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High Temperature Transport Properties at Metal/$SrTiO_3$ Interfaces

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Abstract

High temperature current-voltage characteristics were investigated with a Nb doped $SrTiO_3$ (Nb–STO) single crystal. The conductivity of the 0·5 wt% Nb doped $SrTiO_3$ showed high n-type conductivity with a negative temperature coefficient. The Pt/Nb–STO interface freshly prepared by laser ablation at 973 K in high vacuum condition showed ohmic behavior. However, it turned to show a Schottky type non linearity when annealed in oxygen gas at temperatures higher than 773 K. The I–V *curve in the forward direction was well fitted with the equation based on the thermionic emission model. At high temperatures, the* I–V *behavior was dependent on the oxygen partial pressure. The lower oxygen partial pressure resulted in a lower barrier height. The change in the* I–V *curve with oxygen potential was almost reversible at 873 K, and was frozen below 673 K. Those phenomena suggested that the Schottky barrier formation at the Pt/STO interface has a strong relation with the oxygen transport in Nb–STO. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: $SrTiO_3$, interfaces, electrical properties.

1 Introduction

High temperature electrochemical devices such as solid oxide fuel cells, gas sensors, membrane reactors, etc. are of increasing importance. In those electrochemical devices, key technologies are often related to mass and charge transport at the interfaces. Usually in the electrochemical studies, local equilibrium and local charge neutrality are assumed. Frequently, vanishing effect of energy barrier is considered for electron transport across the interfaces. Most of the electrochemical reaction are successfully explained with this assumption.[1,2] Recently, however, the importance of the effect of the space charge have been imposed in many literature by Maier[3] and coworkers. Denk *et al.*[4] reported the effect of Schottky barrier on the transport at the electrode interface and the grain boundaries of acceptor doped $SrTiO_3$. Klingler and Weppner,[5] Kopp *et al.*[6] and more recently, Kobayashi *et al.*[7] pointed out that the formation of Schottky barrier or internal *p–n* junction makes a significant effect on the Hebb–Wagner polarization measurements. On the other hand, Waser *et al.*[8,9] pointed out the oxide ion transport plays an important role in a lower temperatature application of oxides such as titanate based capacitors. Thus, the both effects of space charge and ionic transport should be considered at the same time to treat metal/oxide interface.

In a previous study, the authors investigated the current—voltage behavior of a $SrTiO_3$ single crystal under oxygen potential gradient.[10] In that case, the interface effect was not clearly observed since the bulk conductivity was too small. In this study, a donor doped $SrTiO_3$ is used to evidence the effect of the interface on high temperature transport properties. Donor doped $SrTiO_3$ is known to form Schottky barrier at the interface with Pt or Au electrodes.[11–13] In this report, as the first part of a sequence of studies, the temperature and oxygen partial pressure dependence of *I–V* behavior is investigated at the Pt/$SrTiO_3$ interface.

2 Experimental

Single crystals of $SrTiO_3$ doped with 0·5 wt% (~1 mol%) Nb were purchased from Nakazumi Crystal Co. The thickness of the pellet was 1 mm, and the diameter was 16 mm. Thin platinum electrodes were deposited on the polished (100) surfaces by the laser ablation method. The ablation chamber was evacuated to about 10^{-8} bar, and the STO-Nb sample was heated at 973 K. The resulting

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electrode thickness was around 500 Å. Working, counter and two reference electrodes were prepared as shown in Fig. 1. The potential difference between the working and the reference electrodes was controlled, and the current through the working and the counter electrodes recorded. Approximately half of the bulk resistance was included in the measured voltage.

3 Results and Discussion

3.1 Electrical Conductivity

Figure 2 shows the electrical conductivity of 1 mol% Nb doped $SrTiO_3$ as a function of oxygen partial pressure and temperature. The temperature dependence indicated metallic behavior; i.e. the conductivity decreased with increasing temperature. If the oxygen vacancy is formed in a reducing atmosphere, the conductivity is expected to increase due to the increase of electronic defects as was reported for La doped $SrTiO_3$ by Moos and Härdtl[14] and for $BaTiO_3$ by Chan and Smyth.[15] However, the conductivity of the present sample with higher dopant concentration was not affected by the generation of oxygen vacancies since the dopant concentration was still higher in all the oxygen potential region in this experiment. In the medium oxygen partial pressure region, a slight conductivity increase was observed, which was reversible in the reduction and oxidation runs. This may be related to the oxidation state of the dopant. Further discussion will not be made in this paper since it gives only minor effects on the present measurements.

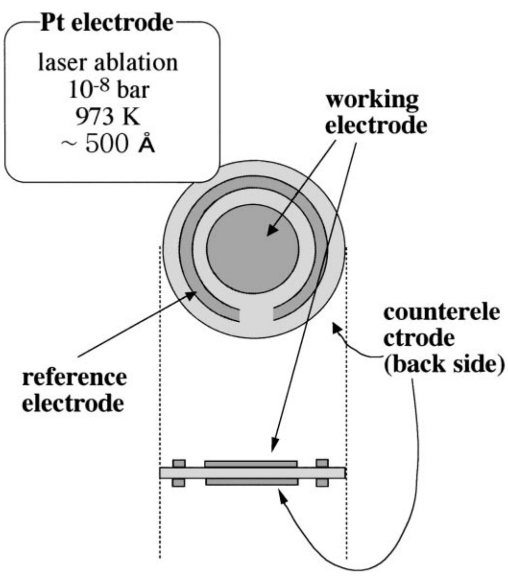

Fig. 1. Configuration of the platinum electrodes deposited by laser ablation method.

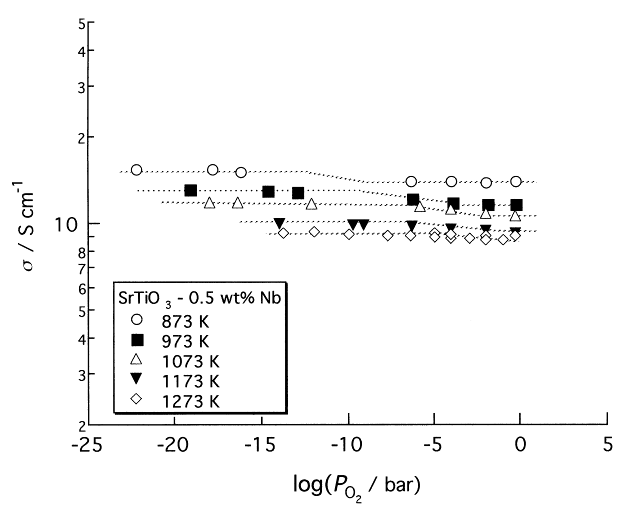

Fig. 2. Electrical conductivity of 1 mol% Nb doped $SrTiO_3$.

3.2 Variation of the interface conductivity by initial heat treatment after Pt deposition

Figure 3 shows the change in the interface specific conductivity measured at zero bias condition in air at varying temperature. The contribution of the bulk resistance is displayed as the upper limit of the data measured in this experiment. The Pt/STO-Nb interface freshly prepared by laser ablation showed relatively high resistance, i.e. low specific interface conductivity. By the initial heat treatment at 573 K, the interface conductivity showed a drastic increase by more than one order of magnitude. After the initial increase, it was close to the upper limit of the measurement. When it is heated to higher temperatures, the interface conductivity decreased dramatically. After heating up to 873 K, the conductivity versus 1/T curve converged to one line with a positive temperature dependence.

Since the Pt electrode was deposited at 973 K at high vacuum condition, it is likely that the STO-Nb was in a reduced state with a high oxygen vacancy concentration. By heating up to 873 K, the

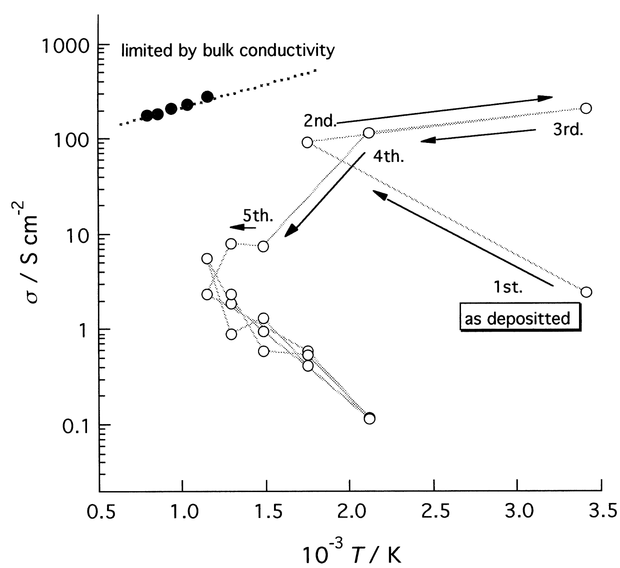

Fig. 3. Variation of the specific interface conductivity of Pt/ $SrTiO_3$ (1 mol% Nb) during heat treatment in air.

sample could be equilibrated with the atmosphere, i.e. 0·21 bar oxygen. This process can oxidize the sample and its interface. Thus, the interface conductivity might have a strong relation with the oxidation state as reported by many other authors.[11–13,16] From the fact that a high temperature was required to form the barrier layer, this may not only be due to the interface (adsorption etc.) but also to the bulk in the vicinity of the interface. On the other hand, the low conductivity observed in the initial state may be due to any surface contamination since it was easily flushed away by heating the sample up to 573 K.

3.3 Oxygen partial pressure dependence of the *I–V* relationship

The oxygen partial pressure dependence of the *I–V* curve was measured isothermally at 873, 773 and 673 K after the heat treatment at 873 K in 1 atm oxygen [Fig. 4(a)–(c)]. An obvious dependence on oxygen partial pressure was observed at 873 K. In high oxygen partial pressures, a nonlinear behavior was observed. In a lower oxygen partial pressure, the interface conductivity increased and the non linearity declined. When temperature decreased, the non-linearity became clearer but the oxygen partial pressure dependence weaker. At 673 K, a clear asymmetrical forward and backward current was observed, and was almost independent of the oxygen partial pressure in this experimental range.

Figure 5(a) shows the oxygen partial pressure dependence of the *I–V* curve observed after the sample was once equilibrated at 873 K and then quenched to 673 K in various oxygen atmospheres. In contrast to the results shown in Fig. 4(c), the current was clearly dependent on oxygen partial pressure. When the oxygen partial pressure was lower, the current was higher in both the forward and the reverse directions. The same data is plotted in log(*J*) versus *E* form in Fig. 5(b). The slope of the forward direction was close to $F/2{\cdot}303RT$, which suggests that the interface resistance is due to the Schottky barrier formation. Since the Schottky barrier of metal/STO interface at ambient temperature has been described well by thermionic emission model,[13] the same model was applied to the high temperature behavior in this study. In the thermionic emission model, the current voltage relationship across the interface is written as,[7]

$$J = A^* T^2 \exp\left(-\frac{FV_b}{RT}\right)\left[\exp\left(\frac{FV}{nRT}\right) - 1\right] \quad (1)$$

where V_b is the effective barrier height, A^* is Rechardson constant which is represented by

$$A^* = \frac{4\pi m^* k^2}{h^3} \quad (2)$$

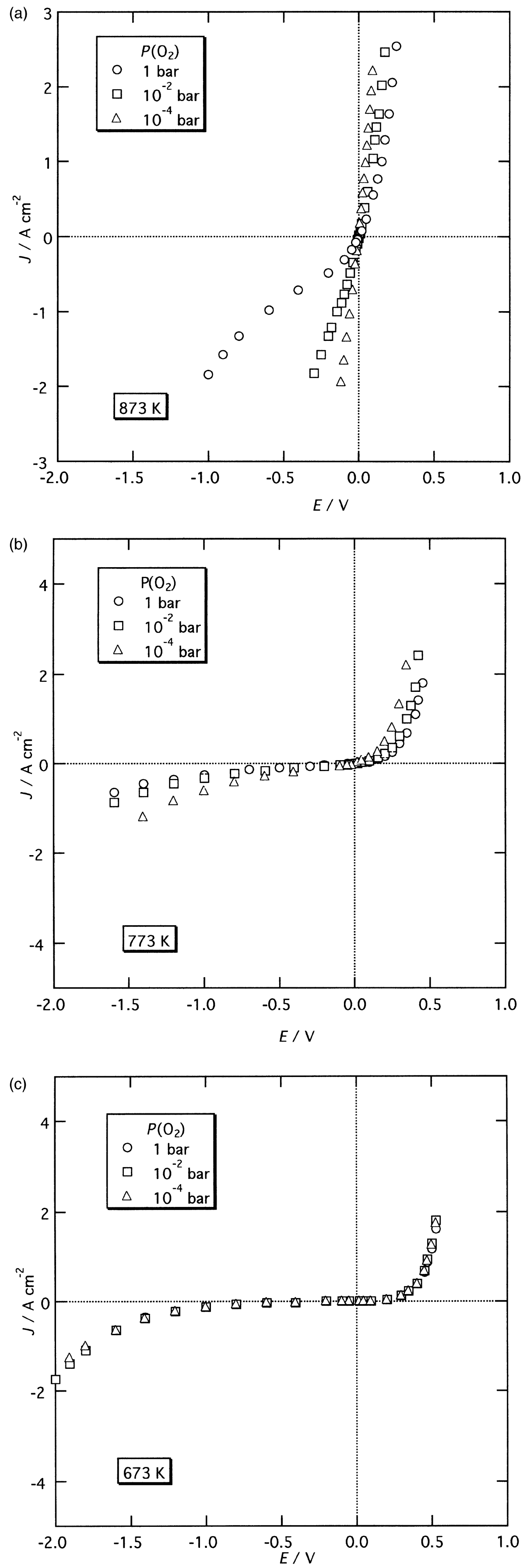

Fig. 4. (a) Oxygen partial pressure dependence of *I–V* curve at Pt/$SrTiO_3$-Nb interface measured at 873 K; (b) Oxygen partial pressure dependence of *I–V* curve at Pt/$SrTiO_3$-Nb interface measured at 773 K; (c) Oxygen partial pressure dependence of *I–V* curve at Pt/$SrTiO_3$-Nb interface measured at 673 K.

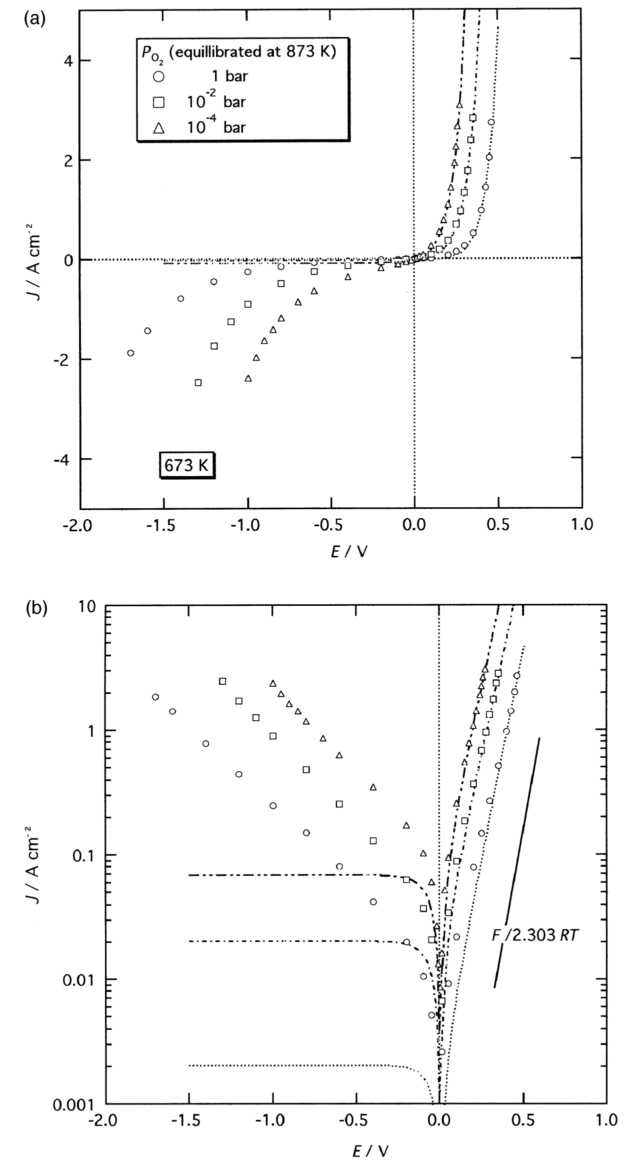

Fig. 5. (a) *I–V* behavior at Pt/SrTiO$_3$-Nb interface measured after the sample was equilibrated at 873 K, and then quenched to 673 K in various oxygen atmospheres. The dashed, dash-dotted, dash-dot-dotted lines are the best fit curve assuming thermionic emission model for the Schottky barrier; (b) Semi-log plot of the data shown in Fig. 5(a).

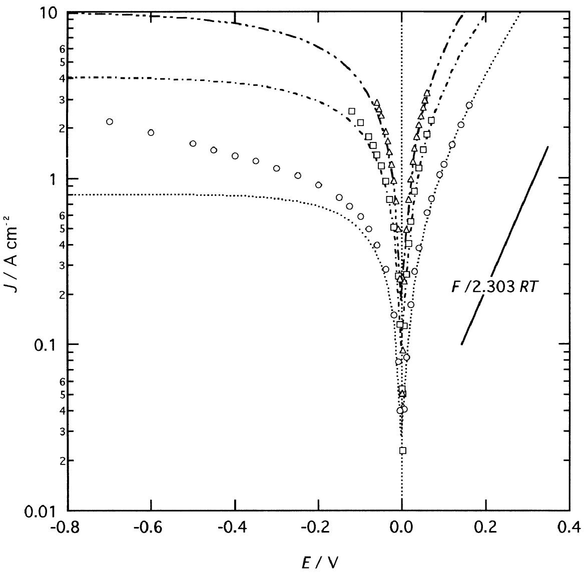

Fig. 6. *I–V* behaviour at Pt/SrTiO$_3$-Nb interface measured in various oxygen atmospheres at 873 K just before the measurement shown in Fig. 5. The dashed, dash-dotted, dash-dot-dotted lines are the best fit curve assuming thermionic emission model for the Schottky barrier.

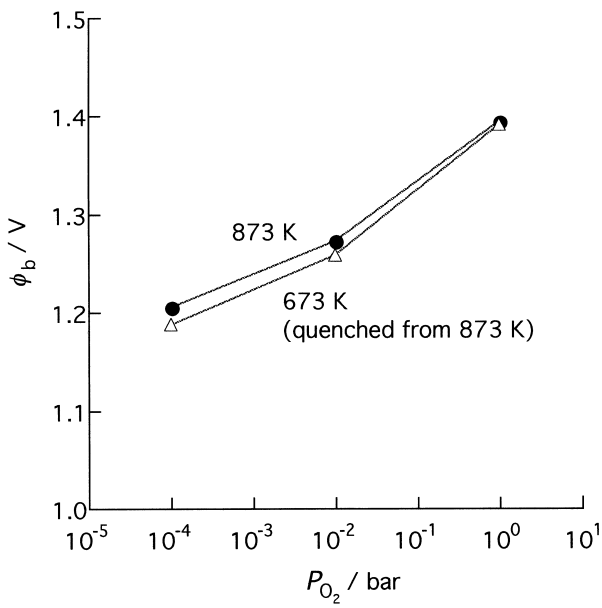

Fig. 7. Calculated Schottky barrier height using thermionic emission model. Rechardson constant, A^*, is assumed to be 120 A cm^{-2} T^{-2}.

and n is the ideality factor which is higher than 1 when the interface is not in an ideal condition. If the Rechardson constant is known, the barrier height can be calculated by fitting the data to eqn (1). In this study, $A^* = 120$ A cm^{-2} is assumed (i.e. effective mass of electron is assumed to be equal to that of free electron). The forward *I–V* curves in Fig. 5 were fitted well using eqn (2) with the ideality factor between 1·12 to 1·22. The calculated barrier height and the ideality factor are plotted in Figs 7 and 8, respectively.

The data obtained at 873 K showed an extremely high ideality factor, n, especially in the reducing atmospheres. In those conditions, the emission model may not be applicable. One possible reason of the deviation is oxygen potential change at the interface under the applied voltage. As pointed out in Ref. 10, the oxide ion distribution can occur under applied voltage even with the sample being a dominant electronic conductor. If the surface reaction rate is limited as reported by Denk *et al.*,[18] the interface oxygen potential will increase with the positive voltage, and decrease with the negative voltage. Since the barrier height decreases with decreasing oxygen potential, the induced low oxygen potential at negative voltage results in the reduction of the barrier height. More experimental studies are necessary to confirm the model for the *I–V* behavior at high temperature.

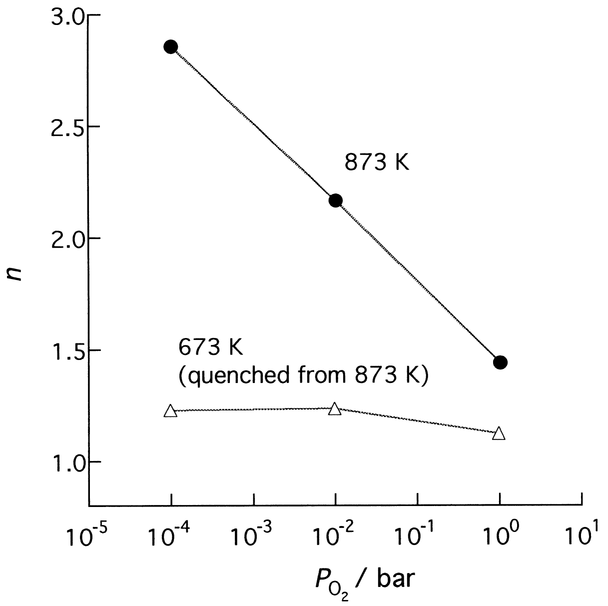

Fig. 8. Ideality factor, *n*, used in fitting the thermionic emission model (eqn (2)) to the data shown in Figs 5 and 6.

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