Defect Equilibrium and Transport Properties of Nb Doped$SrTiO_3$

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INTRODUCTION

Strontium titanate based ceramics are widely used in electronic devices. It is also interesting for high temperature electrochemical applications such as gas sensors and solid oxide fuel cells since it has a wide stability region in oxygen potential. Although many studies have been reported on its electronic transport around room temperature, high temperature bulk / interface transport behaviors are not clear enough especially for donor doped $SrTiO_3$.

The authors reported that the interface between Pt and Nb (1 mol%) -doped $SrTiO_3$ forms Schottky junction even at high temperatures[1]. Recently, we found the rectification behavior is clearer with the samples doped with smaller amount of Nb. In this paper, the electronic and ionic transport behavior of slightly Nb doped $SrTiO_3$ is investigated, and the defect equilibrium is discussed.

EXPERIMENTAL

Single crystals of Nb doped $SrTiO_3$ (Nb: nominally 0.01 wt % = 0.02 mol%) were purchased from Nakazumi crystal Co. Four terminal dc conductivity measurements were performed in oxygen potential range from 10^{-20} to 1 bar at temperatures from 573 K to 1723 K. Oxygen diffusion measurements were performed by isotope exchange technique combined with SIMS (secondary ion mass spectrometry) analysis.

RESULTS AND DISCUSSION

The electronic conductivity of Nb-$SrTiO_3$ is shown in Fig.1. It is constant in a wide oxygen partial pressure range at low temperatures. It showed negative temperature dependence. At high temperatures, drastic increase of the conductivity was observed at low oxygen potential region. It was well described by the formation of electron carrier together with the oxygen vacancies. From the defect equilibrium, the electron concentration is calculated as follows;

$$O_O^{\times} \longrightarrow V_O^{\bullet\bullet} + \frac{1}{2}O_2 + 2e^- \qquad (1)$$

$$K_{red} = \frac{[V_O^{\bullet\bullet}]P_{O_2}^{\frac{1}{2}}n^2}{[O_O^{\times}]} = \frac{\delta\, P_{O_2}^{\frac{1}{2}}n^2}{3-\delta} \qquad (2)$$

$$n = 2\delta + [Nb_{Ti}^{\bullet}] \qquad (3)$$

$$n = \frac{[Nb_{Ti}^{\bullet}]}{3} + \frac{\left(27K' + \sqrt{27K'\left(27K' + 4[Nb_{Ti}^{\bullet}]^3 P_{O_2}^{\frac{1}{2}}\right)} + 2[Nb_{Ti}^{\bullet}]^3 P_{O_2}^{\frac{1}{2}}\right)^{\frac{1}{3}}}{3\cdot 2^{\frac{1}{3}} P_{O_2}^{\frac{1}{6}}} + \frac{2^{\frac{1}{3}}[Nb_{Ti}^{\bullet}]^2 P_{O_2}^{\frac{1}{6}}}{3\left(27K' + \sqrt{27K'\left(27K' + 4[Nb_{Ti}^{\bullet}]^3 P_{O_2}^{\frac{1}{2}}\right)} + 2[Nb_{Ti}^{\bullet}]^3 P_{O_2}^{\frac{1}{2}}\right)^{\frac{1}{3}}} \qquad (4)$$

By fitting the data, the electron mobility and oxidation equilibrium constant were obtained for each temperature. As shown in Fig.2, the mobility was proportional to $T^{-3/2}$ suggesting the existence of phonon scattering. mechanism At the very high temperatures, the mobility appeared to deviate from this behavior. It is probably due to the formation of intrinsic carriers by thermal activation. When the mobility was assumed as the extrapolation of the $T^{-3/2}$ line for the intrinsic region, the band gap width was calculated to be 3.2 eV, which is not far from the expected value from the reported values.

Oxygen vacancy concentration was calculated from the electron and dopant concentrations by using equation (3). It is smaller than estimated from the result of the oxygen isotope diffusion, which suggests the existence of intrinsic disorder or impurity acceptor.

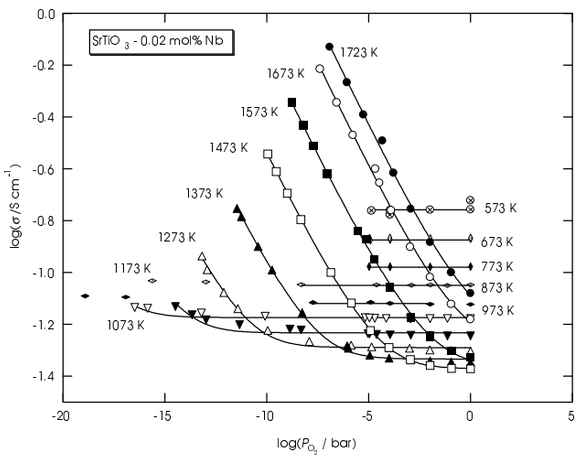

Fig.1 Temperature and oxygen partial pressure dependence of conductivity.

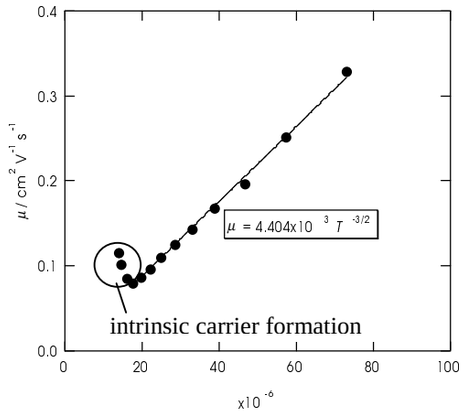

Fig.2 Temperature dependence of electron mobility.

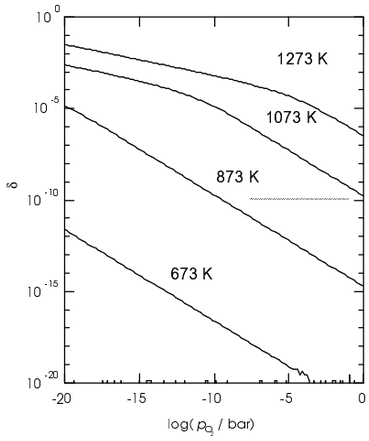

Fig.3 Estimated oxygen vacancy concentration.