

論文の内容の要旨

論文題目

Strain and Chemical Engineering of Electrical Properties in Perovskite Oxynitride Epitaxial Thin Films

(歪および化学組成制御によるペロブスカイト型酸窒化物エピタキシャル薄膜の電気物性開拓)

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Introduction

Perovskite oxide ABO_3 is one of the material groups studied most intensively in the field of oxide electronics. While chemical substitution on the A and B cation sites is a well-established way to achieve new functionalities in perovskite oxides, less attention has been paid to anion substitution until the recent improvements of synthetic technique. Among the anion substituted perovskite oxides, perovskite oxynitrides $ABO_{3-x}N_x$ are especially expected as functional materials: optical usage as pigments and visible light active photocatalysts. In addition, recent studies have also reported their unique electrical properties including high dielectric constant and large magnetoresistance. However, the difficulty in synthesizing dense samples of oxynitrides has frequently prevented evaluation on their intrinsic electrical properties.

In this thesis, I demonstrated epitaxial growth of perovskite oxynitrides as a solution for the problem. Because epitaxial thin films are single crystalline, they can be applied to precise electrical evaluation. The technique of epitaxial growth enabled me to seek for the way to develop novel functionalities in oxynitrides. Firstly, ferroelectricity of $SrTaO_2N$ was investigated from the viewpoint of nitrogen arrangement in the TaO_4N_2 octahedral structure. Next, artificial control of the anion arrangement was demonstrated in $Ca_{1-x}Sr_xTaO_2N$ thin films based on the results of the above-mentioned study. As another topic, I examined the function of nitrogen ion as electron acceptor due to its larger negative charge (-3) than oxygen ion (-2) and performed filling control of conduction band of $SrNbO_{3-x}N_x$ by varying nitrogen content x systematically.

Epitaxial growth of perovskite oxynitrides

Heteroepitaxy is a powerful method to address single crystalline specimens in thin film form and has been widely adopted for basic evaluations and applications in the field of oxide electronics. Although several attempts for epitaxial growth of perovskite oxynitrides have been reported, the quality of the obtained films was much worse than oxide films. This is because the technique to introduce nitrogen in thin films has not been established. I adopted nitrogen plasma

assisted pulsed laser deposition (NPA-PLD) technique. Because past reports have demonstrated doping only a few at% of nitrogen in oxide films with the technique, I investigated the condition to grow perovskite oxynitrides containing nitrogen as a major element targeting SrTaO₂N and CaTaO₂N as model systems.

SrTaO_{3-x}N_x thin films were prepared on the (100) plane of Nb:SrTiO₃ (NSTO) single crystal substrates by NPA-PLD with changing variable parameters. Optimization of growth condition was performed through evaluation on crystal structures with X-ray diffraction (XRD) and nitrogen content x with nuclear reaction analysis (NRA). CaTaO₂N thin films were prepared on the same substrate based on the optimum condition. Surface morphology of films was evaluated with reflection high energy electron diffraction (RHEED) and atomic force microscopy (AFM) and crystal structure was observed transmission electron microscopy (TEM).

I found the tendency nitrogen content x highly depends on partial pressure of introduced nitrogen gas and deposition rate of films and obtained phase-pure stoichiometric SrTaO₂N epitaxial thin films by optimizing these parameters. CaTaO₂N was also possible to be synthesized with the technique and showed quite high quality. The CaTaO₂N films showed a sign of layer-by-layer growth in RHEED measurement and atomically flat surface and high crystallinity were observed with AFM and TEM, respectively (Fig. 1). These films possessed enough high quality allowing reliable dielectric capacitance measurement.

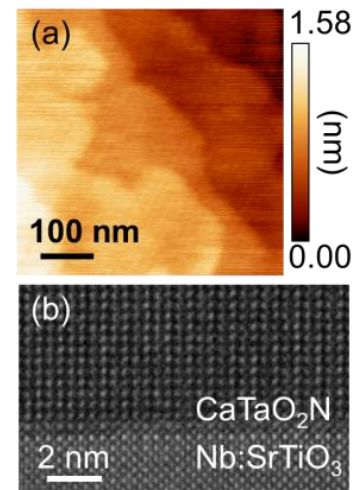


Figure 1 (a) AFM and (b) TEM images of CaTaO₂N epitaxial thin film.

Ferroelectricity and anion arrangement in the SrTaO₂N epitaxial thin films

I investigated ferroelectricity of the SrTaO₂N epitaxial thin films motivated by a suggestion given in a study based on first principles calculation: In SrTaO₂N, two types of anion arrangements, *cis*- and *trans*-types, are allowed for a TaO₄N₂ octahedron. Page *et al.* calculated the stability of these structures and reported that a paraelectric *cis*-type structure is the most stable [1], which agrees with neutron structural analyses on the bulk samples [2]. At the same time, they suggested that the metastable *trans*-type structure, which possesses spontaneous polarization, would be stabilized by biaxial compressive stress because of its large tetragonal distortion ($c/a > 1$) in its optimized structure (Fig. 2). Based on this idea, I investigated the spatial inhomogeneity in ferroelectricity, which may be caused by the spatial distribution of these two different anion arrangement, by combining detailed piezoresponse force microscopy (PFM) measurement and first principles calculation on phase stability under epitaxial stress.

XRD measurements confirmed that the SrTaO₂N ($a \approx 4.03$ Å in a pseudo cubic approximation) epitaxial thin film was strained by NSTO substrate with smaller lattice constant ($a = 3.905$ Å) and showed higher c/a of 1.02 than that reported for bulk samples ($c/a = 1.002$), though the films were partially relaxed from the substrates.

Fig. 3a is a PFM image of the SrTaO₂N film taken on the virgin state. I clearly observed spatial inhomogeneity in the PFM image: tiny regions in the scale of tens to few hundreds nm exhibited relatively high piezoresponse, while the surrounding matrix part did not show piezoresponse. I chose two representative points from the former (A) and the latter (B) and conducted local switching spectroscopy (Fig. 3b). The resultant piezoresponse curve observed at point A depicted hysteresis beginning at a polarized state with finite piezoresponse

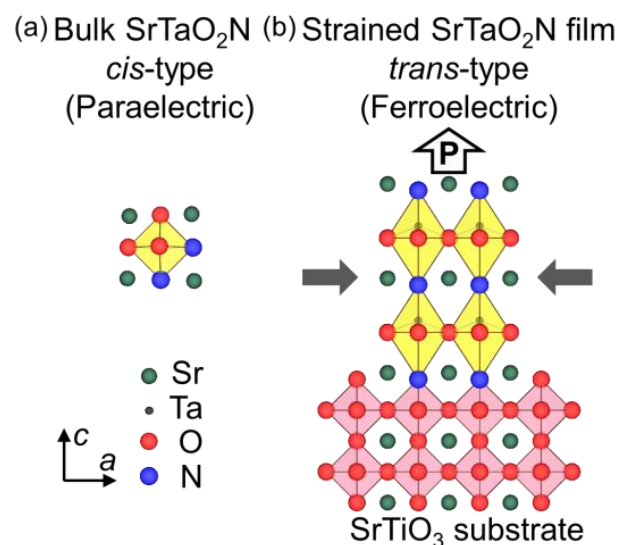


Figure 2 Schematic illustration of (a) unstrained *cis*-type and (b) strained *trans*-type structures of SrTaO₂N.

corresponding to classical ferroelectricity. On the other hand, the curves at point B showed relaxor-like behavior where no polarization existed at the initial state and switchable polarization was induced by external DC bias.

Because a *cis* structure with spontaneous polarization has never been reported both in experimental and computational studies, the tiny regions including point A can be plausibly assigned to the ferroelectric *trans*-type phase stabilized by the epitaxial stress from the substrate. I also suggest that the matrix region including the point B is constructed with thermodynamically stable *cis*-type structures, taking the partial lattice relaxation of the films from substrate into account. Though the origin of the relaxor-like behavior in the matrix region is still under discussion, the lack of long-range anion order in the *cis*-type structures, being a common characteristic of relaxor ferroelectric materials, may play an essential role.

This model was further verified with first principles calculation, because the suggestion by Page *et al.* [1] was based on the calculation of unstrained crystal structures. Fig. 4 shows the relative total energy of the *cis*- and *trans*-type structures under biaxial strain (calculated by a collaborator). It can be seen that the *trans* structure is much less destabilized than the *cis* structure by reducing in-plane lattice parameter, although the *cis* structure remains the most stable even in the case of fully-strained SrTaO₂N film on NSTO. These tendencies supported the model derived from the PFM experiments.

Artificial control on anion distribution in Ca_{1-x}Sr_xTaO₂N

As discussed above, the SrTaO₂N thin film grown on NSTO substrate would mostly consist of a thermodynamically stable *cis*-type structure because of the partial relaxation of epitaxial strain as a consequence of too large lattice mismatch. This situation made it difficult to access experimental evidences for the presence of epitaxially stabilized *trans*-type anion arrangement. To give a larger strain to the film, the film lattice should be perfectly locked to the substrate lattice. Thus, I prepared Ca_{1-x}Sr_xTaO₂N epitaxial thin films, of which lattice parameters were systematically controlled by changing the amount of smaller Ca²⁺ ions on the A-site. The anion arrangement in the films was investigated by spectroscopic structural measurements based on X-ray absorption and transmission electron microscopy.

A series of epitaxial thin films of Ca_{1-x}Sr_xTaO₂N ($x = 0, 0.1 \dots 0.7$) were grown on (100) plane of NSTO and (110) plane of DyScO₃ (DSO, $a_c \approx 3.94 \text{ \AA}$ in pseudo cubic approximation) single crystal substrates by NPA-PLD. Lattice constants of the films were examined with XRD. Average anion distribution on axial and equatorial anion sites was investigated by X-ray absorption linear dichroism (XLD) of N K-edge and O K-edge. Local elemental analysis on axial and equatorial anion sites was conducted with electron energy loss spectroscopy (EELS) combined with high angle annular dark field scanning transmission electron microscopy (HAADF-STEM).

The Ca_{1-x}Sr_xTaO₂N films grew coherently on NSTO substrates in the range of $x = 0$ to 0.5. The tetragonal distortion c/a increased along with Sr content x and reached up to 1.05 at $x = 0.5$ on NSTO substrate. The XLD of O K-edge and N K-edge spectra revealed that for both oxygen and nitrogen the difference in site occupancy between axial and equatorial anion sites becomes larger by increasing epitaxial strain. To gain a closer insight into the local distribution of oxygen and nitrogen on these two sites, EELS spectroscopy combined with HAADF-STEM was conducted on the

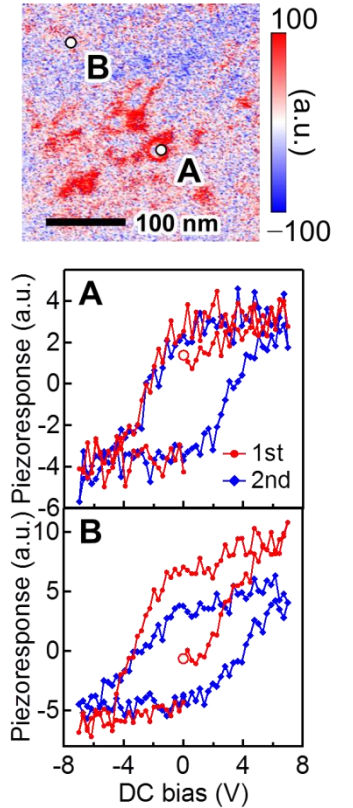


Figure 3 (a) PFM image of SrTaO₂N epitaxial thin film in the virgin state. (b) Local piezoresponses as functions of DC bias observed at points A and B in (a), respectively.

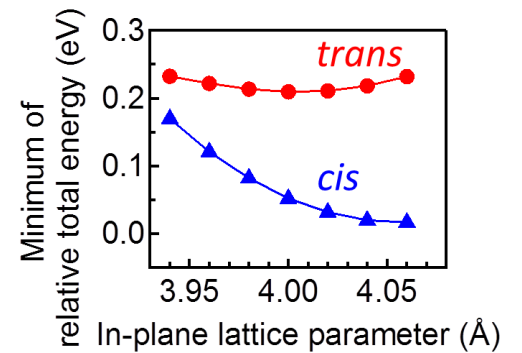


Figure 4 Relative total energies of *trans*- and *cis*- type structures of SrTaO₂N as functions of in-plane lattice parameters.

Ca_{0.5}Sr_{0.5}TaO₂N thin film, which showed the largest tetragonal distortion. The averaged EELS spectra at axial sites and equatorial sites depict that the axial sites are more (less) occupied by nitrogen (oxygen) than the equatorial sites as expected from the *trans*-type anion arrangement. These results clearly prove that epitaxial strain is effective for the control of anion arrangement in perovskite oxynitrides.

Filling control on the conduction band of SrNbO_{3-x}N_x

In transition metal oxides, valence state of cations has a fundamental influence on their functionalities. In perovskite oxides, control of valence state with A-site cation substitution has been established, while the effect of anion substitution is rarely understood. To investigate the effect of nitrogen substitution, I chose SrNbO_{3-x}N_x as a prototypical system including Nb ions with flexible valence states in contrast to *d*⁰-stable Ta. Electronic states of the system were examined based on electrical conductivity and optical absorption measurements.

SrNbO_{3-x}N_x (*x* = 0–1) thin films were prepared on the (100) plane of KTaO₃ single crystal substrates by NPA-PLD. The nitrogen content *x* in the films was controlled by changing the in-put current of the nitrogen plasma source. Resistivity was evaluated with 4-probe method. Optical absorption was examined with an UV-Vis-NIR spectrometer.

SrNbO₃, an end member of the system with *d*¹ electronic configuration, grew coherently on the substrate. It showed low resistivity in the order of 10⁻⁶–10⁻⁵ Ωcm and metallic temperature dependence (*dρ/dT* > 0). By introducing nitrogen, lattice relaxation was induced even with the small amount of *x* = 0.07, and resistivity increased with higher nitrogen amount. Temperature dependence of *ρ* was changed from metallic to semiconducting at a critical composition of *x* = 0.38. At the same time, broad free electron absorption in infrared region was suppressed. Both of the electrical transport and optical properties indicate that the SrNbO_{3-x}N_x system can be described by the rigid band model, in which the band filling is tunable with nitrogen content.

In addition the SrNbO_{3-x}N_x system showed high positive magnetoresistance (MR) at low temperature. While the end member SrNbO₃ showed MR which can be described with classical theory of electromagnetics, oxynitride thin films exhibited anomalous behaviors: MR monotonically increased with nitrogen content despite the decrease in conductivity. The highest MR observed in the SrNbO₂N thin film raised with decreasing temperature and reached about 50% at 2 K under magnetic field of 9 T.

6. Summary

I have demonstrated strain and chemical engineering of physical properties in perovskite oxynitride epitaxial thin films. The research on SrTaO₂N and Ca_{1-x}Sr_xTaO₂N films revealed that it is possible to control anion arrangement artificially by applying external stress and to develop new functionality like ferroelectricity. At the same time, nitrogen introduction is effective to tune electronic state of transition metal compounds as shown in the study on SrNbO_{3-x}N_x. These results indicate that thin-film based approach is significantly effective to reveal the mechanism nitrogen anions cause unique electrical properties and seek for new functionality in oxynitride materials and can lead to future electronics based on them.

References

- [1] K. Page *et al.*, Chem. Mater. **19**, 4037 (2007).
- [2] M. Yang *et al.*, Nat. Chem. **3**, 47 (2011).