SOLID STATE CHEMISTRY

Annual Research Highlights

(1) Possible ferroelectricity in perovskite oxynitride $SrTaO_2N$ epitaxial thin films

Perovskite oxynitrides have attracted much attention because of their novel electronic functionalities, such as visible light absorption, photocatalytic activity, colossal magneto-resistance, and high dielectric constant. It has been suggested that the dielectric properties of ABO_2N are related to anion arrangement in BO_4N_2 octahedra: for example, ferroelectricity may be caused by the off-center displacement of Ta ions in trans-type anion-ordered $ATaO_2N$ (A = Sr or Ba) phases. In this study, we realized room-temperature ferroelectricity in compressively strained $SrTaO_2N$ thin films epitaxially grown on $SrTiO_3$ substrates by nitrogen-plasma assisted pulsed laser deposition. Local piezoresponse measurements revealed the incorporation of small classical ferroelectric domains with dimensions of 10^1–10^2 nm in a relaxor ferroelectric-like matrix (Fig. 1). The ferroelectric domains and the relaxor-like matrix were identified as *trans*- and *cis*-type phases, respectively, based on results of first-principles density functional theory (DFT) calculations that mapped the total energy of $SrTaO_2N$ for various lattice parameters.

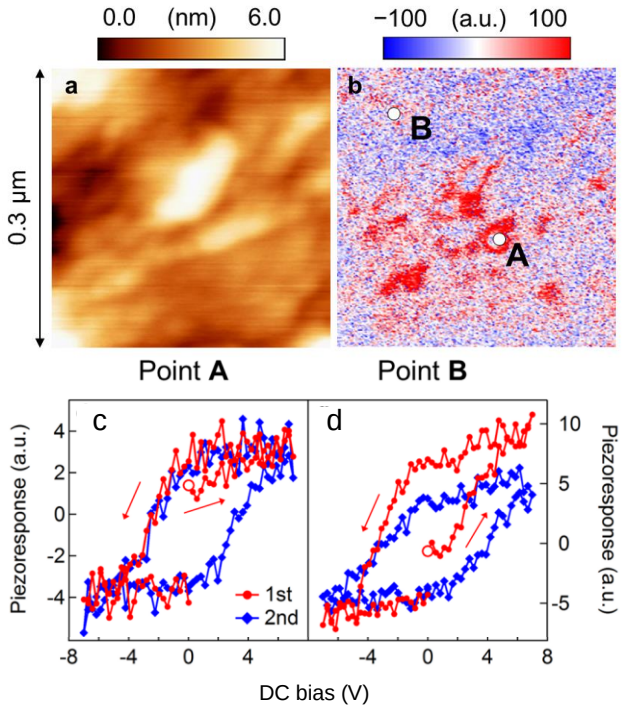

Fig. 1 (a) Topographic and (b) piezoresponse ($A\cos\theta$) images of the $SrTaO_2N$ thin film grown on $SrTiO_3$ (100) substrate measured by a piezoresponse force microscope. (c, d) Local piezoresponse examined by switching spectroscopy with an AC bias of ±1 V at positions A (c) and B (d) indicated in (b). Open circles represent the initial point of the measurements.

1.(1)-9) *Sci. Rep.*, **4**, 4987 (2014)

(2) Large perpendicular magnetic anisotropy in ferrimagnetic Mn_4N epitaxial thin films

Materials with perpendicular magnetic anisotropy (PMA) have attracted considerable attention because of their potential applications in spintronics. While CoPt-based alloy thin films are widely used as perpendicular magnetic recording media, development of noble metal-free PMA materials is strongly desired from the viewpoint of element strategy. In this study, we focused on an antiperovskite-type manganese nitride Mn_4N, which shows ferrimagnetism with a Néel temperature of 738 K. We successfully fabricated highly-crystalline Mn_4N (001) epitaxial thin films grown on MgO (001) substrates using a pulsed laser deposition method, and investigated the electronic transport and magnetic properties. The fabricated Mn_4N thin films were tetragonally distorted with a ratio of out-of-plane to in-plane lattice constants of 0.987. We observed large PMA with an effective magnetic anisotropy constant of 0.16 MJ/m^3, and metallic transport with a room temperature resistivity of 125 μΩ cm. In addition, the Mn_4N thin films exhibited a large anomalous Hall effect at room temperature, where the Hall resistivity and the tangent of the Hall angle were 2.8 μΩ cm and 0.023, respectively. These values are comparable with those of typical PMA materials.

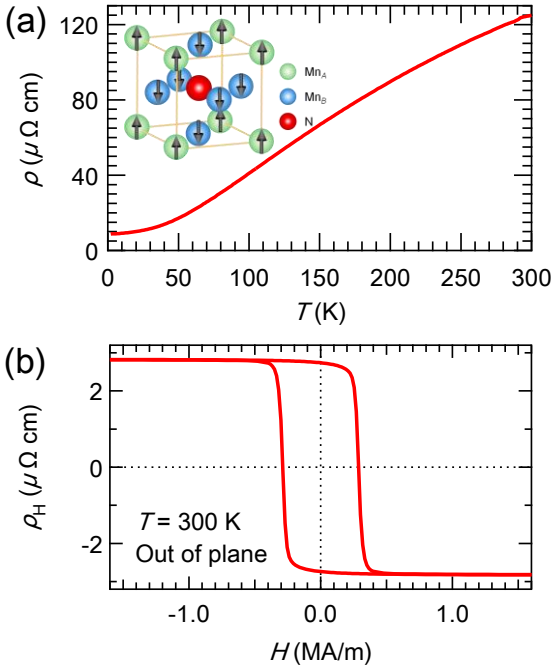

Fig. 2 (a) Resistivity vs. temperature and (b) Hall resistivity vs. temperature curves of 35-nm-thick Mn_4N thin film. The inset shows the schematic of antiperovskite structure of Mn_4N composed of Mn_A (green circles), Mn_B (blue circles), and N (red circle) atoms. Arrows indicate the direction of electron spin.

2.(1)-16) *App. Phys. Lett.*, **105**, 072410 (2014)

固体化学研究室

研究ハイライト

(1) ペロブスカイト型酸窒化物 $SrTaO_2N$ 薄膜の強誘電体的挙動

ペロブスカイト型酸窒化物は、顔料や光触媒、誘電材料などとして盛んに研究がおこなわれている。中でも、ABO_2N 型のペロブスカイトでは、BO_4N_2 八面体中のアニオン配列と誘電特性の関係に興味が持たれている。例えば、*trans* 型の $ATaO_2N$ (A=Sr or Ta) では、強誘電性を示す可能性が報告されている。本研究では、面内方向に圧縮歪みを印加した $SrTaO_2N$ 薄膜を窒素プラズマ支援パルスレーザー堆積法により合成し、室温強誘電性の観察に成功した。導電性の Nb ドープ $SrTiO_3$ 基板上に作製した薄膜の圧電応答顕微鏡像を図 1b に示す。通常の強誘電性を示す 10-100 nm 程度の微小な領域(A)とリラクサー強誘電体的な応答を示すマトリクス領域(B)からなることがわかる。格子歪みとアニオン配列、強誘電性に関する第一原理計算を行い、*cis* 型のマトリクス領域中に *trans* 型の強誘電性領域が局在しているモデルを提案した。

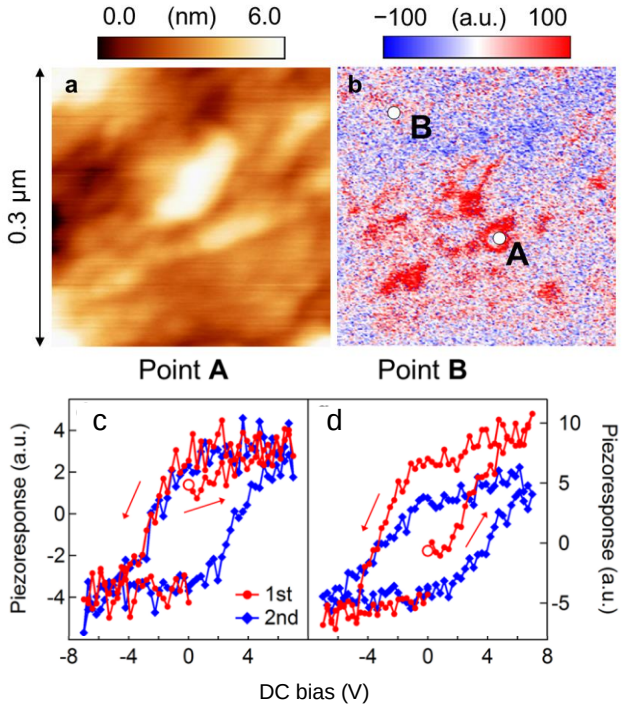

図 1 $SrTiO_3$ 基板上に作製した $SrTaO_2N$ 薄膜の(a)凹凸像と(b)圧電応答像。(c, d)図 b 中の A および B 点における局所スイッチング挙動。

1.(1)-9) *Sci. Rep.*, **4**, 4987 (2014)

(2) フェリ磁性体 Mn_4N エピタキシャル薄膜の大きな垂直磁気異方性

垂直磁気異方性(PMA)薄膜は、薄膜表面に垂直な方向に磁化容易軸を持つ。この特性をハードディスクの磁気記録様式に応用することで、メモリ容量の格段な増加が実現された。近年では、スピントロニクス分野において、スピンバルブや磁気トンネル接合素子にも PMA 薄膜が応用されている。現在、PMA 材料として希少金属元素で構成される CoPt 合金等が広く使用されているが、元素戦略的な視点から、希少金属を使わず大きな PMA を示す材料の開発が切望されている。本研究では、ネール温度 738 K のフェリ磁性を示す逆ペロブスカイト型構造 Mn_4N に注目し、パルスレーザー堆積法を用いて高い結晶性を持つ Mn_4N エピタキシャル薄膜の作製と磁気輸送特性の評価を行った。

MgO 基板上に堆積させた Mn_4N エピタキシャル薄膜は、面内に対する面直の格子定数比が 0.987 である正方晶的な歪みを有しており、室温で 125 μm の電気抵抗率を持つ金属伝導と大きな PMA (0.16 MJ/m^3)を示すことを明らかにした。さらに、この薄膜が従来の PMA 薄膜に匹敵する 2.8 $\mu\Omega$ の異常ホール抵抗と 0.023 のホール角の正接を持つことを見出した。

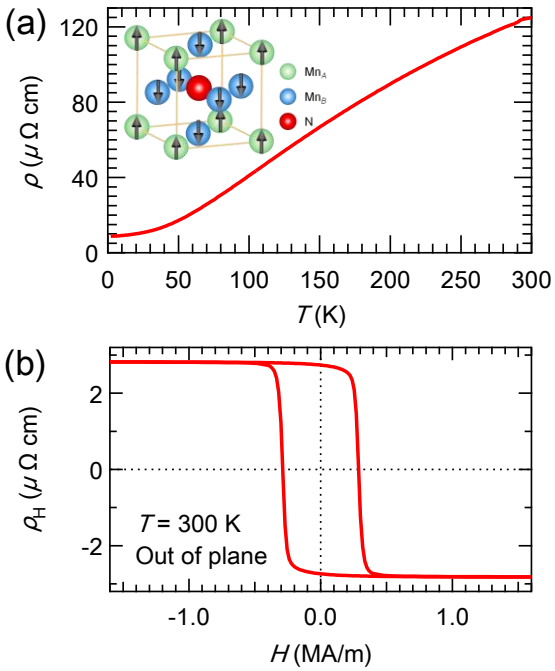

図 2 Mn_4N 薄膜(35 nm)の(a)電気抵抗率と(b)ホール抵抗率の温度依存性。(挿入図) Mn_4N の逆ペロブスカイト型構造（Mn_A (緑丸)・Mn_B (青丸)・N (赤丸)・スピンの向き(矢印)）。

2.(1)-16) *App. Phys. Lett.*, **105**, 072410 (2014)

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3. 著書

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