

2008年3月

The influence of crystal defects on the photoconductivity of SrTiO₃

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キーワード：酸化物エレクトロニクス、Photoconductivity、SrTiO₃

Introduction

SrTiO₃ is often used as a substrate material for novel oxide electronics devices because of its relatively high crystal quality and a good lattice match with many perovskite-type oxides. Additionally, SrTiO₃ has a number of interesting physical properties, such as a very high dielectric constant, metal-insulator transition at very low carrier concentrations, superconductivity at low temperature, and unusually high carrier mobility at cryogenic temperatures. For these reasons, SrTiO₃ has been used as a channel material in field-effect transistors [1]. In order to utilize SrTiO₃ in oxide electronics, it is important to understand how crystal defects affect the carrier transport in SrTiO₃, because the presence of defects can significantly affect device properties. Nondoped SrTiO₃ is a band insulator with $E_{\text{gap}} \approx 3.2$ eV, and therefore carriers need to be injected somehow before transport properties can be studied. There are several possible methods to inject carriers into SrTiO₃, such as impurity doping [2], field effect [3], and photocarrier injection [4]. Impurity doping is the most common technique, but defects are also induced by doping with impurities like La or Nb. In this study, photoconductivity of nominally pure and also defect-rich SrTiO₃ crystals was investigated. The amount of defects in SrTiO₃ was changed by several techniques, and the effects that the defects have on conductivity of the crystals were studied.

Experiment

The surfaces of SrTiO₃ single crystal were etched by phosphoric acid, in order to remove a defect-rich layer from a crystal surface, thus reducing the effective defect density in the probed crystal volume. The etching rate was 35 nm / min at an acid temperature of 133°C. On the other hand, in order to intentionally increase the density of defects, crystals were either annealed at high temperature or grown from nonstoichiometric precursor powder mixtures. Sr-deficient SrTiO₃ single crystals were obtained by annealing at up to 1400°C in air. The precursor powder Sr/Ti ratios used in the non-stoichiometric crystals grown by Shinkosha were 0.98, 1.00, 1.02, 1.04 and 1.06. The cation ratios of the final crystals deviated slightly from these numbers. As a general rule, a loss of a few percent of Sr can be expected to occur in the Verneuil growth process. The crystals were cut into approximately 2 mm x 5 mm pieces and stripe-shaped Ti electrodes were evaporated on the surface. Samples were attached to the cold finger of a flow-type liquid helium-cooled cryostat and illuminated through a quartz viewport with ultraviolet light. Monochromatic light was obtained by passing light from a 1 kW Xe lamp through a double monochromator. An optical chopper was mounted in the light path between the monochromator and the cryostat so that time dependent photoconductivity measurements could be made.

Results and Discussion

(A) Influence of crystal defects introduced by the manufacturing process

As shown in Figure 1, at photon energies between 3.0 and 3.3 eV, a sharp onset of photoconductivity was seen in all samples as expected, since the band gap of non-doped SrTiO₃ is 3.2 eV. A distinct band tail was seen in the photon energy dependence of photoconductivity. This type of behavior can be understood if electronic states exist near the band edge, for example impurity states, from where carriers can be thermally excited to the conduction band. The gradual increase of conductivity below the band gap shows that defect states exist to some extent in all samples. This can be considered a common feature for most oxides. Band tail features were seen clearly in all cases. A larger detected photocurrent at energies below the band edge energy means that a higher density of in-gap states is present. In Figure 1, it is clear that only the cleaved surface shows a very low photocurrent below 3.28 eV at 30 K.

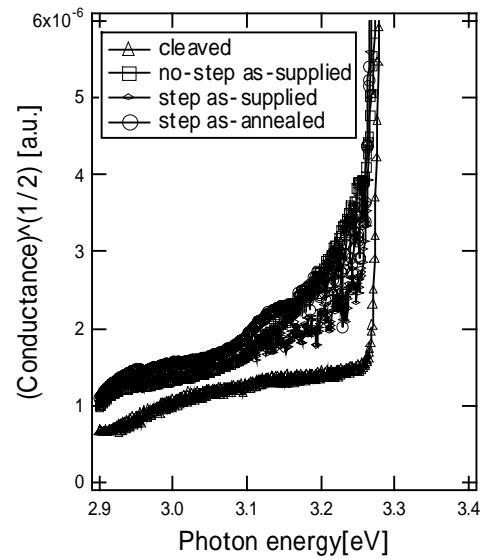


Fig. 1 Photon energy dependence of SrTiO₃ photoconductivity 30 K

(B) Influence of intentionally induced crystal defects on photoconductivity

Figure 2 shows the temperature dependence of sheet resistance of the non-stoichiometric samples under 360 nm illumination.

All samples showed a sharp resistance change at around 30 to 40K, as did other etched and annealed samples. Earlier published work [4] suggests that such a sharp change in current over a narrow temperature range is caused by thermal freeing of holes trapped at sensitizing centers. An additional kink was seen only in the sample made from Sr/Ti=1.00 powder. It should be noted that the stoichiometric source powder composition likely resulted in a slightly Sr-deficient crystals. Empirical tests show that the sample grown from a Sr/Ti=1.04 powder is likely to have nearly ideal stoichiometry. Indeed, that sample showed the lowest sheet resistance over the whole temperature range. It is also interesting to look at the height of the resistivity jump at around 35K in the low-temperature plots. The resistance ratio between 20 K and 40 K are shown as a function of raw powder composition in Figure 3. Since the height of the transition presumably probes hole localization at defect sites, it is not surprising that the minimum again occurred at

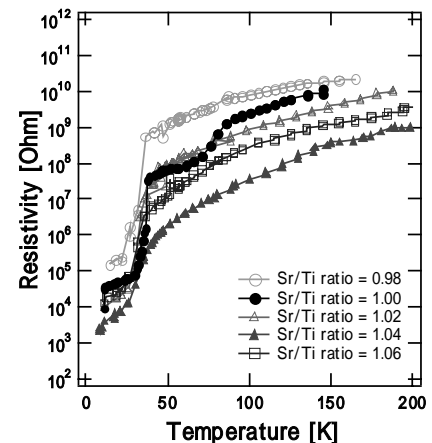


Fig. 2 Temperature dependence of the sheet resistance of non-stoichiometric SrTiO₃ crystals. The compositions of the raw material powders is shown for each sample.

a point that corresponds to a stoichiometric crystal that would be expected to have the lowest defect density.

(C) Photocurrent dynamics of SrTiO₃

In photoconductivity dynamics measurement, the difference of current response to the illumination was observed at several temperatures. In current dynamics, no precursor composition dependence was seen. The photocurrent response became slower at higher temperature, with a sharp slowdown of the photoresponse in the transition region close to 35 K. At even higher temperatures, the response times recovered to nearly the same values as at 10 K. The longest photocurrent risetime occurred at around 35K, which coincides with the large step of the resistivity, as shown in Figure 4. One possibility for the appearance of the rise time peak is that to the time needed to fill the trap sites up to a steady-state equilibrium level changed rapidly at a temperature where the hole trapping starts to occur. The probabilities of releasing carriers from trap sites and trapping carriers from the conduction band would be balanced in that temperature range.

Summary

In this study, photoconductivity of SrTiO₃ was investigated to see how the defects affect the transport properties of nondoped insulating crystals. Influence of defects from mechanical processing was seen as a band tail at low temperature. Resistance value and low temperature transition height were affected by nonstoichiometry of the crystals. Intrinsic defects affected mostly the photoconductivity dynamics. Several different defect are apparently present in SrTiO₃, each affecting conductivity differently.

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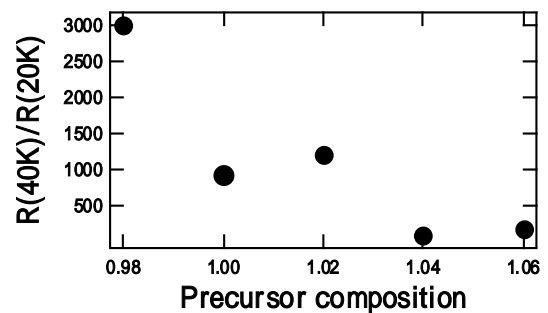


Fig. 3 Composition deviation versus sheet resistance ratio at 20 K and 40 K.

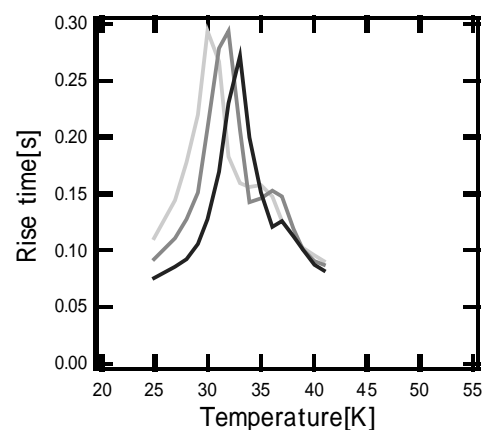
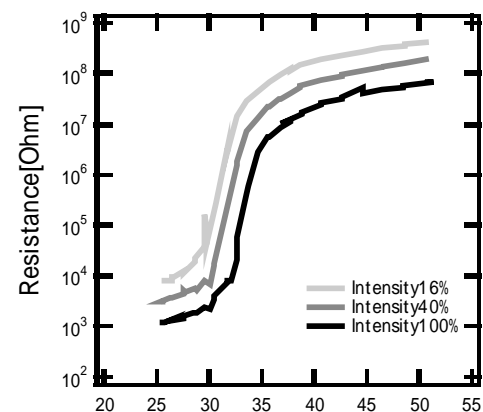


Fig. 4 Temperature dependence of resistance and rise time in SrTiO₃