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# Study on Interfacial Redox Reactions of Tantalum as a Good Scavenger Material in ReRAM Devices

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**Abstract**

**A high functionality as a scavenger material and its close relationship with the interfacial reactions are revealed for Ta and $TaO_x$. From the structural and chemical analyses for Ta interfacial layers in ReRAM-like cells, we observe that Ta scavengers show very active interfacial reactions with oxide layers, and facilitate the resistive switching. The origin of the active scavenging of Ta is not explained by any conventional models for scavenging phenomena, but can be attributed to the high homogeneity of the interfacial reactions. Continuous control of the resistance state and a large increase in the switching yield are also demonstrated by using Ta scavengers, and the involvement of the interfacial reactions are discussed.**

## 1. Introduction

Pushed by recent developments of resistive random access memory (ReRAM) based on redox reactions, increasing attention has been paid to interfacial reactions between metal and oxide. The previous studies have shown that defect formation at the electrode/oxide interface plays important roles in the operation of redox-based ReRAM, and a new device component of "scavenger" layer has been proposed for the devices. Scavenger layers are supposed to provide oxygen defects to a switching oxide through the interfacial reactions (Fig. 1), and have been employed in many recent ReRAMs. The properties of scavenger materials have been discussed based on the formation free energies of the stable oxide per oxygen atom ($\Delta G^{\circ}_{ox}$: $\Delta G^{\circ}/x$ for $M + xO \rightarrow MOx + \Delta G^{\circ}$) (Table I), and a metal with a small $\Delta G^{\circ}_{ox}$ (such as Al and Ti) has been used in ReRAM fabrications [1]. On the other hand, we have recently demonstrated that a very active oxygen scavenging is achieved by Ta scavenger layers rather than metals with a smaller $\Delta G^{\circ}_{ox}$ [2, 3]. To understand the origin of the anomalous oxygen scavenging by Ta layers, we performed detailed analyses of the interfacial reactions in this study. Based on the microscopy observations for ReRAM-type reaction cells with Ta scavengers, the mechanism and potential usage in ReRAM devices were discussed.

Table I $\Delta G^{\circ}_{ox}$, $\phi$, and $X$ of Scavenger Metals

| Materials | $\Delta G^{\circ}_{ox}$ [kJ/mol] | $\phi$ [eV] | $X$ |
|---|---|---|---|
| Al | −526 | 4.28 | 1.5 |
| Zr | −519 | 4.05 | 1.5 |
| Ti | −441 | 4.33 | 1.6 |
| Ta | −394 | 4.25 | 1.7 |
| Pt | −82 | 5.65 | 2.1 |

## 2. Experimental Methods

Test cells of Pt(100 nm)/M(10 nm)/$SrTiO_3$(STO,100 nm)/Pt(100 nm) were fabricated on $SiO_2$(200 nm)/Si substrates by radio frequency sputtering at room temperature. Other than Ta, various scavenger materials (M) of Al, Ti, and Zr were used for the cells for comparison. Note that we intentionally fabricated large-scale cells with thick (100 nm) layers of STO for clear observation of the interfacial reactions. The electrical properties were measured with a semiconductor parameter analyzer (Keysight, B1500) with the bottom electrode grounded. Structural characterization and chemical analysis of the cells were performed by high-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray spectroscopy (EDX) on Titan3 G2 60-300.

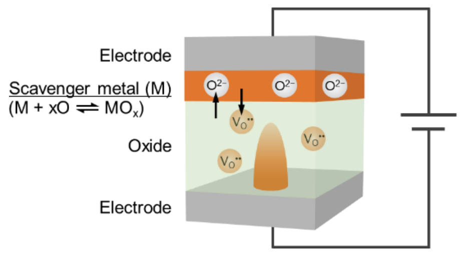


Fig. 1 Schematic illustration of a redox-based ReRAM cell having an interfacial scavenger layer of a reductive metal.

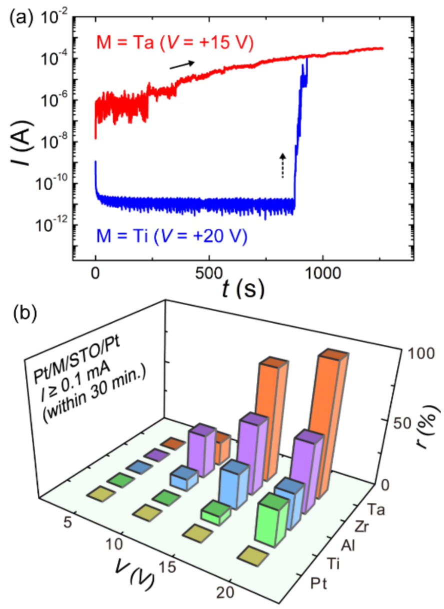


Fig. 2 (a) Time dependence of currents in Pt/Ta/STO/Pt and Pt/Ti/STO/Pt cells under constant voltages. (b) Yields ($r$) of the resistance decrease for various Pt/M/STO/Pt cells.

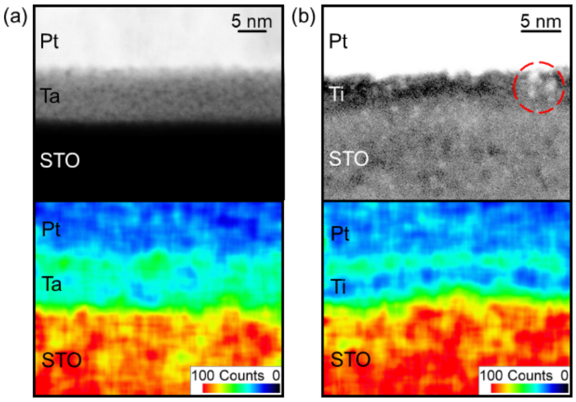


Fig. 3 HAADF-STEM images (top panels) and corresponding EDX mappings of oxygen K-line intensity (bottom panels) for (a) Pt/Ta/STO/Pt and (b) Pt/Ti/STO/Pt cells before voltage applications.

### 3. Results and Discussion

Although Ti and Al have often been used as an oxygen scavenger in redox-based ReRAMs, the occurrence of less active reactions was suggested at the interfaces. As shown in the current–time characteristics [Fig. 2(a)], the resistance of Pt/Ti/STO/Pt cell did not change with time, and a sudden jump of the resistance was only observed in a small number of cells. In contrast, when Ta was used as the scavenger, a gradual decrease of the resistance appeared by voltage applications, and continuous (analog-like) control of the cell resistance became possible. By inducing a resistance decease of ≤~1 M Ω, hysteretic behavior (i.e., resistive switching) was started to be observed in the current–voltage ($I$–$V$) characteristics. The material dependence of the yield ($r$) of the resistance decrease ($I \geq 0.1$ mA within 30 min.) was summarized in Fig. 2(b). The highest $r$ was demonstrated for M = Ta, although the largest $\Delta G^{\circ}_{ox}$ among the four tested materials has been reported for it (Table I). The high $r$ of Ta is also not explained by other conventional models for scavenging based on the work function ($\phi$) or electron affinity ($X$) (Table I), suggesting the uniqueness of the interfacial reactions.

The high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of Ta and Ti scavengers, for which active and less active interfacial reactions were suggested, are shown in Fig. 3. We found that Ta layers have a uniform structure and forms a flat interface with STO [Figs. 3(a)]. However, a rough and wavy structure with unoxidized Ti grains [denoted by a red dotted circle in Fig. 3(b)] were formed in Ti layers. The EDX images showed that oxygen ions have a uniform distribution in the Ta layer [Fig. 3(a)] whereas the Ti layer is only partly oxidized at around the interfaces [Fig. 3(b)]. We observed that the uniformity of oxygen distributions in Ta layer increases with the gradual decrease of the cell resistance, and separate into two regions having a light and dark contrast in the HAADF-STEM images (Fig. 4). These observations suggest that the scavenging reactions of Ta layers uniformly progresses in the thickness direction with changing the fraction of two stable oxidation states of $TaO_x$. The uniform (not local) progress of the interfacial reactions will result in the increases of the net amount of scavenged oxygen in Ta, which may explain the high activity in

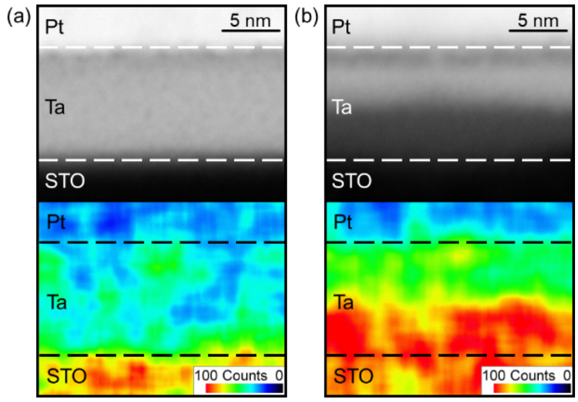


Fig. 4 HAADF-STEM images (top panels) and corresponding EDX mappings of oxygen K-line intensity (bottom panels) at Pt/Ta/STO interfaces after inducing gradual resistance deceases to (a) 8 MΩ and (b) 0.3 MΩ by applications of a constant voltage of +10 V.

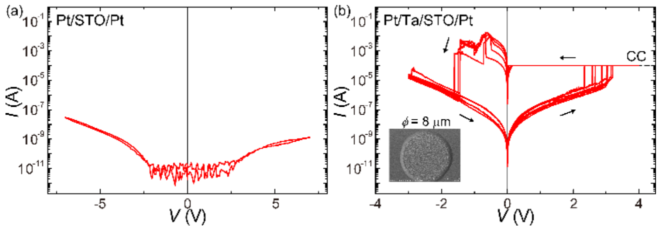


Fig. 5 $I$–$V$ characteristics of (a) Pt/STO(20 nm)/Pt and (b) Pt/Ta(10 nm)/STO(10 nm)/Pt devices having a via-hole structure (inset) .

oxygen scavenging.

In separately fabricated ReRAM devices with smaller thicknesses of STO, we observed that the use of Ta scavenger drastically changes the $I$–$V$ characteristics of the device and offers the stable switching cycles (Fig. 5). The application potential of Ta scavenger is suggested also from the results.

### 3. Conclusions

Ta and $TaO_x$ were shown to have a high activity as an oxygen scavenger for a resistive switching oxide. TEM observations showed that Ta scavenger layers have high structural uniformity, and allow very uniform progress of the interfacial redox reactions. Our findings suggest that Ta and $TaO_x$ have significant advantages as a scavenger material in redox-based ReRAM, such as reduction of the switching voltage and time, and improved uniformity of the switching characteristics by the insertion.

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