Effect of oxygen concentration and metal electrode on the resistive switching in MIM capacitors with transition metal oxides

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Abstract. The influence of the oxygen content in the dielectric layer and the effect of the bottom electrode on the resistive switching in Au/Pt/TaOₓ/TiN and Au/Pt/TaOₓ/Ta structures have been studied. The sputtered TaOₓ layers have been prepared by using oxygen concentrations of 10 or 7% O₂ in the Ar+O₂ working ambient as well as by a gradual variation of the O₂ content in the deposition process from 5 to 10%. Two deposition regimes for TiN electrodes have been investigated: reactive sputtering of Ti target in Ar+N₂ ambient, and sputtering of TiN target in pure Ar. Bipolar resistive switching behavior is observed in all examined structures. It is demonstrated that the resistive switching effect is affected by the oxygen content in the working ambient as well as by the type and the deposition conditions of the bottom electrodes. Most stable effect, with ON/OFF ratio above 100 is obtained in TaOₓ deposited with variable O₂ content in the ambient. The obtained switching voltage between the high resistive and low resistive state (SET) is about -1.5 V and the reverse changeover (RESET) is ~2 V. A well pronounced resistive switching is achieved with reactively sputtered TiN while for the other bottom electrodes the effect is negligible.

1. Introduction

The wide spread in the recent years of portable digital devices as well as the general trend in the mainstream computer industry for increasing the speed of the data transfers of internal mass storage devices and their durability defined the significant interest of the semiconductor industry to non-volatile memory (NVM) technology. The current NVM devices are based on the flash technology incorporating floating gate field effect transistor cell. To satisfy the ever increasing demands for higher data volumes stored, lower power consumption and faster data exchange, the dimensions of floating gate cell are constantly shrunk. Although the flash technology can fulfill the requirements to NVM currently, in the long term its inherent limitations will hamper future scaling [1]. Several alternative NVMs involving different memory effects were proposed including: charge trapping memory, phase change memory, ferroelectric field effect transistor; resistive switching memories; nanoelectromechanical memory; spin transfer torque devices. The use of resistive switching (RS) effect for information storage offers some attractive advantages in respect to the floating gate technology: i) simpler memory cell based on metal
insulator metal (MIM) structure, the so-called memristor; ii) smaller cell size, hence high scalable potential; iii) power consumption, high speed and better endurance/retention; iii) lower production costs.

RS effect, found in the 1960s, is a phenomenon of abrupt non-volatile change of the resistance of the dielectric from high resistive state (HRS) to low resistive state (LRS) and vice versa. At specific electrical stress conditions a reversible dielectric breakdown can be obtained, altering the insulating properties of the material. The memory effect is achieved by transferring the structure in HRS (logical “0”) or LRS (logical “1”) through applying to the two terminals voltage with certain value and polarity. The switch between HRS to LRS is referred to as “SET” operation and the reverse process is called “RESET” operation. RS is obtained either by a creation of conductive filament (the nature of the filament depends on the used material) in the dielectric or by the barrier height modification at the interface with the electrode(s) [2]. RS can also be classified by the voltage polarity required to execute SET and RESET operations. Two types of RS can be distinguished in this case: unipolar where SET and RESET do not depend on the polarity of $V$ but only on its value; and bipolar where SET and RESET operations occur at different voltage polarity.

The resistive switching is observed in many materials, but its existence in the binary transition metal oxides is of particular interest for the semiconductor industry [3,4]. These oxides have dielectric constant higher than that of SiO$_2$, and as high-$k$ dielectrics they were extensively investigated as a replacement of SiO$_2$ in the advanced ultra-high density integrated circuits. It was found that they exhibit some unexpected properties which could be implemented in other microelectronics devices. One of these effects is RS. Among the various high-$k$ oxides, Ta$_2$O$_x$ attracted a lot of attention as a dielectric in the storage capacitors of dynamic random access memories [5]. The resistive switching was also observed in Ta$_2$O$_x$ offering a unique possibility for combining the dynamic random access memory with non-volatile resistive random access memory in a single device.

In this work we present experimental results on RS in Ta$_2$O$_x$-based MIM structures with different electrodes in dependence on the oxygen content in the deposition ambient.

2. Experimental procedure

The test MIM structures were fabricated on p-type (100) Si wafers. After a standard chemical cleaning TiN or Ta bottom electrodes were deposited on Si. Two types of sputtered TiN bottom electrodes were prepared by: i) reactive sputtering of Ti target in Ar+N$_2$ ambient at substrate temperature of 200 °C; and ii) magnetron sputtering of TiN target in Ar without substrate heating. Ta bottom electrodes were also fabricated by magnetron sputtering of Ta target in Ar. The thickness of the bottom electrodes were 70 nm. Next, Ta$_2$O$_x$ layers with a thickness of about 10 nm (as determined by ellipsometry) were deposited through reactive magnetron sputtering of Ta target in a mixture of Ar and O$_2$. During the deposition substrates were not intentionally heated. In order to evaluate the effect of the oxygen concentration on RS working gas mixtures with 10 and 7% oxygen were used as well as gradual variation of the O$_2$ content in the range of 5 to 10% in the deposition process. Previously, it was established that at oxygen concentration above 10% the obtained tantalum oxide is stoichiometric [6]. So, the lower O$_2$ concentration in the ambient is suggested to result in a substoichiometric oxide with increased density of oxygen vacancies, thereby facilitating the resistive switching effect. During the Ta$_2$O$_x$ preparation part of the substrate area was shielded to prevent oxide deposition there and ensure access to the bottom electrode. MIM structures were defined by e-beam evaporation through a shadow mask of circular 30 nm thick Pt top electrodes capped with 30 nm thick Au layer (figure 1). The current voltage ($I-V$) characteristics were measured with Keithley 4200 SCS in a dark chamber at room

![Figure 1. Schematic cross section of the test memristors.](image-url)
3. Results and discussion

Figure 2 shows the comparison of the density of initial leakage current $J$ of capacitors with reactively sputtered TiN bottom electrodes and TaO$_x$ films obtained at different O$_2$ concentrations. As seen the increase of the oxygen concentration in the working gas decreases $J$ implying an improved stoichiometry of the layer. At applied voltage, $V$ below about -1.7 V a slight reduction of $J$ is observed which is further followed be a sharp increase at higher negative $V$ (not shown here). The results on the resistive switching effect of these structures are presented in figure 3 for the used O$_2$ concentrations. As evidenced, bipolar resistive switching is observed for all investigated structures. The SET and RESET operations require different voltage polarity. SET occurs under negative $V$, while RESET appears at positive $V$. In order to obtain RS, however, a forming procedure has to be executed. At this procedure negative voltage linearly increasing from 0 to -3 V (in case of TaO$_x$ obtained at 7% O$_2$ content in the ambient) or -5 V (for films deposited at Ar+10% and (5 to 10)% O$_2$ was applied to the structure with compliance function of the measurement unit turned on at certain level in order to prevent the permanent (hard) breakdown of the dielectric. The aim of the forming is to generate oxygen vacancies or conduction path, activating RS behaviour of the device. In tantalum oxide the main type of defects governing the leakage currents thorough the films are the oxygen vacancies, $V_{O}^{n+}$ [5] which are positively charged. During the forming the existing and the generated by the electrical stress through breaking weak Ta-O bonds O vacancies move towards the inert cathode (Pt), while the negative oxygen ions O$^{n-}$ drift towards the anode (TiN) where they are stored [7]. The generated vacancies and O ions are further used to switch the films resistance. As seen in figure 3 the voltage needed for the forming process is higher than corresponding SET voltage, $V_{SET}$, hence it is critical to limit $J$ during the process to avoid device destruction. The need of a forming to achieve RS suggests that despite decreased O$_2$ concentrations in the working ambient in respect to the one for stoichiometric Ta$_2$O$_5$, the amount of initially embedded $V_{O}^{n+}$ is not enough for visible resistance modulation, and Ta/O ratio of the dielectric layers obtained at the chosen conditions is probably close to the stoichiometric one. In case of layers obtained at 10 and 7% O$_2$ up to three forming cycles (see figure 3(b)) have to be performed to found RS effect. Note that for the samples prepared at 7% O$_2$ the maximum applied voltage for forming is lower than for the rest of the samples, indicating that probably the density of $V_{O}^{n+}$ is higher and/or the rupture of Ta-O bonds occurs at lower electric fields because the bonds are weaker. For the memristors fabricated at 10% and (5 to 10%) O$_2$ resistive switching is achieved at one and the same maximum forming voltage. This might be related to the fact that part of the film in the latter case is deposited at 10% O$_2$. Then higher initial $J$ of the samples
produced with O₂ variation (figure 2) could be explained by the smaller thickness of the layers part corresponding to 10% oxygen. The lower compliance level used for the 10% O₂ samples reflects the tendency for hard electric breakdown, i.e. irreversible loss of the insulating properties for these layers. The obtained $V_{SET}$ is between -1.1 and -1.9V. The lowest value (-1.1 V) correspond to the samples with gradient of the oxygen concentration and the highest to the structures deposited at 7% O₂. The transition from LRS to HRS occurs at about 2.5V and does not seem to depend on the TaOₓ deposition conditions.

**Figure 3.** $J$-$V$ characteristics of TaOₓ memristors with reactively sputtered TiN bottom electrodes, fabricated at a different O₂ content of the working ambient: (a) 10% O₂; (b) 7% O₂; and (c) variable from 5 to 10% O₂.

The resistance in high and low resistive state determined at 0.5 V as a function of the SET/RESET cycles of memristors with TaOₓ fabricated with variable oxygen concentration of the working ambient and reactively sputtered TiN bottom electrodes. R_HRS and R_LRS are the resistance at high and low resistive state, respectively.
The variation of $J$ between HRS and LRS (so called ON/OFF ratio) is an important parameter of the resistive switching memory devices. It was evaluated at 0.5 V for the first SET/RESET cycle. The lowest ON/OFF ratio (7.6) is obtained for the layers prepared at 10% O$_2$ and for the films deposited at 7 and 5-10% O$_2$ it is ~104 and 135, respectively. Although the RS has been observed for all types of Ta$_2$O$_5$ films the effect is not stable in case of 10 and 7% O$_2$. RS effect in the memristors with Ta$_2$O$_5$ deposited at 10 and 7% O$_2$ extinguishes after a few SET/RESET cycles, (figure 3(b) depicts J-V curves corresponding to first and second SET/RESET and 13th cycle clearly indicating that the difference between HRS and LRS diminishes for higher number of cycles). The most stable resitive switching is obtained for the films deposited with gradual change of the ambient oxygen content, as demonstrated in figure 4. The comparison of figures 3(c) and 5 reveals the dependence of the RS effect on the type of the bottom electrode. The difference in HRS and LRS for the structures with Ta$_2$O$_5$ deposited by magnetron sputtering of Ta target in pure Ar (figure 5(a)) is significantly lower than the corresponding one for reactively sputtered TiN (figure 3(c)). The ON/OFF ratio at 0.5 V is 4.8. In case of Ta bottom electrodes RS is hardly observed. Note that presented data are obtained without applying a forming process, and J-V curves in SET direction before the ON state represent the initial current of the structures which is ~6 orders of magnitude higher than the current for reactively sputtered TiN. Most likely, because of the preferential sputtering the deposition of TiN from TiN target in pure Ar atmosphere results in Ti-rich layer which can further react with the tantalum oxide layer and thereby increasing the oxygen vacancies (hence conductivity) to a level at which RS is difficult to be obtained. The same can be also applied to the case of Ta bottom electrodes, as a consequence Ta partial oxidation by O from the overlying Ta$_2$O$_5$ occurs.

In order to acquire some understanding on the nature of the RS effect we briefly discuss the conduction mechanism of memristors with Ta$_2$O$_5$ deposited at 10 and 7% O$_2$ with reactively sputtered TiN electrodes in negative $V$ region where SET operation occurs. Films obtained at variable O$_2$ are not considered as J-V curves were measured with applied compliance. For memristors produced at 10% O$_2$ the conduction in the low $V$ region ($V$< -1V) is Ohmic in both HRS and LRS (slope log$J$-log$V$ is close to 1.0), figure 6(a). At higher negative $V$, however, the conduction is governed by other mechanism (indicated by the change of the slope). The symmetry of the J-V curves in respect to 0V (figure 3(a)) suggests that it is bulk limited. The different slope of high voltage part of HRS and LRS curves generally infers either a change of the mechanism or modification of its parameters upon SET. Space charge limited current (SCLC) or Poole-Frenkel (PF) mechanism (inset of figure 6(a)) could be invoked in case of LRS. SCLC theory [8] predicts slopes of log$J$-log$V$ above 2.0 in case of traps with levels distributed into the band gap or deep traps lying below the Fermi level. In case of PF conduction the obtained (with a compensation factor of 2) refractive index, $n$ of the layers is ~5 which is higher than $n$ for Ta$_2$O$_5$ (2.2). The presence of non-oxidized Ta in the layer, however, increases $n$ and values as high as ~11 have been detected [9]. So, the data suggests that conductive filament between electrodes is probably not formed.
and the RS in these films is due to a modification of the defect states and/or increase of their density. For the layers obtained at 7% O$_2$ the conduction in HRS is also Ohmic at low negative $V$. At higher applied $V$ it can be attributed to either SCLC (Child’s law [9]) or PF effect (inset figure 6(b)). The obtained $n$ in case of PF mechanism is 9.3 which correlates with the expected higher non-stoichiometry. In LRS, however, $J$ has an almost Ohmic behaviour in the all voltage region, which is indicative for a formation of conductive filament through the film at the SET. Hence, the RS effect in the deposited at 7% O$_2$ films is most likely due to a creation and a rupture of a conductive filament.

Thus, the overall resistive switching mechanism in the investigated system could be described as follows. At negative applied voltage some positively charged oxygen vacancies are generated by breaking weak Ta-O bonds. The oxygen vacancies move to the Pt electrode where a vacancy rich region already exists as a result of forming process. The negative oxygen ions drift to the bottom electrode (TiN). When the applied voltage reaches a certain value ($V_{SET}$) there are enough vacancies to form a conductive path between the electrodes turning the memristor in LRS. The positive applied voltage causes the backward drift of oxygen ions to the Pt electrode. The oxygen ions interact with the vacancies reoxidizing Ta atoms. At $V_{RESET}$ part of the conductive filament is cut off and the structure returns in HRS.

4. Conclusion
The possibility to obtain resistive switching with an ON/OFF ratio above 100 in tantalum oxide films was demonstrated. It was found that resistive switching effect is very sensitive to the oxygen concentration of the dielectric. In order to achieve stable resistive switching substoichiometric tantalum oxides with carefully optimized Ta/O ratio have to be used. This is further supported by the conduction analysis indicating that lower oxygen concentrations facilitate the creation of an Ohmic conductive filament. The best results are obtained for layers with a varying along the thickness oxygen concentration from almost stoichiometric to oxygen depleted. The type of the used electrodes as well as the means of their deposition has a significant impact on the resistive switching.

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References
[1] Zhao C, Zhao C, Taylor S and Chalker P 2014 Materials 7 5117
[2] Pan F, Chen C, Wang Z, Yang Y, Yang J and Zeng F 2010 Prog. Nat. Sci.: Mater. Int. 20 1-15
[3] Lanza M 2014 Materials 7 2155-2182

Figure 6. Log$J$-Log$V$ plots of memristors with reactively sputtered TiN electrodes and TaO$_x$ deposited at: (a) 10% O$_2$; and (b) 7% O$_2$. Insets Poole-Frenkel plots of the $J$-$V$ curves at high negative $V$. 

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[1] Zhao C, Zhao C, Taylor S and Chalker P 2014 Materials 7 5117
[2] Pan F, Chen C, Wang Z, Yang Y, Yang J and Zeng F 2010 Prog. Nat. Sci.: Mater. Int. 20 1-15
[3] Lanza M 2014 Materials 7 2155-2182
[4] Paskaleva A, Hudec B, Jančovič P, Fröhlich K and Spassov D 2014 *Facta Universitatis: Electronics and Energetics* **27** 621

[5] Atanassova E and Paskaleva A 2007 *Microelectron. Reliab.* **47** 913-923

[6] Atanassova E, Dimitrova T and Koprinarova J 1995 *Appl. Surf. Sci* **94** 193-202

[7] Xu N, et al. 2008 *Appl. Phys. Lett.* **92** 232112

[8] Demiryont H, Sites J and Geib K 1985 *Appl. Opt.* **24** 490-495

[9] Kao K 2004 *Dielectric phenomena in solids* (San Diego: Elsevier Academic Press)