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# Role of tantalum nitride as active top electrode in electroforming-free bipolar resistive switching behavior of cerium oxide-based memory cells

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ABSTRACT

Electroforming-free cerium oxide-based bipolar resistive switching memory devices have been deposited using radio frequency magnetron sputtering technique. These devices demonstrate two types of forming-free cells: some in the low-resistance state and the others in high-resistance state. The transmission electron microscopy and X-ray diffraction analyses illustrate the formation of tantalum oxynitride layer between tantalum nitride (TaN) and cerium oxide ($CeO_x$), which looks to be responsible for the two types of cells as well as their memory performance. Ohmic and Poole–Frenkel conduction mechanisms are found to be responsible for charge transport in the low- and high-resistance states. The current–voltage characteristics and temperature dependence of resistance suggest that resistive switching mechanism in our $TaN/CeO_x/Pt$ devices may be explained by the model of connection and disconnection of filamentary paths made of oxygen vacancies. The reliability characteristics of $TaN/CeO_x/Pt$ devices indicate better endurance and stable retention performance at relatively lower programming voltages and larger memory window (OFF/ON resistance ratio ~$10^3$) at room temperature and at 100 °C.

## 1. Introduction

In general, resistive switching (RS) devices normally require an electroforming process, which involves high-voltage sweep to switch the device from its pristine state (very high-resistance state (HRS) due to high insulating properties of the active layer) to low-resistance state (LRS). This electroforming process, however, might cause reliability problems associated with the generation and distribution of large number of defects on applying high electric field. Because of this fact and filamentary conduction, conventional resistive random access memory (RRAM) cells show low yield, high operating (set/reset) current/voltage and large variations in switching characteristics [1,2]. In order to avoid such problems, promising forming-free RRAM devices based on redox/interface reaction mechanisms have been anticipated [3,4]. Switching mechanisms in these devices involve the formation of local conductive filaments resulting from the generation/redistribution of oxygen vacancies/ions [5–7], charge trapping [8] or polarization switching [9,10]. Moreover, the nature and geometry of top electrodes play vital role in forming-free switching. Recently, some RRAM devices based on transition metal and rare-earth oxides (REO), such as $Ru/REO_x/TaN$ [11], $Zr/CeO_x/Pt$ [7], $Pt/Gd_2O_3/Pt$ [12], $TiN/Ti/HfO_x/TiN$ [13], $Ti/Ga_2O_3{:}Cr/Pt$ [14], Ti/SiN/Pt [15] and $Pt/CeO_x/TiN$ [16], have shown such electroforming-free switching behavior with high-resistance ratio, relatively low operation voltage, long retention times and good endurance. In addition, deliberate oxide-layer engineering through metal doping, non-stoichiometry and grain geometry have demonstrated their roles in such memory devices, which do not require the initial formation of conductive filaments throughout their bulk [17]. It is a verified fact that a highly nonstoichiometric $CeO_x$ nanostructured active layer does not necessitate an electroforming step but maintains excellent device performance [8,16]. Therefore; it is valuable to further explore the forming-free RS phenomena in $CeO_x$ films for the improvement of their reliability, OFF/ON ratio, uniformity and stability characteristics for their possible utilization in nonvolatile memory devices.

In this work, we have fabricated $CeO_x$-based RS memory devices using a radio frequency (RF) sputtering method. A forming-free bipolar resistive switching in $TaN/CeO_x/Pt$ devices has been investigated for their reliable RS characteristics with high OFF/ON resistance ratio of ~$10^3$ at room and elevated temperatures along with good endurance and retention (>$10^4$ s) properties. It is noteworthy that our devices exhibit forming-free behavior which makes them suitable for relatively low power consumption and excellent write/erase performance during nonvolatile memory applications.

## 2. Experimental details

$CeO_2$ thin films (~15 nm) were deposited on $Pt/Ti/SiO_2/Si$ substrates at room temperature in an RF sputter using a ceramic target made of cerium oxide powder (99.999% pure by Aldrich). During deposition a

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flow of Ar + $O_2$ (Ar:$O_2$∷20:10) gas mixture was maintained at 1.33 Pa in the chamber with a base pressure of ~ $4.26 \times 10^{-4}$ Pa. To study electrical properties of $CeO_2$–based memory devices, TaN circular top electrodes (diameter: 150 μm) of ~100 nm thickness were deposited on $CeO_2$ films in a DC-sputter operating at 75 W using metallic perforated mask. All processing steps of the TaN/$CeO_2$/Pt memory devices were performed at room temperature. The crystal structure of these $CeO_2$ based devices was determined by X-ray diffractometer (XRD; Bede D1, Bede PLC, London, UK) operated at 40 kV and 30 mA at a grazing angle of 3° using Cu $K_\alpha$ ($\lambda = 1.542$ Å) radiations in the $2\theta$ range from 20° to 80° with a step of 0.01°. Film thickness and interfacial reaction between TaN and $CeO_2$ layers were confirmed by cross-sectional high-resolution transmission electron microscopy (HRTEM) operated at 300 kV. To perform cross-sectional HRTEM, specimen was prepared by focused ion beam (FIB) because FIB can micro-machine samples very precisely from some specific area of interest in a sample. Current–voltage (I–V) characteristics of TaN/$CeO_2$/Pt devices were evaluated using Agilent B1500A (Agilent Technologies, Santa Clara, CA, USA) semiconductor parameter analyzer. During electrical characterization, Pt bottom electrode was grounded and a bias voltage was applied to the TaN top electrode.

## 3. Results and discussion

Fig. 1(a) shows typical grazing angle (3°) X-ray diffraction (XRD) pattern of TaN/$CeO_x$/Pt RRAM devices fabricated on Ti/$SiO_2$/Si substrates. Diffraction pattern depicts some broad peaks illustrating that $CeO_2$ film possesses weak polycrystalline fluorite cubic structure (JCPDS #: 34-0394) showing only (111), (200) and (311) reflections corresponding to diffraction angles at 28.5°, 32.5° and 56.5°, respectively. Broadening of the preferably oriented (111) reflection may be caused by significant reduction in grain size [17] or due to very small thickness of $CeO_2$ films [16]. In addition, few weak XRD reflections corresponding to (110), (200), (111), (201), (002), (102), (212) and (410) planes of tantalum oxynitride (TaON) hexagonal structure (JCPDS #: 72-2067) are also visible in this pattern. Presence of TaON interlayer between $CeO_2$ and TaN top electrode can also be confirmed through HRTEM observations as displayed in Fig. 1(b). Sputtered conductive TaN electrode is known to be easily oxidized into TaON because of oxygen getting tendency of tantalum metal [18]. That is why it looks quite reasonable to identify the bright gray area of non-uniform thickness as the TaON interlayer in Fig. 1(b), which lies between the top TaN electrode (black area) and $CeO_2$ layer (gray region). The formation of TaON interlayer is expected during sputtering through local oxidation of the incoming TaN molecules as tantalum possesses much greater affinity than cerium to react with oxygen. This situation may lead to nonuniformity of the interfacial layer. In addition, as the top TaN layer may not be uniform in density, the places rich in TaN show high nucleation and those poor in TaN depict low nucleation leading to nonuniformity of the TaON layer. The formation of such an interlayer (TaON) during deposition has already been described by Zhou and Zhai [19] in Pt/$GdO_x$/TaN and by Zhou et al. [20] in TaN/$CuO_x$/Cu memory devices through X-ray photoelectron spectroscopy analyses. This TaON interlayer is expected to play key role in the bipolar RS behavior.

*I–V* characteristics of TaN/$CeO_x$/Pt cells studied at room temperature (25 °C) are shown in Fig. 2. In the as-prepared state, some cells of a device are noticed to be in LRS and the others in HRS. For those cells found initially in LRS, current switches gradually from LRS to HRS by applying negative biasing as illustrated in Fig. 2(a). However, for those devices which were found in HRS in their pristine state (Fig. 2b), current switches to LRS on the application of positive biasing voltage. In both cases, devices show bipolar resistive switching, irrespective of their pristine resistance states. It is well known that almost all oxide films capable of showing resistive switching require “electroforming” prior to exhibit the repeatable RS behavior [21]. However, TaN/$CeO_x$/Pt devices have displayed bipolar resistive switching behavior without requiring any initial electroforming process for their activation in both cases. Thus, the cells which initiated with low-resistance (ON-state) by applying negative bias and RS established through a RESET process (Fig. 2a) are hereafter called low-resistance state “forming-free” (LRSFF) devices. While those cells that show switching in resistance from HRS to LRS during initial sweep of positive voltages are hereafter named as high-resistance state “forming-free” (HRSFF) devices. A reverse bias causes these devices to switch back to HRS as depicted by sudden decrease in current illustrating typical bipolar-type switching (Fig. 2b). To verify such LRSFF and HRSFF behaviors, up to about thirty different cells from one $CeO_2$ film were tested. Among them, about 70% of the cells showed forming-free character in their LRS while other 30% depicted forming-free behavior in their HRS. No doubt, the LRSFF and HRSFF devices differ in their pristine resistance states, and there are however practically no significant differences (in terms of endurance, retention, set/reset voltages, conduction mechanism in the ON- and OFF-states as well as the temperature dependence of $R_{ON}$ and $R_{OFF}$) between them once they have initiated their initial switching cycle. In addition, both types of cells illustrate multistep switching from LRS to HRS (RESET process) during negative voltage sweep as seen in Fig. 2. Such multistep RESET processes observed in our devices correspond to the rupture of multi-filaments formed at different electric fields, and make these devices suitable for multilevel data storage [20]. The bipolar nature of switching process indicates that the write (erase) process occurs only with a positive (negative) bias. Different behaviors of the two types of devices may be related to the nonstoichiometric

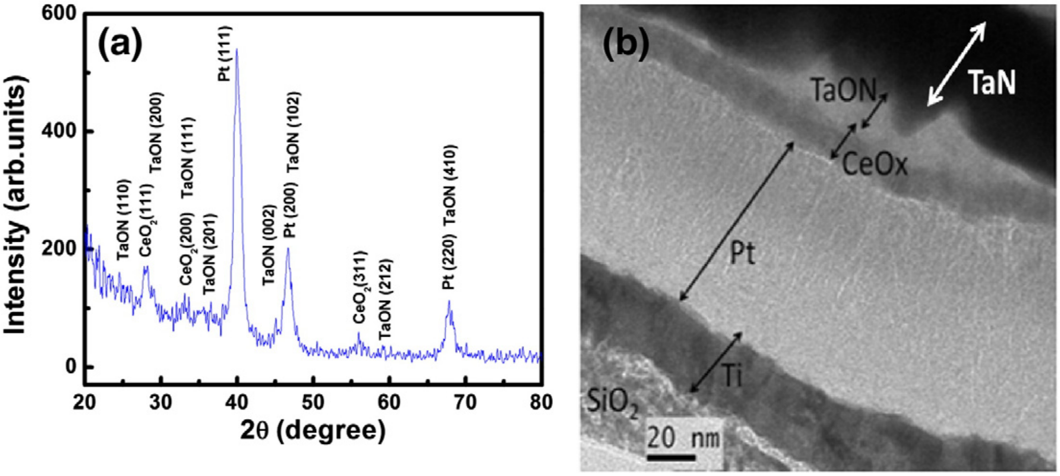

**Fig. 1.** (a) XRD pattern of the fabricated TaN/$CeO_x$/Pt memory devices at room temperature. (b) Cross-sectional HRTEM image of TaN/$CeO_x$/Pt devices depicting TaON interlayer.