4. Experimental details

4.1 Preparation of tubes or wires from porous templates

As described in Chapter 2, 1D nano- or microtubes can be formed within the porous templates. The detailed preparation procedures of inorganic ferroelectric tubes are described in Chapter 5 of organic P(VDF-co-TrFE) tubes in Chapter 6 as well as metallic Pt and multi-layer tubes in Chapter 7. In order to study the morphology and application potentials of these structures, it is necessary to get released tubes or wires as powders or free-standing tubes or wires with one end embedded in a support. In case of macroporous silicon templates, they can be dissolved in a strong base such as aqueous potassium hydroxide (KOH). In the case of porous alumina templates, the selective etching can be realized via a controlled process by using solutions of either a base such as KOH, or an acid such as $H_3PO_4$. The details are listed below:

- In case of macroporous silicon as template matrix, it can be etched with 30 – 40 wt % KOH at 60 °C for 30 to 40 minutes. To prepare arrays, we glued the wetted templates on conducting copper substrates prior to the removal of the matrix material using a conductive glue. The arrays could be handled with tweezers and thus be washed by immersing them into liquids. To remove residual KOH, the solution was washed several times with diluted hydrochloric acid, deionized water, and ethanol successively. To obtain released tubes as a powder, we removed the residual material on the top of the template prior to etching. We moved the wetted templates into cuvettes filled with aqueous KOH. The resulting suspension within the cuvettes was centrifuged after the complete decomposition of the matrix material. Then, the lye was removed with a syringe. The powder samples were washed by adding deionized water and ethanol. After centrifuging, the liquids were separated from the precipitation consisting of tubes with target materials. Finally, they were prepared as ethanolic suspensions which can lead to further characterizations. To prepare free-standing tubes or wires with one end fixed to the macroporous silicon template, a relatively shorter etching time, on the order of 5 – 10 min, was applied. Then, the whole wafer was immersed into de-ionized water to remove the residual KOH before further characterization.

- In case of porous alumina as template matrix, the underlying aluminium was first removed by dipping the whole sample into $CuCl_2 + HCl$ solution. After washing carefully the remaining alumina membrane, it was etched with 5 wt % $H_3PO_4$ solution for 10 hours in a beaker. Because of the interactions among the polymeric nanotubes, they still agglomerated as a membrane in the solution even after the complete removal of the alumina template. Then, the $H_3PO_4$ solution could be replaced by de-ionized water carefully until the pH value of the solution reached 7. A shaking of the beaker made the aggregation of the tubes disappear and a homogeneous suspension formed containing tubes with target materials and could be characterized further.
4.2 Characterization methods of 1D micro- and nanostructures

4.2.1 Electron microscopy

The first method to characterize the overall morphology of the nano- and micro-objects with different parameters was by electron microscopes, including scanning electron microscope (SEM) and transmission electron microscopy (TEM). As the tubes and wires could be obtained in desired forms, e.g., either free suspending in de-ionized water or in ethanol, or free-standing from a template, different investigation methods concerning the electron microscopes, as listed below, were explored to study their morphology:

- SEM (Scanning Electron Microscopy, JSM-6300F) with its basic unit consisting of an electron optical column mounted on the main console, a control and display system, a power supply unit, and a pump box. The main console incorporates a vacuum system, and the control and display system incorporates the control panels, keyboard, and display system. Tubes in different forms can be investigated directly under a SEM provided that they are attached to a highly conductive substrate, such as a doped silicon wafer or copper substrate. For the observation of non-conductive materials such as copolymer P(VDF-co-TrFE), low acceleration voltages, e.g., $1.5 \text{ eV} \sim 5 \text{ eV}$, are used in order to avoid severe electron charges at the sample surface. For inorganic and metallic tubes or wires such as PZT, BTO or Pt, higher acceleration voltages, e.g., $10 \text{ eV} \sim 20 \text{ eV}$, are used to get higher resolution in the images obtained.

- EDX (Energy-Dispersive X-ray Analysis), which is one of the most useful features of SEM analysis. This analytical tool allows simultaneous non-destructive elemental analysis of the sample. When the incident beam in the SEM bounces through the sample creating secondary electrons, it leaves the sample atoms with holes in the electron shells where the secondary electrons used to be. If these “holes” are in inner shells, the atoms are not in a stable state. To stabilize the atoms, electrons from outer shells will drop into the inner shells. However, the atom must lose some energy in this way because the outer shells are at a higher energy state. It does this in the form of X-rays. The X-rays emitted from the sample atoms are characteristic in energy and wavelength to the element of the parent atom, which shells lost electrons and which shells replaced them.

- TEM (Transmission Electron Microscopy, JEM-1010), which can be used to study the morphology of tubes both on their surface topology or cross-section. In the former case, released tubes are placed directly on a holey copper grid coated by carbon films. In the latter case, tubes either released or still residing in template membranes, are embedded in epoxy resin – a mixture of bisphenol A/M epoxy resin, a single component B which is a hardener, a single component C which is an accelerator and a dibutylphthalate D, all of them from Durcupan ACM Fluka – and subsequently cured under $60^\circ C$ for 48 h. Slices measuring 70 nm or thinner can be prepared using an ultra-microtome equipped with a diamond knife. The slices were transferred onto carbon coated copper TEM grids for TEM investigations.

- ED (Electron diffraction), which provides important information on the atomic or molecular arrangement of crystalline nanotubes. The spacings between the spots or rings, much can be learned about the molecular structure and compositions of the samples investigated. The spacing between lattice planes on an ED pattern give information on the atomic structure of the samples investigated. The spacing between lattice planes can be
calculated from the diffraction pattern using the equation: \( r_d = L\lambda \), where \( d \) is the spacing between crystallographic planes, \( \lambda \) is the wavelength of electron, \( L \) is the camera length and \( R \) is the distance from center spot to bright dots on negative. The \( d \) calculated can be compared to the values obtained by the diffractogram of X-ray diffraction (XRD). Thus the crystalline direction of each bright spot can be determined.

### 4.2.2 X-ray diffraction (XRD)

XRD was performed by using a Philips X’pert MRD diffractometer with cradle and secondary monochromator for Cu K\( \alpha \) radiation with a wavelength of \( \lambda = 0.15405 \text{ nm} \). \( \Theta/2\Theta \) scans are carried out in the reflection mode with a small 2\( \Theta \) increment (0.05°) and a long integration time (1 s \( \sim \) 20 s). When the tubes are still residing in the pores of the template membrane, the sample is placed in the diffractometer in such a way that the template surface with the pore openings is arranged perpendicular with respect to the plane defined by the incident and the scattered X-ray beams (in figure 4.1, \( \Psi = 0^\circ \)). The tubes are well aligned within the templates during the measurements. If it is necessary to investigate the textures of the samples, an additional scan, so-called \( \Psi \) scan, can be carried out. The settings of \( \Psi \) (incident beam) and 2\( \Psi \) (detector) were fixed to specific values. The sample was tilted by an angle \( \Psi \) around the axis defined by the intersection of the plane of the incident and the scattered X-ray beams with the template surface. The setup is displayed schematically in figure 4.1. \( \Psi \) equals zero if the two planes are oriented perpendicularly. The scattering intensity is measured as a function of the tilting angle \( \Psi \). This method allows to record a fiber diffractogram in reflection mode.

![Figure 4.1: Schematic depiction of the setup used for the X-ray diffraction experiments.](image)

For the \( \Theta/2\Theta \) scans, the samples were placed in the device in such a way that the surface of the wetted template was oriented perpendicular to the plane of incident and scattered X-ray beams. To perform the \( \Psi \) scans, the setup was adjusted to selected 2\( \Theta \) angles. Then, the samples were tilted by an angle \( \Psi \) around an axis defined by the intersection of the template surface and the plane of the incident and the scattered X-ray beam. The scattering intensity was measured as a function of the tilting angle \( \Psi \).

### 4.2.3 Scanning force microscopy (SFM)

The main technique used for the investigation of ferroelectric materials is the scanning force microscope (SFM). Several modes of operations can be used, including topography mode, friction mode, non-contact mode, lift mode and piezoresponse mode. By using SFM, such information as topology, spontaneous polarization, piezoelectric domain wall as well as phase on a ferroelectric material sample can be obtained.
**Topology investigation by AFM**

The AFM used consists of a cantilever with a sharp tip at its end. The tip is brought into mechanical contact to a sample surface. The force between the tip and the sample leads to a deflection of the cantilever according to Hooke’s law. Typically, the deflection is measured using a laser spot reflected from the top of the cantilever. A feedback mechanism is employed to adjust the tip-to-sample distance to keep the force between the tip and the sample constant. This can be achieved by mounting the sample on a three-dimensional piezoelectric actuator. The tip is then scanned across the sample surface and the vertical displacement necessary to maintain a constant force on the tip is recorded. The resulting map of $s(x, y)$ represents the topography of the sample (c.f. figure 4.2).

![Figure 4.2: Schematic of the set-up of AFM.](image)

**Poling of ferroelectric domains**

An unpoled ceramic initially displays no net piezoelectric response (as shown in figure 4.3a) because the piezoelectric tensors of the randomly oriented grains produced by the fabrication process average to close to zero over the volume of an engineering component such as a piezoelectric actuator. Poling endows the ceramic with its global piezoelectric properties. In this process a direct current (dc) electric field with a strength larger than the coercive field strength is applied to the ferroelectric ceramic at a high temperature, but below the Curie point. On application of the external dc field the spontaneous polarization within each grain gets orientated towards the direction of the applied field, as shown in figure 4.3b. During the poling process, ferroelectric switching occurs in many grains. The grains’ crystallographic axes retain the orientation fixed by the sintering process. However, the high value of electric field applied during poling causes ferroelectric switching such that the average polarization becomes biased along the direction of the electric field vector $E_i$. After poling, there is an overall bias in the average of the grains’ polarization vectors, which gives rise to an overall remanent polarization and a non-zero overall piezoelectric tensor. Note that poling is usually carried out at a temperature which is too low for significant creep or recrystallization to occur.
Piezoresponse Force Microscopy (PFM)

Among all the operation modes listed above, the one which interests us most is the last one: scanning force microscopy operated in the piezoresponse mode, first introduced by Güthner and Dransfeld [115]. Integrated with a lock-in technique (as depicted in figure 4.5), SFM is a powerful tool to probe the local polarization status and electromechanical properties of ferroelectric structures in the above-mentioned piezoresponse mode.

In PFM, an ac voltage is applied between the conductive tip and the electrode on the back side of the ferroelectric. The electric field underneath the tip and the inverse piezoelectric effect causes a periodic thickness change with the same frequency as the applied voltage. This local vibration is transferred by the nanomechanical contact between tip and ferroelectric into a periodic cantilever bending and is detected by the laser deflection signal of the SFM. The further analysis of this signal is performed with a dual channel Lock-In amplifier which measures the values of amplitude($A$/phase($\Phi$) or real-part($A \sin \Phi$)/imaginary part($A \cos \Phi$) relative to the applied ac voltage. In piezoresponse mode the frequency of the imaging should be far lower than the cantilever resonant frequency to avoid mechanical resonance of the cantilever. The driving ac voltage should also be significant below the coercive voltage of the ferroelectric to avoid distortions of the original domain structure.

Two intercalating types of information can be drawn from the SFM investigations on polarized domains:

- Information on domain orientation:

  As pointed out earlier, the sign and magnitude of the piezoelectric constants depend on the value and vectorial orientation of the spontaneous polarization. Therefore, the phase lag between the excitation voltage and the piezoresponse of opposite domains amounts to $0^\circ$ or $180^\circ$, respectively. This can be illustrated by figure 4.5 with two ferroelectric domains having opposite orientations of polarization, perpendicular to the sample surface and sandwiched between a bottom electrode and the conductive SPM tip. In figure 4.5a, no voltage is applied between the electrodes and the two ferroelectric domains have the same dimensions in z-direction, only governed by the spontaneous strain which is the same for the two domains. When a voltage is applied to the tip, the electric field generated in the sample causes the domains with the polarization parallel to the field to extend and the domains with opposite polarization to contract. The images (b) and (c) in figure 4.5 illustrate the z-deformation of the domains when a respectively positive and negative
voltage with respect to the bottom electrode is applied to the tip.

Figure 4.4 illustrates the principle of obtaining the information on the polarization state from the piezoresponse signal. It is based on the detection of the local electromechanical vibration of the ferroelectric sample caused by an external ac voltage. The voltage is applied through the probing tip, which is used as a movable top electrode. The modulated deflection signal from the cantilever, which oscillates together with the sample, is detected using the lock-in technique, as in the case of the noncontact imaging. However, in the piezoresponse mode the frequency of the imaging voltage should be far lower than the cantilever resonant frequency to avoid mechanical resonance of the cantilever. An external voltage with a frequency $\omega$ causes a sample vibration with the same frequency due to the converse piezoelectric effect. Vibration of the sample under the ac voltage also has a second harmonic component at $2\omega$ due to the electrostrictive effect and dielectric constant. The domain structure can be visualized by monitoring the first harmonic signal (piezoresponse signal). The phase of the piezoresponse signal depends on the sign of the piezoelectric coefficient (and therefore, on the polarization direction) and reverses when the coefficient is opposite. This means that regions with opposite orientation of polarization, vibrating in counter phase with respect to each other under the applied ac field, should appear as regions of different contrast in the piezoresponse image.

![Figure 4.4: Demodulation of the information on the polarization state from the piezoresponse signal.](image)

By this method, not only the cantilever movements normal to the sample surface but also lateral shear oscillations (piezoelectric $d_{15}$ constant) can be measured, so that the direction of the spontaneous polarization is detected even when it is parallel to the surface.

It should be mentioned that the vibration of the sample under the ac voltage also has a second harmonic component due to the electrostrictive effect and dielectric constant. Therefore it would be possible to measure electrostrictive properties with the same experimental setup. However, the work in this thesis focuses on the characterization of ferroelectric and piezoelectric properties.

- **Information on domain wall:**

As the tip, held at some distance from the surface, scans over the ferroelectric sample, surface polarization charges induce an image charge $Q_p$ in the probing tip, which results in an additional contribution to the attractive force due to Coulomb interaction. The resulting force gradient is proportional to the product of the electric field due to the polarization and the charge $Q_p$ induced in the tip and, therefore, depends only on the polarization
magnitude and not the sign. This implies that the contrast of opposite 180° domains will be the same and that domain walls will only be visible due to the spatial variation of the charge density in the vicinity of a 180° domain boundary. The tip experiences a change in the force gradient when it is above the wall and the feedback loop alters the tip-sample distance to keep the gradient constant, thus producing a variation of contrast in the feedback signal image, which can be interpreted as an image of the domain wall. Image contrast depends essentially on the external bias voltage applied to the probing tip and on the tip material. By varying the bias voltage, the contrast of domain boundaries can be eliminated and contrast between opposite domains can be observed.

![Diagram](image)

**Figure 4.5**: Principles of piezoresponse SFM. (a) No topographic contrast if no voltage is applied. (b) A change in thickness occurs for neighboring domains with opposite polarization in opposite directions during the positive half period and (c) during the negative half period.

### 4.2.4 Differential scanning calorimetry (DSC)

DSC is a thermoanalytical technique, by which the difference in heat flow (power) to a sample and reference is monitored against temperature while the temperature of the sample, in a specified atmosphere, is programmed. DSC is the most widely used thermoanalytical technique, which enables to determine a number of parameters connected with the physical or chemical processes in condensed phase. Temperatures of phase transitions of first and second order, enthalpies of phase transitions, polymorphism, liquid crystalline transitions, phase diagrams, thermoplastic polymer phase changes, glass temperatures, purity measurements and kinetic studies can be mentioned as examples where DSC is highly efficient.

In order to see the phase transition as well as the melting of ferroelectric materials such as P(VDF-co-TrFE) copolymer, power compensation DSC investigations were carried out. In such a calorimeter, the heat to be measured is compensated with electric energy by increasing or decreasing an adjustable Joule’s heat. The measuring system consists of two microfurnaces of the same type made of platinum-iridium alloy, each of which contains a temperature (platinum resistance thermometer) and a heat resistor (made of platinum wire). For a *Perkin-Elmer DSC 7* used in the experiment, the microfurnace is about 9 mm in diameter, 6 mm in height and has a mass of approximately 2 g. The time constant is slightly smaller than 2 s, and the isothermal noise is about 2µW. The maximum heating power of a microfurnace is about 14 W and the maximum heating rate is 500 K/min. For the evaluation of the curvatures obtained, the program *Pyris Manager* is used.
4.3 Summary of the chapter

In this chapter, the methods to get either released or arrays of 1D nano- and micro-objects, depending on the different porous templates used, were presented first. Then, several characterization techniques, including electron microscopy, energy-dispersive X-ray analysis, X-ray diffraction, scanning force microscopy and differential scanning calorimetry were depicted. These methods and techniques will be used in the next chapters during the fabrication and characterization procedures of 1D nano- and micro-objects.