Hydrothermally grown copper oxide thin films for memory applications

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INTRODUCTION

Cupric oxide is a p-type semiconductor with a direct and narrow band gap in the range of 1.2 – 2.1 eV. It is considered as a suitable material for applications in various fields, eg. in photovoltaics, lithium-ion batteries as well as memory devices.

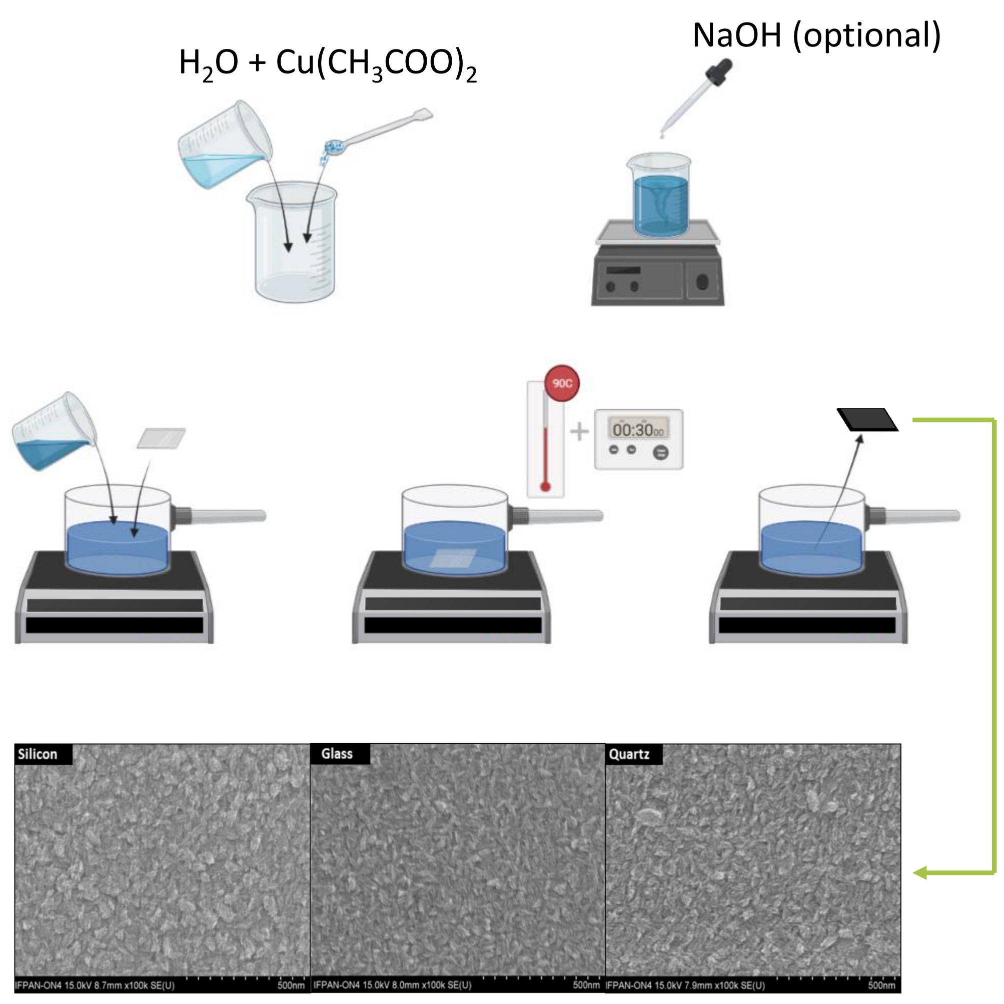
We developed a new growth technology of CuO thin films from aqueous solution. Comprehensive investigation on material properties was carried out [1]. The results forced further work on the technology, consisting of sequencing the growth processes and rapid thermal annealing. Electrical measurements of so-prepared CuO thin films showed the occurrence of switching and memristive effects, what makes our material suitable for potential applications in memory devices.

GROWTH TECHNOLOGY

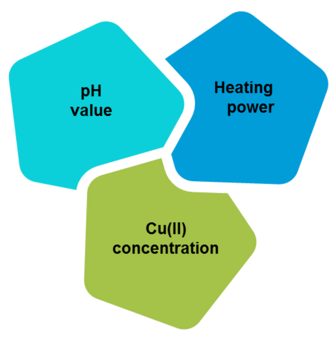
A new, extremely fast and simple technology for the growth of CuO thin films from an aqueous solution was developed (patent application P.429066). The process takes place in an open system (in a pot), and the mixture is uniformly heated using an induction cooker. The growth process consists of 3 key steps: (1) preparation of the reaction mixture, (2) nucleation of the substrate using Au nanoislands, (3) heating the mixture with the substrate inside. Single process lasts from ~30 s up to 6 minutes and growth is possible on different substrates. Based on speciation diagram [2] the Cu fraction responsible for growth is $Cu(OH)^{+}$. We propose growth mechanism that can be described by following reactions:

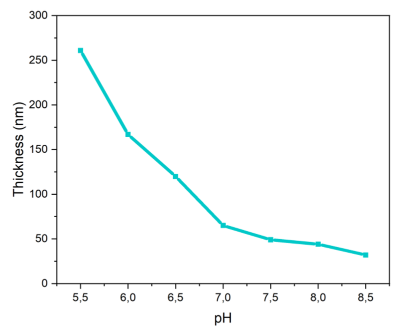
$$Cu(CH_3COO)_2 + H_2O \longrightarrow \boldsymbol{Cu(OH)^{+}} + CH_3COO^{-} + CH_3COOH$$

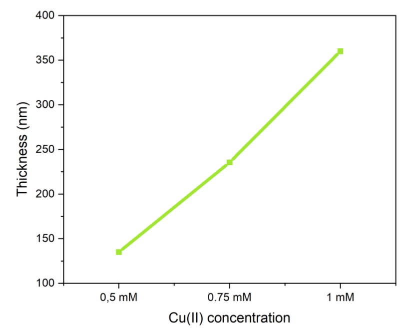
$$Cu(OH)^{+} + CH_3COO^{-} \xrightarrow{temp.} \boldsymbol{CuO} + CH_3COOH$$

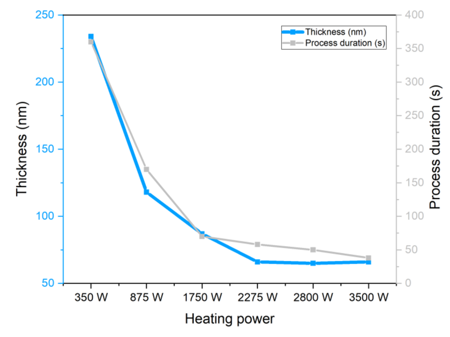


The method allows to control the thickness of the films by modifying the values of the mixture parameters as shown below:

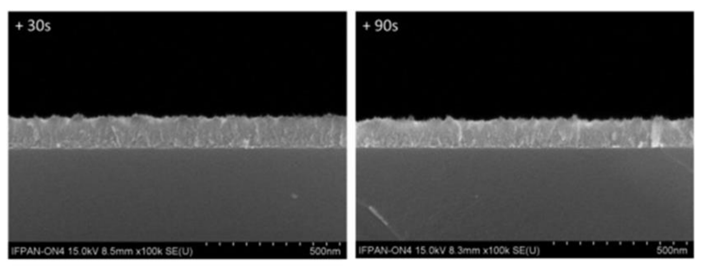








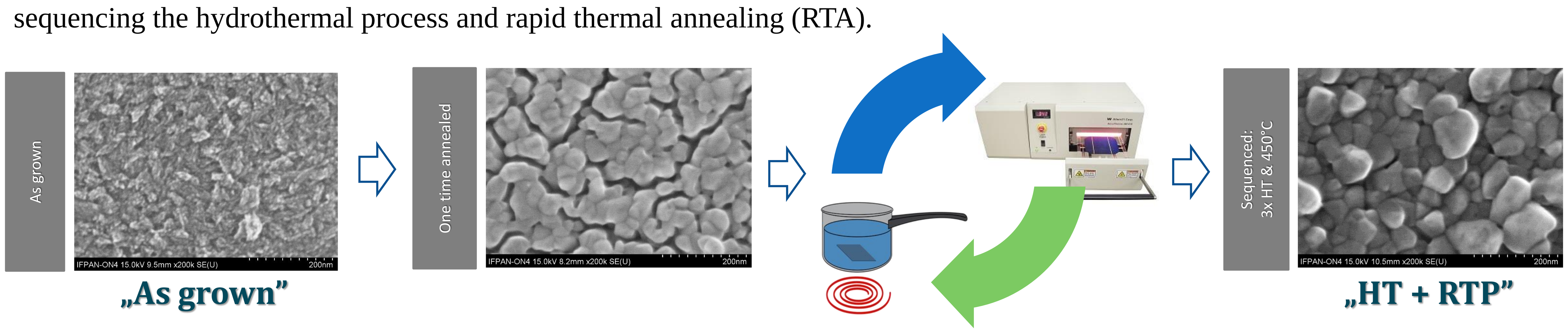
No effect of process duration



Detailed description of growth method can be found in [1].

SEQUENCING HT PROCESSES & RTA

Recently, we have focused on the problem of crack appearance during the SEM observations. According to our thesis it is related to the presence of built-in organics. The natural way to dispose of the organic compounds from the layer is annealing, but it also causes the crack of the layers. Subsequent works concern on obtaining continuous, organics-free and cracks-free CuO films by sequencing the hydrothermal process and rapid thermal annealing (RTA).

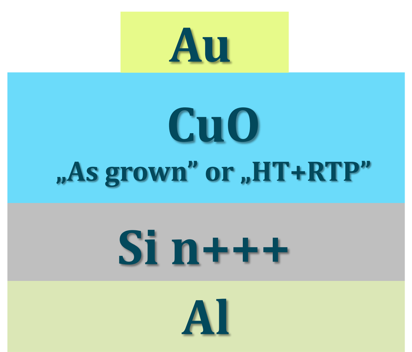


MEMRISTIVE EFFECT

The representative I-V characteristics of the investigated structures are depicted below. After the 'forming' procedure, the voltage loop starts at a positive voltage value, crosses the 0 V, and traces towards negative voltage values. The devices are then switched from LRS to a high-resistant state (HRS), and the current sweeps back up to the maximum positive voltage value. The data presented distinctly show I-V traces' superior stability and repeatability over time, especially in the case of MIM devices with 'HT+RTP' CuO films. The HRS/LRS ratio is about one order of magnitude measured at ± 1 V, proving the possibility of low voltage applications of fabricated devices.

We also present the comparison of set/reset states retention of MIM devices. The resistance (R) values were calculated using I-V characteristics measured at ± 1 V. The I-V curves were measured in a limited range of Vg after a particular time to limit the undesirable switch of the device to the other state. In the case of MIM devices with a 'HT+RTP' material, the approximation of achieved resistance values up to ten years revealed good stability confirmed by the HRS/LRS ratio ~10. However, it must be considered that measurements were performed at room temperature and demonstrated a noticeable drift of the R values. Full information concerning measurements and technology can be found in [3].

MIM structures



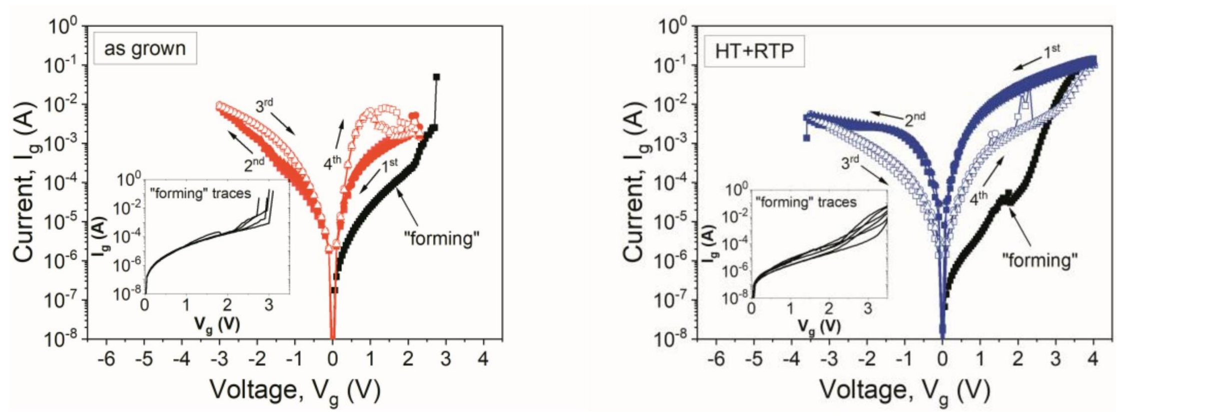


Fig. Comparison of resistive switching I-V curves of investigated in this work MIM devices after ten duty cycles; insets show the family of "forming" traces.

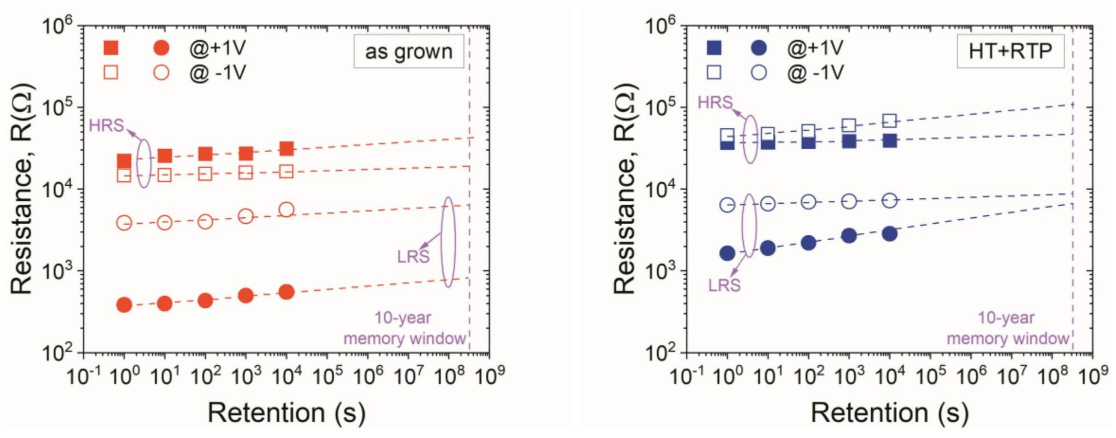


Fig. Retention characteristics of studied in this work RRAM structures with CuO thin films; resistance values were taken at ± 1 V.

CONCLUSIONS

In summary, the feasibility of applying hydrothermally formed CuO thin films in MIM structures was demonstrated. Structural and optical investigations of fabricated materials have shown distinct differences in chemical compositions of 'as grown' and thermally annealed CuO, i.e., 'HT + RTP' film. These differences strongly influence the electrical behavior of fabricated MIM structures. It was shown that fabricated devices with 'HT + RTP' layers are characterized by the improved stability and repeatability of RS characteristics compared to 'as grown' layers and good retention of LRS/HRS states. Moreover, the obtained memory window of MIM structure with 'HT + RTP' layer revealed the good stability confirmed by the HRS/LRS ratio ~ 10 approximately to ten years. However, these are the preliminary results revealed without any examinations of electrical performance at elevated temperatures. Thus, the presented findings have shown the potential application of CuO technology employed in MIM structures for RRAM devices but after further research and technology development.

References

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