Abschlussbericht zu den in den wettbewerblichen Verfahren der Leibniz-Gemeinschaft geförderten Vorhaben

Titel des Vorhabens: Physics and Control of Defects in Oxide Films

Projektnummer/Aktenzeichen: K211/2016

Executive Summary

Within this project we joined the excellence in materials synthesis, comprehensive materials characterization, and profound knowledge in the field of semiconductor physics that is present at IKZ to establish a new mechanism of resistive switching in $SrTiO_3$. Within the project we established, as the first group worldwide, the growth of phase pure and single crystalline $SrTiO_3$ by MOCVD. The material can be grown with controlled Sr off-stoichiometry up to 20 % and is compensated by Ti antisites. Due to the size mismatch between Sr and Ti these antisites are off center defects that induce ferroelectric polarization and cause a midgap defect. Our electrical measurements show a hysteretic behavior that increases with increasing off-stoichiometry. We measure on-off ratios of up to 10^3 at room temperature and 10^7 at 10 K. The resistive switching occurs above 2 V without a forming step and the on-off ratio increases with increasing voltage. The switching is stable in pulsed measurements and the retention time decreases with decreasing off-stoichiometry. Analytical and *in-situ* TEM measurements show that the dipoles due to the Ti antisites couple and form nanopolar domains under applied voltage. The formation of conductive filaments, often observed to induce resistive switching, is observed in our samples above 7V, i.e., far beyond the range (2-5V) where electrical measurements show resistive switching in our samples. Our studies enabled not only a new state of the art in growth of $SrTiO_3$ by the technological most relevant growth method MOCVD but also established a methodology for *in-situ* TEM to characterize electrically contacted devices in the TEM. The latter will offer us new opportunities to perform fundamental studies in device degradation or of ferroelectric switching mechanisms. As regards MOCVD growth, our achievements within the project trigger attempts in our institute to grow this material on Si substrates, which could make it relevant for integration of oxides into Si technology.

Besides $SrTiO_3$ we studied growth of single crystalline NbO_x layers. While we have been successful in growing Nb_2O_5 by MOCVD, NbO_2 a material known to induce resistive switching by a metal insulator transition can only be grown by pulsed laser deposition. Despite its promises the electrical resistivity of the NbO_2 thin films produced so far has been too low to achieve high on-off switching ratios. Therefore, in this project our aim was to grow NbO_2 films with high electrical resistivity. These films may be used in vertical device structures having a higher integration density compared to lateral devices as well as enabling the usage in memristive crossbar arrays. With the vertical structures, high electric field strengths can be achieved, allowing easy switching between the states. Correlating electrical measurements and TEM investigations we concluded that the conductivity of the as-grown layers is dominated by a percolation conductivity along conductive grain boundaries present in the material. Postgrowth annealing of samples, lead to an increased grain size. Thus, we succeeded to achieve resistivities of up to 945 Ωcm, which is only one magnitude below the reported resistivity value for bulk single crystals. Though we produced optimized material, which has been used to get some fundamental insight into the metal insulator transition in this material, we decided to concentrate on the more promising $SrTiO_3$in the second phase of our project.

The project has been part of the ScienceCampus GraFOx and of the EFRE Application Lab Oxide Electronics. In addition to the personal hired from the project an additional PhD student from GraFOx developing the MOCVD growth of $SrTiO_3$ has been allocated to fulfill the tasks of the project. The EFRE Application Lab provided additional equipment for growth (MOCVD), *in-situ* TEM (electrical biasing holder, fast camera, piezo driven stage) and an additional X-ray diffractometer. The project profited from these investments. All other costs were perfectly inline with the project.

The new switching mechanism that has been discovered within this project have been submitted as a German, European and as an international patent. Within the new strategy of the institute, we will develop the material to a technological level and will measure technological important parameters like switching time, retention time and endurance.

1. Zielerreichung und Umsetzung der Meilensteine

The project had three main missions

1) **Within the first mission, we aimed at a new state of the art in structural perfection of $SrTiO_3$ and Nb_2O_5 by using MOCVD.** MOCVD growth of $SrTiO_3$ was a long-term desire in the field of oxide electronics though challenging. At the beginning of the project corresponding reports are missing completely in literature. In case of NbOx, the growth of single-phase films is particularly challenging by both MOCVD and PLD.
2) **Within the second mission, we aimed at studying electrically active point defects, their influence on the formation of Schottky barriers and their role in the formation of the stable high and low resistive switching states.** The first goal has been to show that we can deliberately adjust the desired electrical conductivity, electron concentration and mobility. Second, we wanted to clarify the nature of the electrically active point defects and determine their concentration. Based on this we aimed at establishing a defect specific model of the conductivity in the oxide films. This in turn had to be considered in conjunction with the Schottky barrier formation at the metal-semiconductor interface and the interplay between the point defects in the semiconductor bulk and the interface defects during resistive switching
3) **The third mission was to study defects at an atomic scale and *in-situ*.** State-of-the-art *in-situ* environmental/electrical biasing and ex-situ aberration corrected transmission electron microscopy, both available at IKZ, had to be applied. We aimed at establishing the microscope as a nanoscopic lab to study (i) the fundamental thermodynamic parameters of intrinsic atomic defects in complex oxides and in binary metal oxide crystals, (ii) kinetics of diffusion, defect clustering as dependent on temperature, atmosphere, and an applied electric field and (iii) the role of atomic defects in the process of resistive switching. High resolution TEM and STEM investigations had to be assisted by respective image simulations based on ab-initio calculated atomic defect models to obtain quantitative results on concentration and spatial distribution of atomic defects.

Ad1) Within mission 1 we achieved the tow main goals, i.e., to set a new state of the art in growth of both $SrTiO_3$ and NbO_x by MOCVD and PLD. The work on NbO_x has been performed by 2 Postdocs, the work on $SrTiO_3$ has been done by 1 PhD student, that was paid by the Science Campus GraFOx and the IKZ and have been assigned to the projects.

NbO_x: Niobium oxides are of technological interest for different potential applications, such as energy storage applications due to their intercalation pseudo capacitance. In addition, niobium oxides can be used as selectors or data storage elements in future nonvolatile memory applications. Fundamental investigations of the properties of niobium oxides are, however, hindered by the availability of materials with sufficient structural perfection.

Nb_2O_5 films. The most thermodynamically stable niobium oxide is niobium pentoxide (Nb_2O_5) which has many different polymorphs. The most important polymorphs are the low-temperature polymorph, T- Nb_2O_5, which has an orthorhombic symmetry with a superstructure, and the high-temperature polymorph, H-Nb2O5, which is the most stable polymorph and has a monoclinic symmetry. Of these two, T-Nb_2O_5 is the most relevant for practical applications, because it can be formed at lower temperatures and exhibits intercalation pseudo capacitance. Unfortunately, the availability of niobium oxides with high structural perfection, such as bulk single crystals or as a single-crystalline layer, is limited, to date. Our aim the project was to obtain high-quality T-Nb_2O_5 films using heteroepitaxial growth. Therefore, we investigated the epitaxial growth of T-Nb_2O_5 on a prototype perovskite oxide, $SrTiO_3$. These materials have a significant difference in crystal structure ($SrTiO_3$ is cubic, whereas T-Nb_2O_5) is orthorhombic. At first, we could show that stable growth conditions can be realized for the epitaxial growth of T-Nb_2O_5 on different $SrTiO_3$(100) and (110) surfaces by means of metal-organic vapor phase epitaxy (MOVPE). We verified that the difference in lattice symmetry of Nb_2O_5 and $SrTiO_3$ results in differently oriented film surfaces and the formation of domains that have the T- Nb_2O_5 c-axis aligned with the $SrTiO_3$<001> in-plane directions. Since the number of domain orientations is four and two for the growth on (100)- and (110)-oriented substrates, respectively, the films on $SrTiO_3$(110) exhibit smoother surfaces then the Nb_2O_5 films on $SrTiO_3$(100)

NbO_2 films. Niobium dioxide (NbO_2) has recently gained increasing interest since it exhibits a metal-insulator transition (MIT) at about 1080 K which can be utilized in devices like optical switches, sensors, transistors, or memory devices. This MIT comes along with a structural phase transition from the low temperature, semiconducting distorted rutile structure to a metallic undistorted rutile structure. A dimerization of the Nb–Nb d-orbitals along the [001] direction in distorted rutile leads to the formation of a bandgap. In this direction, the strongest change in resistivity due to the metal-insulator transition can be observed, making this crystal orientation interesting for device applications. However, the electrical resistivity of the NbO_2 thin films produced so far has been too low to achieve high on-off switching ratios. Therefore, it was our aim in this project to grow NbO_2 films with out-of-plane c-orientation and high electrical resistivity. These films may be used in vertical device structures having a higher integration density compared to lateral devices as well as enabling the usage in memristive crossbar arrays. With the vertical structures, high electric field strengths can be achieved, allowing easy switching between the states.

NbO_2 thin films were grown on MgF_2(001) substrates by pulsed laser deposition (PLD). A post-growth annealing step at 880°C increased the grain size of the NbO_2(001) layers. Furthermore, we showed that the resistivity is correlated to the grain size and is in annealed layers up to two orders of magnitude higher than in the as-grown layers resistivities of up to 945 Ωcm were shown, which is only one magnitude below the reported resistivity value for bulk single crystals. We concluded that the conductivity of the as-grown layers is dominated by a percolation conductivity along conductive grain boundaries. By reducing these conductive channels by enlarging the grains, the conductivity is now dominated by the semiconducting NbO_2 grains, which is a crucial step in the realization of resistive switching devices.

$SrTiO_3$ Within this project the epitaxial growth of strontium titanate (SrTiO3) thin films by liquid delivery-spin metal-organic vapor phase epitaxy (MOVPE) is realized for the first time. During the MOVPE growth process, the Sr and Ti gas phase species can be independently controlled, and high oxygen partial pressures can be achieved. Combined, these enable the growth of stoichiometric, as well as pointedly off-stoichiometric, $SrTiO_3$ thin films with a fully occupied oxygen site. In addition, low defect concentrations are obtained due to the near thermodynamic equilibrium growth conditions as compared to other deposition techniques such as MBE and PLD, which are commonly used. Using precursor solutions of $Sr(tmhd)_2$-tetraglyme and $Ti(OiPr)_2(tmhd)_2$ solved in toluene, phase-pure $SrTiO_3$ thin films were epitaxially grown with vaporization temperatures of T_V = 210°C and substrate temperatures of T_S = 710 °C. The gas phase composition is controlled by the concentration ratio of the precursor solutions $(Sr/Ti)_{liq}$ and led to growth of stoichiometric and off-stoichiometric (Sr-deficient) thin films. This deliberately introduced Sr-deficiency is compensated by Ti ions on the vacant Sr-site (Ti_{Sr} antisite defect) without a remarkable concentration of oxygen vacancies. This characteristic is different to the deficiency compensations in films from pulsed laser deposition (PLD) and molecular beam epitaxy (MBE).

Moreover, the epitaxial growth of smooth and well-ordered $SrTiO_3$ films on various lattice mismatched substrates demonstrated that films with a lattice mismatch in the range of $-1.2 < f < 1.1$ % are grown pseudomorphically with vertical lattice parameters matching calculations for ideal stoichiometric and fully strained thin films. Films with lattice strain beyond this range deviate from the Poisson relation, which is assumed to appear either due to relaxation or TiO_6 octahedron tilt. Furthermore, A-site doping of $SrTiO_3$ with La^{3+} has successfully been performed by using $La(tmhd)_3$ as a third precursor. Electrically conductive thin films with a charge carrier density of $5.5x10^{18}$ cm^{-3} to 4.3 10^{20} cm^{-3} with a Hall mobility ranging from 2.0 $cm^2(Vs)^{-1}$ to 0.6 $cm^2(Vs)^{-1}$ were achieved. In this charge carrier density range, Seebeck coefficients in the range of 260 V/K to 550 V/K are determined, which is like values observed in MBE films and single crystals.

Ad 2) Within this mission the impact of crystal defects on the resistive switching materials $SrTiO_3$ and NbO_2 has been investigated. The work on electrical properties of NbOx and SrTiO3 has been performed by a PhD student paid through the project and the IKZ in its last year. The thesis has been defended at HU Berlin 2021.

In the first part of the project, NbO_2 (001) thin films were studied. As described above, NbO_2 is a material that exhibits an insulator-metal transition, which can be induced thermally at 1080 K, or by external electric fields at room-temperature. So far, resistivities measured for NbO_2 thin films in the insulating phase are by a factor of 200 lower than the 10 kΩ cm resistivity measured in NbO_2 single crystals. To make this material applicable for resistive switching, the resistivity in the insulating phase must be increased to effectively block the current in the high resistive state. Through the investigations in this project, it is shown that conductive percolation paths along the grain boundaries are responsible for the decrease in resistivity. Temperature-dependent conductivity measurements identified defect states responsible for the reduction in resistivity from the theoretical value. At temperatures above 650 K, the intrinsic conductivity of the thin film is demonstrated and a band gap of 0.88 eV is determined. Absorption spectroscopy and spectroscopic ellipsometry are also used to determine an optical band gap of 0.76 eV at room temperature.

In the second part of this project, the influence of the Ti antisite defect on resistive switching in $SrTiO_3$ thin films grown by metal-organic vapor phase epitaxy was studied in both stoichiometric and strontium deficient thin films. We have shown via temperature-dependent permittivity measurements that crystal defects harden the soft phonon mode and polar nano regions are formed in highly strontium deficient films, which was attributed to the formation of Ti antisite defects. In addition, highly strontium deficient $SrTiO_3$ films are shown to exhibit stable resistive switching with an on-off ratio of 2×10^7 at 10 K, whereas stoichiometric thin films do not show stable switching. A diode-like transport mechanism based on Schottky emission in the high-resistance state and dominated by defect-assisted tunneling current in the low-resistance state is identified. From this, a new model for resistive switching based on the Ti antisite defect and the induced ferroelectricity is developed. The polarization charge at the interface between the substrate and thin film creates or suppresses a space charge region, which blocks or allows current transport, respectively.

Ad 3) Within this mission we addressed atomic scale investigations of $SrTiO_3$ by combining high-resolution and analytical (S)TEM with *in-situ* TEM to obtain a comprehensive view of structure, electronical properties, and compositions. Our aim here was to address the structural origin that caused the resistive switching in off-stoichiometric samples. By quantitative STEM high angular annular darkfield and low angular annular darkfield measurements we could prove that off stochiometric samples that showed the most pronounced resistive switching were characterized by Ti_{Sr} antisite defects. EELS and EDX showed that layers had a Sr deficiency of up to 16%. Half of the Sr vacancies were occupied by Ti. This resulted in charge neutrality of the layer. In a next step we performed *in-situ* studies in the TEM. This required serious methodological developments in preparation and contacting samples in the TEM. Sample preparation was done by a specially developed method using focused ion beam directly on the electrically contacted chip. Another approach was mechanical wedge polishing with final cutting and transfer of the sample to the chip. For this preparation we cooperated with the company Protochips, who developed special chips for the project. For the measurements we could rely on a significant upgrade of our TEM equipment such as a double tilt in situ biasing holder, a fast camera (<400 fps) and a piezo driven sample stage as well as software that allowed to keep the sample in place and focus during the biasing, which were part of the investment paid by the application lab for oxide electronics financed by the fund for regional development of the European union. Using this advanced equipment, we were able to show resistive switching of our TEM samples linked to ferroelectric switching of nanopolar domains that were induced by the statistically distributed antisite defects in the off-stoichiometric samples. A quantification of the polarization charge as well as spectroscopical analysis of the defects are still ongoing and are topic of follow-up projects.

2. Aktivitäten un Hindernisse

The project in the beginning was focused on establishing the methods and developing MOCVD growth of the two key material systems. Since the development of TEM characterization techniques required material from the start of the project growth, of both material systems by pulsed laser deposition had been established. This allowed to establish a methodology to study atomic defects in the material. We used approaches that had been previous been used by other colleagues, especially based on STEM high angle annular darkfield (HAADF) and low angle annular darkfield (LAADF)imaging. While HAADF imaging provides atomic number contrast, LAADF provides information regarding the lattice distortion induced by defects. We could prove established relations between the contrast and an increase lattice parameter for $SrTiO_3$. However, we were not able to confirm the established assignment of the defect performing image simulations. By contacts to colleagues in Lawrence Livermore National Lab in the US we were provided a number of additional possible defects that were used in further simulations which resulted in a new assignment of the defect to a Ti antisite.

While growth of Nb_2O_5 by MOCVD was straight forward due to the established growth of $NaNbO_3$ growth of single phase and single crystalline $SrTiO_3$ was challenging. Establishing the growth window in terms of temperature fluxes and chamber pressure required a tedious iteration, accompanied by comprehensive XRD and TEM characterization. This was a roadblock for the electrical characterization of this material as well as for the TEM *in-situ* work. Once established this material became the key achievement of this project and provided for a novel principle in resistive switching with potentially high impact for neuromorphic computing. The fact that this material has been established only in the last phase of the project explains, why several crucial parameters like endurance and retention could not been measured with the required reliability. In parallel NbO_2 had been developed, which had been considered as a promising material for resistive switching. Though material with high resistivity could be obtained after optimization of growth and annealing process we decided in the last phase of the project to concentrate on the more promising material system $SrTiO_3$ for two reasons: (i) the material can be grown by controlled stoichiometry using the technological relevant growth technique MOCVD, (ii) $SrTiO_3$ can be grown homoepitaxially on doped $SrTiO_3$ substrates, (iii) we found a new switching principle in this material system.

The development of both material systems was accompanied by comprehensive electrical characterization. A detailed defect spectroscopy especially of $SrTiO_3$ by deep level transient was hampered for two reasons. First of all, it was found that the dielectric response of the material is field and temperature dependent, second it required $SrTiO_3$ layers with controlled doping. Controlled doping of $SrTiO_3$ is up to now not well established and usually layers are highly doped and compensated. Controlled doping was attempted to achieve by PLD within a Bachelor thesis but with little success. Only at the very end of the project La doping of $SrTiO_3$ of MOCVD grown samples had been established and the DLTS work could not be accomplished. However, the field and temperature dependence of the dielectric constant could be measured for bulk material and a model could provided, which has been published in the thesis by Julian Stöver and could be used in future projects. The measurements of the dielectric response of MOCVD grown materials showed also that it is strongly dependent on the materials stoichiometry.

The *in-situ* TEM work required besides excellent material the development of a sample preparation technique that allowed to contact a thin sample in the TEM, that is thin enough to obtain atomic resolution. The optimization process for this process went through different steps using mechanical wedge polishing as well as focused ion beam preparation. Through cooperation with the Protochips company special electrically contacted chips have been developed that provide for the final thinning on the chip. Using this approach, we were able to follow resistive switching at atomic resolution. We could show that the often-considered dielectric breakdown that is accompanied by formation of conductive filaments occurs at voltages of 7 V far beyond voltages where switching is observed in our samples (>2V). Our finding that ferroelectric switching of nanopolar domains plays a crucial role will be part of further studies in future projects.

3. Ergebnisse und Erfolge

The project resulted in a number of breakthroughs in terms of materials synthesis, methodological developments. These are

- Growth of NbO_2 thin films with high resistivity
- Growth of $SrTiO_3$ with controlled cation stoichiometry
- Memristive material which can be tuned without a forming process and exhibits on/off-ratios up to 10^7
- A new approach to prepare samples for in situ TEM measurements with atomic resolution

The new principle of resistive switching has been submitted for application as an international patent under PCT/EP2021/082505. IKZ has discussed these ideas with IBM and NaMLab in Dresden. Both confirmed that the basic properties of this material system, i.e., a high on-off ratio, forming-less switching, analog tunability of the switching are of particular interest for application in neuromorphic computing. They encouraged us to focus on testing device relevant data such as switching frequency, endurance, and retention times. Now we are establishing a formal collaboration with NaMLab Dresden in the framework of a common project.

The project resulted in 2 PhD and 2 bachelor theses. The project contributed to the GraFOx summer school in Italy. The topic resistive switching has now also been established within the ScienceCampus GraFOx 2. An SAW project has been granted together with the Solid-State Theory Groups at Fritz-Haber-Institut Berlin and Humboldt-Universität. The idea is to develop novel materials with optimized properties that follow the new established principle in a "Materials by Design" fashion. Based on the experimental data provided by this project we aim at developing a descriptor that allows us to predict better materials following the same switching mechanism.

4. Chancengleichheit und Internationalisierung

We are keenly aware of the special challenges that women face in pursuing a scientific career and several of the partners have excellent records in employment of female researchers. In the present project we have to admit that we did not meet the goals to hire a relevant number of female students. Among the PIs only Jutta Schwarzkopf is female. At the beginning Laura Bogula participated in the project as a PhD student that has been paid by the ScienceCampus GraFOx. The bachelor student Min Pei joined the project later.

However, a family-friendly work environment and human resources policy at IKZ is documented. IKZ has been certified "beruf und familie" GmbH. Internal mentoring of female students by female PIs has been implemented within the ScienceCampus GraFOx. Career mentoring for female PhD students and post docs is being offered.

5. Strukturen und Kooperationen

The present project was fully located at IKZ. It was also allocated in the ScienceCampus GraFOx. This provided an established environment for cooperation. In the institute daily exchange on a short term was possible, which provided an efficient project environment. Regular meetings took place monthly. Access to methods not available at IKZ like EELS, Seebeck measurements or special Raman measurements were provided through GraFOx partners HU Berlin and Paul Drude Institut. Within the project we could rely on an ongoing cooperation with partners at Lawrence Livermore Lab in the US, which provided us with ab initio calculations necessary for TEM image simulation. In a later stage of the project, we established contacts to the groups of Catherine Dubourdieu at HZB Berlin, to research labs of IBM in Zürich and Yorktown Heights as well as to NaMLab in Dresden. We also exchanged with the group in Forschungszentrum Jülich working in the field of memristive devices lead by Regine Dittmann and Rainer Waser.

6. Qualitätssicherung

Quality control of the project is assured by a few measures that have been introduced with the start of the project. The overall progress of the project and its tasks has been evaluated by the PIs and during monthly project meetings. In addition to that internal meeting with the director of the institute were made to report on the progress of the project. The project was part of the Science Campus GraFOx and therefore under supervision of its Scientific Advisory Board (SAB). The members of the board are international experts who have pioneered oxide electronics and cover the interdisciplinary fields of research of GraFOx from bulk and epitaxial growth, characterization, and theory to devices.

A high quality of the recruited PhD students and Post Docs is a key requirement for the progress of the project. At the beginning of the project the PIs initiated the recruitment process. All open positions were announced on the GraFOx webpage, were advertised within the network and globally. The PIs of the respective research projects interviewed the eligible candidates. A career development plan has been signed with each PhD student and its institution that contains (i) a brief overview of the research project and the major accomplishments expected, (ii) long term career objectives (over 5 years), (iii) short term career objectives (publications, conference participations), research skills and techniques, research management and communication skills. The partners agreed on a dual advisorship for the PhD students. From IKZ and a university partner (HU and TU), to contribute different backgrounds.

To guarantee a high-level dissemination of scientific results all publications of projects are submitted to peer-reviewed journals. Publications were subject to an internal review system at the institute. Prior to submission, publications are provided internally in the institute and to the GraFOx community via the protected server. Presentations for international conferences are rehearsed in front of the research groups and GraFOx members prior to the conference presentation.

7. Zusätzliche Ressourcen

To establish the project significant additional resources have been allocated to the project. These were 1 PhD student with 48 month that established the MOCVD growth of $SrTiO_3$, 36 month of that were paid by the Leibniz ScienceCampus GraFOx 12 month by IKZ. Throughout the project additional equipment has been installed such as an MOCVD, a fast camera for *in situ* TEM, an *in-situ* TEM biasing holder, a piezo driven stage for TEM and an X-ray diffractometer that has in part been financed by European Regional Funds in the framework of Application Lab Oxide Electronics. The total budget of this project amounts to 1.999 Mio €.

8. Ausblick

The achievements of this project are the base of future work in the field of neuromorphic computing. This will focus on one hand on improving the technology, i.e., of contacts and on measuring relevant technological parameters like switching frequency, retention and endurance on a reliable basis. Based on our patent it is our aim to establish cooperation with industrial partners at the international and European level in terms of projects. To find materials with improved properties that rely on that switching mechanism we established a cooperation with our partners FHI and HU in the framework of the SAW project "Memristor Materials by Design. Here modern artificial intelligence approaches are used to screen the space of possible materials and link them to our established experimental approaches.