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Feature article

Structural and electrical properties of $Sr_2NaNb_4O_{13}$ thin film grown by electrophoretic method using nanosheets synthesized from $K(Sr_2Na)Nb_4O_{13}$ compound

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ABSTRACT

$Sr_2NaNb_4O_{13}^-$ ($SNNO^-$) nanosheets were exfoliated from the $K(Sr_2Na)Nb_4O_{13}$ compound that was synthesized at 1200 °C. The $SNNO^-$ nanosheets were deposited on a $Pt/Ti/SiO_2/Si$ substrate at room temperature by the electrophoretic method. Annealing was conducted at various temperatures to remove organic defects in the SNNO film. A crystalline SNNO phase without organic defects was formed in the film annealed at 500 °C. However, a $SrNb_2O_6$ secondary phase was formed in the films annealed above 600 °C, probably due to the evaporation of Na_2O. The SNNO thin film annealed at 500 °C showed a dielectric constant of 74 at 1.0 MHz with a dielectric loss of 2.2%. This film also exhibited a low leakage current density of 9.0×10^{-8} A/cm^2 at 0.6 MV/cm with a high breakdown electric field of 0.72 MV/cm.

1. Introduction

Miniaturization and performance enhancement are required for future microelectronic devices, including dynamic random-access memories, embedded capacitors, gate insulators, and tunable devices [1,2]. These devices can be realized using dielectric thin films with large dielectric constant (ε_r) and low loss (*tan* δ). The ε_r value of most of the dielectric thin films is too low for future microelectronic devices [3–6]. Although some of the dielectric thin films, such as $(Ba_{1-x}Sr_x)TiO_3$ and $Pb(Zr_{1-x}Ti_x)O_3$, have large ε_r value, the value decreases with the decrease of film thickness [7–11]. Therefore, it is necessary to develop a new type of thin film material for future microelectronic devices.

Recently, investigations of two-dimensional materials, such as graphene, boron nitride, metal disulfides, and metal oxides, have increased, because of their innovative electronic, magnetic, and optical properties [12–14]. In particular, interest in metal oxide nanosheets has increased, because the dielectric thin films deposited using metal oxide nanosheets exhibited large ε_r value with low *tan* δ, indicating that they can be used for future microelectronic devices [15–19]. These metal oxide nanosheets can be easily produced from layered-structure compounds through exfoliation processes, and can be deposited on substrates using layer-by-layer (LBL), Langmuir-Blodgett (LB), and electrophoretic methods [15–23].

The LBL method, which uses oppositely charged polyelectrolytes, is a useful method to grow the high dielectric thin films using oxide nanosheets, and the $Ti_{0.87}O_2$ thin film grown by LBL method exhibited large ε_r with low *tan* δ [15]. The LB method is also known as a simple and effective deposition method for nanosheets. Perovskite and titano-niobate nanosheets deposited using the LB method exhibited large ε_r (>200) with low *tan* δ (1 ~ 5%) [16–19]. Moreover, the decrease of ε_r value with decreasing film thickness was not observed in thin films deposited by the LB method [16–19]. Although LBL and LB are effective methods to deposit thin films using nanosheets, they require a long processing time, indicating that these methods could be unsuitable for large-scale production.

Nanosheets can also be deposited using the electrophoretic method. The crystalline quality of thin films grown by the electrophoretic method is not very good, compared with that of thin films grown by the LB and LBL methods [15–19,23].

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However, the growth rate with the electrophoretic method is much faster than those of the LBL and LB methods [24,25]. Furthermore, the electrophoresis can be used to deposit nanosheets on substrates of various types and shapes [25]. Therefore, the electrophoretic method is a useful method for mass production and deposition on irregular substrates. In this work, $Sr_2NaNb_4O_{13}^-$ ($SNNO^-$) nanosheets, which have four oxygen octahedral layers, were exfoliated from a $K(Sr_2Na)Nb_4O_{13}$ (KSNN) compound, and subsequently deposited on Pt/Ti/SiO_2/Si (Pt-Si) substrate using the electrophoretic method. Furthermore, the synthesis and exfoliation process for the precursor compound, and the structural and electric properties of the SNNO thin films were systematically investigated.

2. Experimental section

K_2CO_3, Na_2CO_3, $SrCO_3$, and Nb_2O_5 powders (>99%, High Purity Chemicals Co., Japan) were mixed using ball-milling with ethanol for 24 h, and then dried at 90 °C. The dried powders were calcined at temperatures between 500 °C and 1300 °C for 10 h. The KSNN compound calcined at 1200 °C was mixed with 4.0 M HCl solution, and stirred for 3 days at 200 rpm to exchange the K^+ ions for H^+ ions. After a filtration process, a homogeneous $H(Sr_2Na)Nb_4O_{13}$ (HSNN) powder was obtained. In order to form the $SNNO^-$ nanosheets, 2.0 g of the HSNN powder was delaminated in the 400 mL solution consisting of distilled water and tetrabuthylammonium hydroxide (TBAOH: 40 wt%, Sigma Aldrich, USA). Finally, the residual HSNN compound was eliminated by centrifugation. The SNNO thin films were fabricated using the electrophoretic method in polar acetone medium. During electrophoresis, an electrical voltage of 100 V was applied on Pt-Si substrate at room temperature (RT). A 200 W ultraviolet C light (main wavelength of 254 nm) was irradiated on the deposited films to eliminate organic TBA^+ ions. All of the films were annealed at temperatures between 300 °C and 800 °C for 24 h to remove the organic defects.

X-ray diffraction (XRD: Rigaku D/max-RC, Japan) was used to determine the crystal structure of the specimens. Microstructures of the KSNN (or HSNN) powders and the SNNO films were studied using scanning electron microscopy (SEM: Hitachi S-4800, Japan). For the SEM measurement, the specimens were fixed on the SEM specimen holder using carbon tape. High resolution transmission electron microscopy (HRTEM: Jeol JEM 2100F, Japan) was also used to investigate the structural properties of the specimens. Colloidal suspension of $SNNO^-$ nanosheets was dropped onto the Holey carbon TEM grid (Ted Pella Inc., USA) for the TEM analysis. Moreover, TEM specimen of the SNNO film was prepared by the focused ion beam (FIB: Tescan LYRA3, Czech Republic) method. The surface of thin films was analyzed by atomic force microscopy (AFM: Park Systems NX-10). Compositions of specimens were identified by inductively coupled plasma atomic emission spectrophotometry (ICP-AES: Horiba Jobin Yvon Ultima 2, France) and energy-dispersive X-ray spectroscopy (EDS: EMAX, Horiba, Japan) attached to the SEM. Thermogravimetric-differential scanning calorimetry (TG/DSC: TA instruments Q600, USA) and Fourier transform infrared spectroscopy (FTIR: Thermo Fisher Scientific iS 10, USA) were used to investigate the organic defects. Pt top electrodes with a diameter of 300 μm were deposited on the films using the DC sputtering method for the measurement of the electrical properties of the thin films. Capacitance and dielectric loss were measured in the frequency ranges from 75.0 kHz to 1.0 MHz using a precision LCR meter (Agilent 4285A, USA). A programmable electrometer (Keithley 6517B, USA) was used to measure the leakage current of thin films.

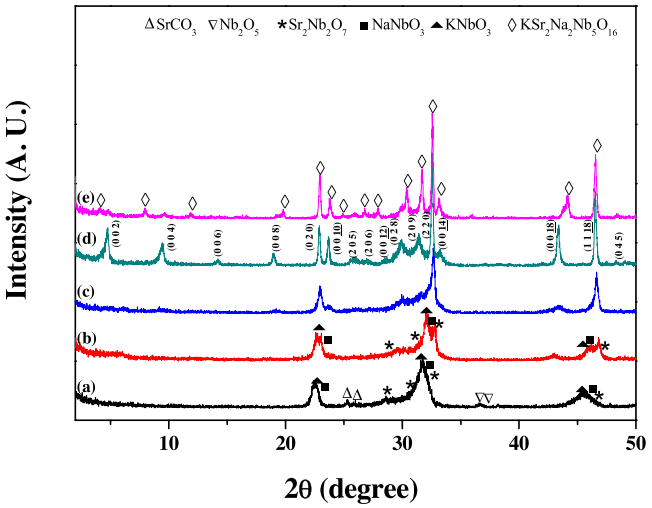

Fig. 1. XRD patterns of the KSNN compounds calcined at various temperatures for 10 h: (a) 500 °C, (b) 800 °C, (c) 1000 °C, (d) 1200 °C, and (e) 1300 °C.

3. Results and discussion

Fig. 1a–e shows the XRD patterns of KSNN specimens that were calcined at various temperatures to investigate the formation processes of the KSNN phase. For the specimens calcined at low temperature (≤800 °C), $Sr_2Nb_2O_7$ [JCPDS # 70-0114], $KNbO_3$ [JCPDS # 71-0947] and $NaNbO_3$ [JCPDS # 89–6654] phases were formed (see Fig. 1a and b). For the specimen calcined at 1000 °C, a small amount of the KSNN phase began to form (see Fig. 1c), through the following reaction: $KNbO_3 + NaNbO_3 + Sr_2Nb_2O_7 \rightarrow K(Sr_2Na)Nb_4O_{13}$. For the specimen calcined at 1200 °C, the KSNN phase was well formed with high intensity (00*l*) reflections (*l* = 2, 4, 6, 8, 10, 12, 14), as shown in Fig. 1d, indicating that it has grains with a large (002) plane. In addition, the crystal structure of the KSNN phase could be the same as that of the $K(Ca_2Na)Nb_4O_{13}$ phase with increased lattice parameters [26,27], as shown in Figs. S1a-f of Supplementary Information 1. However, for the specimen calcined at 1300 °C, a $K(Sr_2Na_2)Nb_5O_{16}$ phase with five NbO_6 octahedral layers was developed (see Fig. 1e). The formation of a $K(Sr_2Na_2)Nb_5O_{16}$ phase can be explained by the evaporation of K_2O, as shown in Figs. S2a and b of Supplementary Information 2.

The KSNN compound calcined at 1200 °C was used to synthesize the $SNNO^-$ nanosheets, because a homogeneous KSNN phase with a large (002) plane was formed in this specimen. HSNN powders were obtained from the KSNN precursor after the exchange of K^+ ions for H^+ ions in HCl solution, and Fig. 2a shows the XRD pattern of the HSNN powders. A homogeneous HSNN phase was formed in this specimen, and a high intensity of (00*l*) reflections was also observed, due to the formation of grains with large (00*l*) planes [26,27]. The inter-planar distance of the basal plane of the HSNN phase is approximately 19.9 Å. Fig. 2b and c show the SEM images of the KSNN precursor and the HSNN specimen, respectively. The average grain size of the plate-like KSNN precursor is approximately 0.5 μm, and the HSNN specimen also has similar shape and size of grains, suggesting that the protonic exchange process hardly damaged the grains of the KSNN precursor. The chemical composition of each specimen was investigated using ICP-AES, and the ratio of K^+ and Sr^{2+} ions in the KSNN specimen was approximately 1:2, which is similar to the stoichiometric ratio of KSNN phase. However, the ratio of K^+ and Sr^{2+} ions in the HSNN specimen was approximately 0.2:2, indicating that 80% of the K^+ ions in the KSNN precursor were replaced by H^+ ions during the protonic exchange

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