**Supporting information**

# High-throughput investigation of a lead-free AlN-based piezoelectric material, $(Mg,Hf)_xAl_{1-x}N$

*Hung H. Nguyen,[1*] Hiroyuki Oguchi,[2] Le Van Minh[1], Hiroki Kuwano[1]*

[1]Department of Robotics, Tohoku University, Sendai, Japan

[2]Advanced Institute for Materials Research (AIMR), Tohoku University, Japan

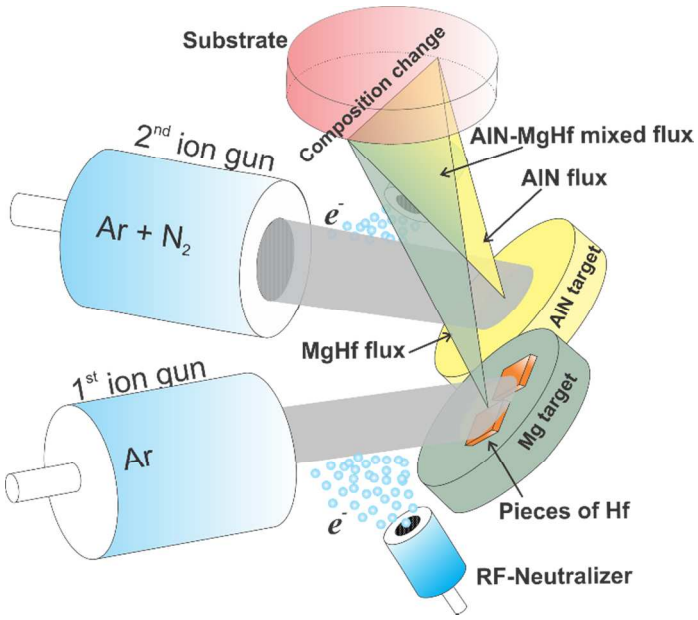


**Figure S1.** Schematic of combinatorial deposition using AlN target and Mg target with pieces of Hf on top.

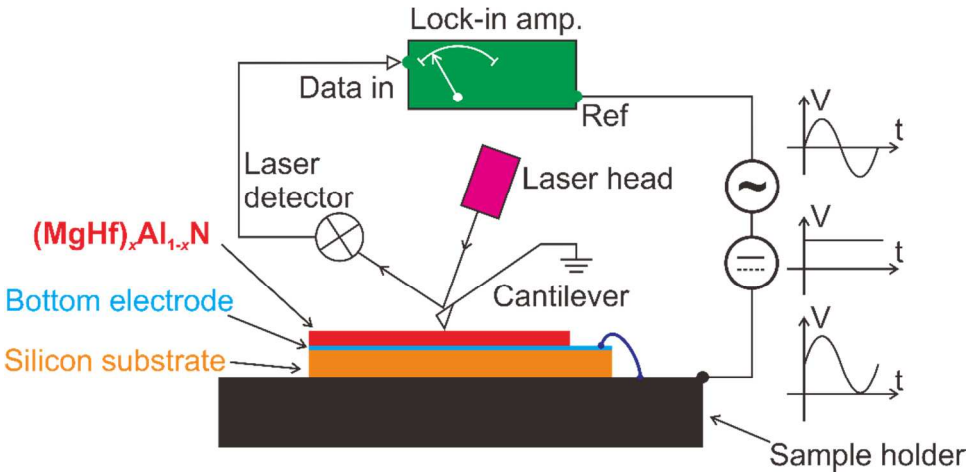


**Figure S2.** The illustration of PRM measurement, in which an AC voltage (*V*) was applied along *c*-axis of the thin film by using an AFM conductive cantilever and bottom electrode. The AC voltage induce a displacement (*D*) on sample surface which was accurately followed by the tip in contact mode. The amplitude of the tip vibration could be measured by lock-in technique. Thus, the piezoelectric coefficient of materials ($d_{33}$) could be determined by $d_{33} = D/V$.

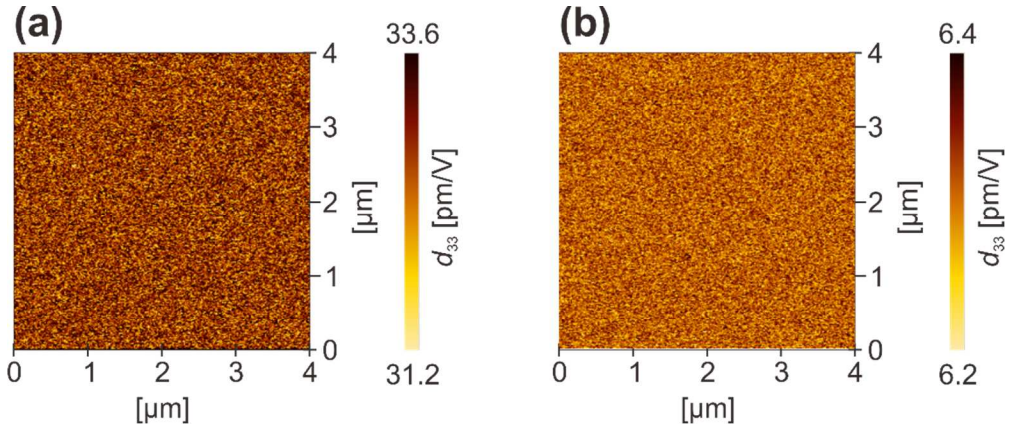


**Figure S3.** PRM images for $LiNbO_3$ (a) and $SiO_2$ (b) single crystal. The $d_{33}$ values were determined by taking average for the observed area. The obtained values for $LiNbO_3$ and $SiO_2$ were 32.7 and 6.3 pm/V, respectively, which agree with widely accepted values. [31, 32]

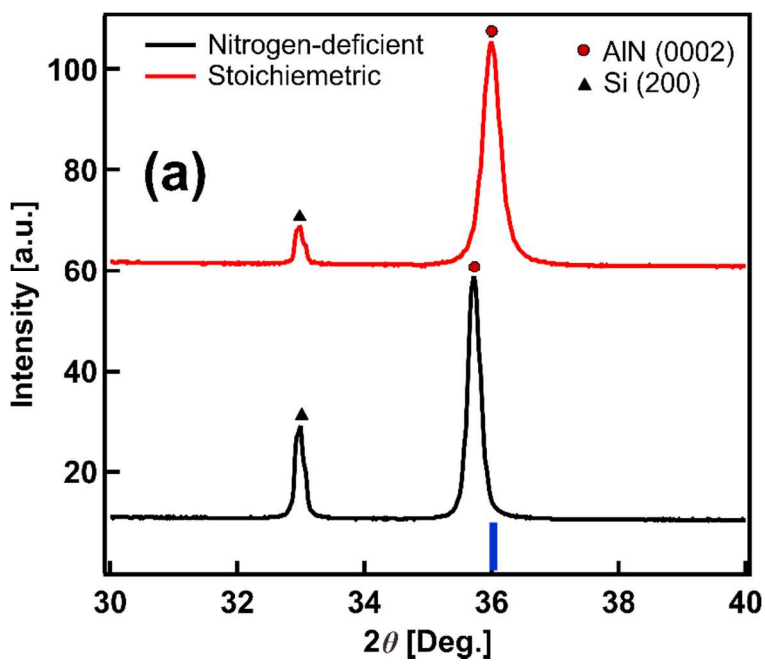


**Figure S4.** XRD patterns for AlN thin films with and without the nitrogen deficiency. Stoichiometry was confirmed by observing (0002) peak of the AlN at $2\theta \sim 36°$, which corresponds to the reference peak position of hexagonal AlN (solid blue line). [7, 8]

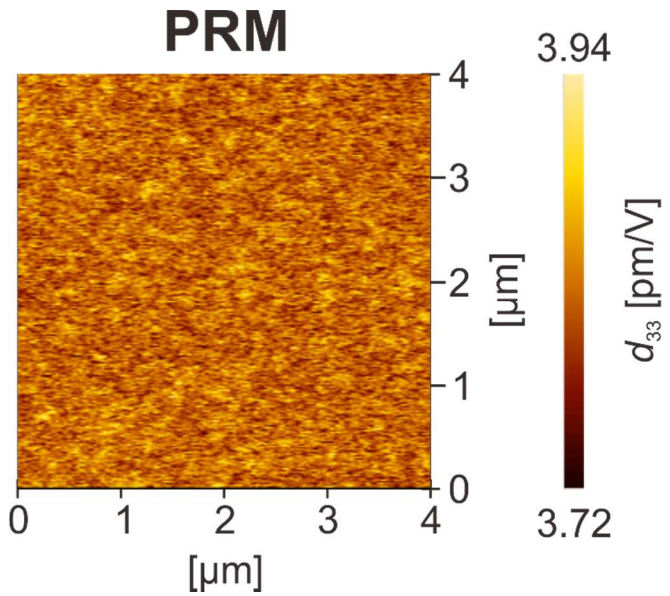


**Figure S5.** PRM image of stoichiometric AlN thin film. The average $d_{33}$ value for measured area is 3.9 pm/V. The obtained value was comparable with reported value of AlN thin films. [1, 7, 17]

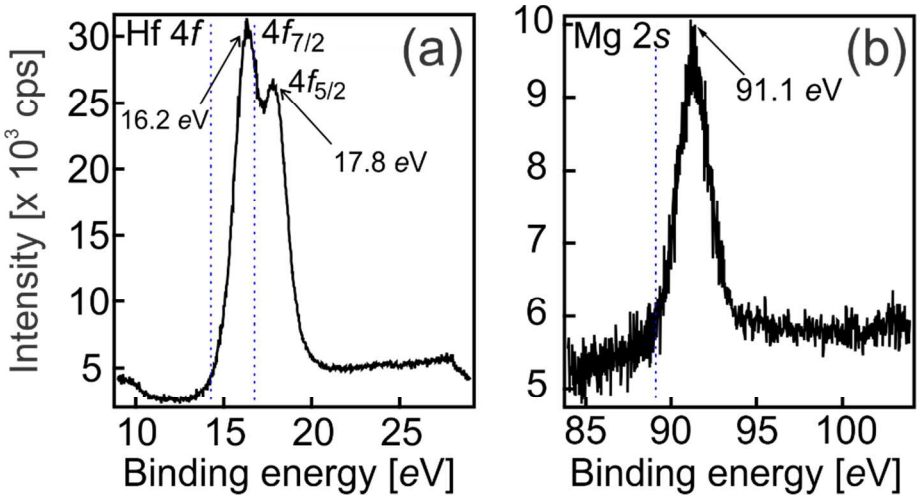


**Figure S6.** High-resolution XPS spectra of (a) Hf 4*f* and (b) Mg 2*s* core-levels obtained for the $(Mg,Hf)_xAl_{1-x}N$ ($x$ = 0.21) film. Blue dotted lines denote reference peak positions. The peak positions were calibrated beforehand by using peak of carbon deposited on sample surface. The spectrum of Hf 4*f* (a) showed two singlet peaks located at 16.2 and 17.8 *e*V, corresponding to Hf $4f_{7/2}$ and Hf $4f_{5/2}$, respectively. These values were 1.8 eV higher than those of the references for

metal Hf (14.4 eV for Hf $4f_{7/2}$ and 16.0 eV for Hf $4f_{5/2}$), and agreed well with the reported values for HfN film. Similarly, the XPS spectrum of Mg 2*s* (b) showed a peak at 91.1 eV, which was shifted by 2.5 eV to a higher energy than that of Mg metal (88.6 eV). The size of this shift agreed well with the reported value for $Mg_3N_2$. These results indicated that Mg and Hf had directly replaced Al and formed bonds with nitrogen.

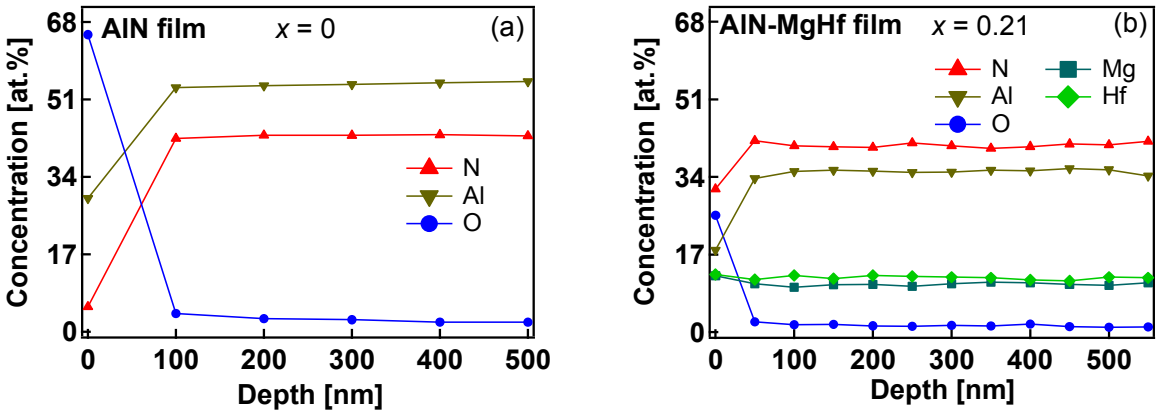


**Figure S7.** Depth profile of the $(Mg,Hf)_xAl_{1-x}N$ films for $x = 0$ (a) and $x = 0.21$ (b) obtained by Ar ion sputtering at a sputtering rate of ~ 5 nm/min using XPS. The higher levels of Al than N observed in these profiles indicated that the films were N-deficient. The extent of the deficiency was roughly uniform (~ 13 at.%) for different *x*.