Memristive effect in CuO thin films grown by hydrothermal method

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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 gas and bio sensors.

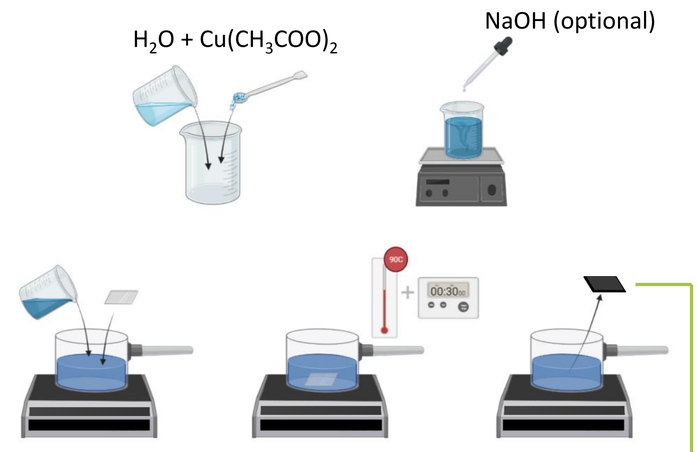
We developed a new growth technology of CuO thin films from aqueous solution. As grown films showed unclear electrical properties. It was impossible to determine, eg. the electrical parameters of the films (and therefore also optimization for application in PV cells). Multiple results indicated that the films obtained by sequencing growth process and annealing allow to obtain more electrically stable films. The investigation of Au/CuO/Au structures showed the occurance of a memristive effect in films. It extends the areas of possible applications eg. in electronics.

GROWTH TECHNOLOGY

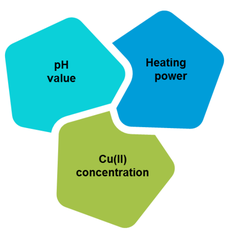
A new, extremely fast and simple technology for the growth of CuO thin films from an aqueous solution was developed (patent application P.429066). The process takes place in an open system (in a pot), and the mixture is uniformly heated using an induction cooker. The growth process consists of 3 key 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 48s up to 6 minutes and growth is possible on different substrates. Based on speciation diagram [1] the Cu fraction responsible for growth is $Cu(OH)^+$. We propose growth mechanism that can be described by following reactions:

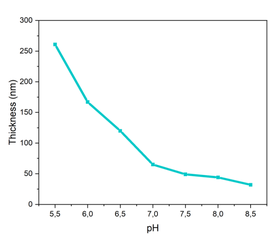
$$Cu(CH_3COO)_2 + H_2O \longrightarrow \boldsymbol{Cu}(\boldsymbol{OH})^+ + CH_3COO^- + CH_3COOH$$

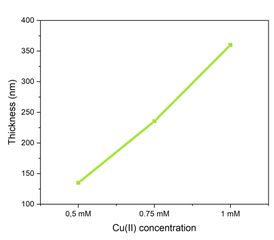
$$Cu(OH)^+ + CH_3COO^- \xrightarrow{temp.} \boldsymbol{CuO} + CH_3COOH$$

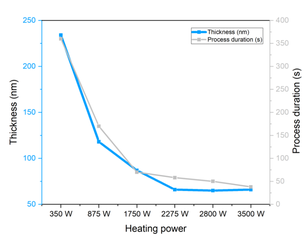


The method allows to control the thickness of the films by modifying the values of the mixture parameters as shown below:

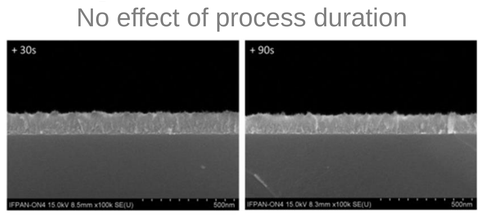


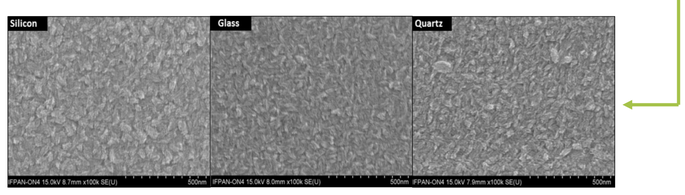






No effect of process duration

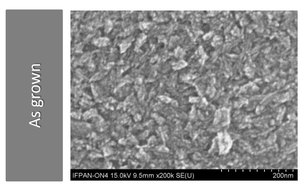


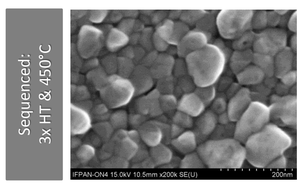


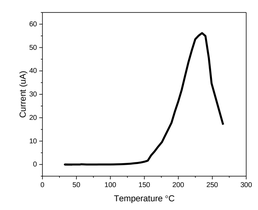
Detailed description of growth method can be found in [2]

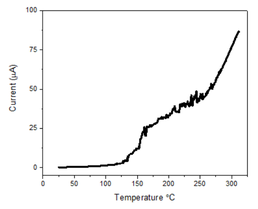
SEQUENCING HT PROCESSES & RTA

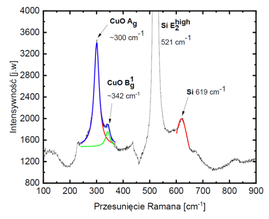
Recently, we have focused on the problem of crack appearance under the electron beam. According to our thesis it is related to the presence of built-in organics, as similar effect was observed for annealed samples. Subsequent works concern on obtaining continuous, organics-free and cracks-free CuO films by sequencing the hydrothermal process and rapid thermal annealing (RTA).

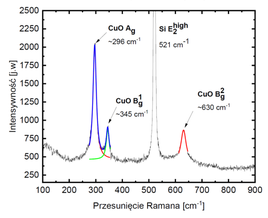


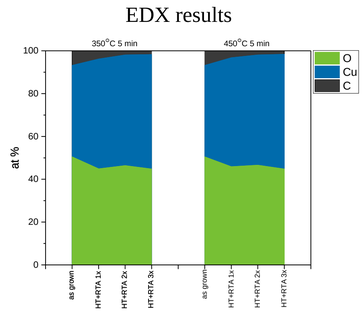








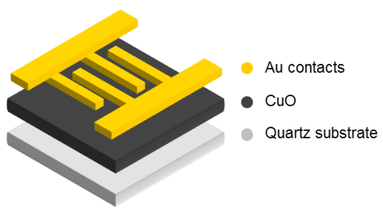


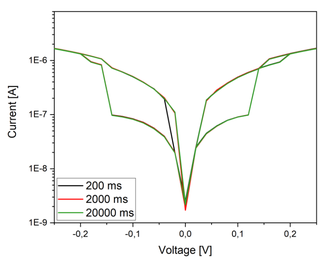


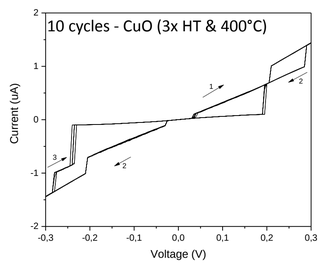
The first tests of sequenced films shows that shape of the I(T) curve is „peak-free” (in comparison to as grown samples) and close to exponential, which mean that in that way we obtain more electrically stable films. Raman spectroscopy measurements show that sequencing doesn't affect the crystalline structure and doesn't cause the formation of the Cu_2O phase. Phonon modes: A_g, B_g^1, B_g^2 which are very well exposed in the Raman spectra, proves the good quality of the crystalline CuO films, both as grown and seqenced. EDX measurements have shown that sequencing leads to a reduction of the at% of carbon in films.

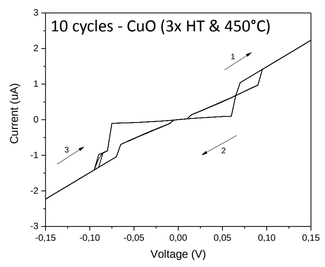
MEMRISTIVE EFFECT

Determining the electrical properties is the greatest challenge in characterization of these films. Recent studies of sequenced films indicated the presence of switching effects. Therefore, I-V characteristics were made for the lateral structures (Au/CuO/Au), and results indicate that it is a typical bipolar memristor system.









The IV characteristics recorded at different rates of voltage change doesn't show essential changes in shape, which proves that the hysteresis is essentially caused by the memristive effect. The subsequent results show that by appropriately selecting the annealing temperatures, we can also control the voltage for which resistance switching is observed.

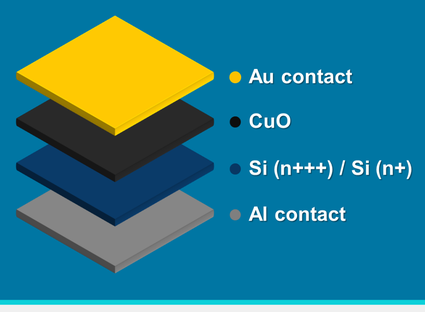
CONCLUSIONS

We developed technology that can be characterized by:

- Ultra fast growth rate
- Growth in low temperatures (below 100°C)
- Growth possible on different substrates
- Possibility of thickness control in wide range
- Low cost reactor & precursors

Sequencing of the hydrothermal process and RTA allows obtaining continuous, free of cracks films and reducing the carbon content in the layers. This makes sequenced CuO thin films more electrically stable.

An extremely promising result is the observation of the memristive effect in the films. This extends the application possibilities of the obtained CuO thin films. Currently, in cooperation with Warsaw University of Technology, we're working on vertical MIM and MIS memristor structures (as shown below) to further research on memristive effect in our material. In the final stage, we plan to create a working memory device based on CuO thin films.



references

[1] F. J. Cerino-Córdova et.al., International Journal of Enviromental Science and Technology, vol.10, 3 (2013) 611-622 DOI 10.1007/s13762-013-0198-z

[2] M. Ozga et. al., Materials Science in Semiconductor Processing, vol. 120, 105279 (2020) DOI 10.1016/j.mssp.2020.105279