様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

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研究課題名（和文）Ultra-high performance and environment-friendly micro-energy harvesters towards self-powered micro/nano-systems for the Internet of Things

研究課題名（英文）Ultra-high performance and environment-friendly micro-energy harvesters towards self-powered micro/nano-systems for the Internet of Things

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交付決定額（研究期間全体）：（直接経費）　　3,200,000円

研究成果の概要（和文）：(DeepL Translator)
本研究は、新規高出力FoM鉛フリーAlN系圧電薄膜と非線形動作アーキテクチャの融合により、超高性能かつ環境に優しいマイクロエネルギーハーベスターの実現を目指すものです。プロジェクトの成果を要約すると、 (1) 非レアアースのTaMgドープAlN薄膜： (2)開発したAlN系圧電薄膜の微細加工によるマイクロデバイスの製作(3) ダブルクランプ型ドープAlN/Si構造による超広帯域動作の高性能(Ta、Mg) ドープAlNエネルギーハーベスタの開発に成功した。

研究成果の学術的意義や社会的意義
I proposed and successfully demonstrated novel high-performance micro-energy harvesters exploiting codoped AlN films and nonlinear device structure. The high-power density and ultra-wide bandwidth EHs will open a new door for compact self-powered wireless sensor nodes toward the Internet of Things

研究成果の概要（英文）：This research aims to integrate novel high-power-figure-of-merit (FoM) lead-free AlN-based piezoelectric films and nonlinear-operating architecture to create ultra-high performance and environment-friendly micro-energy harvesters. The project ’s results can be summarized: (1) Non-rare-earth TaMg-doped AlN thin films: By doping Ta and (Ta, Mg) into AlN wurtzite unit cell, the doped AlN films possessed higher FoM compared with the pure AlN; (2) Microfabrication of the developed AlN-based piezoelectric thin films for making the micro-devices; (3) High-performance (Ta, Mg) doped AlN energy harvesters with ultra-wide bandwidth operation were successfully developed with the doubly clamped doped-AlN/Si structures.

研究分野：Nano/Microsystems

キーワード：Micro-energy harvesters　piezoelectric thin film　piezoelectric device　aluminum nitride　nitride piezoelectricity　MEMS　Power MEMS　doped AlN

１．研究開始当初の背景 (Background at the beginning of research)

A quest for environment-friendly onsite power generators for autonomous micro/nano-systems toward the Internet of Things (IoTs)

In recent years, the quest for alternative power sources for autonomous wireless sensor nodes has been the focus of scientists and engineers. Current batteries are still less than optimal and often present drawbacks related to scalability, reliability, and safety. An ideal power source for self-powered micro/nano-systems should take advantage of onsite energy resources to produce power continuously and reproducibly. Piezoelectric energy harvesters, which can convert onsite waste vibrations into electrical energy, have been deemed a potential solution to the drawbacks of batteries. Still, the power density requirements for micro/nano-systems have not been widely met yet to prove critical for the advancement of the field. ***This proposal aims to integrate novel high-power-figure-of-merit (FoM) piezoelectric nitride thin films and nonlinearity-operating architecture to create ultra-high performance and environment-friendly micro-energy harvesters.***

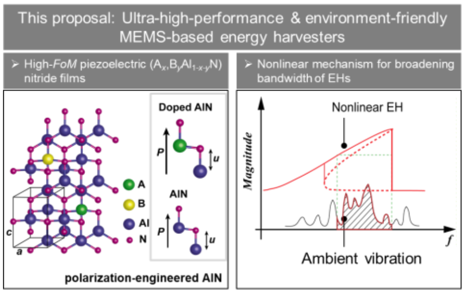

Fig. 1: The proposed research

[A] Highly FoM lead-free piezoelectric films

Piezoelectric thin films offering a high *FoM* value *($FoM = e^2_{31}/\varepsilon$; e_{31} is a piezoelectric coefficient, ε is a permittivity)* are strongly desirable for vibrational energy harvesting. Current harvesters utilize well-developed PZT-based films on Si with *FoM* of up to 30 GPa [K. Wasa et al., *J.Microelectromech.* **21**, 2 (2012)]. From an environmental perspective, toxic lead-based materials are less suitable for widely distributed applications. An attractive alternative is a lead-free piezoelectric thin film of Sc-added AlN solid solution. Sc requirement of greater than 30 at. % for the FoM of 22 GPa on average makes the material extremely expensive [M. Akiyama et al., *Adv. Mater.* **21**, 593-596 (2009)]. Theoretical calculation [Y. Iwazaki et al., *Appl. Phys. Express* **8**, 061501 (2015)] and experimental results [L. Van Minh et al., *IEEE Trans.Ultrason. Ferroelectr. Freq.Control*] prove alternatives from *non-rare-earth elements also significantly enhance piezoelectricity and FoM, leading to significant output power density (PD) of micro-energy harvesters (μEHs).*

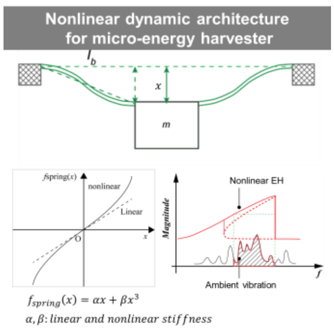

Fig. 2: Clamped-clamped beam for broadening the bandwidth of μEHs.

[B] Nonlinear dynamic architecture for broadband operation (high FB)

Almost all energy harvesters operating linear resonant oscillations have a small bandwidth (*BW*) of below 5 Hz [L. Van Minh-1,2,3,10,11]. Hence, applying *nonlinear dynamics to broaden the bandwidth oscillators* is a more effective approach to converting onsite vibrations into electricity. Most macro-scale devices use external magnetic force for increasing *BW* or fractional bandwidth *(FB: = BW/f_r; f_r: center resonant frequency)* [A. Erturk et al., *Appl. Phys. Lett.* **94**, 254102 (2009)]. PI [L. Van Minh et al., *Jpn. J. Appl. Phys.* **52** 07HD08 (2013)] successfully introduced *nonlinear stiffness of clamped-clamped structures to boost FB of μEHs (Fig. 2)*.

２．研究の目的 (Purpose of research)

This work aims to integrate *novel high-power-figure-of-merit (FoM) piezoelectric nitride thin films with non-rare-earth dopants and nonlinearity-operating architecture to create ultra-high performance and environment-friendly micro-energy harvesters*. The nitride films composed of AlN and *scandium-free cations that substitute Al to engineer the polarization magnitude* present significantly increased piezoelectricity and FoM, increasing vibration-electricity transduction for significant output power. The *nonlinear device mechanism inherently increases wide bandwidth*, consequently suppressing the frequency mismatch with onsite vibrations for an increase in the overall performance of the harvesters. Furthermore, MEMS-based architectures and rare-earth-element-less materials will enable reproducible fabrication and low cost of micro-energy harvesters. ***Aim 1:* Development of high-FoM piezoelectric nitride films; *Aim 2:* Evaluation of piezoelectric properties of the nitride system; *Aim 3:* Development of the prototype of ultra-high performance nonlinear micro-energy harvesters**

３．研究の方法 (Research method)

Doped AlN-based piezoelectric films use a dual magnetron system with a positive plasma column with an alternating current power applied between metallic targets in Ar/N_2 ambient. I proposed and developed a new approach using the dopants-embedded target to produce high-quality doped-AlN piezoelectric films. The experiments were conducted by *doping Ta and Mg in AlN*. Ta with a large ionic radius and bonding with N was considered to distort AlN unit cell effectively with a small amount of the dopant. And Mg was added to compensate for the charge generated by adding Ta. For highly piezoelectricity of doped-AlN nitride films, high-(002) c axis orientation is required. The as-deposited films were evaluated the crystallinity by X-ray diffractions with $2\theta/\theta$ and rocking curve θ/ω scans. EDS and FE-SEM evaluated the doping concentration and surface morphology. FoM was determined via evaluations of piezoelectric coefficients, permittivity, and Young's modulus by using micro-cantilevers (with or without proof mass). The piezoelectric coefficient e_{31} was determined from the relationship between the piezoelectric voltage and the cantilevers' deflection at the steady-state. The permittivity was measured using an Impedance/Phase analyzer. Young's films of 3 μm were grown on 4in Pt/Ti/Si wafers for developing the device prototypes. Doped-AlN etching technique was also devised to release the micromachined structures. Nonlinear-energy harvesters using the clamped-clamped structure of the d_{31}-mode doped-AlN/Si suspension systems with a proof mass.

４．研究成果(Research results)

(4-1) Development of TaMg-doped AlN thin films

The targets with desired dopants and concentrations were crucial for this research. Mg's low melting

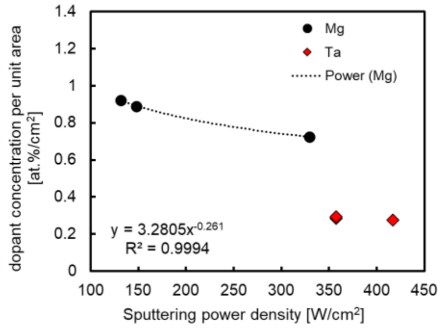

Fig. 3: Ta, Mg doping concentration per the dopant unit area as a function of sputtering power density.

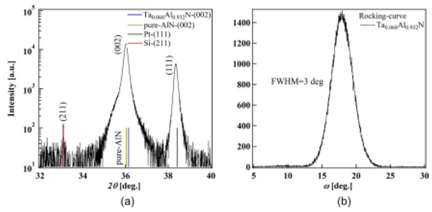

Fig. 4: A typical XRD pattern (a) and rocking-curve (b) of doped-AlN films.

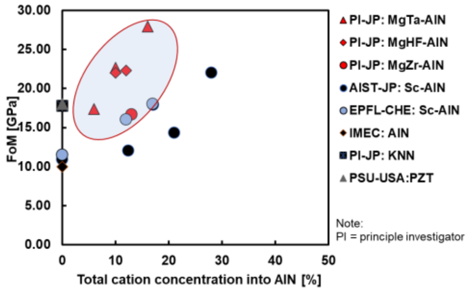

Fig. 5: FoM of the developed doped-AlN and in the piezoelectric field development.

point temperature caused the plasma instability in an inappropriate setting. Also, the Mg surface nitridation impeded doping high dopant concentrations into AlN. Those problems were more serious when increasing the sputtering power of 5 kW.

I proposed and succeeded with the target configuration to overcome those limitations (patent in preparation) for manufacturing the same high-quality films. The approach also made the wide range of dopant concentrations and inclusive low-melting-point elements possible with a wide range of AC power and growing pressure. Fig. 3 shows the Mg and Ta dopant concentration per the unit surface area as a function of the sputtering power density. The high deposition rate of 66 nm/min on average was achieved. Fig. 4 shows the typical XRD diffraction and rocking curve of the doped-AlN films. *The large distortion of the AlN unit cell was confirmed with a small amount of Ta-dopant concentration*. FoM was determined via evaluations of piezoelectric coefficients, permittivity, and Young's modulus by using micro-cantilevers. The TaMg-doped AlN was able to achieve 17 GPa to 27 GPa. Fig. 5 shows the FoM of this work concerning the development of the field.

(3-2) Establishment of device fabrications process

(i) Low residual stress doped AlN thin films on Pt/Ti/Si wafers

All the devices and property evaluation specimens used piezoelectric films with d_{31}-mode in which the piezoelectric films were sandwiched between the two electrode layers. Low residual nitride films were fabricated to avoid the feeling off and large initial deflection of micro-structures. The residual stress was controlled by gas pressure (Ar and N_2 flow rate adjustment). Figure 6 shows

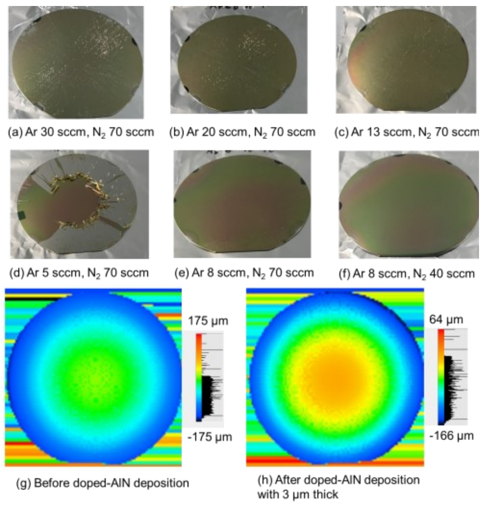

Fig.6: Tunning the residual stress of (Ta,Mg)-doped AlN films with 3 µm in thick for energy harvesters.

the 3-um-thick doped AlN on Pt/Ti/Si wafers with various Ar/N_2 gas flow rates for tunning the residual stress. The films with low residual stress of ± 200 MPa were used for device fabrication. Fig. 6 (g, h) were shown 13 MPa residual stress of the doped AlN determined from Stoney's equation.

(ii) Etching process for doped-AlN films

There are two approaches for etching pure AlN films. Wet etching of AlN with TMAH is typical and can cooperate with the micro-fabrication process of energy harvester devices. The latter is etching AlN with dry etching using Cl_2-based gases. However, the doped AlN was difficult to etch in TMAH despite increasing the etchant temperature. Therefore, the Cl_2-based reactive ion etching was utilized in this research. An inductive coupled plasma RIE (ICP RIE, Samco) was used with the mixed Cl_2/$SiCl_4$/Ar gasses. The etching rate of 200 nm/min at 1Pa, 600 W ICP power, and 75W bias power was achieved. The technique was successfully applied to fabricate various microdevices (Fig. 7).

(3-4) The prototype of ultra-wide bandwidth nonlinear micro-energy harvesters

Nonlinear-energy harvesters using the clamped-clamped structure of the d_{31}-mode doped-AlN/Si suspension systems with a proof mass (Fig. 7(a)). The combination of doped-AlN and Si structural layer was implemented to obtain the high-performance nonlinear energy harvesters (Fig. 8). The fractional bandwidth of 0.2 to 0.5 was achieved compared with 0.001 for the linear devices. The *PD x FB* of 2 to 3 mW.cc^{-1} was achieved at the standard applied acceleration of 1*g*. Fig. 9 shows this work achievement compared with the state-of-the-art piezoelectric energy harvesters.

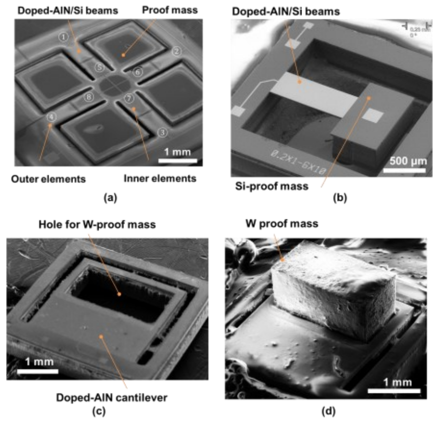

Fig. 7: Doped-AlN based energy harvesters: (a) Ultra-wide bandwidth EH with nonlinear doubly doped-AlN/Si beams; (b) Cantilever-type EH with Si proof mass, (c) Cantilever-EH with a hole before embedding W-proof mass, (d) Cantilever-EH with W- proof mass.

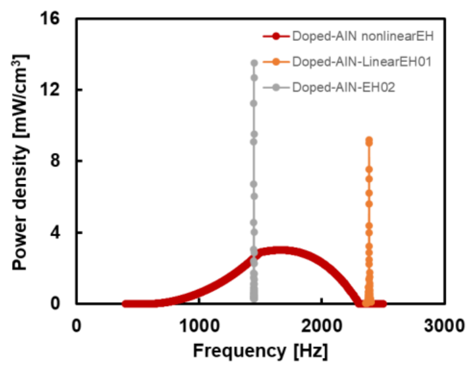

Fig. 8: Power spectra of nonlinear and linear doped-AlN energy harvesters at the standard acceleration of 1g (g =9.81m/s^2).

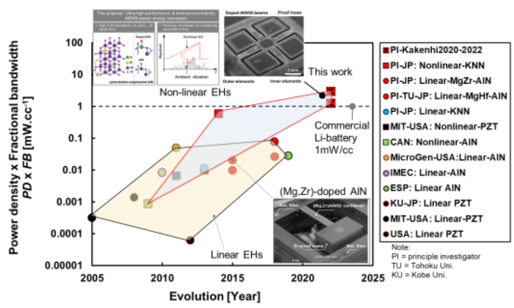

Fig. 9: Performance of piezoelectric energy harvesters at the standard acceleration of 1g (g =9.81m/s^2).

５．主な発表論文等

〔雑誌論文〕　計2件（うち査読付論文　2件／うち国際共著　2件／うちオープンアクセス　0件）

１．著者名 Van Minh, L., Kuwano, H.,	４．巻 9375199
２．論文標題 Piezoelectric Tantalum Aluminum Nitride Films for Vibrational Micro Energy Harvesters	５．発行年 2021年
３．雑誌名 Proceedings of the IEEE International Conference on Micro Electro Mechanical Systems (MEMS)	６．最初と最後の頁 242-245
掲載論文のDOI（デジタルオブジェクト識別子） 10.1109/MEMS51782.2021.9375199	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Van Minh, L., Kuwano, H.	４．巻 10007086
２．論文標題 Piezoelectric Tantalum Aluminum Nitride Grown on Stainless Steel for Low-Frequency Vibration-Driven Energy Harvesters	５．発行年 2022年
３．雑誌名 International Conference on Micro and Nanotechnology for Power Generation and Energy Conversion Applications, PowerMEMS 2022	６．最初と最後の頁 154-157
掲載論文のDOI（デジタルオブジェクト識別子） 10.1109/PowerMEMS56853.2022.10007086	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

〔学会発表〕　計4件（うち招待講演　2件／うち国際学会　2件）

１．発表者名 L. Van Minh and H. Kuwano
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３．学会等名 2021 IEEE 34th International Conference on Micro Electro Mechanical Systems (MEMS)（国際学会）
４．発表年 2021年

１．発表者名 Le Van Minh, Hiroki Kuwano
２．発表標題 Piezoelectric wurtzite nitride thin films for green, high-performance MEMS applications
３．学会等名 The 5th International Conference on Advanced Materials and Nanotechnology, Hanoi, Vietnam（招待講演）
４．発表年 2022年

1．発表者名 Hiroki Kuwano, Le Van Minh, Nguyen Hoang Hung
2．発表標題 Vibration-driven micro energy harvesting with piezoelectric materials for IoTs and SDGs
3．学会等名 The 5th International Conference on Advanced Materials and Nanotechnology, Hanoi, Vietnam（招待講演）
4．発表年 2022年

1．発表者名 Le Van Minh, Hiroki Kuwano
2．発表標題 Piezoelectric Tatalum aluminum nitride grown on stainless steel for low-frequency vibration-driven energy harvesters
3．学会等名 The 21st International Conference on Micro and Nanotechnology for Power Generation and Energy Conversion Applications (PowerMEMS 2022), USA（国際学会）
4．発表年 2022年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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6．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

7．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

8．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関