Programme

Wednesday 22 April

12:00 Registration and refreshments
National Physical Laboratory

12:50 Lunch

13:50 Welcome
Markys Cain, National Physical Laboratory, UK (Conference Chair)

14:00 (Plenary) Have we reached the zenith of Dielectric Science?
Paul Benishai, Hebrew University of Jerusalem, Israel

Quantum Technologies session
Session chair – Markys Cain

15:00 (Invited) Dielectric scaling from hydrogen to silicon donors for High Field Magnetic White Dwarf spectroscopy
Ben Murdin, University of Surrey, UK

16:00 Superconducting micro-resonators fabricated on a rare-earth ion implanted dielectric for quantum information technologies
Ilana Wisby, National Physical Laboratory/RHUL, UK

16:30 Refreshments

16:50 Dielectric low frequency noise probed by high-Q superconducting resonators at mK temperatures
Jonathan Burnett, University College London, UK

17:20 Coupling to individual two-level fluctuators using coherent near-field microwave microscopy
Sebastian de Graaf, National Physical Laboratory, UK

18:00 Poster session
Foyer area

19:00 Free evening
Thursday 23 April

Dielectric Breakdown Session
Session chair – Tony West

08:30 Refreshments
09:00 *(Invited) What do we know, what don’t we know and how do we prevent it anyway*
Alun Vaughan, University of Southampton, UK
10:00 Weakly ferroelectric behaviour in AgNbO$_3$ bulk materials
Ye Tian, Queen Mary University of London, UK
10:30 Refreshments
11:00 Electrical breakdown of dielectric elastomer actuator materials
Bin Chen, Queen Mary University of London, UK
11:30 Dielectric breakdown and resistive switching of acceptor-doped barium titanate: a common mechanism?
Anthony West, University of Sheffield, UK
12:00 Lunch and posters

Hi-K Dielectrics and Applications Session
Session chair – Alun Vaughan

13:30 *(Invited) Controlling domain walls in ferroelectrics for new devices*
Marty Gregg, Queen’s University Belfast, UK
14:30 Novel, high capacitance nanocomposite dielectrics for printed electronics
Sheida Faraji, University of Manchester, UK
15:00 Refreshments
15:30 On the capacitance nonlinearity in high-k oxides
Herbert Kliem, Saarland University, Germany
16:00 Dielectrics constants of bulk ferroelectric PZT measured by THz time-domain spectroscopy
M Naftaly, National Physical Laboratory, UK
16:30 Poster session (continued)
19:30 Conference Dinner
Friday 24 April

Experimental Techniques Session
Session chair – Sillas Hadjiloucas

08:30 Refreshments
09:00 (Invited) Ultra-High Q dielectrics that led to a room temperature MASER
Neil Alford, Imperial College London, UK
10:00 Improved loss measurement using a microwave microscope
Andrew Gregory, National Physical Laboratory, UK
10:30 Refreshments
10:50 (Invited) Localised impedance measurements using photocurrent measurements at field-effect capacitors
Steffi Krause, Queen Mary, University of London
11:20 A calibration algorithm for multi-port network analysers
Timothy Hodgetts, National Physical Laboratory, UK
11:50 Giant dielectric constant: All an illusion?
C Bowen, University of Bath, UK
12:20 Prize Presentations
12:40 Closing remarks and lunch
Poster session 1

Quantum Technologies

Dielectric Breakdown

P:01 TBA

P:02 Hydrogen induced rupture of Si-O bonds in amorphous silicon dioxide
A M El-Sayed, University College London, UK

Experimental Techniques

P:03 Using high frequency LIMM to characterise the poling state of piezoelectric ceramic thin films
M Stewart, National Physical Laboratory, UK

P:04 A new method to measure the clamped indirect piezoelectric effect of thin piezoelectric films
M Stewart, National Physical Laboratory, UK

P:05 Ti-suboxides structures for water splitting
V Adamaki, University of Bath, UK

P:06 Manufacture of porous electrically conductive ceramics for energy applications
V Adamaki, University of Bath, UK

Poster Session 2

Hi-K Dielectrics and Applications

P:07 Microwave and optoelectronic memristive dielectric metamaterials and their applications to secure communications
H Alyami, University of Reading, UK

P:08 Bond-graph input-state-output port-hamiltonian formulation of RLCM networks
I Al-Mashhadani, University of Reading, UK

P:09 High dielectric performance of Ag/cyanoethylated O-(2,3 dihydroxypropyl)-cellulose nanocomposites
N Madusanka, University of Cambridge, UK

P:10 Engineering reliability in new high temperature capacitors for power electronics
P Weaver, National Physical Laboratory, UK

P:11 Characterization of high temperature piezoelectric materials using interferometry and resonance methods
P Weaver, National Physical Laboratory, UK
(Plenary) Have we reached the zenith of Dielectric Science?

P Benishai and Y Feldman
The Hebrew University of Jerusalem, Israel

The main descriptive spectral functions in Dielectric Spectroscopy were established over 30 years ago (Cole-Cole 1941, Havriliak –Negami 1967, Dissado-Hill 1979, Jonscher 1983). The seminal work on dielectric strength is dated to the end of the 1940s (“The Theory of Dielectrics”, H. Froehlich). One could argue that we have reached a zenith from which Dielectric Science can classify materials and their dynamics, yet not provide a microscopic insight to them. This argument is further strengthened when considering the stagnation of accepted dielectric theory as hinted to above.

This paper will argue most definitely that Dielectrics is still far from its zenith. The reasons for saying so are rooted in the concept of universality in dielectric response. The dynamic behavior of dielectric relaxations in many complex systems looks surprisingly similar, be the system a glass forming liquid or a ferroelectric crystal. Yet the language used to describe the relaxation in each system can be very different. Does this simply reflect their different natures or, at the mesoscopic scale, does it hide a universality of Nature? We will explore this point.

(Invited) Dielectric scaling from hydrogen to silicon donors for High Field Magnetic White Dwarf spectroscopy

B Murdin
University of Surrey, UK

Shallow Group V donors in silicon, such as Si:P, once frozen out at low temperature, share many properties in common with free hydrogen atoms [1]. The Group IV host is tetrahedrally bonded, and the Group V impurity has an extra valence electron that orbits around the singly positively charged ion in much the same way. The primary difference is that the host is a dielectric, with electrons that screen the Coulomb force, (a smaller secondary effect is that the host is a crystal with bands that have an “effective mass” that is less than the free mass). The energy scale that defines the Lyman series absorption lines is proportional to $1/\varepsilon^2$, and whereas these transitions are in the UV for hydrogen, for silicon donors they are in the far-IR or THz. The Bohr radius is similarly affected, and is correspondingly larger – the ground state radius is 3nm, and the first excited state is 20nm.

The similarity between hydrogen and Si:P and the scaling due to the dielectric provides several interesting avenues of research. The large atomic radius is comparable with silicon CMOS structures in commercial use, and implies that silicon devices might be made with a single atom as the active structure, and this is crucial for silicon quantum technologies. Such devices will rely on the ability to produce long lived superposition states just as in free atoms in vacuum, and we have shown that this is indeed possible [2]. Secondly, it provides a very interesting spectroscopy laboratory, for testing theories about extreme environments that would be difficult or impossible to reproduce experimentally for hydrogen. For example, the scaling means that it is very much easier to achieve magnetic fields strong enough that the cyclotron energy equals the binding energy. For hydrogen, this only occurs at 100,000T, a field that has been inferred only on the surface of some white dwarf stars, but for Si:P it occurs at 32T, which is achievable terrestrially. We used this dielectric scaling to test the magneto optical theory for hydrogen [1] and to investigate the properties of a helium-like object, the Group VI double donor Si:Se [3]. In this case there are very few calculations of the high field spectrum because the theory including the electron-electron interactions is so complicated. Thus, our results represent the only experimental study of helium transitions for High Magnetic Field White Dwarfs.

Superconducting micro-resonators fabricated on a rare-earth ion implanted dielectric for quantum information technologies

I Wisby1,4, S de Graaf1,2, R Gwilliam3, A Adamyan2, S Kubatkin2, P Meeson4, A Tzalenchuk1 and T Lindstrom1

1 National Physical Laboratory, UK, 2 MC2, Chalmers University of Technology, Sweden, 3 University of Surrey, UK, 4 Royal Holloway University of London, UK

Systems exhibiting coherent coupling between spin ensembles in solids and superconducting quantum circuits are an exciting area of research for applications in quantum information processing. These hybrid systems make it possible to exploit the long coherence times of electron spins as e.g. quantum memories, while at the same time allowing for a high degree of control via the microfabricated superconducting circuit. Rare-earth ions are a particularly interesting spin system, which have unique spin transition accessibility in both the microwave and optical regime, providing the potential for microwave-to-optical quantum transducers.

We demonstrate the successful integration of a rare-earth ion (Gd3+) spin ensemble, locally doped within a sapphire (Al2O3) dielectric alongside a superconducting micro-resonator.

The hybrid device is fabricated by a controlled ion implantation process which utilizes a hard SiN mask atop the Al2O3 substrate during implantation, allowing micron-sized control of the implantation area. The ensemble couples to a superconducting NbN lumped element microwave resonator which is aligned and fabricated atop the implanted dielectric.

The technique is found not to degrade the internal quality factor of the resonators which remains above 105. Using microwave absorption spectroscopy, we observe electron-spin resonances corresponding to a collective coupling of the order of 3 MHz and linewidths of 50 MHz, in good agreement with numerical modelling.

Dielectric low frequency noise probed by high-Q superconducting resonators at mK temperatures

J Burnett1,2,6, L Faoro3,4, I Wisby1,2, V L Gurtovoi5, A V Chernykh5, G M Mikhailov5, V A Tulin5, R Shaikhaidarov2, V Antonov2, P J Meeson2, A Ya Tzalenchuk1,2 and T Lindström1

1National Physical Laboratory, UK, 2Royal Holloway, University of London, UK, 3Universites Paris, France, 4Rutgers The State University of New Jersey, USA, 5Institute of Microelectronics Technology and High Purity Materials, Russia, 6University College London, UK

Superconducting circuits represent an attractive route for quantum technologies and their performance has dramatically improved over the past decade. However, ultimate device performance is still limited by the relatively high rate of decoherence. There is now substantial evidence that the main source of decoherence originates in the dielectric layers of the circuits, e.g. the substrate and surface oxides. Specifically this is due to the presence of parasitic two level systems (TLS) in the dielectric. Many properties of these parasitic TLS can be understood using the standard tunnelling model (STM) of TLS which dates back to the 1970s. Significantly, the model assumes that the TLS interact with the superconducting circuits, but not with one another. An important consequence of this assumption is that the 1/f noise caused by TLS should vanish at low temperatures.

In attempts to understand the origin of decoherence in superconducting devices, superconducting resonators are commonly used to probe their dielectric environments. Here we study slow fluctuations in the dielectrics through the use of an ultra-stable frequency-tracking technique, revealing a 1/f noise spectrum due to the presence of parasitic TLS. Below 1K – where superconducting quantum devices operate – these parasitic TLS can be stimulated by either absorption of microwave photons or thermal excitation, leading to measurable effects in the 1/f noise.

Ultimately the level of 1/f noise is found to increase as temperature decreases — an observation that is directly incompatible with the STM of TLS. We introduce a generalised tunnelling model (GTM) which takes into account the interaction between the TLS and is able to fully explain both the temperature and power dependence of noise in our measurements.


Coupling to individual two-level fluctuators using coherent near-field microwave microscopy

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1National Physical Laboratory, UK, 2Chalmers University of Technology, Sweden, 3Royal Holloway, University of London, UK

Two-Level Fluctuators (TLFs) are material defects that exhibit energy splittings in the GHz range and are known to cause noise and decoherence in solid state quantum circuits[1]. A large number of experiments have addressed both individual TLFs and their ensembles through coupling to the electromagnetic modes of either a qubit or a superconducting resonator [1,2]. The ability to obtain the exact location of each individual TLF together with their coherence properties would be of great importance in the quest to fully understand the nature of TLFs. Here we
propose that the technique of coherent Near-field Scanning Microwave Microscopy (coherent NSMM) can be used to fulfill both these goals. NSMM features a microwave resonator integrated with a scanning probe microscope for nanoscale imaging and has the ability to couple strongly to a TLF located directly underneath the scanning probe tip. Based on quantum-mechanical modelling we estimate that individual non-interacting TLFs could be resolved in materials where the dielectric loss tangent and is less than $10^{-3}$. Such a tool could therefore find a variety of applications in quantum technologies. Not only can it be used to characterise and improve dielectrics used in solid state quantum circuits but also, for example, to develop technologies for controllably introduce single (spin) defects for high density quantum memory applications. We also discuss the requirements of such a ‘coherent NSMM’ and the progress in developing the needed instrumentation [3].


(Invited) Dielectric Breakdown: What do we know, what don’t we know and how do we prevent it anyway?

A Vaughan
University of Southampton, UK

Dielectric materials constitute a critical element in devices that range from field effect transistors (FET) to high voltage plant and, therefore, the reliable long term performance of such items relies critically on the long term reliability of the dielectric. In the case of a FET, the insulation thickness is of the order of a few nanometres while the switching voltage is a few volts, such that device operation involves applied fields of the order of 1000 kV mm$^{-1}$; in the case of thin film capacitors, the dielectric thickness may be of the order of 1 µm and may experience applied fields in excess of 100 kV mm$^{-1}$. In general, as the size of the device increases in response to increasing applied voltages, so the electric field that can be reliably withstood decreases. This is a particular issue in the case of power transmission applications, where the desire to increase the power rating whilst minimising losses favours operating at the highest voltages possible. Consequently, research into dielectric breakdown under such conditions is a topic that is of both academic interest and technological, economic and environmental importance.

Currently, the bulk of technologically-relevant high voltage solid insulation systems are based upon polymers. In such materials, the latter stages of breakdown involve the growth of defect structures termed trees and, because of their macroscopic scale, these structures are readily described. However, the underlying physics and chemistry of the process are less well understood. While it is possible to hypothesise about the processes that occur in the laboratory prior to the formation of visible trees, where defects are deliberately introduced, how degradation is initiated in the absence of such features remains unclear. As such, it is reasonable to say that the fundamental processes that induce electrical degradation and ultimately lead to failure are still poorly understood. Despite this, considerable efforts continue to be made to develop materials that offer improved electrical characteristics, such as increased breakdown strength. While much of this work is essentially empirical, changing material characteristics in a systematic way does, however, provide a means of exploring underlying failure mechanisms.

This paper sets out to discuss two related areas. First, it will review our current understanding of a number of fundamental issues relating to dielectric breakdown in solid polymers. Then it will address strategies that are currently being developed in an attempt to develop new high performance dielectric systems and, in particular, will highlight some very recent developments at Southampton that provide new insights into the linkages between material formulation and breakdown performance.
Weakly ferroelectric behavior in AgNbO$_3$ bulk materials

Y Tian$^{1,2}$, X Wei$^2$, L Jin$^2$ and H Yan$^1$

$^1$Queen Mary University of London, UK, $^2$Xi’an Jiaotong University, China

The structure of AgNbO$_3$ has been augured for decades. The structure is center symmetry with antiferroelectric (AFE) ordering in most literatures. However, the recent paper suggested non-center symmetry, which is compatible with antiferroelectric ordering. In our work, the AgNbO$_3$ ceramics with high-quality were successfully prepared. The polarization-field and current-field hysteresis loops were investigated. The low field data of fresh samples confirmed that a weakly ferroelectric (FE) state exist below the dielectric anomaly (denoted as M$_1$-M$_2$ phase transition). Meanwhile, a field-induced weakly FE state also was observed near the phase transition especially in M$_2$ phase region. The field-induced FE state at low field was more obviously when the sample was poled till the occurrence of double P-E loops. These results indicated that the AgNbO$_3$ should be bi-phase (FE+AFE) systems instead of any single phase at room temperature (RT). So, it showed the weak FE and AFE feature.

Electrical breakdown of dielectric elastomer actuator materials

B Chen$^1$, M Kollosche$^2$, M Stewart$^3$, M Cain$^3$, J Busfield$^1$ and F Carpi$^1$

$^1$Queen Mary University of London, UK, $^2$University of Potsdam, Germany, $^3$National Physical Laboratory, UK

Dielectric elastomer actuators (DEAs) are a kind of deformable capacitors that undergo large voltage-induced deformation of more than 100% in area. Subject to an electric field, the layer of the dielectric elastomer film reduces in thickness and expands in area. The key properties such as large-strain, fast and efficient actuation properties are under investigation for a wide range of possible applications, such as artificial muscles, tuneable optical devices and tactile displays.

The performance of DEAs is limited by electric breakdown. As the voltage across the elastomer increases, the film thins down, with a positive feedback on the increase of the electric field. When the electric field rises to a critical value, the dielectric thins down excessively, causing instability and subsequent electrical failure.

Therefore, in order to measure the electric breakdown strength of dielectric elastomers, a set-up was built at the National Physical Laboratory and extensive measurements showed that the breakdown strength of a 300% pre-stretched acrylic elastomer film (VHB 4910 from 3M) is much higher than that of the un-stretched elastomer film. Also, for the 300% pre-stretched elastomer a different size of the electrodes was found to affect the breakdown strength. This presentation describes these results and discusses possible sources of measurement error.
Dielectric breakdown and resistive switching of acceptor-doped barium titanate: a common mechanism?

A R West and N Maso
University of Sheffield, UK

It has been shown recently that a range of acceptor-doped titanate perovskite ceramics show a gradual increase in p-type conductivity of 1-3 orders of magnitude at temperatures above approximately 300°C on application of a small dc bias in the range 1-50 V/cm. The conductivity decays to its original state on removal of the dc bias. No effect is seen with undoped materials.

Dielectric breakdown of such ceramics is generally observed at room temperature on application of larger bias voltages; the mechanism appears to be not well-understood, although migration of oxygen vacancies are believed to play a role.

This talk will discuss the mechanism proposed for the resistive switching and specifically, the mechanism for increasing the hole concentration under the action of a dc bias and propose that a similar mechanism could be responsible for the onset of degradation.

(Invited) Controlling domain walls in ferroelectrics for new devices

M Campbell, R G P McQuaid, A Kumar and J M Gregg
Queen’s University Belfast, UK

We stand on the verge of a potential revolution in functional materials: conductivity and even superconductivity along ferroelectric domain walls [1] means that functionally active low dimensional sheets (with all their potentially exotic physics) could conceptually be controllably deployed and moved (using electric or stress fields) at will, to create a new generation of active electronic devices – so called “domain wall nanoelectronics”.

This talk will concentrate on two areas of research, which attempt to push forward domain wall electronics as a research field: firstly, experiments revealing fundamental insight into domain wall conduction mechanisms will be described. Specifically, the use of scanning probe microscopy to determine Hall voltages at domain walls will be discussed, as will the active carrier types, mobilities and densities implied in both rare earth manganites and metal-halide boracites (both improper ferroelectrics with transport-active “head-to-head” and “tail-to-tail” walls). Secondly, various ways in which domain wall injection and motion [3] have been controlled, using sample morphology, electric and stress fields, will be described which have culminated in the successful creation of a ferroelectric domain wall diode [4].

References:


Novel, high capacitance nanocomposite dielectrics for printed electronics

S Faraji, M L Turner and L A Majewski

University of Manchester, UK

The rapid development of organic semiconductor materials that can be processed from solution opens up the possibility of printing organic field-effect transistors (OFETs) onto a wide range of substrates to enable the development of low-cost, large area electronics. However, typical solution-processed OFETs operate at voltages that are too high for use in wearable/portable electronic devices or notably as aqueous sensors (V > 5 V). For these applications, transistors working in the range of 1.5 to 1 V are highly desirable. Lowering the operational voltage of OFETs can be achieved by reducing the threshold voltage and the subthreshold swing. These device parameters are largely controlled by the gate dielectric and the density of charge traps at the dielectric-semiconductor interface. Therefore, to achieve ultralow-operational voltages, high-capacitance, solution-processable gate insulators that form trap-free interfaces are essential.

With great promise in hybrid materials, a high-$k$ dielectric material based on alternative organic-inorganic nanocomposite materials is developed that combines very high dielectric constant values intrinsic to ferroelectric ceramic materials (nanoparticles) with mechanical flexibility, low-cost and easy processing of polymers. A novel, solution processed high-$k$ nanocomposite bilayer gate dielectric that enables the fabrication of organic field-effect transistors (OFETs) operating effectively at as low as 1 V in high yields is reported. High-$k$ nanocomposite suspensions are prepared by meticulously incorporating a selection of high-$k$ nanoparticles into poly(vinylidene fluoride-co-hexafluoropropylene) P(VDF-HFP) polymer matrix. The solution-processed nanocomposite layer is subsequently coated with a thin capping layer to improve the surface roughness and dielectric-semiconductor interface and reduces the leakage current. OFETs are fabricated using solution-processed semiconductors, poly[3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione]thieno[3,2-b]thiophene] and a blend of 6,13-bis(triisopropylsilylthynyl) pentacene and poly($\alpha$-methylstyrene), in high yield (> 90 %) with negligible hysteresis, low operational voltage (< 3 V) and low leakage current density (10^{-9} A cm^{-2} at ± 1 V).
On the capacitance nonlinearity in high-k oxides

H. Kliem and L. Kankate
Saarland University, Germany

Metal oxides with a high permittivity are thought to replace SiO₂ to allow a thick insulator with a low leakage current while the capacitance maintains its value. However, several oxides like Pr₂Ti₂O₇, HfO₂, Y₂O₃, or Al₂O₃ [1] show in metal-insulator-metal structures a quadratic-like increase of the small signal ac capacitance in static bias fields. The strength of this nonlinearity decreases with increasing frequency. Here we focus on Al₂O₃ and HfO₂, where we also find a decrease of the permittivity in zero bias fields from the mHz to the MHz range [2]. In the time domain this refers to the well known Kohlrausch time dependence of the polarization currents. A variation of sample thickness and electrode material as well as the measurement of the imaginary part of the permittivity with its also quadratic-like increase reveals that the effects are caused by a relaxational volume polarization.

In Al₂O₃ for the microscopic description we use an asymmetric double well potential where protons fluctuate between the wells by phonon assisted tunneling for temperatures below room temperature. For higher temperatures also a thermal activation can come into play. Such double wells are found between next neighbour oxygen ions (Fig. 1). In the amorphous state the oxygens have a distance distribution characterized by the pair distribution function. This results in a distribution of the distances R between the wells. Therefore the transition probabilities of the protons are also distributed. Since the transition probabilities decrease exponentially with R and the barrier height increases with R we get a broad distribution of relaxation times from a small distribution of R around 0.1 nm resulting in the decrease of the permittivity with frequency.

In the amorphous state it can be expected that the next positive charges (Al⁺) close to the negative oxygen pairs have also different distances causing the intrinsic asymmetry of the double well systems. The asymmetry is changed by an external bias field and causes the nonlinearity of the capacitance. Taking account of the distribution of relaxation times we calculate the frequency dependence of this nonlinearity.

In HfO₂ we find similar properties. Here the decrease of the permittivity with increasing frequency as well as their nonlinearity is by a factor of about 3 to 5 stronger than in Al₂O₃.

[2] L. Kankate, H. Kliem, IEEE-TDEI accepted
Dielectric constants of bulk ferroelectric PZT measured by THz time-domain spectroscopy

M Naftaly¹, M Cain¹, S Lepadatu¹, T Buchacher¹ and J Allam²

¹National Physical Laboratory, UK, ²University of Surrey, UK

The complex permittivity of bulk ceramic ferroelectric of nominal composition PbZr₀.₄Ti₀.₆O₃ was measured in the range 0.2-2 THz using transmission time-domain spectroscopy. The results indicate strong absorption and dispersion in this frequency range often seen in highly disordered and polar materials. The data are compared to equivalent thin film data in the literature and significant differences in the real and imaginary permittivity suggests that substrate clamping and degree of polarisation of the ferroelectric thin film materials affects dielectric properties even at these high frequencies.

(Invited) Ultra-High Q dielectrics that led to a room temperature MASER

N Alford¹, J Breeze¹, J Sathian¹, B Richards¹, K J Tan¹, M Oxborrow¹, C Kay² and E Salvadori²

¹Imperial College London, UK, ²University College London, UK

In this talk we will look at the problem of dielectric loss (the tan δ) in oxides and specifically methods to beat the dielectric limit. We do this using a Bragg reflector in which the Bragg layers, which are made of sapphire, are of equal thickness. In this case the Q factor (or the inverse of the tan δ) saturates to a plateau after around 3 layers. Surprisingly we find that if the layers are aperiodic in thickness there is no saturation and the Q factor rises quadratically to reach remarkably high values of Q=0.6x10⁶ at 30GHz [1]. This result suggested that it might be possible to reach the threshold for masing and indeed we demonstrated recently that in P-terphenyl doped with pentacene when located inside a very high Q sapphire resonator maser action can be observed. This is the first time a solid state maser has been demonstrated at room temperature and in the earth’s magnetic field [2]. Recent work [3] has shown that miniaturisation is feasible and considerable reduction in pumping power is possible by using a strontium titanate resonator which by virtue of a higher relative permittivity leads to a factor of over 5 in size reduction. Importantly, the Purcell factor which is the ratio of the Q factor to the mode volume, remains high and this is a key factor in the ability to exceed the threshold for masing.


**Improved loss measurement using a microwave microscope**

A P Gregory\(^1\), J F Blackburn\(^1\), K Lees\(^1\), R N Clarke\(^1\), T E Hodgetts\(^1\), S M Hanham\(^2\) and N Klein\(^2\)

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Recent progress in the development of a Near-Field Scanning Microwave Microscope (NSMM) for measurement of permittivity and loss at the micron scale will be described. NSMMs \(^1\) have found applications in the electronics industry, and in combinatorial studies for the development of new functional materials and low-loss electroceramics. The NPL instrument uses Q-factor and resonant frequency measurements on a microwave cavity from which complex permittivity may be determined. Improvements to the calibration process have for the first time made it possible to obtain traceable and accurate measurement of loss. This is demonstrated by measurements on polar liquids (via a thin window) \(^2\). The improved calibration algorithm applies the Laplacian ‘complex ‘frequency’ in the image-charge model \(^3\). Technical modifications to the microscope to allow contact mode between the probe tip and specimen to be obtained by an optical beam-deflection system as an alternative to a tuning fork will also be discussed.


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**(Invited) Localised impedance measurements using photocurrent measurements at field-effect capacitors**

J Wang\(^1\), F Wu\(^1\), I Campos-Sanchez\(^1\), L Chen\(^1\), Y Zhou\(^1\), M Watkinson\(^2\) and S Krause\(^2\)

\(^1\)Peking University, China, \(^2\)Queen Mary, University of London, UK

AC impedance spectroscopy is a valuable tool in the characterisation of electrochemical systems and new materials. However, the results obtained using this method are always surface averaged. Previous attempts to develop a Local Electrochemical Impedance Spectroscopy have been restricted to flat surfaces in electrolyte solutions and provide only limited resolution. Photocurrent measurements at electrolyte/insulator/silicon field effect structures are suitable for imaging the complex impedance and electrical potentials of electrochemical and solid state systems. Good lateral resolution of photocurrent measurements was achieved by using silicon-on-sapphire (SOS) substrates \(^1\). To improve the sensitivity of LAPS and SPIM, the traditional insulator was replaced with an organic monolayer such as undecylenic acid or 1,8-nonadiyne that was bound to hydrogen terminated silicon \(^2\). The validation of the technique will be demonstrated with a number of model systems.

An SU-8 photoresist pattern on the anodic oxide was used to assess the resolution of SPIM and LAPS. To obtain quantitative values for the resolution, the laser was focused through the sapphire substrate into the 0.5 μm thick silicon layer and scanned from the uncoated to the coated part of the sample (Figure 1).
The results show that the resolution obtained using a single photon effect can be improved by reducing the laser wavelength. A two-photon effect was used to achieve submicrometer resolution at a wavelength of 1250 nm.

Surface potential imaging using photocurrent measurements at field-effect structures was validated by studying micropatterns of poly(allylamine hydrochloride) (PAH) and DNA on a PAH template. The technique has also been used for the imaging of living cells. It will be shown that the system can produce two-dimensional electrochemical images of parameters such as local cell impedance under the opening or closing of ion channels, membrane-surface potential and two-photon fluorescent images of the cell-attachment area.


A calibration algorithm for multi-port network analysers

T Hodgetts\(^1\), F Smith\(^2\) and J Ellis\(^2\)

\(^1\)National Physical Laboratory, UK, \(^2\)QinetiQ, UK

It is well known in microwave measurement theory that, when a vector network analyser (VNA) observes a 1-port device-under-test (DUT) through a 2-port network, the reflection coefficient measured by the VNA is a bilinear transform of the DUT's true reflection coefficient. To be specific, \(\Gamma_M = (a\Gamma_T + b)/(c\Gamma_T + 1)\), where \(\Gamma_T\) is the true reflection coefficient, \(\Gamma_M\) is its measured counterpart, and the quantities \(a\), \(b\) and \(c\) are parameters of the 2-port network. This straightforward relationship applies whether the 2-port network is a real device or a representation of an imperfect VNA's linear internal architecture (a so-called "error box"), and all conventional calibration and "de-embedding" algorithms for 2-port VNAs are ultimately based on its use with measurements on known DUTs.

It is much less well known that a generalised form of this relationship also exists, relating the true S-parameters of an N-port DUT directly to their counterparts concurrently measured on an N-port imperfect linear VNA (whose imperfections may include "leakage" paths). The generalised form is \(SM = (AST + B)(CST + D)^{-1}\), where the true S-parameters \(ST\), the measured S-parameters \(SM\) and the parameters \(A\), \(B\), \(C\) and \(D\) are now all \((NxN)\) matrices, and the superscript \(-1\) denotes a matrix inverse.

This relationship was introduced into microwave measurement theory by Speciale in the 1970s (Helton & Speciale (1983) and references therein), but his early attempts to apply it to calibration problems were frustrated by mathematical difficulties. The roots of these were identified in the 1983 paper, but its method of determining \(A\), \(B\), \(C\) and \(D\) by matrix eigenvalue techniques was numerically unstable, and the microwave community abandoned the idea. It was revived about ten years ago by two independent groups, one of them involving one of us (Lederer, Szwarnowski & Hodgetts (2005); Zhang, Silvonen & Zhu (2007)), but its numerical stability was still questionable. However, the need for stable \(N\)-port calibration remains.

The structural complexity of some modern microwave materials, e.g. materials with metalised inclusions, causes the common 2-port measurement process to provide incomplete data on a material's electromagnetic behaviour. To this end, recent work has been undertaken with the intention of applying the generalised form for \(SM\) to full 4-port VNA calibration. The VNA system comprises 4 potentially non-reciprocal VNA ports coupled to 2 ortho-mode transducers (OMTs). The DUT sits between the square ports of the OMTs. The numerical instability can now apparently be handled using techniques of advanced numerical analysis (Schur matrix transformations). These will be described, together with test results of 2-port VNA measurements and preliminary work on 4-port VNA measurements.

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Giant dielectric constant: All an illusion?

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Recently, a giant dielectric constant has been reported [1] in lead halide perovskite solar cells. The dielectric permittivity in the dark was found to be $\sim 10^3$ when measured at very low frequencies (<1 Hz) and to decrease to $\sim 20$ at frequencies above $\sim 10$kHz. Under the illumination of 1 sun the permittivity was found to rise to $\sim 10^6$ at low frequencies and to decrease to the same value of $\sim 20$ at frequencies above 10kHz. The authors suggest that that the giant dielectric constant results from structural fluctuations.

In this work we note that somewhat similar dielectric phenomena are observed in many other materials that exhibit “low frequency dispersion”. These materials all have a significant conductivity that that rises with frequency in a power law fashion but with a very small power law exponent, typically $<0.1$. We will suggest that this can be explained as being characteristics of materials that have microstructures containing conducting and dielectric phases.

The lead halide perovskite solar cell results will be compared with measurements of porous lead zirconate titinate (PZT) samples with pore volume filled with water. The latter was used previously to test the validity of modelling the AC response of a material by a large network of randomly positioned resistors and capacitors. These networks simulate the complex microstructures of real materials containing a mixture of conductive and insulating/dielectric phases. Measurements of PZT-water samples extended to low frequencies show a permittivity rising to above $10^7$ at 0.1Hz and falling in a similar way to those of lead halide perovskite solar cells at high frequencies. The AC conductivity of these samples also shows low frequency dispersion with a power law exponent of 0.036. Application of the Kramers Kronig relationships shows an associated permittivity diverging in a power law fashion at low frequencies to values $\sim 10^7$ that are similar to those measured. It is concluded that such high measurements of permittivity are an illusion because they are not measurements of a true capacitive material. It is suggested that the conductivity of the material rises slowly with frequency because it contains numerous potential water filled conducting percolation paths that are blocked by short lengths of insulating/dielectric PZT. These act as capacitors that become increasingly conductive as frequency rises, accounting for the low frequency dispersion. As a result the conduction process is predominantly conductive but contains capacitive components that increase with frequency. Indicative of this is a phase angle that is a few degrees below zero.

It will be noted that reports of exceptionally high permittivity are invariably of materials containing a significant conductive phase.

Poster session 1

P:02 Hydrogen induced rupture of Si-O bonds in amorphous silicon dioxide

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The interaction of hydrogen with amorphous silicon dioxide (a-SiO₂) is important for many applications due to its widespread use in optical and electronic device fabrication processes. Hydrogen, in its more prevalent forms (H₂ and water), is known to induce hydrolytic weakening of quartz and degradation phenomena in optical fibers and SiO₂-insulated electronic devices. However, the involvement of atomic hydrogen in silica network degradation mechanisms is still poorly understood.

Density Functional Theory (DFT) calculations were used to model the interaction of hydrogen atoms and molecules with strained bonds in amorphous a-SiO₂. We show that the interaction of atomic hydrogen with strained Si–O bonds in a defect-free a-SiO₂ network results in the formation of a new defect structure consisting of a 3-coordinated Si atom facing a hydroxyl group which we refer to as the hydroxyl E′ center. This defect adds to the density of dangling bond defects, such as conventional E′ centers. To study the distribution of defect properties, 116 configurations of the defect were calculated. We find that this defect is preferentially generated at bridging O sites where the oxygen forms a statistically long Si–O bond. In order to understand the origins and reactions of this defect, the kinetics of formation, passivation and de-passivation have been calculated. The energy barriers to form this defect from interstitial H atoms range between 0.5 and 1.3 eV, while depassivation occurs with an average barrier of 0.5 eV. This discovery of unexpected reactivity of atomic hydrogen may have significant implications for our understanding of processes in silica glass and nano-scaled silica, e.g., in porous low-permittivity insulators, and strained variants of a-SiO₂.
P:03 Using high frequency LIMM to characterise the poling state of piezoelectric ceramic thin films

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The LIMM method, (Laser Intensity Modulation Method), was developed in the late 1980’s as a technique to measure the through thickness polarisation of polymer films [1]. An intensity modulated laser is used to generate a thermal wave in the film and the resultant pyroelectric signal is measured using lock-in techniques. The depth sensitivity comes through varying the intensity modulation frequency and thus the penetration of the thermal wave. Although techniques such as PFM (Piezoresponse Force Microscopy) have excellent lateral x-y spatial resolution, the LIMM technique remains one of the few techniques with through thickness capability. Although initially developed for polymer films, the method has also been used on ceramic thick and thin films. One of the challenges in using the technique on PZT thin films is that the thermal diffusivity is higher compared with piezoelectric polymers such as PVDF, therefore the modulation frequency to achieve the same depth resolution increases. This poses severe constraints on the instrumentation, requiring lockin amplification into the 100’s of MHz range, high bandwidth and high sensitivity current amplifiers, and linear laser intensity modulation. In this work we have extended the frequency of the tests into the 10’s of MHz range to enable the characterization of thin ceramic piezoelectric films of thicknesses down to 100nm.

P:04 A new method to measure the clamped indirect piezoelectric effect of thin piezoelectric films

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Piezoelectric thin films are used in applications ranging from ferroelectric memories to pyroelectric thermal imaging systems and the success of these applications arises from the successful retention of the functional response of the bulk material to the thin film. In many, if not all cases, this response (polarization, effective piezoelectric coefficients, dielectric properties and more) is not adequately transferred down to the 2D thin film structures and this is primarily due to the constraining effect of the substrate.

The clamping of the film to its supporting substrate can introduce several problems when trying to measure the piezoelectric activity of the film. Firstly there is the tendency for the entire sample to bend, and inflated measures of activity are often obtained if this bend is not accounted for. Kholkin et al [1] introduced the double beam interferometer method to circumvent this. Secondly there is the issue of a finite top electrode size, where the results are largely dependent on the electrode geometry. More recently several workers have claimed that it is possible to measure the thin film piezo coefficient using a single sided measurement on laser vibrometer, [2,3]. In this work we use Finite Element Analysis to show the errors associated with both these methods, particularly the effects of the boundary conditions and finite sized top electrodes.

Here we propose a new method to determine the piezoelectric activity of a thin film. This method involves using a single sided measurement, but the key is to measure the step height at the edge of the electrode, at the interface between the active and inactive material. We develop an analytical expression to relate this step height to material properties and show its applicability using FEA. Experimental results will be shown to that this measurement method is indeed independent of electrode size and sample boundary conditions.

P:05 Ti-suboxides structures for water splitting
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The photo-electro-chemical (PEC) splitting of water requires semiconductors with minimum energy gap of 1.23 eV and with conduction and valence bands overlapping the oxidation of H$_2$O and the reduction of H$^+$ respectively. Titania (TiO$_2$) has been extensively investigated as photo-anode for PEC water splitting due to its suitable band-edge position, chemical resistance, environmental suitability and low cost. The main limitations of stoichiometric TiO$_2$ are its wide band gap (3.2 eV) and electron-hole recombination. Previous work on Ti-suboxides has shown that it is possible to control the extent of oxygen vacancies and the electrical conductivity can be altered from 10$^{-9}$ S/m (TiO$_2$) to 10$^4$-10$^5$ S/m (Magnéli phases). It has also been shown that the oxygen vacancies in the structure of Ti-suboxides increase the carriers' density and thus the photocurrent efficiency.

Other parameters to increase the efficiency is to increase the surface area and use composites structures (i.e. thin films on ferroelectrics) to enhance electron-hole separation. The approach of this work is investigating both parameters and measuring the photocurrent efficiency. TiO$_2$ nanostructures were grown on a Ti mesh that were then heat-treated in a reducing atmosphere introducing oxygen vacancies in the structure. The structures on a Ti mesh offer very high surface area. The water-splitting efficiency of sub-stoichiometric functionally graded titania fibres was also investigated. The PEC measurements were performed in a three electrode system using CSE as reference electrode and Pt wire as counter electrode. Linear voltage sweeps were collected in 1M KOH electrolyte under UV light (318 nm).

P:06 Manufacture of porous electrically conductive ceramics for energy applications
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Electrically conductive ceramics are of interest as electrodes, since they are corrosive and high temperature resistance. The low cost of the manufacturing process is another important parameter. In this work we investigate Magnéli phases as candidate material for electrodes in flow batteries. Magnéli phases have high electrical conductivity, good mechanical properties, high chemical resistance and simple and inexpensive production method [1]. Additionally, it is very important for the electrode to have high surface area that leads to an increase of the catalytic reaction rate, improving the response and power of the battery [2]. The majority of the work on Magnéli phases as electrodes involves their use as substrates for catalytic coatings or as thin films [1,3]. The current work focuses on bulk samples and fibres with increased surface porosity and the initial electrochemical characterisation in a three-electrode electrochemical cell. The porosity was controlled by changing the binder content in the feedstock and for the electrochemical measurements a Pt mesh was used as the reference electrode and a saturated calomel electrode (SCE) as the counter electrode in an aqueous solution of potassium ferricyanide (5.0 mM K$_3$Fe(CN)$_6$) in potassium nitrate (0.1 M KNO$_3$).

This work will discuss the potential of novel dielectrics with memristive behavior as building blocks for future cybersecurity applications. The sigmoidal I-V hysteretic loop response of the device may be used as a fundamental building element of an artificial neural network that can be part of a neuromorphic processor, capable of supervised learning tasks as part of a machine learning solution to cybersecurity e.g., in image recognition, network cluster analysis, as an intrusion detection system of cyber attacks, in evolutionary computation or for the implementation of genetic algorithms [1,2]. Memristor based neural networks are efficient at vector classification where the neural network maps an input vector to a particular output class e.g. the N-tuple classifier. They are also efficient at vector association, mapping a particular input vector to a particular output vector. An application of the MCP neuron is the MCP perceptron model. DARPA’s new memristor-based approach to AI consists of a chip that mimics how neurons process information.

Third order optical nonlinearities lead to the possibility of memristive responses if the new state can be kept for a certain period of time. This may achieved using quantum wells, four-level atomic systems (via electromagnetically induced transparency), semiconductor resonators and amplifiers, liquid crystals etc. Photonic memristors in which sub-wavelength artificial structures provide a mechanism for tailoring, patterning, and manipulating local electromagnetic fields and displacement vectors in a sub-wavelength domain, lead to new possibilities of information carried by electromagnetic wave being processed on the sub-wavelength scale. Engheta et al. [3,4] introduced the pioneering notion of circuit lumped elements at optical frequencies for nanocapacitors, nanoinductors, and nanoresistors, which are based on the interaction of the nanostructures with an optical field. Other approaches [5] suggest the possibility of developing nanoscale plasmonic memristors. Nonlinear responses can also be achieved at microwave frequencies using varactor diodes in the capacitive gaps of split ring resonators. Alternatively, the Mie resonance-induced thermodielectric effect in dielectric meta-atoms can be used to produce hysteretic transmission-power plots in a similar manner the I-V curves found in electrical memristors [6].

Spacetime or event cloaks [7-9] work simply by speeding up and slowing light down. To open a cloak we need to split the propagation wave into an early part and a latter part. The early part will speed up and pass the chosen space-time location before the specified time, whilst the latter part will slow down and pass the chosen space-time location after the specified time. Lukens et al., [10] demonstrated a technique for temporal cloaking, which operates at telecommunication data rates and, by exploiting temporal self-imaging through the Talbot effect, hides optical data from a receiver. Fridman et al. [11] also discussed alternative temporal cloaking approaches. It is clear that dielectrics with memristive behavior may be used to conceal information in new ways. Such opportunities and threats to cybersecurity will be discussed at the conference.


Although in standard $R$, $L$, $C$ circuit analysis, voltage and current vectors satisfy linearly independent relations (Kirchoff's voltage and current laws) and there are single variable relations between flow (current), effort (voltage), generalized momentum (flux) and generalized displacement (charge), there are additional variables associated with mem-based circuits. The discovery of flux controlled memristors by Leon Chua in 1971 [1] as the missing element relating generalized momentum with generalized displacement promises the development of a new class of novel dielectrics over the coming years. Well established dielectric structures such as metal-insulator-metal thin films with thickness between the nanometer and the micrometer scales have been used in several applications and also display memristive and capacitive effects simultaneously. Similar effects are observed in nano-dielectrics where a formation of local dipoles is observed in nanoscale resistors. Incorporation of mem-based elements into circuits containing $R$, $L$ and $C$ components leads to circuits with far more complex 'emergent' behaviors than normal dielectrics display. Interesting phenomena such as self-sustained non-linear oscillators capable of super-critical Hopf bifurcations can be conveniently observed in this new class of dielectrics. From a modeling perspective, such circuits can also mimic dielectric responses of biological materials such as dielectrically excited membranes.

Because of the non-linearity associated to the response of memristive, mem-capacitive and mem-inductive components, Laplace transforms may not be used to derive transfer functions that would uniquely relate the input with the output function of these 2-port devices. Their dynamics may be studied instead, using differential algebraic models arising from descriptor representations derived from nodal analysis associated to the underlying circuit topology. State space models of the circuit dynamics are made possible by adopting a input-state-output port-Hamiltonian formulation (ISO-PHS) from bond-graph analysis [2-5]. The bond graph analysis [6, 7] provides the geometric relations between the memristive elements and the rest of the circuit. Flow and effort variables at all the ports of the network described using the causal bond graph methodology are split into power-conjugated input-output pairs. The general structure of the port is shown in figure 1:

![Figure 1 General structure of a causal bond graph](image)

and the corresponding matrix interrelating the parameters of the port is given from:
where $X_i = [x_{i,1}, x_{i,2}, \ldots, x_{i,n}]^T$ is the state vector in integral causality, $X_d = [x_{d,1}, x_{d,2}, \ldots, x_{d,l-n}]^T$ contains the energy variables in differential causality, $Z_i = [z_{i,1}, z_{i,2}, \ldots, z_{i,n}]^T$ and $Z_d = [z_{d,1}, z_{d,2}, \ldots, z_{d,l-n}]^T$ contains the co-energy variables associated to $X_i$ and $X_d$, and variables $D_i$ and $D_o$ entering and exiting from resistive elements and $U$ containing the efforts and flow variables imposed by the sources. The incorporation of a memristive structure in the above formulation will be discussed at the conference.


P:09 High dielectric performance of Ag/cyanoethylated O-(2,3 dihydroxypropyl)-cellulose nanocomposites

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A novel dielectric nanocomposite based on high permittivity polymer; cyanoethylated O-(2,3 dihydroxypropyl)-cellulose (CRS) and Ag nanoparticles was successfully prepared with different weight percentages (2%, 3%, 4% and 5%) of Ag. The intermolecular interactions and morphology within the polymer nanocomposites were analysed using ATR-FTIR, TGA, SEM and AFM. Ag/CRS nanofilms on SiO$_2$/Si wafers were used to form metal-insulator-metal (MIM) type capacitors. Capacitance and loss factor in the frequency range of 1 kHz to 1 MHz were measured. At 1 kHz, Ag/CRS nanocomposites exhibited dielectric constant enhancement of over 10 times compared to pure CRS films. Furthermore, prepared Ag/CRS nanocomposites show a loss factor < 1 and low leakage current densities. However, Ag/CRS nanocomposites with higher Ag loading (> 5%) showed very high dielectric losses as high concentration of conductive particles could form a conductive path in the composite. A new class of ultra high dielectric constant hybrids using nanosized conductive nanoparticles dispersed in a high permittivity polymer suitable for energy storage applications is reported.
Engineering reliability in new high temperature capacitors for power electronics

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Increasing electrification of power systems in aircraft and other transport systems is driving the development of smaller, lighter, more efficient power conversion technologies which require operation at high temperature. Wide bandgap semiconductors like silicon carbide enable high power switching at high temperature, but existing capacitor technology is unable to provide a suitable, cost effective combination of high operating temperature, compactness, high capacitance and filtering capacity, and reliability for use in high temperature power converters. This paper presents results on the performance of a new ceramic multi-layer capacitor combining high density of capacitance, low loss and temperature stable properties above 200 °C. This paper also reviews the challenges of development of high temperature capacitors and related piezoelectric materials for high temperature sensing and actuation.

Characterization of high temperature piezoelectric materials using interferometry and resonance methods

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Currently available high performance piezoelectric materials, predominantly based on lead zirconate titanate (PZT), are typically limited to operating temperatures of around 200 °C or below. There are many applications in sectors such as automotive, aerospace, power generation and process control, oil and gas, where the ability to operate at higher temperatures would open up new markets for piezoelectric materials as sensors, actuators and transducers. New materials are being actively developed to meet this need, and this effort needs to be supported by reliable properties measurement under these challenging conditions.

Piezoelectric resonance is a widely used method to measure piezoelectric, elastic and dielectric properties under small field excitation. The method is standardized in EN50324-2:2002. These methods are applicable to room temperature measurements with low loss materials. There are several methods [1] for analyzing piezoelectric resonance with lossy materials models, but the extent of their applicability to high temperature measurements is uncertain. At high temperature conductive losses become significant, and factors such as frequency dependence of permittivity and bulk conductivity, and evaluation of materials properties affect the evaluation of piezoelectric properties from resonance spectra.

The accuracy of measurements based on resonance depends on the accuracy and relevance of the electro-mechanical models on which the method is based. For high temperature measurements at high electric field, the resonance method may be unsuitable or at least requires verification. This paper also presents the development of new interferometer systems for direct measurement of piezoelectric strain under high electric field and at temperatures up to 500 °C. New results on piezoelectric resonance measurements on novel high temperature piezoelectric materials, and conventional PZT materials, at temperatures up to more than 500 °C. Results are presented on the influence of factors such as frequency dependence of permittivity and bulk conductivity, and evaluation of materials properties using the EN50324 and software evaluation using lossy models.
