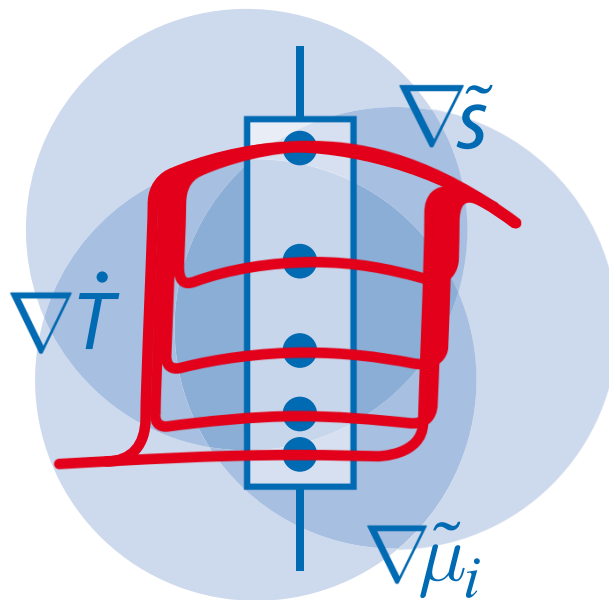


Sonderforschungsbereich

SFB 917

Nanoswitches

Resistively Switching Chalcogenides
for Future Electronics –
Structure, Kinetics, and Device Scalability



Abschlussbericht
2019/2–2020–2021–2022–2023/1

Collaborative Research Center 917

**Resistively Switching Chalcogenides
for Future Electronics –
Structure, Kinetics, and Device Scalability**

RWTH Aachen University

Final report

2019/2-2020-2021-2022-2023/1

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1 Summary

The goal of SFB 917 has been the development of novel nanoswitches that can be reproducibly and reversibly changed between two states on very short time and length scales. Such nanoswitches can enable new storage and memory devices as well as neuro-inspired architectures for information technology. In the third and final funding period of SFB 917 we have witnessed and contributed to three major trends. The exponential growth in the demand for data storage and processing has continued. Hardware improvements are therefore urgently needed to meet the increased demands for data storage and processing as well as the related increase in energy consumption. SFB 917 strives to realize novel storage devices by exploiting the full potential of chalcogenide-based nanoswitches. Yet, it has become increasingly clear in the last few years, that improvements in device performance alone are insufficient to deal with the exponential growth mentioned above.

The advance of Large Language Models (LLMs) like ChatGPT and related software has produced a further increase in data processing related energy consumption. This is a major challenge considering the expected further increase of professional and private usage of such machine learning tools. To minimize the related energy consumption, particularly energy-efficient software and hardware developments are mandatory. Within SFB9917, we have intensified our efforts to work on effects related to a reduction in energy consumption. While energy-efficient devices can help, an improvement in hardware architecture offers significantly more leverage. We have thus explored the potential of chalcogenide based nano-switches in neuro-inspired computer architectures. To this end, several new large-scale research projects have been initiated (NeuroSys and NeuroTec), which extend our research on these devices in increasingly more complex architectures, offering new opportunities to harvest the findings of SFB 917 in new applications.

To tailor chalcogenide-based nano-switches, major advances in instrumentation as well as an in-depth understanding of the origin of underlying phenomena and unconventional properties in these materials have been mandatory. Challenges included the characterization of switching in these materials on nanosecond time and nanometer length scales. Sophisticated tools have been built and utilized. Understanding unconventional properties are required building a bridge between concepts of inorganic chemistry and material properties leading to novel treasure maps which help to identify and tailor chalcogenides for specific applications. These successes are described in detail in the present report. To demonstrate that these findings are also relevant for industry, close cooperation with industrial partners has been established to ensure that the findings made within SFB 917 can also be implemented on the shortest possible time scales.

Zusammenfassung

Das Ziel des SFB 917 war die Entwicklung neuartiger Nanoschalter, die auf sehr kurzen Zeit- und Längenskalen zwischen zwei Zuständen geschaltet werden können. Solche Nanoschalter ermöglichen die Realisierung neuer Speicherbauelemente sowie neuroinspirierte Architekturen für die Informationstechnologie. In der dritten und letzten Förderperiode des SFB 917 haben wir drei wichtige Trends mitgestaltet. Der exponentielle Anstieg des Bedarfs an Datenspeicherung und -verarbeitung hat sich fortgesetzt. Hardwareverbesserungen sind daher dringend erforderlich, um den gestiegenen Anforderungen an die Datenspeicherung und -verarbeitung gerecht zu werden sowie dem damit verbundenen erhöhten Energieverbrauch möglichst zu reduzieren. Der SFB 917 strebt die Entwicklung neuartiger Speicherbauelemente an, indem er das volle Potenzial von Nanoschaltern auf Chalkogenidbasis ausschöpft. In den letzten Jahren wurde jedoch immer deutlicher, dass Verbesserungen der Bauelementeleistung allein nicht ausreichen, um das oben erwähnte exponentielle Wachstum zu bewältigen.

Der Vormarsch von Large Language Models (LLMs) wie ChatGPT und entsprechender Software hat zu einem weiteren Anstieg des Energieverbrauchs bei der Datenverarbeitung geführt. Dies ist eine große Herausforderung in Anbetracht der zu erwartenden weiteren Zunahme der professionellen und privaten Nutzung solcher Werkzeuge des Maschinellen Lernens. Um den damit verbundenen Energieverbrauch zu minimieren, sind besonders energieeffiziente Software- und Hardwareentwicklungen notwendig. Im Rahmen des SFB 917 haben wir daher unsere Bemühungen verstärkt, an Effekten zu arbeiten, die mit einer Reduzierung des Energieverbrauchs verbunden sind. Während energieeffiziente Geräte helfen können, bietet eine Verbesserung der Hardware-Architektur eine wesentlich größere Hebelwirkung. Wir haben daher das Potenzial von Nanoschaltern auf Chalkogenidbasis in neuroinspirierten Computerarchitekturen erforscht. Zu diesem Zweck wurden mehrere neue groß angelegte Forschungsprojekte initiiert (NeuroSys und NeuroTec), die unsere Forschung an diesen Schaltern in immer komplexeren Architekturen erweitern und neue Möglichkeiten bieten, die Erkenntnisse des SFB 917 in neuen Anwendungen zu nutzen.

Um Nanoschalter auf Chalkogenidbasis maßzuschneidern, waren große Fortschritte bei der Instrumentierung sowie ein tiefgreifendes Verständnis des Ursprungs der zugrundeliegenden Phänomene und der unkonventionellen Eigenschaften dieser Materialien erforderlich. Zu den Herausforderungen gehörte die Charakterisierung der Schaltvorgänge auf der Nanosekundenzeitskala und der Nanometerlängenskala. Dazu wurden

avancierte Messmethoden entwickelt und eingesetzt. Um unkonventionelle Eigenschaften zu verstehen, muss eine Brücke zwischen Konzepten der anorganischen Chemie und den Materialeigenschaften geschlagen werden. Dies führte zu neuen Schatzkarten, die helfen, maßgeschneiderte Chalkogenide für spezifische Anwendungen zu identifizieren und maßzuschneidern. Die daraus resultierenden Erfolge werden in dem vorliegenden Bericht ausführlich beschrieben. Um zu zeigen, dass diese Erkenntnisse auch für die Industrie relevant sind, wurde eine enge Zusammenarbeit mit Industriepartnern aufgebaut, um sicherzustellen, dass die im SFB 917 gewonnenen Erkenntnisse auch in kürzester Zeit umgesetzt werden können.

2 Published Results

The 50 most important papers (in chronological order):

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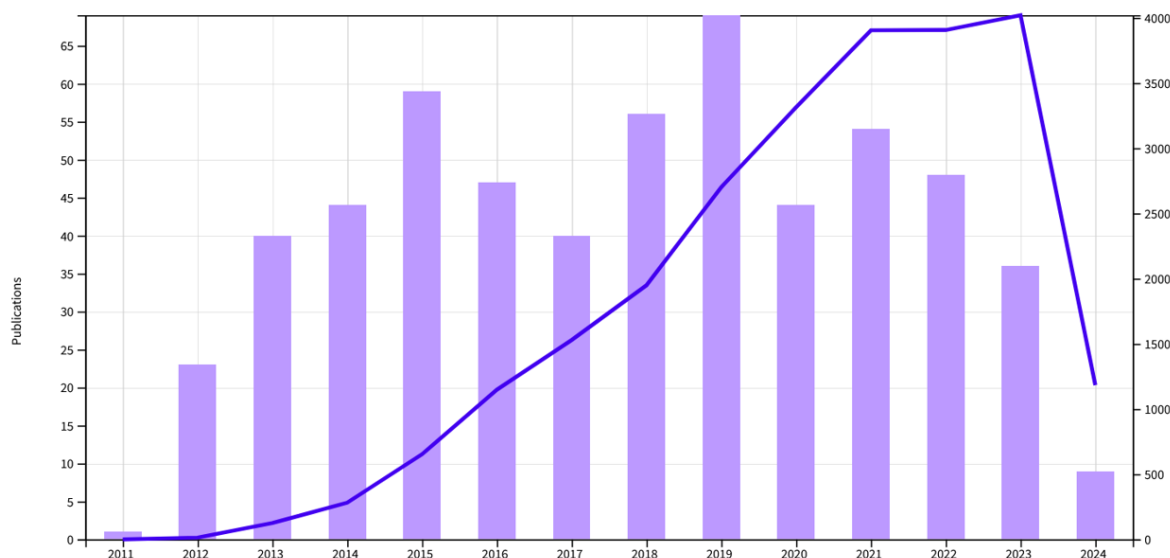
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Patents:

- V.S.P. Jonnalagadda, B. J. Kersting, W. Koelmans, M. Salinga, A. Sebastian, *Resistive Memory Device*, United States Patent: Patent No.: 10,600,958 B2, Date of Patent: March 24, 2020
- S. Wei, M. Wuttig, Y. Cheng, J. Pries, X. Lu, Patent No. 11817146 (Granted)

D. Wouters, V. Rana, RERAM-VORRICHTUNG UND VERFAHREN ZUR HERSTELLUNG EINER RERAM-VORRICHTUNG“, filed on 24.04.2023 with the reference number DE10 2023 110 363.6.

2.1 Publications with scientific quality assurance



In total, we have written so far (as of April 2024) about 570 peer reviewed publications related to SFB 917. These papers are referenced in the reports of the various projects and will thus not be listed here again. Instead, we only present a summary of the annual distribution and the resulting citations. We are pleased that the publications of SFB 917 have resulted in about 25.000 citations so far. At the same time, one also notes a slight reduction in paper productivity in 2020 and the following years, which might be related to Corona effects.

2.2 Other publications and published results

We have also looked for other ways to disseminate our findings. A rough estimate shows that the PIs of SFB 917 have given more than 300 invited talks at national and international conferences. As shown on the previous page, three patents have also been granted / filed. A software package has been made public, which enables a quantitative characterization of bonding in solids employing orbital-based computations (Journal of Computational Chemistry 37, 1030 (2016)). Finally, a first version of a treasure map has been developed which relates chemical bonding descriptors with material properties. <https://materials-map.rwth-aachen.de/>

3 Overview of Projects

Project groups and projects

Topical area A: Structure and material complexity

Project	Status	Title	Research area	Project leader(s)
A1		From structure-property correlations to tailor-made chalcogenide materials	experimental and computational solid state physics, materials science, thin films	Prof. Richard Dronskowski IAC, RWTH Prof. Matthias Wuttig I.Phys.Inst.1A, RWTH
A2		Correlation between the atomic structure and electronic states in resistively switching oxides	solid state physics, thin films	Prof. Regina Dittmann PGI-7, FZJ Prof. Rainer Waser IWE2, RWTH
A3	E	Scanning tunneling microscopy and angle-resolved photoelectron spectroscopy of phase change materials	condensed matter physics	Dr. Marcus Liebmann II.Phys.Inst.B, RWTH Prof. Markus Morgenstern II.Phys.Inst.B, RWTH
A4	E	Local confinement of switching filaments in transition metal oxides in electrical, chemical, mechanical and thermal gradients	solid state physics, electronic materials	Prof. Kristof Szot PGI-7, FZJ
A5		High-temperature, high-pressure structural and thermodynamic properties of chalcogenides and low-valent transition-metal oxides	computational chemistry, crystallography	Prof. Richard Dronskowski IAC, RWTH Dr. Karen Friese PGI-4 and JCNS-2, FZJ
A6	E	Resistive switching of amorphous, non-stoichiometric oxide films	physical chemistry of solids and surfaces	Prof. Manfred Martin IPC, RWTH

Topical area B: Kinetics and switching speed

Project	Status	Title	Research area	Project leader(s)
B1		Fast transient electrical analysis	solid state physics, materials science, electrical engineering	Dr. Ulrich Böttger IWE2, RWTH Dr. Stephan Menzel PGI-7, FZJ Dr. Martin Salinga I.Phys.Inst.1A, RWTH
B2		Electrocolouration: The electroformation process made visible	materials science, crystallography, crystal growth	Prof. Georg Roth Inst. f. Kristallographie Prof. Rainer Waser IWE2, RWTH
B3		Resistive switching in complex oxides: direct investigations of ion transport	physical chemistry of solids and surfaces	Prof. Dr. Roger A. De Souza IPC, RWTH Dr. Susanne Hoffmann-Eifert PGI-7, FZJ
B4		Exploring the relationship between bonding and structure as well as its effect on defects and kinetics	experimental and computational solid state physics, materials science, thin films	Prof. Riccardo Mazzarello Inst.f.Theor.FkPhys., RWTH Prof. Matthias Wuttig I.Phys.Inst.1A, RWTH
B5		Investigating the influence of defects on charge carrier properties in resistive switching with near-field optical microscopy and spectroscopy	condensed matter physics	Prof. Thomas Taubner I.Phys.Inst.1A, RWTH
B6		Electronic structure and phase formation in resistive memory materials	electronic structures, microspectroscopy	Prof. Claus M. Schneider PGI-6, FZJ
B7		Continuum modelling of phase formation	materials science, simulation of phase transformation	Dr. Markus Apel Access ce.V. Aachen Dr. Efim Brener PGI-2, FZJ
B8		Theory and modeling of valence-change based resistive switching	solid state physics (theory)	Prof. Stefan Blügel PGI-1 and IAS-1 FZJ Prof. Christoph Jungemann ITHE, RWTH Dr. Marjana Ležaić PGI-1 and IAS-1, FZJ
B9		<i>In situ</i> transmission electron microscopy of resistive switching devices	solid state physics, phase transformations	Prof. Rafal E. Dunin-Borkowski ER-C and PGI-5, FZJ
B10		Resistive switching mechanism in Mott oxide insulators	condensed matter physics, materials science, electrical engineering	Dr. Dirk J. Wouters IWE2, RWTH

Topical area C: Device technology and scalability

Project	Status	Title	Research area	Project leader(s), institution(s), location(s)
C1		Size effects on the phase stability and switching properties of chemically synthesized HfO ₂ and Sb-based phase change nanoparticles	nanoparticles, metal oxides, chalcogenides, electrical measurements	Prof. Ulrich Simon IAC, RWTH
C2		Defect engineering and scaling of resistively switching oxide thin films	solid state physics, thin films	Prof. Regina Dittmann PGI-7, FZJ
C3		Self-assembled phase-change nanowires	solid state physics, thin films	Dr. Hilde Hardtdegen PGI-9, FZJ
C4		Effects of nanoscale confinement on the properties of phase change materials	solid state physics, materials science, device fabrication	Dr. Martin Salinga I.Phys.Inst.IA, RWTH
C5	E	Highly textured phase change nanostructures for low power devices	solid state physics, thin films	Dr. Hilde Hardtdegen PGI-9, FZJ Dr. Peter Jost I.Phys.Inst.IA, RWTH
C6		Growth, structure and switching of phase change materials in reduced dimensions	Growth, structure and switching of phase change materials in reduced dimensions	Dr. Oana Cojocaru- Mirédin I.Phys.Inst.IA, RWTH Prof. Matthias Wuttig I.Phys.Inst.1A, RWTH
C7	N	Atomic scale imaging and manipulation of transition metal Oxides	physical chemistry of solids and surfaces	Dr. Sylvia Karthäuser PGI-7, FZJ
C8	N	Study of localized defects in phase change materials and oxides with atom probe tomography and correlative microscopy	solid state physics, nanocharacterization, defects	Dr. Oana Cojocaru- Mirédin I.Phys.Inst.IA, RWTH

Cross-topical projects

Project	Status	Title	Research area	Project leader(s), institution(s), location(s)
Z1	E	Integration and nanopatterin techniques	solid state physics, thin films	Prof. Detlev Grützmacher PGI-9, FZJ Prof. Larissa Juschkin Fraunhofer ILT, Aachen
Z2		Characterization of atomistic and electronic structures with ultra-highresolution TEM	Materials science, condensed matter physics, electron microscopy	Prof. Chunlin L. Jia PGI-5 and ER-C, FZJ Prof. Joachim Mayer GFE, RWTH and ER-C, FZJ
Z4	N	Nanoscale technology platform for ReRAM and PCM devices	solid state physics, materials science, and electrical engineering	Dr. Vikas Rana PGI-7, FZJ Dr. Dirk J. Wouters IWE2, RWTH
MGK		Integrated Research Training Group		Dr. Oana Cojocaru-Mirédin I.Phys.Inst.IA, RWTH Prof. Joachim Mayer GFE, RWTH and ER-C, FZJ
Ö		NanoScienceOpen: Bringing nanoswitches to the public and the nature of science to pupils	physics education	Dr. Ralf Detemple I.Phys.Inst.IA, RWTH Prof. Heidrun Heinke I.Phys.Inst.IA, RWTH
Z		Central tasks of the Collaborative Research Center		Prof. Matthias Wuttig I.Phys.Inst.1A, RWTH

Transfer project

Project	Status	Title	Research area	Project leader(s), institution(s), location(s)
T1	N	Failure mechanism and reliability of valence change memories	solid state physics, material science, electrical engineering	Dr. Stephan Menzel PGI-7, FZJ Prof. Rainer Waser IWE2, RWTH

4 Research Achievements of the CRC

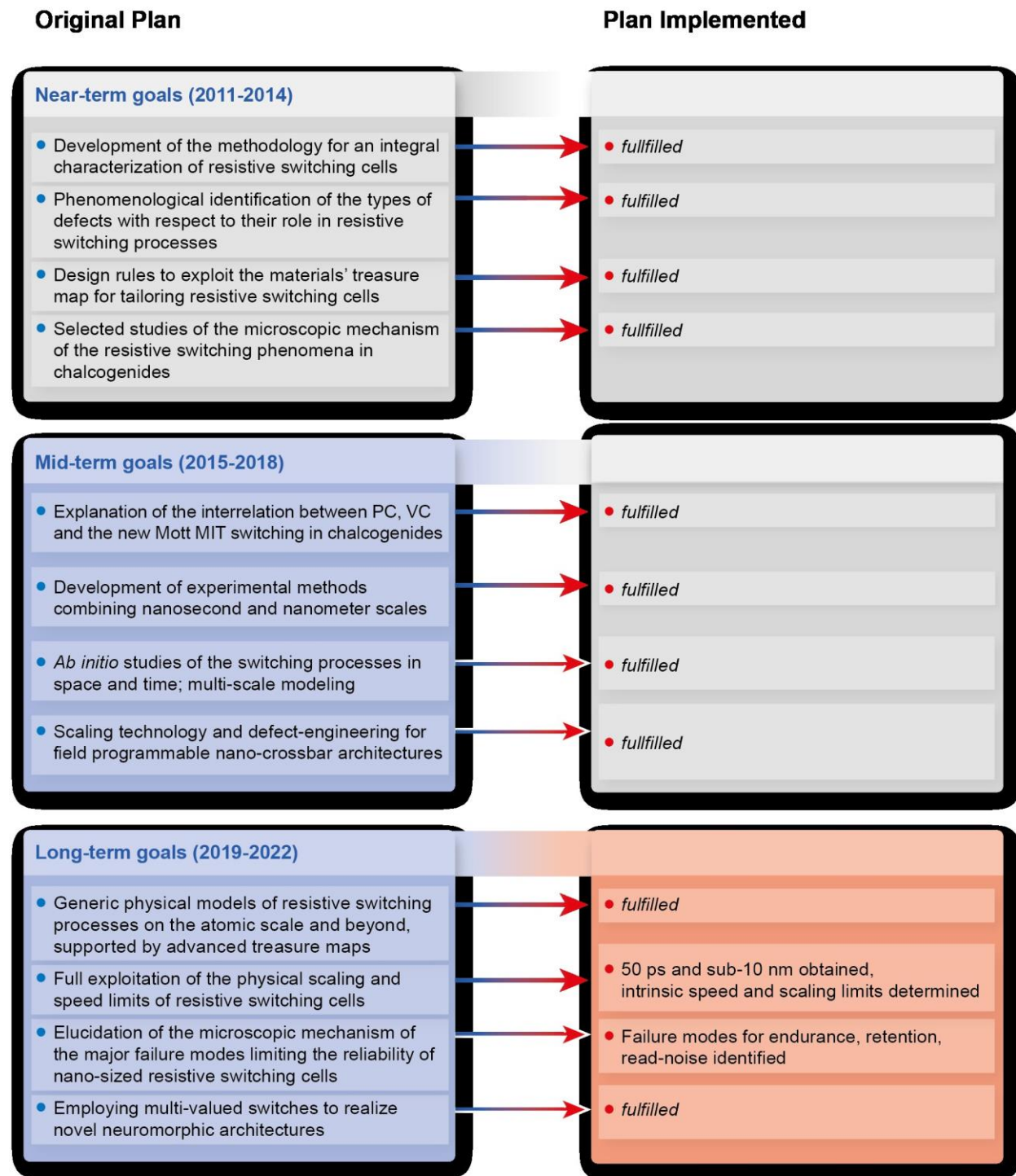


Figure 2: Comparing our original research plan and its implementation.

SFB 917 set itself ambitious goals at the start of the project. To develop and make resistively switching chalcogenides available for future electronics a number of demanding goals had to be identified. These goals for the whole 12 years are summarized in Figure 2. To our satisfaction, the vast majority of goals, even the most demanding ones, identified in 2011 have been met by 2023. This is described in detail in the reports of the different projects. In the third funding period we have explored the ultimate limits of resistive nano-switches in

terms of reliability, scaling and speed. Selected highlights are presented in the following to demonstrate to the public some of the main accomplishments of SFB 917.

As one of the long-term goals we have promised generic physical models of the resistive switching processes on the atomic scale supported by advanced treasure maps. In the following, we briefly outline how we have achieved this goal for one of these classes of switching processes. Phase-change materials (PCMs) exhibit an uncommon contrast between their crystalline and amorphous phases, which makes them promising candidates for new storage-class memory materials. While they have traditionally been used in optical data storage [1], they recently gained profound interest for electronic memory applications, too [2]. PCMs can be rapidly switched between the amorphous and crystalline state. In conjunction with the pronounced property change upon crystallization, they can be employed in data storage and beyond. Presently they constitute one of the most promising variants of a storage class memory featuring characteristics between the fast, yet volatile storage solutions and the slower, but non-volatile Flash memory [3,4]. Interestingly, PCMs are also characterized by rather unconventional properties in the crystalline state, such as an unusual atomic arrangement; rather soft, anharmonic bonds; a high Born effective charge (a measure of chemical bond polarizability) as well as a strong optical absorption in the near infra-red. Early on, we had the suspicion that concepts of chemical bonding might hold the key to understand these properties. While this idea appears obvious in hindsight, it was difficult to implement [5,6]. Thus, one of the PIs in our SFB (Prof. Dronskowski) and his team developed a program suite to quantify chemical bonding in solids relying on orbital-based calculations, which is available to the public [7]. For us, this is a major accomplishment for several reasons. This program suite enables a precise quantification of chemical bonds in solids and hence allows to build a bridge between chemical bonds and physical properties. Equally important, the results of this program can be compared with the results of density-based calculations as done for example in another group in A1. This comparison eventually provides both similarities and dissimilarities. It provides further credit for the chosen strategy to quantify bonds and correlate the corresponding quantum chemical bonding descriptors to physical properties.

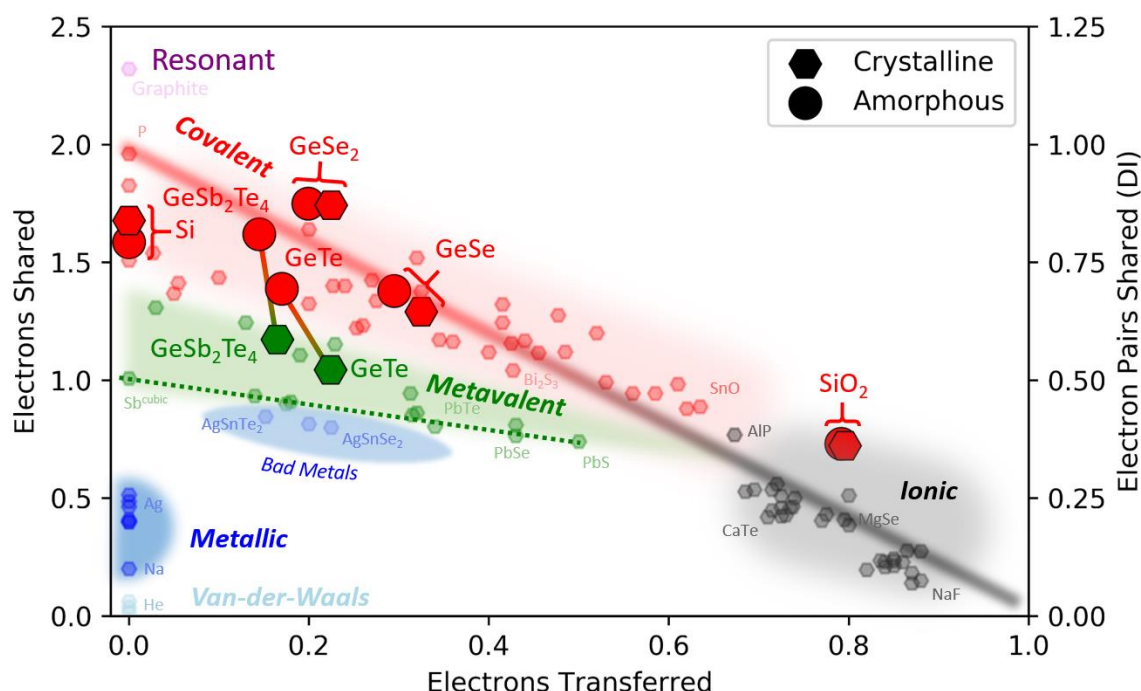


Figure 3. 2D map classifying chemical bonding in crystals and glasses. The map is spanned by the number of electrons shared (Left y-axis) between adjacent atoms and the electron transfer renormalized by the formal oxidation state (x-axis). Different colors characterize different material properties and have been related to different types of bonds. The glasses of three solids are characterized by a bonding mechanism which closely resembles the crystal (GeSe_2 , SiO_2 , and GeSe). On the contrary, for GeTe , Sb_2Te_3 , and GeSb_2Te_4 , pronounced property changes occur upon crystallization. While crystalline GeTe , Sb_2Te_3 , and GeSb_2Te_4 have been phrased as metavalent solids, their glasses are covalently bonded. Metavalent crystals show characteristic features of quantum materials, i.e., they show a pronounced change of properties upon external stimuli like pressure or temperature-[8].

With both program suites similar maps, yet different interpretations are obtained (as discussed in more detail in A1). Interestingly, crystalline phase change materials are all located in a peculiar region of the map located between covalent and metallic solids. Hence, it has been suggested to denote these crystals as incipient metals. Within project A1, a large range of activities by both PIs has been devoted to characterize the bonding in these crystalline chalcogenides. Yet, to understand phase change materials, we also need to understand

the difference between the glass (amorphous phase) and the crystalline phase, both in terms of their atomic arrangement, properties and bonding. Figure 3 shows that the chemical bonding descriptors in phase change materials like GeTe, Sb₂Te₃ and GeSb₂Te₄ change significantly upon crystallization [8]. This finding helps to understand the observed property contrast which is employed in applications of phase change materials. It also explains where to find suitable solids which change their properties upon crystallization. This is the green area of figure 3. Hence, we can now offer a recipe how to locate possible phase change materials.

While this is helpful information, for applications it is even more important to understand property trends within the region of so-called metavalent solids. In particular, it is crucial to know how the most relevant characteristics of PCMs change with stoichiometry. This question has been answered together with American semiconductor manufacturer Micron, for whom the answer obtained is particularly important [9]. Figure 4 shows the crystallization of 5 different amorphous PCMs. Striking differences in crystallization speed are observed, which differs by several orders of magnitude. Interestingly, not only the crystallization speed differs significantly, but also the stochasticity. While Ge₂Sb₂Te₅ and Ge₃Sn₂Te₅ crystallize very rapidly and reproducibly, this is not the case for AIST and Ge₂SeTe which crystallizes much more slowly and stochastically.

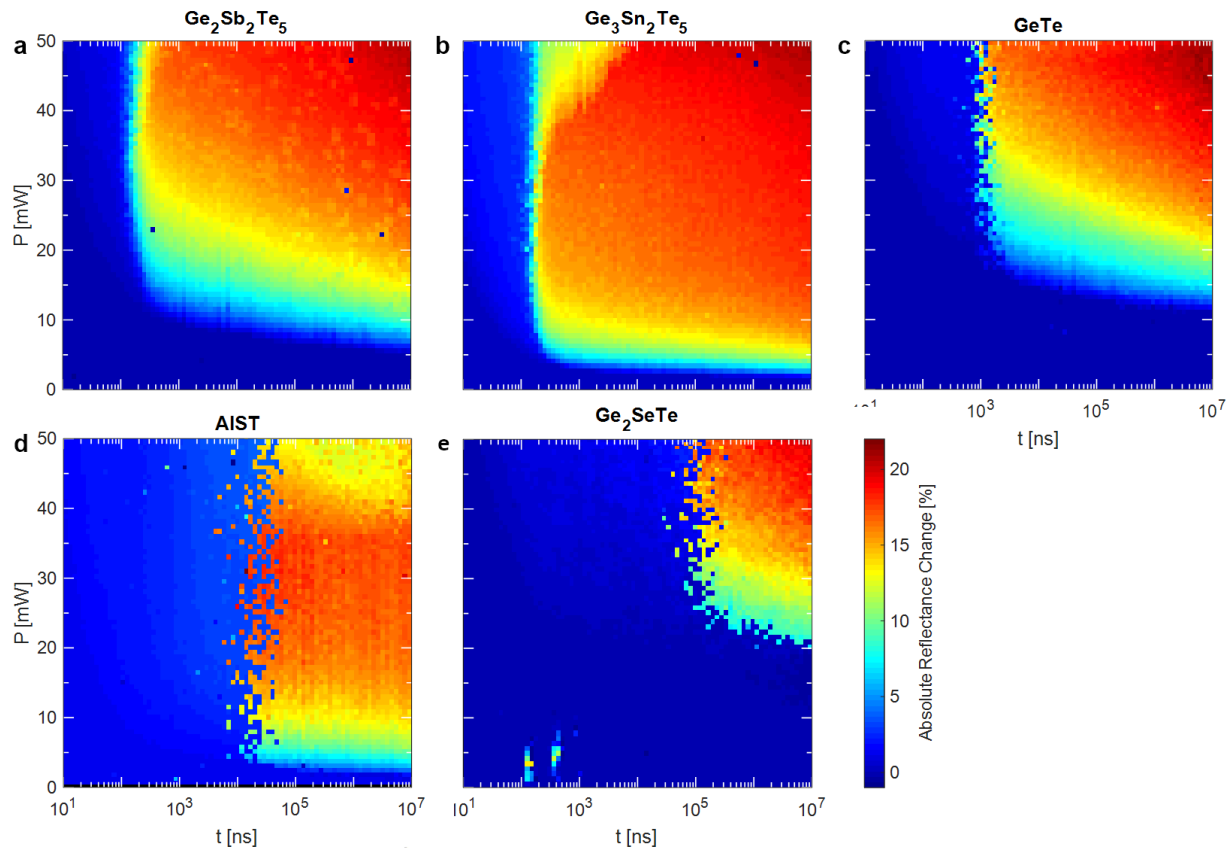


Figure 4. Power-Time-Effect (PTE) diagrams for five different phase change materials: Ge₂Sb₂Te₅ (a), Ge₃Sn₂Te₅ (b), GeTe (c), AIST (d) and Ge₂SeTe (e). Crystallization of the materials leads to a significant increase in reflectance. All materials exhibit a vertical edge, implying that the crystallization speed which results from the combination of nucleation rate and growth velocity is independent of applied power. Significant differences in the minimum time (pulse length) needed to crystallize as well as the stochasticity of this process are observed for the five different materials. The two spots of reflectance change observed for Ge₂SeTe at very low powers and very short pulses can be attributed to local impurities on the sample surface since they are also already observable before the crystallization laser pulse. These impurities seem to be affected already at low pulse powers [9].

This raises two interesting questions. How can the difference in crystallization speed and stochasticity be explained and which stoichiometry trends can be identified? The latter question has been answered together with Micron [10] and is presented in more detail in B4. In summary, the fastest materials are located close to the dashed green line and have significant electron transfer. Such materials are also particularly bad glass formers. To explain this trend, we have determined the mechanism of crystallization decoupling nucleation and growth processes performing experiments which combine nanosecond temporal resolution and several nanometer spatial resolution [10]. These experiments reveal that the pronounced differences in crystallization are due to differences in nucleation rate, while the growth rate hardly differs for the five different compounds.

Interestingly, these changes can be attributed to differences in the bonding of the crystalline phase. This conclusion is also supported by our multiscale simulation of crystallization, confirming that with our understanding we have also reached the goal of multi-scale modeling [10].

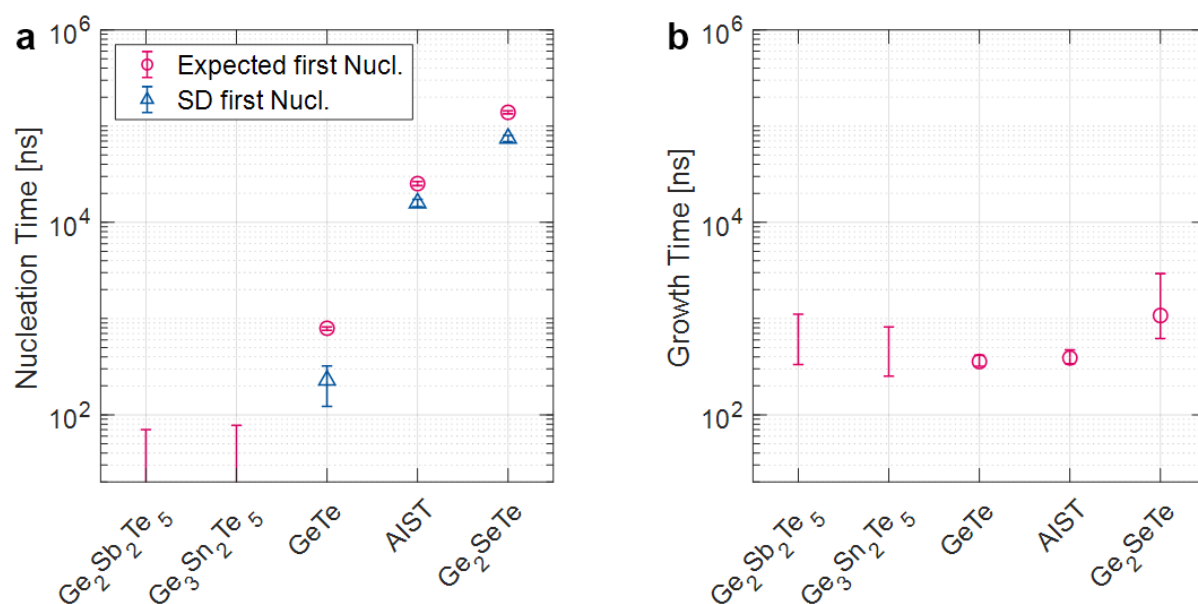


Figure 5: (a) Time required for the first nucleation event for different phase change materials. A significant stoichiometry dependence is observed. For slow-nucleation materials, the standard deviation for the probability distribution is given as well. (b) Growth time for all materials, showing only a marginal dependence on stoichiometry [10].

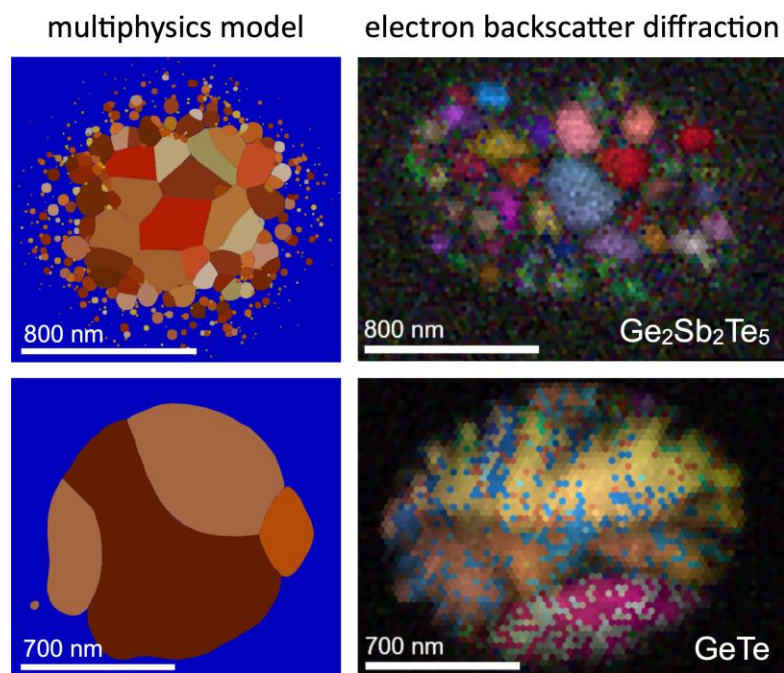


Figure 6: Simulation of nucleation and growth and comparison with data obtained by electron back scattering for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe . Good agreement between experiment and simulation is reached, showing the high nucleation rate in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ [10].

The findings presented above have motivated us to look for techniques which can verify the change of the electronic structure upon crystallization on a nanometer length scale. Please keep in mind that the experiments obtained to get the data in figure 5 and 6 were obtained on a length scale of several 10 nanometers. Unexpectedly, we have noticed that atom probe tomography provides this information. The principle of atom probe tomography is depicted in figure 7. A large electrical field is applied to a sharp tip, creating a large electrical field at its apex. Upon excitation with a short laser pulse fragments (atoms and molecules) can be ejected from this tip. Two different processes can be distinguished upon bond rupture. Depending on the solid investigated, a certain fraction of fragments are molecules, instead of atoms. This is denoted as the material specific probability to form molecular ions (PMI). A second characteristic is the probability of multiple events (PME), which characterizes the probability that more than one fragment is formed at the apex of the tip upon bond rupture.

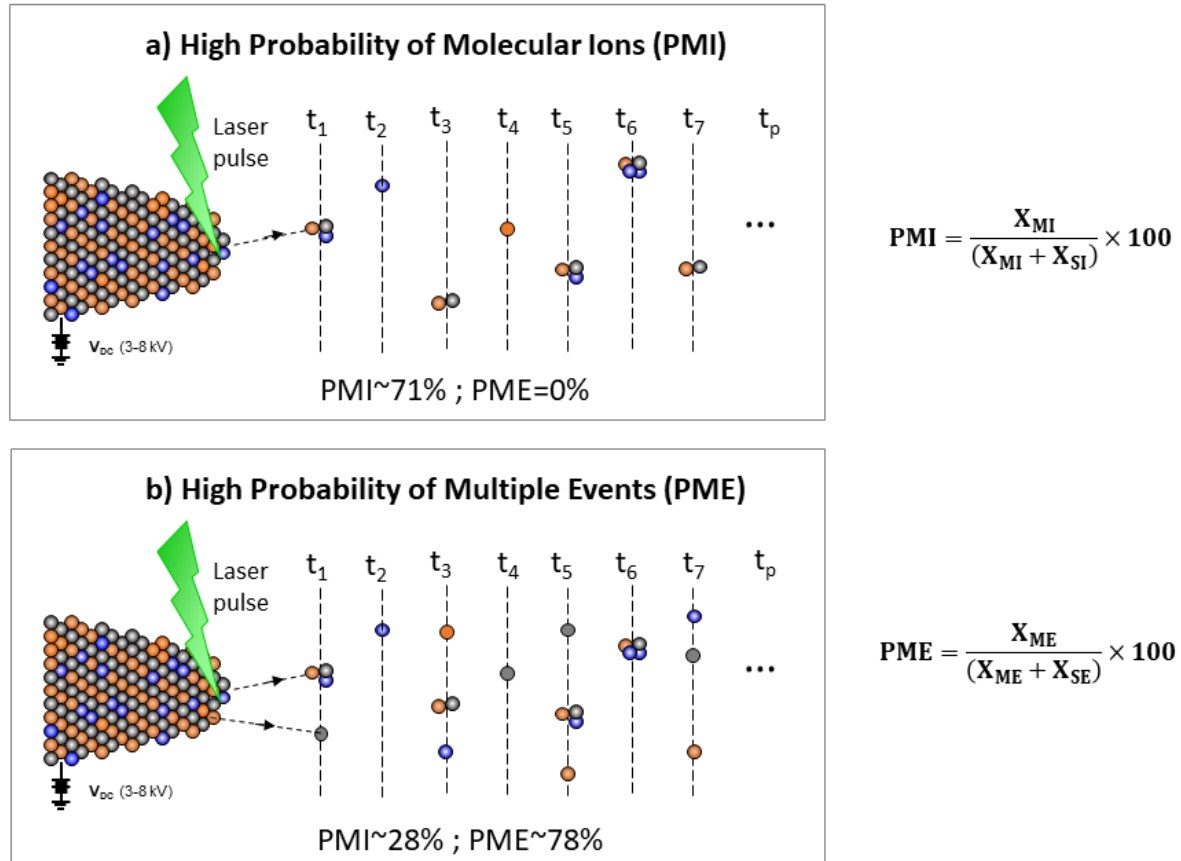


Figure 7. Graphic presentation of the “Probability of Molecular Ions” (PMI) and the Probability of Multiple Events” (PME). Sketch of a bond-breaking experiment for a sequence of successful pulses (pulses for which one or several events took place) exhibiting a) high PMI as well as b) high PME. SI stands for an ion which consists of a single ion, while SE stands for a single event (fragment) to be dislodged upon bond rupture.

With these two quantities, it can be proven that multivalent solids have a unique bond rupture as shown in figure 8, which differentiates them from ordinary two-electron two-center covalent and also metallic solids, a striking observation indeed. While this confirms our conclusion about the unconventional bonding in crystalline phase change materials, it even enables a more inference. As shown in figure 8, the bond rupture in ordinary solids like Si and GeSe does not change upon crystallization, while this is different from the three phase change materials studied so far in both phases, confirming that the electronic structure in these materials indeed changes upon crystallization. This finding offers exciting possibilities to study crystallization in phase change materials where the subcritical nuclei which initiate nucleation are in the nanometer range. On this length scale, atom probe tomography can determine the PMI and PME (figure 8) as well as the stoichiometry in the nucleus. We can hence determine if nucleation of a glass is linked to changes in bonding and stoichiometry on a nanometer scale, an exciting prospect indeed.

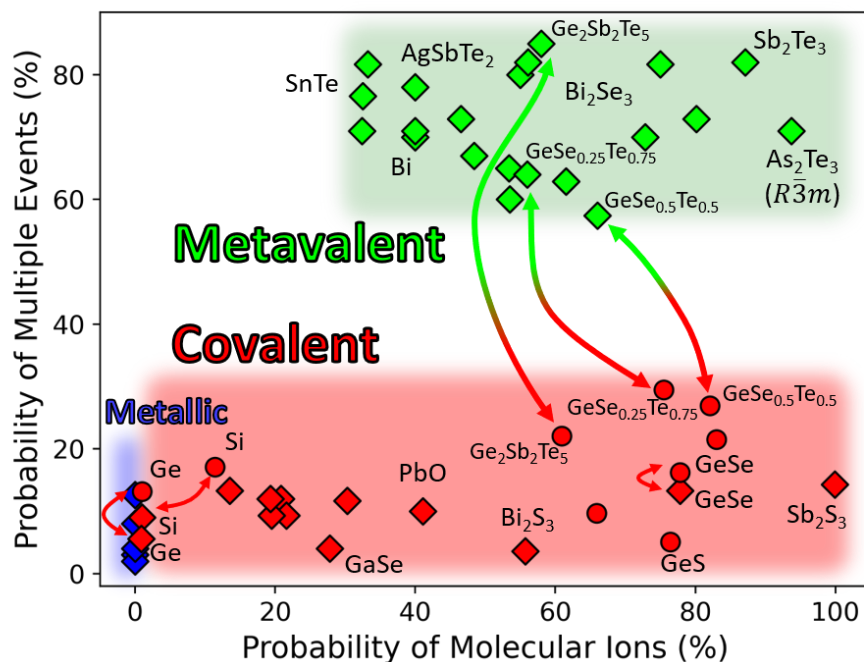


Figure 8: Changes of bond rupture upon crystallization (arrows). Crystals are characterized by diamonds, glasses by circles. We employ two parameters (PMI and PME) to quantify the bond rupture in atom probe tomography [11].

Main achievements resistively switching oxides:

Design rules and predictable models

At the starting date of the SFB, memristive oxides were an emerging field of research. The SFB researchers pioneered the idea that the basic mechanism of the process is based on the movement of oxygen vacancies.[12] However, direct experimental proof which provides quantitative information of the spatial distribution of oxygen vacancies and its changes during switching was missing at that time. Within the SFB, we developed a platform of methods for *operando* analysis of memristive valence change memory (VCM) devices by a large variety of different techniques available within the SFB consortium (see figure 9). This provided us with complementary information about the defect density, the composition and the electronic structure on different length scales, in bulk and surface-near regions and enabled us to develop quantitative models of the switching and failure mechanism of VCM devices. While these methods have been used to understand the VCM model system SrTiO_3 in the first periods of the SFB, **this universal toolbox** has been applied to a large variety of materials including **industrial relevant materials such as TiO_2 , Ta_2O_5 and HfO_2 .**

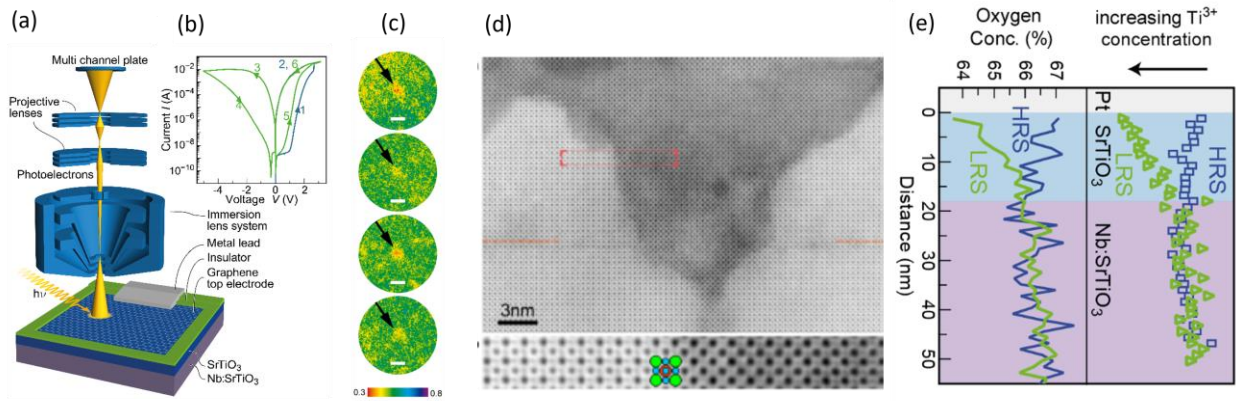


Figure 9: (a) Device and measurement setup schematic for operando PEEM measurement with graphene electrodes. (b) Forming step (blue line) and following reset-set (green line) operation for a STO device with graphene top electrode. (c) PEEM images of the switching filament (indicated by the black arrows) in the LRS 1, HRS 1, LRS 2, HRS 2 (top to bottom) for a photon energy of 531.6 eV. Scale bars are 1 μm . [13] (d) High-resolution ABF of an area across the boundary between the film matrix and the largest filament. The lines denote the interface between the film and the substrate. Bottom: Magnified part of the ABF image marked in red. Atomic columns are indicated by the projected unit cell of SrTiO₃ (Sr: green, Ti: red, O: blue). [14] (e) EELS analysis during in situ switching experiment in the TEM: Upper panel: Intensity of the L₃ edge as a function of depth into the specimen for the LRS and HRS to a depth of 55 nm into the device. Lower panel: Oxygen concentration profiles acquired by integrating the oxygen EELS edge for the same region in the HRS and LRS.[15]

Complemented by simulations of defect chemistry (B3), electronic and ionic transport (B1, B3 and B8), we have gained a detailed, quantitative understanding of the switching processes of VCM cells and their kinetics. In particular, we gain quantitative numbers of the oxygen vacancy concentration upon biasing and used these numbers as input for device simulations [14] (see figure 9). The strong chemical and thermal interaction between the switching oxide, the electrodes and possible interfacial layers **has led to a strategy for the rational design of VCM cells based on the stacking of layers with tailored defect formation energies, ionic, electronic and thermal conductivity** [16]. Based on this concept, we have been able to increase the switching speed by up to 3 orders of magnitude (A. Sarantopoulos under review) [17,18] or avoid retention failure [19].

During the runtime of the SFB, the consortium (A1, B1, B8) **has developed simulation models for resistive switching devices to the scientific community which are available for the public at <https://www.emrl.de/JART.html>**. The focus of this dissemination activity is on compact models which even comprise variability and read-out disturb for use by circuit designers or device engineers, which is particularly important for neuromorphic circuits.

Approaching the speed and scaling limits

In order to investigate the ultimate time limits for the switching speed, we developed within project B1 an automated electrical characterization system for measurements in the sub-100 ps regime (Fig. 10 (a),(b)). This enabled us to establish **a new speed record by demonstrating for the first time SET transitions down to 50 ps** [20] (see Fig. 10(b)). It is important to note that 50 ps is not an intrinsic switching speed limit but caused by the electrical charging time of the device [21]. By further scaling the devices, faster switching (20 ps) is possible as demonstrated later by a different group [22]. This is an important trend as our simulation also predicts that device scaling will increase switching speed from the point of view of thermal acceleration.[23]

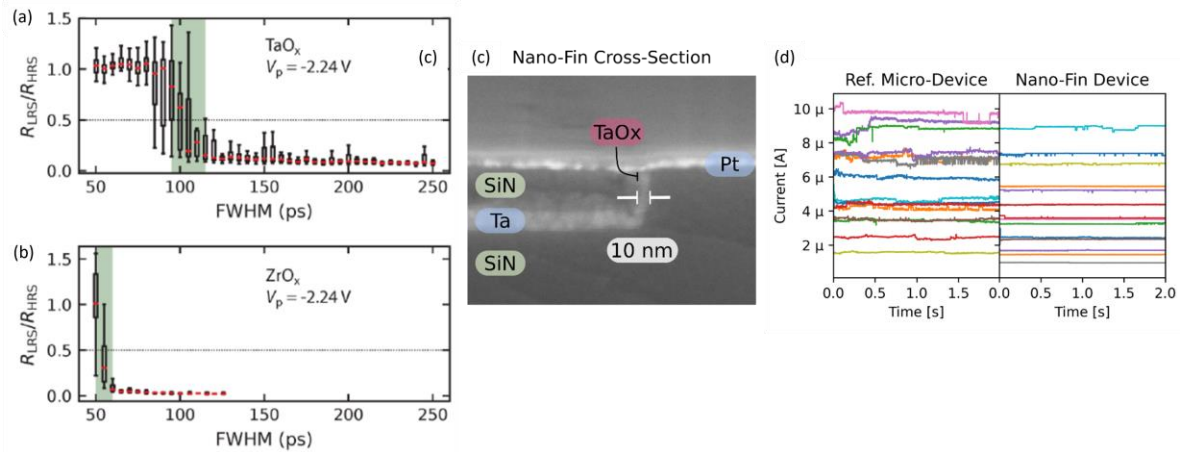


Fig. 10: Boxplots of the ratio R_{LRS}/R_{HRS} at different pulse widths for TaOx (a) and the ZrOx device (b). The green shaded area indicates the determined transition time. Reproduced from (b) (c) (d) (c) Cross-section of the oxide nano-fin device; (d) Noise improvement for the confined filament (right) compared with a reference micro-device (left) with unscaled oxide volume. Adapted from reference [24]

In order to approach the scaling limits of VCM devices we successfully **fabricated sub-nm HfO₂ nanoparticles (C1) and nanoislands (C7)** and characterised their electrical properties by nanogap-electrodes and scanning probe microscopy, respectively [25, 26]. From these investigations, we gained a deep understanding of the role of moisture, carbon contaminations, oxygen vacancies and grain boundaries on the current transport and the forming voltages of ultra-scaled HfO₂ devices.

In order to investigate the impact of scaling on the device performance of integrated devices, we introduced a device design that laterally confines the *switching oxide volume* and thus the filament to **10 nm** (Z4). Using this concept, a TaO₂-oxide based nano-fin device was fabricated (see fig. 10(c)). A comprehensive full factorial measurement approach, with >100,000 modulated current-voltage sweeps demonstrated a 50 % reduction in the write-variability for the oxide nano-fin device compared to a standard large oxide-volume device. Additionally, ionic noise measurements indicate an improvement in filament resistance stability against diffusive processes, as evidenced by higher signal-to-noise ratios for the confined filament (see fig. 10(d)). Kinetic Monte Carlo simulations support our empirical observation for confined filaments and promise further improvements by full lateral filament confinement, which we implement with our oxide nano-pillar device design (Patent filed: Stasner et al., DE10 2023 110 363.6, 24.04.2023). **The results set a new direction for memristive device optimization, extending beyond traditional electrode scaling to address the oxide volume and its immediate lateral surroundings.**

An important international development during the course of the SFB was the start of mass production of Ta₂O₅-based memristive cells for embedded non-volatile memory by Samsung in 2014. On the way to the commercial application of filamentary ReRAM, we have included the T1 project with Infineon Technologies to **address all relevant reliability aspects**. Besides characterizing the intrinsic variability of filamentary ReRAM, the long-term stability (retention) has been experimentally investigated on 2.5 Mbit of 28 nm integrated ReRAM devices and modelled for physical understanding [27] and for extrapolation [28]. Furthermore, the endurance has been measured for 2 Mbit ReRAM, showing no terminal device failures. Nevertheless, the study revealed a rare failure mechanism where the RESET process fails (temporarily) which could be understood via Kinetic Monte Carlo (KMC) modelling [29]. Finally, with the **AURIX™ TC4x product family for automotive applications**, Infineon Technologies announced a commercial product based on the ReRAM technology studied in the collaboration in the framework of T1 (<https://www.infineon.com/cms/de/about-infineon/press/market-news/2022/INFATV202211-031.html>).

Accomplishments through interdisciplinary research.

One key goal of this project was an in-depth understanding of the materials which can be employed in small and fast nano-switches. This goal has been reached for oxides as well as higher chalcogenides and has enabled us to produce treasure maps, which help us to understand, explain and predict even unconventional material properties. These successes would have been impossible if we would not have managed to closely interact across diverse disciplines encompassing material science, chemistry, physics and electrical engineering. We now utilize the concepts developed, for example to tailor chalcogenide based thermoelectrics, or plasmonic phase change materials which can be directly written, enabling active metasurfaces. This possibility is

now developed further with scientists from mechanical engineers which plan to realize novel applications with this functionality.

Within the SFB, we developed a platform of methods for *operando* analysis of memristive devices by different techniques such as soft X-ray photoemission electron microscopy (PEEM) (cooperation with B6), scanning near-field optical microscopy (B5), transmission X-ray microscopy (TXM) and transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) (cooperation with B9). This large variety of techniques provided by the different disciplines within the SFB consortium, combined with the multi-scale simulations performed in B8 have been crucial for the elucidation of the switching and failure mechanisms in VCM devices. This would have been impossible without the joint interdisciplinary effort of the SFB.

New developments / Neuromorphic computing

Nevertheless, the most obvious development came from yet another area. In addition to the use of memristive devices for digital non-volatile memory, there has been increasing interest in the possibility of stabilising multiple resistance states and operating the memristive devices in a quasi-analogue manner, as this will allow memristive devices to be used as hardware representations of synapses in neural networks. Within the SFB (B1, B3), we could clarify the impact of the switching kinetics on the abrupt SET process in filamentary devices [30,31]. In particular, we have shown that thermal runaway is responsible for the sharp SET process that prevents analogue operation. We have developed ways to suppress the runaway, either by restricting the bias regime or by using non-filamentary devices (A1) based on a purely field-driven switching process [32-34].

By now, neuromorphic computing is one of the key research areas of the university and also a major research topic in the Research Center Jülich within the Helmholtz program "Information". In 2019 we have started the Strukturwandel project "NEUROTEC" funded by the BMBF. The goal was to establish memristive devices (VCM, PCM) for the use in novel energy-efficient hardware for future artificial intelligence (AI). The project was prolonged for 5 additional years in 2021 and currently memristive devices are co-integrated with CMOS circuits to demonstrate their use on a system level. These activities are complemented by the BMBF Zukunftscluster "Neurosys", that fosters the interdisciplinary activities (physics, Computer science, electrical engineering, neuroscience) of RWTH Aachen, Research Center Jülich, AMO and local industry partners with respect to future autonomous AI systems.

We are convinced that these developments would not have been possible without SFB 917.

On a national level, parts of the SFB consortium have initiated the Priority Programme SPP 2262 "Memristec", which is funded by the DFG since 2020 and aims at the development of memristive technical systems for industrial applications. Several of the SFB's Principal Investigators are involved in joint projects with other German groups developing new computing or sensor systems based on memristive devices.

Another area of activity that emerged from SFB 917 is the use of memristive devices in optical neural networks. Research on the use of PCMs as phase shifters for reconfigurable optoelectronic networks is included in NeuroSys as well as in the SFB 1459 "Intelligent Matter" led by former SFB 917 participant Martin Salinga.

The optical stimulation of transition metal oxides is part of the DFG Research group initiative "Electromagnetic stimulation of ion transport in transition metal oxides to tailor interfacial functional properties". This initiative is led by Roger de Souza and includes 3 other former PIs of the SFB. The aim of this joint initiative is to exploit the optical stimulation of transition metal oxides for optoelectronics, energy storage and energy conversion.

We published all our results in peer-reviewed journals and presented the results on international conferences. That stimulated discussions of the results and critical input on an international level. Moreover, to ensure the validity of our findings we have implemented a number of crucial tests. The most demanding one probably was the test of explainability and more so predictability. Can we explain and predict unconventional properties and phenomena? By now, we have a number of publications, as will be presented in our detail project reports, where such predictions have been verified. We also have developed software, which is available to the general public to quantify bonding in solids.

During the 2019 symposium in Hürth, all project leaders of the collaborative research center (CRC) discussed adopting modern data management practices to enhance the handling of research data generated or processed within the consortium. It was agreed to employ several key methods across various sub-projects, though the success of these implementations remains to be fully assessed.

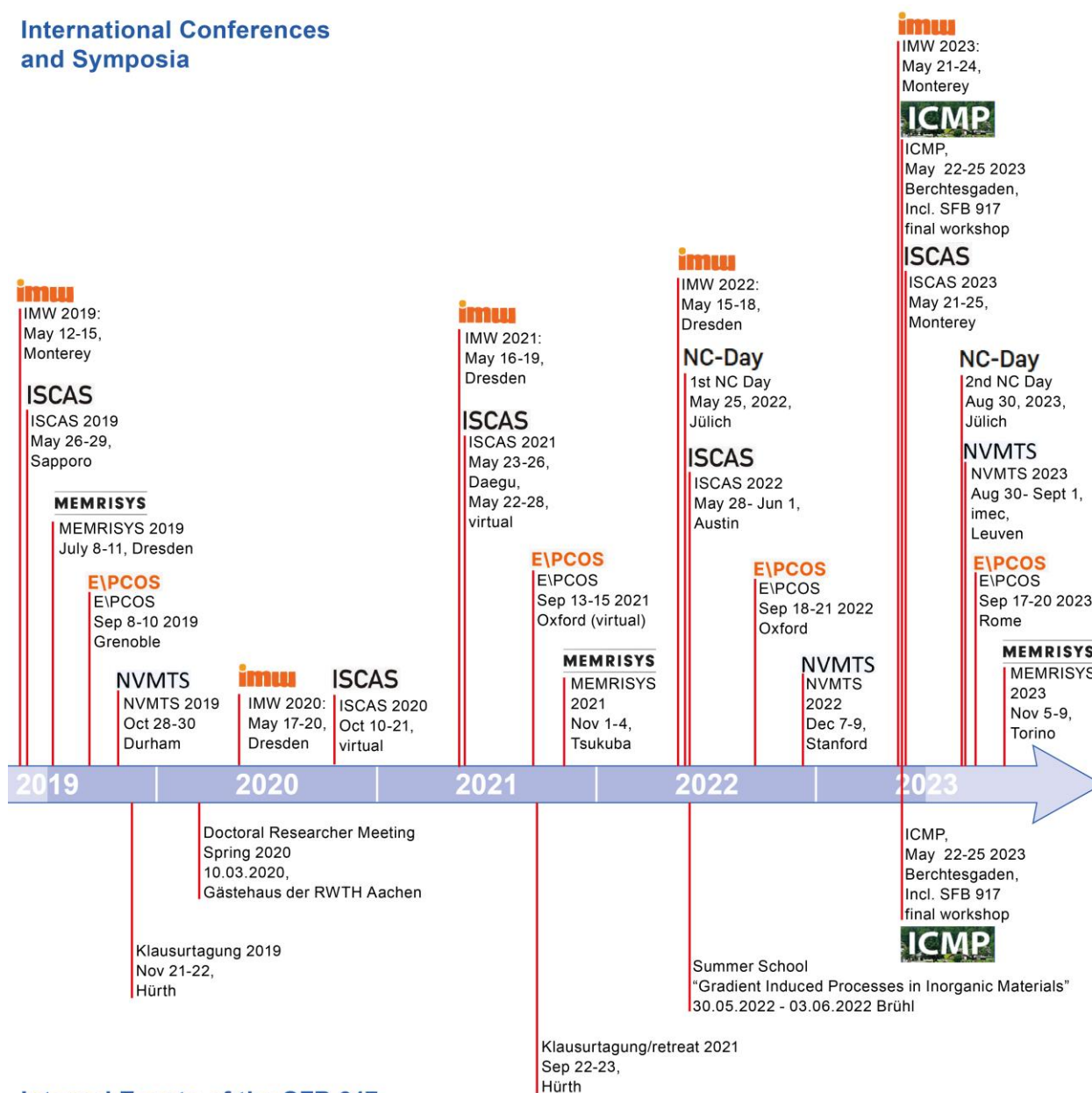
1. **Data Storage and Preservation:** We use robust digital infrastructures for data storage, ensuring both security and longevity. Data is stored in formats that are both accessible and compatible with multiple platforms to facilitate ease of use and interoperability.
2. **Standardization of Data Formats and Metadata:** We have adopted standardized data formats and metadata schemas to enhance data quality and ensure that our datasets are comprehensive and well-documented. This standardization supports the reproducibility of research and enables other researchers to understand and use the data effectively.

3. **Open Access and Sharing Protocols:** Our consortium is committed to open science principles. Research data and associated software are made available through open-access repositories, which are accessible globally. This transparency allows external parties, including researchers and institutions, to access, analyze, and build upon our findings.
4. **Use of Data Management Platforms:** We utilize advanced data management platforms that support the integration, processing, and analysis of data collected from diverse sources. These platforms facilitate collaborative research efforts and enhance the efficiency of data use within the consortium.
5. **Training and Support for Researchers:** To ensure effective use of these data infrastructures, the IT-Center, represented by Mr. Bosse, has offered workshops on data management best practices. This includes providing one-on-one support to address specific data-related challenges.

By employing these methods, our consortium not only aims to enhance the quality and accessibility of research data but also fosters a culture of collaboration and open science. External parties interested in utilizing our data infrastructures can access them via our dedicated online portals, where they can also find detailed documentation and contact information for further inquiries.

4.1 Scientific Event and Science Communication

International Conferences and Symposia



Internal Events of the SFB 917

Figure 10: The different international conferences, workshops and symposia organized or co-organized by SFB 917 as well as internal meetings during the second funding period.

Science Communication Measures:

The science communication measures implemented in this context have focused extensively on engaging both the interested public and the academic community, primarily through the establishment and activities of the educational lab called SClphyLAB_nano. The academic community has been addressed in conferences, the participants of this SFB have given several hundred invited presentations at international conferences, summer schools as well as a high number of publications and press releases.

1. **Educational Lab (SClphyLAB_nano):** This lab was set up during the second period of the Collaborative Research Center (SFB) to facilitate the dissemination of basic scientific principles and methodologies, specifically in the realm of nanoswitches and the nature of scientific work.
2. **Interactive Modules:** Developed in previous funding periods, these modules were designed to help students from grades 8 to 13 understand basic physical principles and the cooperative nature of scientific work. These modules were the primary tools used in the educational lab.
3. **Advanced Equipment Loans:** Equipment such as scanning tunneling microscopes was made available to schools, allowing students to conduct their own project work, thereby deepening their engagement with current research.
4. **Internships and Special Focus Programs:** The lab organized internships for senior students, providing them with first-hand experience in research. Programs targeted at young girls and non-physical science students were also planned, although some were postponed due to the pandemic.

Resonance with Target Communities

1. **High Engagement:** Over 1100 students visited the lab in the last funding period despite challenges posed by the COVID-19 pandemic, demonstrating significant interest and engagement from the target group.
2. **Educational Impact:** A doctoral dissertation by Dr. Fabian Leiß examined the effectiveness of the educational lab in shaping students' perceptions of scientific activities, indicating a positive impact.
3. **Adaptation to Challenges:** Despite the pandemic's disruptions, the project managed to maintain its outreach by adapting its strategies, such as focusing more on bachelor students from non-physical sciences during the pandemic.

University's Internal Communications

1. **Academic Integration:** The project supported a doctoral dissertation and facilitated networking among science communicators nationwide, illustrating strong internal communication and integration within the academic community.
2. **Support for Scientific Exhibitions:** The project extended its outreach by backing scientific exhibitions aimed at the general public, thereby fostering a broader educational environment.

Overall, the measures taken by the SClphyLAB_nano and associated initiatives reflect a comprehensive approach to science communication that effectively engages both targeted educational groups and the broader community. Despite the setbacks due to the pandemic, the programs have shown resilience and adaptability, continuing to make significant educational impacts.

4.2 National and international collaboration

In the last 12 years we have worked together with many other institutions worldwide. Instead of a detailed list (which we have provided in our last two reports), we would like to describe these collaborations from a more strategic perspective. In particular, one can distinguish three types of cooperation:

- a) **Industrial partners:** We have had close contacts with many major industrial players in the semiconductor industry. We are very proud that many of the big international semiconductor device companies have worked with several project leaders of this SFB, even leading to joint products, pap. This list includes Intel, Micron, IBM, Samsung, HK Hynix, Micronix, NXP, ST Micro, AMD, Infineon and many more.
- b) **University partners:** In Germany, Europe, the US and Asia, there are several other universities with a similar research agenda. In the US, one of the largest players is Stanford University, likely due to proximity to the industry in Silicon Valley. We have close contacts to this university, but also to universities and research centres in China (Xian, Shanghai, Beijing, etc.), Korea (Seoul, Yonsei, SKKU, and KAIST), Singapore, and in Europe (Milano, CNRS France, Dresden, Zurich).
- c) **National and International Research Centres,** in particular synchrotron sources. For our research close contact was also necessary with brilliant light sources which help to unravel the functionality of our

materials and devices on short time and small length scales. To this end, we have in part worked with the responsible beamline scientists of the most advanced beamlines in the world, including DESY and XFEL in Hamburg, BESSY in Berlin and SLAC at Stanford.

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5 Impact on Research Priorities and International Visibility

SFB 917 has had significant impact on the research priorities of both RWTH Aachen and Research Center Jülich. It has been seen as a role model for close cooperation between the natural sciences and the engineering sciences, united by the goal to understand and tailor chalcogenide-based nanoswitches. This is the key goal of RWTH Aachen university, which strives to become an integrated, interdisciplinary university. Within SFB 917, we were and still are convinced that chalcogenide-based nanoswitches can play a prominent role as an integral part of the storage hierarchy in modern computers and hand-held devices.

At the same time, members of SFB 917 (relatively) early-on recognized the potential of these devices in neuromorphic computing. For almost 10 years now, Pls of this SFB have approached the rectorate of RWTH Aachen and the Board of Directors of Research Center Jülich to create a research thrust in the area of neuromorphic computing. Such an activity should ideally encompass a broad range of disciplines, ranging from

device-oriented work in material science, chemistry and physics, to system-oriented work in electrical engineering, computer science and the neurosciences. Indeed, it was quite easy to convince both RWTH Aachen and Research Center Jülich to strengthen this research topic. Several new colleagues were hired as full professors to strengthen this research field (Gemmeke, Strachan, Neftci). This has helped to build large teams, which span a wide range of competences ranging from materials science, to electrical engineering, neuroscience and computer science. By now, many of the PIs of this SFB have close interactions with colleagues from computer science and neurosciences. In the last few years, these activities have secured two major funding schemes, NeuroSYS and NeuroTec. Without the strong support of RWTH Aachen and Research Center Jülich in hiring new professors from abroad these successes would not have been feasible. At the same time, it seems fair to say, that these major funding accomplishments would not have been possible without the preliminary work within SFB 917.

SFB 917 had a significant impact on the international visibility and significance of the two host institutions. This can best be shown with the number of invited talks that PIs of this SFB has given in the last 12 years. A very conservative estimate has led to a list of more than 300 such invited talks in Europe and beyond. Also, the number of publications and their citation impact (so far about 25.000 citations) can be described as quite strong as has already been briefly mentioned in chapter 2.

We also believe that the relatively large number of awards received is further evidence for the high visibility of the PIs and their research output. Furthermore, we consider the fact that many major semiconductor manufacturers have and had joint R&D activities with various PIs of SFB 917 in recent years (Infineon, ST Micro, NXP, Micron, Intel, IBM, Samsung and several more) is further evidence for the high visibility and strength of these research activities.

Clearly, key ingredients to promote awareness where publications and presentations of various PIs of this SFB. This has apparently worked very well, as can be seen from the large number of invited presentations and the large number of citations secured so far. In addition, press releases have further helped to increase the national and international visibility. Yet, also other strategies to increase awareness were tested, too. Prof. Dronskowski and team developed a novel DFT-based program suite, which enables quantification of bonding in solids. In Matthias Wuttig's team a new map has been developed, which characterizes bonding in solids and predicts relevant property trends. It is now utilized to design phase change materials, thermoelectrics and other advanced functional materials.