Metal and metal oxide nanoparticles for emerging memories

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We present prototype memory devices using metallic and metal oxide nanoparticles obtained by a physical deposition technique which will be described. The two memory device examples demonstrated concern the use of gold nanoparticles for flash-type memories with large memory windows and the use of titanium oxide nanoparticles for resistive electroforming free memories made at room temperature. Both approaches have a potential for 3-D integration and also reveal interesting nanoparticle properties associated with memory phenomena which will be discussed.

The use of metallic nanoparticles is first demonstrated for charge storage in flash type memory structures. In our flash-type memory structures metallic nanoparticles are embedded in a mixed gate stack structure with SiO_2 tunneling oxide and high-k HfO_2 control oxide. The motivation of this particular investigation is double: 1) mixed gate stack structure enhance the electric field in the tunneling oxide, thus lowering the operating voltages of the devices, and 2) the large variety of available metals (and thus work-functions) used to fabricate metallic nanoparticles allow to engineer the depth of the storage well to improve the programming and retention device characteristics. In this work it is demonstrated that the high-k control oxide can be fabricated using a low thermal budget process (T_{max} < 400°C) in order to avoid the diffusion of metallic atoms from the nanoparticle layer into the dielectrics [1]. Using such process, reference devices present negligible hysteresis while non-volatile memory devices with Au nanoparticles present large hysteresis of up to 8 V with low programming voltages (<10V) and long retention times. Representative TEM images, device structure used for testing and electrical results are shown in fig. 1-3. The physics that control np growth and charge per np will be discussed.

In another direction, non-volatile memories (NVMs) based on the electrically switchable resistance of materials located in between two-terminal electrodes, also called memristors and initially proposed by Chua, referred to as resistive random-access-memories (RRAMs or ReRAMs) have attracted considerable attention because of their potential application in crossbar resistive memories. RRAMs makes use of binary and ternary metal oxides in a metal-insulator-metal (MIM) device configuration where the low and high resistive states can be programmed by application of voltage pulses of same (unipolar switching) or opposite (bipolar switching) polarity to the metal electrodes. Here, we introduce MIM bipolar memristors using titanium oxide (TiO) NPs formed in vacuum by a physical process and deposited on metal electrodes at room temperature [2]. We demonstrate that application of an external electric field during NP deposition modulates the structural (fig 4) and electrical properties (fig.5) of the produced memristive films. The two terminal devices are electroforming free and operate at low voltages. We discuss then the operation of these devices through Grain boundaries formed in the nanoparticle layer that facilitates oxygen vacancy diffusion.

References

[1] E. Verreli et al 'Nickel nanoparticle size and density effects on non-volatile memory performance' J. Vac. Sci. Technol. B **31**, 032204 (2013)

[2] E. Verreli et al. 'Forming free resistive switching memories based on titanium oxide nanoparticles fabricated at room temperature' Appl. Phys. Lett. **102**, 022909 (2013)

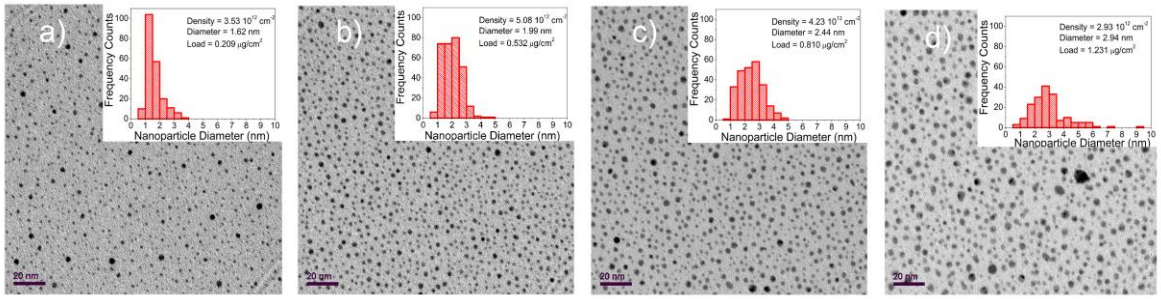

Fig.1 High density Au nanoparticles of small diameter (< 3nm) and high density (> 3. 10^{12} cm^{-2}) obtained using various process conditions. These conditions result in large memory windows that exceed 8v for 10 V programming voltages as shown in Fig.3.

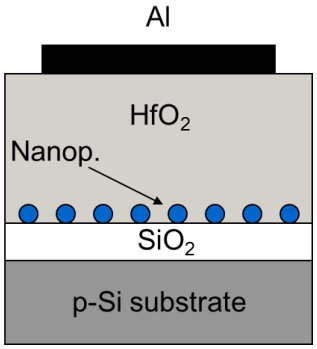

Fig. 2 Capacitors used for Electrical characterization

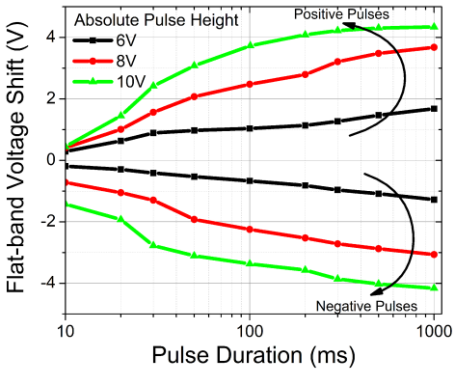

Fig.3 Representative electrical results of the device showing the large memory windows obtained

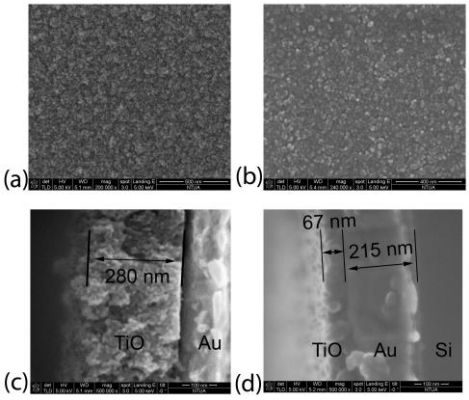

Fig. 4 a) SEM plan view image of as deposited titanium oxide nanoparticle film b) SEM plan view image of high-voltage titanium oxide nanoparticle film, larger grains are visible compared with case (a). Images c) and d) represent cross section SEM images of the as-deposited and high voltage samples respectively. Although the nominal thickness of the two NP films is the same (40 nm), the different fabrication conditions used produced films with different porosity and thus, physical thickness.

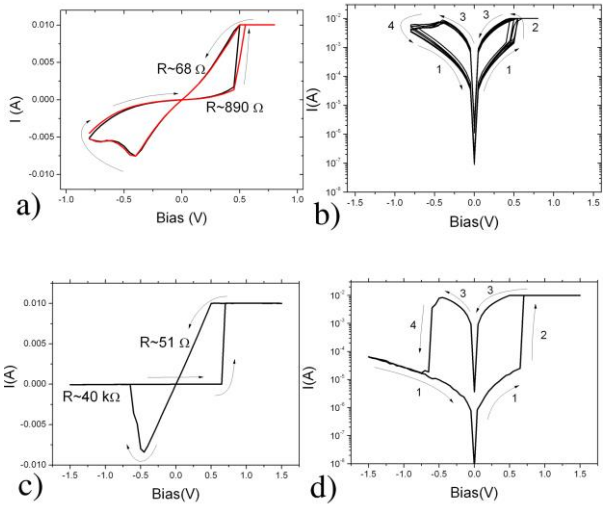

Fig. 5 Characterization of the as-deposited (a and b) and high-volltage samples (c and d). I-V forward and backward sweeps showing the continuous transition between the HRS (forward sweep) denoted with 1 and the LRS (backward sweep) denoted with 3. The set and reset regions are denoted with 2 and 4.