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PhD thesis booklet

# Resistive switching in ultrasmall nanogap devices

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## Introduction

The semiconductor device fabrication will reach the 10 nm spatial resolution soon. On such a small scale the quantum mechanical effects, such as quantum tunneling, limit the operation of the current CMOS devices [8]. In order to sustain Moore-law we need electrical components which exploit the different behavior of the material in nanoscale [5]. The resistive switch or memristor is a passive electronic device whose resistance can be reversibly controlled by applying voltage between its two terminals [6, 7]. They are promising candidates to replace the conventional CMOS devices. Their usage as a simple memory cell (RRAM) is close to commercialization, memristors have approached or exceeded the contemporary flash memories in many parameters. However, their more promising and complex applications such as integration of memory and the processing unit or the neuromorphic computing are still challenging. Despite of the intensive researches their achievable smallest size has not been clarified yet. My PhD work is related to study how the characteristics of these devices are modified at ultrasmall ($< 10\,\mathrm{nm}$) dimensions.

Besides the fabrication of nanodevices, the formation of stable electrical contacts is also challenging since electrodes with similar spacing ($\approx 5\,\mathrm{nm}$) is needed. This is below the current lithography resolution. The surface diffusion of some metals could have significant effect in nanoscale which makes it difficult to establish stable electrical contact [8]. Using graphene as the electrode can provide a solution since it has atomic stability even at room temperature due to the strong covalent bonds [9].

A possible way to create nanometer sized gap is to break electrically an initially continuous wire made by lithography process. In case of metals this method is called electromigration and is already a proven technique. However, for graphene there have been only some initial measurements, and the exact mechanisms were not investigated in detail. Prior to our study the nanogap formations were performed on small, multi-layer graphene which is not ideal for application [10].

## Objectives

The goal of my research is to fabricate and study resistive switching devices below the resolution of present lithographic techniques. The initial structures were made by electron-beam lithography on silicon wafer, whose dimensions were further decreased by controlled breakdown. Finally the resistive switches were established in the few nanometer sized gaps, formed by the breakdown process. During my PhD work I studied two different memristive systems ($Ag_2S$ and $SiO_2$).

So far the $Ag_2S$ memristors were fabricated by using two different electrode materials, an active and a passive one. STM measurements, performed at my research group, revealed that stable resistive switching can be induced if the same material (Ag) is used but geometrical asymmetry is presented in Ag-$Ag_2S$-Ag system. The single material electrodes makes the lithographical fabrication procedure uncomplicated. However mechanical stability of the STM arrangement is rather limited. During my research I formed a few 10 nm sized $Ag_2S$ region in a nanofabricated pure silver samples and I could reproduce the same stable resistive switching as was observed in other measurement arrangements, which ensured the role of the geometrical asymmetry in the switching dynamics. Later I also participated in the optimization process of these devices.

Certain metals show large surface diffusion at nanoscale, which can cause stability problems. Furthermore the metal ions can diffusive inside the switching region, which modifies their operation [8, 11]. Using graphene as the electrode material can provide a solution since it has atomic stability due to the strong covalent bonds and the carbon atoms do not contaminate the active region. The high yield fabrication of nanometer sized gap in single layer, CVD graphene has not been demonstrated. During my work I established a procedure for the fabrication of nanometer-sized gaps with a very high yield and I revealed the mechanism of the breakdown under different environmental conditions.

The $SiO_2$ is also a resistive switching material. If the substrate under the graphene is covered by $SiO_2$, a switching region can be formed around the gap when voltage is applied ($8-10$ V) to the graphene terminals. Since the gap has only few nanometers width the resistive switch also has extreme small size ($\approx$ 5 nm). The switching properties of such a small $SiO_2$ based memristor and the time resolved dynamic of this system has not been demonstrated yet. My real time pulsed measurements revealed multiple physical timescales, among others the dead time, which has an essential role in the device operation. Compared to the experiences, published in the literature, the extreme small size of the switching region did not affect the properties of the device.

## Methods

The nanometer sized contacts were patterned by standard electron beam lithography (EBL) for both silver and graphene samples. Due to the simplified single material device structure the fabrication of Ag-$Ag_2S$-Ag memristor was performed by single lithography step. The silver layer was evaporated by electron-beam physical vapor deposition technique. The width of the asymmetric junction at the narrowest part was under 100 nm. The graphene sheets were grown by chemical vapour deposition (CVD) on copper foil at the University of Basel. The graphene is single layer, polycrystalline and few $cm^2$ in size. Afterwards the graphene was transferred onto Si substrate covered by $SiO_2$ or $Si_3N_4$ using wet etching technique. The devices were fabricated by two lithography steps, in the first one the graphene was etched by $Ar/O_2$ plasma and in the second one the metal layers (Ti/Au) were deposited to establish electrical contact to the graphene. The narrowest width of the graphene constrictions were varied between 100 and 600 nm. During one sample fabrication process more than hundred device could be fabricated, which allows us for statistical analysis.

Most of the electrical measurements were performed by a self-developed measurement control program implemented in C#. It can communicate with the National Instruments data acquisition card, oscilloscope or function generator connected to the computer. The breakdown process of the nanojunctions is performed by applying voltage pulses with increasing amplitude, while the current is monitored. When narrowing of the graphene stripe begins the current drops suddenly and the bias voltage has to be removed quickly, otherwise the gap being formed gets too wide. The implementation of the controlled breakdown process to the measurement control program was an important part of my work.

The few nanometer sized gaps can be characterized by electrical measurement based on quantum tunneling effect. The gap can be described by a potential barrier and its height ($\Phi$) and width ($d$) can be extracted from the I-V measurements [12]. During my visit in Basel atomic force microscope (AFM) and scanning electron microscope (SEM) measurements were also performed. For more accurate characterization, I performed electrical measurements at the temperature of liquid helium (4.2 K).

Depending on the speed of the driving voltage I used data acquisition card or function generator as a voltage source. The shortest transition was 50 ns, which was an instrumental limit. Most of the electrical characterization were performed under vacuum condition to preserve the cleanness of the sample and avoid the oxidation of the surface. For this purpose I established a vacuum tight sample holder made for the lithographed devices. For the high frequency measurements a specific measurement setup were used which capable to transmit the ultra short signals.

## New scientific results

1. I developed a novel measurement setup for the controlled electrical thinning and breakdown of nanofabricated junctions. This included the development of a new high vacuum sample holder, the assembly of an optimized measurement

setup and the development of a versatile measurement program. This measurement system enables us to reduce the active region of nanofabricated devices well below the resolution of present lithographic techniques. The specialty of this system is the pulsed breakdown technique, which allows us to expose the device to much shorter voltage intervals than in real-time feedback-controlled systems. Applying this setup I could establish a few nanometers wide gaps in nanofabricated Ag wires. I have extended this method on single-layer chemical vapor deposited graphene nanostripes achieving nanogaps with measurable tunnel current with a yield over ($\approx 98\,\%$). The wafer scale growth of CVD graphene enabled the simultaneous fabrication of a large ensemble of devices on a single chip. The statistical analysis of hundreds of devices reveals typical gap sizes between 0.3 nm and 2.2 nm [1–3].

2. I studied the resistive switching phenomena of nanofabricated Ag-$Ag_2S$-Ag memristors [2]. I have demonstrated that the resistive switching can be established using a simplified sample design lacking the conventionally employed inert electrode. In this design a simple lithographic step is sufficient to fabricate the base structure, which is an asymmetrically shaped Ag nanowire. I have established the ultrasmall resistive switching region by the controlled electromigration of the Ag nanowires, and the in-situ sulfurization of the such created nanogaps. I have demonstrated that these devices exhibit the conventional switching characteristics of nanometer-scale $Ag_2S$ memristors, such that the direction of the switching is governed by the inhomogeneity of the local electric field due to the geometrical asymmetry of the device. In similar devices I have also demonstrated stable room temperature atomic switching phenomenon, indicating that the surrounding $Ag_2S$ matrix stabilizes the atomic switching process.

3. I analyzed the influence of the environmental conditions on the electrical breakdown of graphene nanostripes [3]. The systematic study of the breakdown power as the function of pulse length and pressure revealed two fundamentally different breakdown processes. I have found, that in high vacuum a significantly higher power was needed to achieve the breakdown than in atmospheric pressure air. Using a thermal model I rescaled the breakdown power to the maximal local temperature of the graphene stripe. Assuming thermally activated processes I estimated the activation energies of the physical mechanisms involved in the breakdown. The significantly different activation energies are consistent with oxidation in air and sublimation in high vacuum. Using two different substrates ($SiO_2$ and $Si_3N_4$), I found that the oxygen content of the

$SiO_2$ substrate does not play role in the breakdown process.

4. I investigated the resistive switching phenomena of graphene-$SiO_x$-graphene devices [4]. The intrinsic resistive switching in the $SiO_x$ layer was confined under a few nanometers wide graphene gap, resulting in a yet unexplored, sub-10 nm size-scale switching region of $SiO_x$. My detailed electrical characterizations revealed that these ultrasmall devices exhibit a significantly smaller electroforming voltage than conventional $SiO_x$ switches, such that the further beneficial properties of larger devices, like fast switching speed, excellent endurance and data retention are maintained. I have performed detailed time resolved measurements to identify the physical timescales governing the device operation. I have demonstrated, that the switching is not a gradual transition: the device keeps its initial state for a certain period of time after the voltage is applied, and finally an abrupt resistance change is observed, which is faster than the $\approx 50$ ns temporal resolution of the measurements. I demonstrated that a modest, linear decrease of the set/reset voltage induces an exponential slowdown of the set/reset operation. I have also identified another fundamental time-scale, the dead time. I found, that after switching OFF the device, it cannot be set to the ON state again as long as the dead time has not passed, even if the driving signal is sufficient for a set transition. The detailed study of the dead time revealed that its length does not depend on the driving conditions, however it could be decreased significantly by a modest increase of temperature, indicating a thermally activated rearrangement of the switching region.

## Utilization of the results

The all-Ag structure of Ag-$Ag_2S$-Ag memristors makes the lithographic device fabrication more uncomplicated which may help its commercialization. The dead time in the $SiO_2$ integrates the advantages of the unipolar and bipolar switches, both states can be achieved using only unipolar pulses. Owing to the multiple physical timescales in this system various switching patterns can be generated These properties ensures complex device operation with low power consumption and device area.

Besides the data storage, the most promising applications of resistive switches is the implementation of neural networks, where each synapses would be realized by a resistive switch [13]. Since they can be switched fast, exhibit non-volatile behavior and show high endurance, new type of memories can be created, for example the

Storage Class Memory filling the gap between DRAM and FLASH memory [14]. It is also possible to use them as logical gateways to enable the implementation of a computer other than the Neumann architecture [15].

# Publications related to the thesis statements


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