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科研費 KAKENHI

科学研究費助成事業　　研究成果報告書

令和　６ 年　６ 月 １８ 日現在

機関番号：８２６２６
研究種目：基盤研究(C)（一般）
研究期間：2021～2023
課題番号：２１Ｋ０４１６８

研究課題名（和文）Controlling the polarity of ScAlN via formation of cation/anion vacancy

研究課題名（英文）Controlling the polarity of ScAlN via formation of cation/anion vacancy

研究代表者
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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）：本研究でケイ素（Si）,ゲルマニウム（Ge)およびスズ（Sn)添加によるScAlNの圧電薄膜の分極は、アルミ極性（Al-polar)から窒素極性（N-polar)に反転した。SiまたはGe添加による極性反転した際の圧電定数d３３の値は大きく変わらなかった。しかし、SiまたはGe添加の方法で高濃度Sc薄膜の極性は反転しなかった。炭素（C)を添加すると、ScAlNの極性は変わらず、分極反転は起こらなかった。SiまたはGeを添加するとアルミニウム欠陥（カチオン欠陥）を発生することで分極反転し、Cを添加する場合は窒素欠陥（アニオン欠陥）を発生することで分極反転は起こらない、と考えております。

研究成果の学術的意義や社会的意義
This study has successfully develop N-polar ScAlN-based thin films, including elucidate polarity control mechanism, which is expected to accelerate the realization of next-generation of radio frequency (RF) filter that will be useful for future telecommunication.

研究成果の概要（英文）：The polarity of scandium aluminum nitride (ScAlN) piezoelectric thin film was inversedby addition of either silicon (Si), germanium (Ge) or tin (Sn). Addition of 10 at.% Si or Ge inversed the polarity of ScAlN from Al-polar to N-polar, without significantly affect the piezoelectric response d33.However, polarity inversion in ScAlN via Si or Ge was observed when scandium (Sc) concentration was below 40 at.%.The inability of Si or Ge addition to inverse Sc0.4Al0.6N was found to correlate with phase transition occuring at higher Sc concentration. Aside from Si or Ge, addition of carbon (C) into ScAlN yielded in thin films with Al-polarity suggesting that addition of C could not inversed the polarity of ScAlN. In this study, we found that polarity inversion corresponds with the ability of Si or Ge to from aluminum vacancy (cation vacancy), while addition of C seems to tend to form nitrogen vacancy (anion vacancy)which could not cause polarity inversion.

研究分野：piezoelectric thin films

キーワード：piezoelectric　polarity inversion　thin films　sputtering　nitride

１．研究開始当初の背景

As a wurtzite-structured piezoelectric materia, aluminum nitride (AlN) can be grown in [0001] direction known as metal (M) or aluminum (Al)-polar or in [000-1] direction known as N-polar (Fig. 1). Addition of scandium (Sc) into AlN (ScAlN) resulted in 500% larger piezoelectric charge constant (d_{33}) and higher electromechanical coupling coefficient (k_{eff}) than AlN [1-2]. This means radio frequency (RF) filter using ScAlN can work at wider bandwidth than that using AlN, which is why, ScAlN is currently widely employed in RF filter for popular smartphone such as iPhone. However, the development of RF filter using the currently available material has reached its limitation and it can only work within 5G network range. Meanwhile, 6G technology will be introduced from 2030 and a more advanced network system requires filter that can work at higher frequency and wider bandwidth. One way to improve the performance of RF filter is by stacking multilayer of piezoelectric thin films with opposite polarization direction. Stacking M-polar and N-polar thin film enable the RF filter to generate signal at higher frequency [3]. By considering this concept and since the use of ScAlN allows the filter to work at wider bandwidth, stacking ScAlN thin films as Al-polar and N-polar thin films is expected to result in RF filter that can operate at wider bandwidth and can function at frequency ranges suitable for 6G network. Since the presence of N-polar ScAlN thin film will give a significant impact on development of next-generation RF filter with wider bandwidth and suitable for 6G technology, it is important to control the polarity of ScAlN.

Recently our group has reported that the addition of elements in group 14 in the periodic table, such as silicon (Si) or germanium (Ge) can successfully inverse the polarity of AlN from Al-polar to N-polar [3-4]. It is hypothesized that the addition of elements in group 14 such as Si or Ge into ScAlN also can inverse the polarity of ScAlN from M-polar to N-polar. Polarity inversion in AlN has been reported to correlate with the presence of cation vacancy and the effect of cation or anion vacancy on polarity inversion will be clarified in this study. Given the importance of polarization engineering to develope highly functional nitride-based materials, it is also important to reveal the role of cation or anion vacancy on polarity inversion.

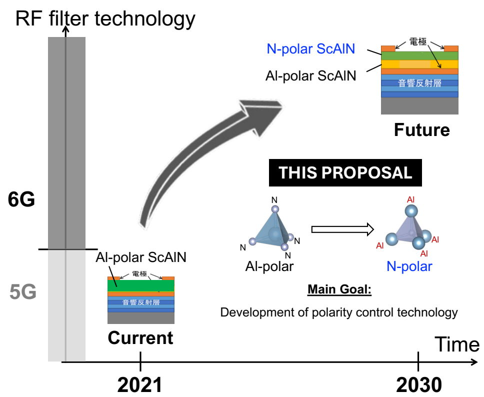

Figure 1 The main goal of this research is to inverse the polarity of ScAlN from M-polar into N-polar

２．研究の目的

i. Control the polarity of ScAlN thin films by doping with other element to promote the formation of cation or anion vacancy.
ii. Clarify the effect of cation/anion vacancy on polarity inversion.

３．研究の方法

All thin films were fabricated via reactive sputtering and polarity control was investigated by:

① Synthesis of ScX-doped-AlN (X is 4+ cation = Si, Ge, Sn, C)

Since doping with element that has higher oxidation state than Sc^{3+} or Al^{3+} can theoretically form cation vacancy (aluminum vacancy/V_{Al}), element that has oxidation state of 4+, i.e. carbon (C), Si, Ge, tin (Sn)) were added into ScAlN.

② Synthesis of ScX-doped-AlN (X is 2+ cation = Mg, Zn)

Since doping with element that has lower oxidation state than Sc^{3+} or Al^{3+} can theoretically form anion vacancy (nitrogen vacancy/V_N), element that has oxidation state of 2+, i.e. magnesium (Mg) or zinc (Zn)) were doped into ScAlN.

All fabricated thin films were then characterized to study changes in piezoelectricity constant (d_{33}), polarity distribution, crystal structure and oxidation states of each element.

４．研究成果

4.1 Synthesis and evaluation of piezoelectricity of ScMAlN (M = Si, Ge, Sn, C)

The positive d_{33} values exhibited by the thin films suggest that the polarity of $Sc_xAl_{1-x}N$ thin film is Al-polar and negative d_{33} indicated N-polar thin films. As shown in Fig. 2, when the concentration of Sc was fixed at 10 at.% (0.1), addition of either Si in the range of 3-26 at.% or Ge in the range of 5-20 at.% or Sn in the range of 5-16 at.% into $Sc_{0.1}Al_{0.9}N$ resulted in thin films with negative d_{33} values, indicating that addition of Si or Ge or Sn could inverse the polarity of $Sc_{0.1}Al_{0.9}N$ (Fig. 2(left)). However, addition of C into ScAlN was found to results in thin films with positive d_{33}, which means addition of C into ScAlN is unable to inverse the polarity of ScAlN. Furthermore, similar d_{33} magnitude between $Sc_{0.1}M_yAl_{0.9-y}N$ and that of $Sc_{0.1}Al_{0.9}N$, was obtained when approximately 10 at.% Si or Ge was added into $Sc_{0.1}Al_{0.9}N$, suggesting addition of each of Si or Ge is could inverse the polarity of ScAlN without significantly lowering the d_{33}. Meanwhile addition of Sn into ScAlN resulted in thin film with N-polarity, but the value of d_{33} is slightly lower than that of ScAlN. Effect of Sc concentration was examined by fixing dopant concentration at 0.1. As can be seen in Fig. 2 (*right*), it is evident that addition of either Si, Ge or Sn was only effective to inverse the polarity of ScAlN when the concentration of Sc is less than 40 at.%. Thus, it can be inferred from these results that the formation of N-polar ScAlN is controlled by both concentration of each additive element (in this case: Si, Ge, Sn) and that of Sc [5-12].

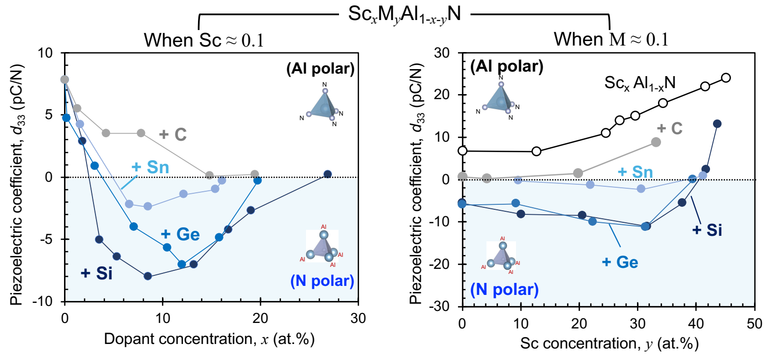

Figure 2 Effect of addition of each element on the polarity of $Sc_xM_yAl_{1-x-y}N$, when (left) Sc was fixed at 0.1 or (right) when dopant concentration was fixed at 0.1.

4.2 Synthesis and evaluation of piezoelectricity of ScXAlN (X = Mg, Zn)

As shown in Fig. 2 (*a*), addition of 4+ cation such as Si in the range of 7-20 at.% into $Sc_{0.3}Al_{0.7}N$ resulted in N-polar thin films, meanwhile addition of either Mg or Zn at the same concentration range was found to results in thin films with positive d_{33}, which means addition of 2+ cation such as Mg or Zn into $Sc_{0.3}Al_{0.7}N$ could not inverse the polarity of ScAlN. Fig. 2(b) summarize the results where it is shown that addition of 2+ cation that theoretically form anion vacancy (V_N) could not promote polarity inversion. Addition of 4+ cation that theoretically form cation vacancy (V_{Al}) could inverse the polarity, except for C [9-10].

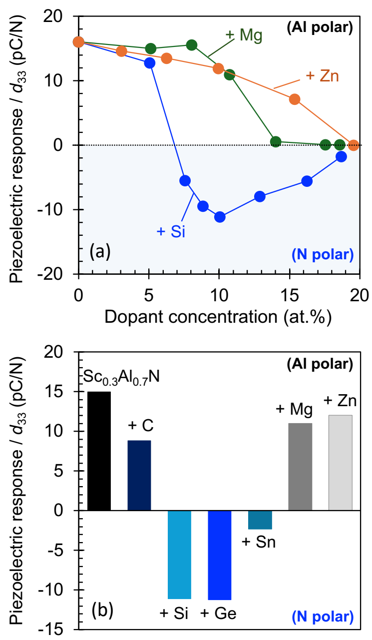

Figure 2 (a) Effect of Mg or Zn concentration on polarity of thin films and (b) Effect of addition of different element on the polarity of $Sc_xM_yAl_{1-x-y}N$

4.3 Effect of element addition on polarity distribution

Effect of element addition on polarity distribution was investigated using $Sc_xGe_yAl_{1-x-y}N$ as representative. The d_{33} values presented in Fig.3(a) were obtained from Piezometer shows that addition of Ge inversed the polarity of $Sc_xAl_{1-x}N$ for $x < 0.4$. Changes in polarity distribution upon changes in Ge addition was further examined using piezo response microscopy (PFM) (Fig. 3(b)) [7-8]. While $Sc_{0.3}Al_{0.7}N$ without Ge addition exhibited Al-polar thin film, gradual addition of Ge resulted in changes in polarity gradually into N-polar with increasing Ge concentration from 2 to 8 at.%. Interestingly when 5 at.% Ge was added into $Sc_{0.3}Al_{0.7}N$, the thin film exhibited d_{33} of zero, but polarity distribution results showed that the thin film comprised 50 % Al-polar and 50% N-polar component which cancel out each other and resulted in d_{33} of zero. Addition of 8 at.% Ge evidently resulted in homogenous N-polar thin film. Results from PFM measurements are found to be consistent with that obtained from Piezometer [7-8].

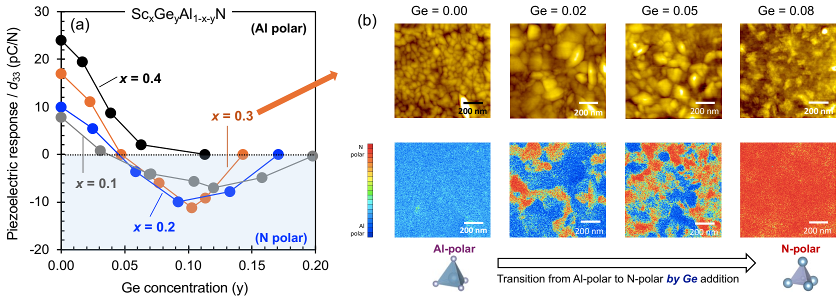

Figure 3 Effect of Ge addition on (a) piezoelectricity of $Sc_xGe_yAl_{1-x-y}N$ and (b) polarity distribution of $Sc_{0.3}Ge_yAl_{0.7-y}N$ thin films.

4.4 Effect of element addition and concentration on changes in crystal structure

Effect of element addition on changes in crystal structure of ScAlN is presented in Fig.4(a) where addition of either Si or Ge could maintain a better wurtzite crystallinity when compared with Sn or C addition, which is why addition of Si or Ge could maintain a better piezoelectric response than addition of Sn or C [9-10]. Effect of element concentration on crystal structure was further studied on $Sc_{0.2}Si_yAl_{0.8-y}N$ and $Sc_{0.4}Si_yAl_{0.6-y}N$ as representatives. The peak at 36° which corresponds with (002) reflection of wurtzite structure was found to be barely shifted by addition of 5 or 10 at.% Si into $Sc_{0.2}Al_{0.8}N$. Meanwhile, addition of 20 at. % Si into $Sc_{0.2}Al_{0.8}N$ resulting in broader peak with lower intensity (Fig. 4(b)), suggesting a decrease in crystallinity at higher Si addition. This explains why addition of Si with concentration greater than 16 at.% into $Sc_{0.2}Al_{0.8}N$ resulted in lower d_{33}. Meanwhile, incremental addition of Si into $Sc_{0.4}Al_{0.6}N$ resulted in a gradual shift of (002) peaks toward lower 2θ, concurrent with the emergence of rocksalt ScN phase (*) (Fig. 4(c)), suggesting incremental addition of Si into $Sc_{0.4}Al_{0.6}N$ encouraged the formation of new phase. Thus, addition of Si into $Sc_{0.4}Al_{0.6}N$ is hypothesized to cause phase transition from wurtzite to a different phase rather than facilitating polarity inversion, which is why polarity inversion could not be observed when Si was incorporated into $Sc_{0.4}Al_{0.6}N$ [5,6,11].

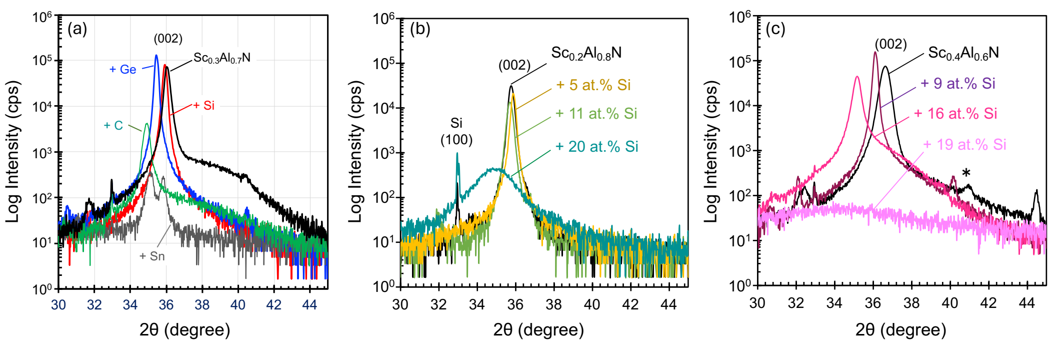

Figure 4 Effect of (a) different element addition on crystal structure and effect of Si concentration on crystal structure of (b) $Sc_{0.2}Si_yAl_{0.8-y}N$ and (c) (b) $Sc_{0.4}Si_yAl_{0.6-y}N$ thin films.

4.5 Investigation on plausible mechanism of polarity inversion

In case of AlN, we have reported that polarity inversion in AlN that was occurred after addition of Si can be elucidated using model proposed by Youngman and Harris [4], where doping with element that has higher oxidation state than Al^{3+} , such as Si^{4+}, into AlN will promote the formation of aluminum vacancy (V_{Al}) and large concentration of V_{Al} can induce the transformation of Al bonding coordination

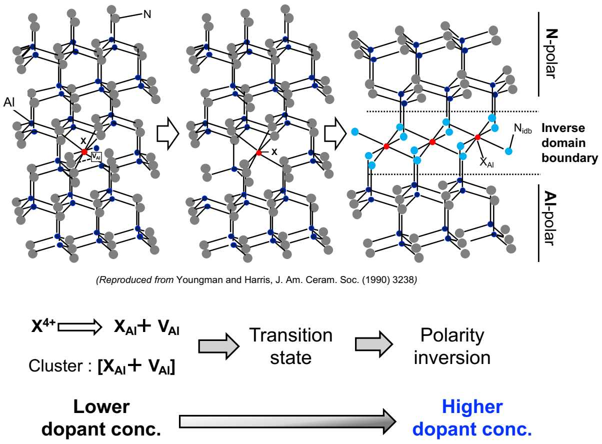

Figure 5 The predicted role of cation vacancy (V_{Al}) on polarity inversion, as proposed by [4].

from tetrahedral to octahedral and eventually cause polarity inversion (Fig. 5). To confirm whether similar mechanism was also occurred in case of addition of 4+ cation into ScAlN, XPS measurements were then conducted to study element state at each thin film. From XPS spectra shown in Fig. 6(a-b) of Si*2p* and Ge*3d*, it was confirmed that both Si and Ge exist as 4+ cation, which means addition of this cation may induce the formation of V_{Al} [5-8,11]. Since $Sc_{0.3}Si_{0.1}Al_{0.6}N$ and $Sc_{0.3}Ge_{0.1}Al_{0.6}N$ exhibited N-polarity, it is evident that addition of 4+ cation is highly likely induce the formation V_{Al} and eventually inverse polarity. The XPS spectra of Sn*3d* can be deconvoluted into 2 doublets and the binding energy of each peak corresponds with the presence of Sn^{2+} and Sn^{4+} (Fig. 6(c)) [9-10]. The presence of multiple components is believed to be responsible for poor wurtzite crystallinity which led to lower d_{33} despite the thin film exist as N-polar. However, the XPS spectra of C*1s* for ScCAlN showed that there are multiple carbon components including one that contain carbon bonded with metal (peak *c*) (Fig. 6(d)) [9-10]. Unlike Si^{4+} or Ge^{4+} that is occupied Al site and form cation vacancy (V_{Al}), the presence of carbon-metal bond suggested that C occupied N-site forming anion vacancy (V_N). This may explain why addition of C could not inverse the polarity of the thin film. These results further confirm that the key to polarity control of nitride, particularly for ScAlN, piezoelectric thin film is the formation of cation vacancy (V_{Al}) which can be promoted by substituting Al or Sc with other element, particularly one that has higher oxidation state than Al or Sc.

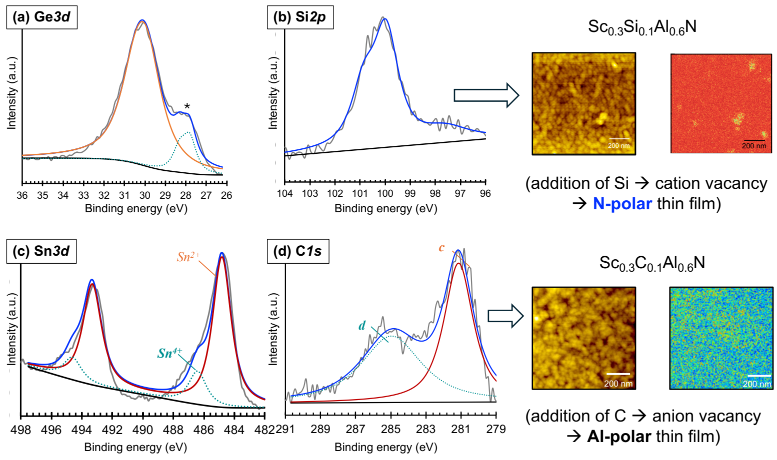

Figure 6 (a) Ge3d, (b) Si2p, (c) Sn3d and (d) C1s spectra of $Sc_{0.3}M_{0.1}Al_{0.6}N$ where M= Si, Ge, Sn, C including the polarity distribution of $Sc_{0.3}Si_{0.1}Al_{0.6}N$ and $Sc_{0.3}C_{0.1}Al_{0.6}N$ thin films

We have presented these results in **6 (six) conferences** (domestic and international) and our work on polarity inversion has also gained a lot of attentions since **2 (two) Best Poster Awards** were received from Japan Society for Applied Physics (JSAP) in Fall 2021 and Spring 2023.

References

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[6] S. A. Anggraini et al, *MRS Fall Meeting 2021.*
[7] S. A. Anggraini et al, *JSAP Fall Meeting 2021, 22a-P01-4.*
[8] S. A. Anggraini et al, *MRS Fall Meeting 2022.*
[9] S. A. Anggraini et al, *JSAP Spring Meeting 2023, 17p-PB01-4.*
[10] S. A. Anggraini et al, *MRS Fall Meeting 2023.*
[11] S. A. Anggraini et al, *Scripta Materialia (under review).*
[12] S. A. Anggraini et al, *ACS Applied Electronic Materials (to-be-submitted).*

５．主な発表論文等

〔雑誌論文〕　計1件（うち査読付論文　1件／うち国際共著　1件／うちオープンアクセス　0件）

1．著者名 Sri Ayu Anggraini*, Masato Uehara, Kenji Hirata, Taisei Motomura, Hiroshi Yamada and Morito Akiyama	4．巻 -
2．論文標題 Effect of Si addition on polarity inversion in scandium aluminum nitride piezoelectric thin films	5．発行年 2024年
3．雑誌名 Scripta Materialia (under review)	6．最初と最後の頁 -
掲載論文のDOI（デジタルオブジェクト識別子） なし	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6件（うち招待講演　0件／うち国際学会　3件）

1．発表者名 Sri Ayu Anggraini
2．発表標題 Controlling the Polarity of Scandium Aluminum Nitride (ScAlN) Piezoelectric Thin Films by Using Ge Addition
3．学会等名 MRS Fall Meeting 2022（国際学会）
4．発表年 2022年

1．発表者名 Sri Ayu Anggraini
2．発表標題 Effect of addition of elements in group IVB (C, Si, Ge, Sn) on polarity inversion of Scandium Aluminum Nitride (ScAlN) piezoelectric thin films
3．学会等名 JSAP Spring Meeting 2023
4．発表年 2023年

1．発表者名 Sri Ayu Anggraini, Masato Uehara, Kenji Hirata, Hiroshi Yamada, Morito Akiyama
2．発表標題 Polarity inversion of scandium aluminum nitride (ScAlN) piezoelectric thin films by using Ge addition
3．学会等名 The 82rd JSAP Autumn Meeting 2021
4．発表年 2021年

１．発表者名 Sri Ayu Anggraini, Masato Uehara, Kenji Hirata, Hiroshi Yamada, Morito Akiyama
２．発表標題 Inversing the polarity of scandium aluminum nitride (ScAlN) piezoelectric thin films by using Si addition
３．学会等名 MRS Fall Meeting 2021（国際学会）
４．発表年 2021年

１．発表者名 Sri Ayu Anggraini, Masato Uehara, Kenji Hirata, Hiroshi Yamada, Morito Akiyama
２．発表標題 Controlling the polarity of scandium aluminum nitride (ScAlN) piezoelectric thin film via Si addition
３．学会等名 JSAP Spring Meeting 2021
４．発表年 2021年

１．発表者名 Sri Ayu Anggraini, Masato Uehara, Kenji Hirata, Hiroshi Yamada, Morito Akiyama
２．発表標題 Polarity Inversion of Scandium Aluminum Nitride (ScAlN) Piezoelectric Thin Films via Addition of Elements in Group IVB (C, Si, Ge or Sn)
３．学会等名 MRS Fall Meeting 2023（国際学会）
４．発表年 2023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