The influence of metallic contacts on electrical properties of nickel and bismuth complexes

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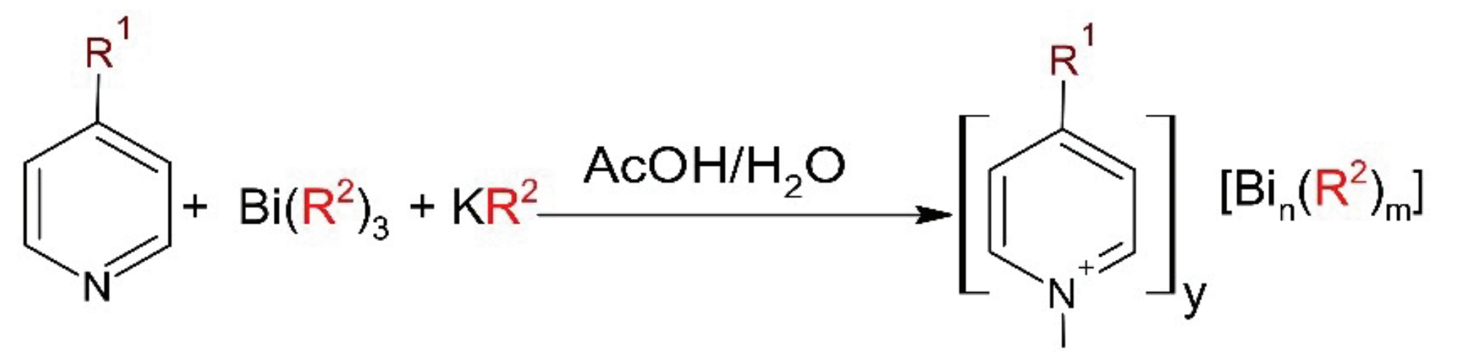
INTRODUCTION:

Memristors are passive electronic components predicted theoretically in 1971 by L. Chua. Due to the high capacity, low current consumption and size, memristors are considered to be key elements in the development of neural networks. The ability to take advantage of resistive memory implies that these elements can perform a synaptic function – constitute memory cells and modulate the signal passing between neurons. This creates opportunities for the use of memristors to create advanced computing systems. The systems proposed in the project are based on Schottky junction memristors of the coordination compounds. The project was focused on the influence of metallic electrodes on the properties of memristors.

METHODS:

Synthesis: BiI_3 (0.66 mmol) and KI (1 mmol) were dissolved in acetic acid / deionized water (1:1) and with 1 mmol of appropriate pyridine derivative (1 mmol). The same scheme was followed for $BiCl_3$/KCl and $BiBr_3$/KBr. The product was precipitated. After 24 hours, the mixture was filtered and the solid part was washed with the same solvent which was used in the reaction mixture. The reaction with iodides resulted in red crystals (Fig. 1), with chlorides in white crystals and bromides gave yellow products.



R^1 = -CN, $-NH_2$, $-CH_3$, $-N(CH_3)_2$
R^2 = -I, -Cl, -Br

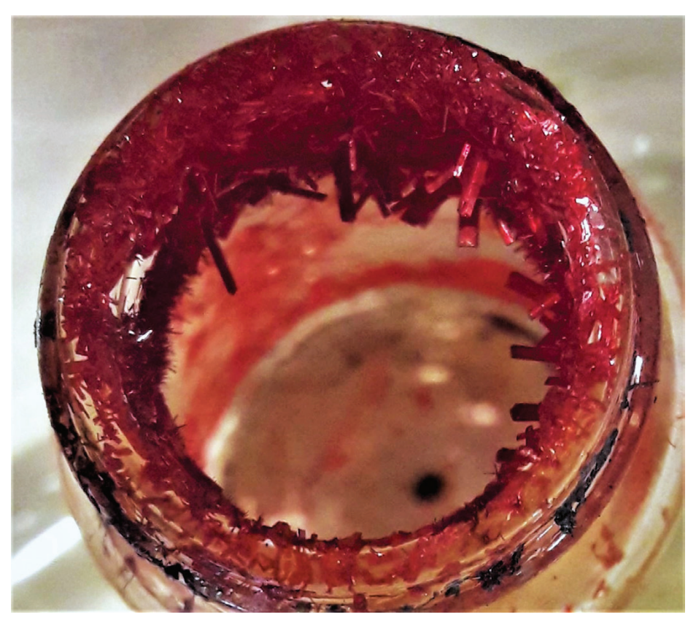
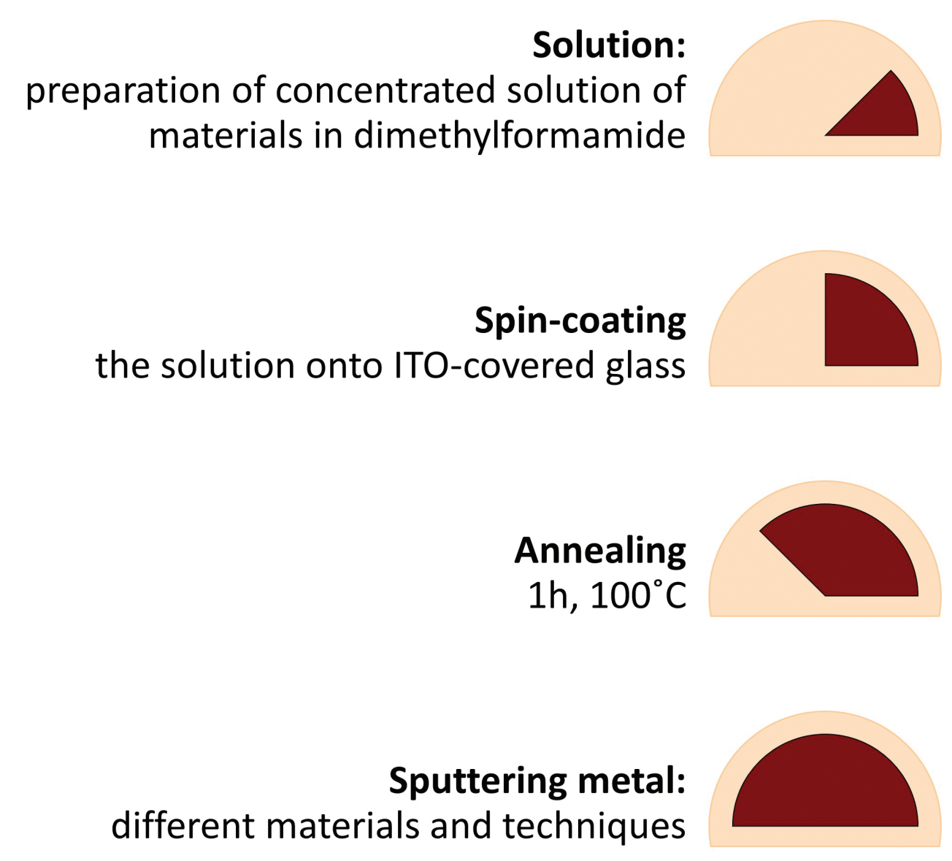


Figure 1. Crystalline product of bismuth iodides synthesis.

To evaluate the purity of the products, the Attenuated Total Reflectance (ATR) was measured. UV/Vis spectra were compared for compounds in solid state (mixed with $BaSO_4$) and liquid state (dissolved in propylene carbonate or dimethylformamide).
Memristors: The devices were made with selected materials. The concentrated solution of each material in dimethylformamide was stirred and dropped onto indium tin oxide (ITO) covered glasses. By spin-coating method, thin layers of materials were formed. The devices were annealed to evaporate the solvent. Different electrodes were thermally evaporated and magnetron sputtered. The electrical properties of the memristors were evaluated with Biologic SP-300 potentiostat.



Solution:
preparation of concentrated solution of materials in dimethylformamide

Spin-coating
the solution onto ITO-covered glass

Annealing
1h, 100°C

Sputtering metal:
different materials and techniques

Figure 2. Memristor fabrication process.

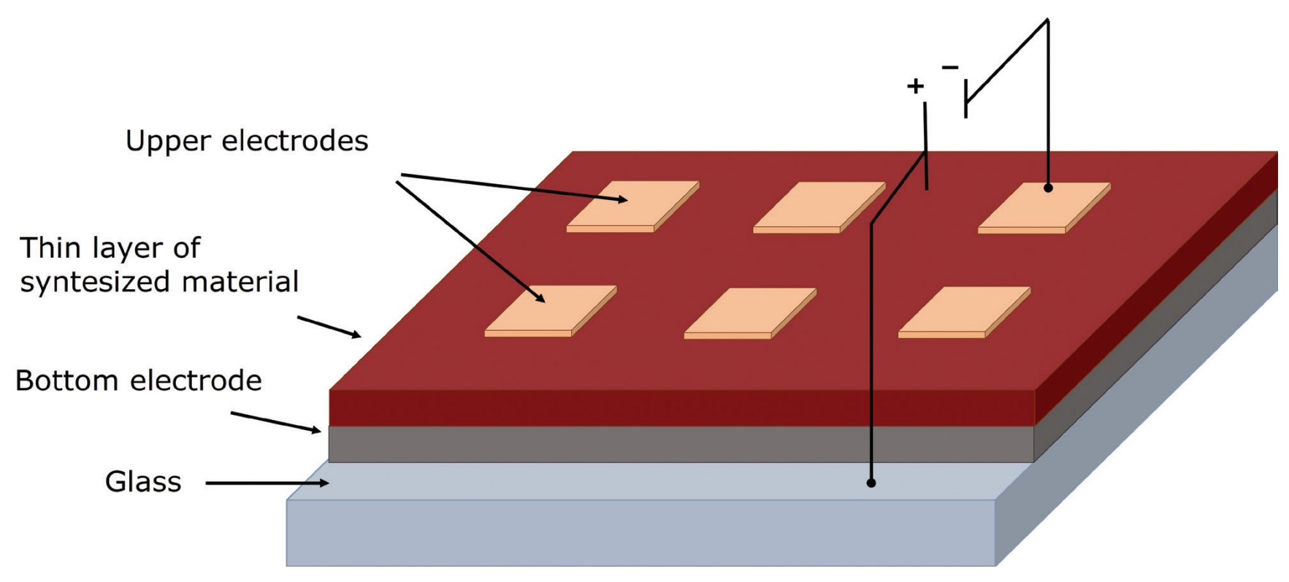


Figure 3. The scheme of memristive device.

RESULTS AND DISCUSSION:

As shown in Table 1, the bandgap energy differs slightly with various ligands. Compounds with 4-dimethylaminopyridine have the highest bandgaps (E_g), while 4-methylpydirines cause lowering of the E_g energy. Significant changes were observed for the three main families, where iodides have shown the best semiconducting properties (< 2 eV). This is a desired feature for memristive materials, since lower electric field is needed to promote electrons to excited states. As shown on Fig. 4 all of the iodide complexes exhibit two main absorption bands: around 470 nm and 340 nm. Negligible shift is observed while changing the ligand from 4-cyanopiridine to 4-dimethylaminopyridine. Due to absorption in visible range, materials may be suitable for optoelectronic applications.

Table 1. Bandgaps energies in eV calculated from Tauc plots

	$-NH_2$	-CN	$-CH_3$	$-N(CH_3)_2$
BiI_3	1.65	1.85	1.63	1.85
$BiBr_3$	2.67	2.67	2.58	2.74
$BiCl_3$	3.25	3.22	3.19	3.26

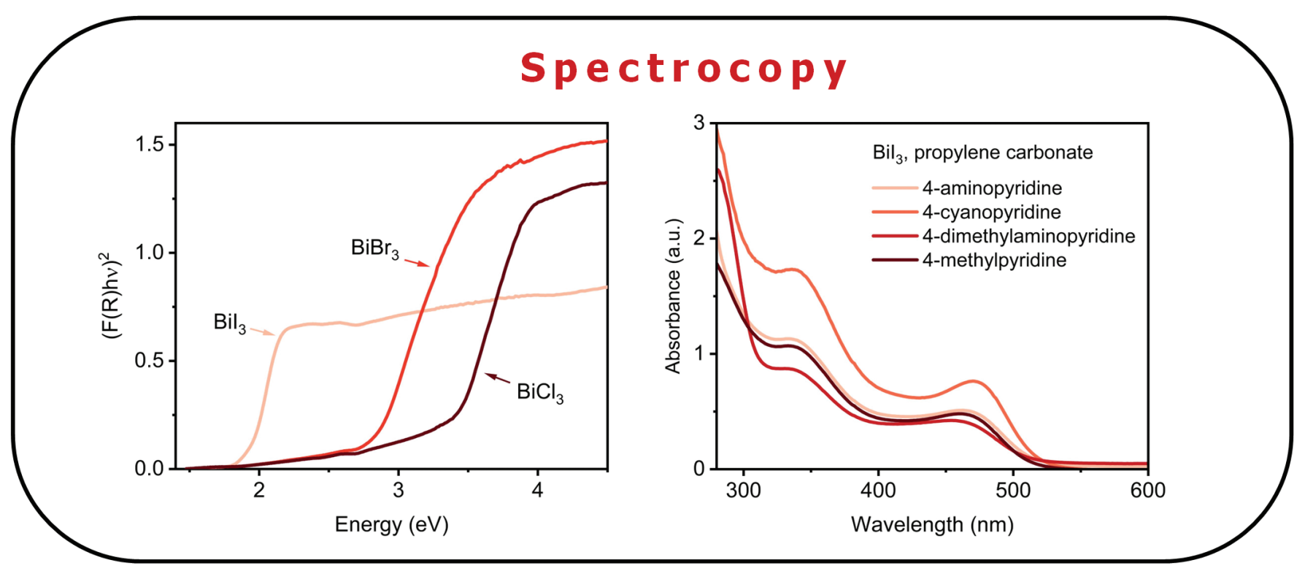


Figure 4. Tauc plot, where F(R) is proportional to Kubelka-Munk function and absorption spectra in propylene carbonate.

Material of the upper electrode influences the Schottky barrier width at the metal/semiconducting material interface. Metal with the highest work function (W_{Cu}=4.51) allowed for the fabrication of a memristor with the widest hysteresis loop. Other metals resulted in more linear and ohmic behaviour of the device. The same characteristics was observed after magnetron sputtering, which short-circuited the sample. The possible cause is high energy of sputtered metal, therefore thermal evaporation was used for further studies.

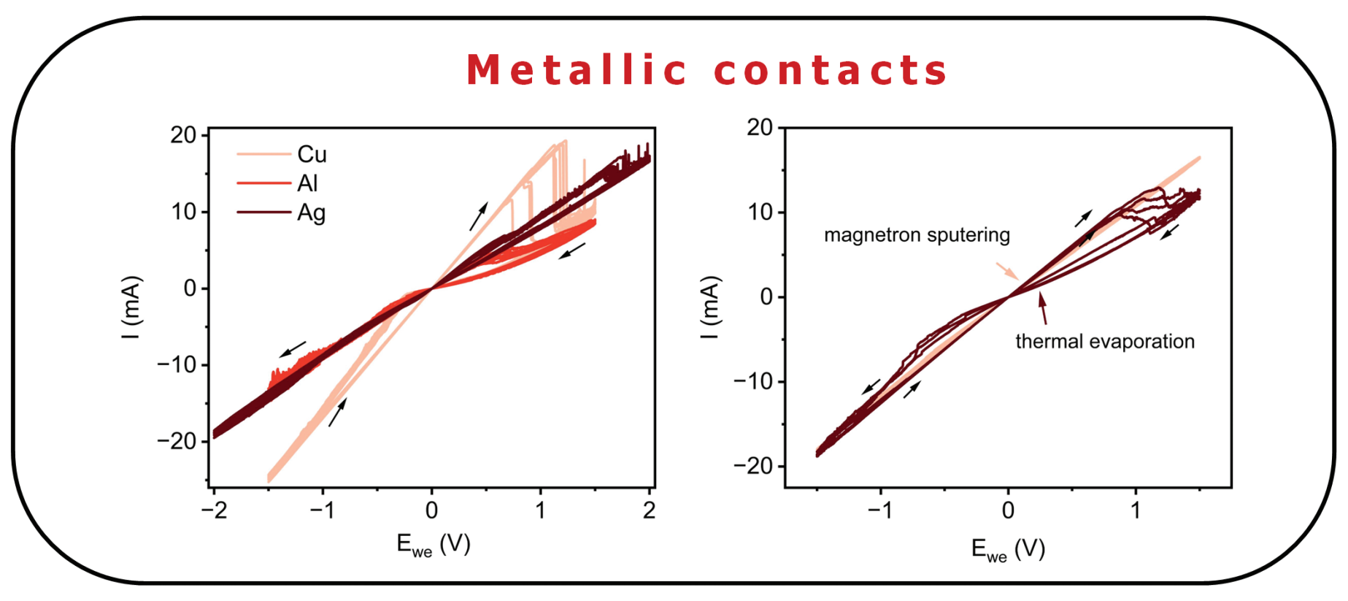


Figure 5. Cycle voltammograms of a material with different metals used for upper electrodes and comparison of two electrode sputtering methods.

Memristors based on bismuth iodide family exhibited pinched electrical hysteresis loop. Different scan-rates were used to determine the best working conditions of memristors. The hysteresis loop was observed from +/- 0.5 V in case of 4-cyanopyridine ligand, from +/- 1.5V for 4-methylpyridine and above 3 V for 4-aminopyridine. It is compatible with electron donation of functional group on pyridine moieties. Moreover, samples were stable for 200 switching cycles with high current difference between both resistive states (ON and OFF).

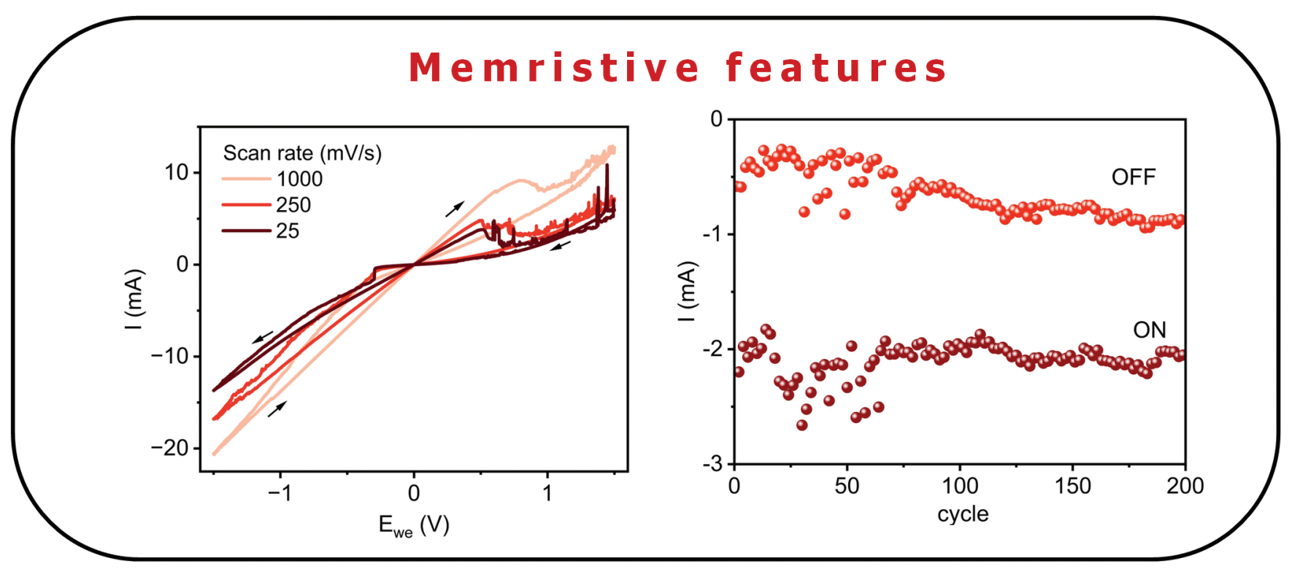


Figure 6. Memristive features of bismuth iodide devices: cyclic voltammogram with different scan rates and chronoamperogram of two resistive states of the device (OFF and ON).

SUMMARY:

Twelve bismuth complexes were synthesized and characterized spectroscopically. Four materials of iodide family were chosen for memristor fabrication thanks to their high solubility, purity and low bandgap values. Therefore, the influence of pyridinium-based ligands in bismuth iodides was further investigated. Optimization of upper electrode material and sputtering technique allowed for the development of stable memristors. High on-off ratio and stability of electrical hysteresis loop open a path for further development of coordination compounds-based memory devices.