Resistive switching phenomena in Ag_2S based nanojunctions

Summary of the Ph.D. thesis

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Introduction

Currently widespread CMOS-based devices face their boundaries concerning miniaturization due to the material properties of the applied compounds and limitations of fabrication techniques. The ongoing demand for improving computation speed and expanding data storage capacities generates an intensive competition in the innovation of novel architectures. Reversible solid state electrochemical reactions have been proposed to form tunable atomic scale junctions between metallic electrodes [Waser, 2009]. The resistive state of such a memory element, called memristor, is altered by biasing the device above its writing threshold. Readout is performed at lower signal levels which preserve the stored information. Memristive devices have been demonstrated not only to be suitable for logical and non-volatile resistance switching random access memory (ReRAM) operations but they are promising candidates for neuromorphic computations and neural network modelings [Ohno, 2011].

The work presented in this thesis focuses on the resistance change phenomena taking place in Ag_2S solid state electrolyte. The development of conducting filaments in this medium is attributed to electrochemical metalization. The insulating Ag_2S is placed between an electrochemically inert and an active (typically silver) electrode. Upon suitable biasing conditions, a metallic filament builds up in the silver-sulfite medium due to electric field effects.

Preceding results demonstrated that filaments formed in thin (20-30 nm) Ag_2S layers show switchings between metallic states at room and cryogenic temperatures [Geresdi, 2011]. The resistance change is attributed to the variation of the junction diameter taking place in the range of 2 - 5 nm.

Objectives

The conducting filaments formed in Ag_2S consist of silver atoms and silver-rich Ag_2S islands as well. Previously the complete formation and rupture of the filaments were investigated where the high resistance states were typically higher than 1 MΩ. Such devices, however, could only be operated at reduced switching speeds due to their fundamental RC limitations. Therefore the resistance changes of the fully constructed filaments form the basis of my research work. The highly non-equilibrium processes dominating this regime were not investigated before. I studied the dynamics of switchings from higher to lower resistances in devices utilizing Ag and PtIr electrodes. A particular attention was paid to high frequency operation and to the long-term stability of the low and high resistance states since these are of primary importance in terms of memory applications. The voltage polarity of the resistive switchings in $Ag/Ag_2S/Ag$ cells was investigated in order to eliminate the need for the inert electrode and thus simplify the on-chip fabrication methods. The first proof of principle structures showed an increased stability facilitating high-density integrability and applicability of the devices. Furthermore, switchings were monitored as a function of temperature at different biasing conditions in order to reveal the dominating driving force of the resistance change.

Methods

Ag thin films deposited on top of a silicon substrate were sulfurised in a low pressure atmosphere. Most of the measurements were carried out in an STM (Scanning Tunneling Microscope) arrangement were a mechanically sharpened tip was gently touched to the surface of the Ag/Ag_2S heterostructure. Temperature dependent measurements ranging from cryogenic to room temperatures were performed in order to reveal the un-

derlying physical phenomena of the observed resistive switchings. A VTI (Variable Temperature Insert) was used to set and monitor the environmental conditions. Experiments utilizing the mechanically controllable break junction technique were also done using in-situ and ex-situ sulfurization to create $Ag/Ag_2S/Ag$ junctions.

Measurement control programs were implemented in C# and Labview in order to achieve a fully automatic control of sample positioning and contact realization. Instrumental communication is also carried out via these programs along with the backup of the experimental data and main instrumental settings. Data analysis is done by Matlab scripts designed for specific tasks.

New scientific results

1. I have developed a room temperature, 3D-tunable point contact measurement setup including the design of the sample holder and the implementation of measurement control programs. I have studied the resistance change behavior of metallic nanofilaments formed in Ag_2S thin films situated between Ag and PtIr electrodes. I have shown that it is possible to induce reproducible resistance changes by bipolar voltage pulses of the width of 10 ns. Utilizing a unipolar, custom built avalanche pulse generator I have demonstrated that significant resistance changes also occur due to 500 ps long voltage pulses. [O1]

2. I have investigated the dynamics of the resistive switching process in $Ag/Ag_2S/PtIr$ nanojunctions. I demonstrated that – at a fixed R_{OFF}/R_{ON} ratio – linearly increasing the driving amplitude results in an exponential acceleration of the switching process over six decades in the frequency domain. I showed that the resistance change exhibits a strongly nonlinear time dependence upon a constant driving voltage

acting on the memristive cell and a conventional serial resistor. High voltage drop on the cell induces a fast switching while low voltage signals slowly modify the resistance state. This results in an elongated transition taking place over at least 11 orders of magnitude in the time domain. Consequently, it is not possible to attribute a well-defined characteristic time to the switching process. This elongated transition was accounted for by numerical simulations which revealed the direct connection between the bias dependence of the R_{OFF}/R_{ON} ratio and the temporal evolution of the resistance change. All parameters of the simulations were deduced from experimental data. [O2]

3. I have studied the voltage polarity of set and reset processes in $Ag/Ag_2S/Ag$ cells. The generally accepted models attribute the polarity of the switching to the specific sequence of inert and active electrode materials. In contrast, I found that the polarity can be solely determined by the local inhomogenity of the applied electric field at the active volume of the junction in agreement with molecular dynamical simulations. This inhomogenity arises from the geometrical asymmetry of the electrodes. Consequently, stable reproducible switchings with well-defined switching polarity were achieved in an STM setup using a silver tip and an Ag/Ag_2S thin film sample. On the other hand, break-junction experiments utilizing silver wires and post-rupture sulfurization revealed a random initial switching polarity in agreement with the stochastic nature of the rupture process. [O4]

4. I have performed temperature dependent measurements to reveal the role of the ambient temperature and Joule heating in the fundamental properties of the hysteretic I(V) traces in $Ag/Ag_2S/PtIr$ cells. My measurements demonstrated that the switching threshold voltages increase with decreasing temperature while the metallic nature of the ON and OFF states is preserved down to cryogenic temperatures.

This behavior was attributed to an excessive heat dissipation taking place in the active volume of the junction facilitating a structural transition of the Ag_2S medium to its superionic argentite phase where rapid changes in the filament structure can occur. This implies that the dominating driving force of the non-isothermal resistance change is self-heating assisted electric field driven ionic transport. [O3]

Utilization of the results

The resistance of the nanometer scale conducting filaments formed in Ag_2S can be continuously tuned by GHz frequency signals in a technologically optimal bias and current range. The high significance of these features is illustrated by the wide range of possible applications from fast and compact memory devices to novel neural network modeling schemes. Combining with other materials, the memristive behaviour can be beneficial in sensors, for example in light detection. One can build logical gates based on a network of memristors, where data processing and storage functionalities are integrated on the same platform realizing a novel hybrid architecture [Yang, 2013].

Publications related to the thesis points

[O1] Attila Geresdi, Miklós Csontos, Agnes Gubicza, András Halbritter and György Mihály. *A fast operation of nanometer-scale metallic memristors: highly transparent conductance channels in Ag_2S devices.* Nanoscale **6**, 2613 (2014).

[O2] Agnes Gubicza, Miklós Csontos, András Halbritter and György Mihály. *Non-exponential resistive switching in Ag_2S memristors: a key to nanometer-scale non-volatile memory devices.* Nanoscale **7**, 4394 (2015).

[O3] Agnes Gubicza, Miklós Csontos, András Halbritter and György Mihály. *Resistive switching in metallic Ag_2S memristors due to a local overheating induced phase transition.* Nanoscale **7**, 11248 (2015).

[O4] Agnes Gubicza, Dávid Zs. Manrique, László Pósa, Colin J. Lambert, György Mihály, Miklós Csontos and András Halbritter. *Asymmetry-induced resistive switching in Ag-Ag_2S-Ag memristors enabling a simplified atomic-scale memory design.* Scientific Reports **6**, 30775 (2016).

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