7. Conclusions and outlook

In this work a comprehensive study of the local piezoelectric response behavior of ferroelectric single crystals, thin films and nanostructures has been carried out, applying the technique of voltage-modulated scanning force microscopy. In view of the significance of ferroelectric thin films and nanostructures for the prospective development of high-density ferroelectric random access memories (FeRAMs) for use in advanced microelectronics, emphasis was put on the local ferroelectric properties of thin films and nanostructures of the most promising ferroelectric materials, viz. $Pb(Zr,Ti)O_3$ (PZT) and different members of the bismuth-layer structure family (BLSF), or Aurivillius phases. Members of the Aurivillius family with both an even and an odd number n of perovskite-type octahedra between Bi_2O_2 layers (even Aurivillius parameter), viz. $SrBi_2Ta_2O_9$ (SBT) and $BaBi_4Ti_4O_{15}$, and $Bi_4Ti_3O_{12}$, respectively, have been studied, because these two sub-groups of the BSLF fundamentally differ in their crystal symmetry and therefore also in the anisotropy of their ferroelectric properties. The investigations included imaging ferroelectric domains, recording local piezoelectric hysteresis loops, and measuring piezoelectric coefficients, all with a lateral resolution down to 10 nm and a high sensitivity. This measurement performance has been achieved by adding a homemade piezoresponse module to a commercial scanning force microscope, by carefully optimizing the measuring procedures, and by studying some of the basic mechanisms and conditions underlying the piezoresponse-mode of scanning force microscopy. Among the results obtained, the following deserve particular attention either in terms of the possibilities and limitations of the piezoresponse-SFM technique, of new facts of fundamental character, or of formerly unknown properties of films and nanostructures significant to the future development of FeRAMs:

1. Making use of a simultaneous or subsequent visualization of both the out-of-plane and in-plane components of the piezoelectric response of a certain sample area, the ferroelectric domain structure of $BaTiO_3$ single crystals, known from many investigations of various authors, was fully reproduced using the piezoresponse-mode SFM setup. In this way, the overall performance and reliability of the setup and the validity of the measuring procedures used were fully confirmed.

2. The domain structure and local piezoelectric hysteresis loops of different grains in polycrystalline PZT thin films were studied and compared with each other. Film thickness and grain size of the films both ranged from 100 nm to 600 nm. The investigations showed that a strong variation of the properties occurred from grain to grain within the same film, and even within the same grain. In particular, it was found that the saturation piezoelectric coefficient may differ drastically from one grain to another, and that the switching process, *viz.* nucleation and growth of domains with reversed polarization, occurred differently when the same grain was probed at different places. The most probable reasons for this variability were found to be the different crystallographic orientations of the grains and crystallites implying variations of the effective piezoelectric response, and the fact that the switching nucleated by the SFM tip evolves according to the local environment. In view of the demonstrated spatial variation of the properties within polycrystalline films, the growth

of *epitaxial* films of these materials is necessary in order to achieve uniform properties over the entire film area.

3. Comprehensive investigations were carried out on individual grains of different well-defined crystallographic orientations within epitaxial thin films of different BSLF members, both with even and odd Aurivillius parameters n. In this way, it was confirmed that even-n BLSF members have no polarization component along their [001] axis, even not in the close vicinity of grains with other orientations, and that they cannot be polarized along the [001] axis under any local conditions. Accordingly, (001)-oriented films of even-n BSLF materials cannot be used in a planar-capacitor type FeRAM. In contrast, odd-n BLSF members have a small component of the polarization along their [001] axis, as was confirmed by local switching experiments in (001)-oriented regions of $Bi_4Ti_3O_{12}$ films. As a consequence, the odd-n BLSF members are in principle suitable for an application in a planar-type geometry even if they are (001)-oriented.
4. A study of the domain structure within individual grains was performed knowing the crystallographic directions in the investigated grains from comparative transmission electron microscopy (TEM) and selected area electron diffraction (SAED) studies of the same BLSF films. The main results are that small grains of the order of 100 nm in lateral size can posses a fine and stable domain structure with the domain sizes at the lateral resolution of the setup. Well defined, rectangular-shaped hysteresis loops were recorded from these grains indicating that individual ferroelectric structures with lateral sizes in the 100 nm range posses excellent properties for the application in non-volatile memories. It was found that the domain walls in these non-*c*-oriented grains are preferentially parallel to the *c*-axis and that, under certain circumstances, interaction of domain walls with different orientation caused the irreversible pinning of the adjacent domains. These results show that the domain sizes in thin films can attain much smaller values than believed previously and, therefore, the lower limit of the smallest structure still exhibiting ferroelectric behavior is well below 100 nm in case of BLSF materials.
5. For FeRAMs with a memory density in the Gigabit range, well-ordered ferroelectric nanostructures with lateral sizes in the 100 nm range are required. To find out whether or not such small structures are still ferroelectric (i.e. possess a spontaneous polarization that is switchable), a study of the local piezoresponse of such manufactured structures was performed. It was found that fine-grained $100\,nm \times 100\,nm \times 100\,nm$ ferroelectric structures exhibit a well-defined piezoelectric hysteresis comparable to that of larger structures, up to $1\,\mu m \times 1\,\mu m \times 100\,nm$. Since these structures were *separate* ferroelectric entities, the results clearly demonstrate that ferroelectricity scales well down with size, without deterioration of the switching behavior, at least in terms of the hysteresis loop parameters $2P_r$ and $2E_C$.
6. Switching experiments were performed on *individual* polycrystalline PZT structures $500\,nm \times 500\,nm \times 100\,nm$ in size that were part of a regular array, with a spacing of 500 nm between them. The experiments showed that these structures could be addressed individually, that they switch entirely, i.e. different ferroelectric domains are not usually forming within one structure, and that no crosstalk occurs between neighboring structures.

Accordingly, there is no obstacle of physical nature to the realization of FeRAMs with a high memory density in the Gigabit range.

7. From the experimental piezoresponse results it was possible to derive certain components of the piezoelectric tensor of the ferroelectric epitaxial thin films investigated. Their values turned out to be about two to five times lower than the values measured macroscopically on the same materials, but comparable to the values obtained by other authors using piezoresponse SFM. The origins of the low values measured were discussed in terms of the complex electromechanical interaction between the ferroelectric sample and the probing SFM tip. For the case of bismuth titanate, which has a nonzero component of polarization along the *c*-axis, the ratio d_{11}/d_{33} determined was same as that measured macroscopically on single crystals, therefore validating the numerical values obtained from the piezoresponse data. A more complex model of the tip-to-sample interaction, including also the elastic properties of the tested material, is definitely needed in order to explain the small effective values measured.
8. A basic imaging mechanism has been studied taking into account the anisotropy of the tensor of the piezoelectric coefficients d_{ij} (matrix notation) in order to establish how the piezoresponse signal really reflects the out-of-plane component of the spontaneous polarization. It was found, by computing and drawing three-dimensional plots of the longitudinal piezoelectric coefficient d_{zz} along the probing direction that only in a restricted number of cases the magnitude of the piezoresponse signal correspond to the magnitude of the polarization.
9. The investigations also demonstrated a fundamental electrical asymmetry of the ferroelectric film-semiconductor electrode structure. The local piezoelectric hysteresis loops were always shifted in the vertical (d_{zz}) direction, indicating a preferential orientation of the polarization towards the bottom electrode. As the main reason, it was established that a region depleted from charge carriers is present at the interface between the ferroelectric film and the *n*-type $SrTiO_3$ substrate causing a built-in field, which favors the aforementioned polarization state. Moreover, it was observed, for the individual structures patterned on the same substrates, that this asymmetry increases with a decrease in size of the structure. The latter effect was explained assuming the presence of oriented dipolar defects in the fine-grained PZT cells, defects located mainly at the surface of the nanostructure.

In conclusion, the successful application of the piezoresponse-mode of scanning force microscopy to a variety of thin films and nanostructures of different composition, crystallographic structure and morphology has contributed to a better understanding of the piezoelectric and ferroelectric properties of these films and structures. Although a number of open questions remains, which are especially related to the details of the field distribution within the material volume under the SFM tip, it can be concluded that voltage-modulated scanning force microscopy has proven a powerful tool to characterize ferroelectric films and nanostructures on the lateral nanometer scale, a performance which is required for future developments of ferroelectric high-density memories in advanced microelectronics.