Optical and Dielectric Properties of Reduced SrTiO$_3$ Single Crystals

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Abstract

The optical band gap energy for SrTiO$_3$ by reduction at high temperature was 3.15 eV. The reflectivity of reduced SrTiO$_3$ single crystals showed little variation, however, the reflectivity by the reduction condition had no effect. For the phonon mode at about 790 cm$^{-1}$, a blue-shift took place upon N$_2$ reduction and the decreased. However, a red-shift took place upon a H$_2$-N$_2$ reduction and the increased at the same phonon mode. With decreasing temperature the dielectric constant decreased rapidly. The thermal activation energies were 0.92-1.02 eV.

Key words: Reduction, Optical band gap, Infrared reflectivity, Thermal activation energy

1. Introduction

Strontium titanate (SrTiO$_3$) is a well-known perovskite structured material which has a cubic paraelectric phase. It can achieve a reasonable charge storage density for high density memory application caused by temperature independent of dielectric constant. SrTiO$_3$ is chemically and compositionally very stable and has excellent dielectric and optical properties which make it an excellent insulating device. In addition, the role of oxygen vacancies in perovskite oxides is important in fatigue degradation and long-term degradation when these materials are used as switching devices such as memory devices. SrTiO$_3$ can be easily grown with a low concentration of point defects and then treated in a reducing atmosphere to produce a controlled amount of oxygen vacancies in a wide range of concentrations. SrTiO$_3$ doped with niobium, or reduced under hydrogen at high temperature, becomes an n-type conductor, thus also being interesting in the field of electronic devices. An n-type conductor is regarded as a bipolaronic material. The polaron formation is obvious due to its low carrier concentration and huge dielectric polarizability. The existence of polarons in SrTiO$_3$ has provided at its surface. There are nevertheless many obscure problems for the physical properties of n-type SrTiO$_3$.

The purpose of the present study was to investigate the details of the reduction effects in high temperature reduction conditions on SrTiO$_3$ using linear absorption and infrared reflectivity measurement. We also present the results of measurements of the dielectric constant for high temperature and describe the thermally activated behavior through the Arrhenius law of conductivity.

2. Experimental Procedure

To investigate the optical and dielectric properties, (100) or (110) pure SrTiO$_3$ and (000) 0.7 wt% Nb : SrTiO$_3$ single crystals with two sides epi-polished (Ra < 7 Å) were used (MTI Inc.). The dimensions were 5 x 5 x 0.5 mm$^3$. Reduction treatment of the SrTiO$_3$ was performed in N$_2$ or H$_2$(5%) + N$_2$(95%) atmosphere for 3 h at 1000°C.

The optical band-gap and infrared reflectivity spectra of the reduced SrTiO$_3$ single crystals were measured using a UV/Vis spectrometer (Optizen 2120UV, Mecasys Co.) a Nicolet avatar 330 FT-IR (Thermo Electron Co.) in a range from 1600 to 400 cm$^{-1}$. The surface treated sample for dielectric measurements was a plane parallel plate with Ag-Pt pastes and wasannealed at 400°C for 1 h. The temperature dependence of the dielectric constant and conductivity were estimated from room temperature to 1000°C in a N$_2$ atmosphere, using a Hioki 3532 LCR HiTester at 50-5 MHz. The heating and cooling rate of the sample was 0.2°C/min.

3. Results and Discussion

The optical transmittance spectra for the reduced (100) or (110) pure SrTiO$_3$ and (000) 0.7 wt% Nb : SrTiO$_3$ single crystals in a wavelength region of 200 to 1100 nm are shown in Fig. 1. The optical band gap of the crystals was determined from the optical transmittance or absorption spectra. The edge of the fundamental absorption was near 395 nm for both pure and Nb-doped SrTiO$_3$ single crystals. However, 0.7 wt% Nb : SrTiO$_3$ single crystals of 0.5 mm thickness are not optically...
transparent in visible region. From the well-known formula between the absorption coefficient and the optical band gap, the value of $E_g = 3.15$ eV obtained for the surface treated samples investigated in the present study is a slightly different shade from that of the previous studies. In our reduction conditions the optical edge brings about a red-shift.

Fig. 2 shows the infrared reflection spectrum of (100) and (110) SrTiO$_3$ prepared by treating with N$_2$ or H$_2$ reduction at 1000°C for 3 h in a tube-type furnace. In the (100) SrTiO$_3$ surface, the reduction atmosphere brought a variation of the absorption for the surface. The physical and chemical properties of the surface must be greatly influenced by the surface morphology and surface termination. We suggest that the (100) surface can be terminated by the domain of the SrO- or TiO$_2$-alternative layer during the reduction. The surface termination of (100) SrTiO$_3$ by the reduction was investigated. However, the reflectivity of the (110) SrTiO$_3$ surface by reduction showed little variation and the surface reflectivity by the reduction condition had no effect. The ideal (110) SrTiO$_3$ surface consists of alternating positively charged SrTiO$_3$ and negatively charged O$_2$ layers. The increased or decreased reflectivity of IR region for the sample heated in N$_2$ or H$_2$ reduction is ascribed to the large number oxygen vacancies produced during the experiment. Different (100) and (110) surfaces were observed resulting in TiO$_2$-terminated ridges. Infrared reflectivity spectra of Nb-doped SrTiO$_3$ single crystals at room temperature are shown in Fig. 3. For the phonon mode at about 790 cm$^{-1}$, a blue-shift took place upon N$_2$ reduction and the decreased. However, a red-shift took place upon a H$_2$-N$_2$ reduction and the increased at the same phonon mode. This is considered an experimental feature of a coupled phonon-plasmon system. Owing to the coupling between the highest frequency phonon mode and the free carrier plasma, the strength and of the absorption band changed. Although its origin is not clear, the peak similar to the defect mode could be related to oxygen vacancy resulting from Nb doping. That is to say, it can be associated with a small polaron. The appearance of the peak is the metallic character of SrTi$_{1-x}$Nb$_x$O$_3$ on the crystal surface. Moreover, there is a little Nb induced local structure distortion. The kind of distortion from the impurity doping effect has been extensively related to formation of small polarons.

Fig. 4 shows the temperature dependence of the dielectric
constant for the reduced (100) SrTiO$_3$ single crystals. The dielectric constant is almost frequency independent at all temperatures. The static dielectric constant reached about 7000. However, the value was smaller than in previous research. With a decreasing temperature the dielectric constant decreased rapidly. These features explain the well-known quantum paraelectric behavior. In addition, the dielectric constant as a function of the reciprocal absolute temperature can be parameterized in certain temperature ranges using the Curie-Weiss law $\varepsilon' = (T - \Theta)^{-1}$, where $\Theta$ is the Curie-Weiss temperature. However, an inspection of $1/\varepsilon'$ shows a change of slope at $T \sim 760$ K. The loss factor $\tan \delta = \varepsilon''/\varepsilon'$ reveals that dispersion effects appear in the region of $T \gtrsim 760$ K and is usually ascribed to dissipation effects due to domain-wall motions.

4. Conclusions

The optical band gap energy for the reduced samples was 3.15 eV and in our conditions of reduction, the optical edge brought about the red-shift. The (100) surface can be terminated by the domain of SrO- or TiO$_2$-alternative layer during the reduction. The reflectivity of (110) SrTiO$_3$ surface by reduction showed little variation, however, the surface reflectivity by the reduction condition had no effect. For the phonon mode at about 790 cm$^{-1}$, a blue-shift took place upon N$_2$ reduction and the decreased. However, a red-shift took place upon a H$_2$-N$_2$ reduction and the increased at the same phonon mode.

With a decreasing temperature the dielectric constant decreased rapidly. These features explain the well-known quantum paraelectric behavior. In addition, the dielectric constant as a function of reciprocal absolute temperature can be parameterized in certain temperature ranges using the Curie-Weiss law. The thermally activated behavior can be described by the Arrhenius law of conductivity, $\sigma = \sigma_0 \exp(-E_a/kT)$.

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REFERENCES


