Crystallographic investigation of aluminium nitride thin films on stainless steel foil for highly efficient piezoelectric vibration energy harvesters

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Abstract. This study reports piezoelectric properties and crystallographic microstructures of aluminium nitride (AlN, wurtzite structure) thin films on 50 μm thick stainless steel foil. The transverse piezoelectric coefficient $d_{31,f}$ and $e_{31,f}$ of 10 μm thick AlN films were estimated as $-1.42 \pm 0.08 \text{ pm/V}$ and $-0.48 \pm 0.03 \text{ C/m}^2$ from a tip displacement of the piezoelectric cantilevers. Dielectric constant $\varepsilon_{33}$ was measured as 10.5 ± 1.0. An electron beam diffraction pattern by a high-resolution transmission electron microscope and x-ray diffraction pattern showed that abundance ratio of the orientation such as <101>, <102> and <103> of AlN crystal on stainless steel foils increased with increasing thickness.

1. Introduction
Recently, there have been growing research and development activities of a power source of MEMS-based wireless sensor modules. Aluminium nitride (AlN) films are expected to be the most attractive piezoelectric material due to relatively high electromechanical coupling coefficient and no environmental pollution in comparison with lead zirconate titanate [1]. A structural layer constitution of AlN on stainless steel foil (SUS304) which features high fracture toughness in contrast to Si-based MEMS is useful for mm-scale MEMS applications. And it also has the advantage of process compatibility based on a traditional mass-production technology. Therefore, we have been developing the piezoelectric vibration energy harvesters using AlN/ SUS304 foil [2].

In this study, piezoelectric properties of AlN thin films on SUS304 foil deposited by reactive RF-magnetron sputtering were measured from a tip displacement of the cantilevers. And the crystalline structure was investigated using a x-ray diffractometer, a scanning electron microscope (SEM) and HR-TEM in order to discuss the relationship between it and piezoelectric properties.

2. Experimental procedure
Two micrometer thick AlN thin films on 50 μm thick mirror polished SUS304 foil substrate were deposited by reactive RF-magnetron sputtering. The AlN crystal growth process on SUS304 and Si (as a reference sample) substrates in same batch is shown in figure 1 as SEM images. X-ray diffraction (XRD) patterns and x-ray rocking curves (XRC) of AlN films including a 10 μm thick sample for the cantilevers were measured by x-ray diffractometer (Bruker D8 ADVANCE) as indicated in figure 2.
and 3. The electron beam diffraction patterns with bright field and dark field TEM images of 2 μm thick AlN thin films on SUS304 foil obtained by HR-TEM (JEM ARM 200FB) are shown in figure 4. 

The fabrication process flow of a piezoelectric cantilever for the measurement of the piezoelectric properties of AlN films is shown in figure 5. First, ten micrometer thick AlN films were deposited at the same condition as the above samples on both-sides of 4 inch mirror polished SUS wafers. The AlN film on the back side of the SUS substrate is the layer for suppressing the warpages of wafers. Next, AlN films were etched by a heated TMAH solution (b). Thirdly, upper electrode of 0.2 μm Au/2 μm Ni/3.0 μm Cu was patterned on the entire wafer by electroplating using thin Cu/Ti seed layer as a power feed electrode and adhesive layer (c). Then, a patterning of the SUS substrate into the cantilever shape was carried out by a ferric chloride solution (d). Finally, the SUS wafers were diced (e) and the piezoelectric cantilever chips were adhered on printed circuit boards by a epoxy resin (f). The dimensions of a cantilever were 6.5 mm length and 3.0 mm width.

Piezoelectric vibration was generated by applying sine wave voltage with the half DC bias voltage between upper and bottom electrodes, and its frequency was 500 Hz which was much less than the mechanical resonance frequency 1650 Hz. The tip displacement as a function of applied voltage in figure 6 was measured by the setup using laser vibrometer (Onosokki LV-1710) [3]. The electrical properties were evaluated by semiconductor characterization system (KEITHLEY 4200-SCS).

![Figure 1](image1.png)

**Figure 1.** SEM images of the AlN crystal growth process on SUS304 and Si (as a reference sample) substrates in same batch.

![Figure 2](image2.png)

**Figure 2.** XRD pattern of the AlN films on SUS and Si substrates.

![Figure 3](image3.png)

**Figure 3.** X-ray rocking curves of AlN(002) of the AlN films on SUS and Si substrates.
Figure 5. Schematics of the fabrication process for the piezoelectric cantilevers.

Figure 6. Tip displacement and estimated $-d_{31}$ of the two cantilevers as a function of the applied voltage. The length between the laser spot and fixed end was 6.35 mm.

3. Results and discussion

The x-ray crystal structural analysis in figure 2 and 3 indicates the difficulty of the AlN(002) orientation growth on the SUS304 substrate focusing on its intensity and the value of full width at half maximum (FWHM) of XRC. As shown in figure 1, Stranski-Krastanov growth of AlN was occurred on the Si substrate. On the other hand, Volmer-Weber growth was observed in case of the SUS304 substrate. Because the roughness values of the Si and SUS304 substrate were almost same $\sim$ Ra = 0.3 – 0.6 nm, it is thought that one of the reasons is difference of chemical potential of the substrate surface. SUS304 is the alloy which consists of about 10 % Ni, 20 % Cr and Fe. It is estimated that the distribution of adatom interactions depending on the difference of the element at substrate surface...
caused Volmer-Weber growth on the SUS304 substrate. There is possibility that the ± 10 deg. tilting and the low abundance ratio of the AlN(002) orientation shown in figure 4 were occurred on the same mechanism. The lateral size of AlN columns was in the range of less than 50 – 300, and the random orientation including AlN(101), (102) and (103) was seen in a crystalline column. In addition, there are no single-oriented crystalline columns. This is striking difference between the AlN film on Metal/Si and on SUS substrate [4], [5]. And the results shows the piezoelectric properties of AlN on the SUS304 substrate could not be estimated from the crystallographic film quality such as the value of FWHM of AlN(002) peak based on the relationship in case of Si substrate [6].

The transverse piezoelectric coefficient $d_{31f}$ and $e_{31f}$ of the AlN films were estimated from a tip displacement of the piezoelectric cantilevers using the constituent equation for multiple layer cantilever [7]. The structural layer constitution was defined as 0.2 μm Au/ 2 μm Ni/ 3.0 μm Cu/ 15 nm Ti/ 10 μm AlN/ 50 μm SUS/ 10 μm AlN, and the mechanical properties of bulk were used for the calculation [2], [8]. The results as a function of the applied voltage were shown in figure 6. The comparison of the electrical and piezoelectric properties of various AlN films on Si substrates [9], [10] and on the SUS304 substrate was summarized in table 1. The piezoelectric coefficient of the AlN film on the SUS304 substrate was significantly less than the values of AlN films on Si substrates. It is thought that the complicated crystalline structure as above caused the low piezoelectric properties in this experiment.

Table 1. Comparison of the electrical and piezoelectric properties of various AlN films on Si and SUS304 substrates. Symbol ※ means that the value was calculated by the author. $E_{\text{Bulk}}$ = 340 GPa.

| Ref. | Growth method | Substrate | Dielectric constant | Piezoelectric coefficient $d_{31f}$ [pm/V] | $e_{31f}$ [C/m²] |
|------|---------------|-----------|---------------------|---------------------------------------------|-----------------|
| M.-A. Dubois et al. [6] | Pulsed DC sputtering | Pt/Si$_3$N$_4$ /SiO$_2$/Si | 10.4 ± 0.4 | ※$d_{31f}/2$ = -1.7 ± 0.12 | -1.02 ± 0.04 |
| A. Ababneh et al. [7] | DC magnetron sputtering | (100) Si | Unclear | -1.0 to -1.8 | ※$d_{31f} \times E_{\text{Bulk}}$ = -0.34 to -0.61 |
| In this study | RF magnetron sputtering | Stainless steel SUS304 | 10.5 ± 1.0 | -1.42 ± 0.08 | -0.48 ± 0.03 |

4. Conclusion

Piezoelectric properties and crystallographic microstructures of AlN thin films on 50 μm thick SUS304 were investigated. The transverse piezoelectric coefficient $d_{31f}$ and $e_{31f}$ of 10 μm thick AlN films were estimated as -1.42 ± 0.08 pm/V and -0.48 ± 0.03 C/m², and its dielectric constant was 10.5 ± 1.0. It is thought that these low piezoelectric properties were due to the complicated crystalline structure including the fine grain and the random orientation of AlN<101>, <102> and <103>.

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