Doping effect of Nb on ionic polarization of SrTiO₃

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THz dielectric spectra of Nb-doped SrTiO₃ single crystals were measured using the far-infrared spectroscopic ellipsometer to understand the doping effect of Nb on ionic polarization. The frequency of the Slater transverse optical (TO) mode increased with the doping amount of Nb, meaning the decrease in the ionic polarization by Nb doping. From the change in the Slater TO mode frequency, it was estimated that the ionic polarizability of 1% Nb-doped SrTiO₃ was 10.4% lower than that of undoped SrTiO₃. This result suggested that the intrinsic permittivity of Nb-doped SrTiO₃ is lower than that of that of undoped SrTiO₃. First principles calculations revealed that the Nb 4d-orbitals contributes to the covalency between B-site cations and O ions, however, the covalency is suppressed due to the electron carrier doping. The doped electrons causes the decrease in the long-range Coulomb force and the increase in short-range elastic force, and therefore the ionic polarizability is decreased by Nb doping.

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1. Introduction

The dielectric and ferroelectric properties of perovskite-type oxides (ABO₃) strongly depend on constituent elements, microstructure, and defects etc. Various approaches such as modification of chemical composition,¹¹⁻¹⁵ engineering of domain or grain boundary structures,¹⁶⁻²⁰ and defect control²¹⁻²⁷ have been studied to improve these properties. In this study, we focused on the electron carrier doping effect on dielectric property of perovskite-type oxides. The knowledge concerning the dielectric properties of the carrier-doped perovskite-type oxide is required for device design. For example, Nb- and La-doped SrTiO₃ has been used as a material of barrier-layer capacitors and conductive substrates.²⁸⁻⁴⁰ In order to precisely control the height and thickness of the Schottky barrier at the interface which determines device characteristics, it is necessary to know the dielectric properties of the carrier-doped oxides. In addition, ferroelectric perovskite-type oxides with electron carriers have been actively studied for applications such as photovoltaic and photocatalytic element in recent years.³⁶⁻⁴² It is thought that knowledge on the dielectric properties of carrier-doped perovskite-type oxides in these fields is useful. However, since the electron carrier-doped material is a semiconductor, it is difficult to measure the intrinsic dielectric permittivity.

Recently, we developed a far-infrared spectroscopic ellipsometer for measuring the complex permittivity of high-permittivity materials in THz region.⁴⁵⁻⁴⁹ This technique provides the ionic polarization which predominantly determines the intrinsic dielectric properties of high-permittivity materials. The ellipsometry is a direct measurement technique, therefore, it is possible to evaluate semiconductors as well as insulators.

In this study, THz dielectric spectra of Nb-doped SrTiO₃ single crystals using the far-infrared ellipsometer and changes in the ionic polarization due to the Nb doping were observed to understand the dielectric properties of carrier-doped SrTiO₃. In addition, first-principles calculation was carried out in order to understand the electronic and bonding states of Nb-doped SrTiO₃.

2. Experimental procedure

We used undoped, 0.1% Nb- and 1% Nb-doped SrTiO₃ single crystals purchased from Shinkosha, Japan. The resistivities of undoped, 0.1% Nb- and 1% Nb-doped SrTiO₃ crystals were 1 × 10¹¹, 8 × 10⁻⁵, and 5 × 10⁻³ Ω cm, respectively. The sizes of the samples were 15 × 15 × 0.5 mm³, and the surfaces were mirror polished. The THz complex permittivities of the samples were measured by the far-infrared spectroscopic ellipsometer. The measurement principle and the detail of the ellipsometer are described in our previous reports.⁴³,⁴⁴ We measured the
Ionic polarization originating from the Slater mode which is the soft mode of SrTiO$_3$\textsuperscript{44,48–51} and discussed doping effect of Nb on the intrinsic dielectric property of SrTiO$_3$. In addition to the experimental approach, first-principles calculation was carried out using the Vienna Ab-initio Simulation Package code.\textsuperscript{52,53} The density functional theory calculation was performed using projector augmented wave method\textsuperscript{54} and the generalized gradient approximation with PBEsol exchange–correlation potential.\textsuperscript{55} The plane-wave cutoff energy was 500 eV and $3 \times 3 \times 3$ k-point mesh was set in the Brillouin zone. A model consisting of $2 \times 2 \times 2$ supercell (8 perovskite unit cells) was constructed, and then one of the 8 titanium atoms was replaced with a niobium atom to express Nb-doped SrTiO$_3$. Geometry optimization was performed using the conjugate-gradient technique based on the Hellmann–Feynman theorem. The structure optimization was carried out so that the symmetry of SrTiO$_3$ did not change by substitution with Nb, that is, the cubic system was maintained. The partial charge density was calculated and visualized using VESTA software.\textsuperscript{56}

3. Results and discussion

Figure 1 shows the complex permittivities of undoped, 0.1% Nb- and 1% Nb-doped SrTiO$_3$ single crystals at 35–200 cm$^{-1}$ (1.05–6.00 THz). The Slater and Last modes were observed as resonant-type dielectric dispersions in the measurement frequency region.\textsuperscript{44,48–51} In Fig. 1(b), there are two maxima in the imaginary part of permittivity $\varepsilon''$. In the spectrum of undoped SrTiO$_3$ crystal, the maxima at 91.8 and 173 cm$^{-1}$ correspond to the transverse optical (TO) mode frequencies ($\omega_{\text{TO}}$) of the Slater and Last modes, respectively. On the other hand, the maximum in the Im($1/\varepsilon''$) spectrum shown in Fig. 1(c) corresponds to the longitudinal optical (LO) frequency ($\omega_{\text{LO}}$) of the Slater mode. Form the THz dielectric spectra, the TO mode frequency of the Slater mode depended on the doping amount of Nb, while the LO mode frequency was almost the same value at 171 cm$^{-1}$. The Slater TO mode frequency increased with increasing the doping amount of Nb, while the LO mode frequency was almost the same value at 171 cm$^{-1}$. The Slater TO mode frequency increased with increasing the doping amount of Nb from 91.7 to 96.9 cm$^{-1}$ as shown in Fig. 2. This result suggested that the static permittivity decreases by 10.4% with 1% Nb substitution, assuming that the 1% Nb substitution hardly affects the electric polarization and the dielectric permittivity follows the Lyddane–Sachs–Teller (LST) relation,

$$\varepsilon(0) = \frac{\omega_{\text{TO}}^2}{\omega_{\text{LO}}^2},$$

where $\varepsilon(0)$ is the static permittivity, and $\varepsilon(\infty)$ is the permittivity due to electric polarization. It was possible to estimate the intrinsic permittivity of a semiconductive material using the far-infrared ellipsometer. Incidentally, the resonant peaks of the Slater and Last modes broadened by Nb substitution, suggesting the increase in phonon damping due to the presence of different elements. Moreover, the increase in conductivity by Nb doping was observed as the increase in $\varepsilon''$ outside peak. The increase in $\varepsilon''$ may be represented by the Drude model,\textsuperscript{57,58} however, analysis using the model was not performed in this study.

The substitution of Ti ions with Nb ions means the increase in effective mass of ions, and the increase in effective mass contributes the decrease in the Slater TO mode frequency. Contrary to this hypothesis, the result of the THz dielectric spectroscopy indicated the increase in the Slater TO mode frequency, suggesting the increase in the short-range elastic force and/or the decreasing in the long-range Coulomb force. To discuss the bonding state between B-site cations and O ions, first-principles calcu-

![Fig. 1. THz dielectric spectra of undoped, 0.1% Nb- and 1% Nb-doped SrTiO$_3$ single crystals.](image1)

![Fig. 2. Slater TO mode frequency as a function of doping amount of Nb in SrTiO$_3$.](image2)
The structure optimization revealed that the lattice constant expanded from 0.38911 to 0.39125 nm by 12.5% Nb substitution. **Figure 3** shows total and projected density of states (DOS) for SrTiO₃ and 12.5% Nb-doped SrTiO₃. In SrTiO₃, oxygen p-orbitals give the primary contribution to the valence band and the top of the valence band is created by O 2p-orbital. The bottom of conduction band is formed by Ti 3d-orbital. Ti 3d-orbitals also contribute to the lower half of valence state spectrum and the admixture of Ti 3d-orbitals and O 2p-orbitals indicates the covalency between Ti and O ions.⁵⁹ On the other hand, in Nb-doped SrTiO₃, the Nb 4d-orbitals exists in the valence band and contributes to the covalency. However, the Fermi level moves into the conduction band which is consisted of Ti 3d-orbitals because of excessive electrons, meaning that a part of Ti ion is reduced to Ti³⁺. The doped electrons accommodated in the Ti-3d orbitals increase the electron clouds around the Ti atom, expanding the radius of the Ti ion. The reason why the lattice constant is increased by Nb substitution is considered to be caused by the larger ionic radii of Nb⁵⁺ and Ti³⁺. In molecular orbital theory, the valence band is constructed by bonding orbital, and the conduction band is constructed by anti-bonding orbital. Therefore, it is thought that the covalent bonding is weakened when electrons occupy the conduction band. **Figure 4** shows the partial charge density distribution of valence band which contribute to the covalent bonding. Paying attention to the expansion of the charge distribution between B-site cations and O ions, the covalent bonding of Ti-O is especially reduced by Nb substitution. In general, the covalent bonding of Ti-O affects the Slater mode (the soft mode of SrTiO₃), and it is considered that the increase in the Slater mode frequency (hardening of the soft mode) is related to

![Figure 3](image-url)
the decrease in the covalency of the Ti–O bonding. As is already explained, the Nb 4d-orbitals contribute to the covalency between B-site ions and O ions, however, the doped electrons suppress the covalency. Uchida and co-workers have studied the electron-doping effect of SrTiO₃ by first principles calculations, and have reported that the electron doping destabilizes the ferroelectric phase of SrTiO₃. In addition, they have mentioned that the decrease in the long-range Coulomb force is a cause of the instability of ferroelectricity. The doped electrons reduce the positive electric charge of the Ti ions, and the smaller electric charges lead to smaller electric dipole moments when displaced by the same distance, causing the decrease in the Coulomb interactions. On the other hand, we also think that changes in the short-range elastic force can not be neglected, since the lower covalency leads to the increase in the short-range elastic force against long-range Coulomb interactions. However, we do not have effective means to separate the elastic and Coulomb effects, and further research is required.

4. Conclusions

In this study, the THz dielectric spectra of Nb-doped SrTiO₃ single crystal were measured using the far-infrared spectroscopic ellipsometer. The frequency of the Slater TO mode increased with the doping amount of Nb, meaning the decrease in the ionic polarization by Nb doping. From the change in the TO mode frequency, it was estimated that the ionic polarizability of 1% Nb-doped SrTiO₃ was 10.4% lower than that of undoped SrTiO₃. First principles calculations revealed that the Nb 4d-orbitals contributes to the covalency between B-site cations and O ions, however, the covalency is suppressed by the effect of electron carrier doping. The doped electrons causes the decrease in the long-range Coulomb force and the increase in short-range elastic force, and therefore the ionic polarizability is decreased by Nb doping.

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