One-dimensional ferroelectrics: Nanowires and nanotubes

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Abstract

An overview of some general features of the fabrication of one-dimensional (1D) ferroelectric structures is given. Included are positive and negative template-assisted fabrication methods, along with some examples and properties of the obtained ferroelectric nanowires and nanotubes, in particular from the group of the authors. The contribution of Professor James F. Scott to the development of the field of nano-ferroelectrics at MPI-Halle is briefly highlighted.
Considerable attention has been paid in the last 15 years to nanowires and nanorods as one-dimensional nano-systems. Most of the effort was directed towards the synthesis of one-dimensional nanostructures comprising carbon nanotubes\textsuperscript{1}, semiconductor, metallic, and simple oxide nanowires.\textsuperscript{2,3,4,5} A somewhat smaller amount of work has been performed to synthesize one-dimensional nanostructures from functional complex oxide materials. This is most probably due to the chemical and structural complexity of these materials, such as BaTiO\textsubscript{3} (BTO) or PbTiO\textsubscript{3} (PTO) which are perovskite oxides, or YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} - a high-T\textsubscript{c} superconductor, in all of which stoichiometry and structure play a most important role in achieving functional properties.

At the general level, there are two main methods to fabricate nanoscopic and mesoscopic one-dimensional structures: self-assembly, or bottom-up methods, used for instance by Urban et al. to fabricate BTO ferroelectric nanowires\textsuperscript{6}, and template-mediated approaches described, e.g., by Martin et al.\textsuperscript{7} In principle, self-assembly fabrication methods offer a higher crystalline quality and smaller dimensions mainly due to the bottom-up building of the structure using atoms and molecules. On the other side, the template-mediated methods offer a number of advantages in terms of tunability of the characteristic dimensions, as well as a better control of stoichiometry and a higher flexibility. Most of the template methods to obtain tubular or rod-like structures use porous templates in conjunction with infiltration or conformal deposition to partially or entirely fill the pores. This paper will address some general features of the fabrication of one-dimensional (1D) ferroelectric structures along with some examples and properties of obtained ferroelectric nanowires and nanotubes, in particular from the group of the authors. For more comprehensive reviews on one-dimensional ferroelectric and
perovskite nanostructures, see, e.g., refs. \(^8,^9\) Before turning to 1D ferroelectrics, however, a historical remark referring to the significant role James F. Scott played in initiating the studies of nanosize ferroelectrics will be given.

1. Historical remark

It was as early as in 1997 that Professor James F. Scott joined the Max Planck Institute of Microstructure Physics (MPI) in Halle, Germany, for a half-a-year research stay within the framework of a prestigious Alexander von Humboldt Research Award. At that time the authors of the present paper were coworkers of Professor Ulrich Gösele's department at MPI, working with ferroelectric thin films and heterostructures, mainly grown on silicon wafers. This research had been initiated by Gösele who had a strong background in silicon materials science and microelectronics, and who clearly saw the promising perspectives of high-k and ferroelectric complex-oxide materials for the future downsizing of silicon-based thin-film devices. Jim Scott brought along not only an important experience in ferroelectric thin films and integration of them into silicon technology, but, most importantly, his joy of discovery and open mind. Soon after his arrival at Halle, he immediately noticed that the department had not only state-of-the-art deposition equipment available (like MBE, PLD, MOD, etc.), but also quite some equipment to structure and analyze thin films down to the nanosize region as, e.g., electron-beam lithography, reactive ion etching, as well as powerful infrastructure and knowledge in electron microscopy. In the discussions with the present authors, Professor Scott turned their attention to the fact that – different from the semiconductor area, where the micro and nano aspects had already found considerable attention – ferroelectric
nanostructures had not yet been in the proper focus of international research at that time. He suggested moving into this direction, and – apart from participating in the running activities of the group\textsuperscript{10,11} – he actively took part in the first steps done by the Halle group into the nano area. The title lines of the first three papers\textsuperscript{12,13,14} reporting on corresponding results of this joint activity in 1998 and 1999, clearly indicate the direction chosen: „Self-patterning nano-electrodes on ferroelectric thin films for gigabit memory applications“ (Ref. 12), „Nano-phase SBT-family ferroelectric memories“ (Ref. 13), and “Switching properties of self-assembled ferroelectric memory cells” (Ref. 14), with SBT meaning SrBi\textsubscript{2}Ta\textsubscript{2}O\textsubscript{9}. Whereas that work was related to self-assembled nanostructures, i.e. a bottom-up path, the subsequent activities of the group were also focussed on the top-down approach, \textit{viz.} the preparation of ferroelectric nanosize islands by help of electron-beam direct writing, and the investigation of their structural and physical properties\textsuperscript{15,16}. Later, among the various activities of the group related to the preparation and investigation of many different ferroelectric nanostructures (see, e.g., Refs. 17,18,19,20) there were also various one-dimensional ferroelectric nanostructures as described below. The cooperation with Jim Scott continues until present days addressing different topics such as nanotubes, which are within the scope of the present paper, or vortex structures.\textsuperscript{21} The present authors acknowledge with great respect and gratefulness the impact received by Professor James F. Scott.

\section*{2. Ferroelectric nanowires}

A good example for the growth of perovskite nanowires using bottom-up fabrication methods is the preparation of BaTiO\textsubscript{3} and SrTiO\textsubscript{3} nanowires by Park's group.
at Harvard University. The synthesis of perovskite nanowires is performed by solution-phase decomposition of complex alkoxide precursors in the presence of coordinating ligands.\(^6,^{22}\) In a typical reaction, an excess of \(\text{H}_2\text{O}_2\) was added at high temperature (100°C) to a heptadecane solution containing the Ba-Ti or Sr-Ti bimetallic alkoxide and oleic acid. By heating up the resulting solution to 280°C for 6 hours, anisotropic nanorods grow most likely due to decomposition and crystallization in an inverse micelle medium formed by the precursor and the oleic acid. The reaction yields well-isolated nanorods with diameters varying from 6 to 30 nm and lengths of over 10 µm. Ferroelectric domains as small as 10 nm in diameter have been written on a single wire using ultra-high vacuum electric force microscopy (EFM), i.e. by applying an external field via a conductive tip.

More recent examples for the growth and investigation of ferroelectric nanowires comprise PbTiO\(_3\),\(^{23}\) KNbO\(_3\),\(^{24}\) BaTiO\(_3\),\(^{25}\) and lead-free bismuth-based complex perovskites.\(^{26}\) It should be noticed that also theorists have discovered ferroelectric nanowires as an attractive research subject, see, e.g. refs. 27, 28, 29, with the latter reference also extending into the area of multiferroic nanowires.

### 3. Ferroelectric nanotubes

From fundamental physics as well as from the application point of view the tubular geometry, respectively nanotubes, might be more interesting than the simple wire geometry. The intricate tubular geometry along with a high aspect ratio and one additional variable parameter, i.e. the wall thickness, as well as the larger surface-to-bulk ratio...
ratio might influence the ferroelectricity in such structures. There are fundamental questions that immediately arise:

- Is the polarization direction influenced by the geometry?
- Which would be the aspect ratio at which the surface effects would become important?
- If the polarization is perpendicular to the tube axis, what would be the ferroelectric domain pattern?
- In which way the obvious non-planar geometry and stress distribution influence the polarization switching?

The most interesting aspect of the nanotube system is the characteristic geometry, viz. one dimension that can extend into microscopic sizes along with the toroid-type cross-section, which in certain cases might have the aspect ratio of a thin film. This abnormal geometry correlated with the actual crystalline orientation will define the ferroelectric properties of the tube in terms of polarization orientation and switching ability. It has to be stressed that the "top" and the "bottom" surface of that "thin film", i.e. the outer and inner surfaces of the tube shell, have different curvatures. This might not be a real problem in the case of bulk tubes, but in the nanotube case this might generate a highly non-uniform field. To answer the above questions properly it is necessary to handle proper fabrication processes which allow an easy and convenient way to fabricate nanotubes of different materials, geometries, and sizes. In the following we will summarize fabrications methods of ferroelectric nanotubes available up to the date.
3.1. Hydrothermal synthesis

The hydrothermal method to obtain ferroelectric nanotubes follows the same general route of hydrothermal synthesis that allows the preparation of ferroelectric perovskites at low temperatures, i.e. the reaction of oxide or hydroxide precursors in an aqueous solution under controlled pH value and temperature to obtain an ABO$_3$-type compound.

One strategy to obtain perovskite nanotubes is to use simple-oxide nanotubes as bona fide precursor and to let these react, under hydrothermal conditions, with a compound which contains the second cation. For a ferroelectric perovskite a good precursor is TiO$_2$ which allows to obtain the important ferroelectric perovskite oxides such as $A$TiO$_3$, where A can be Ba, Sr, Pb, etc. Using TiO$_2$ nanotubes rather than "normal" crystalline TiO$_2$ for a reaction in a hydrothermal environment might be an easy route to fabricate perovskite nanotubes. There are several ways to achieve TiO$_2$ nanotubes. One of these uses a simple hydrothermal treatment of crystalline TiO$_2$ with an NaOH aqueous solution. Another approach uses a nanocrystalline atanase phase, which can be easily obtained by hydrolysis of titanium alkoxide. Titania nanotubes down to 10 nm diameter can be obtained by hydrothermal reaction of this nanocrystalline phase in an NaOH solution at about 150°C. TiO$_2$ nanotubes can also be obtained by rolling up crystalline TiO$_2$ sheets exfoliated from TiO$_2$ crystals during hydrothermal annealing as it is proposed by Yao et al. To obtain perovskite nanotubes one can simply let react these titania nanotubes with Ba(OH)$_2$ and/or SrCl$_2$ to obtain (Ba,Sr)TiO$_3$. The hydrothermal reaction is performed at ambient pressure by refluxing the solution for a period of 20 to 60 h. BaTiO$_3$ and SrTiO$_3$ nanotubes with 8 to 15 nm outer diameter, 4 to 7 nm inner diameter, and several hundred nanometer length were obtained. In a similar way, PbTiO$_3$ nanotubes were recently
prepared by a reaction of prefabricated TiO₂ nanotubes with PbO vapour at between 300 and 600 °C.³³

An alternative approach is proposed by Padture and Wei.³⁴ The starting material is self-organized TiO₂ nanotubes obtained by anodization of Ti metal sheets. The anodization process is similar to the one used to obtain ordered porous alumina.³⁵,³⁶,³⁷ Briefly, a polished Ti foil is anodized in an aqueous HF solution at 16°C by applying a direct voltage between the Ti foil and a Pt cathode.³⁸ A honeycomb-type array of amorphous TiO₂ nanotubes of about 100 nm diameter and 200-300 nm length is obtained. These nanotubes can lateron be reacted with Ba(OH)₂ under hydrothermal conditions (at a pH value of 13.2 and a temperature of 200°C for 80 min) to obtain an array of polycrystalline nanotubes. Remarkable is the preservation of the nanotubular shape after the reaction of the amorphous titania with the Ba ions and the transformation of the initially amorphous walls into polycrystalline BaTiO₃ or (Ba,Sr)TiO₃.³⁹ The above fabrication method along with the methods to fabricate large-area, perfectly ordered nanoporous alumina arrays⁴⁰ might develop into an interesting way to fabricate well-ordered nanoporous ferroelectrics, regular composite materials, ordered nanotubes, etc. - in other words a new class of materials.

**3.2. Template-based synthesis**

A general approach to fabricate nanoscale structures of complex materials is to use existing structures that are easily obtained from simple materials such as silicon or aluminium, and to deposit, react and/or etch them in order to obtain new materials which would keep the geometry of the initial structure, the latter usually being called "template". In other words, the existing nanoscale materials are used as skeleton for the fabrication of
new structures with new materials that are more complex in structure and eventually rich in functional properties.

Any adroit technique is here allowed. Any material from well-known silicon to biological materials such as viruses\textsuperscript{41} can be suitable to play the template role. Generally, the initial template can be negative or positive, i.e. holes in a substrate, or wires grown on a substrate, respectively. The fabrication process shown below comprises three different stages:

- Template fabrication
- Coating of the template
- Crystallization annealing
- Etching away the host template

\textbf{3.2.1. Negative (porous) templates}

There are two major templates used for nano-fabrication, \textit{viz.} macroporous silicon and nanoporous alumina. Different approaches are being used to obtain the templates, depending on the material of choice. For instance, for the preparation of macroporous silicon, which is one of the most used templates due to various reasons (including the availability of high-quality silicon and the eventual compatibility with silicon microelectronic technologies, as well as possible applications in photonics, e.g., as bi-dimensional photonic band-gap material), there is now a relatively well-established technology, and good reviews are published.\textsuperscript{42}

Template fabrication from macroporous silicon is a different field and we will not detail this, but we can briefly say that a careful control of the etching parameters can make the silicon pores absolutely straight up to a depth of several hundreds of microns or
can modulate or tune the pore diameter in a desired way as it is shown in Figure 1 (from ref. 43).

**Figure 1:** Diameter-modulated pores etched into silicon (left), and a corresponding gold wire obtained by electrochemical deposition (right). ⁴³

The pore diameter in macroporous silicon can vary from 0.4 µm up to 2-3 µm and the depth can range from several microns up to 250-300 µm. The main advantage of macroporous silicon is the possibility of wafer-scale processing. Wafers of four-inch diameter are nowadays standard in macroporous silicon processing, yielding perfect pore arrays over the whole wafer.

Nanoporous alumina is as well an established template used in the fabrication of one-dimensional nanosize structures made out of different materials including multi-segment nanotubes. Nanoporous alumina is obtained by anodization of an aluminium foil using different electrolytes. The anodization of aluminium has been studied for a century now, but only in the last 15 years - after Masuda and Fukuda ³⁵ discovered that the pores are self-assembling into ordered arrays after long anodization times - it became really intensively studied and applied in photonic crystals and other nanotechnology-related
fields. Self-ordered alumina pores are arranged in a hexagonal pattern with the lattice constant varying from 60 nm to 500 nm, depending on the actual etching conditions. The size of the self-organized domains is in the range of few microns. For example, Choi et al.\textsuperscript{40} using an imprint technique to induce pore nucleation in the form of a regular array have successfully obtained large–area (in the centimeter range) single domain, well-ordered nanoporous alumina. By etching away the aluminium substrate, a nanoporous Al\textsubscript{2}O\textsubscript{3} membrane with straight and well-aligned pores from the top to the bottom can be relatively easily obtained.

It is important that these porous materials, macroporous silicon and nanoporous alumina, can act as templates to fabricate one-dimensional functional materials. Taken together, these two types of templates offer a wide range of diameters ranging from 40 nm to several microns and a high aspect ratio, sometimes reaching several orders of magnitude.

### 3.2.2. Nanotubes and nano-shell tubes obtained by infiltration

Tubes of different materials and dimensions can be relatively easily obtained by infiltration of porous substrates such as porous silicon, nanoporous alumina, or other porous materials, with polymers or other precursor solutions. For instance, polymer nanotubes have been fabricated by infiltration of macroporous silicon with a polymer material at the glass transition temperature. The infiltration of the high-aspect ratio porous template is performed by wetting the inner surface of the silicon pores with a polymer.\textsuperscript{44}

Inorganic nanotubes or nanowires are similarly obtained, if a precursor solution is used to infiltrate the template, followed by an appropriate thermal annealing. In such a
way, nano-shell tubes of BaTiO₃, Pb(Zr,Ti)O₃ (PZT), and SrBi₂Ta₂O₉ (using a “mist” solution deposition approach) and corresponding arrays were fabricated. Fig. 2 shows an array of nano-shell tubes obtained by partially etching the host silicon template away, and also a single wire showing the high aspect ratio.

**Figure 2:** Array of BaTiO₃ nano-shell tubes obtained by partially etching the host silicon template away (left), and a single BaTiO₃ tube arranged on a silicon wafer (right).⁴⁵

A single-step infiltration yields tubes with about 90 nm wall thickness. The outer diameter and the length correspond to the template, i.e. 400 nm and 150 µm, respectively. Piezoelectric properties and ferroelectric switching of PZT and BTO nanotubes were measured by PFM after they had been arranged onto a Pt-coated silicon substrate. Individual ferroelectric tubes of PZT and BTO were probed by a conductive tip and electrically characterized by measuring the local piezoelectric hysteresis. The as-prepared nanotubes showed only weak ferroelectric properties; however by a one-hour annealing at 700°C the switching properties were significantly improved, resulting in rectangular hysteresis loops with sharp ferroelectric switching at a coercive voltage of about 2 V (see Figure 3).
Figure 3: Piezoresponse hysteresis loop of a single PZT nanoshell tube after annealing.

The effective remanent piezoelectric coefficient was estimated to about 90 pm/V which is higher than in thin films. Morozovska et al. have theoretically shown that the transition temperature could be higher in long ferroelectric nanotubes than the one of the bulk material for a negative electrostriction coefficient, and predicted preservation and enhancement of the polarization.\textsuperscript{47} The possible reason of the enhancement of the polar properties in these confined ferroelectric nanotubes and nanowires is the radial stress coupled with polarization \textit{via} the electrostriction effect under the decrease of the depolarization field for long cylindrical nanoparticles.

Alternative solution-based deposition methods might also be used in uniform coating of the template. Morrison et al. have used “mist” (liquid-source) deposition and similar macroporous silicon templates to obtain SrBi\textsubscript{2}Ta\textsubscript{2}O\textsubscript{9} nano-shell tubes\textsuperscript{46}. Alternatively, nanoporous alumina templates and a similar infiltration process can be used to obtain either nanotubes\textsuperscript{48} or nanowires\textsuperscript{49} depending on the precursor solution wetting properties and infiltration time.\textsuperscript{50}
Various physical properties of negative template-made ferroelectric nanotubes are now under investigation worldwide. For example, mechanical fracture in relation to domain structure\textsuperscript{33}, resistive switching\textsuperscript{51}, and retention-loss dynamics\textsuperscript{52} have recently been investigated on PZT and PbTiO\textsubscript{3} nanotubes, respectively, made by applying nanoporous alumina templates.

### 3.2.3. Positive templates: nanowires

However, the negative-template approach described above has a number of drawbacks when real applications, mostly in microelectronics, are envisaged. One of the most serious ones is the relatively difficult control of the wall thickness of the tube. Additionally, real devices need electrodes on both inner and outer sides. This would require several precursor infiltrations of the porous templates in the above process. These turned out to be more difficult and more laborious than a single-step infiltration.

An alternative approach to the fabrication of one-dimensional nanoscale ferroelectric structures has been proposed a few years ago.\textsuperscript{53} Instead of porous templates, positive templates, such as epitaxially grown nanowires, are used. One layer or many layers can be easily deposited on the nanowires by conventional vapor deposition methods, as typically used in microelectronics industry. Finally, tubular structures can be obtained by selectively etching the initial nanowires away. An important advantage offered by the vapor deposition methods compared to the infiltration methods is a better control of the wall thickness due to the inherently better control of the film thickness in vapor deposition processes. For many reasons, including geometric and hydrodynamic reasons, it is much easier to perform vapor deposition on skyscraper-type structures than into deep trenches.
Multi-wall nanotubes have been prepared using two types of templates, i.e. silicon nanowires and ZnO nanowires (Figures 4 and 5). The silicon nanowires (SiNW) used have an average diameter ranging from 20 nm to 50 nm and a length of 200 nm up to 600 nm, whereas ZnO nanowires have a hexagonal cross-section with an equivalent diameter of 100 nm up to 150 nm and a length in the micron range. Details on nanowire template fabrication were published elsewhere.\textsuperscript{54,55} Platinum and SrRuO\textsubscript{3} were used as metals and BaTiO\textsubscript{3} and PZT as ferroelectric materials in a sequential deposition to obtain metal-ferroelectric-metal (MFM) structures.

**Figure 4:** SEM image of a cross-section sample prepared by focused ion beam thinning of a Pt-PZT-Pt tri-layer structure deposited on a silicon nanowire template. The inset shows a zoom-in image of a coated single Si nanowire.
Figure 5: SEM image of a ZnO nanowire template covered with a SrRuO$_3$(10 nm)/PZT(60 nm) bi-layer film (left); top-view of a PZT nanotube obtained by etching the silicon template away (right).

Ferroelectric switching of a single PZT/Pt nanotube of about 250 nm outer diameter was measured by piezoresponse scanning probe microscopy (PFM). Hysteresis loops acquired on a tube as well as on the free surface of a ferroelectric film similarly processed as the tubes are shown in Figure 6.

Figure 6: Piezoelectric hysteresis loop acquired on a PZT/Pt nanotube arranged on a Pt-coated Si wafer (triangular dots) and on a 60 nm thick PZT film deposited on a Pt-coated Si wafer and processed in the same run as the nanotubes (square dots).
The hysteresis loop shows relatively good switching properties of the ferroelectric thin film, whereas the effective piezoelectric coefficient is about ten times lower compared to the values acquired using the same measurement setup on high-quality epitaxial films.\textsuperscript{56} A lower quality of the polycrystalline ferroelectric layer due mostly to the low deposition temperature and the thickness below 50 nm might be responsible for these low values of the effective piezoelectric coefficient. The cylindrical geometry of the tube, in which the inner electrode is at a floating potential, gives a relatively intricate field distribution within the ferroelectric shell. This effect along with the mechanical boundary conditions increases the effective piezoelectric coefficient as well as the measurement noise, deteriorating the shape of the hysteresis loop. Nevertheless, a switching process together with a strong imprint in the positive direction is confirmed.

The fabrication method based on nanowires is appropriate to fabricate three-dimensional ferroelectric capacitors (see Fig. 7) for storage devices. This is mostly due to the fabrication processes and materials which are similar to the ones used in nowadays microelectronic industry. The gain in the cell surface of a ferroelectric capacitor made from nanowires in the stacked architecture is simply the ratio between the surface with and without nanowires:

$$G = \frac{S_{nw}}{S} = \pi/2 \cdot R_a$$

Where $S_{nw}$ and $S$ are the surface with and without nanowires, respectively, the latter being given by $L^2$, and $R_a$ is the aspect ratio of a single nanowire. For nanowires with 100 nm diameter and 1 µm length the aspect ratio is 10 and the gain is about 15, which practically means that the active surface is 15 times larger than in the planar case.
The nanowire-based fabrication method in combination with the template-assisted large-scale ordered growth of nanowires (viz. ZnO nanopillars 57) might be an alternative to the trench-based fabrication of 3D ferroelectric capacitors.

Figure 7: Proposed memory cell based on 3D ferroelectric structures built on silicon nanowires.

### 4. Conclusions

In summary, we have shown here the possibility to obtain ferroelectric tubular structures, including multilayer structures such as metal-ferroelectric-metal capacitors, with a high aspect ratio and characteristic dimensions (diameters) ranging from about 100 nm up to several micrometers. The presented methods are suitable to fabricate single nanotubes and ordered nanotube arrays. Potential applications are manifold and comprise micro- and nano-fluidics, mesoscopic piezoelectric actuators and scanners, storage devices and tunable photonic crystals, 58,59 or, as recently shown by Jim Scott, terahertz emitters. 60
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**References**


