Nanostrain

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

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Welcome

Welcome to the seventh edition of the EMRP Nanostrain project newsletter.

The Nanostrain project closed in June 2016, so this newsletter is the final update on the work of the project. If you have any outstanding questions relating to the project please contact Graham Baker: graham.baker@npl.co.uk

Project news

Micro-scale Scanning Measurement of Piezoelectric Coefficients

M. Stewart[1], J. Wooldridge[1], S. Scott-Wildman[1], M. Cain[1]

Much of the Nanostrain project has focussed on the indirect piezoelectric effect, where the application of an electric field creates a useful strain, for instance to move the scanner head in an Atomic Force Microscope. However, the original discovery of the piezoelectric effect by the Curie brothers in 1880 showed that by compressing certain crystals a charge was released, and the term "piezo" derives from the Greek word to press. This is the direct piezoelectric effect and it wasn't until several years later they found it was reversible, and so discovered the indirect effect.

The Curie brother's experiments developed a sensitive electrometer to measure the generated charge, and many years later this method is still one of the simplest methods to measure the piezoelectric coefficient. The method is susceptible to thermal drift, and to overcome this, Don Berlincourt developed an instrument to apply a sinusoidal force and measure the AC charge. His name became synonymous with this method and it is used in industry to measure mm to cm sized samples. The problem with the instrument is because of its size it is difficult to measure thin films and small samples.

At NPL we have developed a prototype microscale instrument based on this principle, which can be used in an SEM (Scanning Electron Microscope) and so measurements can be made on the sub micrometre scale and additionally scanned across a sample. The prototype uses a MEMS (Micro-Electro-Mechanical-Systems) based force sensor (figure 1) to measure the applied AC force, generated using a simple piezoelectric buzzer mounted underneath the sample. The sample in this case is a 1 m thick film of PZT on a 20 m thick silicon membrane, and the force sensor can be positioned anywhere on the sample using a combination of the SEM stage and a

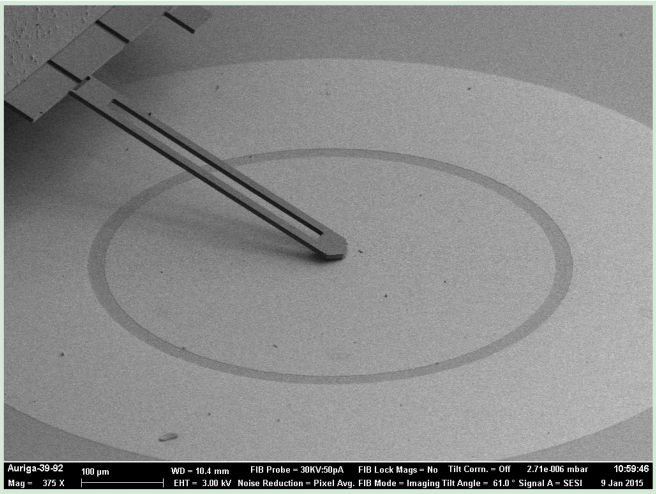

Figure 1 SEM image of the PZT film membrane with the force sensor touching the centre of the sample. The centre electrode is isolated, but the outer electrode has a connection, (hidden by the sensor), that is used to collect the charge.

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micromanipulator. Normally the top probe would also be used to collect and measure the generated charge, but in this prototype the sample top electrode, the central disc figure 1, is connected to the charge amplifier, and the force sensor is electrically isolated.

The sample measured, with a piezoelectric film on a passive silicon substrate, is essentially a micro sized version of the piezoelectric buzzer and so will move like a drumskin at the first fundamental frequency and below. The application of an AC field causes the membrane to move up and down, with the maximum displacement at the centre of the disc. This can be measured separately using a vibrometer (figure 2) which shows a linescan across the centre and plots the AC displacement as a function of distance.

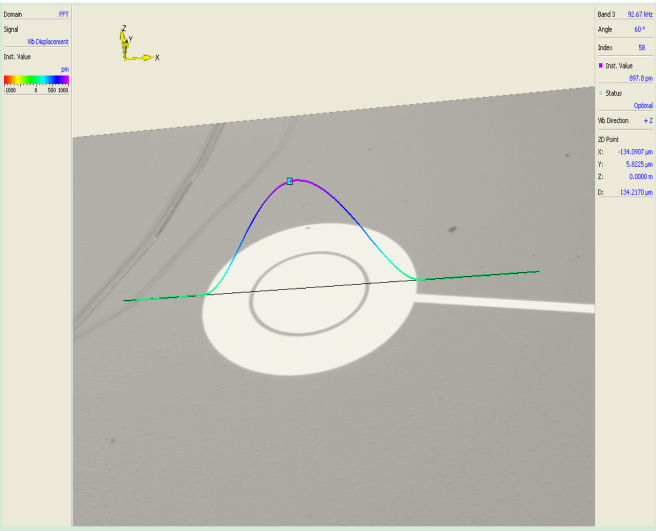

Figure 2 Mode shape data from the vibrometer showing the fundamental mode of the membrane at 92.67 kHz.

Initially, to make each measurement point with the system, the probe was raised and the sample moved across by 10 µm and then repositioned, however, more consistent results were seen when the probe was dragged across the surface. The results from the two methods agree very well, although the Berlincourt results are slightly noisier. The prototype suffered from two minor problems, a very low applied force, maximum of approximately 2 µN, and crosstalk between the applied force driving signal and the generated charge. These issues can be addressed in the next iteration, however this instrument has shown for the first time the reversibility of the direct and indirect piezoelectric coefficients at this small length scale.

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Differential phase-contrast dark-field electron holography for strain mapping [1]

T. Denneulin[1], F. Houdellier[1], M. Hÿtch[1]

Electron holography is an interferometric experiment conducted in a transmission electron microscope (TEM) which allows the reconstruction of the phase and the amplitude of a wave. It is used to map electrostatic, magnetic and strain fields at the nanometer scale. Strain charaterisation is important to understand the properties of materials, such as the charge carriers mobility in semiconductors or piezoelectricity in metal oxides, and relate them to fabrication parameters.

There are many different optical configurations for electron holography [2]. The most widespread is the off-axis configuration where a Möllenstedt-Düker biprism is placed after the specimen. Fig. 1(a) illustrates the off-axis configuration for strain mapping in epitaxial thin films, so-called dark-field electron holography (DFEH) [3]. The beams diffracted by the substrate are interfered with the beams diffracted by the epitaxial layer. The hologram is recorded using a CCD camera and the phase is numerically reconstructed by Fourier processing. A strain map is then obtained by differentiation of the phase in the direction of the chosen reciprocal lattice vector.

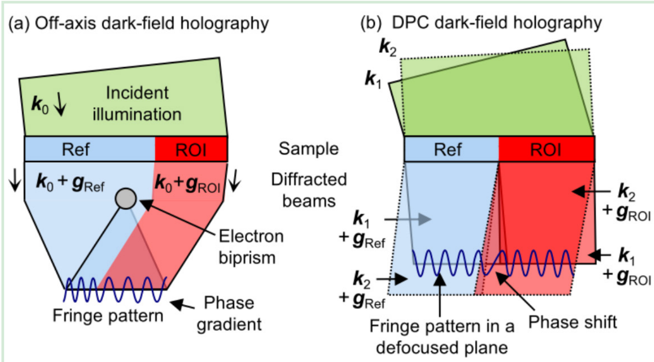


Figure 1 (a) Dark-field off-axis electron holography. Beams diffracted by a reference region (Ref) are interfered with beams diffracted by a region of interest (ROI) thanks to an electron biprism below the specimen. (b) Differential-phase contrast (DPC) dark-field holography. Two incident beams with a different angle are created by a pre-specimen biprism (not shown here). Beams diffracted by slightly distant regions interfere in a defocused plane.

In the article, we developed an alternative dark-field holographic configuration that uses a biprism located before the specimen. This configuration is called differential-phase contrast, based on the work of McCartney *et al*. [4]. Two incident beams with a different angle are created by the pre-specimen biprism. The hologram is then recorded in a defocused plane where beams diffracted by slightly distant regions of the specimen interfere (Fig. 1(b)). One advantage of this technique is that the DPC phase reconstructed from the hologram is directly proportional to the strain, providing that the biprism is oriented perpendicularly to the reciprocal lattice vector. Another advantage is that the reference region does not need to be as large as the region of interest.

Experiments were carried out using the Hitachi I2TEM-Toulouse microscope equipped with multiple biprisms, double stages (Objective and Lorentz) and an image corrector (CEOS B-COR). Fig. 2(a) shows an example of (004) hologram obtained on a Si/SiGe superlattice with different Ge concentrations. When grown by epitaxy on a Si substrate, SiGe layers are compressed in the in-plane direction and stretched in the growth direction by Poisson's effect (see Fig. 2(b)). The DPC phase reconstructed from the hologram (Fig. 2(c,d)) increases with the Ge concentration in the layers, proportionally to the growth strain. The strain can then be calculated if the defocus and the angle between the two incident beams are determined (see paper for details).

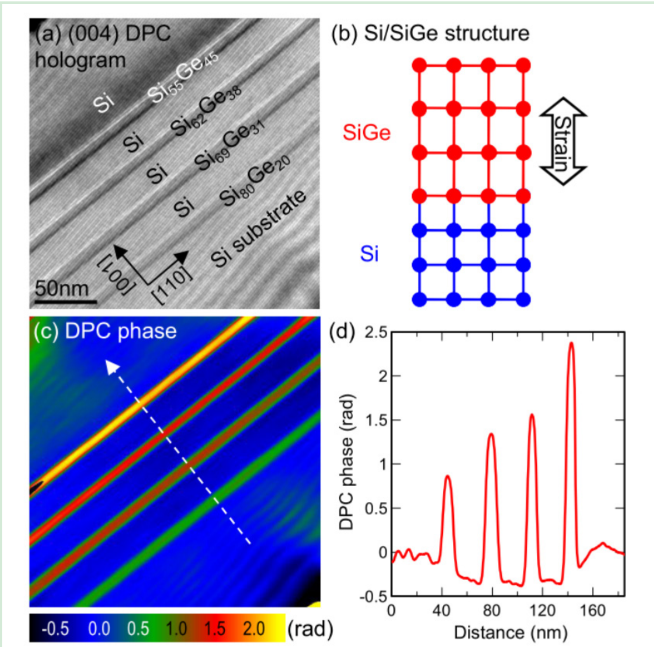


Figure 2 (a) (004) DPC dark-field electron hologram obtained on a Si/SiGe superlattice with different Ge concentrations (20%, 31%, 38% and 45%). (b) Representation of the lattice structure. (c) DPC phase reconstructed from the hologram by Fourier processing. (d) DPC phase profile extracted from the map along the growth direction according to the arrow.

The sensitivity of the technique can be controlled with the defocus. The larger the defocus is, the better the sensitivity but the poorer the spatial resolution. Fig. 3(a) shows a defocus series acquired on a dummy p-MOSFET device with recessed SiGe source/drain. The SiGe source/drain are used to apply a compression to the Si channel [5]. The signal in the DPC phase maps (Fig. 3(b)) increases with the defocus. Therefore, the noise in the strain maps (Fig. 3(c)) decreases when the defocus increases. The standard deviation of the strain calculated in the substrate (indicated below the strain maps) is used to estimate the sensitivity and varies between 0.06% to 0.03% for a defocus range Δf=+4.7 µm to +14.1 µm.

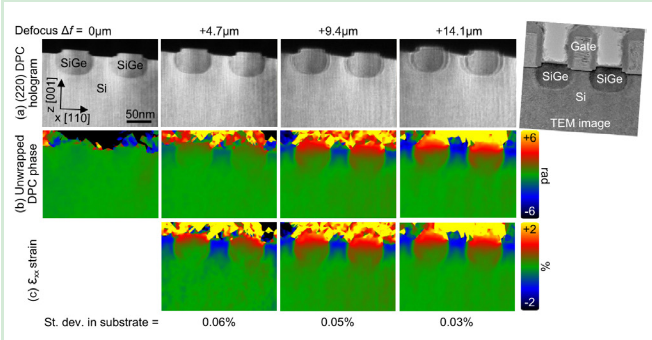


Figure 3 (a) (220) DPC dark-field electron holograms obtained on a p-MOSFET-like devices with recessed SiGe sources and drains for a defocus range Δf = 0 to +14.1 µm with 4.7 µm step. (b) Reconstructed and unwrapped DPC phase images. (c) εxx in-plane strain maps. The standard deviation of the strain calculated in the substrate is indicated below.

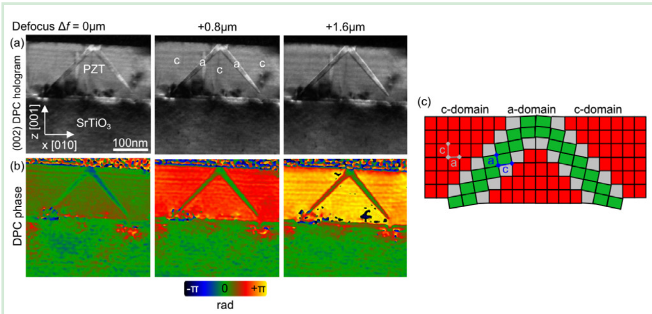


Figure 4 (a) (002) DPC dark-field electron hologram of a Pb(Zr0.2,Ti0.8)O3 layer grown on SrTiO3 substrate for a range of defocus (Δf=0 to +1.6 µm). Holograms contain two a-domains with opposite inclination bounded by c-domains. (b) Reconstructed DPC phase image. (c) Representation of the lattice structure.

This technique was also used to investigate the strain in piezoelectric materials within the Nanostrain project. Fig. 4(a) is a defocus series of (002) DPC holograms obtained on an epitaxial Pb(Zr0.2,Ti0.8) O3 thin film epitaxially grown on a SrTiO3 substrate.

It contains c- and a-domains (or 90° domains, see representation in Fig. 4(c)). The a-domains are needle-shaped and inclined by 45° relatively to the STO interface. The DPC phase (Fig. 4(b)) is proportional to the growth strain and then increases more rapidly in the c-domains than in the a-domains as a function of the defocus (a being closer to the substrate lattice parameter than c).

In conclusion, DPC dark-field holography provides a quick access to strain maps with about 5 nm spatial resolution and 0.05% sensitivity. It should be helpful to characterise residual strain and eventually dynamic strain in piezoelectric devices when applying a bias to the sample inside the microscope.

[1]CEMES - CNRS

[1] T. Denneulin, F. Houdellier and M. Hÿtch, "Differential phase-contrast dark-field electron holography for strain mapping", Ultramicroscopy 160 (2016), pp. 98--109.

[2] J.M. Cowley, "Twenty forms of electron holography", Ultramicroscopy 41, 4 (1992), pp. 335--348.

[3] M. Hÿtch, Houdellier, F. Hüe and E. Snoeck, "Nanoscale holographic interferometry for strain measurements in electronic devices", Nature 453, 7198 (2008), pp. 1086--1089.

[4] M.R. McCartney and P. Kruit and A.H. Buist and M.R. Scheinfein, "Differential phase contrast in TEM", Ultramicroscopy 65, 3-4 (1996), pp. 179--186.

[5] S.E. Thompson *et al*., "A logic nanotechnology featuring strained-silicon", Electron Device Letters, IEEE 25, 4 (2004), pp. 191--193.

Characterization of Stress and Strain in Semiconductor Materials by correlative confocal Raman and IR-near-field Techniques

Imaging and Stress Characterization by IR-SNOM and synchrotron-based near-field Spectroscopy

Since the first successful demonstration of synchrotron-based nano-FTIR spectroscopy at the PTBs low-energy storage ring Metrology Light Source (MLS) in 2012 [1] the sensitivity of the technique has been further increased. This was achieved by adapting the MLS storage ring optics especially to the requirements needed for performing near-field IR spectroscopy, thus enabling high-resolution IR spectroscopic characterization of materials used in semiconductor technology over a much broader wavelength range than accessible with laser-based radiation sources.

Recently PTB researches demonstrated within the scope of EMRP IND 54 Nanostrain project the sensitivity of this relatively new non-destructive technique for strain characterization. For this purpose strain was induced in graphene coated crystalline silicon carbide (6H-SiC) (provided by PTB 2.53) by applying the Vickers micro-indentation technique (Czech metrology institute (CMI).

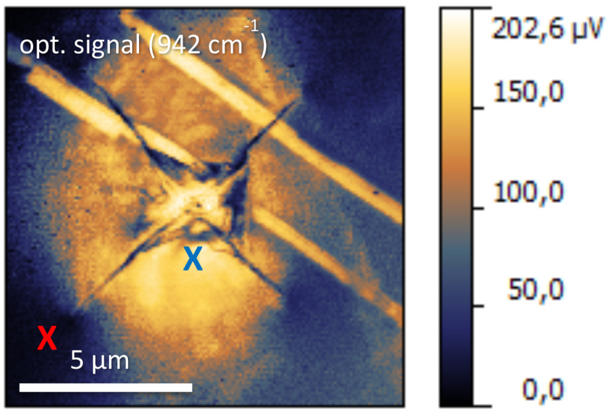


Figure 1 IR-SNOM image recorded with at a wavelength of 10,6 µm (942 cm^{-1}). Optical images recorded by IR-SNOM images reveal residual stress fields around the indentation in the SiC crystal. The two position marked with X (blue and red) indicate the measurement position of the nano-FTIR spectra presented in Figure 2 in the corresponding color.

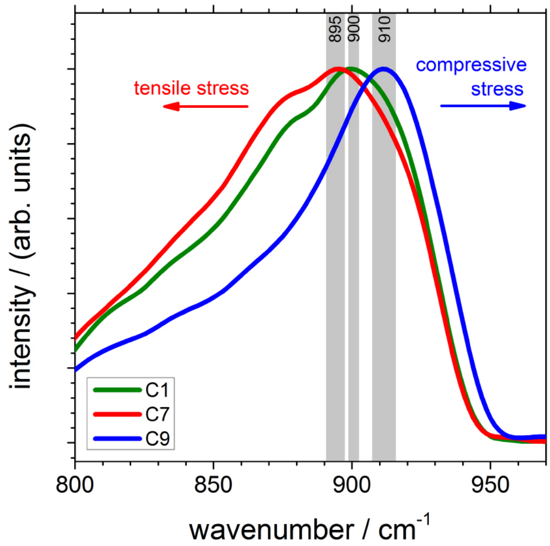


Figure 2 Synchrotron-based nano-FTIR spectra recorded from different positions around the indent in bulk Si. The near-field IR reference spectrum (green) was recorded from a stress-free position far away from the indent. The other two spectra were obtained from the position indicated in Figure 1 in the corresponding color. Compared to the stress-free reference the spectral position of the phonon-polariton band is shifted to higher or lower wavenumbers thus indicating compressive or tensile stress at the measurement positions, respectively.

IR-SNOM images recorded with a laser-irradiated Au-coated near-field probe at different wavelengths reveal in optical images residual stress fields around the indented SiC crystal. For demonstrating the strain sensitivity of synchrotron-based nano-FTIR spectroscopy near-field spectra were recorded at selected positions where strong tensile or compressive strain field are expected. The strongly enhanced optical near-fields around the tip apex excite surface phonon-polaritons which can be regarded as optical lattice vibrations within the polar SiC crystal. This strong near-field interaction occurs at a material specific frequency around the longitudinal optical phonon frequency and provides information about the local dielectric function of the investigated material. Since strain or stress induced changes of the crystal lattice lead to modifications of the dielectric function of the sample the acquired near-field IR spectra show a shift compared to the stress-free reference spectrum as presented in Figure 2. Compressive stress induces a spectral shift of the phonon band to higher wavenumbers while tensile stress results in a shift to smaller wavenumbers. In combination with an appropriate stress model the stress distribution can be calculated from the measured shift of the phonon resonance in near-field IR spectra. Compared to earlier work by Huber *et al.* and Gigler *et al.* [3,4] the use of an ultra-broadband IR synchrotron radiation source enables the acquisition of the full SiC phonon resonance thus enabling a much more accurate determination of the spectral band shifts than with previously used laser-based sources.

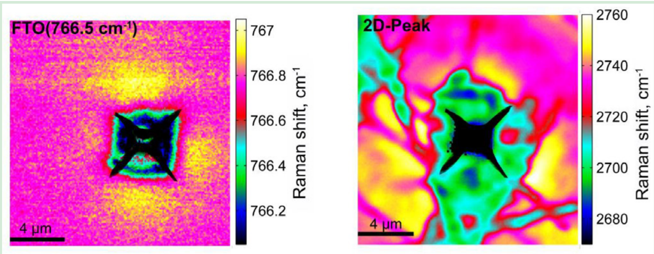


Figure 3 Raman mappings of 6H-SiC and epitaxial graphene around the indentation area. The colorbar indicates the peak position of the respective Raman peak.

The strain characterization by synchrotron-based nano-FTIR spectroscopy can be further improved by modeling the near-field distribution around the tip-apex and the contribution of different phonon modes to the observed shifts of the phonon-bands. This will be a possible subject for the Nanostrain follow-up EMPIR project

Revealing the spatial strain distribution by high resolution confocal Raman imaging

Residual strain in 6H-SiC and epitaxial graphene, which causes a change in their vibrational energy states, is particularly observable by means of Raman spectroscopy. The different types of strain such as compressive or tensile strain even influence the behavior of Raman shift direction, so that the presence of compressive (tensile) strain induce a phonon hardening (softening) of the phonon modes in the Raman spectrum. In this case, the Raman shift direction in the Raman spectrum can act as a strain indicator and might be an effective tool to distinguish the different types of strain or even to indicate the different strain directions (e.g. uniaxial and biaxial strain, respectively). Nevertheless, a high resolution confocal Raman mapping is needed to study the spatial strain level distribution across the examined area. Therefore, PTB induced strain in 6H-SiC and epitaxial graphene using the Vickers micro-indentation technique to show the Raman spectroscopic strain sensitivity and the need of a software solution for multiple data evaluation. Spatial Raman mapping across the 6H-SiC area of (30 x 30) μm^2 was performed with a piezo sample stage enabling an increment of 0.1 µm, whereas the laser power was kept at a level that avoids local heating of the graphene sample. A total of ~24,000 Raman spectra was recorded. The spectra were evaluated by means of a Matlab™ -Tool "EvalMap" developed at PTB which allows non-linear curve fitting procedure to be applied to the spectra to determine characteristic peak properties such as the intensity, peak position and peak width (FWHM) of Raman bands in every single Raman spectrum. The software also provides methods for despiking and smoothing of the spectra as well as hyperspectral evaluation techniques.
The Raman shift calibration was done according to the recommendations given in the ASTM E1840-96 ("Standard Guide for Raman Shift Standards for Spectrometer Calibration).

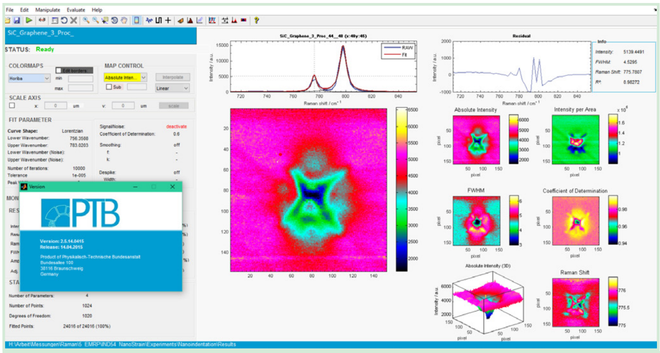


Figure 4 Matlab™ -Tool „EvalMap" (proprietary software developed by Physikalisch-Technische Bundesanstalt).

Low strain sensitivity of micro-Raman spectroscopy appeared in bulk 6H-SiC due to its high stiffness and its transparency with respect to visible light. However, small yellow "clouds" above and below the indentation spot in the Raman mappings of the Raman active FTO-band related to 6H-SiC (Fig. 3) indicate slight changes in their Raman shifts of ~0.5 cm^{-1}. These areas near the micro-indentation spot enclose small amounts of compressiv strain, which is proved by Raman shifts towards larger wavenumbers and clearly indicates a phonon hardening in the Raman spectrum. In contrast, the average Raman shift distribution of the 2D-Peak (normally relaxed at ~ 2668 cm^{-1}) indicates a larger variation in the Raman spectrum (± 20 cm^{-1}) compared to the values obtained for the bulk material 6H-SiC, showing that 2D materials are highly sensitive to the applied strain (Fig. 3). Subsequently, all peak positions in the evaluated Raman mapping can be converted into strain values by solving the secular equation of the force constants matrix to estimate the amount of strain [5,6,7].

The Raman mapping of epitaxial graphene on 6H-SiC clearly shows the need of a software solution for multiple data evaluation to reveal the non-homogeneous strain distribution across the mapping area. The Matlab™ - Tool "EvalMap" could support the strain characterization in solids using Raman or nano-FTIR spectroscopy, but it is currently under development. Nevertheless, PTB aims to release this software probably in the next Nanostrain EMPIR project.

[1] P. Hermann, A. Hoehl, P. Patoka, F. Huth, E. Rühl, and G. Ulm, Opt. Express 21(3) 2913-2919 (2013).

[2] P. Hermann, A. Hoehl, G. Ulrich, C. Fleischmann, A. Hermelink, B. Kästner, P. Patoka, A. Hornemann, B. Beckhoff, E. Rühl, and G. Ulm, Opt. Express 22(15) 17948-17958 (2014).

[3] A. J. Huber, A. Ziegler, T. Köck, and R. Hillenbrand, Nat. Nanotechnology 4 153-157 (2009).

[4] A. M. Gigler, A. J. Huber, M. Bauer, A. Ziegler, R. Hillenbrand, and R. W. Stark, Opt. Express 17(25) 22351-22357 (2009).

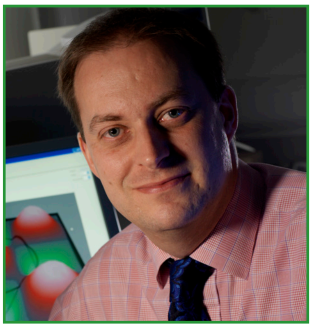
[5] C. Androulidakis *et al*., Sci. Rep. 5, 18219 (2015).

[6] J. Liu & Y. K. Vohra, Phys. Rev. Lett. 72, 4105 (1994).

[7] I. De Wolf, Semicond. Sci. Technol. 11 139–154 (1996)

Big Interview:

Prof Markys Cain - PETMEM



Prof Markys Cain is the Technical Leader for PETMEM (Piezoelectronic Transduction Memory Device), a European partnership of universities, research institutions, and industry that will focus on the development of new materials and characterization tools to enable the fabrication of an entirely new low-voltage, memory element. He also runs scientific consultancy firm Electrosciences Ltd and whilst Science Leader for Functional Materials at NPL was originator for Nanostrain and oversaw Work Package 1 of the Nanostrain project for its first two years.

What do you believe will be the lasting legacy of the Nanostrain project?

I hope the lasting legacy will be fast, low-power computing and telecommunications technologies that could see iPhones that last for a week on one charge, laptop computers that can run at 100GHz for super computer speed calculations, or domestic applications of wearable electronics that require very low power. One of the key features of piezoelectronic transistor (PET) technology is low power so I can also see energy harvesting technologies coming on stream much, much faster than they currently do.

In what way is the work of Nanostrain being built upon by the PETMEM project?

The PETMEM project has two aims: firstly to build a proof of concept prototype PET memory device; and secondly to develop within Europe the tools and processes to allow other people to design with and make Piezoelectric transistor technology.

Nanostrain was really the first European project that took some of the ideas from IBM and elsewhere (where strain affects electronic properties of material systems) and developed the metrology, measurement tools and modeling understanding of this important technology. So Nanostrain laid the foundations for PETMEM, as Europe would not have had the consortia to put together PETMEM without Nanostrain.

What is the PETMEM project and what problem does it seek to address?

The key challenges that PETMEM is trying to address are the development of robust industrial tools for being able to process the piezoelectric and the piezoresistive parts of a PET. Currently they cannot really be done at an industrial scale. The key aims of PETMEM are to develop industrial scale processes and tools that are robust, standardized, reliable and commercially accessible. Parallel to this is a huge focus on the development of new materials that exhibit piezoelectric and/or piezoresistive properties. This is important, as there are not many piezoresistive materials out there that can operate in the conditions we need them to operate in – this is the big technical challenge. The final outcome is that the project will demonstrate a scalable PET-based memory cell.

What will this mean to industry?

It will mean that they have access to the industrial tools they need to design their own devices based on low-power, high-speed piezo technology. This will be for a whole range of different applications such as memory devices and RF switches. The project will develop the process tools so people can reliably and accurately deposit piezoelectric materials onto 12inch substrates in an industrial processing way. So this is not an academic pursuit, but one to create industrial toolsets for Europe.

In what sectors could this have the biggest impact?

Having spoken to the consortia of Nanostrain and PETMEM our view is the market where PET technology could have the biggest impact is likely to be in radio frequency (RF) mobile telecoms. This is where you can switch between different frequency bands using ultra low power PET devices that can be manufactured at the same scale as CMOS technology. This means the first big impact is likely to be the RF switch market in mobiles and base stations. We are by no means restricted to this market though, as a recent paper on nuclear fusion shows the potential impact we could have in emerging energy markets.[i]

What will this mean to your average consumer?

My view is that the man in the street will be able to stream live video on multiple channels simultaneously (without wireless access) as they will be able to quickly switch and access a lot of free bandwidth space you can't currently access. So the average consumer will have a mobile phone that can get faster data streaming, and a longer lasting battery, but they will also be able to go and buy a laptop that can run at 50GHz – getting beyond that *little* Moore's Law blip - PET technology should go beyond that. My Macbook runs at 3GHz, the battery, with a solid state hard drive lasts about 6 hours – imagine it running at 50GHz and a battery life of a week! Imagine what I can do with such a step change, for example in materials simulation or in atmospheric simulation for climate change or anything that is impacted by big data? I will be able to use a laptop instead of having to access a supercomputer for many applications.

What timescale is the PETMEM project working towards?

It is a three-year project started in Dec 2015, ending in Dec 2018. Once finished we will have processes, tools, models, new materials, patents and IP and two device demonstrators made by IBM in Zurich. We are planning on other research proposals to accelerate the development of the RF transistor (in parallel to PETMEM).

IBM considered the PET was 7-10 years away from when PETMEM started, so the impact might be seen in a few years (in the mobile phone sector first) as long as everything works! It is first and foremost a research project, after all.

What is the role of metrology in the PETMEM project?

Metrology is a very important part. NPL is focused on materials modeling, especially across length scale. Then there will be a series of measurement tools developed by aixACCT Systems, who were also involved in Nanostrain. They are developing a range of tools to characterize material properties under PETMEM – and using some of the tools that Nanostrain helped to develop throughout the process.

Are any other research projects developing the work of the Nanostrain project?

There are smaller research activities, possibly a product idea for a radiation detector, a high physics particle radiation detector that came out of Nanostrain. Then there is the EMPIR proposal, JRP-g04 "Metrology for advanced energy-saving technology in next-generation electronics applications" which as of 28th November 2016, has been selected and will be consequently funded. We have put together a consortium under the EMPIR energy call including some of the Nanostrain partners that is all to do with low-powered high efficiency microelectronics. That would look at developing the suite of metrology needed for industry to develop and to use low powered materials, electronics, components and systems. One of the key focuses of this is on RF transistor, which is very exciting.

[i] M. G. Cain, P. M. Weaver, and M. J. Reece, "Ferroelectric materials for fusion energy applications," J. Mater. Chem. A, vol. 4, no. 27, pp. 10394–10402, 2016.

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