Barium stannate based heterostructures for electronic applications

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Executive Summary

Data processing is based on temporary and permanent data storage and has until now been realized by CMOS technology. Recently, the speed gap between fast volatile memories for code storage and execution (SRAM, DRAM) and the slower non-volatile devices (magnetic hard discs drive, flash memory) has become a critical issue, the so-called memory wall. Establishing novel concepts for non-volatile memories that could overcome this speed gap triggered research in device technology, materials science and fundamental physics in the last years. The ferroelectric gate field-effect transistor (FeFET) based on a semiconductor channel and a ferroelectric gate, is among the emerging concepts and has attracted much attention due to its potential advantages such as high speed (response times of ns), low power consumption, high density and non-volatility. A promising material that appeared in the last years for these applications is $BaSnO_3$. $BaSnO_3$ has room temperature mobilities of 200–300 $cm^2V^{-1}s^{-1}$ in single crystals in a broad doping range from 1.0 × 10^{19} cm^{-3} to 4.0 × 10^{20} cm^{-3}. This is the highest mobility ever observed for any perovskite oxide, and about two orders of magnitude larger than that of the widely used $SrTiO_3$. Within this project it was the goal to explore the technological potential of this system, its basic science, and set a new state of the art in its materials mastery.

Based on a cross disciplinary work between materials growth, experimental characterization and solid-state theory we have achieved a number of scientific mark stones that reach far beyond the materials system under study. At IKZ a reproducible crystal growth process for $BaSnO_3$ has been established that allows it to produce 5x5 mm^2 substrates with high crystalline perfection and excellent electrical and optical properties. In parallel growth of bulk $LaInO_3$ has been developed and substrates with 10x10 mm^2 in size were realized. This material served not only as a substrate but also to establish fundamental materials parameters like bandgap, dielectric constants, effective masses. Successful attempts in homoepitaxial growth on these substrates have been made by pulsed laser deposition (PLD) and resulted in record mobilities as regards PLD grown samples. At PDI a mixture of Sn and SnO_2 has been used as a novel Sn source overcoming limitations of conventional cells. Thereby PDI succeeded to grow stoichiometric $BaSnO_3$ layers on various oxide substrates. PDI established absorption-controlled growth of $LaInO_3$ and realized the first time the full $BaSnO_3/LaInO_3$ heterostructures by molecular beam epitaxy (MBE). This resulted in superior transport properties of the 2D electron gases (2DEGs) (sheet electron concentrations up to 6x$10^{13}$$cm^{-2}$ and mobilities up to 110 cm^2/Vs) compared to reported values of competing $BaSnO_3$-based 2DEGs and to well established interfaces like $SrTiO_3/LaAlO_2$. Major advances have been made also in understanding surfaces of $BaSnO_3$ and the interface between $BaSnO_3$ and $LaInO_3$ by combining atomic resolution transmission electron microscopy (TEM) and ab-initio theory. First we could show that it is the adaption of the octahedral tilt between the perfectly cubic Perovskite $BaSnO_3$ and the orthorhombic $LaInO_3$ and the shift of the cations along the growth direction that causes the so called critical thickness for the formation of the 2DEG at the interface. The polar distortions compensate the polar discontinuity and thereby hamper the necessary charge transfer. This newfound mechanism is adoptable to any polar/nonpolar interface. Second, we showed that the interface chemistry may outbalance the effect of strain and thus control the epitaxial relationship between an orthorhombic and a perfectly cubic Perovskite. Though ferroelectric switching of the 2DEG was hampered due to leakage caused by interface states, first principle theory could show that addition of an even unpolarized ferroelectric may further increase the 2DEG charge carrier density.

1. Achievement of objectives and milestones

The aim of the project has been to (i) develop the $BaSnO_3/LaInO_3$/ (Na, K)NbO_3 epitaxial layer system to prove its suitability for application as nonvolatile memory devices, (ii) achieve a new state of the art in materials perfection in the system $BaSnO_3/LaInO_3$, (iii) study basic materials properties of these materials and (iv) get insight into the physics of the interfaces between $BaSnO_3/LaInO_3$ and $LaInO_3$ and (Na,K)NbO_3. To reach this goal the following milestones have been defined and reached in the project

***MA1 Crystal Growth Process developed for $BaSnO_3$ and MA2 (Increased diameter)**. Wafers of size 5x5 and 3x5 mm^2 were fabricated from bulk $BaSnO_3$ crystals and served as substrates for homoepitaxial growth experiments by MBE and PLD. These crystals are up to now the largest single crystals available at the international level. The crystal size is limited by the maximum crucible diameter that allowed to control the decomposition of the compound by any growth atmosphere.*

***M B 2.1.(Coherently grown $BaSnO_3$ with improved mobility)** La-doped $BaSnO_3$ layers were grown by MBE on $SrTiO_3$, DyScO3 as well as lattice-matched $LaInO_3$ and $BaSnO_3$. While state-of-the art electron mobilities*

(~100 cm^2/Vs) for layers on $SrTiO_3$ and $DyScO_3$ were achieved, growth on lattice matched $LaInO_3$ and $BaSnO_3$ unexpectedly resulted in significantly lower electron mobilities due to contaminations from the substrate.

MB2.2(Growth of $LaInO_3$ by MBE with controlled electrical properties). *The MBE growth of $LaInO_3$ has been developed and applied to grow of $LaInO_3/BaSnO_3$ heterostructures. This is to the best of our knowledge the first time that $LaInO_3$ has been grown by MBE.*

MB2.3 (Growth of $LaInO_3$ on $BaSnO_3$ with abrupt interfaces and 2DEG). *Combining annealing experiments, atomic force microscopy and TEM a proper annealing regime has been developed that promotes surfaces formed of regular monoatomic steps and atomically flat terraces. Structures grown by this recipe showed an improved mobility of the 2DEG. MBE structures contained 2DEGs with electron concentrations in the order of $3x10^{13}cm^{-2}$ and mobilities of ~$100cm^2/Vs$.*

MB3.1/3.2 (MOCVD of coherently strained (Na,K)NbO_3). *Pulsed lase deposition was used to deposit the full stack consisting of $BaSnO_3/LaInO_3/(Na,K)NbO_3$ in the same run. 100 nm thick layers of $(Na,K)NbO_3$ were grown on La doped $BaSnO_3$ as well as $(K,Na)NbO_3/LaInO_3/BaSnO_3$. The $(K,Na)Nb0_3$ films were plastically relaxed when grown as topmost layer of the intended FeFET heterostructure. This is due to the lattice mismatch to $LaInO_3$ and $BaSnO_3$ of more than 2.5 % and leads to high density of structural defects at the interface. To avoid plastic lattice relaxation and defect formation or even to incorporate compressive strain in the thin film, a ferroelectric material with a larger lattice parameter is required.*

M B 3.4 (Reduction of leakage current by aliovalent doping e.g. with Cu, Ba, Mn). *Attempts to reduce the leakage in the $(K,Na)Nb0_3$ layer failed. This can be assigned to the high density of interfaces states between $(K,Na)Nb0_3$ and $LaInO_3$ caused by misfit dislocations.*

M C 4 (Switchable 2DEG). *While the low structural perfection did not allow for switching of the 2DEG, first principle studies of the $BaTiO_3/LaInO_3/BaSnO_3$ heterostructures performed within the project could show that adding a paraelectric $BaTiO_3$ increases the achievable density of the 2DEG to 0.38 e/a^2, i.e. by a factor of 3. Switching the polarization direction to pointing outward the $LaInO_3/BaSnO_3$ interface depletes the 2DEG charge to 0.14 e/a^2 indicating the possibility of tuning the charge density within the $BaSnO_3$ layer by switching the ferroelectric polarization*

2. Activities and obstacles

The work has been performed in close collaboration between all partners by exchange of samples, results and by discussions. Regular project meetings were organized on a 3-month basis. Individual exchange was organized spontaneously and between theory characterization and experiment according to the needs. Al participants were member of the ScienceCampus GraFOx and took part in seminars, meetings and secondary skills trainings or the summer school at Villa Vigoni in Italy offered by the network. This opened also the perspective to cooperate with other partners in the network, using their expertise (e.g., characterization methods) and to get contact to guest scientists or international renown experts in the field. At the beginning of the project we became aware that for the groups active in theory and characterization the delay in realizing the full epitaxial structure within short time could be a strong roadblock for developing their work. This holds especially for the HU theory group, working on electronic and structural properties of interfaces, that required experimental input of the interfaces for structural and electronic modelling. This holds as well for TEM activities at IKZ that were focused on the interfaces and for the TU group that works on surfaces and interfaces by scanning tunneling microscopy and scanning tunneling spectroscopy. To overcome this potential hurdle K. Char from Seoul National University, Korea was invited to join our activities. He provided heteroepitaxial layers on $SrTiO_3$ substrates and produced samples on demand. Within the collaboration we were able to optimize surfaces and interfaces. By exchange of personal we were able to establish PLD growth of the full structure at IKZ. The work performed between Seoul National University, HU (theory) and (IKZ) and PDI provided new insights into the physics of the 2DEG at the $BaSnO_3/LaInO_3$ interface and resulted in a number of common publications. Based on this fruitful collaboration Kookrin Char was awarded the Humboldt Research award hosted by IKZ in 2022. International cooperation that had not been foreseen were established during the project with Shanghai University. Due to a Postdoc funds by the China Scholarship Council and National Natural Science Foundation of China we were able to hire an additional postdoc in the field of first principle calculations that worked on the ferroelectric switching of the 2DEG by theory. The epitaxial activities at IKZ and PDI were driven by strong interaction between bulk growth at IKZ, epitaxial growth at IKZ and PDI and TEM characterization at IKZ that helped to understand stoichiometry and epitaxial growth in this system. To support the activities in growth, a master student worked at IKZ and was integrated into the PLD activities. The COVID pandemic and the lockdown in the beginning of 2020 and the following restrictions in access to experimental facilities were serious challenges to an experimentally driven project like ours. Due to cost neutral extension of the project by the Leibniz-Association and by finances of the Leibniz Institutes (IKZ, PDI) the project has been exceptionally successful in terms of scientific output and publications in high impact journals as can be seen below.

3. Results and successes

The main success is based in the field of the scientific results achieved. These are:

1) Bulk materials as substrates and for fundamental basic materials research.

Within the project we developed three different lattice matched substrates for the growth of $BaSnO_3/LaInO_3$ heterostructures, i.e. (i) $BaSnO_3$ single crystals by directional solidification with sizes up to 5x5 mm^2, (ii) $LaInO_3$ by the vertical gradient freeze method with sizes of 10x10 mm^2 [1] and Czochralski growth perovskite-type (La, Nd)(Lu,Sc)O_3 single crystals with sizes of 17 mm diameter. [2]

2) MBE growth of $BaSnO_3$ and $LaInO_3$

Within the project MBE growth of $BaSnO_3$ and $LaInO_3$ has been established which allowed the first time to grow the full heterostructure by MBE. MBE grown materials is typically less affected by atomic defects than PLD grown materials. The latter suffer from the damage by fast ions generating atomic defects especially in highly ionic materials. Our heterostructure grown by MBE set a new standard with respect mobilities of the 2DEG (110 cm^2/Vs) and charge carrier densities (6 x 10^{13} cm^{-3}) at the $BaSnO_3/LaInO_3$ interface. Within the project a novel approach to grow $BaSnO_3$ has been developed using an efficient SnO source consisting of *a mixture of SnO_2 and Sn and provides for a better control of growth. In contrast to the conventional MBE approach used by other groups that is forced to use high cell temperatures it provides higher fluxes, i.e. higher growth rates at lower temperatures. The approach is of general interest and applicable also to other oxide semiconductors.* [3,4] Furthermore *$LaInO_3$ has been grown the first time by MBE. We used absorption-controlled growth conditions, where the control of fluxes is less critical to obtain stoichiometric material.* [5]

3) Growth of $BaSnO_3$ on lattice matched $BaSnO_3$ and $LaInO_3$ substrates

Threading dislocations until now strongly influence mobilities of epitaxial $BaSnO_3$ layers. Reducing them to get close to theoretical predicted values was one of the goals of this project. The development of novel lattice-matched $BaSnO_3$ and Ba doped $LaInO_3$ Ba for the first time enabled the growth of $BaSnO_3$ thin films with a threading dislocation density of $1 \cdot 10^7$ cm^{-2} and thus the lowest threading dislocation density published in the literature to date. This allowed for temperature-dependent Hall-effect measurements, where a carrier mobility of 99 $cm^2V^{-1}s^{-1}$ could be determined for a charge carrier density of $3.8 \cdot 10^{19}$ cm^{-3} at 20 K. These values are among the best that could be obtained for PLD grown layers. They are, however, still lower than that of MBE grown layers MBE grown films with significant higher dislocation densities. We assign this to fact that PLD suffers from unavoidable formation of atomic defects induced by high energetic ions. MBE films grown on $BaSnO_3$ and $LaInO_3$ films on the other hand suffered from impurity segregation from the substrate due to the higher growth temperature. [6]

4) Physics of the polar/nonpolar interface between $BaSnO_3$ and $LaInO_3$ by experiment and theory

The origin of the 2D electron gas at the interface between polar and nonpolar interfaces is focus of a longstanding debate. A common experimental finding is the observation that the 2DEG forms after a "critical thickness" of 4 ML. The same has been observed in the case of $LaInO_3/BaSnO_3$. the Different models have been proposed to explain this finding, among them the polar catastrophe model and the charge transfer model from surface states. TEM observations of samples from the group of Kookrin Char showed that this transition is linked to a changing octahedral tilt at the interface between cubic$BaSnO_3$ and orthorhombic $LaInO_3$ accompanied by cation shift across the interface. [7] *Theory performed within this project by Aggoune and Draxl explain this by an upward shift of cations to counteract the nominal polarization ($LaInO_3$) and minimize the polar discontinuity ($BaSnO_3$). This hampers the electronic charge transfer up to a thickness of 4 monolayers. Essentially the polar distortions compensate the polar discontinuity.* [8]

5) Understanding of the domain structure in the growth of orthorhombic $LaInO_3$ on cubic $BaSnO_3$

The epitaxial orientation relationship of heteromorphous materials in general is assumed to be controlled by strain energy minimization. In case of Perovskites strain can be compensated by changes in rotation or tilt of the octahedra in addition to tetragonal distortion. By combining first principle calculations and in depth quantitative TEM studies we could show that the interface chemistry of bonding may balance the energetics of the system and counteract the strain accommodation. Our finding highlights the remarkable influence of the interface chemistry on the epitaxial relationship in heterostructures of different ABO_3 perovskites with different symmetries. [9]

6) An in-depth study of the surface termination of $BaSnO_3$ and of the $BaSnO_3/LaInO_3$ interface.

The interface termination is a key to promote 2DEG or 2D hole gas at the polar/nonpolar interface of Perovskites. Combing transmission electron microscopy and ab-initio theory we could show, that BaO termination is energetically most favorable for the free surface over a wide range of chemical potentials. Overgrowth with $LaInO_3$ promotes SnO_2 termination, consistent with the observation of 2DEGs at that interface. First principle theory confirms our experimental findings that at the interface between $LaInO_3$ and $BaSnO_3$ Sn- termination is energetically favorable. By growing 4 monolayer thin $LaInO_3$ layers on $BaSnO_3$ we could prove by TEM the presence of a BaO layer on the surface of $LaInO_3$ caused by surface segregation of Ba.

7) Measurement and determination of fundamental materials parameters.

At the beginning of the project there were e.g., little information on the bandgap of $LaInO_3$, which is crucial for model calculations regarding 2DEGs. Based on the excellent bulk crystals that have been produced within this project, comprehensive and modern characterization tools, and excellent theory we determined the band structure of $LaInO_3$ [10] and $BaSnO_3$ [11] and fundamental parameters such as dielectric constants and effective masses by experiment.[1] These values are new references and are reliable data to design devices based on these materials.

8) Ferroelectric Tuning of a Two-Dimensional Electron Gas at the Interface of $LaInO_3$ and $BaSnO_3$

Due to the prominent leakage that coms from interface states caused by plastic relaxation we cannot present a working device. However, a thorough first principle study that has been performed by funding from our cooperation partner at Shanghai University during a 2 years stay of a postdoc in the group of our project partner Claudia Draxl we were able to gain important insight into this interface that could in future be exploited by experiment. We find that aligning the ferroelectric polarization toward (outward) the $LaInO_3/BaSnO_3$ interface leads to an accumulation (depletion) of the interfacial 2DEG. Varying its magnitude, we find a linear effect on the 2DEG charge density that is confined within the $BaSnO_3$ side. Analysis of the optimized geometries reveals that inclusion of the ferroelectric layer makes structural distortions at the $LaInO_3/BaSnO_3$ junction less pronounced, which, in turn, enhances the 2DEG density. Thicker ferroelectric layers allow for reaching higher polarization magnitude. Experimentally ferroelectric materials with a lattice parameter of more than 4.12 Å as $PbZr_xTi_{1-x}O_3$ with a high Zr-ratio could provide an opportunity to realize switchable 2DEGs with improved structural properties.

4. Equal opportunities, career development and internationalisation

Bastet is part of GraFOX and therefore follows identical rules regarding equality and internationalization. The recruitment of PhDs and Postdocs ensures clear and transparent procedures as well as equal opportunity in terms of nationality and gender fully complying with the guidelines of the Leibniz Association. In the recruitment process, all open positions were announced on the GraFOx webpage, advertised within the network and worldwide via the EURAXESS platform, which includes a gateway to Science4Refugees.The international character of the project reflects not only in the recruitment process, but also in visits of guest scientists, in collaborations as well as the organization of international conferences. During the project a strong collaboration with Seoul University developed. This included exchange of samples mutual visits in Seoul and Berlin. Daniel Pfützenreuter, one of the PhDs spent a 3-month period at Seoul University as a guest scientist, Kookrin Char from Seoul University visited Berlin twice for periods of 1 month each. Further visits were planned but hampered by the COVID. Regarding gender, 50% of the PhD students, 66% of the Postdocs and 40% of The PIs are female. 3 out 7 additional hired persons in the project are non-German. As in the GraFOx level carrier development is secured by a career development plan that is set up at the beginning of the PhD. It is updated at an annual level with the supervisor. Secondary skills training is provided through GraFOx and Forschungsverbund Berlin. Students present their results in the GraFOx seminar, in PhD seminars and at national and international conferences

5. Structures and collaboration

The cooperation between all partners is already well established through GraFOx. Within the project it is based on the exchange of samples, mutual characterization of these samples, modelling of surfaces and interfaces and common discussion of the results and common publication of these results in peer reviewed journals and at international conferences. The project was coordinated by M. Albrecht at IKZ. Regular meetings took place on a 3-month basis at IKZ. These meetings served for exchange of scientific results, samples and planning of experiments. For exchange of data a cloud-based server is maintained at PDI. Besides the regular meetings, exchange is organized based on actual needs. These meetings took place as personal or after COVID pandemic based on Skype or Zoom based meetings. Besides these meetings with project partners regular meetings during GraFOx seminars or annual and biannual meetings took place.. These meetings within the GraFOx network offer the opportunity for exchange with other partners of the network and to make use of the various characterization facilities allocated in the network. Results were presented in the monthly GraFOx Update seminar, where recent results are presented on the working level. Strategic cooperation with K. Char from Seoul University who spent three periods of 2 month each at IKZ, has been established. This cooperation is partially supported by Samsung. A Humboldt fellowship for K. Char has been granted based on his expertise and the results of the cooperation. In the second half of the project a close collaboration with Shanghai University has been established in the field of solid state theory. A postdoc financed through Chinese government fonds worked in the group of Claudia Draxl at HU Berlin on the ferroelectric switching of 2D electron gases.

6. Quality assurance

Quality management within the project follows the routines established within GraFOx, i.e. (i) Internal refereeing, i.e., each publication is before submission subject of an internal refereeing within GraFOx before submission, (ii) scientists are encouraged to publish their results in high impact journals and open access. (iii) presentations at scientific conferences are rehearsed and open for all members of the project.

7. Additional resources

An amount of 210.000 € additional resources have been allocated to the project by all partners. TUB, HU IKZ and PDI supported the project mainly by additional personnel. IKZ pays students 75% E13 positions and adds the required funds from the institutes budget. HU added an additional postdoc position to the project. Le Fang, a Postdoc working since 11/2019 in the project focuses on the interface between $LaInO_3$ and ferroelectrics and is paid in the framework of an exchange between Humboldt-University and Shanghai University by funds of the government of the P.R. of China.

8. Outlook

This project established a new state of the art for 2DEGs at the polar/nonpolar interface $BaSnO_3/LaInO_3$. The system can be grown homoepitaxially and by MBE and shows superior properties in terms of the 2DEG mobility and the sheet carrier density. While first principle calculations show the potential to switch a 2DEG by a ferroelectric gate and to enhance the sheet carrier density further by combining the polar/nonpolar heterostructures with ferroelectrics an experimental prove is still missing. This would require a ferroelectric that is lattice matched to $BaSnO_3$. Ferroelectric materials with a lattice parameter of more than 4.12 Å are typically lead containing materials, such as $PbZr_xTi_{1-x}O_3$ with a high Zr-ratio. As an alternative approach would be to use $(K,Na)NbO_3$ as the ferroelectric layer and $SrSnO_3$ instead of $BaSnO_3$, could be used since it exhibits smaller lattice parameters. $SrSnO_3$ was already investigated in the frame of this project and could be grown fully strained on (110) $NdScO_3$ substrates. $La(In,Ga)O_3$ also exhibits smaller lattice parameters than pure $LaInO_3$. This would enable the growth of a fully strained dielectric $La(In,Ga)O_3$ film on the semiconducting $SrSnO_3$ layer to form a 2DEG at their interface. The formation of a 2DEG was already reported for the $La(In,Ga)O_3/BaSnO_3$ interface and is assumed to exhibit similar properties for the $La(In,Ga)O_3/SrSnO_3$ interface.

References

[1] *Z. Galazka et al., Melt Growth and Physical Properties of Bulk $LaInO_3$ Single Crystals, Phys. Status Solidi A, 218, 2100016 (2021), DOI: 10.1002/pssa.202100016*

[2] *C. Guguschev et al., Czochralski growth and characterization of perovskite-type (La, Nd)(Lu,Sc)O3 single crystals with a pseudocubic lattice parameter of about 4.09 Å, J. Cryst. Growth 536, 125526 (2020), DOI: 10.1016/j.jcrysgro.2020.125526*

[3] *G. Hoffmann et al. Efficient suboxide sources in oxide molecular beam epitaxy using mixed metal + oxide charges: The examples of SnO and Ga_2O. APL Materials, 8(3), 031110 (2020), DOI: 10.1063/1.5134444*

[4] *G. Hoffmann et al., Drastically enhanced cation incorporation in the epitaxy of oxides due to formation and evaporation of suboxides from elemental sources. APL Materials, 9(11), 111110 (2021), DOI: 10.1063/5.0058541*

[5] *G. Hoffmann et al., Adsorption-controlled plasma-assisted molecular beam epitaxy of LaInO3 on DyScO3(110): Growth window, strain relaxation, and domain pattern. arXiv:2212.11736*

[6] *D. Pfützenreuter et al., Epitaxial $BaSnO_3$ thin films with low dislocation density grown on lattice matched $LaInO_3$ substrates, Nanotechnology 32 505609 (2021), DOI 10.1088/1361-6528/ac291c*

[7] *Young Mo Kim et al., Interface polarization model for a 2-dimensional electron gas at the $BaSnO_3/LaInO_3$ interface, Scientific Reports 9, 16202 (2019), DOI: 10.1038/s41598-019-52772-8*

[8] *W. Aggoune and C. Draxl, npj Computational Materials 7, 174 (2021), DOI: 10.1038/s41524-021-00646-x*

[9] *M. Zupancic et al., Role of the interface in controlling the epitaxial relationship between orthorhombic $LaInO_3$ and cubic $BaSnO_3$, Phys. Rev. Materials 4, 123605 (2020); DOI: 10.1103/PhysRevMaterials.4.123605*

[10] *W. Aggoune et al., Fingerprints of optical absorption in the perovskite LaInO3: Insight from many-body theory and experiment; Phys. Rev. B 103, 115105 (2021), DOI: 10.1103/PhysRevB.103.115105*

[11] *W. Aggoune et al., A consistent picture of excitations in cubic $BaSnO_3$ revealed by combining theory and experiment, Communications Materials 3:12 (2022); DOI: 10.1038/s43246-022-00234-6*