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Research paper

Tuning the switching behavior of conductive-bridge resistive memory by the modulation of the cation-supplier alloys

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ABSTRACT

Conductive bridge random access memory (CBRAM) represents a promising technology under consideration for future non-volatile memory. These devices rely on a reversible formation and dissolution of metallic filaments inside a dielectric that is sandwiched between two electrodes. The metal cations needed for the formation of the filament, are generally provided by one of the two electrodes whose chemical composition can affect the properties of the switching behavior. The impact of various layers acting as cations-supplier is investigated at the nanoscale by means of atomic force microscopy (AFM) in terms of filament's formation and stability for three different Cu-based electrodes. Three samples are investigated: pure Cu, C-doped $Cu_{0.6}Te_{0.4}$ and Cu_2GeTe_3. We show different effects on the conductive filaments when the Cu chemical composition approaches the 40 at.% in the material. In particular, the observed switching behavior ranges from non-volatile to volatile by reducing the fraction of Cu inside the cation supplier electrode. A simple method based on AFM is demonstrated for the comparison of the filament stability across different samples. The latter can be applicable for the rapid assessment of the non-volatility of a given material system. We observe the appearance of unstable filaments using Cu_2GeTe_3 that represents the material containing the lowest Cu fraction among those screened. Finally, the AFM-based analysis is linked to the electrical behavior of CBRAM stacks showing volatile or a non-volatile operations depending on the selection of the cations-supplier electrode. Our results indicate that the selection of such electrodes can lead to the direct tuning of the electrical properties of the generated filaments and thus to the overall resistive switching (RS) operation.

1. Introduction

Conductive bridge random access memory (CBRAM), often referred to as programmable metallization cells (PMC) or electrochemical memory (ECM) is attracting substantial interest for non-volatile storage application for the low operating voltages (<2 V), fast switching times (≈ns), high memory density and excellent scalability [1–3]. The mechanism of the resistive switching phenomenon in these devices has been identified as the formation and rupture of conductive filaments (CFs), which are related to ionic migration and nanoscale chemical reactions [4,5]. A basic CBRAM cell consists of an inert counter electrode, a switching layer and a cation supplier electrode often referred as the active electrode. A positive voltage applied to this latter element, activates the injection and migration of the cation species through the switching layer, resulting in the growth of the metal filament when the cations are reduced [6]. Particularly, the active electrode layer has the important role to provide the building blocks to the CF and for this reason it has been at the center of various studies [7–11]. For example, Jameson et al. [9] reported on the possibility to induce CFs containing Te to exploit the low 1-atom conductance of semiconductors compared to metals, and achieve a stable low current operations. Here we investigate the resistive switching as induced by conductive atomic force microscopy (C-AFM) in three different Cu-based cation supplier layers. The chemical composition of the three electrodes is modulated from Cu-rich to Cu-poor by changing the Cu at.% inside the alloy. The reduced dimension of the area probed by the C-AFM tip enables the understanding of effects which are important for the further scaling projection of this memory technology. The main advantage of this approach is the possibility to form and inspect the shape and size of scaled CFs after their formation [12]. The continuous read-out of the induced CFs by subsequent C-AFM scans enable also the direct observation of the filament stability in time. Finally, we relate the appearance of unstable switching events to the decrease of the metal cations supplied by the active electrode.

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2. Materials and methods

The three samples investigated in this work are reported in Fig. 1a. The progressive variation of the Cu-content in the active electrode is achieved by using different material systems: (1) pure Cu with a 3 nm-thick Ta layer, (2) C-doped $Cu_{0.6}Te_{0.4}$ and (3) Cu_2GeTe_3 [10,13]. To replicate a small memory cell the tip of the C-AFM is used as a scaled inert counter electrode [14]. The tip-sample system is schematically shown in Fig. 1b where a high resolution TEM image of the tip-apex and Cu/Al_2O_3 is shown in the inset. The switching layer is the same for all the samples, and is constituted of 3 nm-thick amorphous aluminum oxide deposited using a plasma enhanced atomic layer deposition technique (PE-ALD) at 45 °C, using O_2 plasma and Tri-Methyl Aluminum (TMA) precursor. In case of pure Cu (Fig. 1a) we insert a 3-nm thick Ta layer between the Cu layer and the Al_2O_3, in order to prevent the undesired in-diffusion of Cu causing the irreversible over injection of Cu. The intermediate Cu at.% is achieved by a carbon doped $Cu_{0.6}Te_{0.4}$ layer, deposited by a DC-magnetron sputtering [10]. This layer has shown superior performance and does not require any liner between active electrode and dielectric. Finally, the relatively low Cu composition is obtained by a Cu_2GeTe_3 layer, deposited by a DC-magnetron sputtering. During the C-AFM analysis, the sample is back-contacted and the bias is applied to the active electrode while the conductive tip is grounded [15]. The AFM system is a commercial D3100 equipped with a C-AFM sensor. We use our in-house fabricated full diamond tips [16].

3. Results

Fig.1c shows one switching cycle as induced on the $Cu/Ta/Al_2O_3$/tip-system. When the sample is positively biased the filament formation (set) triggers the low resistive state (LRS) and conversely the high resistive state (HRS) is restored during reset in the opposite polarity. In this configuration the tip-sample resistance provides the actual current limitation during the filament formation as reported elsewhere [12]. This generally leads to a low current compliance (≈10 μA) due to the relatively high tip resistance offered by our diamond tips. For a direct comparison among the samples, multiple switching cycles are recorded and compared for each of the three materials. Fig. 2a shows the comparison of three reset curves for the three samples. The reset current shows a decrease as the Cu at.% is reduced. The latter is reported for a population of 20 CFs in Fig. 2b where a net trend is observed for the reset current. Consistently, in Fig. 2c also the reset voltage shows a clear dependence with the Cu-content in the active electrode. In this case, a shift toward lower values of the reset voltage is observed as the Cu is reduced. In other words, since the Cu^{n+} represent the building blocks of the CF as the availability of Cu is decreased the resulting CFs are weaker and require less current for their rupture. This trend confirms the previous experimental observations in integrated devices and potentially can represent an option to reduce the power dissipation of the switching event by reducing the switching current [2,17]. In the case of Cu_2GeTe_3 we observe very small values for the reset current (≈tens of nA) and the reset voltage (≈200 mV). Despite the small required switching power, these properties can represent a serious limitation for non-volatile application as the CFs will likely spontaneously dissolve. Not surprisingly this reflects also in a strong rectifying behavior of the I–V characteristics recorded for this material as discussed later.

Leveraging the capability of the C-AFM to directly probe the CFs after their formation, we design a simple experiment for the assessment of the CF stability. The CF is first created, and subsequently stressed by continuous AFM scans at a fixed read-out bias. During these scans the tip is positively biased (100 mV) thereby combining on each passage on the CF a read-out and the application of a single reset pulse. The latter has to be considered as applied on every single passage of the tip onto the CF, therefore the number of pulses delivered will depend on the number of AFM scan-lines crossing the CF area. In this way, we can count the number of pulses required to change the shape and conductivity of a given CF. It has to be noted that this procedure does not reflect directly a retention test done on a fully fabricated device, in particular due to different stress condition of the CF which in this case is exposed to air and not enclosed inside a cell. However, the direct relationship between the structural stability over time of the CF and the device's data retention allows a qualitative benchmark of different materials. Fig. 2d shows an example of such experiment on a standard Cu/Al_2O_3 blanket sample. After the CF is created (not shown), the AFM tip is scanned over the area biased with 100 mV (Cu negatively biased). Each time the tip passes on

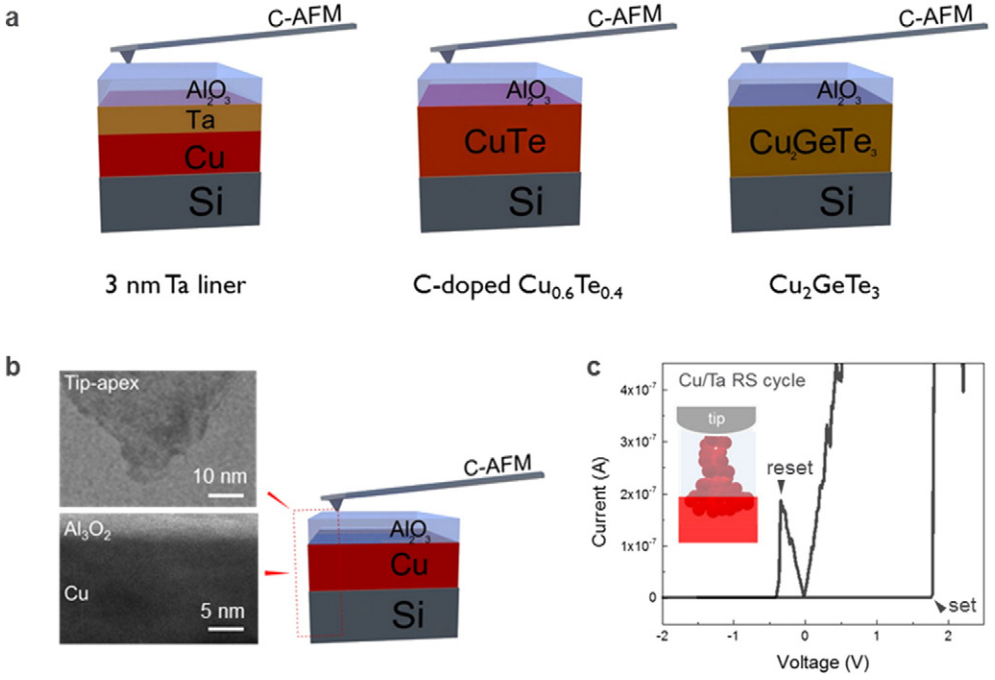

Fig. 1. (a) Schematic of the three samples investigated in the work. The fraction of Cu at.% in the active electrode is modulated from high to low, respectively using pure Cu capped with 3 nm Ta layer, C-doped $Cu_{0.6}Te_{0.4}$ and Cu_2GeTe_3. (b) Schematic and TEM images of the tip-sample system. (c) Tip-induced I–V characteristic measured for a $Cu/Ta/Al_2O_3$/tip-device.