

Alloyed electrodes for enhanced memristive performance

Iliia Valov and Yuchao Yang

Simultaneous electrodeposition of metals facilitates the realization of memristive devices with high yield and improved reliability.

Nanoionic memristive devices are one of the most promising building blocks for next generation hardware architectures for cognitive type data processing. These highly scalable, low power, fast operating units, offer a broad spectrum of functionalities at various operation conditions. This makes them ideal for direct applications such as sensors, selectors, short and long-term memories and more complex systems such as internet of things (IoT) and artificial intelligence (AI). Significant progress has been achieved implementing memristive devices in circuits for neuromorphic computing, demonstrating capabilities of pattern classification¹, signal/image processing², context-dependent network formation³, recognition of spatiotemporal patterns⁴ etc. However, despite this highly encouraging progress the full potential of the memristive technologies is yet to be reached. Main advantage of the nanoionic memristive devices compared to classical semiconductor technologies is their operation principle, relying on redox-reactions and transport of ions/atoms instead of electrons. This fact has been mostly underestimated during the race for fast integration and product developments, and fewer efforts have been dedicated to material design through a thorough understanding of the underlying physical processes.

In contrast to electrons, fundamental properties and behaviour of ions and atoms within a solid electrolyte matrix such as their activity, bond strength, activation energy, size, mass and oxidation state vary, depending on the chemical element used. For example, the half-cell redox reactions Ag/Ag^+ , Cu/Cu^+ , Cu/Cu^{2+} and $\text{Cu}^+/\text{Cu}^{2+}$ have different standard electrode potentials (activation energies) and polarizability. This is used in the classical electrochemistry not only as a criteria to select appropriate metal electrodes, but also to deposit materials with new properties such as alloys (Cu-Ag, bronze (Cu-Sn), brass (Cu-Zn) etc.)⁵, or using metal alloys to electrochemically form composite oxides⁶. Moreover, ions including Ag^+ , Cu^+ and Cu^{2+} have different mobility within e.g. SiO_2 films due to different bond strengths they form with the oxide matrix⁷. Thus, filament properties can be tuned by electrochemical alloying.

Different metal electrodes, i.e. Ag, Cu, Ni, Au, Fe, Ti, Zr, V, Al and Ta as well as alloys, for example CuTe and CuGeTe have been studied in terms of electrochemical reactions⁸ and as improved supply for active metal ions⁹ in memristive cells. However, using alloys where both components are redox-active and mobile may bring significant advantages in electrode materials design.

Writing in Nature Nanotechnology H. Yeon and colleagues¹⁰ now demonstrate the power of using alloyed electrodes to significantly improve performance and reliability of memristive devices based on electrochemical metallization effect and to increase their yield to 100%.

The authors use as switching matrix 6 nm thin film of amorphous Si with pre-formed conduction channels. In this work, Ag alloyed with Cu, Ni, Cr and Ti have been tested as active electrodes. The criteria for selecting alloying elements are based on fundamental requirements accounting for the redox reaction rate, mobility (and the related bond strength) of the ions within the a-Si, and the miscibility of the metal components i.e. whether they form a solid solution or not. This approach allows to extract more general rules for a suitable composition of the active electrode material.

The authors found that 1) the ions of alloying components should have comparable or higher mobility compared to Ag in order to form the backbone interacting with Si, possibly, before Ag-ions have arrived

there. 2) The alloying metals must form solid solution with Ag. In this way, Ag atoms in the filament are stabilized in Si-channel, diminishing its reactivity and mobility. 3) The amount of the alloying component should be small enough to preserve the dominance of Ag switching properties. Details on the operation principle of the alloyed memristors are provided in Figure 1.

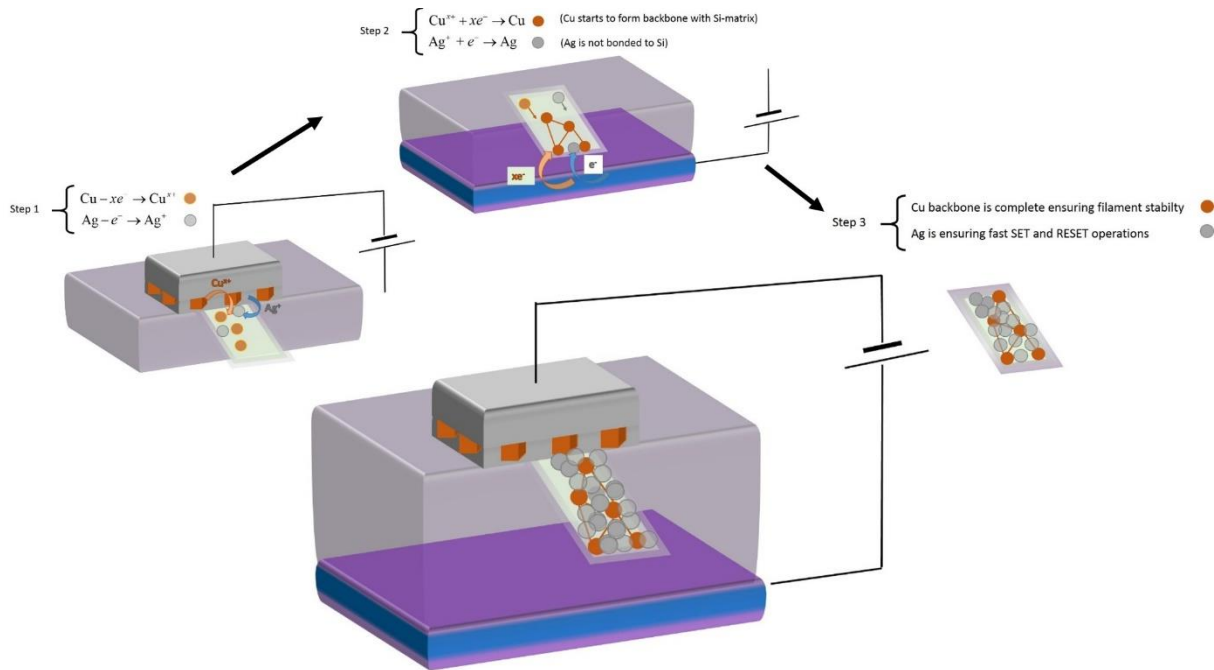


Figure 1. Alloyed memristors mechanism. **Step 1)** At the active electrode Cu and Ag are anodically dissolved and diffuse within the channel. Cu-ions move faster compared to Ag-ions. **Step 2)** At the bottom electrode Ag-Cu filament begins to grow following the electrochemical reduction. First, Cu-atoms start to form backbone binding to the Si-matrix. Ag-atoms are slower and not bonded to Si. **Step 3)** Complete alloyed Ag-Cu filament is formed during the SET process. Bonded Cu ions are now slower and Ag-component is ensuring fast SET/RESET operation, whereas Cu-backbone is responsible for the stability of the filament. Alloyed filaments improve the yield and entire device performance.

The analog switching performance is tested on 32x32 transistorless arrays. Using a 256-level greyscale image, superior weight storing capability of Ag-Cu-based devices at low programming current was acknowledged. Further, the authors have tested the capabilities of Ag-Cu arrays by programming convolution kernels into them, performing image-processing tasks. Due to the enhanced retention, faithful image processing was demonstrated for sharpen, box blur, vertical and horizontal edge detection, highlighting the effectiveness of the alloying approach for superior device performance.

The significantly improved device performance is certainly promising and suggests that this approach could be applied to other memristive systems and extended to reach new features. For example, using alloyed compositions with two, three or even more elements could allow tailoring the filament behaviour with different electrodes and changing its mechanical, physical and chemical properties, such as density, microstructure, melting temperature, absorption of oxygen or other species, corrosion resistance etc. To this end, alloying may minimize the absorption and mobility of protons as a disturbing factor. These advantages of alloyed electrodes offer the chance of programming desired functionalities, adapting it to particular applications. However, the highly attractive concept of functionalities on demand can meet several challenges.

Most of the typically used switching films are binary, ternary or quaternary compounds such as Ta₂O₅, SiO₂, SrTiO₃, etc. where the interactions between the ions/atoms of the active electrode/filament and the solid electrolyte matrix are complex and influence the defect-chemical and electronic properties not only of the conducting channel but also of the whole matrix. Thus, finding an alloy composition fulfilling all requirements for compound layers and predicting/controlling all reactions and effects may be difficult. Further, the harsh conditions during devices operation, characterised by high electric fields in the range of 10⁸ V m⁻¹ and current densities of about 1 MA cm⁻² may lead to phase instabilities, dealloying and finally, degradation. Another issue is the translation of the macroscopic definition for solid solution to nanometer scale devices (in both lateral and vertical direction), where the number of atoms constituting the conducting filament may drop below 50.

Another important question is whether other widely used types of memristive devices such as valence change memories or thermochemical memories can be improved using this approach. Finally, the role of the counter electrode material and reaction polarizability should be studied in more detail as it may play important role during the formation of the alloyed conduction channels. Nevertheless, the design strategy proposed in this work is an important step forward toward the rational design of materials properties for high performance nanoionic memristive devices.

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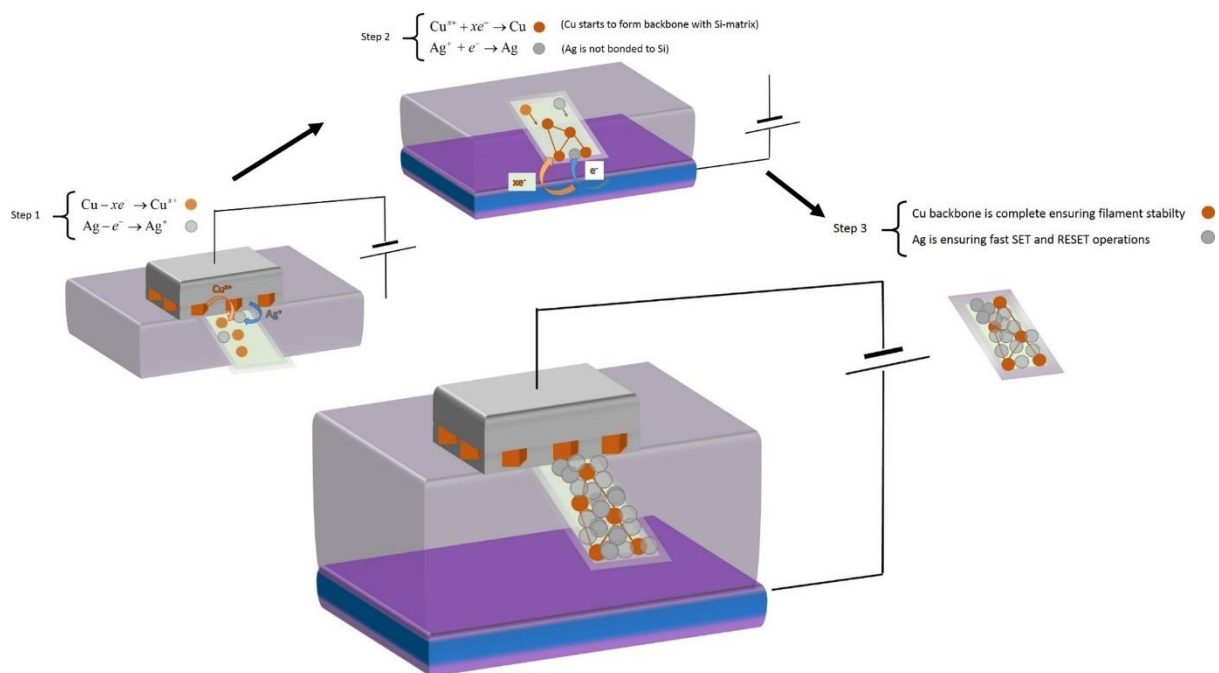


Figure 1. Alloyed memristors mechanism. **Step 1)** At the active electrode Cu and Ag are anodically dissolved and diffuse along the channel. Cu-ions move faster compared to Ag-ions. **Step 2)** At the bottom electrode Ag-Cu filament begins to grow following the electrochemical reduction. First, Cu-atoms start to form backbone binding to the Si-matrix. Ag-atoms are slower and not bonded to Si. **Step 3)** Complete alloyed Ag-Cu filament is formed during the SET process. Bonded Cu ions are now slower and Ag-component is ensuring fast SET/RESET operation, whereas Cu-backbone is responsible for the stability of the filament. Alloyed filaments improve the yield and entire device performance.