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Electroceramics: looking ahead

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Abstract

Research and development in the field of electroceramics is driven by technology and device applications. It includes research on a broad spectrum of inorganic materials, and it covers all scales from the level of the crystalline lattice to that of final devices. The applications find a place in an increasing number of domains, ranging from environment monitoring and transportation, through medicine and health-care, to electronics and communications. Two tendencies are emerging: surface and interface phenomena play an increasingly important role, motivated by the interest to integrate electroceramic functions into microelectronics and MEMS technologies as well as by the evolution of bulk products from discrete components into materials systems. Electroceramics are following conventional semiconductors with respect to down-scaling. Nano-size effects, nanotechnology related processes, and the use of new characterization techniques to reveal nanometric scale features are therefore gaining in importance. Recent research in electroceramics and evolving trends for the future are discussed in the context of these two issues.

Keywords: Dielectric properties; Electrical properties; Films; Functional applications; Interfaces

1. Introduction

The field of electroceramics is application driven and technology centered. Its foundations are the science of ceramic processing, chemistry, and solid state physics, and its products find applications in as diverse fields as industrial process control, health-care, consumer electronics and environment monitoring. The tools at the hands of the electroceramist include the majority of the periodic table, inorganic, organo-metallic and solid state chemistry, crystallography and other structural and chemical characterisation tools, experimental physics, modeling and device engineering. The field is truly a trans-disciplinary one in both its fundamentals and its applications aspects.

Electroceramics includes dielectric and conductive ceramics. Dielectric ceramics can be divided into linear and non-linear dielectrics, each counting a large number of materials. Conductive ceramics are even more numerous, encompassing super-conductors, conductors and semiconductors, and including both ionically and electronically conductive ceramics. Additional groups, not entirely separated from the ones mentioned above, are magnetic ceramics and optical ceramics.

For a decade, electroceramic materials have been introduced into microelectronic products: integrated capacitors, but also electroceramics memories, have already reached the market, and researchers are at present also developing ferroelectric transistors (so called 1T memories or FeFET). In parallel, the vast area of electroceramic sensors and actuators is expanding, or rather 'contracting', into the field of microsystems: highly performing microsensors and microactuators based on electroceramics are being demonstrated, in which ceramic films and microtechnology are combined to form efficient microdevices for production control, environment monitoring, and biomedical applications.

In recent years the trend of miniaturisation has had an important impact on the field: electroceramic thin films are at the focus of current R&D work. As part of the interest in thin films, but also beyond thin films towards thick films, the evolution of the industrial interest from discrete components into electroceramic systems and multifunctional electroceramic becomes significant. With this trend, integration technology and

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surface and interface phenomena gain importance. Another, more recent, trend is that of the downscaling of electroceramic based components and devices. Nanosize effects, nanotechnology related processes, and the use of new characterization techniques to reveal nanometric scale features are therefore gaining in importance.

The short review on current state of the art and trends in the field of electroceramics focuses on these two important issues of integration and nanotechnology: the impact of electroceramics in information and communication technologies is outlined first, followed by a brief description of selected examples of applications of electroceramics in microsensors and microactuators. Then integration issues that are important for electroceramic based systems are discussed, and finally some examples that illustrate results in the new research field of nanoscience and nanotechnology of electroceramics are presented.

2. Electroceramics in communications and information technologies

2.1. Information storage: memories

For a decade electroceramics have been developed for a number of memory applications. They offer advantages such as increased memory density for DRAMs, and low-voltage and high speed for non volatile memories.[1]

Dynamic random access memory (DRAM) is the most important solid state memory due to its simplicity, high bit density, fast read/write speed, and low power consumption. As the DRAM density reaches gigabit, scaling becomes very challenging. Modifications of the capacitor geometry, to increase or at least to maintain capacitance, in spite of the reduction of cell floor area, seem to have arrived at their limit, hence the need to replace the low permittivity SiO/SiN dielectric, by higher permittivity materials. Ta_2O_5 with medium permittivity of 25 is being implemented, and $(Ba,Sr)TiO_3$ (BST) having dielectric constant over 200 is studied since some time.[2] A number of technological issues, such as acceptable processing temperature,[3] and conformal deposition on three dimensional structures were solved to a high degree, but issues such as reliability and high throughout/high yield unit processes are not yet completely established.

Ferroelectric non volatile random access memories (FeRAMs) are obtained when ferroelectric films replace the dielectric layers of the DRAMs.[4] Writing and reading are made by switching the ferroelectric capacitor. In the last decade FeRAMs are being developed for stand alone applications and for embedded applications. In comparison to Flash memories, FeRAMs are of a low voltage operation as well as shorter write times. The materials proposed for FeRAM applications are based on $Pb(Zr,Ti)O_3$ (PZT) compositions as well as on $SrBi_2Ta_2O_9$ (SBT) layered perovskite Aurivillius phase systems.

Requirements of FeRAMs include operating voltages below 3 V, endurance cycles $>10^{10}$, and long storage time with out degradation. While SBT films are more stable against fatigue (freezing of the polarisation upon increasing number of switching cycles), PZT has the advantage of a lower processing temperature. The replacement of the Pt electrodes by oxide electrodes, such as IrO_2, eliminates the fatigue problem, but increases the leakage of the capacitor. Recently, suppression of fatigue, without degradation of the leakage properties has been demonstrated[5] by the modification of the ferroelectric/electrode interface. In a similar way also the switching voltage has been reduced.[6] Imprint effect (imprint is the shift of the hysteresis loop along its voltage axis during rest time, that results in unachievable switching) are still more severe in PZT than in SBT. Numerous integration problems of FeRAMs have been solved in last years, and others are still being solved: bottom and top electrodes, contact technology and diffusion barriers, conformality, etching, isolation, and yield. For low density memories, the capacitor is placed aside from the transistor [Fig. 1(a)], and higher processing temperatures are permitted. For high density memories [Fig. 1(b)], the ferroelectric capacitor is located above the transistor, and the processing conditions are much more demanding. For further development of high density non volatile memories, a lower deposition temperature, multi level metalisation, and reduction of cell size have to be achieved. Reliability problems are still to be completely solved.

Applications of embedded FeRAM are in contactless smart IC cards and RF–ID cards. Ferroelectric memory technologies are expected also to be used in reconfigurable devices as programmable interconnect switches (able to reconfigure logic in a system under operation mode). Matsushita, Panasonic, NEC and Rohm are producing and selling smart cards. Other manufacturers like Hundai are at different stages of developments. Applications of stand alone FeRAM are expected in computer memories, in high speed telecommunications, and are developed by companies like Samsung, and Siemens.

Development is made presently in 1T (1 transistor) ferroelectric memories. The memory is a ferroelectric field effect transistor (FeFET) in which a ferroelectric layer is deposited above the gate. After applying a pulse voltage to the gate, the FE is polarised in a given direction. The drain current is then controlled by the state of the polarisation of the ferroelectric layer. While FeRAM operates in a destructive read out mode and therefore the read/write cycle is long, requiring rewrite after each read operation, FeFET has a non destructive read-out. In addition FeFET is small, containing only a single

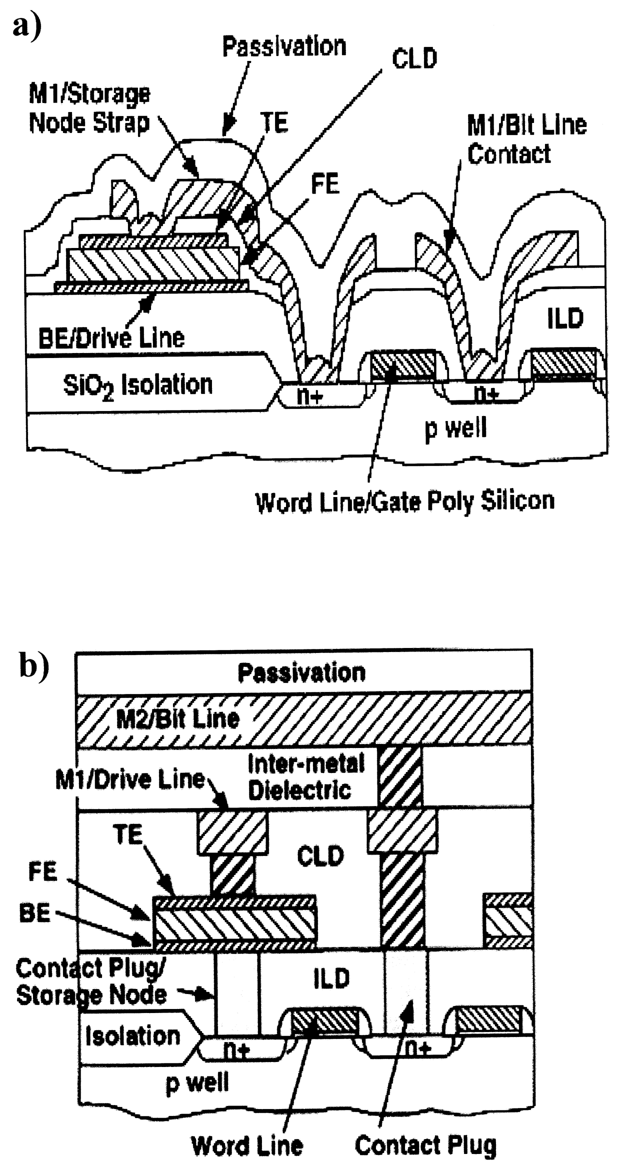

Fig. 1. Structures of non volatile ferroelectric memories: (a) lateral architecture for low density applications e.g. smart cards and RF–ID cards, (b) vertical architecture for very large scale integration in computer memories.[7]

transistor, and no capacitor. FeFET is scalable and fast and therefore very interesting for high density memories. At present there are two directions of development: One in which the ferroelectric layer is directly deposited on the Si (e.g. $BaTiO_3$), and a second in which the layer is separated from the silicon by a buffer layer (e.g. Si_3N_4 for SBT).[8] At present retention time is not yet sufficient.

2.2. Communication technologies: high frequency applications

The expansion in microwave communications in parallel with the advances of thin and thick film technologies lead to accelerated developments in the field of integrated devices and multi-component modules that contain electroceramic passive components. Low temperature cofired ceramics (LTCC) are an example of size reduction and improved functionality gained in RF/microwave packaging due to these recent technological advancements. LTCC — based multilayer multichip modules embed passive components and dense interconnects, reducing the area occupied by monolithic microwave integrated circuits (MMICs). LTCCs are made of layers of ceramic tapes, often containing glassy phase, that are fired at a relatively low temperature of about 900°C. This low temperature allows the use of convenient conductors like silver or gold. Inductors, capacitors, resistors, and other passive components are embedded in between the layers. Advanced modules contain cofired layers of different compositions, such as low permittivity and high permittivity (Fig. 2).

In parallel to the advances in thick films applications, attention has been focused recently on the development of thin film based passive components. Ultimately passive integrated circuits combining various thin films to form capacitor, resistor and inductor networks will be produced. Presently, the development of thin film capacitors is advancing rapidly. At the simplest level, discrete thin film decoupling capacitors have been incorporated in multichip module since some time.[9] The design, which replaces circuit boards with a miniaturized module, uses arrays of decoupling capacitors made of PLZT thin films. The thickness of the capacitor arrays, similar to that of IC, makes them efficient for packaging purpose. Advances towards fully integrated capacitors with IC were reported by a large number of manufacturers including Alcatel, GEC Marconi, TI, and Nipon Telegraph. Matsushita have reported products containing integrated BST decoupling capacitors in monolithic microwave integrated circuits on GaAs MMICs.[10]

Recently there has been an increased interest in ferroelectric thin films for high frequency applications. The interest can be divided into two directions: consumer portable communications and radar systems. For mobile phones the interest is in voltage dependent capacitors (to replace Varactor diodes at higher frequencies) and for tunable and/or adaptive bandpass filters. The potential advantage of ferroelectric thin films over present semiconductor varactors are the lower losses and better power handling, and the advantage over ferrites are lower losses, and lower power consumption.

The tunability (K) can be defined as $K = (\varepsilon_{ro} - \varepsilon_{rv}) / (\varepsilon_{ro} tg\delta_o)$ where ε_{ro} and ε_{rv} are the dielectric constant at zero and at maximum dc bias voltages and $tg\delta_o$ is the loss at no dc bias. The interest in ferroelectric thin films is due to the fact that high tunability is achieved at low voltage; however, losses are still a major issue.

Ferroelectric films could also be useful in phased array antennas. Presently this application is confined to military use, but ferroelectric array technology could lead to a cost and size reduction that will widen the market toward civil antena applications.

Whereas bulk dielectrics filters are best at lower MW frequencies integrated piezoelectric filters devices are emerging for the intermediate MW frequency range (2–10 GHz): currently piezoelectric filters, based on surface acoustic wave (SAW) devices made of $LiNbO_3$ crystals, are used for low MW frequencies. The operation frequency is determined by the separation between the interdigitated electrodes on the crystal surface, and therefore, the utilisation at increased frequencies encounters technological difficulties. An alternative design, using bulk acoustic waves (BAW) has been demonstrated recently by Dubois and Muralt.[11] The devices are made of piezoelectric AlN films deposited onto a micromachined Si_3N_4/SiO_2 membrane [Fig. 3(a)] and show a high performance, in particular high temperature stability. Further more, the AlN films were also deposited onto an acoustic Bragg mirror on silicon [Fig. 3(b)], displaying high quality factor and coupling coefficient, and opening the way to a new generation of *integrated* piezoelectric filters for wireless communications. The central frequency of the BAW devices is fixed by the film thickness, and applications in the 2–10 GHz could be feasible.

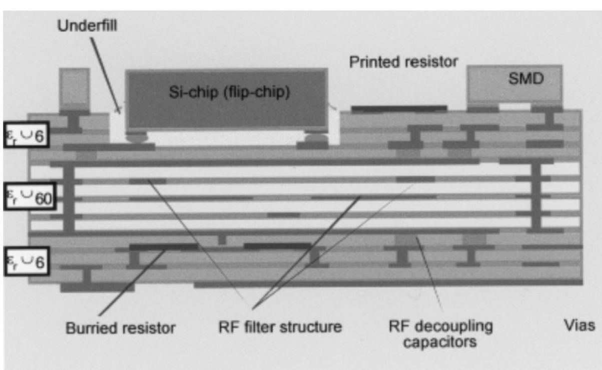

Fig. 2. Advanced LTCC module (courtesy of W. Wersing, Siemens).

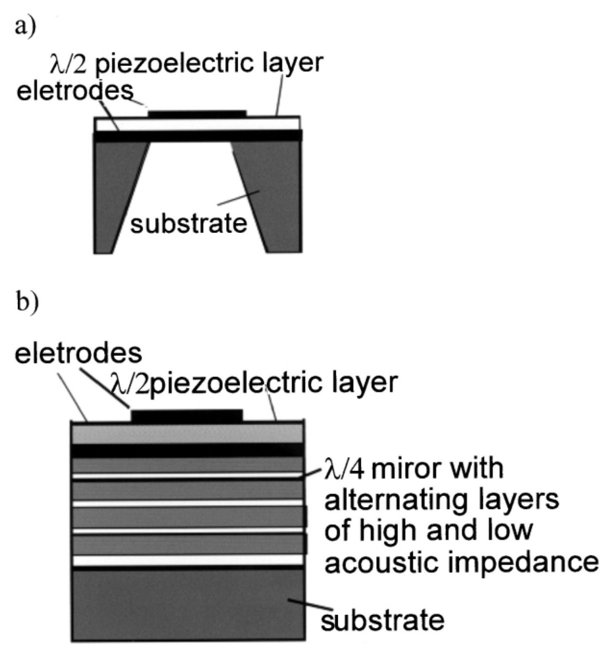

Fig. 3. Schematic drawing of thin film bulk acoustic resonator on Si_3N_4/SiO_2 membrane on micromachined silicone (a) and on Bragg grating integrated onto silicon (b). © 1999 IEEE.[11]

High temperature ceramic superconductors (HTS) thin films are also likely to have commercial impact in microwave communication systems; Due to their superior low-loss performance they are considered for passive components such as filters and resonators. Applications in which advanced tests have been made include multiplexers for mobile communication base stations, Doppler radars, and phased-array radar systems.[12] Applications include also multi-materials such as integrated HTS/ferroelectric structures for electrically tunable microwave filters.[13] High frequency active devices and circuits based on Josephson junctions are also being proposed. The fabrication is by far more challenging than that of HTS films for passive devices and the fabrication of high quality junctions (often multi layers or arrays) with a process suitable for large scale device manufacturing is still to come.

2.3. Information retrieval: novel electroceramic sensors

Sensors and actuators based on electroceramics are known and commercialised since long time: ultrasonic imaging using piezoelectric ceramics, zirconia oxygen sensors, and pumps, pyroelectric smoke detectors, and NTC temperature sensors are well known examples. Their excellent performance and low price make them widely spread.

In recent years electroceramic materials are being added to silicon based MEMS (micro-electro-mechanical systems) resulting in new functionalities. An important benefit is an economical one — batch processing lowers the product price. In a number of applications the MEMS concept facilitates better device quality, e.g. higher sensitivity, better reproducibility and faster response. In some applications an additional advantage is the lower power consumption in comparison with discrete devices. The ease of fabrication of sensor *arrays* is another important advantage. Examples of MEMS having functional ceramics at the 'heart' of the device include chemical micro-sensors on micro hot-plates, pyroelectric IR micro-sensors arrays for thermal imaging, and piezoelectric micro-motors and magnetic field sensors made of high temperature ceramic superconductors (HTS).

A large number of piezoelectric microdevices have been demonstrated to date: microactuators, such as ultrasonic micromotors,[14] micropumps,[15,16] microfilters,[17] PFOMs[18] (piezoelectric coating on optical fibers for use as phase modulators, and coating on optical fibers with Bragg grating for tunable wave filters), and a number of devices based on actuating cantilevers (e.g. mirror tilters), sensors, such as pressure sensors[19] accelerometers[20] and AFM cantilevers.[21,22] An important advantage of integrated piezoelectric technology is the efficient and low cost of fabrication of one- or two-dimensional arrays. Arrays are useful for ultrasonic transducers, and research in this field is being pursued for ultrasonic high-frequency imaging: medical imaging[23] and high frequency hydrophone applications.[24]

An area in which electroceramic thin films on silicon have a clear commercialisation potential is that of pyroelectric sensors. Pyroelectrics respond to changing temperature (or IR radiation) by generating electric current and are widely used as fire alarms, intruder alarms and uncooled IR cameras (thermal imaging). Improved response through the reduction of thermal capacity favors the use of thin pyroelectric layers on thin membranes (bulk micromachining of silicon), or suspended pyroelectric layers on bridges (surface micromachining with silicon). Using silicon as the substrate of the pyroelectric array, a full integration of the sensor with the preamplifiers and the read-out electronics can be achieved.[25] Reported applications of pyroelectric thin film-based sensor arrays include the IR focal plan array for uncooled IR imaging fabricated by Raytheon,[26] Siemens,[27] and GEC-Marconi.[28] A 64-element linear-array IR for gas spectrometer has been developed at the EPFL.[29] Examples are shown in Fig. 4.

MEMS may provide substantial improvements in the field of ceramic chemical sensors.[31] Ceramic sensors, based on semiconductors such as SnO_2, show this potential.[32] These sensors function by conductometric sensing (absorption induced conductance change). They operate at elevated temperatures and suffer from relatively poor selectivity and to a lesser extent, poor stability. A high power consumption is another limitation in portable devices. The use of MEMS technology is therefore advantageous: arrays that contain elements sensitive to different chemicals can be made easily — improving selectivity. Sensitivity is further increased because of the faster thermal response of the microelement sensors, and the power consumption of the devices is reduced due to their reduced size.

Superconducting quantum interference devices (SQ UIDs), based on high Tc ceramic superconductor (HTS) thin films, and related devices, are being developed with applications foreseen in magnetocardiology, and magnetoencephalography, in microscopy, in geophysics, and in nondestructive evaluation of materials (NDE). SQUID based magnetic field detectors for NDE have reached by now the market.[33] The magnitude of the noise, and with it the limit of detection, depend strongly on the crystallinity of the superconducting thin films and on the interface with the insulating layer. Therefore, epitaxial $YBa_2Cu_3O_{7-x}$ (YBCO) films on lattice-matched single-crystal substrates show the highest sensitivity. By using the short coherence length in the order of ang-

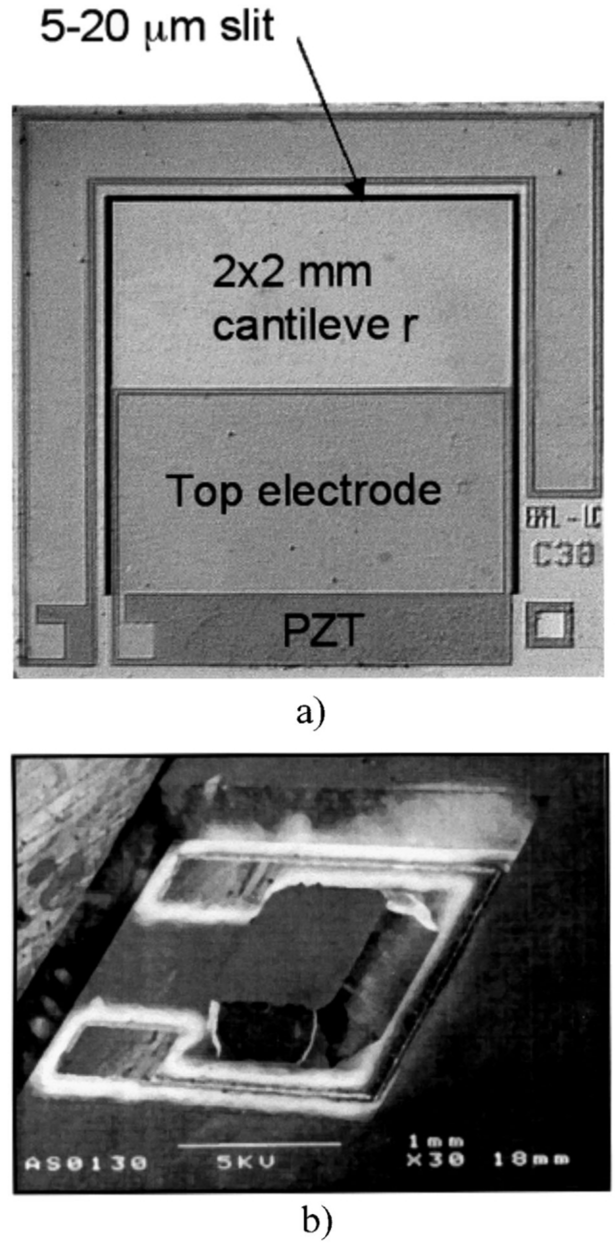

Fig. 4. Examples of piezoelectric microsensors on silicon: (a) microphone[30] and (b) accelerometer. © OPA N.V. with permission from Taylor and Francis Ltd.[20]

stroms of HTSC superconductors and their large anisotropy, a variety of grain-boundary junction devices was developed. All are based on the fact that due to the small coherence length there is only a weak coupling between two superconducting grains, which acts as a Josephson junction. For some applications, multilayers (superconducting and insulating), with vias and cross-overs are required — this technology is not mature yet. Silicon-based SQUIDs are desirable but they do not achieve yet the high performance obtained by epitaxial growth on matching substrates. Therefore flip-chip technology is used for the fabrication of sensitive devices (Fig. 5).

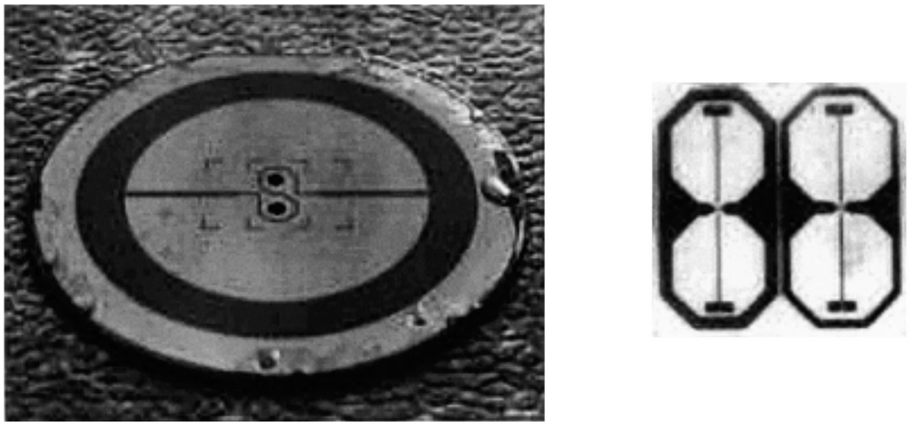

Fig. 5. HTS directly coupled dc SQUID gradiometer with flip-chip flux transformer.[34] (a) The flux transformer is made of a buffered $Yba_2Cu_3O_7$ film on 2″ silicon wafer; (b) the two planar SQUID gradiometers are fabricated on a 10×10 mm $SrTiO_3$ bicrystal.

3. Trends in electroceramic technology: from discrete components to integrated systems

Miniaturisation, frequency and speed increase, product optimisation and increased efficiency resulted in the last decade in an important shift from discrete components into integrated systems: Integrated capacitors, thin film sensor arrays, and LTCC are important examples that were discussed above.

Due to this evolution, electroceramic thin and thick films have become a focus of research in the field of electroceramics since some years. Issues related to surfaces and interfaces are critical and their understanding and control is sought. Integration issues related to compatibility and interdiffusion, metalisation, barriers, adhesion layers, and patterning, constitute central topics in development of electroceramics.

Due to the large scope of this subject, only selected topics will be discussed in this section.

3.1. Thick films

Research in electroceramic thick films is gaining importance. Whereas resistive thick films have been used since long time, and conductive thick layers were introduced since some years, it is only very recently that piezoelectric thick films attracted interest, due to their need in various miniaturized sensors and transducers.

The deposition of thick films on silicon requires a reduction of the sintering temperature. Two directions are pursued: chemical solution deposition (CSD), and powder sintering routes. Multiple coatings of CSD films have been used for films of thickness up to 10 μm (e.g. Ref. 24). Annealing is done for each layer of ~0.25 μm, and the whole process does not exceed 700°C. Automated deposition procedure facilitates the process. Sayer and co-workers[35] developed a composite sol-gel method in which the solution was loaded with commercial PZT having a narrow (<1 μm) size distribution, and then deposited to give a series of successive layers of 3–4 μm thickness each, and annealed at temperatures inferior to 700°C. The films, of 5–100 μm thickness, were deposited on platinized alumina and on aluminum and working ultrasonic arrays with attractive properties for ultrasound medical microscopy have been demonstrated in spite the low density of the films.

Two powder methods were used successfuly to obtain dense thick films: electrophoresis deposition (EPD) and screen printing. With EPD, Van Tassel and Randall[36] deposited PZT thick films on Pt-coated alumina substrates. Using PbO and Li as fluxes, they obtained dense 10 μm films at 900°C. Kosec and co-workers[37] used screen printing to obtain ~40 μm PLZT thick films on Pt-coated alumina at 1100°C, with PbO flux. They report that the films have similar properties to those of HIPed ceramics of the same composition, including low coercive field.

The processing of PZT thick films on silicon substrates will open new perspectives in applications, and is therefore being pursued: Chen et al.[38] added a mixture of Li_2CO_3 and Bi_2O_3 powders as a sintering aid to the PZT-based ink, and sintered the films at 850°C on silicon electroded with Pt/Ti. The sintered films exhibited however low density, hence low remnant polarization, and low peizoelectric activity. Koch et al.[39] have developed a PZT micropump on silicon substrates using screen printing. The films contained a borosilicate glass sintering aid. A crystallizable glass-ceramic thick film was used as a lead diffusion barrier for silicon.[40] Thiele et al.[41] used B_2O_3–Bi_2O_3–CdO sintering aid to sinter PZT thick films on silicon. After sintering at 900°C, a high density was obtained and the films showed a strong peizoelectric activity (poled films have d_{33} coefficient of 110 pV/N).

Kurosawa,[42] using hydrothermal method, obtained thick piezoelectric films of 25 μm thickness at temperatures as low as 160°C. The films grew on titanium substrate from a solution that contained the necessary ions and reacted with the titanium substrate. Different devices such as micro ultrasonic motors and touch probe sensors have been demonstrated using this method.

Patterning of the thick electroceramic films is still an open issue: screen printing is a convenient method when the feature size is large enough; this is true for piezoelectric micro-devices. Thick films prepared by the sol-gel method are wet-etched.[22] In the case of further thicker films, laser micromachining was used to form ultrasonic array device (Fig. 6).[23] Other methods were proposed as well: King et al.[43] developed a direct-write approach which is suitable for small-lot fabrication of multi-material integrated ceramic components. They use a CAD — instructed automated 'pen' for precision printing of ceramic inks. A typical ink nozzle size is 100 μm, and the ink used is similar to that used by conventional screen printing.

Integration issues of thick films are not resolved yet: e.g. working devices that necessitate beam structures and use thick films were rarely reported, therefore the issue of stress control is still open. Oriented films would be of interest, e.g. for the use of uniaxial piezoelectrics or for the use of relaxor-ferroelectrics. Further work in this area is expected.

3.2. Thin films

For thin films, a large number of deposition methods, chemical and physical, are well developed and will not be discussed here. On the contrary, patterning is still under study, therefore, it is of interest to outline here few of the newly developed routes. Substrate effect on the functioning of thin films is still an open question, and will be referred to in this section. Finally, an example of the role of the interface in the functioning of electroceramic thin films will be described, leading into new questions that are emerging presently concerning nanoscience and nanotechnology in electroceramics.

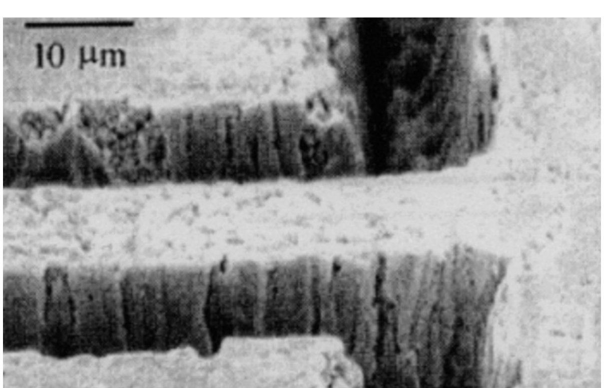

Fig. 6. Laser machined transducer of thick films of PZT sol-gel composites. © OPA N.V. with permission from Taylor and Francis Ltd.[23]

3.2.1. Substrate effects

The clamping of the films to the substrate results in modification of their functional properties. This has been a subject of a number of studies, both theoretical and experimental. For example, the piezoelectric response is strongly influenced, due to the modified boundary conditions: the perpendicular response is substantially smaller than that of bulk ceramics, while the bending response of the sandwich structure (substrate + film) is enhanced.[44] The pyroelectric response is modified as well, since the thermal expansion mismatch between the substrate and the film results in piezoelectric contribution to the pyroelectric effect. Also switching is influenced by the substrate- numerous studies showed that non-180° switching is much weaker in thin films in comparison to the bulk.[45]

Ijima et al.[46] have shown long time ago the influence of stresses in the films on the polar domain configuration of $PbTiO_3$ (PT). Due to thermal expansion mismatch between the film and the substrate, stresses develop when the film is cooled down after its sintering. Ijima showed that in in-plan (100) compressed films, grown on magnesia single crystal substrates, domains switched to position with polar axis perpendicular to the film surface upon cooling, in parallel to the development of stresses in the film. Seifert et al.[47] have shown similar effect for PT film grown on $SrTiO_3$ crystals. This is not possible when the film is grown on silicon, due to its small thermal expansion coefficient. A way to circumvent the problem, when out-of-plan polarisation is needed, is to transfer the film from the magnesia substrate onto the silicon. This solution is suitable only for limited cases, due to the increased cost of production. When out-of-plan polarization is important, and in applications that necessitates silicon substrates the <111> orientation is often preferred, since it guarantees that the polarization will be out of plane, albeit in a inclined direction.[48] Another solution is the growth of the films in condition that introduce compressive stress during in-situ deposition, and optimisation of poling procedure.[49]

The effect of 2D clamping on the ferroelectric phase transition has been studied theoretically by Pertsev et al.[50] who calculated the phase diagram of mono-domain $BaTiO_3$ thin film under a misfit strain relative to its substrate due to the volume discontinuity at the paraelectric/ferroelectric phase transition. They showed that phases and transition temperatures are very different from those of the classical 3D single crystal. This model has been successfully modified to describe the permittivity–temperature behavior of columnar-structured $BaTiO_3$ and $SrTiO_3$ films prepared by chemical solution deposition methods.[51] In a somewhat similar analysis, Streiffer et al.[52] explained the suppression of the permittivity of BST thin films compared to bulk ceramics of the same composition by the effects of non-stoichiometry, stress, and interfacial effect.

3.2.2. Texture and oriented growth

Epitaxially grown oxide thin films are essential in a number of applications: SQUID devices based on high-Tc ceramic superconductors, maneto-optical wave guides based on garnets, high-K gate oxides, etc. This is in particular challenging if, due to functional requirements, the material has to be deposited on Silicon. In this case seeding layers have to be used.

Ramesh et al.[53] used first bismuth titanate (layer perovskite structure) as a template for the textured growth of (100) PLZT and its underlying LSCO electrode on Si. Later, Muralt et al.[54] used lead titanate as template for (100) growth of PZT on platinum. The PZT (111) orientation is favored by the (111) Pt itself and is further enhanced by the diffusion of Ti, used as adhesion layer between Pt and Si, through the platinum grain boundaries.[55] Muralt et al.[56] showed that a controlled growth of (111) PZT is obtained if a crystalline layer of TiO_2, of few nanometers thickness is used as seed layer on top of the platinum electrode. Piezoelectric properties of the differently oriented tetragonal PZT films are shown in Fig. 7.[57] (100) Orientation gives a higher activity than (111) orientation, since in the former orientation all the domains participate, while in the later, some domains are clamped in plane. Recently, truly epitaxial ferroelectric films were grown on Si by various templates. Sharma et al.[58] use a 5-layer heterostructure geometry (TiN/MgO/STO/YBCO/PZT) to grow (100) PZT on Si, including a buffer layer. McKee et al.[59] revealed a way to grow epitaxial $SrTiO_3$ directly on silicon by modifying the growth conditions to obtain $SrSi_2$ at a submonolayer thickness between the silicon and the strontium titanate layer. This is especially important for gate dielectrics in which intermediate low permittivity oxide is deleterious.

3.2.3. Patterning of thin films

Patterning of thin films is accomplished mainly by two approaches, a reductive approach of etching of the annealed continuous layers, and an additive approach in which a treatment of the substrate results in obtention of patterned film prior to the annealing step. For electroceramic films, advances in the first approach are focused on nano-patterning, and are discussed in the following section on nanotechnology.

An intermediate approach is the uv patterning process using photosensitive precursors. Laser UV irradiation with tailored wavelength according to the absorption of the film is irradiated through a patterned photomask to form a hard to dissolve polymer. The unirradiated areas remain soluble and are dissolved prior to the crystallization. Different electroceramic films have been prepared by this method, in particular by Hirano and coworkers who studied the precursors chemistry and patterned in this way $LiNbO_3$,[60] TiO_2,[61] and KTP.[62]

Selective surface functionalisation of substrates by self assembled monolayers that are printed or stamped on the substrate stamps had been originated by Whitesides and co-workers.[63] This method of microprinting was recently used by Payne et al.[64] for the fabrication of a variety of patterned micro-devices based on electroceramic thin films, thus demonstrating a method that eliminates the etching step that is an integral part of conventional device fabrication processes. Payne and coworkers use hydrophobic self assembled mono layers to modify the wetting and tribological character of the substrate surface. The layers are microstamped onto the surface. A subsequent deposition of the electroceramic film is followed by lift-off from the monolayer, on which the films, being comparatively hydrophilic, do not adhere. In this way a patterned oxide thin layers are obtained on the unfunctionalized regions. The so patterned films are then crystallized by appropriate heat treatment. Lateral resolution as fine as 0.5 μm has been demonstrated with oxides. The potential resolution reaches down to several tens nanometers. Micro patterning of PZT, $LiNbO_3$ and Ta_2O_5 on a variety of substrates was demonstrated, and devices made of multi-level layers such as FeCAP made of Pt–PZT–Pt on silicon were realised and characterised.

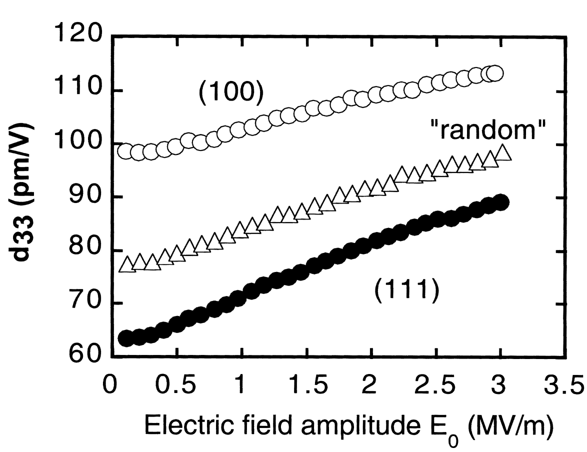

Fig. 7. Orientation dependence of the piezoelectric coefficient in tetragonal PZT films.[57]

3.2.4. Downscaling effects

Downscaling effects in electroceramics have been investigated since a number of years but are still far from being entirely disclosed. All functions, electric, optic, magnetic, etc., are influenced by downscaling.

An illustrative example of size effect and the role of interfaces in electroceramic thin films is that of ferroelectric switching behavior. This problem is being studied intensively for the development of FeRAM. It is manifested by two phenomena: the thickness dependence of the coercive field, and the switching fatigue. Through the analysis of switching, leakage and fatigue, Tagantsev et al.[65] developed a qualitative model explaining the origin of fatigue and size dependence of coercive field: charges that are injected from the electrodes during switching accumulate at the near-electrode region and pin the seeds of the oppositely charged domains that would other wise grow upon switching. Following this model they postulated that furnishing a mechanism for charge release in the near-electrode region of the ferroelectric material will improve fatigue without deteriorating leakage current. Indeed, 5 nm conductive oxide inserted between one of the electrodes and the ferroelectric layer resulted in a significant improvement in fatigue, and in reduction of the coercive field, without deterioration of the leakage behavior (Fig. 8).[5]

The importance of the few first nanometers at the interface of the metal electrode and the ferroelectric film, is an example of the importance of nanometer size scale effects in advanced devices.

4. Nanotechnology and nanoscience of electroceramics

Size effects in electroceramics have been a concern and a subject of detailed studies since long time, but it is the downscaling of devices and components based on electroceramics, that triggered the present interest in nanotechnology. The wealth of newly developed experimental tools for direct observation of nanoscale features and the general current interest in nanoscience, are certainly additional important factors.

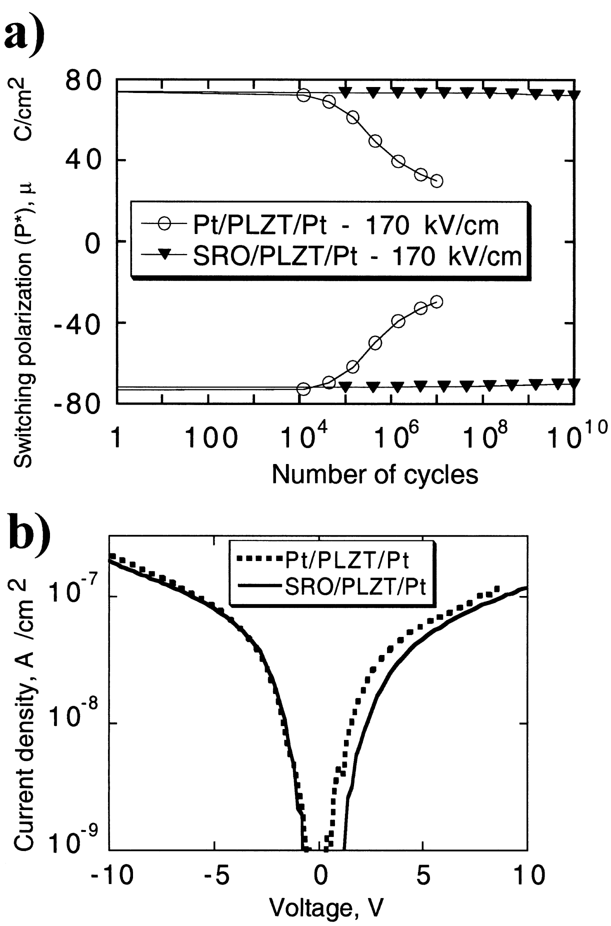

Fig. 8. Switching polarization as a function of number of voltage reversals for PLZT capacitors with and without 5 nm $SrRuO_3$ between the top electrode and the PLZT film (a) and the corresponding leakage (b).[5]

4.1. Nanoanalysis

Functionality of electroceramics is interpreted using structural characterization techniques combined with electrical measurements; as feature size decreases, local probe techniques become essential.

Ferroelectric domain walls can be used for the illustration of advances and recent interest in nanoanalysis of electroceramics; domains and domain walls in thin films have been studied using transmission electron microscopy since some time. Recently the thickness of domain walls, and its variation as the ferroelectric phase transition is approached, were investigated by Foeth et al.[66] by HRTEM and weak beam transmission electron microscopy (WBTEM) showing similar magnitude and behavior to that calculated theoretically by Cao and Cross.[67] The nano polar-regions (10–50 nm size) in relaxors were also studied using TEM, and identified in the ferroelectric relaxor $Pb(Mg_{1/3}Nb_{/23})O_3$ at low temperature,[68] and in $Pb(Sc_{1/2}Nb_{1/2})O_3$ in the relaxor 'window' between the high-temperature paraelectric phase and the room-temperature ferroelectric phase.[69]

Recently scanning probe microscopy (SPM) has been used to determine simultaneously the structures, some times at almost atomic dimensions, and local properties of electroceramics surfaces.

Using SPM it is possible to examine local properties of surfaces by evaluation of contact potential between metals and ceramics, local electrostatic fields at grain boundaries and current flow across boundaries.[70] AFM is being used to image domain patterns at the surface of ferroelectrics materials. The imaging of out of plan antiparallel domains has been studied intensively. It is based on the detection of the piezoelectric vibrations of the ferroelectric domains when activated by an external ac voltage that is applied through the conductive probing tip.[71] In a more complex way, by sensing simultaneously horizontal and vertical direction of vibration of the AFM cantilever in response to voltage modulation of the ferroelectric material by the AFM tip, the 3D domain distribution in a number of ferroelectric crystals, such as $BaTiO_3$ and TGS,[72] was reconstructed. Moreover, the crystallographic orientation of the individual grains at the surface of $BaTiO_3$ ceramics, with down to 40 nm resolution, was reconstructed using this method.[73] In a recent study, in-plane domain structure of thin films has also been observed.[74]

While the resolution of the conventional polarising optical microscope is too poor for observation of domains in thin films, the use of polarizing confocal scanning optical microscope (CSOM) improves the resolution, providing a relatively simple means for observation and analysis of non-180° domain walls,[75] which is complementary to the SPM studies. Hubert and Levi[76] developed a technique based on CSOM which measures small electric field-induced changes in the refractive index n, showing submicron size domains in BST films, and their reorientation under switching fields. Another exciting development is the dielectric microscope developed by Cho and co-workers.[77] Cho is scanning the surface of the sample with a probe measuring, locally, the 3rd order dielectric susceptibility. The detection is made by measuring the changes in the resonance frequency of a MW oscillator that is made of the probe and a coil. Since the nonlinear dielectric susceptibility is sensitive to changes in the polarisation direction, this method gives a map of the domain structure of the surface with nanometer scale resolution.

Domain dynamics is a subject of particular interest for piezoelectric applications and for memories. Mobile domain walls contribute to piezoelectric activity, but reduce stability — therefore their control is important. Damjanovic et al.,[78] in a study of high Tc piezoelectric ceramics, suppressed an undesired non linear response (change of piezoelectric coefficient upon change of ac stress) by the modification of the composition of the ceramics. In parallel to this suppression, a TEM study showed stacking faults sub-grain structure of intergrowth of two different piezoelectric phases.[79] This showed that domain walls were pinned at the lattice defects, and because of this, the non linearity associated with domain wall movements was suppressed. This and similar questions, are the driving force in the pursue of direct observations of the dynamic behavior of domain walls. Indeed, in a recent study, Yang et al.[80] observed, using scanning near field optical microscopy (SNOM), features such as domain wall bending at pinning defects. These studies are likely to intensify in the near future.

Spatial homogeneity of the switching properties of ferroelectric films at the nanoscale level is an important issue for scaling down ferroelectric memory capacitors. For capacitor cells of size equivalent to few grains, the response of individual grains and the subgrain response are of great importance. Domain switching was studied intensively by force microscopy by Gruvermann.[71] Nucleation of reverse domains upon polarisation reversal are therefore of importance and are studied by local methods.[81] Using scanning force microscopy in a piezoelectric mode, information about the fatigue mechanisms is obtained. It was shown, for example, that fatigue proceeds 'region by region' (namely, an 'on/off' process) and not by a gradual reduction in switched polarisation throughout the film.[82] It was shown also that that the capacitor edge region fatigues faster, and also recovers faster than the center of the element upon application of a recovering pulse, probably due to field concentration at the edges.

Doubtless, direct observations at the nanosize scale will increase in importance in relating properties of electroceramics to microscopic phenomena.

4.2. Nanofabrication and nanostructuring

As feature size decreases, integrated electroceramic-based devices require structuring at the nano size scale thicknesswise and latterally.

Ultrathin layers of high permittivity oxides are needed in microelectronic technology. Silica has been the gate dielectric in MOS capacitors since decades. However, feature size reduction imposes now thickness reduction of the gate oxide to a level (<1.5 nm) that results in unacceptable tunneling currents. An alternative gate dielectric is therefore needed. Various materials are being investigated, such as tantalum oxide and strontium tanalum oxide, but the problem is the interfacial silica that forms once the oxide is deposited on the silicon. An approach circumventing this problem was recently shown by McKee et al.[59] who grew alkaline earth and perovskite oxides on silicon, totally avoiding the amorphous silica interfacial phase. From analysis of the thermodynamic data of SrO–Si, the conditions of growth in which $SrSi_2$ is stable were examined. This compound has been successfully grown on the silicon at 850°C, in a submonolayer thickness, and then the growth conditions were changed for those of a stable growth of $SrTiO_3$ without perturbing the underlying disilicide. A MOS capacitor with an equivalent oxide thickness of less than 10 Å was so obtained.

Patterning issues for small size components include also the electrodes. Alexe et al.[83] demonstrated the formation of self-patterning metallic bismuth nano-electrodes on ferroelectric bismuth titanate films that were prepared with excess bismuth oxide. The excessive bismuth migrated to the surface of the film during the high temperature treatment process to form self-organized arrays of epitaxial bismuth electrodes, 200nm in lateral dimension, and 40 nm in height.

In addition to the pure scientific interest in scaling problems there is a practical interest to explore the operational feasibility of ferroelectric capacitors with lateral dimensions of the order of 100 nm and smaller. Capacitors of this dimensions were produced by a number of groups.

Okamura et al.[84] and Alexe et al.[85] used electron beam (EB) direct writing technique to fabricate SBT and PZT structures with lateral sizes <100 nm. In this method chemical reactions are locally induced in the metal–organic thin film by irradiation with an EB having sufficient energy and dose, and the desired pattern is impressed by scanning the EB over the sample. The pattern is developed by dissolving the unexposed area in a specific solvent. The non-dissolved material is than crystallized and sintered. The obtained pattern of films of 100 nm thickness gave capacitors with 1:1 horizontal to lateral dimensions, (Fig. 9a) with film grain size <20 nm. Piezoelectric activity of the films have been verified by force microscopy in the piezoelectric mode (PFM).

Ganpule et al.[86] took another approach, and used focused ion beam milling to define capacitors with submicron lateral dimensions. The advantage of this method is that the patterning is done all through the capacitor stack including the upper electrode. After the milling process, the films were re-annealed to recover the damage. Then, piezoelectric hysteresis was measured by force microscopy (PFM), proving the film can be switched. These results suggest that memory densities exceeding 1 Gbit can be fabricated using ferroelectric films.

Triscone and co-workers,[87] circumvented the patterning problem, and showed another way to possibly produce components such as FeFET: epitaxial PZT/$SrRuO_3$ heterostructures were grown on conductive Nb:$SrTiO_3$ substrate. An AFM tip was used to switch locally the polarization direction in the PZT (Fig. 10a). The electronic density of the underlying metallic $SrRuO_3$ layer was modified by this and the sheet resistance was changed by up to 300 ohms per square (Fig. 10b). This procedure was reversible and allowed sub-micrometer electronic features to be written directly in two dimensions, with no external electrical contacts or lithographic steps required.

4.3. Nanopowders

Another aspect of nanostructuring is the production of ultrafine powders of electroceramics. This research has been successful since some years, and continues to develop. The objective is to obtain fully dense ceramics at low temperatures and/or without coarsening of the powders. This is needed for functional purpose, for improved mechanical properties, or for other reasons such as the densification of thick films on silicon. Coating the fine powder by dopants is a successful approach that allows low sintering temperatures, far below the conventional ones, and results in ultra-fine microstructures, with ceramic grain size below 100 nm, in materials like ceria[88] and zinc oxide.[89] Chen[90] has demonstrated recently a spectacular decrease in sintering temperature of yttria by a simple two step sintering method solely by exploiting the difference in kinetics between grain boundary diffusion and grain boundary migration. With a careful choice of the sintering temperature, ceramics with grain size in the <100 nm range were obtained. As nanocrystalline powders in the size range 5–10 nm are becoming increasingly available, fully dense ultrafine grain-size electroceramics of different compositions will be obtained.

Within the nano-particle technology, a second issue of practical importance is the introduction of nanoscale porosity in electroceramics. Open or close nano porosity is needed, depending on the application. Controlled porosity at 10–1000 nm scale can be obtained using a variety of template materials such as emulsions and polysterene beads.[91] An example of the advantage of the closed porosity was shown by Seifert et al.,[92] who showed that nanoporosity (~ 100 nm pore size) in (Pb,Ca)TiO_3 had increased 4–8 times the sensitivity of the voltage response, of these pyroelectric films. On the other hand, for

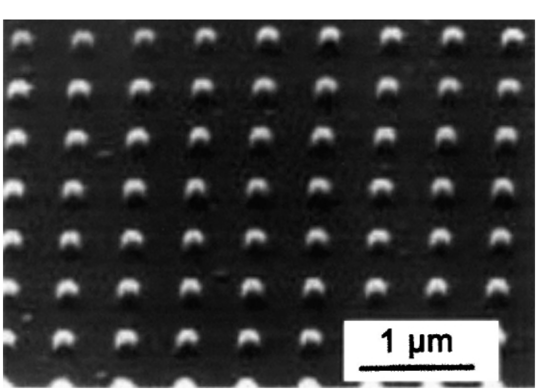

Fig. 9. SEM micrograph showing a PZT cell array on a $SrTiO_3$:Nb conductive substrate.[85]

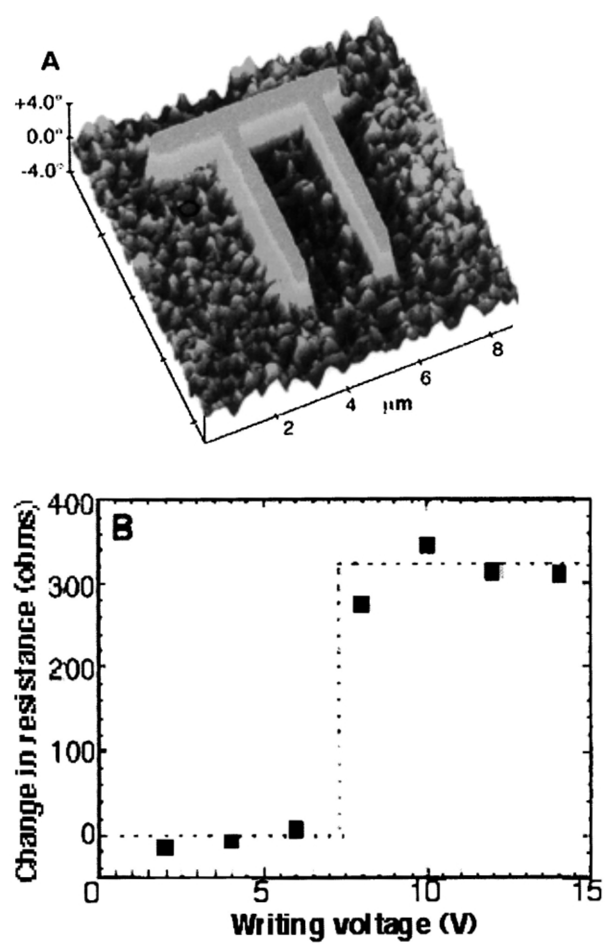

Fig. 10. Direct pattern writing of field effect regions using an AFM probe. (a) Piezoelectric phase image of a structure written with -12 V inside a square written with $+12$ V). (b) resistance change of the underlying $SrRuO_3$ as the voltage on the PZT is increased. Reprinted with permission. Copyright [1998] American Association for the Advancement of Science.[87]

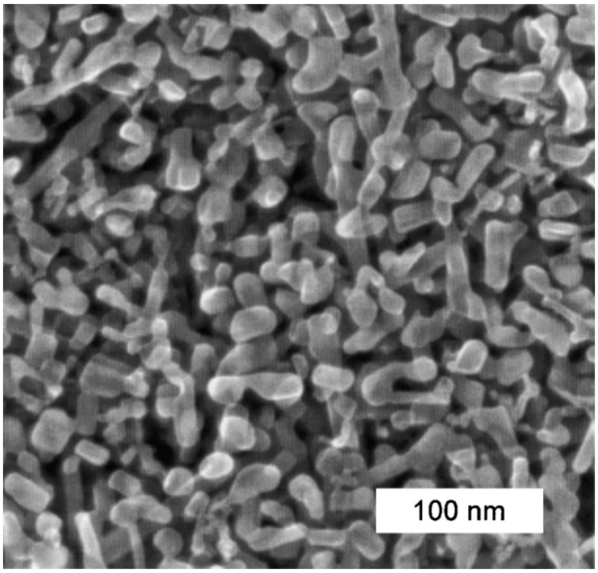

Fig. 11. Mesoporous films obtained by crystallization of hydrothermally prepared Nb_2O_5 gel. Reprinted with permission of the author.[94]

chemical sensors, open porosity is needed as the sensitivity increases with the surface area of the pores. An important illustration of this is the photoelectrochemical cell of Graetzel.[93] For a higher efficiency this cell requires a high surface area of the semiconductor material, onto which the photosensitive dye is adsorbed, and to which the latter transfers the photo-electrons. Fig. 11 shows the nanoporous film of semiconducting Nb_2O_5 produced for this purpose.[94] The films are made of amorphous gels obtained by a hydrothermal sol-gel synthesis. A high porosity with particle and pore size of about 25 nm was achieved.

More complex particles and new nano-ceramics have been synthesised lately. Trends in this respect were set by the discovery of carbon fullerenes and carbon nanotubes. Following this, it has also been shown that nanoparticles of 2D layered metal dichalgogenide compounds such as WS_2, and MoS_2[95] and also V_2O_5[96] can collapse into fullerene-like cages and nanotubes. In addition to applications as solid lubricants, WS_2 nanotubes of <20 nm diameter have been used as AFM tips enabling the imaging of deep nanostructures.[97]

TiO_2[98] nano-tubes were recently synthesized, and so were a number of niobates. In addition, Fulleren-like inorganic structures of MoS_2, WS_2, BN[99] were recently produced by laser ablation. It is too early to predict the application potential of these materials, but the study of their properties is certainly an exciting perspective.

5. Summary

Electroceramics offer an increasing variety of functions, and their use is becoming more widely spread, in particular in microelectronics and communication components and devices. In parallel, the interest in the use of electroceramic sensors and actuators in microsystems is growing. These applications, and the general current trend of miniaturisation, and increase in density, frequency and speed, make integration issues a central theme in R&D of electroceramics. This has been discussed with reference to both thick and thin film technologies. Integration issues lead to an increasing interest in the nanoscience and nanotechnology of electroceramics. Although these latter topics are still at their initial phase, the stimulating results in nanoanalysis, in nanopowder fabrication, and in nanofabrication of devices on silicon obtained so far ensure valuable and exciting developments in the field in the coming years.

Acknowledgements

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References

1. Melnick, B., Cuchiro, J., Mcmillian, L., Paz de Araujo, C. and Scott, J., Process optimization and characterization of device worthy sol-gel based PZT for ferroelectric memories. *Ferroelectrics*, 1990, **112**, 329–351.
2. Sommerfelt, S. R. In *Thin Film Ferroelectric Materials and Devices*, ed. R. Ramesh. Kluwer Academic Publishers, 1997, pp. 1–42.
3. Yoshida, M., Yabuta, H., Yamagouchi, S., Yamaguchi, H., Sone, K., Arita, T., Iizuka, T., Nishimoto, S. and Kato, Y., Plasma CVD of (BaSr)TiO_3 dielectrics for Gigabit DRAM capacitors. *J. Electroceramics*, 1999, **3**, 123–133.
4. Scott, J. F. and Paz de Araujo, C. A., Ferroelectric memories. *Science*, 1989, **246**, 1400–1405.
5. Stolichnov, I., Tagantsev, A., Setter, N., Cross, J. and Tsukada, M., Top-interface-controlled switching and fatigue endurance of (Pb,La)(Zr,Ti)O_3 ferroelectric capacitors. *Appl. Phys. Letters*, 1999, **74**, 3552–3554.
6. Tagantsev, A. K. and Stolichnov, I. A., Injection-controlled size effect on switching of ferroelectric thin films. *Appl. Phys. Letters*, 1999, **74**, 1326–1328.
7. Jones, R. E. Jr. and Desu, S. B., Process integration for non-volatile ferroelectric memory fabrication. *MRS Bull.*, 1996, **21**(6), 55–63.
8. Ishiwara, H. *FED Journal,* 2000, **11**(suppl.), 27–40.
9. Dimos, D. and Mueller, C. H., Perovskite thin films for high-frequency capacitor applications. *Annual. Rev. Mater. Sci.*, 1998, **28**, 397–419.
10. Noma, A. and Ueda, D., Reliability study on BST capacitors for GaAs MMIC. *Integ. Ferroel.*, 1997, **15**, 69–78.
11. Dubois, M.-A., Muralt, P., Matsumoto, H. and Plessky, V., Solidly mounted resonator based on aluminum nitride thin film. In *Proc. of the 1998 IEEE-UFFC Ultrasonics Symposium*, 1998, pp. 909–912.
12. Gallop, J., Microwave applications of high-temperature superconductors. *Supercond. Sci. Technol.*, 1997, **10**, A120–A141.
13. Gevorgian, S. S., Carlsson, E. F., Rudner, S., Helmersson, U. and Kollberg, E. L., HTS/ferroelectric devices for microwave applications. *IEEE Trans. Appl. Superconductivity*, 1997, **7**, 2458–2461.

14. (a) 1st demonstrator — Flynn, A. M., Tavrow, L. S., Bart, S. F., Brooks, R. A., Ehrlich, D. J., Udayakumar, K. R. and Cross, L. E., Piezoelectric micromotors for microrobots. *J. Microelectromechanical Systems*, 1992, **1**, 44-51. (b) ZnO motor — Racine, G. A., Luthier, R. and. Rooj, N. F., Hybrid ultrasonic micromachined motors. In *IEEE-MEMS*. Fort Lauderdale (USA), 1993, pp. 124–129. (c) PZT motor — Muralt, P., Kohli, M., Maeder, T., Kholkin, A., Brooks, K., Setter, N. and Luthier, R., Fabrication and characterization of PZT thin-film vibrators for micromotors. *Sensors and Actuators*, A 1995, **48,** 157-165.
15. White, R. M., *AMD (ASME)*, 1994, **188**, 103.
16. Nguyen, N. T., Meng, A. H., Black, J. and White, R. M., Integrated flow sensor for in situ measurement and control of acoustic streaming in flexural plate wave micropumps. *Sensors and Actuators A*, 2000, **79**, 115–121.
17. Luginbuhl, P. H., Collins, S. D., Racine, G. A., Gretillat, M. A., de Rooij, N. F., Brooks, K. G. and Setter, N., Microfabricated Lamb wave device based on PZT sol-gel thin film for mechanical transport of solid particles and liquids. *J. Microelectromechanical Systems*, 1997, **6**, 337–346.
18. Fox, G. R., Müller, C. A. P., Setter, N., Ky, N. H. and Limberger, H. G., Sputter deposited piezoelectric fiber coatings for acousto-optic modulators. *Journal of Vacuum Science & Technology A*, 1996, **14**, 800–805.
19. Scheeper, P. R., van der Donk, A. G. H., Althuis, W. and Bergveld, P., A review of silicon microphones. *Sensors and Actuators A*, 1994, **44**, 1–11.
20. Baborowski, J., Hediger, S., Muralt, P. and Wuethrich, Ch., Fabrication and characterization of micromachined accelerometers based on PZT thin films. *Ferroelectrics*, 1994, **224**, 283–290.
21. Fujii, T., Watanabe, S., Suzuki, M. and Fujiu, T., Application of lead zirconate titanate thin film displacement sensors for the atomic force microscope. *J. Vac. Soc. Technol. B*, 1995, **12**, 1119–1122.
22. Lee, C., Itoh, T. and Suga, T., Self-excited piezoelectric PZT microcantilevers for dynamic SFM-with inherent sensing and actuating capabilities. *Sensors and Actuators A*, 1999, **72**, 179–188.
23. Luckas, M., Sayer, M. and Foster, S., High frequency ultrasonics using PZT sol gel composites. *Integrated Ferroelectrics*, 1999, **24**, 95–106.
24. Bernstein, J. J., Finberg, S. L., Houston, K., Niles, L. C., Chen, H. D., Cross, L. E., Li, K. K. and Udayakumar, K., Micromachined high frequency ferroelectric sonar transducers. *IEEE Trans. UFFC*, 1997, **44**, 960–966.
25. Beratan, H. R., Hanson, C. M. et al., *International Symposium on Integrated Ferroelectrics* (ISIF), Monterey (CA), 1998.
26. Hanson, C. M., Beratan, H. R., Belcher, J. F., Udayakumar, K. R. and Soch, K., Advances in monolithic ferroelectric uncooled IRFPA technology. *Proceedings of the SPIE*, 1998, **3379**, 60–68.
27. Bruchhaus, R., Pitzer, D., Primig, R., Schreiter, M. and Wersing, W., *5th Infrared Sensors and Systems*. Dresden University Press, Dresden, 1997.
28. Watton, R., Ferroelectric IR bolometers-from ceramic hybrid arrays to direct thin film integration. *Ferroelectrics*, 1996, **184**, 141–145.
29. Willing, B., Kohli, M., Muralt, P. and Oehler, O., Thin film pyroelectric array as a detector for an infrared gas spectrometer. *Infrared Physics and Technology*, 1998, **39**, 443.
30. Ledermann, N. and Muralt, P., Piezolectric cantilever microphone for photoacoustic gas detector. *Integrated Ferroelectrics* (in press).
31. Tuller, H. L. and Micak, R., Inorganic sensors utilizing MEMS and microelectronic technologies. *Current Opinion in Solid State and Materials Science*, 1998, **3**, 501–506.
32. Semanik, S. and Cavicchi, R., Kinetically-controlled chemical sensing using micromachined structures. *Accounts of Chemical Research*, 1998, **31**, 279–287.
33. Koelle D., High transition temperature superconducting quantum interference devices: basic concepts, fabrication and applications. *J. Electroceramics*, 1999, **3**, 195–212 and references within.
34. Tian, Y. J., Linzen, S., Schmidl, F., Dörrer, L., Weidl, R. and Seidel, R., High-T_c directly coupled direct current SQUID gradiometer with flip-chip flux transformer. *Applied Physics Letters*, 1999, **74**, 1302–1304.
35. Luckas, M., Sayer, M. and Foster, S., High frequency ultrasonics using PZT sol gel composites. *Integrated Ferroelectrics*, 1999, **24**, 95–106.
36. Van Tassel, J. and Randall, C., Electrophoretic deposition and sintering of thin/thick PZT films. *J. Eur. Ceram. Soc.*, 1999, **19**, 955–958.
37. Kosec, M., Holc, J., Malic, B. and Bobnar, V., Processing of high performance lead lanthanum zicronate titanate thick films. *J. Eur. Ceram. Soc.*, 1999, **19**, 949–954.
38. Chen, H. D., Udayakumar, K. R., Cross, L. E., Bernstein, J. J. and Niles, L. C., Dielectric, ferroelectric, and piezoelectric properties of lead zirconate titanate thick films on silicon substrates. *J. Appl. Phys.*, 1995, **77**, 3349–3353.
39. Koch, M., Harris, N., Maas, R., Evans, A. G. R., White, N. M. and Brunnschweiler, A., A novel micromachined pump based upon thick-film piezoelectric actuation. *Sensors and Actuators A*, 1998, **70**, 98–103.
40. Maas, R., Koch, M., Harris, N. R., White, N. M. and Evans, A. G. R., Thick-film printing of PZT onto silicon. *Mater. Lett.*, 1997, **31**, 109–112.
41. Thiele, E., Damjanovic, D. and Setter, N., Processing and properties of screen printed lead zirconate titanate piezoelectric thick films on silicon. *J. Am. Ceram. Soc.* (submitted).
42. Kurosawa, M. K., Hydrothermal method PZT film and its application to actuators and sensors. *Integrated Ferroelectrics*, 1999, **24**, 1–12.
43. King, B. H., Dimos, D., Yang, P. and Morissette, S. L., Piezoelectricity in ferroelectric thin films: domain and stress issues ferroelectrics. *J. Electroceramics*, 1999, **3**, 173–178.
44. Lefki, K. and Dormans, G. J. M., *J. Appl. Phys.*, 1994, **76**, 1764–1767.
45. e.g. Trolier-Mckinstry, S., Shephard, J. F., Lacey, J. L., Su, T., Zavala, G. and Fendler, J., Piezoelectricity in ferroelectric thin films: domain and stress issues. *Ferroelectrics*, 1998, **206,** 381–392.
46. Ijima, K., Tomita, Y., Takeyama, R. and Ueda, I., *J. Appl. Phys.*, 1986, **60**, 361–367.
47. Seifert, A., Lange, F. F. and Speck, J. S., Epitaxial growth of $PbTiO_3$ thin films on (001) $SrTiO_3$ from solution precursors. *J. Mater. Res.*, 1995, **10**, 680–691.
48. Kohli, M., Huang, Y., Maeder, T., Wuethrich, C., Bell, A., Muralt, P., Setter, N., Ryser, P. and Forster, M., Processing and properties of thin film pyroelectric devices. *Microelectronic Engineering*, 1995, **29**, 93–96.
49. Kohli, M., Muralt, P. and Setter, N., Removal of 90 degrees domain pinning in (100) Pb(Zr/sub 0.15/$Ti_{0.85}$)O_3 thin films by pulsed operation. *Appl. Phys. Lett.*, 1998, **72**, 3217–3219.
50. Pertsev, N. A., Zembilgotov, A. G. and Tagantsev, A. K., Effect of mechanical boundary conditions on phase diagrams of epitaxial ferroelectric thin films. *Phys. Rev. Lett.*, 1998, **80**, 1988–1991.
51. Pertsev, N. A., Zembilgotov, A. G., Hoffmann, S., Waser, R. and Tagantsev, A. K., Ferroelectric thin films grown on tensile substrates: renormalization of the Curie–Weiss law and apparent absence of ferroelectricity. *J. Appl. Phys.*, 1999, **85**, 1698–1701.
52. Streiffer, S. K., Basceri, C., Lash, S. E. and Kingon, A. I., Ferroelectricity in thin films: The dielectric response of fiber-textured $(Ba_xSr_{1-x})Ti_{1+y}O_{3+z}$ thin films grown by chemical vapor deposition. *J. Appl. Phys.*, 1999, **86**, 4565–4575.

53. Ramesh, R., Gilchrist, H., Sands, T., Keramidas, V. G., Haakenaasen, R. and Fork, D. K., *Appl. Phys. Lett.*, 1993, **63**, 3592–3594.
54. Muralt, P., Maeder, T., Sagalowicz, L., Hiboux, S., Scalese, S., Naumovic, D., Agostino, R. G., Xanthopoulos, N., Mathieu, H. J., Patthey, L. and Bullock, E. L., Texture control of $PbTiO_3$ and Pb(Zr,Ti)O_3 thin films with TiO_2 seeding. *J. Appl. Phys.*, 1998, **83**, 3835–3841.
55. Sreenivas, K., Reaney, I., Maeder, T., Setter, N., Jagadish, C. and Elliman, R. G., Investigation of Pt/Ti bilayer metallization on silicon for ferroelectric thin film integration. *J. Appl. Phys.*, 1994, **75**, 232–237.
56. Muralt, P., Maeder, T., Sagalowicz, L., Hiboux, S., Scalese, S., Naumovic, D., Agostino, R. G., Xanthopoulos, N., Mathieu, H. J., Patthey, L. and Bullock, E. L., Texture control of $PbTiO_3$ and Pb(Zr,Ti)O_3 thin films with TiO_2 seeding. *J. Appl. Phys.*, 1998, **83**, 3835–3841.
57. Taylor, D. V. and Damjanovic, D., Domain wall pinning contribution to the nonlinear dielectric permittivity in Pb(Zr, Ti)O_3 thin films. *Appl. Phys. Lett.*, 1998, **73**, 2045–2047.
58. Sharma, A. K., Narayan, J., Jin, C., Kvit, A., Chattopadhyay, S. and Lee, C., Integration of $Pb(Zr_{0.52}Ti_{0.48})O_3$ epilayers with Si by domain epitaxy. *Appl. Phys. Lett.*, 2000, **76**, 1458–1460.
59. McKee, R. A., Walker, F. J. and Chisholm, M. F., Crystalline oxides on silicon: the first five monolayers. *Phys. Rev. Lett.*, 1998, **81**, 3014–3017.
60. Yogo, T., Takeichi, Y., Kikuta, K. and Hirano, S., Ultraviolet patterning of alkoxy-derived lithium niobate film. *J. Am. Ceram. Soc.*, 1995, **78**, 1649–1652.
61. Kikuta, K., Takagi, K. and Hirano, S., Photoreaction of titanium-based metal-organic compounds for ceramic fine patterning. *J. Am. Ceram. Soc.*, 1999, **82**, 1569–1572.
62. Noda, K., Sakamoto, W., Yogo, T. and Hirano, S., Ultraviolet patterning of $KTiOPO_4$ thin films through metallo-organics. *J. Mater. Res.*, 1999, **14**, 222–227.
63. Berggren, K. K. et al., Microlithography by using neutral metastable atoms and self-assembled monolayers. *Science*, 1995, **269**, 1225–1257.
64. Li-Jeon, N., Clem, P., Young-Jung, D., Lin, W., Girolami, G. S., Payne, D. A. and Nuzzo, R. G., Additive fabrication of integrated ferroelectric thin-film capacitors using self-assembled organic thin-film templates. *Adv. Mater.*, 1997, **9**, 891–895.
65. Tagantsev, A. and Stolichnov, I., Injection-controlled size effect on switching of ferroelectric thin films. *Appl. Phys. Lett.*, 1999, **74**, 1326–1328.
66. Foeth, M., Sfera, A., Staedelmann, P. and Buffat, P.-A., A comparison of HREM and weak beam transmission electron microscopy for the quantitative measurement of the thickness of ferroelectric domain walls. *J. Electron Microscopy*, 1999, **48**, 717–723.
67. Cao, W. and Cross, L. E., Theory of tetragonal twin structures in ferroelectric perovskites with a first-order phase transition. *Phys. Rev. B*, 1991, **44**, 5–12.
68. Yoshida, M., Mori, S., Yamamoto, N., Uesu, Y. and Kiat, J. M., Transmission electron microscope observation of relaxor ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$. *J. Korean Phys. Soc.*, 1998, **32**, S993–S995.
69. Chu, F., Reaney, I. and Setter, N., Role of defects in the ferroelectric relaxor lead scandium tantalite. *J. Am. Ceram. Soc.*, 1995, **78**, 1947–1952.
70. Bonnell, D. A., Local structure and properties of oxide surfaces: scanning probe analyses of ceramics. *J. Am. Ceram. Soc.*, 1998, **81**, 3049–3070.
71. Gruverman, A. L., Auciello, O. and Tokumoto, H., Nanoscale investigation of fatigue effects in Pb(Zr,Ti)O_3 films. *Appl. Phys. Lett.*, 1996, **69**, 3191–3193.
72. Eng, L. M., Friedrich, M., Fousek, J. and Günter, P., Scanning force microscopy of ferroelectric crystals. *Ferroelectrics*, 1997, **211**, 49–52.
73. Eng, L., *Appl. Phys. Lett.*, 1999, **74**, 233–235.
74. Roelofs, A., Böttger, U., Waser, R., Schlaphof, F., Trogisch, S. and Eng, L. M., Differentiating 180 degrees and 90 degrees switching of ferroelectric domains with three-dimensional piezoresponse force microscopy. *Appl. Phys. Lett.*, 2000, **77**, 3443–3445.
75. Bradely, P., Colla, E. and Setter, N. (unpublished).
76. Hubert, C., Levy, J., Carter, A. C., Chang, W., Kiechoefer, S. W., Horwitz, J. S. and Chrisey, D. B., Confocal scanning optical microscopy of $Ba_xSr_{1-x}TiO_3$ thin films. *Appl. Phys. Lett.*, 1997, **71**, 3353–3355.
77. Cho, Y., Kazuta, S. and Matsuura, K., Scanning nonlinear dielectric microscopy with nanometer resolution. *Appl. Phys. Lett.*, 1999, **72**, 2833–2835.
78. Damjanovic, D., Demartin, M., Shulman, H. S., Testorf, M. and Setter, N., Instabilities in the piezoelectric properties of ferroelectric ceramics. *Sensors and Actuators A*, 1996, **53**, 353–360.
79. Reaney, I. M. and Damjanovic, D., Crystal structure and domain-wall contributions to the piezoelectric properties of strontium bismuth titanate ceramics. *J. Appl. Phys.*, 1996, **80**, 4223–4225.
80. Yang, T. J. et al., Direct observation of pinning and bowing of a single ferroelectric domain wall. *Phys. Rev. Lett.*, 1999, **82**, 4106–4109.
81. Ganpule, C. S., Nagarajan, V., Li, H., Ogale, A. S., Steinhauer, D. E., Aggarwal, S., Williams, E., Ramesh, R. and De Wolf, P., Role of 90 degrees domains in lead zirconate titanate thin films. *Appl. Phys. Lett.*, 2000, **77**, 292–294.
82. Colla, E. L., Hong, S., Taylor, D. V., Tagantsev, A. K., No, K. and Setter, N., Direct observation of region by region suppression of the switchable polarization (fatigue) in Pb(Zr,Ti)O_3 thin film capacitors with Pt electrodes. *Appl. Phys. Lett.*, 1998, **72**, 2763–2765.
83. Alexe, M., Scott, J. F., Curran, C., Zakharov, N. D., Hesse, D. and Pignolet, A., Self-patterning nano-electrodes on ferroelectric thin films for gigabit memory applications. *Appl. Phys. Lett.*, 1998, **73**, 1592–1594.
84. Okamura, S., Mori, K., Tsukamoto, T. and Shiosaki, T., Fabrication of ferroelectric $Bi_4Ti_3O_{12}$ thin films and micropatterns by means of chemical solution decomposition and electron beam irradiation. *Integr. Ferroelectr.*, 1997, **18**, 311–318.
85. Alexe, M., Harnagea, C., Hesse, D. and Gösele, U., Patterning and switching of nanosize ferroelectric memory cells. *Appl. Phys. Lett.*, 1999, **75**, 1793–1795.
86. Ganpule, C. S., Stanishevsky, A., Su, Q., Aggarwal, S., Melngailis, J., Williams, E. and Ramesh, R., Scaling of ferroelectric properties in thin films. *Appl. Phys. Lett.*, 1999, **75**, 409–411.
87. Ahn, C. H., Tybell, T., Antognazza, L., Char, K., Hammond, R. H., Beasley, M. R., Fischer, Ø and Triscone, J.-M., Local, nonvolatile electronic writing of epitaxial $Pb(Zr_{0.52}Ti_{0.48})O_3$/$SrRuO_3$ heterostructures. *Science*, 1998, **276**, 1100–1103.
88. Kleinlogel, C. and Gauckler, L.J. In: *Proc. 12th Int. Conf. Solid State Ionics*, Thessaloniki, Greece, in press.
89. Luo, J., Wang, H. and Chiang, Y.-M., Origin of solid-state activated sintering in Bi_2O_3-doped ZnO. *J. Am. Ceram. Soc.*, 1999, **82**, 916–920.
90. Chen, I.-W. and Wang, X.-H., Sintering dense nanocrystalline ceramics without final-stage grain growth. *Nature*, 2000, **404**, 168–171.
91. Xia, Y., Gates, B., Yin, Y. and Lu, Y., Monodispersed colloidal spheres. Old materials with new applications. *Adv. Mater.*, 2000, **12**, 693–713.
92. Seifert, A., Sagalowicz, L., Muralt, P. and Setter, N., Microstructural evolution of dense and porous pyroelectric $Pb_{1-x}Ca_x$-TiO_3 thin films. *J. Mater. Res.*, 1999, **14**, 2012–2015.
93. Bach, U., Lupo, D., Comte, P., Moser, J. E., Weissö, F., Salbeck, J., Spreitzer, H. and Graetzel, M., Solid-state dye-sensitized mesoporous TiO_2 solar cells with high photon-to-electron conversion efficiencies. *Nature*, 1998, **395**, 583–585.

94. Lenzmann, F., *Mesoporous, Nanoparticulate Films of Nb_2O_5 and ZrO_2, Preparation and Characterization*. PhD thesis, EPFL, Lausanne, Switzerland, 2000.
95. Tenne, R., Margulis, L. and Genud, M., Polyhedral and cylindrical structures of tungsten disulphide. *Nature*, 1992, **360**, 444–445.
96. Ajayan, P. M., Stephan, O., Redlich, Ph. and Colliex, C., Carbon nanotubes as removable templates for metal oxide nanocomposites and nanostructures. *Nature*, 1995, **375**, 564–567.
97. Rothschild, A., Cohen, S. R. and Tenne, R., WS_2 nanotubes as tips in scanning probe microscopy. *Appl. Phys. Lett.*, 1999, **75**, 4025–4027.
98. Kasuga, T., Hiramatsu, M., Hoson, A., Sekino, T. and Niihara, K., Formation of titanium oxide nanotube. *Langmuir*, 1998, **14**, 3160–3162.
99. Parilla, P. A., Dillon, A. C., Jones, K. M., Riker, G., Schulz, D. L., Ginley, D. S. and Hebe, M. J., The first true inorganic fullerenes? *Nature*, 1999, **397**, 114–115.