



# Full ALD Ta<sub>2</sub>O<sub>5</sub>-based stacks for resistive random access memory grown with *in vacuo* XPS monitoring



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## ABSTRACT

Ta<sub>2</sub>O<sub>5</sub>-based metal-insulator-metal stacks for resistive random access memory were grown by atomic layer deposition technique only with the emphasis on different top metal–oxide interface engineering. The impact of top TiN electrode growth and NH<sub>3</sub> treatment on dielectric chemical and electrical properties was discussed. In addition the TiN/Ta<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub>/TiN stack with bilayer dielectric was grown and studied too. According to *in vacuo* XPS analysis at top interface both TiN/Ta<sub>2</sub>O<sub>5</sub>/TiN and TiN/Ta<sub>2</sub>O<sub>5</sub> (NH<sub>3</sub>-treated)/TiN stacks comprise the TaO<sub>x</sub>N<sub>y</sub> interlayer which is twice thicker in the case of stack with NH<sub>3</sub> treatment (~1.3 nm) in comparison with untreated one (~0.7 nm). *In vacuo* XPS analysis also showed that 2 nm Al<sub>2</sub>O<sub>3</sub> insert between Ta<sub>2</sub>O<sub>5</sub> and top TiN electrode allowed to completely block formation of TaO<sub>x</sub>N<sub>y</sub> interlayer at TiN/Ta<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub>/TiN stack. As a result it was found that TiN/Ta<sub>2</sub>O<sub>5</sub>/TiN demonstrated gradual and rather slow (~10<sup>-3</sup> s) character of resistive switching while the switching at stack with bilayer Ta<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> dielectric is much more abrupt, faster and it reveals more than one order of magnitude higher endurance.

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## 1. Introduction

Transition metal oxide based ReRAM devices have attracted a lot of attention due to their good scalability, fast speed and high endurance [1,2]. Since 3-D V-NAND Flash memory has been introduced to the market the concept of Vertical ReRAM is also considered to be more cost-effective for the industrial application [3]. However, V-ReRAM architecture requires high conformal deposition of both dielectric and conductive layers on the high aspect ratio substrates. Due to the unique property of ALD technique to produce highly conformal coatings [4] the development of fully ALD based methods for the ReRAM stacks is of great interest.

Amongst the binary metal oxides, Ta<sub>2</sub>O<sub>5</sub> based ReRAM devices have demonstrated encouraging electrical performance, including high endurance, high switching speed, low energy operation and forming-free resistive switching. However, oxygen deficient ion sputtered TaO<sub>x</sub> films are mostly applied for ReRAM stacks [2,5]. Usually ALD metal oxides are highly stoichiometric and their

application for Pt free ReRAM requires scavenging (extracting) thin active metals layers (Ti, Hf, Ta) leading to oxygen deficiency in the dielectric [6,7]. Unfortunately ALD of Ti, Hf, Ta is of great challenge and the creation of full ALD ReRAM stack requires different approaches. One of the possible solutions is an annealing of ALD dielectric in reducing atmosphere accompanied with *in situ* top electrode deposition (TiN) [8]. Another interesting approach is a using of two layer or multilayer ALD Ta<sub>2</sub>O<sub>5</sub> based dielectrics with emphasizing on interface chemical interactions [3,9]. However, the composition of the layers is concealed in these works, thus the clear understanding and particularly the modeling of resistive switching in such stacks become rather difficult. It is evident that the application of *in situ* (*in vacuo*) chemical state monitoring (e.g., using of X-ray Photoelectron Spectroscopy (XPS)) both for the approach with the dielectric reducing annealing and for the approach with the multilayer dielectric including interface barrier layers at interfaces is quite desirable. First it is more convenient to study full ALD ReRAM stacks on planar metal-insulator-metal (MIM) structures. Thus, this work is aimed at the chemical and resistive switching properties investigations of ReRAM planar stacks where both Ta<sub>2</sub>O<sub>5</sub> based dielectrics and electrodes (TiN) are grown by thermo-ALD in combination with *in vacuo* XPS analysis.

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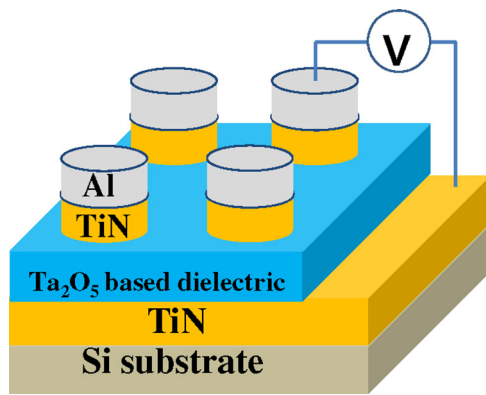


Fig. 1. The general scheme of ReRAM stacks.

## 2. Experimental

The TiN(20 nm)/Ta<sub>2</sub>O<sub>5</sub>(7 nm)/TiN(20 nm)MIM stacks were grown by thermo-ALD using a vertical type Sunale R-100 Picosun OY ALD reactor containing a turbo molecular-pumped ultra-high vacuum transfer system for *in vacuo* XPS analysis. *p*-type ( $\rho = 12 \Omega \text{ cm}$ ) Si wafers with native oxide were employed as substrates. Both bottom and top TiN electrodes were grown by ALD at 400 °C using TiCl<sub>4</sub> and NH<sub>3</sub>. The TiCl<sub>4</sub> and NH<sub>3</sub> pulse durations were 0.1 s and 1.0 s, respectively. For Ta<sub>2</sub>O<sub>5</sub> ALD (300 °C) Ta(OC<sub>2</sub>H<sub>5</sub>)<sub>5</sub> and H<sub>2</sub>O were used. Ta(OC<sub>2</sub>H<sub>5</sub>)<sub>5</sub> and H<sub>2</sub>O pulse durations were 0.5 s and 0.1 s, respectively. On the part of the samples 2 nm Al<sub>2</sub>O<sub>3</sub> layer was grown on Ta<sub>2</sub>O<sub>5</sub> before top TiN electrode deposition. For Al<sub>2</sub>O<sub>3</sub> ALD (300 °C) Al(CH<sub>3</sub>)<sub>3</sub> and H<sub>2</sub>O were used. Al(CH<sub>3</sub>)<sub>3</sub> and H<sub>2</sub>O pulse durations were 0.1 s and 0.1 s, respectively. The other part of samples after Ta<sub>2</sub>O<sub>5</sub> deposition was exposed to treatment (400 °C, 2 h) by NH<sub>3</sub> pulses (1 s, duty cycle 10 s) directly before TiN top electrode deposition.

To study the chemical state of the MIM-stack and its interfaces by *in vacuo* XPS the stack was transferred to the analyzing chamber on the next key stages of the growth: after 3 nm Ta<sub>2</sub>O<sub>5</sub> deposition on TiN electrode (1); after reaching of Ta<sub>2</sub>O<sub>5</sub> total thickness in 7 nm (2); after 4 nm TiN top electrode deposition (3) carried both on the samples with unmodified Ta<sub>2</sub>O<sub>5</sub> and on the samples modified by NH<sub>3</sub> treatment or by insert of Al<sub>2</sub>O<sub>3</sub> interlayer (4). XPS spectra were obtained by Theta Probe Thermo Fisher Scientific spectrometer with a monochromatic Al K $\alpha$  X-ray source (1486.7 eV). The core level spectra were recorded with the 0.1 eV step and 50 eV pass energy. The spectrometer energy scale was calibrated using Au4f<sub>7/2</sub> core level lines located at  $E_b = 84.0 \text{ eV}$ . The base pressure in the analytical chamber was better than  $5 \times 10^{-10} \text{ mbar}$ . The lines corresponding to oxide species were fitted by symmetric convolution of Gaussian and Lorentzian functions and the lines corresponding to the metallic species (bulk TiN) were fitted with the Doniach–Sunjic function, *i.e.*, a convolution of a Gaussian and Lorentzian functions with an additional asymmetry parameter.

For electrical investigation the top TiN electrodes of both unmodified and modified Ta<sub>2</sub>O<sub>5</sub> based stacks were lithographically patterned through the hard Al mask using wet etching processes. The general scheme of ReRAM stack is presented in Fig. 1. The diameters of top electrodes were of 100  $\mu\text{m}$ .

The electrical properties were investigated by current–voltage (I–V) measurements. Direct current (DC) sweep and pulsed I–V measurements were carried out using an AgilentB1500A semiconductor device analyzer. The voltage pulse duration was in a range of  $10^{-3}$ – $10^{-6} \text{ s}$ . Compliance current  $10^{-3} \text{ A}$  was used only during the forming step. At all measurements a bias voltage was applied to the top electrode and the bottom electrode was grounded.

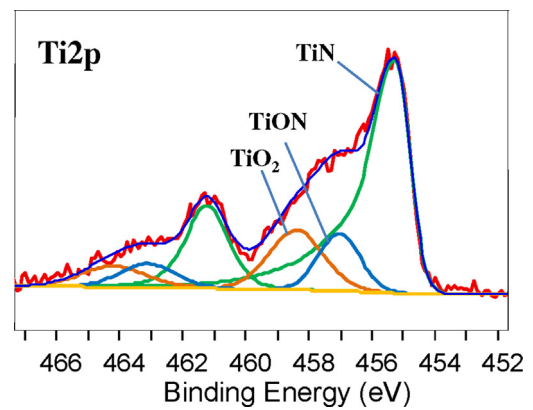


Fig. 2. Ti2p XPS spectra collected at bottom TiN/Ta<sub>2</sub>O<sub>5</sub> interface.

## 3. Results and discussions

Taking into account the importance of the both bottom and top dielectric interfaces analysis we firstly studied bottom TiN/Ta<sub>2</sub>O<sub>5</sub> interface by XPS measurements after ALD of only 3 nm of Ta<sub>2</sub>O<sub>5</sub> to ensure the interface analysis without ion etching. Really, Figs. 2 and 3 represent the Ti2p and Ta4f core level spectra, respectively, measured after 3 nm Ta<sub>2</sub>O<sub>5</sub> ALD on TiN.

The Ti2p spectrum can be fitted with 3 doublets. The first doublet with the 2p<sub>3/2</sub> component centered at  $E_b = 455.3 \text{ eV}$  originates from the bulk TiN [10]. The second doublet with 2p<sub>3/2</sub> component centered at  $E_b = 457.0 \text{ eV}$  is attributed to TiON subsurface layer [10]. The third doublet with 2p<sub>3/2</sub> component is found at  $E_b = 458.4 \text{ eV}$ . This line is usually attributed to TiO<sub>2</sub>, despite that the binding

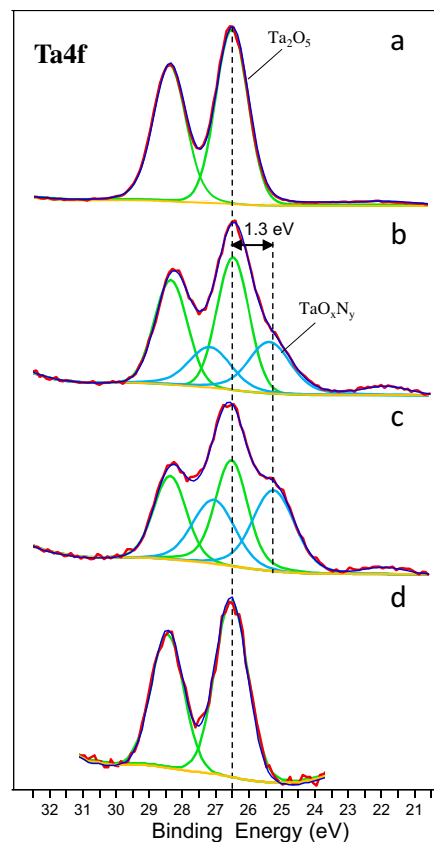


Fig. 3. Ta 4f XPS spectra collected at (a) bottom TiN/Ta<sub>2</sub>O<sub>5</sub> interface; (b) top Ta<sub>2</sub>O<sub>5</sub>/TiN interface; (c) top Ta<sub>2</sub>O<sub>5</sub>/TiN interface with NH<sub>3</sub> treatment prior to top TiN ALD; (d) top Ta<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub>/TiN interface.

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