様　式　C－１９、F－１９－１、Z－１９　（共通）

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研究課題名（和文） トンネリング電気磁気-誘電効果を発現するナノグラニュラー複相膜の創製

研究課題名（英文） Creation of tunneling electro-magneto-dielectric effect of nanogranular composite films

研究代表者

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交付決定額（研究期間全体）：（直接経費）　　4,900,000円

研究成果の概要（和文）：私は、直流電界を用いた交流輸送応答における誘電緩和周波数（fr）のチューニングを可能にする新規誘電体ナノグラニュラー材料を開発しました。この材料は、RFローパスフィルタやアンテナなどのデバイス構造を簡略化・小型化できる可能性があります。構造は、絶縁性マトリックス中に磁性金属ナノ粒子を分散させたものである。直流電界を印加することで、特定の周波数範囲内でfrを調整することが可能である。興味深いことに、電界を増加させると、最初にfrが低周波側にシフトし、その後高周波側に移動する。この現象は、粒状体対のサイズ差を考慮した誘電特性を理論的に検討しました。

研究成果の学術的意義や社会的意義
This work provide insights into the electric polarisation of disordered granular solids to electric fields associated with nanometric structures, which is of importance in the field of dielectric and spintronics physics and may have application in compact filters and antennas.

研究成果の概要（英文）：I have developed novel dielectric nanogranular materials that allow for the tuning of the dielectric relaxation frequency (fr) in the AC transport response using a DC electric field. These materials have the potential to simplify and miniaturize device structures such as RF low pass filters and antennas. The structure consists of magnetic metal nanoparticles dispersed in an insulating matrix. By applying a direct current electric field, it is possible to adjust the fr within a specific frequency range. Interestingly, increasing the electric field initially shifts the fr towards the low-frequency side before moving to the high-frequency side.
To address this issue, I developed an asymmetric electron tunneling model, which provides an explanation for the observed results. I have also theoretically investigated the dielectric properties based on the asymmetric electron tunneling model, taking into account the size difference between granular pairs.

研究分野： nanocomposite; magnetodielectric;

キーワード： dielectric relaxation　granular dielectrics　electric field　electron tunneling　metal-ceramic composites

１．研究開始当初の背景

Nanogranular materials comprise disordered nanometre-sized granular metals dispersed in a host matrix and are a robust platform for studying complex disordered solids. Based on this platform, a variety of intriguing phenomena have been discovered that involve the interplay of electronic, magnetic, optical, and thermal properties, as well as quantum and superconductive behaviour. At diluted granular fractions (typically less than the percolation threshold of 50% vol. percent), the materials are in the dielectric regime, whereby both DC and AC electrical transport properties have been widely studied in this regime. In particular, the study of AC transport provides an in-depth understanding of the electric polarisation associated with the structural configuration.

In this field, I have conducted experimental and theoretical studies to understand the impact of magnetic particle content and film morphology on the tunnel magneto-dielectric (TMD) effect in nanogranular films. I discovered that the peak frequency of the TMD effect changes as the insulation layer thickness varies. This finding established a strong correlation between the applied magnetic field and charge tunneling between granular pairs in the nanogranular film. I also investigated the structure and alloy composition of the films in detail, successfully creating films with the highest TMD value (8.5%) at room temperature. There has been significant research in a wide range of fields investigating how H and E fields can alter material properties, including optical, electrical, and magnetic properties. Progress has been reported in various material systems, such as electric field control of magnetism and magnetic field control of electrical polarization. Thus, the tunnel magneto-electro-dielectric (TEMD) effect, which is the main focus of this study, is based on the premise that TMD and tunnel electro-dielectric (TED) effects can occur simultaneously and independently.

２．研究の目的

This application aims to develop nanogranular films that exhibit a tunneling electro-magneto-dielectric (TEMD) effect. This effect involves a change in the dielectric effect under the influence of both electric (E) and magnetic (H) fields. This research is exciting as it seeks to explore and control the interaction of electrical and magnetic properties in materials under both H and E fields. In this project, the challenge is to create nanogranular films that demonstrate a TEMD effect, where the dielectric effect is influenced by both electric and magnetic fields. This would allow the two properties to be mutually influential, rather than independent.

３．研究の方法

The Co_x-$(MgF_2)_{1-x}$ films was realized by magnetron co-sputtering of Co and MgF_2 targets on Si/SiO_2/Ti/Pt substrates under an Ar gas pressure of 0.5 Pa at room temperature.

Two target sources are located in one chamber with an angle of 45° relative to the substrates. The Co or FeCo content was carefully regulated by increasing the input power from 80 to 120 W at intervals of 10 W with fixed sputtering power of MgF$_2$ target to 150 W. The substrate was rotated at a speed of 10 rpm to achieve a uniform granular state. Structures were observed using a field-emission transmission electron microscopy and a Cs-corrected 200 kV high-angle annular dark-field (HAADF)-type scanning transmission electron microscope (STEM). The magnetic behavior was measured using a vibrating sample magnetometer. The dielectric and magneto-dielectric properties were measured using an inductance-capacitance-resistance meter within a 1-1000 kHz frequency range and an impedance analyzer in the range of 1 kHz-100 MHz, with magnetic fields ranging up to ±10 kOe or dc bias voltage of 0-2.5V.

４．研究成果

成果 1 [Ref.1]：

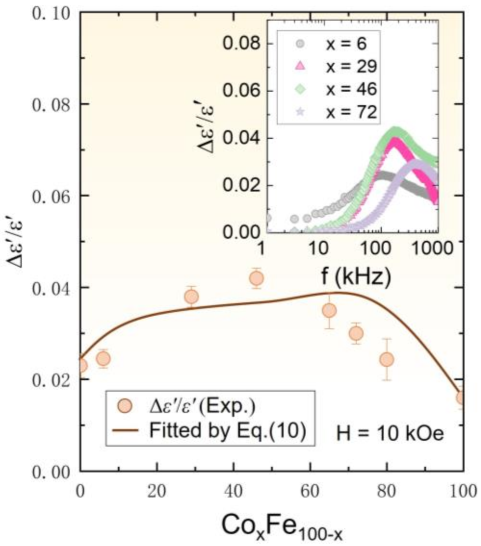

Fig. 1. Tunnel magnetodielectric ratio (Δε'/ε') of the CoFe-MgF$_2$ films at its peak position with various percentages (*x*) of the Co/(Co+Fe) ratio; the error bars denote the deviation of the experimental results measured from two different sputter-deposited samples, and the circles represent their mean values. The solid line is the theoretical fitting. Inset displays the frequency dependence of TMD ratio with selected *x*.

Since the discovery of TMD effect, large experimental effort has been made to improve the magnitude of TMD ratio (Δε'/ε'). For instance, given that the achieved TMD ratio of 0.1% at H = 1 kOe and 0.3% at H = 10 kOe of Fe$_9$Co$_8$-Mg$_{26}$F$_{57}$ nanogranular film was not adequately high, a two-dimensional Co/AlF$_3$ granular heterostructure that permits the introduction of a small fraction of ferromagnetic component was proven to substantially enhance the TMD ratio up to 0.8% at H = 1 kOe; this peak TMD ratio was subsequently increased to 1.45% as the thickness was reduced to the monolayer limit. Furthermore, engineering the refined granule-matrix interfaces further increased TMD ratio up to record highs of 2.1% and 8.5% at H = 1 and H = 10 kOe respectively. Despite these experimental studies on the control or enhancement of TMD effect that have greatly improved the understanding of the structure – property correlation, the prediction of the theoretical limit of TMD ratio has yet to be unravelled so far. On the other hand, although a prior study has illustrated the magnetic-field dependence of TMD ratio, the dependence on the square of the normalized magnetization ($m^2 = M^2/M_s^2$) is yet to be understood despite this correlation (i.e., TMD ratio$\propto m^2$) being centred around the spin-dependent quantum-mechanical charge tunnelling mechanism, which has been observed in numerous nanogranular material systems. Therefore, understanding these behaviours from a theoretical perspective, specifically on how large TMD ratio can attain and how such a correlation can arise, is critical.

In this study, we combine the Debye-Fröhlich model with the spin-dependent charge tunnelling effect to theoretically derive the limit of TMD ratio and show that the TMD ratio can be expressed as TMD ratio = $2P_T^2m^2$, where P_T is the tunnelling spin polarization (P_T) of the magnetic nanogranules and m is the normalized magnetization ($m = M/M_s$). According to this equation, for a sufficiently large magnetic field (m = 1), TMD ratio becomes $2P_T^2$, whereby it allows predicting a theoretical limit of TMD ratio exceeding 200%, and for a small P_T, TMD ratio is proportional to m^2. We finally investigate the x-dependence of TMD ratio in (Co_xFe_{100-x})-MgF_2 films that can be consistently explained by the formulation.

成果2[Ref.2]：

Frequency filters that alter the amplitude and phase of an electrical signal with respect to the frequency are extensively used in electronic applications such as telecommunication and signal processing systems, which can transmit the desired signal in a specific frequency range while rejecting or suppressing signals in the undesired frequency range. In tunable filters, the passband frequency can be effectively tuned via mechanical, magnetic, or electrical approaches, and have been explored using a variety of technologies, including switched capacitor networks, microelectromechanical systems, ferroelectric, and ferromagnetic films. Tunable frequency filters may cover multiple frequencies to meet different scenarios in multiple band operations.

In this work, we demonstrate new dielectric nanogranular materials, where the dielectric relaxation frequency (f_r) of the AC transport response is tuned by a DC electric field. Using dielectric granular materials with electrically tunable frequency response, device structures such as RF low pass filters and antennas may be simplified and miniaturised. The structure comprises nanometre-sized magnetic metals dispersed in an insulating matrix. Using different metallic Co fractions (x) of Co-MgF_2 films, f_r can be tuned by the electric field. Specifically, for $x = 0.24$, f_r is controlled in the range from 1.5 MHz (OFF state) to 2.2 MHz (ON state) by increasing the electric field up to 14 kV/cm, as shown in Fig. 2.

To probe the origin of the electric-field induced tunable f_r in this work, we focus on the Debye-Fröhlich model. As described earlier, charge oscillation is typically considered based on the granular pairs of the same size, forming a double potential well in the AC electric field $E_\omega(t)$. This model explains the distribution of f_r by introducing a distribution function. Nonetheless, the granular size difference and resulting charge energy difference in each granular pair are ignored. In the absence of charging energy difference ($\Delta E_c = 0$), the variation of f_r is monotonically increased as E is gradually applied, which is unable to reproduce and explain the calculation result. By introducing the charging energy difference ($\Delta E_c \neq 0$), which is a natural consequence of granular systems, we propose a generalised asymmetric model. For this model, there exists a difference in granular size ($d_1 > d_2$), which causes the potential shift to be asymmetric in the electric field $E(t) = E_\omega(t) + E$, where $E_\omega(t)$ is the AC electric field and E is the DC electric field. Based on this model, the calculation results indicate that f_r first decreases in small E, and then increases upon further increasing E, which is consistent with the results. Further, the theoretical calculations reveal that the granular size difference ($d_1 - d_2$) is proportional to the decreased magnitude of f_r in small E. In other words, as the size difference increases, f_r decreases sharply. For a specific combination of d_1 and d_2 (*e.g.*, d_1 = 3.0 nm, d_2 = 2.0 nm), an increasingly large intergranular separation (s_{12}) may result in a sharp increase while maintaining a negligibly small decrease in f_r with increased E. This model allows establishing the structure-property relationship in disordered granular solids and quantitively analysing the effect of structural parameters on the tunability of f_r.

This work was recently published on *Advanced Electronic Materials* and was selected as Front Cover.

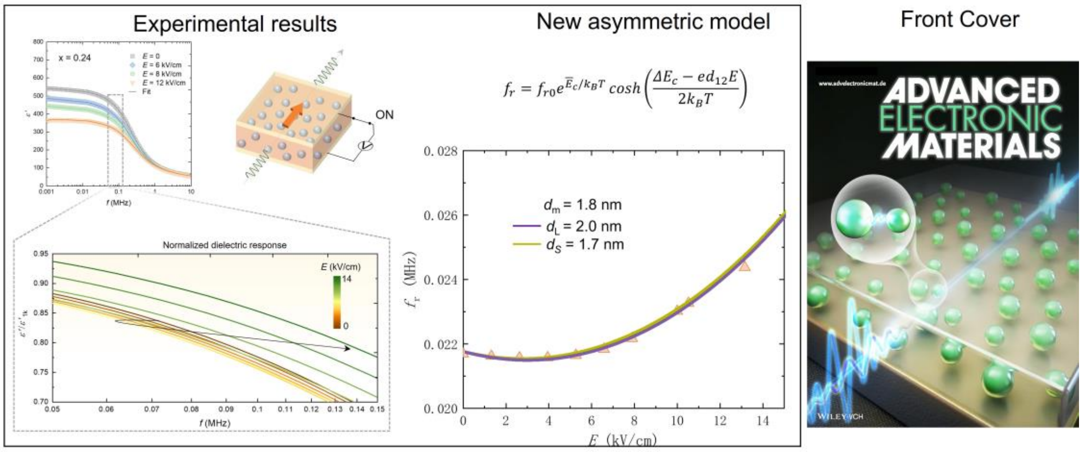

Fig.2. Experimental dielectric variations under different electric field ranging from 0 to 12 kV/cm and newly established asymmetric charge tunneling model to fit the dielectric relaxation frequency. This work was selected as Front Cover in Advanced Electronic Materials.

Reference:

1. Y. Cao, et al, Appl. Phys. Lett. 2022, 120, 082901.
2. Y. Cao, et al, Adv. Electron. Mater. 2023, 2201218.

５．主な発表論文等

〔雑誌論文〕　計5件（うち査読付論文　5件／うち国際共著　1件／うちオープンアクセス　5件）

１．著者名 Kimura Moe、Cao Yang、Kijima-Aoki Hanae、Kobayashi Nobukiyo、Ohnuma Shigehiro、Masumoto Hiroshi	４．巻 63
２．論文標題 Tunneling Magnetodielectric Effect in CoAlO Granular Films	５．発行年 2022年
３．雑誌名 MATERIALS TRANSACTIONS	６．最初と最後の頁 1677～1681
掲載論文のDOI（デジタルオブジェクト識別子） 10.2320/matertrans.MT-M2022098	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

１．著者名 Cao Yang、Kobayashi Nobukiyo、Wang Cheng、Takahashi Saburo、Maekawa Sadamichi、Masumoto Hiroshi	４．巻 2201218
２．論文標題 Novel Dielectric Nanogranular Materials with an Electrically Tunable Frequency Response	５．発行年 2023年
３．雑誌名 Advanced Electronic Materials	６．最初と最後の頁 1-9
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/aelm.202201218	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

１．著者名 Cao Yang、Kobayashi Nobukiyo、Masumoto Hiroshi	４．巻 120
２．論文標題 Tunnel magnetodielectric effect: Theory and experiment	５．発行年 2022年
３．雑誌名 Applied Physics Letters	６．最初と最後の頁 082901～082901
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１．著者名 Cao Yang、Nogawa Kenta、Kobayashi Nobukiyo、Masumoto Hiroshi	４．巻 14
２．論文標題 Fabrication of transition metal (TM=Fe, Co) difluorides carbon nanocomposite films by magnetron co-sputtered deposition of Fe/Co and Teflon targets	５．発行年 2021年
３．雑誌名 Applied Physics Express	６．最初と最後の頁 075502～075502
掲載論文のDOI（デジタルオブジェクト識別子） 10.35848/1882-0786/ac07f0	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

１．著者名 Wang Cheng、Cao Yang、Kobayashi Nobukiyo、Ohnuma Shigehiro、Masumoto Hiroshi	**４．巻** 11
２．論文標題 Structure and tunneling magneto-dielectric properties of CoSrF nano-granular thin films	**５．発行年** 2021年
３．雑誌名 AIP Advances	**６．最初と最後の頁** 085224～085224
掲載論文のDOI（デジタルオブジェクト識別子） 10.1063/5.0058707	**査読の有無** 有
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〔学会発表〕　計4件（うち招待講演　2件／うち国際学会　3件）

１．発表者名 Yang Cao, Nobukiyo Kobayashi, Shigehiro Ohnuma, Hiroshi Masumoto
２．発表標題 Electrical control of tunnel magnetodielectric response in nanogranular films
３．学会等名 日本金属学会（2022年秋）
４．発表年 2022年

１．発表者名 Yang Cao
２．発表標題 Tunnel Magnetodielectric Effect Experimental and Theoretical Progress
３．学会等名 Physics 2022（招待講演）（国際学会）
４．発表年 2022年

１．発表者名 Yang Cao
２．発表標題 Tunable Tunneling Magneto-Dielectric Response via Heterostructure Routes
３．学会等名 Global Summit on Condensed Matter Physics (CONMAT2021)（招待講演）（国際学会）
４．発表年 2021年

１．発表者名 Yang Cao, Nobukiyo Kobayashi, Shigehiro Ohnuma, Hiroshi Masumoto
２．発表標題 Tunneling magneto-dielectric response in nanogranular films: Theoretical and experimental studies
３．学会等名 Material Research Meeting 2021 (MRM2021)（国際学会）
４．発表年 2021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
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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