1. Introduction

1.1 Scope of the thesis

The aim of this thesis is to investigate the physical and structural properties of ferroelectric micro- and nano-tubes which can be potentially used as building blocks to assembly functional devices for the purpose of mass storage. The choice of ferroelectric tubes is based on the following features:

- Their state can be controlled precisely with little energy consumption due to their thin wall thickness;
- They can be easily integrated into device architectures in the form of ordered tube arrays;
- As actuator cantilevers, ferroelectric tubes have more deflection freedom than thin films and wires;
- An individual ferroelectric tube with domains having polarizations perpendicular to the tube walls can act as a barcode;
- The ferroelectricity is scalable, thus, in the long-run, we expect that such ferroelectric nano- and micro-tubes can be used as building blocks in mass storage devices on the nanometer scale.

The method proposed in this thesis to fabricate 1D nano- and micro-objects is based on wetting of ordered porous templates. By a controlled procedure, tubes and wires in the nano- and micro-ranges composed of inorganic ferroelectrics and organic polymers as well as metals have been realized and characterized, respectively. A first step towards an assembly, which is a tri-layer metal/ferroelectrics/metal tubular structure, is also proposed in this work which might lead to such functional devices as a mass storage similar to IBM’s “Millipede”.

1.2 Building blocks of tomorrow’s storage devices

In the 21st century, the information technology will move from structured elements in the micrometer range to those in the nanometer range. The involved nanotechnology is often somewhat arbitrarily defined as containing structural or functional elements on a scale smaller than 100 nm. With the fast evolution of new technology, the nanometer scale is expected to pervade also such fields as data storage. Today, most data storage is realized by magnetism in which no clear-cut way has been shown to achieve the nanometer scale in all three dimensions. With its speedy developments, however, magnetic storage technology will doubtless arrive at a point where fundamental physical phenomena start to become important, e.g., the well-known limit of superparamagnetism. Several ideas have been proposed to overcome this limit.

For key areas in information technology, especially in the areas of nano-electronics and data storage, it is not yet obvious which materials and technologies will offer potential alternatives
to the magnetic storage approach. Any emerging technology which could be considered seri-
ously as a substitute for an already-existing but limited one must be able to provide long-term
perspectives. In the case of storage device, any new technique, which has a better storage capa-
bility than today’s magnetic recording \cite{1}, should possess the long-term possibility for further
scaling.

An available tool well-known today which is suitable as a potential replacement technique and
which offers long-term perspectives is a sharp tip with a dimension in the nanometer range.
Such tips are widely used in atomic force microscopes (AFM) and scanning tunnelling micro-
scopes (STM) for imaging and structuring down to the atomic scale. The main function of the
simple tips lies in the local confinement of interaction between the tip and another medium
which is manipulated or characterized.

In 1992, Mamin et al. at the IBM Almaden Research Center pioneered the possibility of using
an AFM tip for readback and writing of topographic features for the purpose of data storage \cite{2}. In
the scheme developed by them, reading and writing were demonstrated with a single AFM tip
in contact with a rotating polycarbonate substrate, as shown in figure [1.1]. Data was formed by
a thermomechanical process by applying local heating and force to the polymer through the tip.
In this way, densities of up to 30 Gb/in² were achieved. This represented a significant advance
in the storage densities of that day. Later, this system was further refined which included mainly
an increase in the readback speeds to a data processing rate of 10 Mb/s \cite{3}.

![Figure 1.1: Performance of thermomechanical writing with an AFM tip on a rotating polymer surface. A focused laser beam propagates through a transparent Poly(methyl methacrylate) (PMMA) sample and heats the optically absorbing AFM tip. The heated tip softens the substrate, and the local tip pressure creates an indentation. The sample is placed on a precision air-bearing spindle to allow for sample rotation \cite{2}.](image)

There also exist fundamental limits for high data processing rate in exploiting single tips in
AFM operation for storage, at present mainly including, the mechanical resonant frequencies
of the AFM cantilevers limit the data rates of a single cantilever to a few Mb/s \cite{4, 5}. The oper-
ation time of a single AFM at present does not have advantage over the conventional magnetic
storage either. Currently, a single AFM operates at best on the microsecond time scale while
conventional magnetic storage operates at best on the nanosecond time scale. To be competitive
not only with the currently existing magnetic recording but also with future developments, the
AFM data rates have to be improved by at least three orders of magnitude.

1.3 “Millipede” - a new approach for storing data

At the end of 1990’s, the scientists in IBM Zurich proposed a new concept, the so-called “Milli-
pede” \cite{6}, which has the potential to store data at high speed with an ultrahigh density. The
feasibility of this high-density data storage system was suggested to be based on micromecha-
nical components borrowed from AFM: tiny depressions melted by an AFM tip into a polymer
medium represent stored data bits that can then be read by the same tip \cite{6}. This thermomecha-
nical storage technique is capable of achieving data densities in the hundreds of Gb/in² range,
well beyond the expected limits for magnetic recording (60 – 70 Gb/in²). Whereas the readback
rate of an individual probe is limited, high data rates can be achieved through the use of massive parallelism: in the “Millipede” system concept, the read/write head consists of an array of more than 1000 thermomechanical probes, fabricated on a single silicon chip using Very Large Scale Integration (VLSI) microfabrication techniques, which operate simultaneously.

As illustrated in figure 1.2 at the heart of the prototype “Millipede” storage system is an array of 1,024 tiny V-shaped levers with very sharp tips. The whole array lies on an area of $3 \text{mm}^2$. Each cantilever is $0.5 \mu m$ thick and $70 \mu m$ long. The tip at the point of the “V” on the cantilevers is two micrometers long. Beneath the array of cantilevers is a polymer layer that acts as the medium for storing bits of information. Bits are written and read thermomechanically.

Prototype versions of “Millipede” have gone through more than 100,000 write-and-erase cycles to prove the durability of the system. Currently, data can be read and written from the device at a rate of a few $Kb/s$, but the IBM researchers estimate that with refinement the system could boost this to $Mb/s$. The plastic film that data is written on and from is moved around beneath the lever array so that each individual tip addresses an area on the order of $100 \text{mm}^2$.

Using this set-up, the IBM researchers managed to cram $500 \text{Mb}$ of data into each $100 \text{mm}^2$ area. This is approximately 20 times denser than that can be achieved with the best magnetic storage system today. Upon realization, this new technology could bring vast amounts of data which could be stored in the mobile phones, laptop computers and even watches. In the present thesis, I will suggest an approach for an analogous data storage device replacing the individual cantilevers by piezoelectric tubes.

### 1.4 Ferroelectric materials for nano- and microelectronics

#### 1.4.1 Ferroelectricity and piezoelectricity

The word “piezo” originates from Greek, which means “to press” or “to squeeze”. Piezoelectric materials are a class of materials that can be polarized by applying a mechanical stress or an electric field. The direct piezoelectric effect is described as that when an external stress is applied to the material, charges appear [7]. This can be illustrated by a linear relation of the charge density $D_i$ as a function of the stress $X_{jk}$ applied to the piezoelectric material (using the Einstein summation convention):

$$D_i = d_{ijk} X_{jk} \quad (1.1)$$
where $d_{ijk}$ is the third-order piezoelectric coefficients tensor measuring in $[C/N]$. The piezoelectric coefficient measured in the direction of the applied field is usually called the longitudinal coefficient, and that measured in the direction perpendicular to the field is known as the transverse coefficient [7]. Other piezoelectric coefficients are denominated shear coefficients.

The reverse effect is that a strain appears when the piezoelectric material is subject to an external electric field. The corresponding relation is also described by a linear equation which relates the $X_{ij}$ developed in a piezoelectric material and the external electric field $E_k$:

$$X_{ij} = d_{kij}^{\text{reverse}} = (d_{ijk}^{\text{direct}})^t E_k$$

(1.2)

where $t$ denotes the transposed “matrix”. The unit of the reverse piezoelectric coefficient is [m/V].

Practically, it is useful to relate the piezoelectric coefficients to the local spontaneous polarization ($P_S$). For most ferroelectric materials, the paraelectric phase is centrosymmetric, which leads to the disappearance of the linear piezoelectric coefficients. For the ferroelectric phase which is nonlinear, higher order terms give:

$$d_{im} = \epsilon_{ij} Q_{mjk} P_{Sk}$$

(1.3)

where $Q_{ijk}$ are the polarization-related electrostrictive coefficients and $\epsilon_{ij}$ the linear dielectric tensors.

For the particular case of tetragonal symmetry where axis “3” is the polar axis, $P_{S1} = P_{S2} = 0$, $\epsilon_{11} = \epsilon_{22}$, $\epsilon_{ij} = 0$ for $i \neq j$, and the only non-zero electrostrictive coefficients are $Q_{11} = Q_{22}$, $Q_{12} = Q_{21}$, $Q_{13} = Q_{23}$, $Q_{31} = Q_{32}$, $Q_{33}$, $Q_{44} = Q_{55}$, $Q_{66}$. It follows:

$$d_{33} = \epsilon_{33} Q P$$

(1.4)

By this equation, the absolute value of the polarization can be estimated if the electrostrictive coefficient $Q$ and the dielectric constant $\epsilon_{33}$ are known.

In a “standard” dielectrics, positive and negative charges are displaced from their original position by the application of an external electric field. This creates a dipole moment, the polarization. However, this polarization will vanish, if the electric field is switched back to zero. In a ferroelectric material, on the contrary, a permanent displacement is inherent to the material and does not disappear in the absence of the external electric field. The direction of this polarization can be switched by applying an appropriate external field. In fact, the key property of a ferroelectrics is described by the switchable spontaneous polarization by an external electric field. As a result, the polarization will not be a linear function of the applied electric field as it would be in a normal dielectrics. It shows hysteresis behavior. The ideal case is depicted in figure 1.3a. At any point, it is approximately given by

$$P = P_s + (\epsilon - 1)E$$

(1.5)

where the spontaneous polarization $P_s$ is equal to the polarization in the absence of an external electric field within a single ferroelectric domain.

In a real case, the loop is less square due to the presence of nucleation centers, which induce an earlier switching (as depicted in figure 1.3b). At that time, the spontaneous polarization is
obtained by extrapolating the polarization at high electric field linearly down to zero field [8]. \( P_r \) stands for the polarization remaining after the disappearance of the external electric field. It is worth to mention that the remnant polarization is not a material parameter as it would be for the spontaneous polarization. \( P_r \) depends on the history of the sample, e.g., on the amplitude of the last electric field used for poling.

![Figure 1.3](image)

**Figure 1.3:** (a) Hysteresis loop of an ideal ferroelectric domain. (b) Hysteresis loop of a real ferroelectric material [9].

Most ferroelectrics exist in a paraelectric form \( P \) at higher temperatures and transform into a non-centrosymmetric phase \( F \) on cooling below a characteristic temperature, the so-called *Curie point*, \( T_c \). This phase transition can be depicted by a change in point symmetries from \( P \) to \( F \subset P \).

Ferroelectric phase transitions are said to be of the first-order when the spontaneous polarization changes abruptly at the Curie point. Second-order phase transitions are characterized by a smooth disappearance of the spontaneous polarization at the Curie point. The two mostly commonly used materials, barium titanate (\( BaTiO_3 \), *BTO*) and lead zirconate titanate (\( PbZrTiO_3 \), *PZT*), treated in this dissertation, possess a first-order transition.

Upon cooling through \( T_c \), a spontaneous polarization evolves. It will be different in different areas in a crystal. Thus the crystal consists in general of many domains. Neighboring domains are separated by domain walls.

### 1.4.2 Ferroelectric nano- and microtubes - better candidates for cantilevers?

1D ferroelectric structures, such as tubes and wires in nano- and micro-scales, belong to a newly developing category of nano- and microscale ferroelectrics [10]. As illustrated in figure 1.4a, a piezoelectric tube, which could be either an *ABO* \(_3\) perovskite type oxide, e.g., *PZT*, *BaTiO* \(_3\), *PbTiO* \(_3\), *LiNbO* \(_3\), *LiTaO* \(_3\) or *Bi* \(_{12}\)Ge*O* \(_2\), or a ferroelectric polymer, e.g., PVDF and its copolymers, can be fabricated into a new type of cantilever with its inner and outer electrodes in the same configurations as the conventional piezoelectric scanner used in nowadays scanning probe microscopes. With one end fixed onto a substrate and the other end kept freely moving, as well as four properly attached electrodes respectively at the inner and outer pore walls, such a piezoelectric tube could be deflected in the desired direction by the application of an external electric voltage \((\pm V_x, \pm V_y)\) between one inner and one outer electrodes on the opposite sides.
across the tube wall. This allows a 3D movement of the free end of the tip. Vice versa, a controlled deflection can also create voltages.

We propose that such ferroelectric tubes, either composed of inorganic perovskite materials, with a diameter within the micrometer range (0.05 $\mu m$ – 5 $\mu m$) but with a wall thickness in the nanometer range (10 $nm$ – 100 $nm$), or composed of organic polymers, with a diameter from 25 $nm$ to 400 $nm$ and a wall thickness of around 30 $nm$ (when the diameter is larger than 60 $nm$), when mounted with a sharp tip (e.g., a diamond-like carbon tip), could potentially be better candidates for the levers (as shown in figure 1.4(b)) used in mass-storage devices due to the following advantages besides the usual advantages of ferroelectric thin films used in nowadays FeRAMs:

![Figure 1.4](image)

**Figure 1.4:** (a) A piezoelectric tube, either made of an inorganic perovskite material or made of an organic polymer, with its properly attached electrodes, can be manipulated by the application of an external electric field. (b) Schematic of a sub-micron piezoelectric scanner and active cantilever.

- For very thin tube walls, the deflection of the tube can be controlled precisely by small voltages applied to the electrodes. For a piezoelectric tube of 1 $\mu m$ in diameter, 50 $nm$ wall thickness and 100 $\mu m$ in length, 1 V applied between the inner and outer electrodes on the opposite sides across the tube wall can induce a movement of the free end of the tube as much as 2.5 $\mu m$. If voltages are applied to all the four pairs of the inner and outer electrodes across the tube wall in the same direction, e.g., from outer electrode to inner electrode or from inner electrode to outer electrode at the same time, an elongation or shrinkage in the $z$ direction can happen. Calculations show that 1 V applied on all the four pairs of electrodes can induce a change of 600 $nm$ in the length of the tube. This means that only small voltages are required for a manipulation of such a piezoelectric tube.

- Such piezoelectric nano- and microtubes are compatible with the Complementary Metal Oxide Semiconductor (CMOS) driving circuits. As stated above, a movement of 1 $\mu m$ of the free end of the tip of the tube needs 0.4 V as the voltage applied. As a result, such piezoelectric nano- and microtubes can be readily integrated into the already existing CMOS logical circuits. We expect that even more sophisticated functions can be integrated via such a piezoelectric tube on a very local scale.
1.4.3 Ordered arrays of piezoelectric nano- and microtubes: a new route toward mass storage devices

Similar to the concept of “Millipede” depicted in figure 1.2, which is not just a modification of an already existing storage technology, but involves a new concept in which high data rates result from massive parallel operation of arrays of tips, highly ordered arrays of ferroelectric nanotubes also have a large application potential in the same field as mass storage devices, as shown in figure 1.5.

Such a mass storage chip composed of arrays of piezoelectric tubes is based on a mechanical parallel $x/y$ scanning of the individual tubes without movement of the whole chip over a storage medium, which can be the same material as in the case of “Millipede”, a thin polymer film. In addition, a feedback-controlled $z$-approaching and $z$-levelling scheme bring the entire cantilever array chip into contact with the storage medium. This tip-medium contact is maintained and controlled while $x/y$ scanning of the individual tubes is performed in parallel for write/read. It is important to note that this data processing approach is not based on individual $z$-feedback for each cantilever; rather, it uses a feedback control for the entire chip, which greatly enhances the efficiency. That means, in such devices, all the micro-cantilevers (piezoelectric tubes) scan independently their individual area and write/read data in an associated section of the storage medium, which is called a bit array of a storage field. Compared to the conventional mass storage devices, the ferroelectric probe arrays permit a fully random read/write with an increased access speed since the individual storage field is not read out in series, but in parallel. The speed of the proposed device could potentially exceed the present access time limit, which is in the $10 \text{ ms}$ range.

During the storage operation, the chip is raster-scanned over an area called the storage field. The scanning area of an individual tube is equivalent to the cantilever $x/y$ pitch, which is currently $1.5 \mu m$. Each cantilever tip of the array writes and reads data only in its own storage field. This eliminates the need for lateral positioning adjustments of the tip to offset lateral position tolerances in tip fabrication. Consequently, a $32 \times 32$ array chip will generate $32 \times 32 (\sim 1,024)$ storage fields on an area of less than $50 \mu m \times 50 \mu m$. Assuming an areal density of $500 Gb/in^2$, a storage field of one cantilever ($1.5 \mu m \times 1.5 \mu m$) has a capacitor of about $2 \times 10^{-3} Mb$, and correspondingly a $32 \times 32$ array chip has a storage capacity of $2 Mb$ on an area of less than $50 \mu m \times 50 \mu m$. Compared to the concept of “Millipede” which has an $x/y$ pitch of $92 \mu m$, the data access rate might be increased as the area each ferroelectric tubular cantilever reads/writes is much smaller.

![Figure 1.5: A mass storage device which is based on highly ordered arrays of piezoelectric tubes on a large scale. In such a device, all the micro-cantilevers (piezoelectric tubes) scan independently their individual area and write/read data in an associated section of the storage medium, which is called a bit array of a storage field.](image)
In real applications, the space needed for the individual write/read wiring of each tube has to be considered. The row and column time-multiplexing addressing scheme implemented successfully in every DRAM is a very elegant solution to this issue. We propose that in our data storage device which is based on piezoelectric tubes, this can be done in the same way as in the case of the “Millipede”, that is, the time-multiplexed addressing scheme is used to address the array row by row with full parallel write/read operation within one individual row.

1.5 Array design, technology and fabrication

Before any prototype of the above-proposed mass storage device can be fabricated, which is based on arrays of functional piezoelectric tubes, different building blocks must be accomplished. They include the preparation and characterization of:

1. Functional piezoelectric nano- and microtubes composed of materials of either an inorganic perovskite oxide or an organic polymer, adopting a configuration of either released or as arrays.

2. Metallic coatings which could be at specific places at the outer wall and/or inner wall of the piezoelectric nano- and microtubes. These metallic structures also have tubular configurations. Potentially, they could be carried out by the same method as the one used for piezoelectric nano- and microtubes.

3. Individual complex tubular structures with their tube wall consisting of metal/ferroelectrics/metal in radial direction consecutively. This allows for the realization of a prototype of functionality of an individually controllable cantilever.


This thesis will deal with all these steps thought not all details (e.g., separated four electrodes on the outer surface of the piezoelectric tubes) could be solved and realized within the scope of the work. The results of this thesis will be helpful as first steps towards the realization of the suggested mass storage device.

1.5.1 Template-directed approaches to 1D micro- and nanostructures

The fabrication method we chose to use in the fabrication of the above elements is based on template-directed approaches, especially template-wetting.

As a straightforward route towards the fabrication of 1D nanostructures, template-directed approach entails synthesizing the desired materials in desired topology via a wealth of templates. The structures so-obtained are complementary to those of the templates. Notable examples include:

- Templating against features on solid substrates such as described in [11, 12]. By this method, metal nanowires as thin as 15 nm were prepared by shadow sputtering a metal source against an array of V-grooves etched on the surface of a Si(100) wafer.

- Templating against self-assembled molecular structures. It explores the fact that surfactant molecules spontaneously organize into rod-shaped micelles (or inverse micelles) when their concentration reaches a critical value [13].
- Templating against existing nanostructures. For example, gold nanorods are directly coated by polystyrene or silica (5 – 10 nm in thickness) to form cable-like nanostructures [14].

- Templating within the pores of a porous membrane. The most outstanding character of this method is that it is extremely general with regard to the types of materials that can be prepared [15] [16] [17].

Among all the template-related methods listed above, synthesis within the channels of porous materials is of our particular interest. This method has several unique advantages: First of all, it is versatile, with the possibility to prepare nanotubes composed of various materials (e.g., metals [18], semiconductors [19], ceramics [20], and polymers [21]) in a controlled manner. The diameter of the tubes can be as small as 3 nm [22]. The nano- and micro-objects obtained are mono-disperse and can be either released from or connected to the templates used.

With the so-called template-wetting method proposed in this thesis, which exploits wetting phenomena based on the ability of low surface energy liquids to wet high surface energy solids, we are thus able to make the first step towards the fabrication of all the 1D elements necessary to realize such functional-tubes-based mass storage devices.

1.5.2 Basic building blocks for functional devices

We chose the following basic building blocks to be realized first before the fabrication of any complex structures can be attempted:

**Piezoelectric nano- and microtubes composed of perovskite $ABO_3$ ceramics**

The first core building block consists of ferroelectric nano- and microtubes which are composed of perovskite $ABO_3$ ceramics.

Dynamic random access memories (DRAMs) are the workhorses for memory chips. Presently, the most commonly used nonvolatile memories are “flash memories” and electronically erasable programmable read only memories (EEPROM). They have common drawbacks: lack of speed, without easy and unlimited reprogrammability, and they are relatively expensive. To overcome these shortcomings of flash memories and EEPROMs, advanced concepts are explored based on either magnetic or ferroelectric materials. Perovskite oxides are prime candidates for these applications, because of their high permittivity in the paraelectric phase or their ferroelectric properties [23]. They also have such advantages as lower operating voltages, improved read/write time-scale and physical robustness compared to the already existing memory types. In fact, these materials are already on the way to memory densities comparable to those of conventional ferroelectrics. The fabrication of future nanoscale capacitors with improved performance for non-volatile memory applications will very likely rely on the new technology of complex oxides. Ferroelectric random access memory devices (FeRAMs) use the remanent polarization for non-volatile information storage.

As described earlier in this chapter, ferroelectrics belongs to polar materials whose spontaneous polarization, in an attainable range of temperature and pressure, possesses at least two equilibrium orientations in the absence of an external electric field. The direction of the spontaneous polarization can be used to store information. This is employed in nonvolatile random access memories. Ferroelectrics also often exhibit a large dielectric permittivity which can be used in thin film capacitors and DRAMs. The piezoelectricity of ferroelectrics is used in actuators,
microelectromechanical systems (MEMS) and pressure sensors, while their pyroelectricity is used for load-sensitive pyroelectric sensors.

The preparation of functionalized nanotubes from complex oxide ferroelectrics is of general interest in materials science. Recently, ferroelectric nanorods with diameters as small as 5 nm to 60 nm and with lengths of more than 10 µm were obtained by a solution-phase decomposition of bimetallic alkoxide precursors in the presence of coordinating ligands [24]. By means of electrostatic force microscopy, ferroelectric switching was shown in a 12 nm diameter rod [25]. Application advantages of these devices include [26] “enhancing the piezoelectric response of composite materials by five orders of magnitude in comparison with bulk ceramic materials”.

Moreover, the fabrication of such FeRAMs poses significant technological challenges. Naturally, the great interest in nanoscale leads to a question: how small may be a ferroelectric component from a capacitor that is still remaining stable and switchable?

A point to note here is that, for practical applications, especially with diameters in the mesoscale range, ferroelectric oxide tubes are more desirable than the simple rods. A rod cannot be manipulated in the same way as a tube. Especially for tubes with thin walls, they can be manipulated very precisely and thus very sensitively on a local scale.

Compared to the method used in [24], a big advantage of the template-wetting method (which will be described in more details in this thesis) to fabricate these piezoelectric nano- and microtubes lies in the possibility that the large-scale configuration of the tubes can be designed a priori by the design of the template used. That means, free-standing arrays of ferroelectric nano- and microtubes can be accomplished not only on relatively large-scale but also with desired arrangement such as hexagonal or squared which is related to the specific structure of the templates.

Ferroelectric nanotubes composed of organic polymers

1D ferroelectric nano- and micro-objects can also be realized by organic polymers besides inorganic ceramics. In recent years, there has been an increasing recognition of the importance of polymeric materials which can be incorporated as active elements in electric circuits. Among the properties which can be exploited, an important one is piezoelectricity. Due to the molecular, crystalline and morphological structure of polymers, they have the potential to comply with the restrictive requirements of piezoelectricity and its two related properties: pyroelectricity and ferroelectricity. The investigations of Kawai in 1969 [27] on elongated and polarized films revealed a large piezoelectric effect exhibited by poly(vinylidene fluoride) (PVDF) with the molecular repeating unit (CH₂-CF₂).

Ferroelectricity has also been found in certain copolymer compositions of VDF with trifluoroethylene, TrFE [28, 29] and tetrafluoroethylene, F₃E [33]. Specially, copolymers of P(VDF-co-TrFE) are of great interest because of their outstanding ferroelectricity [31, 34, 35], together with a concurrent strong piezo- and pyroelectricity. These polymers exhibit, in addition, an important aspect of ferroelectricity that so far has not been demonstrated in PVDF: the existence of a Curie temperature at which the crystals undergo reversibly a ferroelectric-to-paraelectric phase transition in a wide range of VDF-to-TrFE compositions. In PVDF, the existence of such a ferroelectric-to-paraelectric transition is still uncertain, and, in fact, it is generally believed that melting may intervene before the onset of such a phase transition.

Although piezoelectricity in synthetic polymers is not as high as that in naturally occurring...
single crystal inorganic materials and ceramics, the advantage of these polymeric materials as piezoelectric elements arises because they have lower density, more flexibility, and are easier to process. They also show a much higher dielectric strength and much better chemical resistance than ceramics together with a lower mechanical and acoustic impedance which make them good candidates for building blocks as sensors of mechanical signals. In fact, PVDF has already been used in many applications such as transducers in ultrasonic cardiac imaging, blood pressure and pulse measurements, touch sensors in robotics [36], optical fiber coatings for electric field sensing [37], and, as a programmable neural network system [38]. They can also be used in composites with piezoelectric ceramics to improve their properties in device applications [39].

PVDF nanotubes were prepared by Steinhart et al. [40] by wetting of ordered porous templates. Although crystallization occurring within the nanotube walls exhibits directional crystal growth due to the confined geometry and curvature within the pores of the template, only the non-polar $\alpha$-phase was observed. In order to get better functionality, e.g., piezoelectricity and pyroelectricity, a substitute has to be used.

1D ferroelectric polymeric nano- and micro-objects which will be realized in this thesis are based a copolymer, P(VDF-co-TrFE). The P(VDF-co-TrFE) nanotubes or nanowires obtained by the template-wetting method show piezoelectric properties which makes them promising to be used in parallel to inorganic ferroelectric nano- and microtubes in various applications. Compared to ferroelectric ceramics, the ferroelectric polymers are more readily altered to conform to complex device requirements imposed by the environment, size, shape, reliability and durability. They can also be easily patterned for integrated electronic applications. Ferroelectric polymers adhere well to a wide variety of substrates yet difficult for many other ferroelectric ceramics.

**Metallic nano(shell) tubes**

As shown earlier, in order to move the free end of a piezoelectric tube, it is necessary to apply an external electric voltage via a certain configuration of metallic electrodes. In this sense, to fabricate metallic nano- and microtubes which can be adapted to the configuration of the ferroelectric tubes is necessary. Besides the use as electrodes, metallic nano- and microstructures have a lot of further applications, such as catalysts, hydrogen storage and sensors.

Hollow structures made of metals, so called metallic nanoshell tubes or metallic nanoshell particles, are attractive mainly because they do not only exhibit such important features as surface plasmonic resonances and catalytic activities different from and even superior to their bulk counterparts [41, 42], but also have the potential to serve as electrodes in integrated electronic devices on the nanoscale. Among all the metals, platinum (Pt) is of particular interest as the most widely used catalyst and electrode.

For applications in the field of catalysts and electrodes, it is advantageous to employ Pt nanoparticles [43, 44, 45] and nanotubes [46, 47], with a considerably enhanced surface-to-volume ratio compared to bulk Pt. Particularly interesting are Pt nano(shell) tubes within the pores of a membrane acting as a support. Such hybrid systems may exhibit channels with diameters ranging from a few tens of nm to several $\mu$m and depths up to hundreds of $\mu$m with Pt-coated walls. The advantages compared to dispersed systems are obvious: no precipitating and flocculating of the Pt species reducing its activity occur. Pt-coated porous membranes are easy to handle, and no tedious recovering procedures are necessary as in the case of dispersed Pt nanoparticles. They are ideal building blocks for miniaturized flow reactors. Tubes should be prevented from leaching rather than discrete nanoparticles attached to the pore walls that could be removed by
a flowing medium. Aligned pores within a membrane having blind ends, whose walls being coated with Pt, may allow performing Pt catalyzed reactions within their interior. Such hybrid systems containing functionalized microcavities could be promising materials for the “lab on a chip” technology. Furthermore, Pt coated porous materials may be used as nanostructured electrodes which can in turn be wetted with another material, e.g., ferroelectrics.

Although 1D metallic nanotubes have significant application potential in different fields, few methods have been reported on the preparation of uniform metallic 1D structures. Up to now, two approaches to metallic 1D structures have been proven most successful: template synthesis and step-edge decoration. In the frame of template synthesis, macroporous membranes and nanotubes have been used as sacrificial templates. Recently, a chemical process has been reported to synthesize Au, Ag and Pt nanowires. The second method, step-edge decoration has been employed to synthesize molybdenum and some other metallic 1D structures. Nonetheless, a versatile method is still required to produce mono-disperse metallic nanotubes or nanowires in a controlled manner. The goal lies not only in fabricating metallic nano- and microtubes of the desired materials and studying their properties, but also in making use of them as electrodes for other functional structures.

### 1.6 Organization of the thesis

The purpose of the present thesis is to investigate essential elements required for potential future prototypes of functional devices based on piezoelectric materials, such as a new mass storage device. This includes the fabrication and investigation of the different nano- and micro-elements necessary as well as a proposal of the primary composite functional structures based on these elements.

First of all, since the so-called template-wetting method, which is the method of choice in this thesis, exploits the basic phenomena of wetting, Chapter gives an overview of the wetting theory. Not only general aspects are dealt with but also the specific aspects associated with: the physics underlying the occurrence of wetting within the confinement in the 1D cylindrical pores. The structure formation and tailoring of the morphology of the 1D nano- and micro-objects obtained from this specific wetting phenomena are addressed. Because these cylindrical pores are from the porous templates, the next chapter, Chapter is dedicated to a detailed description of the fabrication as well as the materials properties of such porous templates, including porous alumina and macroporous silicon. We expect that the results of these investigations on the materials properties may have also implications for applications in the areas of sensors and opto-electronics.

Before the description on the fabrication and characterization of all the nano- and micro-elements, an experimental chapter, Chapter describes all the methods used in the characterization, including scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX), transmission electron microscopy (TEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), atomic force microscopy (AFM) and piezoresponse force microscopy (PFM).

In Chapter and Chapter the fabrication and the characterization of two core elements towards the assembly of a mass-storage device are described:

- Inorganic piezoelectric perovskite oxide tubes (Chapter) composed of materials including PZT and BTO. Besides the morphology and crystallinity, their piezoelectric property is also characterized by PFM on an individual tube on a local scale.
• Organic polymeric tubes (Chapter 6) composed of $\beta$-phase P(VDF-co-TrFE). Specific properties, such as temperature-induced phase changes, were measured by DSC, besides morphological, and crystalline properties. Piezoelectric switching as well as ferroelectric domain information is also shown by PFM on an individual nanotube.

The possibility to mount metal electrodes on the ferroelectric nano- and microtubes is depicted in the Chapter 7. A prototype of tri-layer tubes with tube-walls composed of metal/ferroelectrics/metal in radial direction consecutively is also shown in the same chapter.

The last chapter, Chapter 8, gives a summary and an outlook based on the results presented in this thesis. We expect that these basic elements as well as primary composite structures could potentially serve as the essential elements and a major trial step towards complex functional devices for data-storage in the future.