Thermoelectric properties of B-doped SrTiO$_3$ single crystal

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Abstract. Effect of boron on the electric and thermoelectric properties of SrTiO$_3$ has been studied. Boron-doped SrTiO$_3$ was prepared by vacuum annealing of SrTiO$_3$ single crystals in presence of boron vapors. The crystals show low resistivity ~0.1 $\Omega$·cm and high Seebeck coefficient of several hundreds $\mu$V/K at a room temperature. It was estimated that almost every boron atom incorporated in SrTiO$_3$ crystal provided a charge carrier. Temperature dependence of Seebeck coefficient and figure of merit $ZT$ were measured as a function of carrier concentration.

1. Introduction
SrTiO$_3$ (STO) has a simple lattice structure and highly degenerate electronic orbitals. This results in the narrow conduction band and therefore, in relatively large electron mass and a large power factor of 2-3 $\times$ 10$^{-3}$ W/m·K$^2$, comparable to that of the practical thermoelectric material BiTe [1]. However, because of the high thermal conductivity of ~10 W/m·K, the dimensionless figure of merit $ZT$ of SrTiO$_3$ is only 0.1.

Ion substitution can increase $ZT$ through reduction of the lattice thermal conductivity and of electrical resistivity. Indeed, yttrium substitution for Sr provides carrier doping and reduces thermal conductivity, thereby enhancing $ZT$ [2]. Recently, multilayered structures of STO, containing 24 layers of a 4-unit-cell Nb-doped and non-doped STO, were produced by pulsed laser deposition [3]. They exhibited a high value of $ZT = 2.4$, which is attributed to the quantum confinement of electron wave function in a layered structure. Therefore, the electric, thermal and thermoelectric properties of STO and its structure have drawn much attention.

Recently, we found an effect of boron on electric and thermoelectric properties of STO crystal heat-treated with boron vapors: the resistivity was significantly reduced from insulating to conducting, and very high Seebeck coefficient was observed. This boron-related change of STO properties has not been recognized. In this paper, we present resistivity, carrier density and Seebeck coefficient of the
boron-doped STO. In addition, the origin of the conductivity, in terms of boron doping or oxygen vacancies, is discussed by comparing STO samples with and without the boron doping.

2. Experimental procedure

We used single crystals of STO with dimensions $1 \times 1 \times 0.035$ cm$^3$. The largest surfaces were parallel to the crystallographic (100) plane and were optically polished. The crystals were heated at 900 °C in a vacuum chamber, wherein boron was evaporated by electron beam heating. During evaporation, the vacuum was kept at $10^{-4}$ Pa. Evaporation rate was monitored by a film thickness monitor placed near the STO plate and held constant at 1.16 mol/s·cm$^2$. Doping amount of boron was controlled by changing the evaporation time. After the evaporation, the plate was kept at the same temperature for 600 s to diffuse the boron atoms from the surface into the bulk. To characterize the STO samples, we measured Seebeck coefficient, electrical resistivity by four-probe method, as well as carrier concentration and Hall mobility by Hall effect in the Van der Pauw configuration.

3. Results

After the heat treatment with boron vapors, no deposition of boron was detected on the surface by X-ray diffraction. A very weak B$_2$O$_3$ peak, however, appeared on the plate exposed for long period. Resistivity was lower for the samples annealed with boron than without boron, and it decreased with increasing evaporation time. These facts indicate that boron deposited on the plate has incorporated into STO and introduced a substantial amount of carriers to the STO crystal. Secondary ion mass spectroscopy indicated inhomogeneous boron distribution in the samples. Nevertheless, we define the boron concentration as an averaged value, i.e., assuming that the boron homogeneously distributed in the crystal. This assumption is made for convenience of presenting the results and also for understanding the relationship between the boron doping and carrier density.

Figure 1 shows the resistivity of the STO plate as a function of temperature for various boron concentrations. In the figure, we also plotted resistivity of the undoped sample, i.e., treated at the same conditions without boron vapors. The boron-doped samples had lower resistivity than the undoped sample. Their resistivity showed metallic temperature dependence and decreased as boron concentration increased. The Hall measurement indicated that carriers were electrons for all samples. Carrier concentration of the doped samples at 300 K is presented in figure 2 as a function of boron concentration. It is proportional to boron concentration except for the highest concentration. The sample with highest concentration contained B$_2$O$_3$ on the surface. Carrier concentration of the undoped sample was of the order of $10^{16}$ cm$^{-3}$, about two orders of magnitude lower than that of the doped samples. Hall mobility of the doped samples was typically less than 10 cm$^2$/V·s, but it was ~100
cm$^2$/V·s in the undoped sample. Figure 3 displays carrier number per boron atom as a function of the carrier concentration.

Figure 4 shows Seebeck coefficient as a function of carrier concentration. Seebeck coefficient was as high as 700 µV/K and decreased as carrier concentration increased. Dimensionless figure of merit, $ZT$, was evaluated using the obtained Seebeck coefficient, resistivity and the reported thermal conductivity value of 11.2 W/m·K [3]. The thermal conductivity is reported as almost constant below carrier concentration of $10^{21}$ cm$^{-3}$. Therefore, we assume constant thermal conductivity in the evaluation. Figure 5 shows dimensionless figure of merit $ZT$ including the previously reported values [1, 3, 4]. Temperature dependence of Seebeck coefficient is depicted in figure 6.

4. Discussion

Although the boron-doped and undoped samples show comparable resistivity in figure 1, carrier concentration of the boron-doped samples was 30-300 times higher. This indicates that the origin of the lower resistivity of the boron-doped samples is not merely the oxygen deficiency, created by annealing at high temperature in vacuum. In addition, the almost proportional dependence of carrier concentration on boron concentration shown in figure 2 implies that boron atoms incorporated in the STO crystal and acted as carrier dopants. Figure 3 indicates that one boron atom provided almost one
electron, as long as $\text{B}_2\text{O}_3$ was not formed on the sample surface. Therefore, we conclude that high-
temperature annealing with boron vapors incorporates boron atoms and introduces carriers into STO
crystal and that the oxygen vacancies contribute less to the doping than boron atoms.

The Seebeck coefficient and dimensionless figure of merit measured on the boron
doped STO crystals are comparable to reported values on STO. This indicates that heat treatment of STO
with boron vapors is a valid process of STO doping, and that STO is a potential thermoelectric material.

5. Conclusions
STO single crystals annealed in a vacuum at 900 °C with boron vapors exhibit low resistivity ~0.1
$\Omega \cdot$cm, lower than that of the STO annealed without boron. The resistivity decreased as boron
evaporation time increased, and the estimated carrier density in boron-exposed samples was about two
orders of magnitude lower than that of the sample without boron. Therefore, the measured electrical
properties originated predominantly from boron interaction with STO. The carrier concentration
calculated from the Hall measurement is almost proportional to the assumed boron concentration in
the STO crystal. It implies that one boron atom provided one carrier in the STO. Consequently, these
results indicate that boron was introduced into the STO crystal and acted as a carrier dopant.

Seebeck coefficient measured from the boron doped STO crystal was more than several hundreds
$\mu$V/K. Dimensionless figure of merit also showed a similar behavior as in a typical carrier-doped STO.
Quite a few studies have been conducted on the interaction between boron and STO. Therefore,
further investigation on boron-doped STO is necessary for revealing the carrier doping mechanism and
the potential for thermoelectric applications.

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Figure 6 Temperature dependence of Seebeck coefficient.