Barium stannate based heterostructures for electronic applications

PIs Claudia Draxl (C1.6), Holger Eisele (C2.5), Oliver Bierwagen (C3.10), Jutta Schwarzkopf (C3.11), Martin Albrecht (C1.7), Zbigniew Galazka (C3.1)

Participating Institutions: Leibniz-Institut für Kristallzüchtung, Paul-Drude-Institut für Festkörperelektronik, Humboldt-Universität zu Berlin, Arbeitsgruppe Festkörpertheorie, Technische Universität Berlin

Introduction

Novel concepts for non-volatile memories have triggered research in device technology, materials science and fundamental physics in the last years. Based on the wide tunability of their physical properties which can be insulating, semiconducting, matallic, magnetic and ferroelectric, Perovskite oxides are considered to be key players in this field. 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 (with response times in the range of ns and smaller),[1] low power consumption, high density and non-volatility. While the concept of a FeFET is not new in itself, its development has been hindered by a number of issues that require fundamental materials research including development of new materials. Key problems in the realization of FeFETs with retention times comparable to flash memory have been depolarization field, gate leakage currents, mobile ionic charges and the lack of scalable ferroelectric gate dielectrics. Fundamental questions that concern FeFET´s device performance, are far from being well understood and the proper combination of materials among the variety of compounds is still to be found. Critical issues are the huge contrast in dielectric constants of the semiconductor and the ferroelectric layer as well as the band offsets between the layers in the stack. Despite the rapid progress made in the field of perovskite oxide heterostructures during the last years, the realization of room temperature functionality remains challenging until today. This holds especially for the free carrier mobility, a key parameter influencing the performance of any FET. The best room temperature values of the mobility in the model perovskite oxide semiconductor $SrTiO_3$ have remained below 10 $cm^2V^{-1}s^{-1}$ over the last 50 years. Impressive advances in mobilities, achieved through improvement in homoepitaxial growth, have been restricted to low temperatures.[2]

A promising material that appeared in the last years and could overcome these limitations is $BaSnO_3$. $BaSnO_3$ has room temperature mobilities of 200–300 $cm^2V^{-1}s^{-1}$ in single crystals for a broad doping range from 1.0 × 10^{19} cm^{-3} to 4.0 × 10^{20} cm^{-3}.[3,4] This is the highest mobility ever observed for any perovskite oxide, and about two orders of magnitude larger than that of the widely used $SrTiO_3$. Moreover, the conductivity of ~10^4 $\Omega^{-1}cm^{-1}$ reached at 4.0 × 10^{20} cm^{-3} is comparable to the highest value previously reported in the transparent conducting oxides. The high mobility is attributed to a small effective mass resulting from the ideal Sn-O-Sn bonding in a cubic perovskite network, small disorder effects due to the doping away from the SnO_6 octahedra, and reduced carrier scattering due to the high dielectric constant.[5] $BaSnO_3$ can be easily n-doped by La and Sb. P-type doping by K with free carrier concentrations and mobilities similar to CuO_2 have been predicted from theory[6] and first p-n junctions have been realized.[7] Favourable conduction band offsets with structurally similar oxides such as $SrTiO_3$, $LaAlO_3$, lattice matched $LaInO_3$, and many other perovskite oxides promote charge transfer into the $BaSnO_3$ layer, making it a promising candidate for a modulation doped high mobility channel material in oxide heterostructures[8,9] a concept so successfully applied in III-V semiconductors. $BaSnO_3$ has a low lattice mismatch to $(Na,K)NbO_3$, a ferroelectric oxide that combines excellent ferroelectric and piezoelectric properties comparable to those of lead-zirconate-titanate (PZT)[10] with a relatively high Curie temperature (628 K for $NaNbO_3$, 708 K for $KNbO_3$) and a moderately high band gap (between 3.2 and 4.4 eV, depending on strain state

and phase). Heterostructures based on $BaSnO_3$ and $NaNbO_3$ thus hold promise to realize ferroelectric gate control of a 2DEG in a coherently strained structure.

GraFOx is at the moment focused on the analysis of group III-Sesquioxides, but considers Perovskites as an important addition with respect to tuning basic materials properties by going from more covalently bonded materials to more ionic bonded materials.

The favourable properties of $BaSnO_3$ and the fact that unique $BaSnO_3$ bulk crystals are grown at IKZ motivated us to establish a collaborative project in this field. The project BaStEt joins bulk crystal growth, epitaxial growth of ferroelectric layers by MOCVD, with structural and electrical characterization at IKZ, molecular beam epitaxy at PDI, ab-initio theory at Humboldt-University and STM imaging and spectroscopy at TU Berlin. The objective is to develop coherently strained $(Na,K)NbO_3/LaInO_3/BaSnO_3$ ferroelectric–dielectric-semiconducting heterostructures for device applications. In view of the plethora of opportunities that are offered by $BaSnO_3$ based heterostructures and the requirements to establish its basic physical properties for proper device design the project focuses on two main tasks:

(i) Improvement of materials perfection and control of materials properties by growing homoepitaxial layers. This contrast with previous work, where $BaSnO_3$ has mostly been deposited on foreign substrates and the resulting multitude of atomic and extended defects makes it hard to distinguish their role in electronic properties.

(ii) Understanding basic physics of polar-nonpolar interfaces by combining comprehensive characterization from the macroscopic to the atomic scale with ab-initio theory.

Bulk crystal growth

$BaSnO_3$ crystals grown from the flux are very small and obtained in a very small quantity. Therefore they do not permit systematic development of homoepitaxial growth and preparation of heterostructures. Very recently native, grown from the melt have been developed at the Leibniz-Institut für Kristallzüchtung as well as $LaLu_{0.5}Sc_{0.5}O_3$ substrates that are attice matched to $BaSnO_3$.[11] $BaSnO_3$ single crystals were grown directly from the melt by direct solidification within an iridium crucible with the use of high oxygen partial pressure (up to 1 bar). The melting point of $BaSnO_3$ is 1855 °C ± 25 K. The main issue associated with growing $BaSnO_3$ from the melt is a very strong and nonstoichiometric decomposition leading to an intensive evaporation and composition change of the starting material. The size of the obtained single crystals was approaching 1 cm^3 allowing for preparation 5×5mm^2 wafers. High structural quality was confirmed by a single perovskite phase, stoichiometry, narrow rocking curve (FWHM = 26 arcsec) and low EPD ($\leqslant 10^6$ cm−2), several orders of magnitude lower than the dislocation density reported for heteroepitaxial thin films. Depending on growth conditions the as-grown and undoped crystals were insulators or semiconductors, which turned into insulating state after annealing in the presence of oxygen at or above 1200 °C. Doping with La made the $BaSnO_3$ single crystals highly conducting with high electron mobilities above 200 $cm^2V^{-1}s^{-1}$ for electron concentrations exceeding 10^{19} cm^{-3}. The indirect energy gap of $BaSnO_3$, neglecting excitonic effects, was determined to be 2.99 ± 0.04 eV at room temperature and 3.17 ± 0.04 eV at 5 K. Melt-grown $BaSnO_3$ single crystals may open the route for substrate preparation to be used for both homo- and heteroepitaxy. While this is a proof of principle, the technological development of bulk crystals is in a very early stage it is one main goal of the project to make a serious effort in research and development to realize a reproducible growth technology within a reasonably short time frame. Bulk $BaSnO_3$ single crystals constitute a foundation for the homo- and heteroepitaxial film growth and the resulting devices.
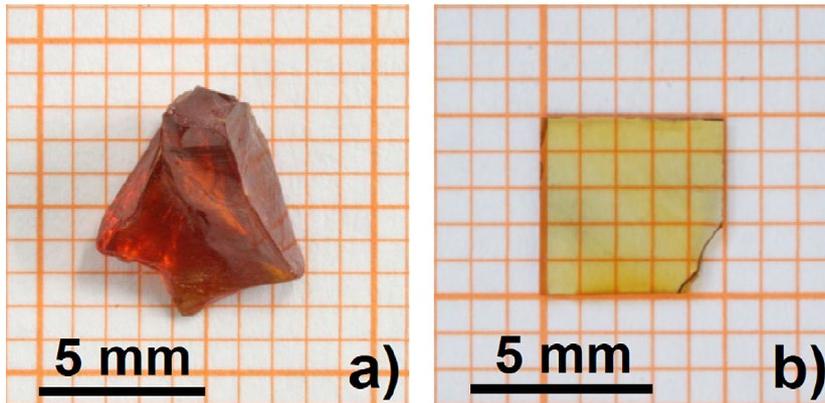
$LaInO_3/BaSnO_3$ Interfaces

The origin of the 2DEG at the interface of Perovskite heterostructures has started with its discovery in the materials system $SrTiO_3/LaAlO_3$. One of the most commonly discussed models is based on the charge discontinuity (and hence the resulting polarization discontinuity) between the polar perovskite $LaAlO_3$, i.e. a material with an alternating sequence of layers with opposite non-zero ionic charge (LaO^+ and AlO_2^-), and the non-polar $SrTiO_3$ (consisting of non-charged SrO^0 and TiO_2^0 layers). The role of surface states and unintentional doping in $SrTiO_3$ has been put forward by other authors. In the framework of the common project "BaStEt" and the GraFOx ScienceCampus we started a collaboration on the role of interfaces between $BaSnO_3$ and $LaInO_3$ with the group of Kookrin Char at Seoul University to establish the specific origin for 2DEGs there. The focus was on the structure of the $LaInO_3$ film itself and on the interface.

$BaSnO_3$ is a cubic Perovskite, while $LaInO_3$ is orthorhombic with a pseudocubic Perovskite structure. The lattice mismatch is low but depends on the epitaxial relation. Essentially three different orientations are possible with the a, b and c lattice parameter out of plane. From cross sectional and plane view HRTEM images of epitaxial films we find that all orientations are present, i.e the films have a domain structure as shown in Fig. 2.
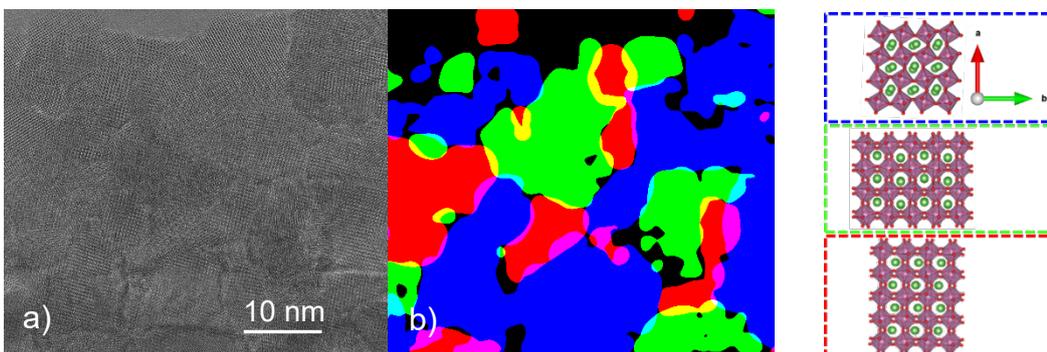

Figure 2: Distribution of domains in $LaInO_3$ (a) HRTEM image. (b) domain distribution obtained from the FFT of (a). (c) Stick and ball models of the different domains seen along the surface normal. Blue: c-orientation, green b-orientation, red: a-orientaion

Quantitative evaluation of the data showed that the c-oriented domains are clearly predominant. We calculated the strain energy for these orientations based on the elastic constants that were obtained from DFT calculations and found that the statistically preferred c-orientation is the one that exhibits the highest strain energy. A possible explanation comes from considering the tilt of the oxygen octahedra in these different orientations. Considering the Glazer tilt pattern, it is hypothesized that $a^-a^-c^+$ pattern present in the c-oriented interface might be energetically more favorable to adopt the strain.

Based on transport measurements that were performed at Seoul University it was found that the electrical properties of the channel depend critically on the thickness of the $LaInO_3$ layer. The conductance of the layer increases as soon as the first unit cell of $LaInO_3$ is deposited, and increases further with layer thickness until it reaches its maximum at an $LaInO_3$ thickness of 4 unit cells (≈16 Å). Beyond this thickness we find a slow decrease of the conductance. The sheet carrier density (n_{2D}) obtained by Hall measurement follows the same trend, i.e. n_{2D} increases until a LIO thickness of four unit cells and then decreases slowly. We observed that the Hall mobility (μ) increases as n_{2D} increases, consistent with the reported behavior of μ in BSO films where μ is limited by the threading dislocations in the BSO film.

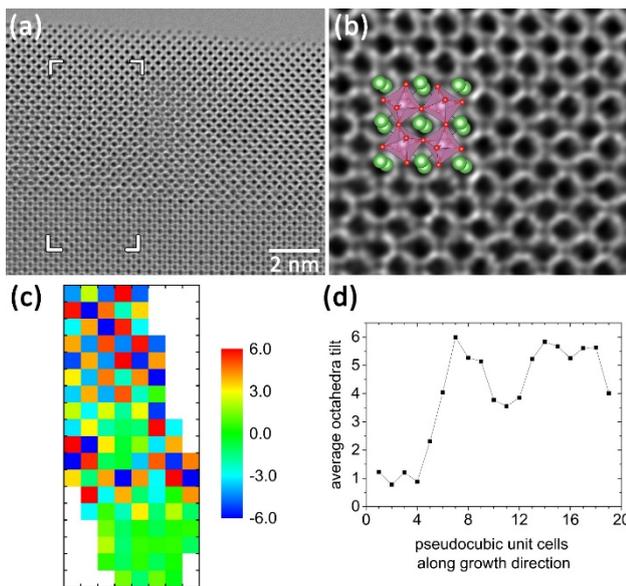*Figure 3.* (a) Cross-sectional HRTEM image of the $BaSnO_3$/$LaInO_3$ interface. (b) Magnified view of LIO from (a) together with a stick-and-ball-model of the orthorhombic crystal structure of $LaInO_3$ indicating the tilt of the oxygen octahedra (violet). Green, violet and red balls represent La, In and O atomic columns, respectively. (c) Map of the oxygen octahedral tilt evaluated from the region indicated by the white frame in (a). (d) Line profile of the octahedral tilt across the BSO/LIO interface.

Analyses of the $BaSnO_3$/$LaInO_3$ interfaces were performed by high resolution transmission electron microscopy. To analyze the octahedral tilt in the layers and at the interface we used exit wave reconstruction, which permits to measure the position of the oxygen atoms. For symmetry reasons octahedral tilt was measurable only in areas of the samples where the $LaInO_3$ layer is oriented along c. The octahedral tilt was measured from amplitude images of the exit wave reconstruction by a peak finding algorithm. Strikingly, the analysis showed that the octahedral tilt in the orthorhombic $LaInO_3$ layer at the interface corresponds to that of the underlying $BaSnO_3$ substrates and gradually changes to the tilt expected for orthorhombic $LaInO_3$. The gradual change of the octahedral tilt extends over 4 monolayers of the pseudocubic unit cell. Such an internal strain gradient will most likely lead to a polarization in analogy to flexoelectricity. Preliminary DFT calculations of the group at Humboldt-University led by Claudia Draxl indicate that the strain induced shift of the La atoms causes octahedral tilts from which we expect significant changes in the intrinsic polarization.

Using self-consistent 1D Poisson-Schrödinger band calculation of the interface based on the above-mentioned graded polarization in LIO produced an excellent fit to the experimental data of the entire thickness and doping dependent variation of n_{2D} of the 2DEG state. Such a 2DEG state at the BSO/LIO polar interface will have high density ($n_{2D} \sim 10^{14}$ cm^{-2}, $n_{3D} \sim 10^{21}$ cm^{-3}) with large spin-orbit coupling energy (~ 0.1 eV) of Sn 5s electrons. Further reduction of defects such as threading dislocations in BSO films will lead to higher mobility at low temperatures, which will enable quantum transport measurement of a unique 2DEG state.

[1]   K. S. Takahashi, M. Gabay, D. Jaccard, K. Shibuya, T. Ohnishi, M. Lippmaa and J.-M. Triscone,
         "Local switching of two-dimensional superconductivity using the ferroelectric field effect",
         Nature **441**, 195 (2006).

[2]   J. Son, P. Moetakef, B. Jalan, O. Bierwagen, N. J. Wright, R. Engel-Herbert and S. Stemmer,
         Epitaxial SrTiO$_3$ films with electron mobilities exceeding 30,000 cm^{2}V^{-1}s^{-1},
         Nature Materials **9**, 482 (2010).

[3]   H. J. Kim, U. Kim, H. M. Kim, T. H. Kim, H. S. Mun, B. G. Jeon, K. T. Hong,W. J. Lee, C. Ju, K. H. Kim, and K. Char,
          "High mobility in a stable transparent perovskite oxide",
         Appl. Phys. Exp. **5**, 061102 (2012).

[4]   H. J. Kim, U. Kim, T. H. Kim, J. Kim, H. M. Kim, B.-G. Jeon, W.-J. Lee, H. S. Mun, K. T. Hong,   J. Yu, K. Char, and K. H. Kim,
         "Physical properties of transparent perovskite oxides (Ba,La)SnO$_3$ with high electrical mobility at room temperature";
         Phys. Rev. B **86**, 165205 (2012).

[5]   D. O. Scanlon, "Defect engineering of BaSnO$_3$ for high-performance transparent conducting oxide applications,"
         Phys. Rev. B **87**, 161201 (2013).

[6]   Y. Li, J. Sun, and D. J. Singh,
         "Infrared absorption and visible transparency in heavily doped p-type BaSnO$_3$",
         Appl. Phys. Lett. **110**, 051904 (2017).

[7]   H. M. Kim, U. Kim, C. Park, H. Kwon, and K. Char,
         "Thermally stable pn-junctions based on a single transparent perovskite semiconductor BaSnO$_3$"
         APL. Materials **4**, 056105 (2016).

[8]   K. Krishnaswamy, L. Bjaalie, B. Himmetoglu, A. Janotti, L. Gordon, and Chris G. Van de Walle,
         "BaSnO$_3$ as a channel material in perovskite oxide heterostructures",
         Appl. Phys. Lett. **108**, 083501 (2016).

[9]   S. A. Chambers, T. C. Kaspar, A. Prakash, G. Haugstad, and B. Jalan,
         "Band alignment at epitaxial BaSnO$_3$/SrTiO$_3$(001) and BaSnO$_3$/LaAlO$_3$(001) heterojunctions",
         Appl. Phys. Lett. **108**, 152104 (2016).

[10]   Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, and M. Nakamura,
         "Lead-free piezoceramics",
         Nature **432**, 84 (2004).

* [11] R. Uecker, R. Bertram, M. Brützam, Z. Galazka, T. M. Gesing, C. Guguschev, D. Klimm, M. Klupsch, A. Kwasniewski, and D. G. Schlom,
         "Large-lattice-parameter perovskite single-crystal substrates",
         J. Cryst. Growth **457**, 137 (2017).

GraFox publications are highlighted by an "*".