Graduate School of Advanced Science and Engineering
Waseda University

博士論文概要
Doctoral Thesis Synopsis

論文題目
Thesis Theme

Atomic Switch Based Tug of War

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In chapter 1, an introduction is given. To make future computers smaller and more efficient, one approach is to build a completely new computer architecture that is inspired of biological brains: a neuromorphic system. Recently, neuromorphic systems using nonvolatile memories as artificial synapses controlled by CMOS neurons attract much attention. However, CMOS circuits only enable sequential operation. As a result, the CMOS-neuron based neuromorphic systems cannot achieve parallel interactive computation, which is the most important function to be emulated. Using an amoeba this function has been shown. That is because the amoeba explores its surrounding by stretching and shrinking its arms in an interactive parallel way. A theoretical algorithm based on this behaviour had been proposed in the past and is called Tug of War principle. Aim of this doctoral study was to implement this Tug of War model into an actual solid-state device based on silver sulphide gap-type atomic switches: Atomic Switch Based Tug of War Devices.

Conventional atomic switches operate by growing and shrinking a Ag filament between two electrodes caused by bias application. The general concept of Tug of War devices, which have three electrodes, is that filament growth and shrinkage from the centre active electrode is linked to one another by a limited amount of silver in the centre electrode, comparable to the amoeba retracting an arm when another one stretches due to a limited body volume. Namely, filament growth is induced by bias application in one channel, but the shrinkage of the previously grown filament in another channel is caused by the depletion of silver atoms in the centre electrode due to the new filament growth.

To realise the concept of the Tug of War devices in this doctoral study, several steps were done that are described in chapter 2 to 6. First, the device design and fabrication process had to be analysed. Then, silver sulphide, which is the material of the centre electrode, and influences on the sulphurization process were examined. Since a gap-material is needed to supply the electrons for the reduction/oxidation reactions that grow/shrink filaments, different conductive polymers were characterised and tested. In preliminary experiments, important influences on later Tug of War switching were pinpointed. And finally, Tug of War operation was demonstrated.

In chapter 2, sample design and fabrication procedure are developed. The device design for these Tug of War devices had to comprise several counter electrodes so that filaments can grow to several directions to later achieve the desired parallel computing. Since the shrinkage due to the depletion of silver atoms is expected to occur when a filament grows a few hundred nanometres, I decided to use e-beam lithography for device fabrication. First, the requirements and issues to achieve the Tug of War operation were identified through the experiments on the electrode material, adhesion layer, upper and lower limits of device dimensions and the form of the electrodes. I also found that it is necessary to add an insulation layer on top of the centre electrode in order to promote filament growth between the electrodes. A channel structure was also added to the design to prevent leakage current between both counter electrodes that could disturb the desired filament growth. The final device design used two platinum counter electrodes and one active silver sulphide electrode with an insulation layer on top, embedded in a channel structure. Titanium was used as adhesion layer. The final fabrication process was: Patterning of platinum counter electrodes → Creation of the channel structure → Deposition of the silver electrodes and the insulation layer → Sulphurization → Covering of the sample with gap-material.

In chapter 3, as a next step in the development of Tug of War devices, properties of silver sulphide were analysed to better understand the occurring electrochemical processes during switching. Furthermore, conditions for the sulphurization of the silver electrode via an annealing process in sulphur vapour were examined and the optimal conditions were pinpointed to be: 180°C for 10 minutes with a certain but not too high sulphur partial pressure. Sulphurization should be done immediately after Ag patterning to avoid unwanted diffusion, corrosion and other effects of the silver on platinum, severe problems that were also revealed and needed to be solved in this doctoral study.

In chapter 4, different materials are analysed on their suitability as gap-material. An electronically conductive gap-material is necessary to supply electrons for the reduction process at the active electrode through the gap between the electrodes. Ionically conductive materials have been used as gap-material in atomic switches with a large gap. However, these cannot be used for Tug of War operation, because they would lead to a transport of silver-cations through the gap-material to the counter electrode and hence to the formation of filament formation from the counter electrode instead of the active electrode. To achieve the Tug of War operation, an electronically conductive gap material is needed for the filament growth from the centre active electrode.

To find a suitable gap-material, several compounds such as PEO, PEO+BTOE, P3HT with short and long polymer chain lengths, P3EHT, ActiveInk N2200, PFP and ESpacer were analysed on their ionic and electronic conductivity and their stability. It was furthermore tested whether these gap-materials would be soft enough to let filaments grow through it. Also, problems such as leakage current were examined.

It was found that: solid filament formation can be achieved by enhancing electronic conductivity. P-type conductive materials can be used for Tug of War devices even though it was believed that n-type polymers are needed to supply the electrons for the redox reactions. The final conclusion is that P3HT seems most suitable as gap-material, but polymer chain length could be further adjusted.

In chapter 5, as preparation for the final Tug of War measurements, preliminary experiments are described that were performed to analyse filament growth through these so far developed devices. For example, requirements to initiate Ag protrusions, how long filaments can maximally grow, and the stability of established connections were examined. It was found that the maximum filament length is not given by the amount of excess silver in silver sulphide as believed before, but that all silver can be extracted from the sulphide.

In many cases, threshold switching was observed, meaning that an established connection breaks below a certain threshold voltage. The reasons for this were examined. It was found that this can happen from the development of a Nernst potential. Another cause for threshold switching was identified to be incomplete connections, meaning when the current flow between the electrodes is not completely given by the silver filament, but partly given by water molecules or current flow through the polymer. The stability of the filaments can be enhanced by applying a bias voltage of a larger value or for a longer time. High currents should be avoided using a series resistance during this procedure because it can damage the devices irreversibly through Joule heating. All these results are important findings to understand and to achieve Tug of War operation with these novel devices.

In chapter 6, after all preparation, finally, the Tug of War operation is analysed and demonstrated. Several challenges had arisen from the above described findings. For example, filament growth was not limited to excess silver in silver sulphide. This missing limitation suggested that it might not be possible to obtain a Nernst potential strong enough to shrink a filament from depletion. Other results however showed that filaments can shrink from that potential if the applied voltage is low enough. Therefore, a first point in proving that the Tug of War principle is possible is to show filament shrinkage without bias application to that side, purely by applying a bias voltage to another side to grow filaments there. This was successfully achieved using PEO, PEO+BTOE and P3HT as gap-material. This is a completely new concept to previous atomic switches.

After successfully showing filament shrinkage due to the Tug of War principle, electrical measurements were performed to show alternating switching between both counter electrodes. As a result, the Tug of War operation using the atomic switch based devices that had been developed in the first chapters has been demonstrated for the very first time. With this the main goal of this doctoral study was achieved.

To figure out the main mechanisms that underlie the Tug of War operation, additional experiments were performed. Switching timing and shrinkage were examined. It was found that switching ON on one side and OFF at the other occurs at a similar timing. However, looking at it more precisely showed that both, the breakage of a connection to one side before the establishment of the connection to the other side and the breakage of a connection after the establishment of a new connection, could be observed. As for the shrinkage, in many cases, positive current while a small negative read voltage was applied, indicated filament shrinkage is caused by a Nernst potential forming when a new filament starts growing towards the other counter electrode.

Summarized, the goal of this doctoral study, namely to demonstrate Tug of War operation on an all solid-state device based on atomic switches, was demonstrated for the first time. Furthermore, details about the switching mechanisms were identified.

In chapter 7, a conclusion about the findings is given. After the development of the Tug of War device design, fabrication and the search of suitable gap-materials, preliminary experiments were done. Finally, shrinkage of filaments due to the Tug of War principle could be visualised and Tug of War operation could be demonstrated in electrical measurements for the first time. Furthermore, mechanisms of this novel switching type were examined.

With this, the goal of this doctoral study was achieved. Additionally, many findings of this doctoral study proved reports from literature and common believes wrong, for example that only n-type gap-materials could be used and that only excess silver is used to form filaments. Also, the general achievement of filament growth from the active electrode is in itself a special finding because common atomic switches use electrolytes as gap-material and hence only achieve filament formation from the inert counter electrodes.

Summarized, this study did not only introduce a completely novel element for future computer hardware, but also contributes a lot of valuable findings to the field of research on atomic switches.

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Paper	○1. C. Lutz, T. Hasegawa, T. Tsuchiya, C. Adelsberger, R. Hayakawa, T. Chikyow: “P-type polymer-based Ag_2S atomic switch for ‘Tug of War’ operation”, JJAP, 56, 06GF03 (2017). ○2. C. Lutz, T. Hasegawa, T. Chikyow: “Ag_2S atomic switch-based ‘tug of war’ for decision making”, Nanoscale, 8, 14031 (2016). 3. X. Zhang, R. Waitz, F. Yang, C. Lutz, P. Angelova, A. Gölzhäuser and E. Scheer: “Vibrational modes of ultrathin carbon nanomembrane mechanical resonators”, Appl. Phys. Lett. 106, 063107 (2015). 4. R. Waitz, C. Lutz, S. Nößner, M. Hertkorn, E. Scheer: “Spatially Resolved Measurement of the Stress Tensor in Thin Membranes Using Bending Waves”, Phys. Rev. Applied 3, 044002 (2015).
Oral Presentation	1. C. Lutz, “‘Tug of War’ devices for interconnection of artificial synapses”, Memrisys Conference, Athens/Greece, 04/2017 (Keynote presentation). 2. C. Lutz, “‘Tug of War’ devices for interconnection of artificial synapses”, Workshop on Molecular Architectonics, Osaka/Japan, 06/2017. 3. C. Lutz, “Organic semiconductors and sample design for Ag_2S based Tug of War atomic switches”, Waseda-NIMS Students Seminar, Tsukuba/Japan, 01/2017. 4. C. Lutz, “p-type polymer based Ag_2S Atomic Switch for 'Tug of War' Operation”, International Microprocesses and Nanotechnology Conference (MNC), Kyoto/Japan, 11/2016. 5. C. Lutz, “Ag_2S atomic switch based Tug of War devices for neuromorphic networks”, JSAP 77th Autumn Meeting in Niigata/Japan, 09/2016. 6. C. Lutz, “Future Computer Architecture: Memristors, Artificial Synapses and Decision Makers”, University of Konstanz/Germany, 09/2016 (Invited). 7. C. Lutz, “A Tug of War - 3 Terminal Atomic Switch for neuromorphic decision making”, RWTH Aachen/Germany, 09/2016. 8. C. Lutz, “Tug of War - Implementation of decision making functionality in atomic switches”, Early Bird Meeting at Waseda University in Tokyo/Japan, 07/2016. 9. C. Lutz, “A Tug of War between nanodots”, Waseda-NIMS Students Seminar, Tsukuba/Japan, 01/2016. 10. C. Lutz, “Decoding of brain activity during mind wandering”, Assessment Centre of the Max Planck Institute for Brain Research/Germany, 03/2014.

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Poster Presentation	1. C. Lutz, T. Hasegawa, T. Chikyow, "'Tug of War' devices for interconnection of artificial synapses", Workshop on Molecular Architectonics, Osaka/Japan, 06/2017. 2. C. Lutz, T. Hasegawa, T. Chikyow, "'Tug of War' devices for interconnection of artificial synapses", MANA Symposium, Tsukuba/Japan, 02/2017. 3. C. Lutz, T. Hasegawa, T. Chikyow, "'Tug of War' devices for interconnection of artificial synapses", Early Bird Meeting, Waseda University, Tokyo/Japan, 02/2017. 4. C. Lutz, T. Hasegawa, T. Chikyo, "A tug of war between nanodots", "6th Waseda-NIMS International Symposium" at Waseda University in Tokyo/Japan, 07/2015. 5. C. Lutz, L. Efremova, C. Kreuter, M. Leist, "Establishment and characterization of a microfluidics platform to study the effect of chemicals on neurites separately from thos on neuronal cell bodies", The Conference "Cellular Nano Sciences" at the Max Planck Institute in Heidelberg/Germany, 07/2011. 6. P. Adelhelm, B. Mogwitz, J. Sann, P. Khamehgir, C. Lutz, J. Janek: "Towards the in-situ Characterization of Model All Solid state Batteries – Preparation of $LiFePO_4$ and LiPON Thin Films via Pulsed Laser Deposition", ZAAC, Volume 636, Issue 11, page 2098, 2010.

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