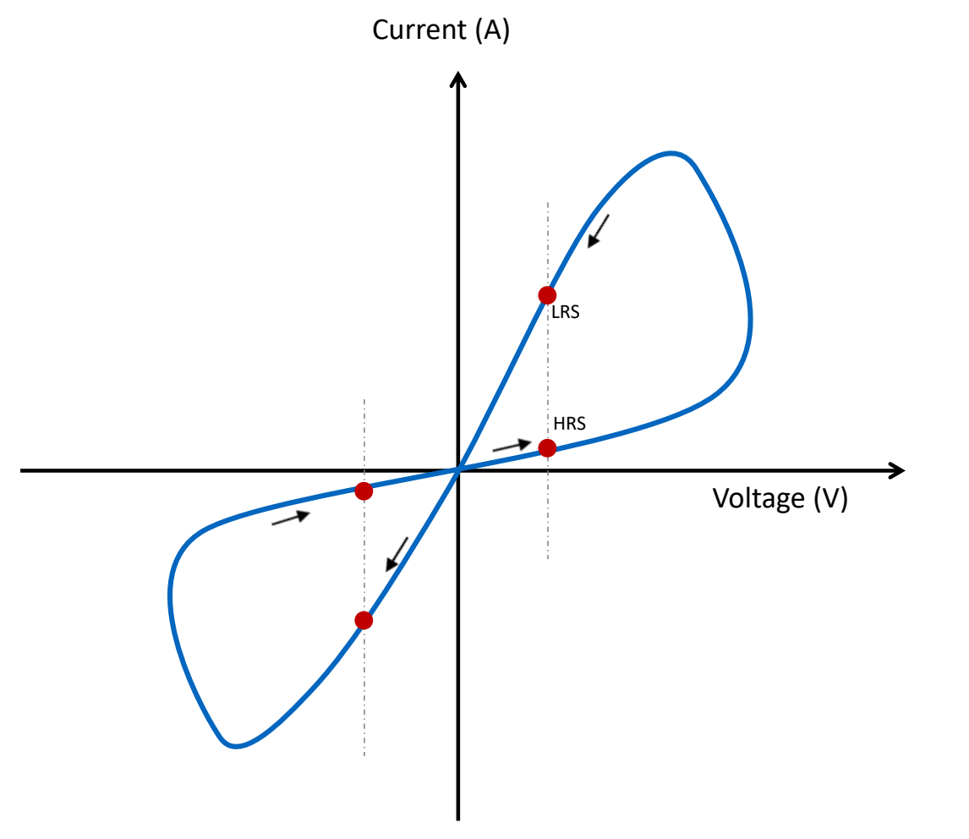
Studies on memristor effects in CuO layers grown by hydrothermal method

Monika Ozga[1], Robert Mroczynski[2], Marek Godlewski[1], Bartlomiej S. Witkowski[1]

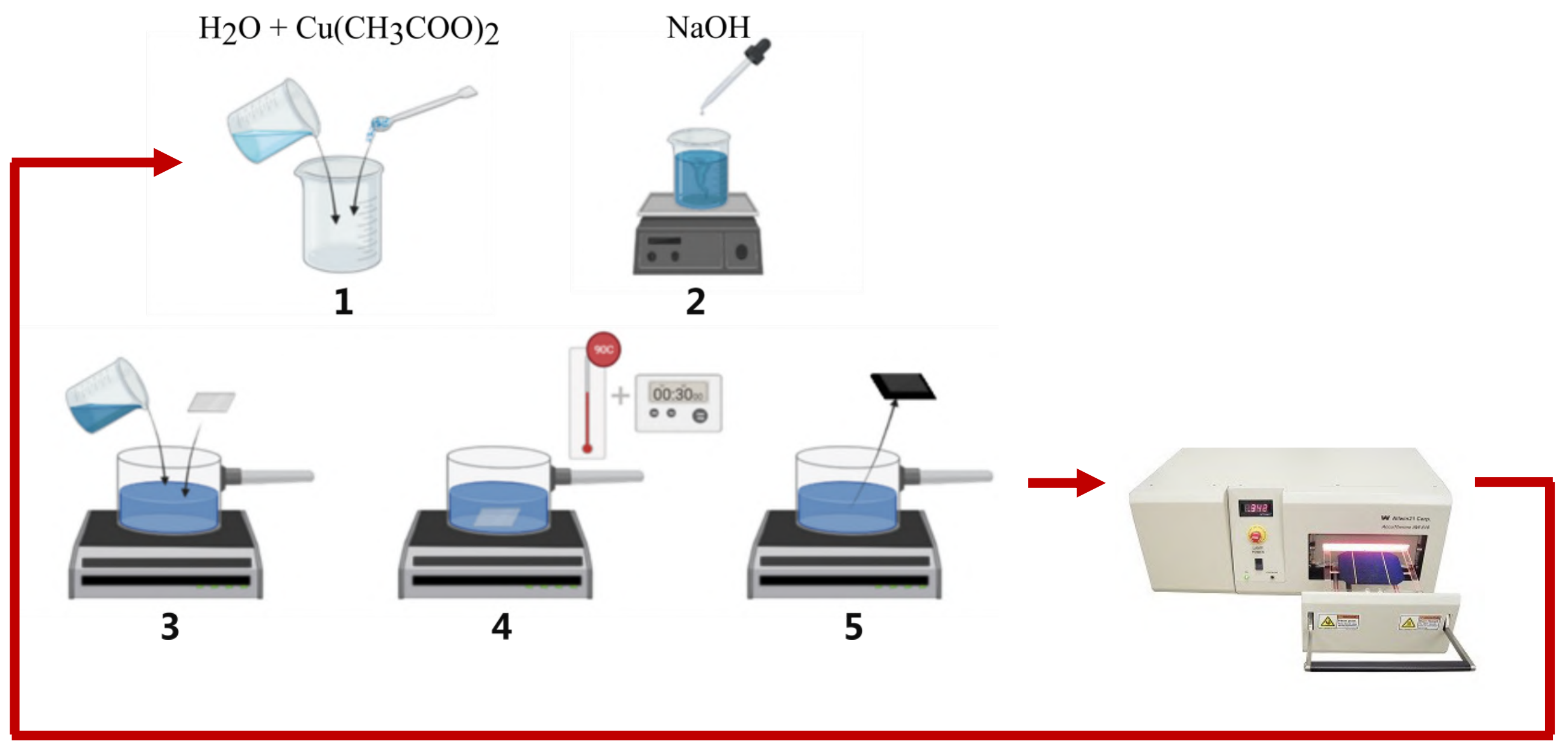
[1] Institute of Physics of the Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warsaw, Poland
[2] Warsaw University of Technology, Institute of Microelectronics and Optoelectronics, Koszykowa 75, 00-662 Warsaw, Poland

INTRODUCTION

Our growth technology enables the rapid development of CuO thin films under mild conditions from aqueous solution. Among its many interesting properties, CuO films grown hydrothermally exhibit the memristor effect, allowing for the switching between two resistance states using electrical impulses. This characteristic positions CuO as an excellent candidate for Resistive Random Access Memory (RRAM) applications. RRAM, an emerging technology, boasts numerous advantages, including high endurance, rapid switching speed, simple structure, scalability, and compatibility with standard CMOS technology. On this basis, RRAM is considered one of the technologies that may revolutionize the digital memory market in the future.



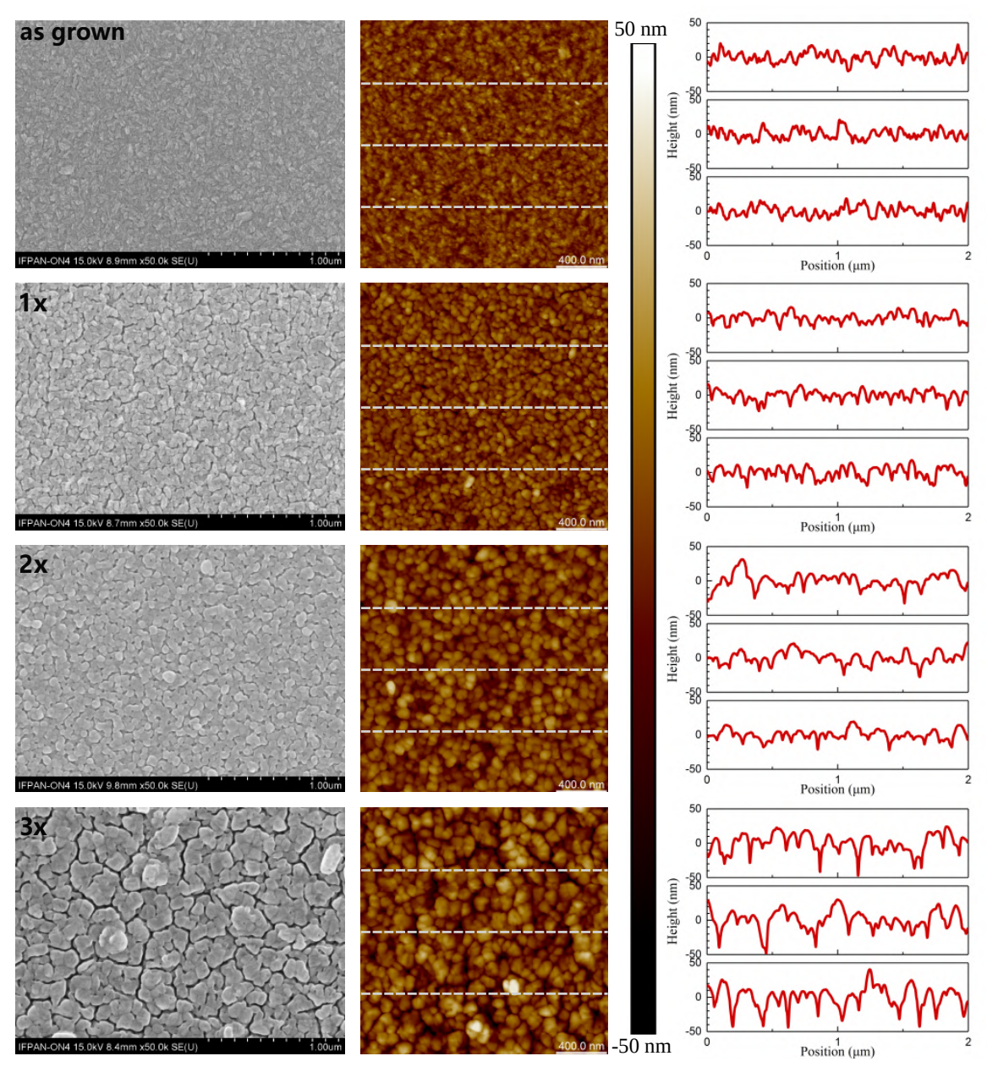
GROWTH TECHNOLOGY



CuO layers are produced hydrothermally, utilizing an innovative approach that allows for ultra-fast growth in mild conditions and within an open system. This approach involves two key steps. Firstly, the reaction mixture is prepared. It comprises water and copper acetate and optionally NaOH for pH adjustment. Subsequently, the so-prepared solution is placed in the reaction vessel along with the substrate and uniformly heated via induction. A single growth process lasts from ~50 seconds up 6 minutes and the temperature does not exceed 100°C.

Recent investigations have revealed that the as grown films are contaminated by carbon compounds originating from the copper precursors. It makes them susceptible to cracking under the influence of temperature, due to the release of trapped between grains impurities. To address this challenge, the HT+RTA procedure, involving cyclic repetition of growth processes and rapid thermal treatment (450°C, 5 min, O_2/N_2 atmosphere), was implemented, resulting in enhanced layer quality and stability.

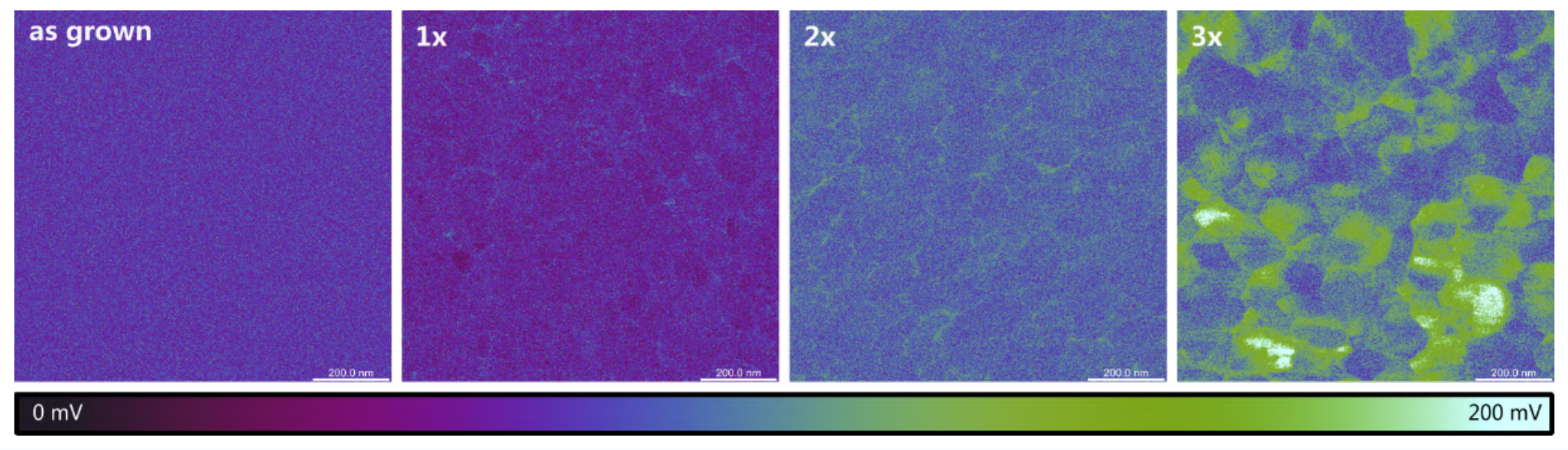
MATERIAL PROPERTIES



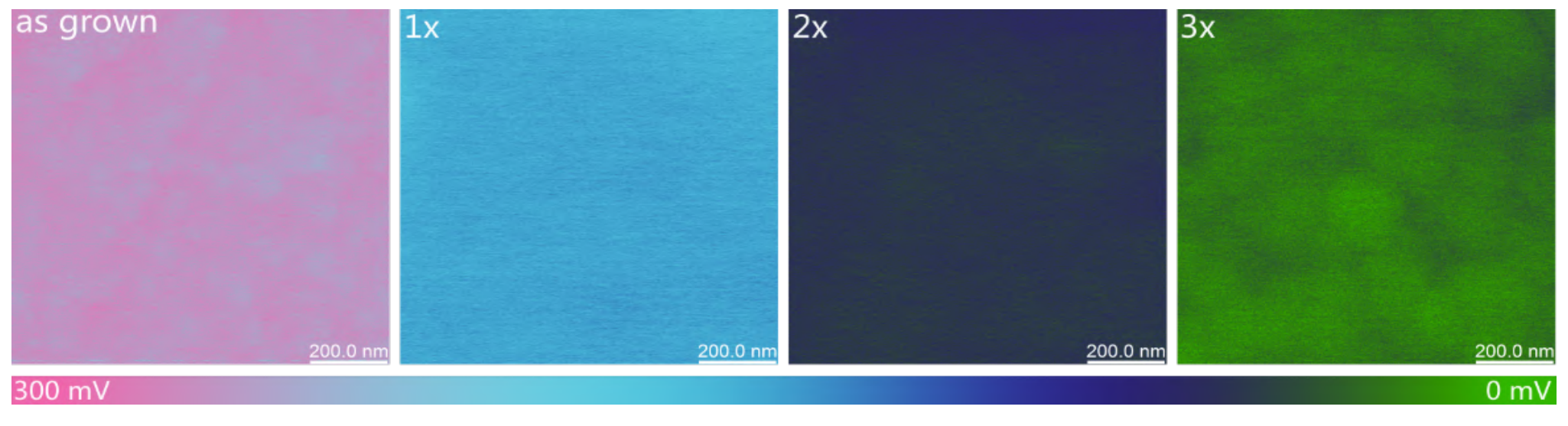
Sequential hydrothermal growth followed by rapid thermal annealing enhances CuO thin film properties.

- ‣Careful parameter selection yields crack-resistant continuous layers
- ‣Elemental analysis shows a significant reduction in carbon compounds with repeated HT+RTA cycles
- ‣HT+RTA procedure does not result in the formation of foreign phases (e.g. Cu_2O)
- ‣SCM demonstrates uniform carrier distribution, with notable changes after three cycles
- ‣KPFM detects surface potential alterations, impacting work function

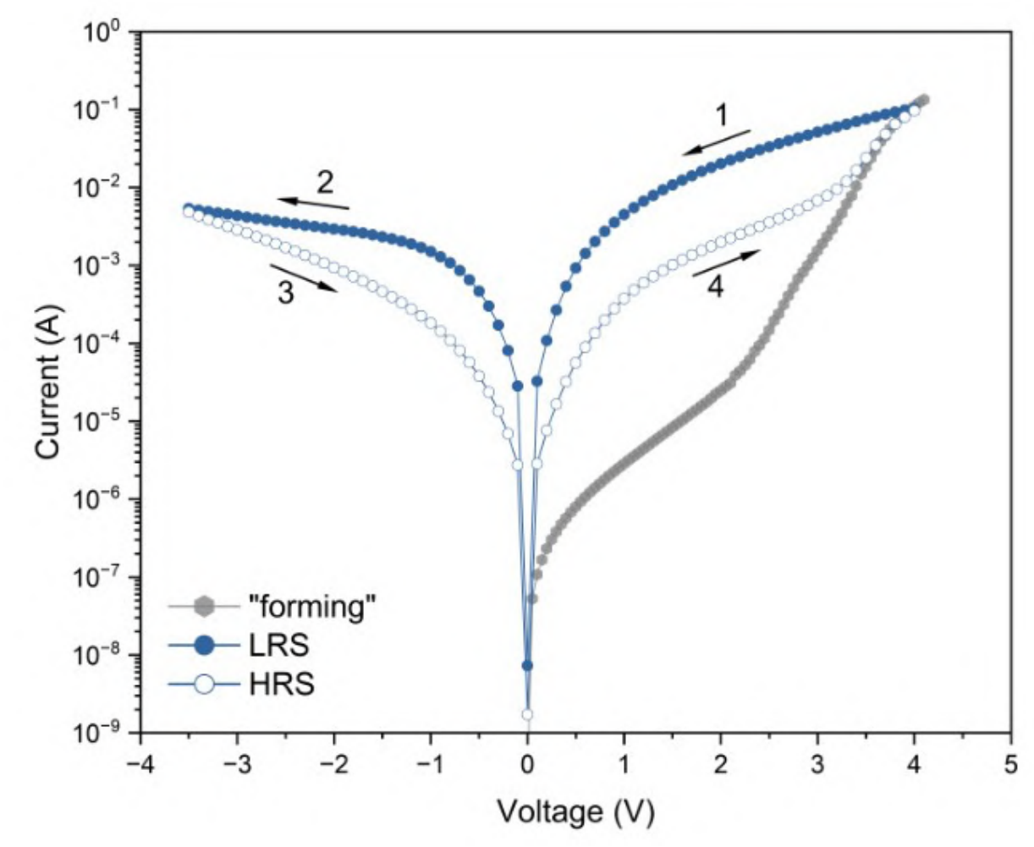
SCM:

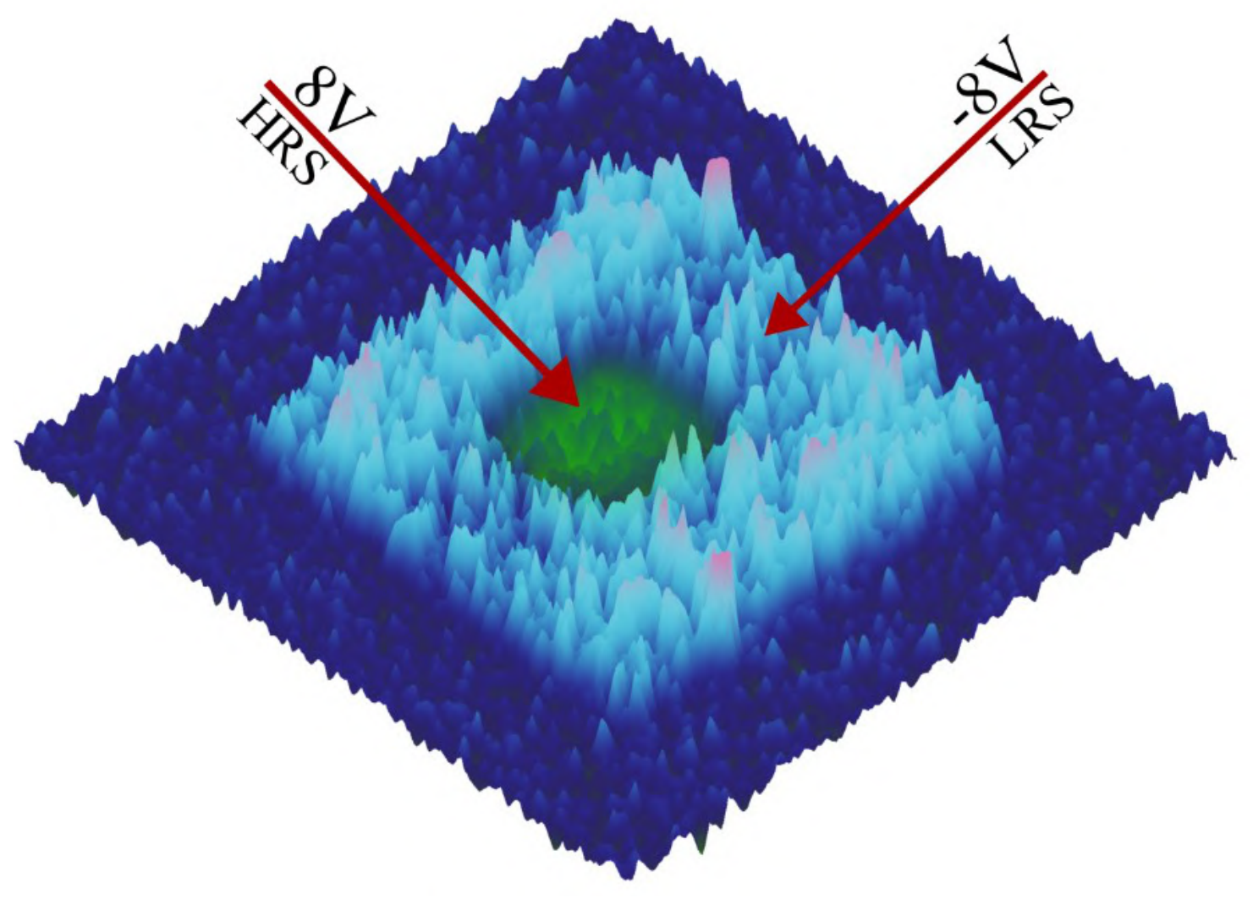


KPFM:



MEMRISTOR EFFECT

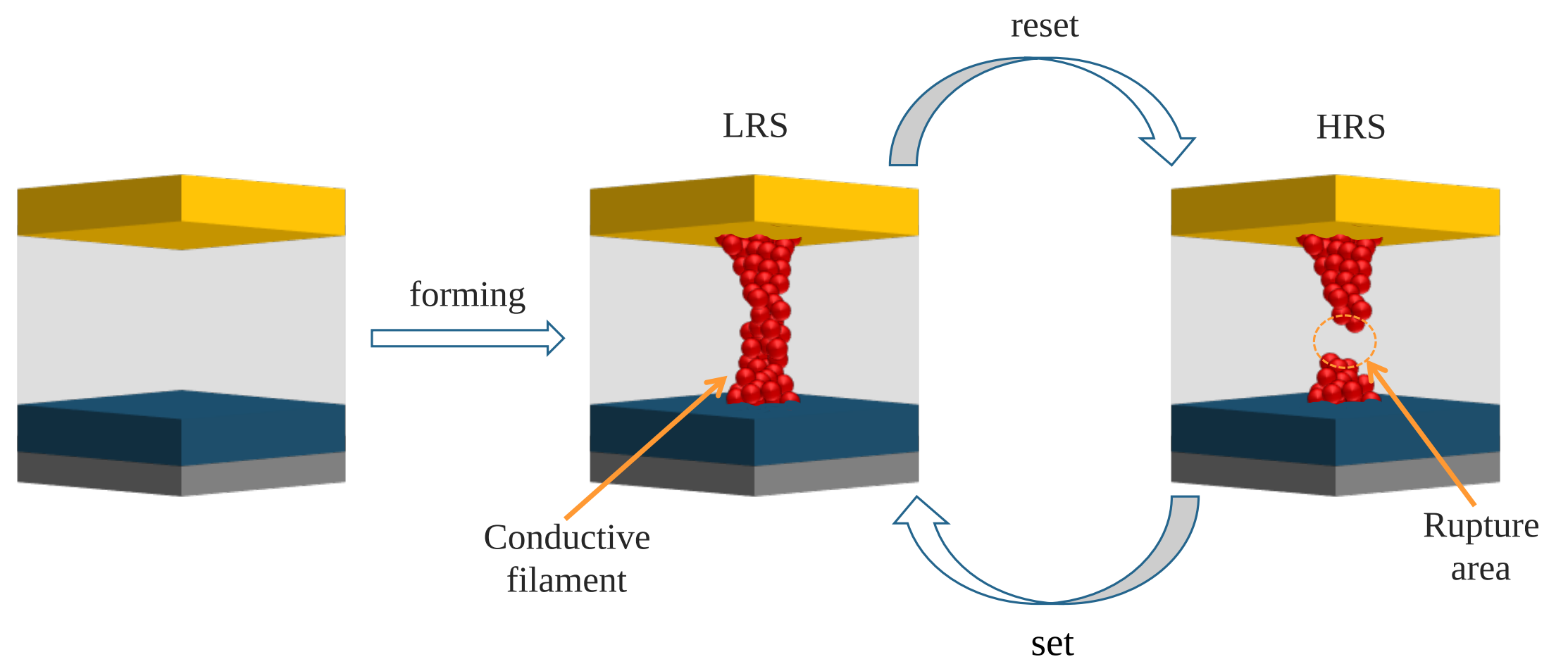




The I-V characteristics, measured through a sequence of steps: 0V ⟶ 4V⟶ -3.5V ⟶ 4V exhibited a pinched hysteresis loop. It implies that the CuO-based MIM structure operates as a bipolar memristor system. The potential application of such structures in RRAM was demonstrated using tunneling AFM (TUNA). The current map allows distinguish between the unwritten region and the areas where data was recorded (LRS and HRS).

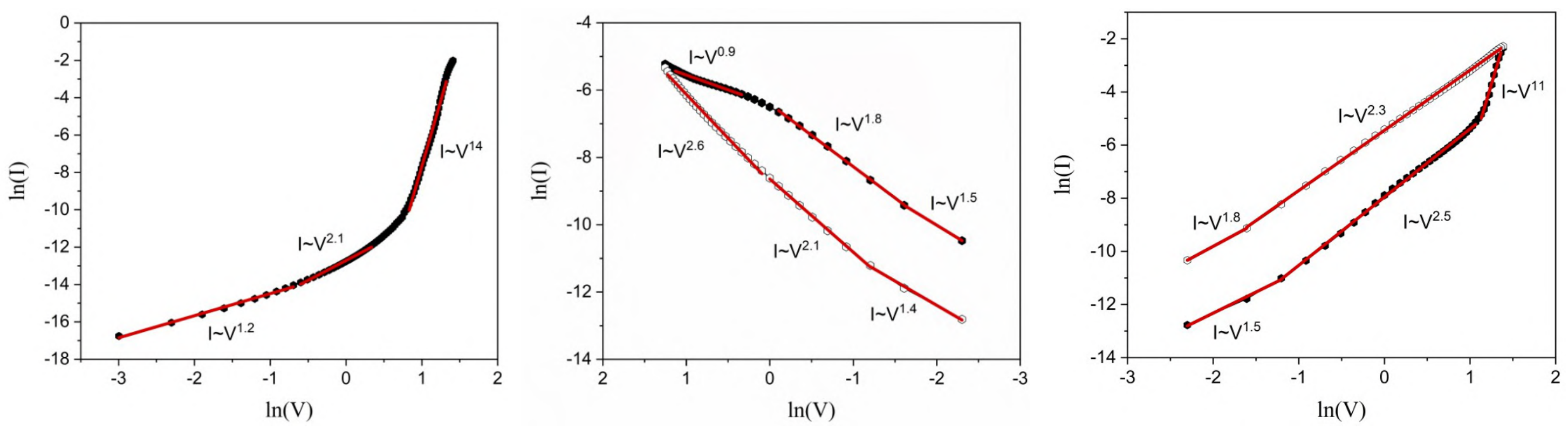
RESISTIVE SWITCHING MECHANISMS

The analysis of resistive switching (RS) and conductivity mechanisms is of fundamental importance for the application potential of memristors based on CuO layers. Understanding them will allow for optimal design of memory structures, which will result in increasing their efficiency and reliability. Despite significant progress and successful demonstrations of RRAM technology, the physics of resistive switching is not fully understood and remains the subject of intensive research.



The findings from the TUNA analysis suggest that the resistive switching mechanism in the examined structures relies on the forming and disruption of a conductive filament (CF) within the CuO layer under the influence of the applied voltage. First, the structure is initiated, i.e. CF is forming as voltage increases. Subsequently, by applying the appropriate voltage (V_{set}/V_{reset}), the pathway can be locally disrupted and reconstructed multiple times, resulting in alterations in the resistance state.

The primary conduction mechanism in the examined structures was verified by comparing experimental data with model slope values and linear fits in coordinate systems representing individual mechanisms. Based on this analysis, space charge limited current (SCLC) was identified as the predominant mechanism. Discrepancies from the model values result from the simultaneous occurrence of other mechanisms within specific voltage ranges, such as Poole-Frenkel emission and hopping conduction.



$I{\sim}V^{m=1}$	Flow of carriers present in the material in the low voltages
$I{\sim}V^{m=2}$	As the electric field increases, the role of the injected carriers increases
$I{\sim}V^{m\gg 2}$	The current completely depends on the injected carriers

CONCLUSIONS

We have developed an innovative method to produce high-quality and stable CuO films exhibiting the memristor effect, making them suitable for RRAM devices. Our focus on understanding the physics of memristors has led to the successful identification of the formation and disruption of conductive filaments as the mechanism of resistive switching. Additionally, we have determined that space-charge-limited current (SCLC) is the predominant conduction mechanism in CuO-based structures. Moving forward, our research will continue to explore the composition of CF and further investigate the co-existing conduction mechanisms to advance our understanding of memristor behavior.

Narodowe Centrum Nauki This research was partially funded by National Science Centre, Poland under research project np. 2022/45/N/ST5/02535