様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科研費 KAKENHI

科学研究費助成事業　　研究成果報告書

平成 ２９ 年　 ５ 月 ２３ 日現在

機関番号：１１３０１
研究種目：若手研究(B)
研究期間：2015～2016
課題番号：１５Ｋ１８２３１

研究課題名（和文）界面拡散層の抑制により大きな磁気誘電および磁気光学効果を有するナノ複相薄膜の創製

研究課題名（英文）The nano-composite films with large magneto-dielectric and magneto-optical properties by interface diffusion layer controlling

研究代表者
張　亦文（Zhang, Yiwen）

東北大学・学際科学フロンティア研究所・助教

研究者番号：３０５７９９５９

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）：電子デバイスや磁気記録の急激な発展に伴い、高誘電率、磁気ー誘電、磁気ー光学効果などの多機能性材料が必要とされている。ナノ複相膜は、セラミックス母相とナノ金属粒子との界面の面積が巨大なことから、多くの機能性が発現する。しかし、相互拡散し易い金属とセラミックス原子同士の場合には、ヘテロ界面に厚い原子拡散層が発生し、機能性発現の大きな障害となっている。本研究では、大きな磁気誘電効果や磁気光学効果などの発現を目指して、新しい開発した差動圧力スパッタ（DPS）法を用いて酸化物と金属粒子界面拡散層を抑制することが成功した。これらの機能性は次世代センサや超高密度記録などへの応用化が大いに期待できる。

研究成果の概要（英文）：Developments of electromagnetic devices require multi-functional materials, such as magnetic-dielectric films, and multiferroic materials. The nanocomposite films consist of magnetic nano-sized metal particles and an insulator phase. These films have significant practical advantage of easy fabrication and have been applied in magnetic sensors. They possess enhanced properties such as the high dielectric constant, magneto-dielectric effects , and magneto-optical effects at room temperature.However, it is usually difficult. Because conventional deposition systems keep the metal and the ceramic deposition in the same atmosphere, which easily induce the intermixing at interface. In this research, I have developed the newly Differential pressure sputtering (DPS) method, and successfully realize controlling the interface of the Oxide-Metal nano-composite films.

研究分野：magnetic and dielectric films

キーワード：nano-composite films　super-paramagnetic　dielectric constant

１．研究開始当初の背景

It is required that multi-functional materials should be developed for novel micro-electronic devices. Recently, a variety of materials have been studied as magnetoelectric systems. However, the properties only show substantial value at low temperature. Among of them, the nanocomposite films consist of magnetic nano-sized metal particles and an insulator phase. These films have significant practical advantage of easy fabrication and have been applied in magnetic sensors. They possess enhanced properties such as the newly discovered magneto-dielectric effects and magneto-optical effects at room temperature.

２．研究の目的

Our early work has found that the MgF-FeCo nano-composite films show giant dielectric properties and TiN-Co nano-composite films show good high-frequency magnetic properties. These results show that the insulation property and superparamagnetic property are important to obtain the magnetic-dielectric properties, which require the small particle size around 2 nm and uniform dispersion of magnetic metal particles in insulator phase. For this aim, $BaTiO_3$ (BTO) is a good candidate as insulator phase owing to its high insulation (ρ), dielectric constant (ε) and good thermal stability. Recently, the BTO-Co nano-composite films have been studied for multiferroic materials, which demonstrate well insulation for dielectric properties. The Co particles size of the films is above 30 nm, which exhibits ferromagnetic property rather than superparamagnetic property. These films with ferromagnetic properties provide high potential for multiferroic materials. Whereas, the films with superparamagnetic property open another door for magnetoelectric coupling effect, such as newly discovered magneto-dielectric effects. Therefore, controlling Co particle size in the BTO-Co films is key point to realize superparamagnetic property and magnetic-dielectric property. In this research, the BTO-Co multi-layer structured nano-composite films have been designed to control the Co particle size for superparamagnetic property. However, the easy oxidation of Co particles with nano-sized diameter could deteriorate magnetic properties of Oxide-Co system. Therefore, the influence of Co oxidation phase between BTO/Co on the properties is important and will be researched here.

３．研究の方法

The BTO-Co nanocomposite and multi-layer films have been produced on Si (100), Pt/Si and quartz substrates by the Differential Pressure Sputtering (DPS), with two separated sputtering chambers for oxide (BTO) and metal (Co) inside one big chamber. The films could be co-deposited by rotation of the substrate. The Ar gas pressure of each chamber was of 6.0×10^{-1} Pa. The thickness of each layer of multi-layer films were controlled by sputtering power and the deposition time in each chamber. The power of BTO target was set at 100 W, and power of Co was changed from 25 to 150 W.

The structure of the as-deposited BTO-Co films was analyzed by X-ray diffraction (XRD, Bruker NEW D8 ADVANCE) using Cu K_{α} radiation and field-emission transmission electron microscopy (FETEM, Hitachi 4300E). The composition of the films were identified by X-ray photoelectron spectroscopy depth profile (XPS, ZSX Primus 2). Film thickness was tested by surface profile-meter (Dektak 8). Electrical resistivity was measured by a conventional four-point probe method. The magnetization curves were identified by a vibrating sample magnetometer (VSM, Rikendensi, BHV-30SS). The dielectric properties were analyzed by inductance, capacitance and resistance (LCR) meter with measurement range in 1 kHz-1MHz. All the measurements reported in this paper were carried out at room temperature.

4. 研究成果

The thickness of each BTO layer keep constant about 2 nm. By changing the sputtering power, the thickness of each Co layer is controlled from 0.3 to 6.3 nm. From XRD, the low-angle region modulation peaks are caused by the periodic multi-layer structure of BTO-Co films, consisting of amorphous BTO layers and Co layers. The thickness of one period of BTO/Co layers can be calculated by the distance between low-angle peaks, which increases from 2.3 to 8.3 nm with the Co sputtering power increasing, which is consistent with our design.

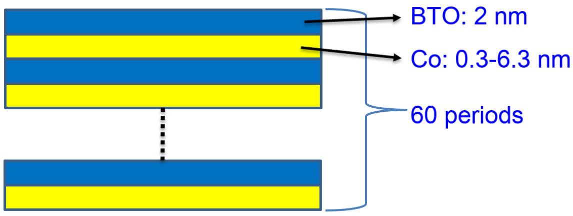

Fig. 1. Schematic drawing of the design of the BTO-Co multi-layer films.

The microstructure of BTO (2 nm)/Co (2.5 nm) film (typical sample) has been investigated by the TEM and HRTEM. As shown in Fig. 2(a), cross-sectional bright-field TEM of BTO-Co films illustrates the clear multi-layer structure of BTO (2 nm)/Co (2.5 nm) film. Figure 2(b) shows the nanometer-sized Co around 2 nm in diameters appear in the Co layers. The Co particles have fcc and/or hcp crystalline structure (difficult to distinguish) with the estimated lattice parameter about 0.205 nm. On the other hand, a small amount of CoO particles also have been observed and the CoO possess fcc crystalline structure with the estimated lattice parameter about 0.244 nm. Comparing to the Co particles size (above 30 nm) of the reported studies, the smaller Co particles of about 2 nm have been realized by Co layer thickness controlling in the BTO-Co films, which show homogeneous dispersion of Co particles. Considering this structure, these BTO-Co films could exhibit the superparamagnetic properties, which is important to obtain the magnetic-dielectric properties.

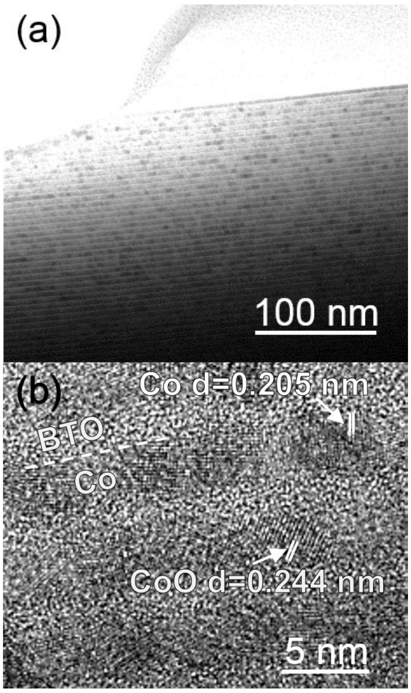

Fig. 2. TEM image from the cross-section view (a), HRTEM image (b) of BTO(2 nm)/Co(2.5 nm) film.

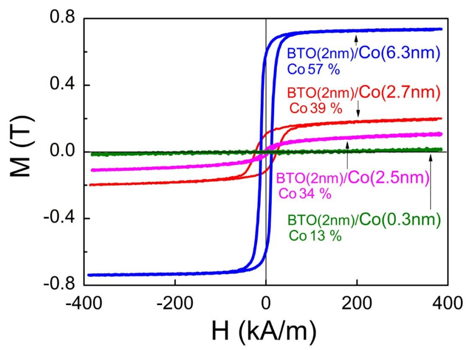

Fig. 3. Hysteresis loops of BTO-Co films with different Co layer thickness from 0.3 nm to 6.3 nm.

Figure 3 shows the magnetic properties of BTO-Co films with different Co layer thickness. The saturation magnetization (M_s) of films increases from 0.01 to 0.73 T, with the Co layer thickness increasing. Note that the films with large Co layer thickness show high Ms, and that M_s/Co_{atom} (the estimated saturation magnetization per Co atom) increases from 0.08 T to1.3 T. This rapid increment of M_s indicates the partially oxidation of Co metal is suppressed in the films with thick Co layer. However, M_s of the films is still lower than that of pure Co 1.8 T, which suggests that the films contain a considerable amount of Co oxidation component, which have been identified by the HRTEM above (Fig. 2). Considering the magnetic hysteresis loops of the films, the films exhibit ferromagnetic properties with Co layer thickness higher than 2.5 nm. Whereas, they shows the superparamagnetic properties with the Co layer thickness lower than 2.5 nm, which have potential for the magnetic-dielectric properties.

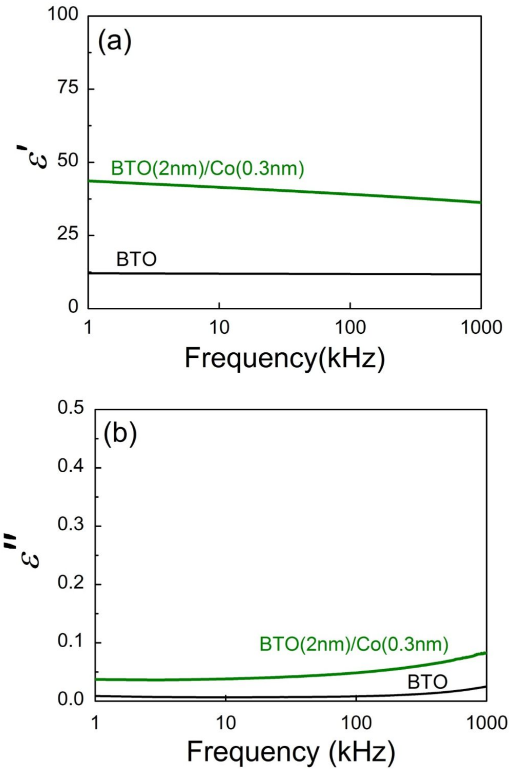

Fig. 4. Dielectric properties of the BTO and BTO-CO films: the real part of dielectric constant (ε') (a), the imaginary part of dielectric constant (ε") (b) at 1 kHz.

ρ of the BTO-Co films was controlled from 10^0 to 10^6 μΩ·m by the Co layer thickness from 6.3 nm to 0.3 nm. This high resistivity BTO-Co films, should have the effect of Co layer on the dielectric properties. Figure 4 shows the real part of dielectric constant (ε') at 1 kHz of the BTO film and BTO-Co film. Comparing to the BTO film, it shows the ε increasing from about 10 to 40 of the BTO-Co multi-layer nanocomposite films with lower Co layer thickness. The imaginary part of dielectric constant (ε") of BTO-Co film also increases, but it is still lower than 0.1 within a frequency range from 1 kHz to 1000 kHz, which indicates that it has less leaking current between the Co layers. However, M_s of this film is small about 0.01 T, owing to the partial oxidation of nano-sized Co particles. The increase of dielectric constant proves that amount of Co metal particles still exist in the BTO-Co films. This newly phenomenon also have been observed in MgF-FeCo nano-composite films of our early work, which is explained by spin-dependent charge oscillation caused by quantum mechanical tunneling between magnetic particles. The further study should be performed for understanding mechanism and realizing high insulating BTO-Co nano-composite films with pure metal Co particles of around 2 nm in diameter. According to this research, I have published the paper of "Magnetic and Dielectric Properties of $BaTiO_3$-Co Multi-layer Nano-composite Films" on the professional journal (***J. of Magn. & Magn. Mater.***). I also have obtained the Award for Best Poster Presentation on the 2016 Annual conference of the ceramic society of Japan.

５．主な発表論文等

〔雑誌論文〕（計４件）

① Y. Cao, N. Kobayashi, **Y. Zhang**, S. Ohnuma, H. Masumoto, Enhancement of low-field magneto-dielectric response in two-dimensional Co/AlF granular films, ***Appl. Phys. Lett.***, 査読有, Vol. 110, No 7, pp. 072902-1–072902-5, Feb., 2017. DOI 10.1063/1.4976743

② Y. Cao, **Y. Zhang**, S. Ohnuma, N. Kobayashi, H. Masumoto, Control of the static and high-frequency magnetic properties in perpendicular anisotropic Co–HfN granular films through insertion of HfN interlayers, ***Jpn. J. Appl. Phys.*** 査読有, (*Rapid communication*), Vol. 56, No 4,

pp. 040307-1–040307-4, Mar., 2017. DOI 10.7567/JJAP

③ **Yiwen Zhang**, Nobukiyo Kobayashi, Shigehiro Ohnuma, Masateru Nose and Hiroshi Masumoto, Structure, Magnetic and Dielectric Properties of $BaTiO_3$-Co Multi-layer Nano-composite Films, ***J. of Magn. & Magn. Mater.*** **査読有**, Vol. 401, pp. 925-928, 2016. DOI 10.1016/j.jmmm.2015.11.006

④ Yang Cao, **Yiwen Zhang**, Shigehiro Ohnuma, Nobukiyo Kobayashi and Hiroshi Masumoto, Structure and isotropic high-frequency response of Co-HfN nanogranular films, ***IEEE Trans. on Magn.,*** **査読有**, Vol. 51, pp. 2801404, 2015. DOI 10.1109/Tmag.2015.2438003

〔学会発表〕（計 5 件）

① **Yiwen Zhang**, Hiroyuki Kosukegawa, Hiroyuki Miki, Nobukiyo Kobayashi, Shigehiro Ohnuma, Toshiyuki Takagi, and Hiroshi Masumoto
Electrical and Magnetic Properties of DLC-Co Nano-composite Films by Hybrid Deposition Method
61st Annual Conference on Magnetism and Magnetic Materials (MMM), 2016.10.31-2016.11.04, New Orleans, USA

② **Yiwen Zhang**, Nobukiyo Kobayashi, Shigehiro Ohnuma, Masateru Nose, and Hiroshi Masumoto
Improvement of magnetic properties of $BaTiO_3$-Co nano-composite films by differential pressure sputtering
9th Pacific Rim International Conference on Advanced Materials and Processing (PRICM9), 2016.08.01-2016.08.05, Kyoto International Conference Center, Kyoto, Japan

③ **Yiwen Zhang**, Nobukiyo Kobayashi, Shigehiro Ohnuma, Masateru Nose and Hiroshi Masumoto
Characterization of Interface State, Magnetic and Electric Properties of $BaTiO_3$-Co Multi-layer Films
The 10th International Conference on Surfaces, Coatings and Nanostructured Materials (NANOSMAT) 2015.09.13-16, Manchester, UK

④ **Yiwen Zhang**, Yiwen Zhang, Nobukiyo Kobayashi, Shigehiro Ohnuma, Masateru Nose and Hiroshi Masumoto
Structure, Magnetic and Dielectric Properties of $BaTiO_3$-Co Multi-layer Nano-composite Films
The 20th International Conference on Magnetism 2015.07.05-10, Barcelona, Spain

⑤ **Yiwen Zhang**, Hiroyuki Kosukegawa, Hiroyuki Miki, Nobukiyo Kobayashi, Shigehiro Ohnuma, Toshiyuki Takagi, Hiroshi Masumoto
Structure and Properties of C-Co Nano-composite Film by Hybrid Deposition Method
日本セラミックス協会 2016 **年会**
2016.03.14-16 **早稲田大学，東京**

〔図書〕（計 0 件）

〔産業財産権〕

○出願状況（計 0 件）

名称：
発明者：
権利者：
種類：
番号：
出願年月日：
国内外の別：

○取得状況（計 0 件）

名称：
発明者：
権利者：
種類：
番号：
取得年月日：
国内外の別：

〔その他〕
ホームページ等

６．研究組織

(1)研究代表者
張 亦文（ZHANG, Yiwen）
東北大学・学際科学フロンティア研究所・助教
研究者番号： 30579959