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Effect of TaOx thickness on the resistive switching of Ta/Pr0.7Ca0.3MnO3/Pt films

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The influence of interfacial structure on the resistance switching behavior of Ta/Pr0.7Ca0.3MnO3/Pt films was investigated by varying the reactive Ta electrode thickness. Structure and component analyses revealed that a TaOx layer formed at the interface and its thickness increased with the Ta thickness in the thin region while staying the same in the thick region. The similar thickness dependences of the negative differential resistance and resistance switching characteristics were observed and interpreted by the TaOx thickness dependent oxidation and reduction reaction across the interfacial region. This study demonstrates that the resistance switching characteristics could be improved by suitable interfacial engineering. © 2012 American Institute of Physics.

Resistance switching (RS) in metal oxides has been extensively investigated due to its potential applications in future nonvolatile memory devices with high performance requirements. Several physical models have been proposed to explain the RS mechanism, including conductive filaments, valence change mechanisms, electric field enhanced ion migration, and Schottky interface modulation. The filament formation and rupture induced by the electric field and Joule heating is thought to be the most likely explanation for the RS effect. Recently, there have been several reports that some metal materials are easily oxidized and reduced when they are used as top electrodes (TEs), which are involved in the growth and dissolution of metallic filaments during RS. In our previous report, we observed that the oxidation of the active metal electrode (Al, Ti, Ta, etc.) and the reduction of some pervoskite oxides, such as Pr0.7Ca0.3MnO3 (PCMO), at the interface will lead to RS behavior in the TE/PCMO/Pt structure but not for non-reactive metals (Pt, Ag, Au). Therefore, it is clear that the RS effect is related to the formation and dissociation of such interfacial metal oxide layers that are involved as part of the conducting path. However, both filamentary and homogenous switching at the TE-oxide interface has been reported to coexist in one sample, exhibiting the opposite switching behavior. Thereafter, it is strongly expected to improve the RS properties of RS devices through the suitable design of the interfacial structure.

This study explores the RS effect of Ta/PCMO/Pt films with respect to interface engineering by varying the reactive Ta layer thickness. We find that an amorphous thin layer forms at the Ta/PCMO interface and its thickness is dependent on the total Ta layer thickness as measured by high-resolution transmission electron microscopy (HRTEM). Electron energy loss spectroscopy (EELS) reveals that the interfacial layers mainly consist of TaOx. The distinct I-V characteristics exhibit an obvious correlation with the thickness-dependent interfacial structure, especially the negative differential resistance (NDR) and switching field, and can be ascribed to the oxidation and reduction reaction across the interfacial region.

A series of Au/Ta/PCMO/Pt-layered structures were prepared in a RF magnetron sputtering system on commercial Si substrates as reported in an earlier paper. A PCMO film of 160 nm thickness was grown on a 180 nm Pt buffer layer. The TE of Ta (film thickness tTa = 1, 3, 5, 7, 9 nm) was deposited on the PCMO/Pt/Si substrate at room temperature. The sample was then covered by a 40 nm Au film to protect it from contamination. An array of TE pads with an area of 80 × 80 μm² was fabricated using a conventional photolithography technique. Keithley 2400 and Agilent 81110 A were used for pulsed I-V characterizations and pulse switching, respectively. For all electrical measurements, the bottom electrode was grounded and the TE was always biased. HRTEM and EELS were employed to investigate the structure and chemical components of the interface sections of the films.

Fig. 1(a) shows the HRTEM image of the top interface between the Au capping layer and PCMO without a Ta interlayer, revealing an extremely sharp interface. The 1 nm-thick Ta film insert reveals that an amorphous layer (a-TaOx) of about 2.6 nm formed between the Au and PCMO (see Fig. 1(b)), similar to previous studies. To increase tTa to 3 and 7 nm, the values of the observed amorphous layer/bulk Ta (metal) thickness, 3.8/2.2 nm and 4/6.2 nm, respectively, are shown in Figs. 1(c) and 1(d). At tTa ≥ 9 nm, the amorphous layer maintains a constant thickness of about 4 nm.

A chemical analysis is then used to identify the amorphous layers in the interfacial region, determining their composition and settling their impact on the RS characteristics. A nanoprobe EELS spectrum was collected from the amorphous interface for the Au/Ta (1 nm)/PCMO sample, as shown in Fig. 2. The EELS spectrum displays a platform of around 14.8 to 24.2 eV (Fig. 2(a)), which is identified as the Ta-O2.3 compared to the reference standard spectrum of TaOx. There is no significant contribution to the spectrum from the 39.5 eV surface plasmon of bulk Ta. Furthermore,
two weak adjacent peaks at 347 and 352 eV appear in an energy range of 300 to 400 eV, which is the characteristic feature of Ca (Ca-L$_{2,3}$), as shown in Fig. 2(b). Therefore, the spectrum taken at the interface includes contributions from a majority of TaO$_x$ and a minority of PCMO. In contrast, for samples with larger $t_{Ta}$, the EELS spectrum exhibits a sharp characteristic peak of Ta at about 39.5 eV in the bulk Ta region (not shown here) in addition to the Ta-O$_{2,3}$ feature in the amorphous region. Similar results have been obtained in other samples at $t_{Ta} \approx 9$ nm. These results clearly demonstrate that the amorphous interfacial layer mainly consists of TaO$_x$. This can be ascribed to the oxidation of Ta TE by the adjacent PCMO during sample preparation, and the interdiffusion of some PCMO into the interfacial region at ambient temperatures seems inevitable. Based on our HRTEM and EELS results, it is clearly demonstrated that only about 1 nm of Ta has been natively oxidized to generate an amorphous TaO$_x$ layer of not much more than 4 nm for a thin Ta film adjacent to PCMO.

The structural characteristics of the amorphous interfacial region do indeed play an important role in RS behavior. The I–V characteristics for the Au/Ta/PCMO/Pt films were measured and the representative results with different $t_{Ta}$ are shown in Fig. 3. For the as-prepared samples, a positive pulsed voltage sweep from 0 to 3 V was performed to carry out the forming process (pulse width: 25 ms, period: 35 ms, 120 steps). Afterwards, a pulsed voltage scan from 3 to $-3$ V and from $-3$ to 3 V was subsequently applied to measure the RS behavior with a current compliance of 100 mA. For the sample with $t_{Ta} = 1$ nm, the resistance of the as-prepared sample was about 9 kΩ (measured at 0.4 V). During the forming process, a distinctive NDR appears, leading to a high resistance state (HRS) of about 6 kΩ, as shown in Fig. 3(a). Afterwards, HRS can be set to a low resistance state (LRS) of about 2 kΩ by applying negative voltage (HRS, LRS measured at $-0.4$ V); see Fig. 3(b). The NDR effect only occurred at the first voltage scan. When the second cycle of voltage scan was applied, the NDR peak disappeared while the RS behavior in the region of negative voltage stayed almost the same. In comparison, for the Au/PCMO/Pt sample without a Ta interlayer layer, the corresponding I-V curve follows Ohm’s law with a resistance of about 4 Ω, indicating that the resistance of the PCMO layer is quite small. These characteristics clearly illuminate that the NDR and RS take place at the amorphous interfacial region.

The results obtained are similar to previous studies of Ta/PCMO/Pt and Ti/PCMO/Pt and can be attributed to the oxidation/reduction process via the motion of oxygen ions at the interfacial region.11–13,15–17 During the forming process, the oxygen ions of PCMO begin to migrate into the natively oxidized TaO$_x$ layer when the positive applied voltage exceeds a critical value $V_P$. Hence, the TaO$_x$ interlayer is further oxidized, which generates the remarkable NDR effect and causes the switching to HRS. When a negative bias is applied to TE, most of the applied voltage will drop across the oxide layer and then result in a large local electrical field.

FIG. 1. HRTEM images of interfaces for samples of Au/Ta/PCMO structure with different $t_{Ta}$, (a) without Ta inserted, (b) 1 nm, (c) 3 nm, and (d) 7 nm. The thicknesses of these amorphous interfacial layers are 0 nm, 2.6 nm, 3.76 nm, and 4 nm, respectively.

FIG. 2. EELS spectrum measured at the amorphous interfacial region for a sample of Au/Ta (1 nm)/PCMO.

FIG. 3. I-V characteristics for Au/Ta/PCMO samples with different $t_{Ta}$. (a) Forming and (b) resistive switching processes measured by pulsed voltage sweep with a current compliance of 100 mA.
that repels oxygen ions from TaOx towards PCMO, and the reduction of the Ta oxide layer causes a switching back to the LRS.

To access the interfacial contribution to the RS characteristics, the Ta layer’s thickness-dependent switching parameters are collected from dozens of samples with different tTa and analyzed. Fig. 4(a) shows the behavior of Vp instability with tTa after statistical summarization. As a result, the Vp of a sample with tTa = 1 nm is about 1.1 V. To increase tTa, the corresponding Vp decreases monotonically with slight variation. However, the “set” voltage (Vs) from HRS to LRS exhibits the opposite thickness dependences, as shown in Fig. 4(b). A similar trend in thickness dependence for HRS and LRS measured at −0.4 V is observed and illustrated in Fig. 4(c).

Obviously, the RS characteristics (Vp, Vs, and HRS/LRS) for an Au/Ta/PCMO/Pt structure with tTa = 1 nm is different from that of a larger tTa, which is believed to originate from the Ta thickness-dependent interfacial structure. Previous experimental results from HRTEM and EELS measurements clearly reveal a similar trend in TaOx thickness (tTaOx) dependence, establishing the apparent correlations between interfacial structure and RS characteristics. First, for increasing tTaOx, sample resistance naturally increases, regardless of HRS or LRS, as shown in Fig. 4(c). Second, the thickness dependence of Vs can also be well understood. Because most of the applied voltage drops across the oxide layer, higher negative voltage is required to complete the reduction of the Ta oxide for the thicker TaOx layer, causing Vs to increase with tTa. The thickness dependence of Vp is counterintuitive and requires further investigation. As previously discussed, the motion of oxygen ions at the Ta/PCMO interface driven by the electric field results in the NDR effect. Therefore, one possible argument is that the TaOx thickness-dependent oxygen vacancy concentration distribution results in this feature. In thinner TaOx without voltage applied, the oxygen vacancy concentration is higher than that of thicker TaOx due to the limited quantities of oxygen vacancies provided by PCMO. Hence, higher positive voltage is needed to overcome the larger chemical potential for thinner TaOx.

Finally, as evidenced by HRTEM results, tTaOx almost keeps a constant value of 4 nm at tTa ≥ 3 nm, leading to the saturation behavior of Vp, Vs, and HRS/LRS.

Moreover, the I-V characteristics (Vp, Vs, and HRS/LRS) in the thicker Ta thickness region remain almost the same, implying that the chemical components and even the thickness of TaOx layers may change a little. In other words, under an electric field, the oxidation of Ta almost changes a little and this variation is insufficient to influence thickness trends.

During the forming and RS processes, although the chemical components and even the thickness of TaOx may be modified to a certain degree, the I-V characteristics (Vp, Vs, and HRS/LRS) in the thicker Ta thickness regions remain almost the same, implying the following points. First, during the RS process tTaOx may keep almost constant for samples with tTa ≥ 3 nm. Otherwise, the observed HRS/LRS for a thicker Ta interlayer will change with tTa. This deduction suggests that the increment of tTaOx is limited, resulting from oxidation prompted by the ion migration driven by the applied electric field and vice versa. Moreover, the fact that RS generates in the thinner interfacial region suggests that it is unnecessary to fabricate thicker oxide layers in real applications of such memristive devices, regardless of whether RS originates from a filamentary conducting path or homogenous interfacial switching. Thus, the improvement of RS characteristics can be expected based on the suitable design and control of the interface structure.

In conclusion, we have investigated the interfacial effect of an Au/Ta/PCMO/Pt structure with varying Ta interlayer thicknesses on RS characteristics. HRTEM and EELS results show that a thin TaOx layer forms at the interfacial region, and its thickness increases with the Ta thickness in the thinner region, maintaining a constant at tTa ≥ 3 nm. The interfacial structure-dependent NDR and RS effects have been observed and are ascribed to the oxidation and reduction reaction across the interfacial region. The improvement of RS characteristics by suitable interfacial engineering are expected, and this unique property of interfacial-dependent devices could be exploited for applications.

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![FIG. 4. The tTa dependence of (a) NDR voltage Vp, (b) set voltage Vs, and (c) HRS/LRS value (measured at −0.4 V). These results were collected and statistically analyzed from samples with different tTa.](image-url)


