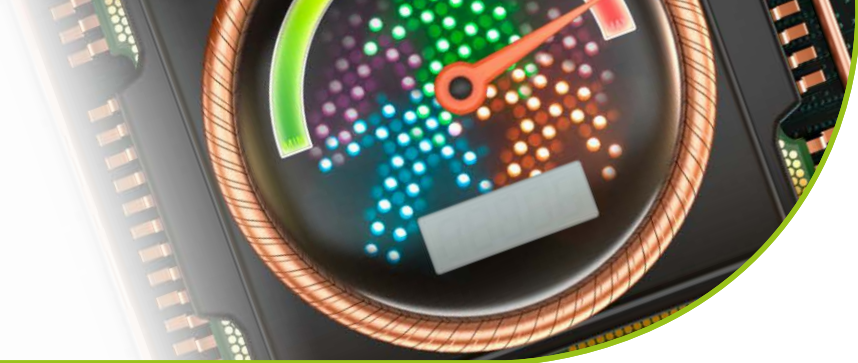




**Nanostrain**

Providing highly accurate measurement of strain in nanoscale systems to drive innovation



e-newsletter • Issue 3 • Summer 2014

# Welcome

Welcome to the third edition of the quarterly EMRP Nanostrain project newsletter. Over the next three years this newsletter will provide you with everything you need to know on the latest project developments, as well as interviews with global industry leaders and a summary of upcoming global events and academic conferences on the exciting technological area of nanoscale piezoelectrics.

## Project news

### *Modelling the piezoelectric properties of ultrathin films*

Nanostrain project partners based at NPL and IBM have produced a model-based methodology for measuring the voltage induced deformation of piezoelectric thin epitaxial films. The work is published in this month's Journal of Applied Physics and represents the first collaborative paper produced by the two institutions.

In the paper, the authors present a model which accurately represents the deformation produced when a voltage is applied across a piezoelectric film perfectly bonded to a linear elastic substrate. Under these conditions, exact analytical solutions can be found that predict the biaxial bending, charge accumulation and thickness changes.

The work represents a significant step forward from previous modelling approaches, which were more limited in the range of physical variables they could predict. By extending the analytical approach to a fuller set of variables, more comprehensive comparisons with experimental data can now be made.

The difficulty now involves finding sufficiently accurate techniques to measure the curvature of the film/substrate bilayer so that the validity of the model can be assessed. Existing wafer

flexure techniques are not sufficiently accurate for the tiny curvatures predicted from the model, and so different methods will need to be found. NPL is currently undertaking research with a number of partners in order to overcome these challenges, exploring the use of Piezoresponse Force Microscopy (PFM) as well as X-ray synchrotron diffraction on the XMaS beam line at the European Synchrotron Radiation Facility (ESRF).

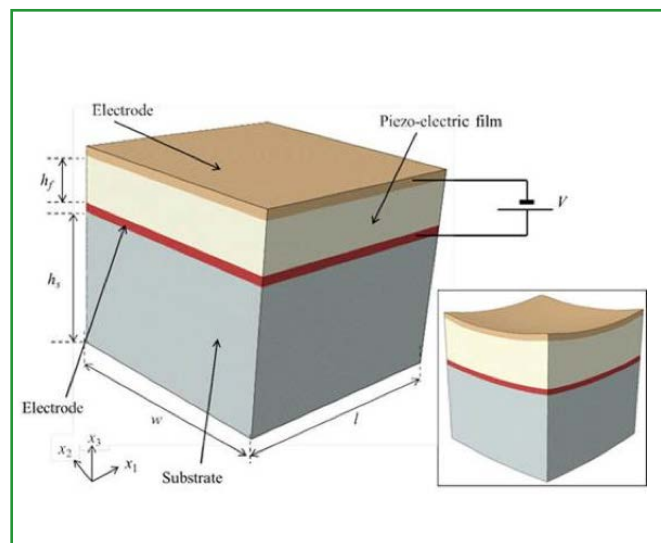


Figure: Schematic diagram of the bilayer and its electrical connection Inset: Bilayer undergoing bending, illustrating equi-biaxial curvature

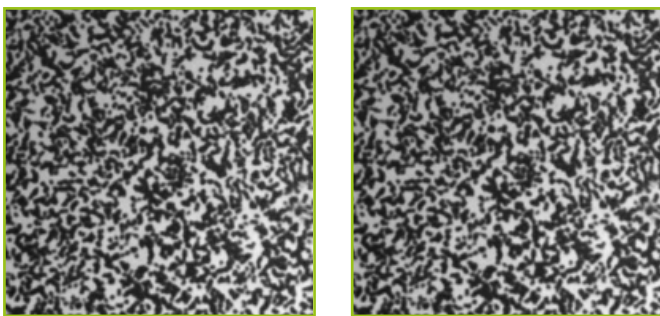
## Visualization of Strain Displacement using DIC on Interleaved AFM Imaging

Digital Image Correlation (DIC) is an important technique to visualise how different samples behave under stress. Developed in the 1980s as a way to visualise local in-plane deformations of an object, it now plays a key role in the Nanostrain project

DIC relies on comparing two images of the sample: one taken under normal conditions (a reference image) and the other when influenced by some external stimulus (a distorted image). The aim of the method is to detect very small changes in sample morphology caused by the external stimulus and then to compare it to sample deformation as predicted by some analytical relation or numerical model.

Until recently images used for DIC were acquired by an optical microscope, but in principle any digital image can serve as an input. This means that the technique can be applied to data obtained from atomic force microscopes (AFM) as well as transmission electron microscopes (TEM).

Within the Nanostrain project the aim is to visualize local displacements of a piezo electric material acquired by AFM and TEM. Project partner Miroslav Valtr and his colleagues at the Czech Metrology Institute (CMI) developed a set of software tools precisely for this purpose. The main tool is a cross-correlation module in Gwyddion open-source software (see <http://gwyddion.net>). Using this module the shifts in the x and y axes were calculated from the reference and distorted images. They then prepared a small script that assembled an input file for Gnuplot (see <http://www.gnuplot.info>) which is an open-source plotting software.



Figures 1 and 2. Sample 3b was downloaded from the DIC Challenge [website](#)

The team then tested the process on a set of generated images known as Sample 3b, where half of the image was shifted by different fraction of a pixel. The reference and distorted images can be found in Figures. 1 and 2, with the resulting displacements denoted by arrows in Figure. 3.

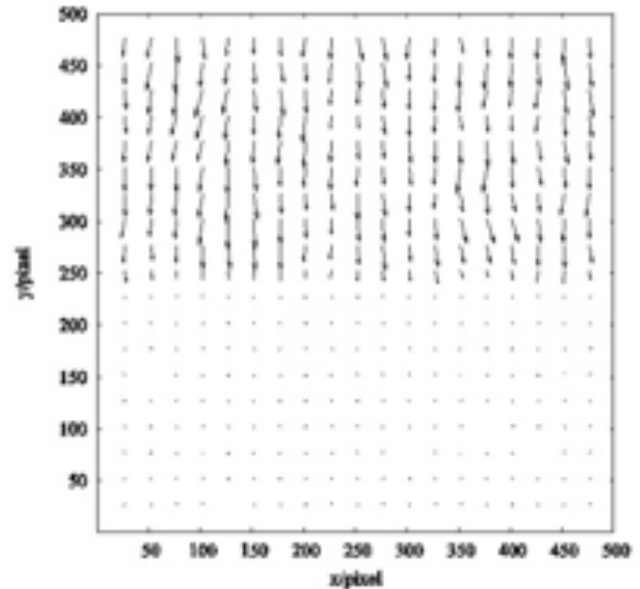


Figure 3. The arrows are not drawn to scale, and have been increased in order to better visualize the displacement. The shift was half a pixel in magnitude.

These tools form a simple but useful alternative to special commercial DIC software packages. With many data loading and data processing options that Gwyddion has it can be useful for processing DIC data acquired through a number of unconventional imaging techniques.

Moreover, using different data synthesis and modification modules in Gwyddion on artificially prepared data with known deformation can help evaluate the sources of uncertainty in DIC results.

In making the transition from theory to practice, one experimental obstacle that needed to be overcome was the fact that samples suffer from drift when placed on the AFM piezo scanner stage as the AFM scans typically require several minutes to obtain. Whilst the scanner drift is very small for state-of-the-art scanning microscopes (around a nanometer or less), this is still significant if sub-nanometer resolution of strain displacement is required as is the case with many piezo- or ferroelectric thin film materials.



Figure 4 – PZT sample with a circular top electrode and AFM probe in contact with the electrode

In order to minimize the drift between reference and modified image, a new method has been developed by Serban Lepadatu and his colleagues at NPL. Here a piezoelectric sample is used with a bonded circular top electrode as shown in Figure 4. By applying a voltage offset to the circular top electrode, an electric field is set up between the top and bottom electrodes. This results in sample strains due to the inverse piezoelectric effect. Rather than obtaining two consecutive AFM scans, one without a voltage offset and one with a voltage offset, a single AFM scan is taken using interleave mode. Thus each line in the AFM image is scanned twice, with and without a voltage offset, resulting in a repeatable sample strain. The normal and interleave scans are then separated and used as inputs for DIC. This method minimizes scanner drift since the time required to scan a single line is around a second.

Initial results are very promising, with an example of this technique shown in Figure 5. Here a  $2 \mu\text{m}^2$  area is scanned on top of the circular Au electrode. This forms a suitable surface for DIC processing as the thermally evaporated Au electrode tends to form into small granules. These provide a suitable texture for the DIC algorithm to track distortions in the sample surface. Figure 5a is the reference image from the interleaved scan and Figure 5b is the modified image where a voltage offset was applied. These two images are fed as inputs into the DIC algorithm and the resulting strain displacement distribution is shown in Figure 5c. The magnitude of strain displacement is of the order 1 nm, which is possible to detect using the interleaved AFM DIC technique. We expect the improved sensitivity of this technique will prove very valuable for measurements of strain distribution in piezoelectric thin film materials, serving as a tool for characterization and evaluation of functional devices based on these materials.

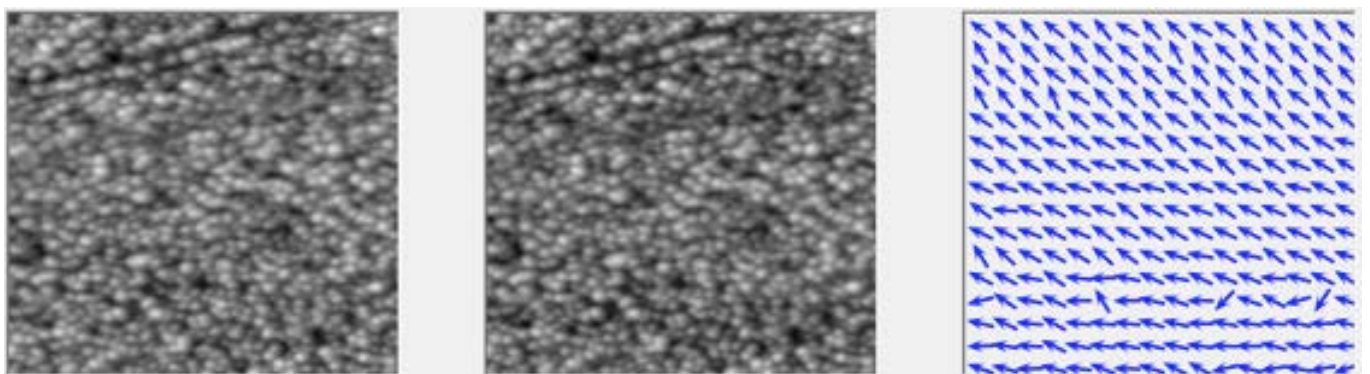
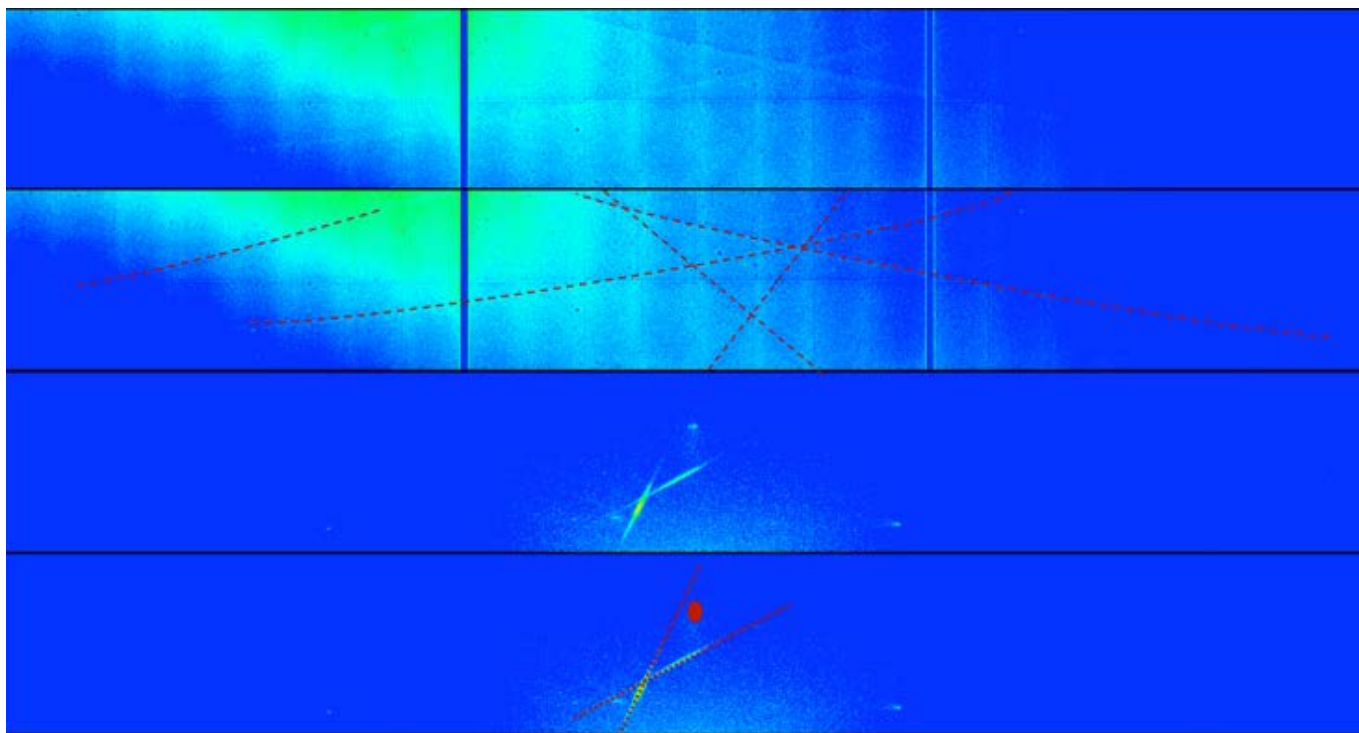


Figure 5 – Interleaved AFM DIC method showing a  $2 \mu\text{m}^2$  AFM scanning area on the Au top electrode, a) reference topography image, b) modified topography image and c) strain displacement direction computed using DIC



### *XMaS beamline experiments test new measurement technique*

In the last edition of this newsletter we reported on the interferometer commissioning process underway on the XMaS beamline in Grenoble. Since those measurements were taken in February, scientists from NPL, the XMaS beamline and the I16 beamline at Diamond Light Source Ltd have returned to carry out the first experiments developing a new measurement technique.

The new approach aims to measure crystallographic lattice parameters and their distribution (intrinsic strain) in thin film heterostructures, although the technique is also applicable to single crystals.

The synchrotron light is shone through thin film samples where it undergoes Diffuse Multiple Scattering (DMS). The DMS gives rise to lines of weak scatter which are similar to the Kikuchi features seen in diffuse electron scattering, and arise from an extended secondary source within the sample. In this case this source is the crystal truncation rods of the substrate in conjunction with the thin film truncation rods.

This opens up the possibility of simultaneous measurements in a single snapshot of the substrate as well as the film lattice parameters and their distribution. This technique could have a resolution on the order of  $10^{-4}$  Ångstroms, which is comparable with

standard techniques, without requiring the sample to be moved. Measurements could also be taken under the influence of external stimuli, allowing the determination of strain in ferroelectric materials as well as the deformation of the substrate induced by the piezoelectric material.

The preliminary experiments carried out in May used a Gold single crystal as an exemplar to calibrate these calculations. The top two panels of Figure 1 show the X-ray data collected on a single-photon counting area detector around the (2.6 2.6 1.6) reciprocal lattice point. The second panel uses red dotted lines to highlight the weak DMS line.

The bottom two panels show the corresponding DMS lines for a sample of technological relevance, such as thin piezoelectric heterostructure on a ceramic substrate. In this case the red circle highlights a crystal truncation rod which, in this instance, is used like a torchlight to enhance the DMS signal. For this sample the data were collected around the (0 2.2 0) reciprocal point in the pseudo-cubic crystallographic unit cell of the piezoelectric thin film.

This data, and subsequent data recorded with electric field induced changes in strain, represents a first for ferroelectric thin films and presents a novel simultaneous method to explore the static and potentially dynamic response of functional films and their substrates.

## Nanostrain at ALTECH 2014

The Nanostrain project was well represented at the ALTECH symposium of the 2014 European Materials Research Society (EMRS) Spring Meeting, held in Lille, France from the 26th-30th May. The conference focused on analytical techniques for precise characterization of nanomaterials, and the peer-reviewed proceedings will be published in *Physica Status Solidi* (a) and (c).

Over 300 attendees were present across the week, with academic participants supplemented by a strong industrial attendance. One of the presentations was delivered by a team from aixACCT, a firm specialising in electrical testing for material development and device qualification. They presented improvements on one of their products which uses a double beam interferometer to measure the thickness change of piezoelectric thin films. As their technique is very dependent on the size of the sample, their work is unlikely to overlap too much with the similar Nanostrain research conducted at NPL.

As reported in the last issue of this newsletter, members of European Metrology Research Programme (EMRP) projects delivered 11 invited talks as well as 24 talks and tutorials. The following partners delivered presentations

- Werner Österle, Nicole Wollschläger (BAM Federal Institute for Materials Research and Testing, Berlin, Germany): Focused Ion Beam Machining for Site-specific Nanocharacterization - Advances and Drawbacks (training tutorial)
- Thomas Hase (University of Warwick, UK): Advanced XRD methodologies (training tutorial)
- Peter Hermann, Arne Hoehl, Bernd Kaestner, Gerhard Ulm and Burkhard Beckhoff (Physikalisch-Technische Bundesanstalt, Berlin, Germany): Characterization of Si-based Nanostructures by Near-Field Imaging and Nano-FTIR Spectroscopy (training tutorial)
- Mark Stewart, Serban Lepadatu and Markys Cain (National Physical Laboratory, UK): A Geometry Independent Approach to the Measurement of the Piezoelectric Coefficient of Thin Films
- Alex Bogdanov (A.P. Vinogradov Institute of Geochemistry SB RAS, Irkutsk, Russia; and Irkutsk State Technical University, Irkutsk, Russia), Anna V. Kimmel (National Physical Laboratory, UK): The effect of mutual order of B-cations on electronic and optical properties of strained  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  (talk)

- Anna V. Kimmel, Markys G. Cain (National Physical Laboratory, UK): Properties of  $\text{Pt}/\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$  interfaces (talk)
- J. Wooldridge, M. Stewart, C. Vecchini, M. G. Cain, M. Gutmann, M. Reece (National Physical Laboratory, UK): Temperature and Frequency Dependence of Electric Field Induced Phase Transitions in PMN-xPT (talk)
- Anna V. Kimmel, Carlo Vecchini, Markys Cain (National Physical Laboratory, UK): Structural properties of  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  (poster)

Read more about ALTECH 2014 [here](#)

The programme of ALTECH is available [here](#)

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## Upcoming events

### EMRS-Strasbourg Fall 2014

Warsaw University of Technology, Poland  
September 15-19

### Third International Conference in Nanotechnology

Bharati Vidyapeeth University, Pune, India  
October 14-15

### Nanocon 2014

Brno, Czech Republic  
November 5-7

### Nanosafe 2014

MINATEC, Grenoble, France  
November 18-20

### Nanotek & Expo

San Francisco, USA  
December 1-3

### Asian Conference on Nanotechnology

Kuala Lumpur, Malaysia  
December 16-17

### 6th NRW Nano-Konferenz

Dortmund, Germany  
January 12 2015

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# Big Interview:

## Thibaud Denneulin, CEMES



Thibaud Denneulin

### What is the DFEH technique?

DFEH was patented by Martin Hýtch and coworkers at CEMES in 2008. Briefly stated, the principle is to interfere electron beams that have been diffracted by a single crystal specimen using a Möllenstedt-Düker electron biprism. The beams diffracted by the strained region of interest are interfered with the beams diffracted by a region of reference (usually the substrate). This gives a fringe pattern that can be seen as a magnified representation of the lattice planes.

### What are the advantages of using DFEH?

There are several strain measurement techniques in TEM. Each one has its own advantages and drawbacks. There is one group of methods based on the analysis of diffraction patterns (such as convergent beam electron diffraction (CBED) and nanobeam electron diffraction (NBED)). These methods provide mainly localised information and require the acquisition of large amounts of data in order to investigate large areas. Other imaging techniques also exist, however, like high resolution TEM (HRTEM), scanning TEM (HRSTEM) and dark-field electron holography (DFEH). The advantage of DFEH is that it has a relatively good sensitivity and a large field of view. The optical configuration is also quite flexible and the spatial resolution can be tuned (1 to 20nm) depending on the sample requirements.

### The technique you are using is a destructive one: by the time you've made these samples, you've thinned them down dramatically and changed their properties. How would you compensate for this damage experimentally?

It is a good question and this is an aspect that remains to be investigated for piezoelectric samples. The thinning of a material using a focused ion beam can introduce irradiation damage at the surface and create amorphous layers. This problem can be investigated by preparing thin foils of different

thicknesses and using different ion beam energies. Another problem is the relaxation of the strain: when a layer is grown by epitaxy and is strained by a substrate, it can relax when it is thinned down. The strain measured in a thin foil can then be lower than in the bulk. This problem can be addressed by comparing the results with mechanical simulations. For the most part, however, the influence of the preparation depends strongly on the material, the preparation conditions, the sample geometry and the strain components being studied.

### Who have you been collaborating with?

We collaborate with BAM (The German Federal Institute for Materials Research and Testing) on the preparation of thin films by Focused Ion Beam. The samples used in our research originate from the University of Wisconsin. We also work with NPL in the UK to compare the TEM images with those obtained via X-ray diffraction and computer simulation.

### Have you had any interesting results?

Before the Nanostrain project our primary focus was on semiconductors (silicon and germanium). At the beginning we weren't entirely sure the same measurement techniques could be transposed onto piezoelectric oxides – which are made of very different materials. The experiments carried out in the first year on thin layers of PZT and PMN-PT have shown that it is possible to obtain deformation maps that are spatially resolved on the nanometric scale with a sensitivity of less than 0.1%. These results came as a surprise to us, and have given us faith in the effectiveness of the system.

These measurements were in large part possible thanks to the latest generation microscope (I2TEM Toulouse) acquired by the CEMES experiment in 2012, and the careful preparation of the experimental samples.

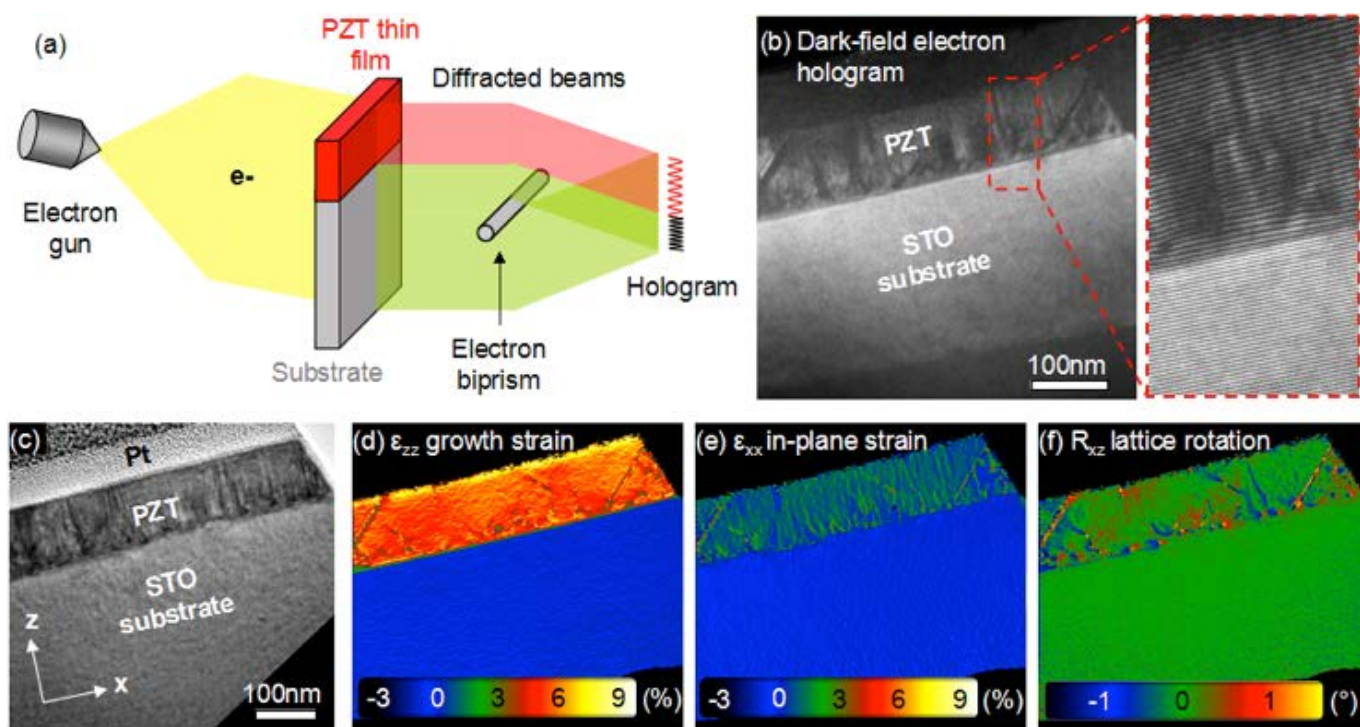
## What will these results mean for the Nanostrain project as a whole?

The development of a new technology is often reliant on new measuring techniques. Measurements of strain undertaken with X-ray diffraction or Raman scattering are known to have high sensitivity but are still not capable of generating a sufficiently high resolution on the nanometre scale. Indeed, many of the piezoelectric properties of nanomaterials depend on ferroelectric nanodomains, structural defects, and other details which are not directly visible under existing techniques. This is where electron microscopy comes in useful, offering us a glimpse of the world on the nano-scale.

## What are the next steps for CEMES?

The major challenge we face is that of applying a bias to a sample in a microscope in situ in order to observe and quantify the piezoelectric deformations. We also hope to observe different mechanisms such as the reversal and movement of the ferroelectric domains.

Another key area of research involves expanding the range of samples we are capable of studying. So far we have uniquely studied thin layers, but over the coming years we hope to collaborate with IBM in order to examine real piezoelectric systems.



(a) Principle of dark-field electron holography. (b) Electron hologram of a  $\text{PbZrTiO}_3$  (PZT) layer grown by epitaxy on a  $\text{SrTiO}_3$  (STO) substrate. (c) TEM image. (d) Reconstructed  $\epsilon_{zz}$  growth strain, (e)  $\epsilon_{xx}$  in-plane strain and (f)  $R_{xz}$  rotation of the lattice.

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**EMRP**

European Metrology Research Programme  
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