

## Inserted-cation-dependent Device Characteristic of SrVO<sub>3</sub>-based All-solid-state Redox Transistor

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### Abstract

Two SrVO<sub>3</sub> (SVO)-based all-solid-state redox transistors were fabricated. A Li<sub>4</sub>SiO<sub>4</sub> (LSO) Li<sup>+</sup> ion conductor and a Y-stabilized-ZrO<sub>2</sub> (YSZ) H<sup>+</sup> ion conductor were chosen as a solid state electrolyte. Although similar electronic carrier doping behavior due to the monovalent cation was expected, the two devices showed completely different electronic conduction characteristic. While the YSZ device showed relatively large drain current enhancement (9%), the LSO device showed very small one (0.2%). The result indicated that inserted H<sup>+</sup> or Li<sup>+</sup> gives different effect on the local environment near V<sup>4+</sup> ions (V-O-V angle).

### 1. Introduction

SrVO<sub>3</sub> (SVO) thin film is promising material for application to next generation nanoelectronics owing to its metal-insulator transition (MIT). MIT in SVO was achieved only for extremely thin film (with a several nm thick) which are not well suited to practical application.<sup>1-3)</sup>

Recently, theoretical calculation (density functional theory plus dynamical mean-field theory) indicated that tensile strain induces MIT in CaVO<sub>3</sub> and related materials.<sup>4)</sup> Furthermore, we experimentally evidenced that, in Ca doped SVO, MIT was achieved even for relatively thick films (with a 50 nm thick), which are safely applied to practical devices.<sup>5)</sup> Hard X-ray photoemission spectroscopy indicated that the origin is the strain from the substrate.<sup>5)</sup> Therefore, even for SVO, the strain is expected to be a key factor for MIT.

Concerning the SVO bulk crystal, Li<sup>+</sup> ions were inserted into the SVO to form Li<sub>x</sub>SrVO<sub>3</sub> (LSVO). The lattice constant of the LSVO expanded as the amount of inserted Li<sup>+</sup> ions increased, which leads the tensile strain.<sup>6)</sup> Also, increase in oxygen nonstoichiometry was reported to cause expansion of lattice constant.<sup>7)</sup> Therefore, electrochemical control of ion insertion and desertion (redox) in SVO thin film, which enables huge variation in both strain and electronic carrier density, can be a powerful method to realize the MIT at room temperature (RT), at which resistivity switching is applied to resistive random access memory.

In the present study, we report SVO-based all-solid-state redox transistors with a Li<sub>4</sub>SiO<sub>4</sub> (LSO) Li<sup>+</sup> ion conductor or a Ytria-stabilized-ZrO<sub>2</sub> (YSZ) H<sup>+</sup> ion conductor as solid-state electrolytes. Since use of liquid electrolytes makes compatibility with other peripheral devices very low, our all-solid-devices are advantageous for practical application. While H<sup>+</sup> ion insertion lead to an enhancement of 9%, Li<sup>+</sup> ion

insertion produced a very small enhancement of 0.2%. The difference is not understood based merely on tensile strain and carrier density, meaning that other factors should be considered. Based on the strong dependence on the kind of electrolyte used, the effect of the inserted cation on the local environment near V<sup>4+</sup> ions was indicated.

### 2. Experimental methods

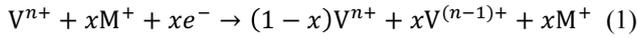
An SVO-based all-solid-state redox transistor is schematically shown in Figure 1. SVO thin film as a channel layer was fabricated by pulsed laser deposition (PLD) using a sintered SVO target pellet prepared by solid phase reaction. Pt thin film for the gate, drain and source electrodes was deposited by RF sputtering. In the transistor with LSO, LiCoO<sub>2</sub> (LCO) was also deposited for gate electrode. YSZ and LSO as the electrolyte were deposited by PLD using a sintered target pellets. Electrochemical measurements were performed using a Keithley 4200-SCS parameter analyzer and an atmosphere/temperature tunable prober system (Nagase). Details of experimental conditions were reported previously.<sup>8)</sup>

### 3. Results and discussion

Figure 2 upper panel shows the electrical conduction characteristic (drain current enhancement vs gate voltage  $V_G$ ) for a constant drain voltage  $V_D$  of 0.1 V at RT.  $V_D$  and  $V_G$  are the voltage between the drain and source, and between the gate and source. In YSZ transistor, drain current enhancement of 9% was observed. This increment resulted from the H<sup>+</sup> insertion into SVO thin film, which induced additional electrons into V<sup>4+</sup> ions. The considerable hysteresis resulted from unsteady state ionic diffusion in the SVO thin film, in which the H<sup>+</sup> ion flux and the H<sup>+</sup> ion concentration gradient in SVO film is not reached to steady state. This suggests that the electrical carrier was modulated by H<sup>+</sup> ion transport in the SVO thin film, with comparably slow kinetics featuring ion migration-related phenomena, at low temperatures such as RT.

In contrast, with LSO transistor, drain current showed very small enhancement (0.2%) compared to that observed with YSZ transistor. The possible reason for this difference is discussed later.

Figure 2 lower panel shows the gate current  $i_G$  dependence on the  $V_G$ . The value of  $i_G$  is several tenth nA, which is much larger than that found in electric-double-layer-transistors (EDLTs). This supports that our device is a redox transistor rather than EDLT. The behavior of  $i_G$  corresponds to redox reaction of V<sup>n+</sup> ions, which is expressed as



We discuss below the possible origin of the difference between LSO and YSZ redox transistor since the variation in drain current behavior for them differed even though both  $\text{Li}^{+}$  ion and  $\text{H}^{+}$  ion are monovalent cation. Schematic illustrations of one-eighth of the unit cell of SVO are shown in Fig. 3. In LSO one,  $\text{Li}^{+}$  ion was inserted into 3c-site,<sup>6)</sup> which is the tetrahedral site surrounded by three oxygen ions and one strontium ion, to form  $\text{Li}_x\text{SrVO}_3$ . As an amount of the inserted  $\text{Li}^{+}$  ion increased, the valence of V ion decreased from  $\text{V}^{4+}$  to  $\text{V}^{3+}$  to maintain electroneutrality, which led to the increase of electronic carrier. The lattice constant slightly increased 0.06% with increase of  $x$  up to 0.6 while crystal structure was kept cubic.<sup>6)</sup> Local distortion of the lattice around the inserted  $\text{Li}^{+}$  ion can affect the V-O-V angle which is the origin of metallic conductivity. Therefore, in  $\text{Li}_x\text{SrVO}_3$ , the variation in V-O-V angle prevents the conductivity enhancement. In YSZ one, when  $\text{H}^{+}$  ion is inserted into SVO,  $\text{H}_2\text{O}$  and oxygen vacancy were created. Due to the emergence of these, relatively large lattice expansion of 0.2% was observed.<sup>7)</sup> This value (0.2%) is far larger than that of LSO one (0.06%).

Based on the gate current applied during device operation, the doped electrons in SVO are estimated to be 0.64 per unit cell for LSO one, and 0.39 per unit cell for YSZ one. Therefore, drain current enhancement with  $\text{Li}^{+}$  ion insertion is expected to be larger than that with  $\text{H}^{+}$  ion insertion. However, the present result is completely opposite. Thus, the carrier density is not main reason for the variation in drain current behavior. One possible reason for the difference is decrease in electron mobility due to lattice distortion. As mentioned above,  $\text{H}^{+}$  insertion into SVO caused relatively large lattice expansion. Although the V-O-V angle is expected to be affected with the lattice expansion, the large expansion can be advantageous for enhancement of conductivity. Since details of this mechanism are not clear at present, we need to clarify in future work.

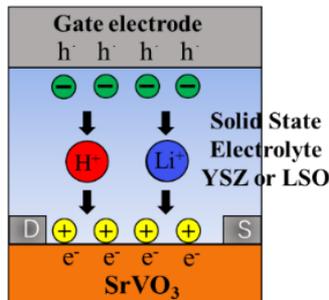


Fig. 1. Schematic illustration of the SVO-based redox transistor with a LSO  $\text{Li}^{+}$  ion conductor or a YSZ  $\text{H}^{+}$  ion conductor.

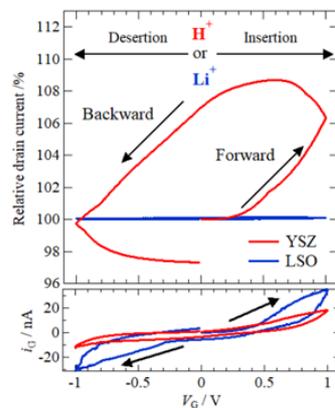


Fig. 2. Relative drain current vs.  $V_G$  (upper panel) and gate current vs.  $V_G$  (lower panel) in the SVO-based redox transistor with YSZ or LSO measured at RT. The  $V_G$  sweeping rate was 6 mV/s.

#### 4. Conclusions

SVO-based all-solid-state redox transistors, with an LSO  $\text{Li}^{+}$  ion conductor or a YSZ  $\text{H}^{+}$  ion conductor, were fabricated to examine whether the induced electronic carrier and strain due to the ion insertion can cause MIT at RT. While the YSZ transistor exhibited drain current enhancement of 9%, the LSO transistor exhibited small one of 0.2%. The small drain current increment in LSO transistor can result from the decrease in electron mobility. Although drain current enhancement was insufficient for MIT at present, the results should indicate the possibility of SVO-based high performance ReRAMs.

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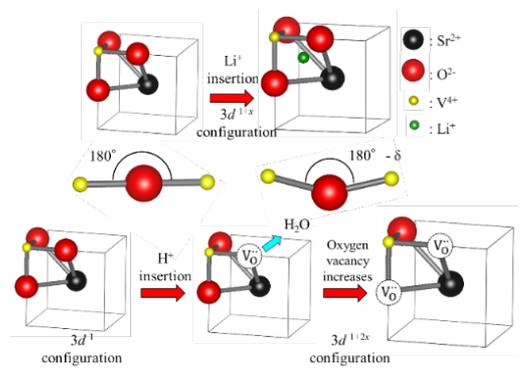


Fig. 3. Suggested models for  $\text{Li}^{+}$  or  $\text{H}^{+}$  ion insertion into SVO