substrate temperature of around 600°C. In order to complete the crystallization to perovskite phase, post annealing was conducted for an hour at 650°C. Subsequently, the Pt top electrode was prepared. Crystalline structure of the PZT thin film on
each metal substrate was examined by X-ray diffraction (XRD) measurement. Fig. 1 shows the XRD patterns of PZT thin films directly deposited on metal substrates. The measurement results indicated that polycrystalline PZT thin films with perovskite structure were successfully prepared on each metal substrate without Pt bottom electrode. Furthermore, the PZT thin films on ASS and FSS substrates were strongly oriented along c axis. Fig. 2 shows the cross-sectional image of the PZT thin film on FSS substrate. We confirmed the dense PZT thin films were grown on the FSS metal foils. Similar cross-sectional structures were observed in the PZT thin films on the other metal substrates.

3. Electric characteristics

3.1 Ferroelectric and dielectric properties

We measured ferroelectric properties of the PZT thin films using a Sawyer-Tower circuit and P-E hysteresis curves are shown in Fig. 3. The PZT thin films showed good ferroelectricity except the PZT on Zr substrates. We measured dielectric properties and results are listed in Table 1. Relative dielectric constant ranges from 180 to 421. Dielectric loss of the PZT thin films on the W substrate was as high as 34.8 %, while that of the PZT thin films on the other substrate was lower than 10 %.

The relationship between dielectric constant and coefficient of thermal expansion (CTE) is plotted in Fig. 4. The CTE of PZT thin film is 6.7 ppm/K [1], therefore the PZT thin films would have compressive stress except that on W substrates. Relative dielectric constant of the PZT thin film on the Ti substrates showed the highest values, probably because the CTE of Ti is close to that of PZT and compressive
stress of the PZT would be the lowest among them. These results suggest that the dielectric properties can be adjusted by the internal stress of the PZT thin films from the metal substrates.

### 3.2 Piezoelectric property

We fabricated 13 mm long bimorph cantilevers of PZT films on ASS, FSS and Ni metal substrates and evaluated the piezoelectric coefficient $e_{31,f}$ from the tip displacement by applying voltage to one side of the PZT layers as unimorph cantilevers. The tip displacement of the cantilevers as a function of applied voltage is shown in Fig. 5. The piezoelectric constant $e_{31,f}$ were calculated from the following equation [2].

$$e_{31,f} = \left[ \frac{h_s^3}{6} \left( \frac{Y_s}{1 - \nu_s} - \frac{Y_p}{1 - \nu_p} \right) \right] \cdot \left( \frac{Y_p h_p + Y_s h_s}{2Y_p h_p^3 + (Y_s + 2Y_p) h_p^2 h_s + Y_s h_p h_s^2} \right) \cdot \left( \frac{h_p}{V} \right) \cdot \frac{2\delta}{x(2l - x)} \quad (1)$$

where $h_p$, $Y_p$, and $Y_s$ are the thickness, Poisson’s ratio and Young’s modulus of piezoelectric layers; $h_t$, $\nu_t$, and $Y_t$ are the thickness, Poisson’s ratio and Young’s modulus of a metal substrate; $s_{11}^{pe}$ and $s_{12}^{pe}$ are elastic compliance of piezoelectric layers; $x$, $l$, $\delta$ and $V$ are the length of the top electrode, the length of

| Table 1. Properties of PZT thin films on metal substrates. |
|---------------------|-----|--------|-----|--------|-----|
| Capacitance[pF]     | ASS | FSS    | Ti  | Ni     | W   |
| Dielectric loss     | 0.102 | 0.104  | 0.116 | 0.036   | unmeasurable |
| Area of electrode [mm²] | 0.218 | 0.198  | 0.197 | 0.224   | 0.206 |
| Relative dielectric constant | 192 | 348    | 421  | 197    | 180 |
| CTE [ppm/K]         | 17.3 | 10.4   | 8.5  | 13.3    | 5.9  | 4.3 |

![Figure 3. P-E hysteresis loops of PZT thin films on (a) ASS, (b) FSS and (c) Ni substrate.](image)

![Figure 4. Relationship between dielectric constant and coefficient of thermal expansion.](image)
cantilever, applied displacement to the cantilever and output electric voltage, respectively. The piezoelectric constant $e_{31,f}$ of PZT films on ASS, FSS and Ni substrates were calculated to be about -1.5, -2.4, -0.67 C/m$^2$, respectively. Those values are almost comparable with those of PZT thin films deposited on Pt-coated metal substrates [3].

4. Conclusions
In this study, we measured crystalline orientation, ferroelectric and electrical properties of PZT thin films which were directly deposited on metal-foil substrates. We successfully prepared the high-quality PZT thin films directly deposited on a variety of metal foils. We selected six kind of metal substrates; austenitic stainless steel (ASS), ferritic stainless steel (FSS), Ti, Ni, Zr and W for PZT depositions. The PZT thin films showed good ferroelectricity except that on Zr substrates. The relative dielectric constant of PZT thin films was ranged from 180 to 421, and it strongly depended on the CTE of substrates. The PZT film deposited on the FSS showed the best piezoelectric coefficient $e_{31,f}$ of -2.4 C/m$^2$, which was comparable to that of the PZT film formed on the platinum-coated metal substrates.

References
[1] Hong E, Smith R, Krishnaswamy S V, Freidhoff C B. and Trolier-McKinstry S 2006 Thin Solid Films 510 213
[2] Hida H, Hamamura T, Nishi T and Tan G 2017 Jpn J Appl Phys 56 10PF08
[3] Nishi T, Ito T, Hida H and Kanno I 2016 J Phys Conf. Ser. 773 012062

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