1. Introduction

Ferroelectric materials gradually enter into the design of microelectronic devices. The ability to increase the packing density of the ferroelectric structures and thus the capabilities of the device is primarily limited by the possibilities to manufacture very small structures in a controlled way, but also by the fact that such tiny ferroelectric structures may not preserve their macroscopic properties at this scale. Recently, the interest in finding a better alternative for random access memories (RAMs) in personal computers has pointed towards non-volatile ferroelectric RAMs (FeRAMs). The new devices should satisfy at least the present requirements for dielectric RAMs (DRAMs), plus non-volatility, a property that will save both energy and time, since the constant need of refreshing the memory state (as it is the case in nowadays DRAMs) disappear. On the more practical side, time will also be saved, as the lengthy transfer of information from the long-time mass storage devices to the dynamic memory (such as the initial boot of a computer after switching on, for instance) will vanish as well.

To compete with DRAMs, the lateral size of an individual non-volatile ferroelectric memory cell should be in the mesoscopic range, i.e. less than 100 nm. It is therefore necessary to understand and to control the processes that lead to a deterioration of the prospected performance of ferroelectric structures having such a small size. Presently, however, the understanding of the ferroelectric phenomena at these sizes is by far not complete and needs to be improved, as it can also be seen from the numerous publications in this field during the last decade.

Taking this into account, the scope of the research presented was to study ferroelectric phenomena on a local scale for different materials in view of their prospective use in non-volatile memories.

A summary of the fundamental elements of ferroelectric and piezoelectric phenomena needed to understand the principle of the experimental technique and the interpretation of the results is presented in Chapter 2.

Special attention has been paid to the description of the experimental technique used to achieve the scope of the present work. The method used for the study of the local ferroelectric behavior is the so-called "piezoresponse SFM", a scanning probe technique based on the converse piezoelectric effect that is present in all ferroelectric materials. This technique allows both the detection and the modification of the ferroelectric state, using the same experimental setup, with a resolution down to 10 nm.

As it is at the heart of the experimental setup, the operating principles of a scanning force microscope (SFM) are reviewed in details in Chapter 3. A short review of the previous experiments and SFM-methods to image ferroelectric domains is also provided in order to put the problem in perspective and to demonstrate that the method chosen is the most suitable under the given circumstances, namely the necessity of imaging and modifying the ferroelectric state.

A separate chapter (Chapter 4) is dedicated to an extensive discussion of the possibilities that this technique provides to probe the local ferroelectric properties. For this purpose a careful analysis of the signals involved in the measuring process was included into Chapter 4. In particular, while various voltage modulated scanning force microscopy techniques are gaining in popularity for ferroelectric imaging, they are usually restricted to image displacements normal to the surface. By using the relatively new capability of imaging shear displacements in SFM, the concept of in-plane domain imaging has been developed. This mode enables to image displacements in the plane of the ferroelectric film surface, and therefore to extend the capabilities of piezoresponse SFM to ferroelectric domains whose polarization is oriented in the plane of the film.

The experimental results and a specific discussion of each of them are presented in Chapter 5. First, the capabilities of the experimental system were tested using barium titanate single crystals, whose properties are well known from the literature, both from macroscopic and microscopic characterization. The good agreement between the local measurements of single crystalline $BaTiO_3$ by piezoresponse SFM and the known published properties is an explicit confirmation of the correct operation of the setup, and therefore an overall validation of the experimental method.

Using this setup, ferroelectricity was then locally investigated on a series of ferroelectric thin films and structures of decreasing size:

1. First, continuous films of lead zirconate-titanate (PZT), one of the most frequently used ferroelectric material for device applications, were investigated. The polycrystalline PZT films consist of randomly oriented grains with sizes in the 100 nm to 600 nm range. The thickness of the films is in the same range, viz. 200 nm up to 600 nm.

2. Then, Individual protruding grains of various bismuth layer structured ferroelectrics (BLSFs) were investigated, a relatively new class of ferroelectric materials that feature a high endurance to switching fatigue, and a complex and highly anisotropic layer structure similar to that of the high-temperature superconductors. These materials are also called bismuth-layered perovskites or sometimes Aurivillius phases (after Bengt Aurivillius, the Swedish scientist that discovered and first studied them). These individual ferroelectric grains were part of epitaxial films with a mixed orientation; i.e. they consisted of individual protruding non-c-oriented grains embedded into a c-oriented matrix. The size of the non-c-oriented grains happens to be in the mesoscopic range (hundreds of nanometers) and is therefore well suited for this study. Also, due to the high anisotropy of the BLSFs, they provided a unique system to study the effects of the anisotropy on the ferroelectric properties and the dependence of the latter on the crystallographic orientation.

3. Finally, ordered periodic arrays of fine-grained individual ferroelectric structures having lateral sizes ranging from 1 µm down to 100 nm, were investigated. On these ordered arrays of mesoscopic structures, both fundamental problems, such as the possible disappearance of ferroelectricity below a critical size and more generally the dependence of the ferroelectric properties on the lateral size, as well as problems of high practical and technical relevance, such as cross-talk between adjacent structures, were addressed.

A more general discussion of the results obtained is provided in chapter 6, where different problems common to all of them are presented. Since sizes of the smallest mesoscopic structures investigated were approaching the experimental resolution limit, a discussion of the limitations of the method as well as of potential improvements is also included.