National Measurement System

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Strategic Capability Programme

Programme Document

April 2012

National Measurement Office

NPL National Physical Laboratory

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Contents

Introduction

The strategic capability programme is a new initiative from the National Measurement System which aims to provide a focus for development of major new measurement capabilities. This programme was proposed and implemented as a response to the launch of the NMS Strategy in July 2011. The purpose of the programme is to:

- Establish major new measurement capabilities at the leading edges of science and technology to ensure the NMS is delivering solutions ready to address the UK's future measurement needs
- Enable major development of existing metrology areas to drive forward science to internationally leading status
- Address significant emerging national challenges
- Delivers world-class science in partnership with the foremost academic research groups internationally

Inauguration of the Strategic Capability programme occurred on 1st April 2012. At inception, the programme consisted of a mix of current work and work being formulated from the NMS programme portfolio that either already met the criteria or could be scaled to meet the full ambition for the programme by the end of the first year of the programme. In addition, there was one major new project on Graphene that was formulated as part of the IRD 2012 programme. This was designed from the outset to be a strategic capability programme project.

It should be noted that the Strategic Capability programme is a virtual programme. As such, all projects in this programme are included in contracts for the NMS Knowledge Base or IRD programmes.

Table 1: NMS projects forming the initial NMS Strategic Capability Programme

Project Identifier		Project Name
IRD\2012\18		Programme formulation for NMS Strategic Capability Programme
IRD\2012\4		Fundamental scaling effects in piezoelectrics – "nanostrain"
IRD\2012\5		Chemical Imaging using Bifunctional Electrochemical Scanning Probes
IRD\2012\9		Metrology for Structured Surfaces
IRD\2012\13		Real-time methods for the measurement of key properties of Graphene at the device scale
CB\2012\12005	Capability consists of these two projects	Ambient imaging mass spectrometry with high resolution
NS001SA2		Ambient and Imaging Mass Spectrometry
TS0040203		Graphene for Metrology
TS003409		Co- funding for EMRP 17e Traceable Radiometry for Remote Measurement of Climate parameters
MAT\2011\21		Grains to Structures
TS0040402		Solid state Quantum Technologies
CB\2012\CF17	Capability consists of these two projects	Traceable characterisation of nanostructured devices (TReND)
NS002SA1a		Surface and Nanoanalysis of Surfaces and Particles (a)

Project No.	IRD\2012\18	**Price to NMO**	£105k
Project Title	Programme Management and Formulation for Strategic Capability Programme	**Co-funding target**	N/A
Lead Scientist	Neil Harrison	**Stage Start Date**	April 2012
Scientist Team		**Stage End Date**	March 2013
		Est Final Stage End Date	
Sector	Management	**Activity**	Programme Management

Summary

This project will formulate proposals of work for the Strategic Capability programme during the 2012/13 year for inclusion in programme contracts from April 2013 and engage with key stakeholders to ensure maximum impact is achieved from the science delivered by the programme. To achieve these objectives the project will:

- Develop the programme strategy and roadmaps;
- Consult with key stakeholders in government, industry, academia, regulators and other end users in order to determine future measurement requirements or other related issues that need to be addressed by the programme;
- Develop a series of project proposals for consideration for inclusion in the Strategic Capability Programme;
- Commission expert reviews of areas of new science and technology to the NMS to assess requirement for NMS intervention to enable development of future applications and markets;
- Provide independent assessment of proposals through use of non-NPL experts to feed into NMO review process.

The Need

New measurement requirements are constantly emerging from all areas of UK life. For example, new technologies require new underpinning metrology and standards, as do new regulations or environmental targets. To underpin areas such as growth in the economy, public health issues or mitigation of environmental impacts these measurement requirements must be successfully addressed as early as possible. In order to achieve these objectives effectively an overview of the research priorities and how to address them is required. Maintaining and developing a programme strategy and roadmaps achieve this objective and allow, in conjunction with knowledge of specific technical requirements obtained through stakeholder consultation, the formulation of a work programme that address UK measurement needs. Both the careful design of any programme of work coupled with the continual review of opportunities for increased impact are essential in order to make sure that the maximum value possible is extracted from the investment made in the technical projects.

Major unmet needs where the NMS has no current capability or where an existing capability requires a major upgrade to stay competitive and continue to address UK needs have to be identified and tackled with a more strategic approach since the investment required is substantial and usually longer term than achievable within a knowledge base or IRD programme.

The Solution

This project differs from the normal programme management projects in that it is concerned with the development of major new capabilities at NPL offering a major step change to existing capability or the development of substantial new capability to address a need as yet unmet by the NMS. As with the formulation of all NMS technical projects the views of a wide range of stakeholders from academia, industry, regulators, government and other end users will be sort through a wide ranging consultation process in order to capture emerging and future measurement requirements. This process will include looking at independent evidence of measurement needs as expressed in government reports, foresight activities, industry roadmaps etc. as well as conducting meetings, surveys and interviews as required that focus on specific topics of interest. Collation and assessment of information from all sources will enable the programme strategy and roadmap to be developed which will guide the future direction of the programme. A series of outline proposals will be developed as a result of this work and external reviews commissioned. The proposals and reviewers comments will then be fed into the NMO's internal review process.

Project Description (including summary of technical work)

- Horizon scanning, capture and analysis of science and technology trends to feed into current and future programme direction;
- Development and updating of programme roadmaps and strategy;
- Engagement with programme stakeholders to:
    - Realise outputs and maximise benefits to the UK;
    - Ensure alignment of programme with UK Government, academia, Industry and Societal drivers;
- Oversee preparation of project proposals for review and assessment;
- Submission of final projects for inclusion in most appropriate knowledge base or IRD programme contract;
- Liaison with the NMO programme supervisor to deliver maximum impact and efficient delivery;
- Identification of exploitable material for increased impact through channels provided by the Pan-Programme KT programme and other exploitation avenues;

Impact and Benefits
Effective programme management will maximise the outcomes to key stakeholder communities from the outset of the technical work and ensure knowledge transfer activities in the programme are efficient and effective. The programme as a whole addresses many measurement challenges across the broad sweep of the UK economy and society. Therefore, the design of knowledge flows and exploitation plans in technical projects which occurs during the formulation process is essential for delivery of the wide benefits of the programme to the broadest possible audience.

Support for Programme Challenge, Roadmaps, Government Strategies
This project underpins the work of the whole programme through development of an overview of key science and technology trend, societal drivers and measurement requirements as captured in the programme strategy and roadmaps. These key programme documents are utilised during development of technical proposals.

Synergies with other projects / programmes
This project will interact with the other NMS programmes so that synergies and common goals can be identified to ensure that the maximum value is returned from the investment in the NMS portfolio.

Risks
Not applicable.

Knowledge Transfer and Exploitation
The main functions of this project are to ensure the development of a new programme of work and to measure and increase the impact of the programme. Improvement of the programme impact will be achieved through proactive intervention in the technical projects within the programme rather than through direct knowledge transfer activity in this project.

Co-funding and Collaborators
Not applicable.

Deliverables

1	**Start: 1st April 2012**	**End: 31st March 2013**	

Deliverable title: Programme Management and Formulation

Project No.	IRD\2012\4	Price to NMO	£1,523k
Project Title	Fundamental scaling effects in piezoelectrics – "nanostrain"	Co-funding target	£900k
Lead Scientist	Markys Cain	Stage Start Date	April 2012
Scientist Team	J.Wooldridge, P.Weaver, M.Vopson, M.Stewart, L.Hao, N.McCartney, J.Blackburn	Stage End Date	March 2015
		Est Final Stage End Date	March 2018
Sector	Advanced Manufacturing	Activity	Strategic Capability
Project Champion	Yong Yan		

Summary: Control of material properties at the nanoscale through application of strain by piezoelectric materials opens up a wide range of innovative new applications e.g. tuneable electronics, sensors and next generation (beyond Moore's Law) transistors. We have assembled an international team spanning the European Synchrotron Radiation Facility (ESRF), IBM (York Town Heights), and NPL to develop new metrology to exploit nanoscale piezoelectric functionality. It presents a major strategic opportunity to work closely with IBM, one of the leading industrial research organisations in the world, who have invited us to collaborate in a large project (open research with fully published outputs) to develop the science of piezoelectric materials in electromechanical transistors. This project will build on key strengths across NPL in functional materials, MEMS (micro-electro-mechanical system) and NEMS (nano-electro-mechanical system) metrology, and nanoscale SPM (scanning probe microscopy) to develop innovative new techniques for the *measurement of piezoelectrically coupled strain at the nanoscale*.

The Need : Nanotechnology presents a major opportunity for growth in UK industry in collaboration with international partners [1]. It is one of the key areas identified by the NMS [2] where the UK is a world leader and advances in metrology can support that strong position. Emerging industrial applications include configurable chemical and optical sensors and electromechanical logic. Nanoscale strain measurement has been described as one of the holy grails of nanocharacterisation [3]. It is challenging because strains of interest (10^{-4} to 10^{-6}) are at or beyond the limit of techniques such as x-ray diffraction (XRD - approximately 10^{-4}). Transmission electron microscopy (TEM) can measure strain at the nanoscale [4] but is destructive so is not suitable for measurements on functional devices. Recent research at NPL [5] and NIST [3] established high resolution electron back-scatter diffraction (EBSD) and confocal Raman microscopy (CRM) as techniques for strain measurement in the micro- to nano- scale. NIST are not able to perform in-situ combined measurements, nor the strain induced by piezoelectric coupling. Thus industrial need for accurate strain measurement at the nanoscale evades the best laboratories worldwide.

[1]Nanotechnology: a UK Industry View 2010, www.materialsktn.net [2] The Strategy for the National Measurement System: 2011-2015 [3] Vaudin, M. D et al. APL, 93, 193116 [4] Hytch M., Nature 453 1086 [5] "Correlation of electron backscatter diffraction and piezoresponse force microscopy…" Burnett, Weaver, Blackburn, Stewart, Cain, JAP108, 042001, 2010

The Solution:

To meet this need requires non-destructive strain measurement in the region 10^{-4} to 10^{-6} in nanoscale devices. We propose an ambitious multinational research endeavour with substantial in-kind support which more than matches the funding from the NMO. We will apply new technologies together with the innovative combination of existing and emerging techniques. The metrological relationships between these techniques and the definition of strain at the nanoscale requires modelling of the fundamentals of piezoelectric strain at the nanoscale and strain transfer in nanostructures. NPL has a track record in nanoscale strain measurement by EBSD, coupled (not in-situ) EBSD / PFM in functional materials [5], piezo-MEMS [6] and NEMS metrology [7], digital image correlation and modelling. NPL has a strategic partnership with the UK beamline 'XMaS' at ESRF and has implemented a unique measurement system for piezo materials into their beamline . This research and multinational support makes NPL uniquely suited to carry out this work, and provides NPL and the UK with a timely opportunity to develop a lead in this area for the benefit of UK industry.

[6] "MEMS metrology for microscale piezoelectric measurement" Wooldridge et al (submitted) [7]Hao, Gallop, Cox "Excitation, detection, and passive cooling of a micromechanical cantilever using near-field of a microwave resonator" APL 2009, 95, 113501

Project Description (including summary of technical work)

1. Piezo-MEMS tools (developed in NMS Materials 2009/2012) will be scaled to down and fitted to NPL's FIB to provide integrated electro-mechanical / EBSD measurements of nano-strain in piezoelectrics.
2. Develop piezo-NEMS for strain measurement using near-field microwave resonator. [Materials, TQEM, NPL FIB]
3. Integrate piezoelectric interferometric measurement system into new beam line development at the ESRF XMaS Synchrotron beam line in Grenoble. [NPL, ESRF, XMaS beamline]
4. Apply nanoscale digital image correlation (DIC) to scanning probe microscopy (SPM). [NPL]
5. Model strain coupling in nanoscale piezoelectrics and nanostructures, multiscale modelling of MEMS / NEMS devices providing traceability to fundamental materials properties [NPL, TYC, IBM]

Impact and Benefits

- Innovation: The DARPA funded work (open publishable) supporting IBM's investigation of nanostrain piezoelectricity for electromechanical logic provides NPL and the UK an opportunity to contribute to a major technological innovation to develop the next generation transistor logic providing benefits to the UK supply chain and R&D base. Capability for nanoscale strain metrology will support a wide range of UK industry and innovation.
- Economic benefit supporting UK growth in nano-functional materials and new technologies based on them ensuring strong UK participation in the $2.6 trillion market for goods incorporating nanotechnology. Collaboration with IBM in a dedicated case study will provide routes to international markets for UK technology.
- Quality of life: Better security and resource efficiency through new sensing and electronic technologies.
- Science and status: Direct industrial relevance through IBM collaboration, UK access to new user facility at ESRF.

Support for Programme Challenge, Roadmaps, Government Strategies: This project directly supports the IRD programme challenge by addressing key innovation-led technology areas as identified in NMS strategy and other UK documents (see Need section). The project is highly interdisciplinary with input from across NPL (materials, quantum), building on capability from Materials, Physical and Pathfinder programmes to develop a new direction where NPL can take an international lead. This project develops our strategy (Functional Materials roadmap) for metrology to support new innovation and emerging industrial technologies within the UK.

Synergies with other projects / programmes: This project builds on previous NMS projects: "nanoferroelectrics" by developing the metrology in a new direction of electro-mechanical coupling in functional materials; "MEMS metrology" – applying techniques developed in this project in innovative combination with EBSD; FM04 harsh environments –apply macroscale metrology of strain coupling to the nanoscale; Pathfinder 'NEMS for multi-property measurement' taken to new areas using piezoelectrically coupled devices.

Risks: Delays in nanofabrication. Mitigated by supply by IBM from their dedicated research fabrication facilities. Programme timing across organisations can lead to delays e.g. recruitment of post-docs. This is factored in to the project plan assuming a delayed start for external collaborators.

Knowledge Transfer and Exploitation: In this project our overarching KT goal is to support the exploitation of the application of piezo strain at the nanoscale through; 1. A managed programme of industrial training workshops (with the Materials and SP-KTN); 2. A case study with partner IBM demonstrating how practical knowledge of piezo strain can be used to design new transistor architectures (published papers) will allow us to develop new metrology for the benefit of UK industry (metrology IP to be retained by NPL); 3. Measurement best practice guides on tasks 1,2,4 above; 4. New service at ESRF for characterising macroscopic and atomic strain. We will work with our IAG that includes UK companies QinetiQ, BAESystems, Queensgate, XAAR, Syfer, Renishaw and Polytec UK and others who have direct need of the metrology set out in this proposal. We will carry out these activities using our extensive KT network of which we either chair, or lead or actively participate in: IOM3 Smart Materials and Systems Committee, European Piezo Institute, IOP Dielectrics Group, EMMA-Club, & VAMAS TWA24.

Co-funding and Planned Collaborators: This project forms part of a wider international open research programme led by IBM which already attracts major in-kind funding to directly support the objectives of this NMS project (IBM $250k, EPSRC ESRF XMaS €400k) plus the wider IBM project (DARPA $9m). Co-funding is also anticipated from EU FP7 (SELECT €311k, ITN Next Gen €300k) and EMRP (2012 Industry &Open) to develop this work at a European level.

Deliverables

1	**Start: 01/04/2012**	**End: 31/03/2015**	
Deliverable title: In-situ Piezo-MEMS tools built into NPL's FIB facility for quantitative strain mapping at the nanoscale.			
2	**Start: 01/04/2012**	**End: 30/09/2014**	
Deliverable title: Piezo-NEMS near-field microwave resonator for strain measurement in nanoscale devices demonstrated.			
3	**Start: 01/04/2012**	**End: 31/3/2015**	
Deliverable title: Piezoelectric measurement system deployed into Synchrotron beam line for microscale strain measurement.			
4	**Start: 01/04/2012**	**End: 31/03/2014**	
Deliverable title: In-plane strain at atomic scales: Nanoscale digital image correlation using scanning probe microscopy.			
5	**Start: 01/04/2012**	**End: 31/03/2015**	
Deliverable title: Models and datasets of nanoscale strain coupling: atomistic approaches based on defect mediated structural dynamics (NPL,TYC, IBM)			

Project No.	IRD\2012\5	Price to NMO	£597k
Project Title	Chemical Imaging using Bifunctional Electrochemical Scanning Probes	Co-funding target	
Lead Scientist	Andy Wain	Stage Start Date	April 2012
Scientist Team	Alan Turnbull, Andrew Pollard, William Kylberg	Stage End Date	March 2014
		Est Final Stage End Date	March 2018
Sector	Advanced Manufacturing, Health	Activity	Strategic Capability
Project Champion	Pankaj Vadgama		

Summary

The aim of this project is to advance the state-of-the-art in high-resolution chemical imaging via the development of novel bifunctional electrochemical probes.

The Need

Controlling the chemically reactive nature of functional materials is a ubiquitous challenge that requires a detailed knowledge of interfacial phenomena over various length scales. The intelligent design of novel materials with tailored chemical properties impacts areas of critical importance across a spectrum of requirements, ranging from the chemically reactive (e.g. heterogeneous catalysts for chemical energy conversion), through to the chemically inert (e.g. corrosion-resistant alloys for oil and gas pipelines). Electrochemically active interfaces are of notable interest and the related challenges in materials and surface science have an extensive impact across UK industry. For example, the discovery and development of cheaper, more sustainable electrocatalysts for fuel cells is one of the bottlenecks to their widespread use.

The behaviour of solid-liquid interfaces is governed by a complex interplay of dynamic processes such as mass transport, charge transfer and reactive chemistry that can only be truly understood through real-time interrogation at a localised level. Whilst tools for the physical and chemical characterisation of surfaces are prevalent (e.g. AFM, EDX analysis), they lack the ability to measure in-situ surface reactivity (speciation, mechanisms and kinetics). Electrochemical scanning probe microscopies offer a solution to this challenge through chemical mapping of reacting surfaces. Currently such techniques suffer from one of two limitations: (i) the lack of topographical feedback to maintain controlled tip-surface separation and (ii) an inherent inability to study the behaviour of reagents that cannot be generated electrochemically. These limitations restrict both the spatial resolution of the technique and the diversity of reactive systems that can be investigated.

The Solution

Building on current NPL capabilities in electrochemical scanning probe microscopy and pooling expertise from both the Materials and Analytical Sciences Divisions, we propose to extend the state-of-the-art by developing a novel high-resolution electrochemical imaging system that addresses the limitations highlighted above. Bifunctional capillary probes with sub-micron sized apertures will be fabricated that utilise ion-conductance as a means of topographical positioning control, whilst enabling intricate local reactivity measurements simultaneously through a secondary channel, which may operate in one of three ways:

- **Redox Electrochemistry**; the second channel will consist of a simple microelectrode and be used to interrogate surface reactivity through amperometric (current) measurement.
- **pH-Measurement**; the second channel consists of a functionalised microelectrode (e.g. iridium oxide deposited on platinum) that enables determination of local pH through potentiometric (potential) measurement.
- **Reagent delivery**; the second capillary barrel contains a "dosing reagent" dissolved within a water immiscible solvent and locally partitions into the solution. Current is then collected at the substrate when the probe passes over active regions.

Preliminary work has been undertaken in the first of these modes, but the application of this dual measurement approach has not been explored in any depth. The advancements offered will significantly broaden the scope of reactive chemistry that can be imaged using electrochemical microscopy, leading to a breadth of applications in fields of commercial importance.

Project Description (including summary of technical work)

The project will focus initially on the development of the novel probes and instrumentation described above and validation of the new methodologies using standard substrates. The utility of the proposed techniques towards the meticulous extraction of surface kinetics through measurement of diffusive concentration profiles will be tested with reference to a model system with known electrode and chemical dynamics, of which there are many examples.

Our aim is to then demonstrate the new measurement capability by application to industrial problems in which identifying surface reactivity on a local scale is a key issue. These may include, for example:

- **Electrocatalysis**; Measurement of electrokinetics at the single catalyst particle level and determination of active sites that control the behaviour of supporting carbon nanomaterials have remained long-standing challenges in the fuel cell industry. The improved working distance control of the proposed bifunctional probes will help resolve issues of spatial resolution and help make such measurement a reality. Furthermore, the reagent delivery mode will allow the study of less conventional electrocatalytic reactions, such as the oxidation of methanol, a reaction of significance to direct methanol fuel cells.
- **Charge Transport in Solar Energy Devices**; Structure-activity relationships are of critical significance in the development of new photocatalytic materials, particularly in the growing field of photoelectrochemical water splitting. The proposed multifunctional probes lend themselves to the simultaneous mapping of surface topography and photocatalytic activity.

- **Advanced Corrosion Monitoring**; Two problems relevant to the oil and gas industry will potentially be explored. The first relates to the visualisation of localised corrosion processes of materials as a function of applied stress to understand better how damage develops in service. The second challenge concerns the efficiency of corrosion inhibitors, wherein we will use the developed methodology to determine the uniformity of inhibitor molecule coverage in situations where non-uniform corrosion has already occurred.

Impact and Benefits

The scientific ramifications of this work are broad and the knowledge and insights generated will enable improved characterisation of surface reactivity in functional materials, indirectly leading to:

- More efficient, cheaper, sustainable electrocatalysts for fuel cell applications
- Higher performance materials for solar energy conversion
- Improved materials selection and inhibitor formulations

Direct Benefits to NPL include:

- Enhanced NPL capability in electrochemical microscopy, establishing world-leading status
- Potential for industrial partnerships through provision of niche measurement service to UK industry

Support for Programme Challenge, Roadmaps, Government Strategies

Strong alignment with NMS strategy in key national challenges, including:

- **Growth** - Advanced instrumentation (characterisation tools, methodologies, scanning probe techniques)
- **Energy** - Measurement and characterisation methods supporting fuel cells and photovoltaics
- **Sustainability** - Transition to a new generation of functional materials with improved efficiency

Synergies with other projects / programmes

The work builds upon the foundation laid through previous projects in the Materials and ChemBio programmes. The advanced local electrochemical measurements promised will support current projects in fuel cells (Materials, TSB, FP7), catalysis (IRD), photovoltaics (Materials, IRD, EMRP) and in the corrosion theme.

Risks

Proof-of-concept has been established in each of the *single* channel modes so risk should be limited to the addition of the topographical channel and the ability to independently measure topography and activity without interference. This should be mitigated through expertise in electronics and ion conductance microscopy both in and outside of NPL. Furthermore, the use of ion current measurement in AC and DC modes will be investigated as a means to circumvent any such signal convolution.

Knowledge Transfer and Exploitation

Our primary objective is to develop a unique capability, so the output focus will be on high impact publication and dissemination to the scientific community via international presentations. The aim is to not only evaluate the versatility of the developed tools but also to explore extended applications beyond those highlighted, leading to potential avenues of new science. Knowledge transfer to/from UK industry will be achieved through current industrial advisory groups, notably in the fuel cell and corrosion themes. These will also provide a springboard for potential future industrial exploitation, e.g. through TSB or direct funding.

Co-funding and Collaborators

Project collaborators will provide support via technical input and/or provision of the required materials:

- **Johnson-Matthey** – world leaders in fuel cell catalyst development
- **BP** – interest/expertise in corrosion inhibition and in-situ stress imaging
- **EMPA** – experience in photoelectrode materials
- **Bath University** – interest in materials for solar energy conversion
- **Cardiff University** – expertise in catalysis
- **Imperial College London** – world experts in ion conductance microscopy

Deliverables

1	**Start: 01/04/12**	**End: 31/03/13**	
Deliverable title: Evaluation of bifunctional probe fabrication and implementation approaches (NPL report)			
2	**Start: 01/04/13**	**End: 31/03/14**	
Deliverable title: Novel high resolution imaging system enabling local surface reactivity measurements through dual channel measurement (peer reviewed publication)			
3	**Start: 01/01/13**	**End: 31/03/14**	
Deliverable title: Demonstration of bifunctional probes to local reactivity measurements for energy applications (peer reviewed publication and conference presentation)			

Project No.	IRD\2012\9	**Price to NMO**	£659k
Project Title	Metrology for Structured Surfaces	**Co-funding target**	£745k
Lead Scientist	Richard Leach/Mark Gee	**Stage Start Date**	June 2012
Scientist Team	John Nunn, Claudiu Giusca, Chris Jones	**Stage End Date**	May 2014
Sector	High Value Manufacturing Energy Efficiency	**Activity**	Strategic Capability
Project Champion	Ben Beake		

Summary This project will facilitate the introduction of structured surfaces in a range of industrial products by enhancing the understanding of the relationship between structure and functional performance. The technical work will be concerned with the development of novel characterisation techniques to enable the fast, validated and traceable evaluation of the 3D topography of patterned surfaces, the measurement of the functional performance of patterned surfaces, and the modelling of the performance of patterned surfaces.

The Need Structuring of surfaces at the nano and micro scale holds the promise of step change improvements in the functional performance of the surfaces of engineering components. Many sectors of industry will benefit from this technology through better control of properties such as, friction, optics, electrical function and fluid flow. Thus this technology will contribute to the drive to transform, e.g., the efficiency of automobile transport identified by the King Report and the International Energy Agency Advanced Materials for Transport Group. The take up of this technology is hampered by the lack of appropriate metrological techniques to assess these surfaces, to characterise their performance, and to model their behaviour. Current metrology methods use sensors that cover a very small area and hence are too slow in industrial applications. Some preliminary products have already been produced using this technology, e.g. piston rings patterned by laser processing, but this work has been carried out by a laborious, time consuming empirical process because of the lack of the necessary knowledge of the relationship between measurements of the surface and their functional performance. Government funding is required for this challenging metrological work as key investment in metrology through this project will have a major effect in transforming the performance of products across wide sectors to industry.

The Solution A step change improvement in characterisation techniques will enable timely introduction of this new technology. As the new functionality depends on the topographic patterning of large (up to metres) of surfaces with nanometre precision, fast, accurate characterisation of large areas of the surface needs to be made, and novel analysis methods will be developed that can address this challenge providing the key information on surface structure that is required. These measurements will be made using new optical (e.g. dispersive coherence scanning interferometry) techniques developed in project EF/2011/06, 2011-2014 (NPL has existing and developing world-leadership in areal surface topography measurement). So that the key parameters that control performance can be identified, the surface structure determined through these measurements needs to be correlated with their functional performance. In this project the focus of the work will be concerned with tribological performance as NPL already has expertise in this area. Modelling will be required to ensure that the necessary understanding of how functional performance can be related to the surface structure is developed in a coherent way so that prediction of performance can be made for a range of patterned surfaces. This challenging interdisciplinary work will draw on both the expertise of the EM Division on topographical characterisation, and the Materials Division on the functional performance of materials. The key deliverables of the project will be:

- Methods developed for fast large scale characterisation of the structure of surfaces with nanometre accuracy.
- Scientific papers on the functional performance of these structured surfaces.
- Modelling methods for the prediction of performance from key surface characterisation parameters.
- Good practice guidance on the measurement to function relationships that can be applied in industry.

Project Description The work will comprise:

- The development of novel characterisation techniques (using existing measurement methods) to enable the fast, validated and traceable evaluation of the 3D topography of patterned surfaces.
- The development of sampling methodologies and data processing to derive 3D surface parameters relevant to applications.
- Measurement of the frictional performance of key pattered surfaces chosen to represent the major types of patterning, correlating the performance to key parameters.
- The development of techniques to evaluate the durability of patterned surfaces under mechanical contact.
- Modelling of the frictional performance of patterned surfaces to develop a fundamental understanding of the relationship between structure and functional performance.

Impact and Benefits This project will deliver the underpinning metrology necessary for manufacturing with deterministic control of surface topography that can improve , e.g. friction, wear, aerodynamics, fuel efficiency, biocompatibility and spectral response. Specifically it will:

- Lead to new science on the characterisation of surfaces and understanding of how the topography of surfaces can give better functional performance.
- Develop NPL's capability in application of metrology to the knowledge-based design of surfaces.

- Enable the effective and efficient design of functional surfaces for applications across manufacturing industry.
- Give a competitive advantage to UK industry, both through better products and through more efficient manufacturing.
- Give surfaces with lower friction leading to considerable increases in fuel efficiency (10 %) and reduced environmental impact.
- Lead to surfaces able to give better control of fluid flow in applications such as medical diagnostic devices.
- Give the ability to engineer new functions into a product such as self-cleaning glass or colouring without paint.

The project has real technological and scientific relevance and, therefore, a large potential to create a positive impact on people's lives through improvements in fields as diverse as medicine, consumer electronics and the energy conservation.

Support for Programme Challenge, Roadmaps, Government Strategies This project addresses several challenges in the strategies of the NMO and the government (TSB High Value Manufacturing, Advanced Materials, Healthcare, Nanoscience, Sustainable Energy) by enabling the development of innovative and energy efficient products, increases in the fuel efficiency of transport systems and reductions of impact on the environment, increases in the efficiency of manufacturing and reducing the waste of materials, and better healthcare products such as diagnostic devices. The project fits with the roadmaps for the M4, Engineering and Flow and EMRP Programmes addressing the requirement for high resolution measurement of structured surfaces.

Synergies with other projects / programmes This project will draw on the capability developed in previous projects in the Materials Programme such as FM01 where preliminary work was carried out on the functional evaluation of patterned surfaces, in the IRD Programme where Project T11 developed techniques to monitor the degradation of surfaces from wear, and in the Engineering and Flow Programme where Project EF/2011/06 is currently developing fast methods for the measurement of the topography of surfaces. Good links with industry will be established so that the methodology that is developed can be taken up by industry. Dissemination will continue after the end of the project to ensure that the maximum impact can be achieved.

Risks The main risk of the project is to develop new characterisation methods to address the major challenge of measuring large areas quickly with micro- to nanometre resolution. This will be mitigated by looking at several different approaches and settling on one method for further development when the feasibility has been confirmed. Another risk is concerned with the development of a universal approach to the modelling of the relationship between the topography of a patterned surface and its function. This will be ameliorated by the careful choice of representative surfaces and by partnering with an academic with appropriate modelling skills.

Knowledge Transfer and Exploitation A coherent plan for knowledge transfer will be implemented that will include the production of good practice and its dissemination by direct contact with industry and publication as an NPL Good Practice Guide. Scientific publications will be made, as appropriate, in peer reviewed journals to disseminate the project results to the scientific and technical communities. Two areas where exploitation is foreseen are the development of new characterisation methods for the assessment of patterned surfaces where the option of licensing the new technology will be explored. Similarly there are likely to be exploitation opportunities with the modelling aspects of the project. Results will be presented at a themed meeting of the Measurement Network. An industrial stakeholder group will also be formed to ensure that industry has the opportunity to inform the project concerning industrial priorities, and to receive key output from the project.

Co-funding and Collaborators This project is of considerable interest to many sectors of industry so direct support of the project will be sought from key industrial stakeholders in the early stages of the project. The value of this direct support is likely to be £40k. One proposal has also been submitted to FP7 on the rapid characterisation of the topography of structured surfaces which fits many of the objectives of this project. The value of this co-funding is £250k. A proposal will also be submitted to the 2012 EMRP Industry call on Patterned Surfaces. The value of this co-funding will be £300k

Collaboration will be through the universities of Southampton (nCATS), Imperial, Huddersfield (EPSRC Advanced Metrology Centre), and Cranfield (EPSRC Ultra-Precision Centre). This will include PhDs, masters students and leverage for EPRSC funding. The collaboration with nCATS at Southampton will be carried out through the support of an EPSRC Postdoc worth £90k that has been agreed under the £2.5M funding that nCATS was recently awarded on Green Tribology, and a short KTS with Southampton and TWI worth £65k. Industrial partners will include Ford, Neuteq, Cranfield Precision, Rolls Royce, Airbus, John Crane and TWI.

Deliverables

1	**Start: 1/6/2012**	**End: 31/1/2014**	
Deliverable title: Characterisation of structured surface - 2 scientific papers			
2	**Start: 1/10/2012**	**End: 31/1/2014**	
Deliverable title: Measurement of the functional performance of patterned surfaces - 2 scientific papers			
3	**Start: 1/9/2012**	**End: 30/5/2014**	
Deliverable title: Modelling and prediction of functional performance of patterned surfaces - 2 scientific papers			
4	**Start: 1/4/2012**	**End: 30/5/2014**	
Deliverable title: Dissemination, management and exploitation - NPL Good practice guide, meetings of stakeholder group			

Project No.	IRD\2012\13	**Price to NMO**	£3.2M
Project Title	Real - time methods for the measurement of key properties of Graphene at the device scale	**Co-funding target**	£1000k
Lead Scientist	J T Janssen	**Stage Start Date**	1/4/2012
Scientist Team	Olga Kazakova, J T Janssen, Ian Gilmore, Debdulal Roy, Chris Hunt, Tim Burnett, Alexander Tzalenchuk , Markys Cain, Andy Pollard	**Stage End Date**	
		Est Final Stage End Date	1/10/2015
Sector	Growth	**Activity**	Strategic Capability
Project Champion	Yong Yan		

Summary: *"Understanding the factors that influence the electrical transport in graphene and it's uniformity at wafer scale under environmental exposure are highly desirable"* .Christos Dimitrakopolous IBM, T.J. Watson research Centre. Recent work at IBM has already demonstrated the feasibility of the first high-frequency graphene electronics circuits, for radio-frequency applications (Lin, Science 332, 1294 (2011); Wu, Nature 472, 74 (2011)).

It is essential to cross the laboratory to production line gap; *"Going from laboratory demonstration to real-life application can be a difficult process and this is where many new technologies have failed in the past. Metrology plays an essential role in this process by providing reliable and reproducible measurement technology which gives confidence in the results of research".* Kostya Novosolev, joint Nobel prize winner for his work on graphene.

Graphene, a single layer of carbon atoms in a hexagonal lattice, has displayed exceptional new physical effects and scientific interest has soared rapidly (70,000 citation of 3000 papers produced in 2010). New applications such as all-carbon electronics, high-frequency transistors, chemical and biological sensors, ultracapacitors, solar cells, etc., require industrially produced graphene which cannot be realised without measurement methods applicable to fabrication lines. The lack of this metrology is therefore a roadblock to progress. The properties of graphene are determined by the morphology and chemistry of the "graphene" as it can be doped or contaminated and it is supported by a substrate. Therefore, techniques need to be developed which can measure essential properties on a local scale and, most importantly, correlate these measurements with performance. _In use these device will have to be "packaged" to protect the Graphene from atmospheric exposure and the effectiveness and compatibility of this packaging needs to be assessed. The project proposed here develops methods for rapid and reliable measurement of electronic, chemical and structural parameters of epitaxial graphene grown on SiC and CVD grown graphene essential to take it from the laboratory to the production line and the quality of any packaging layers.

The Need. New measurement methods will be required in every fabrication line using graphene to enable development at the same pace as academic progress so that industrial companies can turn inventions into products. The potential of graphene (see table in impact and benefits) cannot be exploited without methods that are valid over the large-scale, for example, fast, contactless electrical measurement methods for testing of epitaxial graphene devices. Currently used methods are time-consuming, complicated and expensive and the obtained information is still generalized over the whole device and not correlated with the exact composition and morphology of graphene.

Metrological challenges, such as determination of the graphitization level and layer thickness, quantitative measurement of dopant concentration with sensitivities of better than 10^{10} atoms per cm^2 , need to be coupled with measurement of corresponding changes in electrical and electronic properties to understand the effect of surface functionalisation and contamination on the graphene properties. According to the ITRS roadmap graphene production will move from research to pre-production in the next few years.

Industrially relevant large-area graphene can be produced using two different routes, sublimation of SiC or CVD growth on metal (MBE growth is also possible but still in its infancy). The electrical properties of monolayer graphene are very different from bi-layer or tri-layer graphene and homogenous covering is required for most applications (this is not necessarily the case for applications which rely on the unique structural properties of graphene like high-strength composite materials). In the case of epitaxial graphene grown on SiC and depending on the growth conditions, the percentage coverage of the wafer with mono-, or bi-layer graphene will vary and appears to correlate with the number of step edges present in the SiC crystal. Identification of step edges is easy with AFM based techniques but identification of the number of graphene layers is much more difficult (Burnett, Nano Letters 11, 2324 (2011)) and needs to be combined with other more advanced functional scanning techniques or Raman analyses. The doping of graphene on SiC is determined by charge transfer from the SiC crystal and an interface layer between the substrate and graphene.

The properties of this interface layer and how they control the electron density are unknown. Similar issues exist for CVD growth of graphene on metals. A fingerprint of the domain structure of the metal substrate remains in the graphene layer after growth and lift-off, the different thermal expansion coefficients of metal and graphene cause ripples to be formed. The density of such domains and ripples will dramatically affect the electrical mobility.

The Solution - *To provide validated real-time measurement methods applicable to graphene in fabrication settings.*

In principle all key measurements are possible in the laboratory using dedicated equipment and specifically designed and fabricated samples (Tzalenchuk, Nature Nanotechnology 5, 186 (2010)). Whilst this may be useful in research settings, it does not meet the needs of industry. The challenge is to combine/integrate a number of techniques which can give a meaningful result on the factory floor and apply them to a single sample. The properties of graphene are determined by the structure on the nano-scale but the aim of the industry is to produce graphene by the square metre. Hence high-speed, contactless measurements are required which can be validated against established metrological standards. The methods can be used to investigate "packaged" graphene in combination with novel methods that overcome the challenge of performance assessment of ultra thin packaging material.

Contactless methods - Electron-beam microscopy (i.e. PEEM, LEEM) and functionalised electrical scanning probe microscopy (i.e. SKPM and EFM) have been recently successfully used to identify the number of layers in epitaxial graphene, but they need further development, validation and correlation with large-scale transport properties.

We propose a method that combines electrical measurements with Raman microscopy and spectroscopy techniques. This contactless technique can then be simplified to provide a mapping method for epitaxial and exfoliated graphene. Functional electrical microscopy (EFM, SKPM, SCM) will be applied to measure key data such as the graphitization level, thickness, distribution of the electrical potential and charge, electrical state of dopants and impurities, work function, and capacitance with a very high special resolution (<20 nm). Rapid, large scale laser/ electron beam intensity modulation method (LIMM) and Near field Microwave Microscopy (NFMM) and will be evaluated as candidates for development for high frequency electronic/dielectric and thermal properties of graphene.

Validation methods -Secondary ion mass spectrometry (SIMS) and x-ray photoelectron spectroscopy (XPS), are not currently suitable for Graphene. SIMS is the tool for quantitative measurement of the dopant profile over the first 10 nm of an ultra-shallow implant. XPS is the key tool for non-destructive depth profiles of complex layer structures for high-k dielectrics for smaller device architectures and quanitifaction of surface functionalisation. Graphene presents a new challenge in surface sensitivity with a requirement of a depth resolution of around one atomic layer above and below the graphene and substrate interface which requires new capability development (e.g. ion beam development and new g-ogram method for data interpretation). Micro-Raman spectroscopy is a key metrological tool for graphene to quickly and reliably determine the number of graphene layers and quality of the graphene. Tip-enhanced Raman spectroscopy is a new variant of this technique with potential for non-destructive imaging of the surface chemistry with spatial resolutions of better than 20 nm. TERS could be developed for nanoscale imaging of surface dopants, functional groups and nanoscale contaminations and to study the effect and measurement of graphene layer edge-effects. Helium and neon ion microscopes have recently been shown to be extremely useful for graphene nanofabrication and imaging with sub-nm resolution. The potential of these instruments for quantitative surface elemental analysis through backscattering spectrometry has not yet been developed.

Project Description (including summary of technical work):

This project delivers a step change in the state of the art from a series of methods only suitable for measurement over a small area to an integrated system scanning over a device

1) ***Aim***: Measurement of key electrical parameters and characteristics of epitaxial graphene. ***Realization***: EFM, SKPM, SCM, NFMM and LIMM measurements will be performed in ambient conditions on epitaxial graphene grown by solid-state graphitization of SiC on both C- and Si-sides. Various types of conducting probes and samples with different numbers of layers will be studied. A comparative research on exfoliated graphene on SiO_2 and on CVD grown graphene on suitable substrates will be performed. Interaction and charge exchange between graphene and the substrate, as well as between individual layers will be studied
2) ***Aim:*** Development of EFM/SCM spectroscopic measurement techniques.***Realization***: Optimal conditions for spectroscopy will be developed to enable use over a wide area. The role of capacitance and Coulomb interactions will be understood. Quantum capacitance studies of epitaxial graphene will be performed
3) ***Aim:*** To trial and develop large-scale methods. ***Realization:*** Large-scale (scanning) methods from Aim 1 will be trailed and the best candidates developed to measure carrier-density and mobility. These measurements will be correlated with local methods.
4) ***Aim:*** Metrological methods for the identification of various graphene layers.***Realization***: Identification will be achieved using microscopy and spectroscopy techniques. Correlation of sample morphology (including various complex growth modes) with electrical mapping will be accomplished. Angle resolved XPS can be used to give quantitative measurement of the thickness of a uniform graphene layer with sub-nm precision.
5) ***Aim:*** Measurement tools to investigate the role of transfer doping in the electrical/ electronic properties of graphene. ***Realization***: Electrical microscopy and spectroscopy will be developed and performed on n- (i.e. NH_3, alkali atoms) and p-doped (i.e. N_2O, H_2O, O_2, organic molecules) graphene. Process of decoupling of graphene

from a SiC substrate due to hydrogen intercalation will be studied for extrinsic (from dopants) and intrinsic (from substrate) doping.

6) ***Aim:*** Tools to quantify dopant concentration, defect state and identification of contaminants for correlation with electrical performance. ***Realization (aims 5 and 6)***: Electrical microscopy and spectroscopy will be developed and performed on n- (i.e. NH_3, alkali atoms) and p-doped (i.e. N_2O, H_2O, O_2, organic molecules) graphene. Process of decoupling of graphene from a SiC substrate due to hydrogen intercalation will be studied for extrinsic (from dopants) and intrinsic (from substrate) doping. Fitness for purpose assessments will be made over large areas.

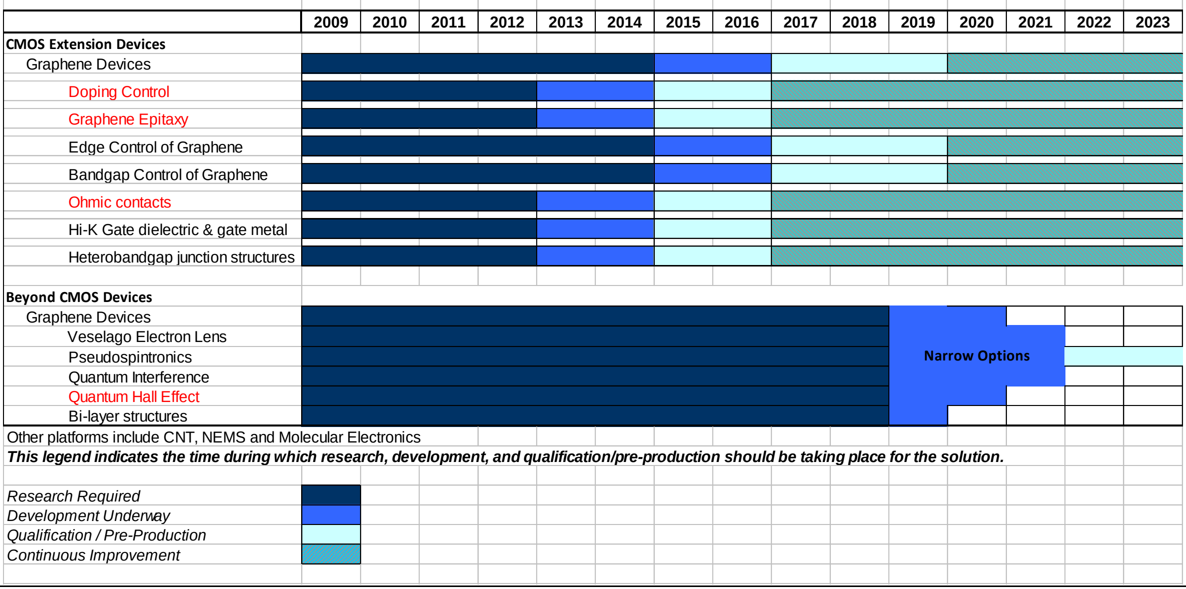
7) ***Aim:*** Establish methods, using metrological techniques, for the assessment of the robustness of "packaged" Graphene in devices operating under real conditions and their compatibility with Graphene. ***Realization***: The performance of exceptionally thin packaging materials will be assessed using sub-micro scale interdigitated combs on a silicon substrate. Compatibility will be assessed by packaging the graphene then using the other tools developed in the project to determine whether the graphene has been affected by the packaging.

Impact and Benefits The electronics sector will be first to exploit the extraordinary properties of graphene in new applications and extending existing technologies which are reaching the and of what is technically possible such as ultra-fast transistor and interconnects for the ICT industry (see ITRS roadmap below. Potential applications of graphene include, ultra-small transistors, super-dense data storage, wearable electronics, ultra-capacitors to store and transmit electrical power and highly efficient solar cells. The ability to dope Graphene will lead to the development of chemical sensor systems. The global market for graphene-based products will be worth an estimated $67 million in 2015 increasing to $675.1 million in 2020 at compound annual growth rate of 58.7%.

Segment	Growth rate %	Value in 2015	Value in 2020
Capacitors	67.2%	$26	$340
structured materials	39.1%	$17.5	$91
displays	-	-	$43.8
photovoltaics	36.1%	$7.5	$35.0
thermal management	8.4%	$15	$22.5

ITRS Roadmap Shows the technical development needs for which metrology has to be delivered in parallel

Table ERD8 Research and Technology Development Schedule proposed for Carbon-based Nanoelectronics to impact the Industry's Timetable for Scaling Information Processing Technologie



Support for Programme Challenge, Roadmaps, Government Strategies The project enables the UK government and European growth agenda for the exploitation of the markets for graphene-based products by supporting the £50m UK national research initiative for graphene announced by the chancellor *"We will fund a national research programme that will develop production methods that take this Nobel-Prize winning discovery from the British laboratory to the British factory floor"* and the £1billion FP7 Flagship project (http://www.graphene-flagship.eu/GF/index.php) proposed to kick-start a graphene based industry in Europe. NPL aims to be the metrology partner in both of these opportunities by delivering the tools outlined in the ITRS roadmap; "non-destructive in-situ measurement methods to improve the balance between measurement speed, accuracy, and precision"

Synergies with other projects / programmes.
The project develops surface analysis capabilities (SIMS, TERS, XPS) from the Chembio programme and electrical methods (EFM, SCM, SKPM, LIMM, NFMM) being developed in the pathfinder and materials programmes.

Risks: The collaborators will provide graphene but the quality may not be exactly as expected.

Knowledge Transfer and Exploitation. Knowledge transfer to stakeholders will be through a new NPL "Graphene Futures Campaign" with a dedicated web space, special interest group, and bi annual meetings. Exploitation of the outcomes will be through a variety of routes and not solely focussed on graphene:

- offering a service to assess very thin packaging materials for the electronics, photonics, sensors and food sectors
- using NPLs combined capabilities for research focussed consultancies on new materials for the sensor and electronic industries (e.g. the new gas exposure capability from Chembio Programme)
- establishing NPL as the prime partner providing metrology for the national research initiative (NRI) and flagship project on graphene seeking joint and additional investment to deliver metrology related technical capabilities
- integrated solutions to metrology challenges for industry through relationships with UK instrumentation suppliers

Our track record shows that we will be able to publish collaboratively in high impact journals.

(1) **Nature Nanotechnology 5, 186-189 (2010).** *Towards a quantum resistance standard based on epitaxial graphene.* A. Tzalenchuk, S. Lara-Avila, A. Kalaboukhov, S. Paolillo, M. Syväjärvi, R. Yakimova, O. Kazakova, T. J. B. M. Janssen, V. Fal'ko et al

(2) **Applied Physics Letters 97, 112109 (2010).** *Charge transfer between epitaxial graphene and silicon carbide***.** S. Kopylov, A. Tzalenchuk, S. Kubatkin and V. Falko.

(3) **Advanced Materials, 23, 878–882 (2011).** *Nonvolatile Photo-Chemical Gating of an Epitaxial Graphene - Polymer Heterostructure* **;**S. Lara-Avila, K. Moth-Poulsen, R. Yakimova, T. Bjørnholm, V. Falko, A. Tzalenchuk, and S. Kubatkin.

(4) **Physical Review B 83, 233402 (2011).** *Anomalously strong pinning of the filling factor ν = 2 in epitaxial graphene***;** T. J. B. M. Janssen, A. Tzalenchuk, R. Yakimova, S. Kubatkin, S. Lara-Avila, S. Kopylov, and V. I. Fal'ko.

(5) **Nano Letters, 11, 2324–2328 (2011)** *Mapping of local electrical properties in epitaxial graphene using Electrostatic Force Microscopy;* T. Burnett, R. Yakimova, O. Kazakova.

(6) **Solid State Communications 151, 1094 (2011).** *Engineering and metrology of epitaxial graphene,* A. Tzalenchuk, S. Lara-Avilla, K. Cedergren, M. Syvajarvi, R. Yakimova, O. Kazakova, T.J.B.M. Janssen, K. Moth-Poulson, T. Bjornholm, et al.

Co-funding and Collaborators: Linkoping and Chalmers Universities, Sweden, Lancaster University, Exeter University (graphene centre), EMRP Graphene project 2012 Industry call, Flagship Graphene (proposed). IMEC, the largest European semiconductor research institute and Samsung.

1	**Start:** 1/4/2012	**End:** 30/9/2012	
Deliverable title: State of the art assessment , initial experiments and review of measurement tools for graphene **Evidence:** Report and project plan ,disseminated to webspace and graphene campaign launch meeting .			
2	**Start:** 1/8/2012	**End:** 32/8/2014	
Deliverable title: Development of wide area measurement tools for the electrical characteristics of Graphene **Evidence: 2** publications in peer-reviewed journals per year.			
3	**Start:** 1/8/2012	**End:** 31/8/2014	
Deliverable title: Development of wide area measurement tools for the structural characteristics of graphene **Evidence: 2** publications in peer-reviewed journals per year.			
4	**Start:** 1/8/2012	**End:** 31/8/2014	
Deliverable title: Validated Measurement tools for the chemical analysis of graphene extended to wide areas **Evidence: 2** publications in peer-reviewed journals per year.			
5	**Start:** 1/6/2012	**End:** 31/7/2015	
Deliverable title: Tools for the assessment of performance and compatibility of "graphene packaging materials" **Evidence:** 2 publications in peer-reviewed journals.			
6	**Start**: 1/8/2012	**End:** 31/8/2015	
Deliverable title: Wide area measurement tools to correlate the electrical, structural and chemical characteristics **Evidence: 1** publication in peer-reviewed journals per year.			
7	**Start:** 1/9/2012	**End:** 30/10/2015	
Deliverable title: Dissemination and knowledge transfer **Evidence: 3 p**roject workshops linked to graphene campaign , demonstration of techniques and engagement with industry, academia and instrumentation sector			

Project No.	NMS/CBM/12005	**Price to NMO**	£1222k
Project Title	NB12: Ambient imaging mass spectrometry with high resolution (NPL)	**Co-funding target**	£750 k
Lead Scientist	Felicia Green, Ian Gilmore	**Stage Start Date**	01/07/2012
Scientist Team	Tara Salter	**Stage End Date**	31/03/2015
		Est Final Stage End Date	2018
Sector	Health - Diagnosis; Advanced Manufacturing & Services - High-value manufacturing & bio-products	**Activity**	Development of Existing Capabilities; Methodology for New Capabilities

Summary

Through close collaboration with academia and industry this project will develop ambient imaging mass spectrometry (AIMS) capability for the rapid analysis of innovative and complex products in nanobiotechnology and advanced manufacturing.

The Need

According to the Co-Nanomet 'European Nanometrology 2020' report, a key objective in metrology is achieving in-situ nanometre resolution imaging from life systems, particularly for detection of low levels of biomarkers and disease markers. In industry there is strong demand for methods to analyse complex mixtures (subtle chemical differences, complex matrices) combined with the ability for rapid ambient analysis (screening, quality control) and surface chemical imaging with spatial resolutions of better than 10 μm to resolve chemical distribution (biomarkers on skin, homogeneity of tablets, pharmaceuticals in tissue sections and agrochemicals on leaves). Consultation with industrial stakeholders confirms this demand, with real excitement around ambient mass spectrometry as a potential solution, with over 20 UK industries becoming involved in the last 5 years. Industrial consultation has stated that AIMS could enable: real time and rapid quality control that takes into account chemical differences; understanding efficacy of products with difficult chemistries; simultaneous direct analysis of small molecules, polymers and organometallics; minimal sample preparation. Yet a common problem was best stated by one stakeholder (Svetlana Riazanskaia, Unilever) 'no facilities and expertise of this sort are presently available in house, so without NPL we wouldn't be able to do this research.' For effective use in industry the first critical need is for repeatability, and through the ChemBio programme we have started to establish the underpinning metrology leading to repeatability's of 10% (a factor of 10 improvement). Presently there is no capability for quantification, a demand from industry, due to a lack in the fundamental underpinning metrology. Improvements in sensitivity and quantification on real world samples need to be developed to enable routine use. Previous ChemBio projects have found spatial resolution typically ranges from 100 μm to 1 mm. New concepts and methods are required to develop high-performance AIMS capability.

The Solution

This project will radically improve the imaging capability of plasma assisted desorption ionisation mass spectrometry (PADI MS) from 1 mm to 10 μm in collaboration with the plasma physics group at Liverpool University (Prof James Bradley). We will address the challenge of sub-micron resolution by establishing new capability using a combination of a focused laser for desorption combined with novel ambient ionisation. With a long-term goal of achieving a spatial resolution of 100 nm we will explore the integration of scanning probe microscopy to give near-field laser ablation. It will be important to ensure that AIMS is quantitative and sufficiently sensitive, so we will develop the fundamental metrology to understand the desorption and ionisation mechanisms to enhance these aspects.

Project Description (including summary of technical work)

Metrology to measure the analytical sensitivity of important ambient MS techniques (DESI, PADI, paperspray). Fundamental study of the desorption and ionisation mechanisms of DESI and PADI and (1) develop methods to enhance sensitivity to 1 ppb (2) measure the quantification accuracy of DESI, PADI and paperspray including determination of matrix effects and (3) interpretation of mass spectra using searching of public chemical databases i.e. PubChem, LipidMaps, KEGG. Characterisation of an imaging PADI capability that radically improves spatial resolution from 1 mm to 10 μm using a novel microfabricated plasma source, developed in collaboration with an EPSRC-NPL funded post doc (Dr. Andrew Bowfield). Establish high-resolution (500 nm) AIMS capability at NPL exploring near-field laser desorption and other novel desorption ionisation mechanisms, suitable for biomolecules from tissues, skin and additives on manufacturing products. With industry collaboration ensure standardisation enables use of AIMS for solving complex industrial problems.

Impact and Benefits

At the end of this project, AIMS will be capable of (a) < 10 μm PADI spatial resolution (b) sensitivity and quantification for 1 ppb trace detection (c) sub-micrometre analysis (d) application to industrial problems in nanobiotechnology and high-value manufacturing (for personal care products such as hair products, laundry, cosmetics, and surface treatments e.g. glass, packaging, food processing). More specifically, this work will impact three areas that have been highlighted as UK Government priorities through the provision of analytical methods that can rapidly analyse complex formulations and systems: life sciences and stratified medicine (through capability for ambient tissue imaging and diagnostics); food and agriculture (rapid in situ analysis of agrochemicals on plants); and advanced manufacturing (increased analytical capability for product development). From the health and biotechnology sector improvements in quantification and sensitivity will be beneficial for rapid point of care (POC) analysis of dried blood spots; enhanced speed for process analytical control; MS miniaturisation; enhanced drug metabolism/pharmacokinetics on tissues; and enable non-destructive, quantitative chemical imaging of irregular samples. Further, the establishment of high resolution AIMS will be a step towards intercellular MS imaging for biological applications.

Support for Programme Challenge, Roadmaps, Government Strategies

The NMS Strategy Document 2011-2015 highlights growth and innovation as a National challenge, emphasising the need to support priority sectors health and advanced manufacturing through 'strategic capability building' of underpinning science for the NMS to be internationally competitive. This project aims to deliver this through measurement science in UK world-leading areas in nanotechnologies, regenerative medicine and new production technologies. It aligns with the ChemBio Nanobiotechnology theme and roadmap through advances in mapping cells and POC devices to leading metrology for diagnostics and regenerative medicines, ultimately supporting regulation in nanomedicine and building a strong UK bioscience sector. This project also aligns with the ChemBio Surface Analysis theme and roadmap and improving analysis of biological tissue through AIMS to improve medical imaging and diagnostics, coinciding with key TSB challenges (Nanoscale Technologies Strategy 2009-2012) in diagnostics, imaging, and drug discovery and disease prevention. The European Technology Platform for Nanomedicine (Roadmaps in Nanomedicine Towards 2020) also highlights the need for improvements in imaging systems and the establishment of translatability of research into product development. Finally, this work will aligns with the biological nanometrology objectives outlined in Co-Nanomet's European Nanometrology 2020 report (2011).

Synergies with other projects / programmes

This project builds on developments in ChemBio projects NB4 "Reliable analysis of skin and tissue using DESI and ambient methods" and SA2 "Ambient and imaging mass spectrometry" which have established international recognition for NPL and the NMS. The proposal is also aligned to the recently won EMRP project "Metrology for the characterisation of biomolecular interfaces for diagnostic devices (HLT-04). Future work would look to move to nano-resolution (< 100 nm) ambient MS; application in the development of POC diagnostics and medical *in vivo* imaging.

Risks - Spatial resolution dependent on sensitivity – Mitigation: research to improve ionisation and collection efficiency in 1.
Large step changes needed to improve quantification - Mitigation: Basic fundamental understanding of techniques.

Knowledge Transfer and Exploitation - Dissemination will be through: 1) Peer-reviewed publications in high-impact journals, organisation of an IUVSTA workshop on ambient MS and oral presentations at international meetings. We will lead the Ambient Surface Mass Spectrometry session at British Mass Spectrometry Society and contribute to the leadership of imaging MS in the American Society for Mass Spectrometry. 2) Development of international ISO standards and CCQM SAWG. ISO TC 201 on surface chemical analysis has recently established a new study group on IMS. 3) A stakeholder workshop enabling industry to conduct trial experiments and provide a good practice guide for AIMS. Direct consultation and guidance to industry, government departments (NHS, FERA, DSTL, HO) and NMIs (KRISS, BAM) to enable establishment of their own analytical capability.

Co-funding and Collaborators -The project has strong stakeholder support from industrial partners (AZ, GSK, Novartis, Unilever, P&G, Dow, Syngenta, Croda, Pilkington, Johnson Matthey, BP, Perkin Elmer, Smith and Nephew, GE healthcare, Molecular Profiles) and instrument manufacturers (Thermo, Waters, Elforlight, KR analytical). The project will benefit from equipment loans and access to equipment otherwise unavailable in an NMI, and industrially relevant samples and materials (in-kind value ~£60k). Collaboration with internationally leading academic groups including Prof Graham Cooks (Purdue), Prof Renato Zenobi (ETH-Zurich), Profs David Barrett and Morgan Alexander (University of Nottingham), Prof James Bradley (University of Liverpool), Prof Colin Creaser (Loughborough University), and Dr Zoltán Takáts (Justus-Liebig University). Co-funding will be sought through TSB, EMRP and FP7 with the companies and academic groups identified above. As part of ChemBio project NB4, NPL already has an EPSRC co-funded (worth £225k) post-doctoral researcher (Dr Andrew Bowfield) to develop imaging PADI.

Deliverables

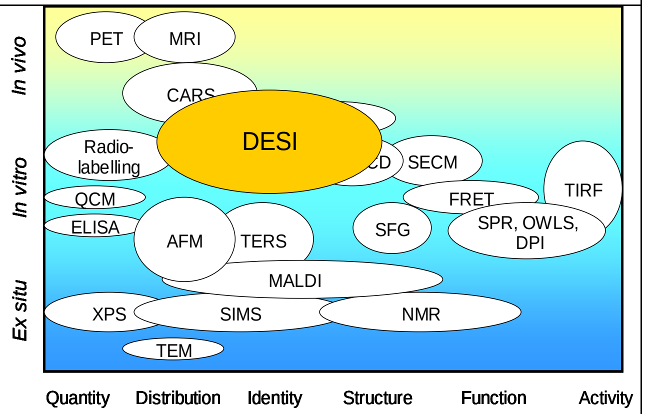
1	**Start: 01/07/12**	**End: 31/03/15**	
Fundamental metrology and quantification of ambient surface MS as evidenced by a good practice guide and 4 peer-reviewed publications			
2	**Start: 01/07/12**	**End: 01/03/14**	
Establish 10 μm resolution PADI imaging capability (iPADI) and 3 peer-reviewed publications			
3	**Start: 01/11/12**	**End: 31/03/15**	
Establish laser ablation imaging and innovative desorption/ ionisation to achieve nanoscale (500 nm) chemical images.			
4	**Start: 01/07/13**	**End: 31/03/15**	
Advance key application areas in ambient MS as evidenced by a stakeholder workshop			

Project No.	**NS001SA2**	**Price to NMO**	£415k
Project Title	Ambient imaging mass spectrometry	**Co-funding target**	
Lead Scientist	Ian Gilmore	**Stage Start Date**	01/10/09
Scientist Team		**Stage End Date**	31/03/13
		Est. Final Stage End Date	
Sector	Underpinning metrology	**Activity**	Methodology for new capability

Summary

For biological studies there is a strong demand for analytical techniques that operate in ambient conditions and there are great benefits if techniques can operate *in vivo*. This has been identified as a major metrology requirement in a recent EU report on needs for standardisation in Research and Development in nanotechnologies. This underpinning knowledge base project will develop the foundations for the use of ambient MS, for reliable and valid measurements across the range of application sectors. This is essential to enable ambient MS to be developed beyond exploratory research and into use at analytical and testing laboratories and production line or field analysis.

The Need



There is a major requirement for analytical techniques with high chemical specificity and sensitivity that can operate in ambient conditions and in a portable unit. For many industrial devices and products, the surface chemistry is critical but the samples are not compatible with vacuum-based surface chemical analytical techniques. Desorption Electrospray Surface Ionisation (DESI) is a powerful mass spectrometry technique that gives full MS/MS information, but directly analyses the samples of interest without sample preparation. Figure 1 shows how different analytical techniques contribute to the biological measurement requirements that span from quantification and identification through to structure, function and activity as well as the operating environment from *in vacuo* through to *in vivo*. It is clear that DESI and related methods are strategically important. However, many users report issues in its robustness and reliability. Typically repeatability is 50% and, for industrial use, this needs to be regularly < 10 %, and results need to be comparable between instruments.

DESI shows great potential in molecular analysis, with the potential for ambient imaging, in field, *in vitro* or *in vivo* instantaneous molecular analysis. To fulfil this potential requires underpinning metrological research, to enhance the usability, robustness and reliability of the technique.

The Solution

To improve DESI repeatability and constancy to better than 10%, to build confidence in the technique for measurements in healthcare, security and pharmaceuticals. To provide a user guide to direct analysts through the range and effectiveness of DESI. To establish the capability of DESI for a range of measurements including analytical area, depth sensing, reaction monitoring and low detection limits.

Project Description

This knowledge base project will build on and grow the successful collaboration with LGC in the current Chem Bio programme that has made significant progress in developing the basic metrology for reliable analysis using DESI. Here, we aim to establish a simple procedure to set optimal DESI conditions; this will lead to improvements in the robustness and comparability of the technique. Then, from this base we will develop a method and procedure for the improvement of DESI repeatability and constancy to better than 10%. This work will develop in collaboration with instrument manufacturers such as ABI, Waters, Thermo and Shimadzu to ensure consistency across MS platforms.

It is essential for industry to have a clear understanding of the regimes of effectiveness when using DESI – which materials it works well for and those for which it does not work. In this work, we develop the understanding to map out which materials may be analysed effectively using DESI. We will provide clear guidance and validated protocols to help analysts optimise DESI for the analysis of different classes of material. A metrological framework will be developed to support and optimise the technique for a range of different issues such as sensitivity or spatial resolution. Firstly we will evaluate sensitivity of DESI, developing standard methods for measuring limits of detection by understanding the erosion of material (analogous to sputtering yields) and efficiency of the DESI process. Secondly a procedure for the characterisation of DESI lateral resolution and optimisation will be extended from our present work to include reference materials to measure resolution. We will also investigate possible ways to improve limits of sensitivity and spatial resolution by sniffers, grids, enclosures or other instrumental improvements. Thirdly we will look into the potential to obtain additional information such as DESI depth resolution and using DESI as a real time probe.

Impact and Benefits - Desorption Electrospray Surface Ionisation (DESI) is a powerful mass spectrometry technique: It has shown the ability to identify pharmaceuticals, explosives, proteins and a range of biological materials [Science 306 (2004) 471]. It is capable of molecular image analysis for a range of samples including tissues [Science 311 (2006) 1566], with optimum spatial resolution of the order of 100 μm. It can give femtomole sensitivity [Anal. Chem. 77 (2005) 6755], high throughput analysis [Anal. Chem. 80 (2008) 6131] and real time analysis for reaction monitoring [Anal. Chem. 79 (2007) 5064]. Molecular detection can be attained from a wide range of materials including creams from skin, explosives on plastics and textiles [J. Forensic Sci.53 (2008) 807], metabolites from dried blood, and lipids from animal and plant tissues [IJMS 259 (2007) 8]. It is possible to couple the technique with mini-MS for a handheld ambient molecular analysis device [Anal. Chem. 80 (2008) 4026]. Molecular examination of complex surfaces, *in situ*, *in vitro* or *in vivo*; to give rapid chemical or biological analysis as well as image analysis is critical in a wide range of novel application areas. There are many strong examples of the potential of DESI and complementary techniques in areas such as high throughput analysis of pharmaceuticals, detection of explosives, forensic analysis, environmental monitoring, counterfeit detection, imaging of cancer tumours or monitoring of catalytic reactions. However, definitions, measurement methods and reference materials are necessary to ensure comparable results from day to day and from laboratory to laboratory. This project will impact all these areas.

Support for Programme Challenge, Roadmaps, Government Strategies

Across a wide range of bio-chemical areas it is increasingly important to use label-free imaging for *in vivo* analysis, and this is stated as a research priority in "Nanomedicine- European Technology platform 2006". A mass spectrometry approach is required such as DESI.

One of the top science and technology priorities for the MoD is advances in "man-portable biological detection systems" (Defence Technology Strategy); ambient mass spectrometry could be key to achieving this aim.

The DIUS ChemBio strategy for 2008 points out that a key aim is to "support innovation and competitiveness through the development of reliable leading-edge measurement". One of the major drivers is "chemical analysis in ambient conditions", where it is suggested that new techniques such as ambient mass spectrometry' may have a major role to play. Consultation with industry showed a strong demand for the development of metrology in Ambient Mass Spectrometry. At the consultation workshop [SAMS V, NPL Report October 2008] this project ranked as one of the highest needs overall projects.

Synergies with other projects / programmes - In this project, which is in collaboration with LGC, we develop the measurement infrastructure for reliable measurements using DESI, to enable industry to make full use of its potential and capabilities. Therefore it will support a wide range of companies, many who are already presently interested in this field, from major companies such as Unilever, Smith & Nephew, Johnson & Johnson, AstraZeneca, GSK, Shell, BP, BAE, Pilkington's, Syngenta, 3M, Proctor and Gamble, Thermo, Applied Biosystems, as well as supporting smaller high-innovation companies and instrument manufacturers such as Intertek, LSA Ltd, CSMA Ltd, and Millbrook instruments and other government departments or national laboratories such as DoH, Dstl and the Institute of Food Research. The programme has very strong academic collaborations in the UK and internationally.

Risks - The project has relatively low technical risk which is mitigated by the range of partners and the extensive expertise within them.

Knowledge Transfer and Exploitation - KT including provision of expert advice to UK industry and academia, 3 publications, presentations at meetings, the production of reference data on the website.

Co-funding and Collaborators - Co-funding opportunities will be utilized where possible to maximize the Government investment. This project is in collaboration with LGC and with a range of stakeholders who wish to utilize the capabilities of DESI across a range of sectors.

Deliverables

1	**Start: 01/10/09**	**End: 31/03/13**	
Deliverable title: Develop methods to improve the repeatability of DESI to better than 10%.			
2	**Start: 01/10/09**	**End: 31/03/13**	
Deliverable title: Identify the classes of materials and substrates for which DESI is effective and provide a guide to analysts.			
3	**Start: 01/10/09**	**End: 31/03/13**	
Deliverable title: Evaluate the detection sensitivity of DESI and measure the rate of material removal, depth resolution and useful lateral resolution.			
4	**Start: 01/10/09**	**End: 31/03/13**	
Deliverable title: KT including provision of expert advice to UK industry and academia, 3 publications, presentations at meetings, the production of reference data on the website.			

Project	TS0040203 - 2.3 (Strategic Capability)		Price to NMO	£421k
Project Title	Graphene for Metrology		Co-funding Target	
			Start Date	01/04/10
			End Date	31/03/13
Lead Scientist	JT Janssen			

Vision
Exploiting the unique properties, in graphene to develop novel quantum metrology. Examples are universality of the quantum Hall effect, and digital electronics beyond CMOS based on charge and/or spin transport.

Impact & Benefits
A redefinition of the SI based on quantum electrical standards remains controversial. If the electrical triangle of quantum standards can be tested in graphene, a completely different system from conventional semiconductor 2DEG materials, this key SI development would be placed on a firmer basis. In addition graphene is a unique material, the strongest known, with a range of properties important for future nanometrology. It has very low spin-orbit coupling making it potential useful for spintronics applications and for quantum spin Hall effect which may in future provide a new standard. Its high thermal conductivity should benefit the semiconductor industry beyond Moore's law.

Support for Programme Challenge
This proposal is precisely aligned with the strategy of the Pathfinder Programme; "*To develop an SI wholly defined in terms of fundamental constants of nature*". It supports the plans of the international community to refine the SI. It will explore novel techniques and carry out a range of targeted R&D to anticipate future NMS requirements thereby supporting the aim "*development of the SI*".

Support for Government Strategies
This project directly supports:
a) the NMS strategy for the DIUS National Laboratory to "maintain NPL's leading international status" "shaping (and leading) European priorities for metrology research"
b) the underpinning metrology strategy "foundation for the SI"
c) Strongly supports government Nanotechnology strategy and digital economy.

The Need
The quantum Hall effect (QHE) currently forms the basis for maintaining the electrical unit of resistance in the SI system. It requires low temperatures (below 1K) for successful operation. A recently discovered material, graphene, could be used to make QHE devices which work at significantly higher temperatures. This creates the opportunity to increase the accessibility of quantum standards beyond the few top-level NMI's. The novel band structure of graphene (massless Dirac fermions) gives a unique opportunity to perform an in-depth study of the universality of the QHE and related effects. This is of fundamental physical importance, and has been given added urgency by the proposed re-definition of some of the SI base units. In addition, there are no known solutions beyond the end of Moore's Law in CMOS; graphene might hold the answer.

Current State of the Art (NMI and elsewhere)
Some preliminary work on the optical and electrical properties of graphene has been undertaken through a SR project at NPL. Other NMIs have also embarked upon graphene studies including an attempt to make a precision measurement of the QHE (incidentally using an NPL built CCC bridge). NPL together with the Brazilian NMI – INMETRO has recently performed an STM study of graphene on SiC. Very recently NPL has made a very accurate measurement of the QHE in epitaxial grown graphene 4 orders of magnitude better than the previous result. This work (arXiv:0909.1220, submitted for publication) puts NPL firmly in the lead internationally in the field of graphene metrology.

The Solution
In single and two-layer graphene the very high mobility of the zero gap semiconductor means that the QHE is observable even at room temperature, though without fully flat plateaux. It is as a result of quite different physics that a comparison between graphene and GaAs is so important for assessing the fundamental nature of *e* and *h* in condensed matter systems. Our focus will be on producing samples with a high mobility using novel fabrication techniques and measuring the QHE at elevated temperatures around 4K which would be possible in a modest (<10T) magnetic field. In addition the success of our epitaxial grown graphene means that we can for the first time embark on proper device design and large-scale integration of graphene electronics.

Metrology Capability to be Delivered
As well as a test of the universality of the QHE, the future applications of graphene to other topological electrical standards involving spin current will also be explored.

Project Description
Preparation and measurement of graphene membranes with varying layer numbers using Raman, optical absorption and SPM. Then fabrication of gated and patterned graphene nanoribbons (GNRs) as planar device prototypes for initial studies of their band gap engineering possibilities and fine-tuning of electronic, magnetic and spin properties. A detailed study the QHE and a comparison between graphene and GaAs. In addition investigation of graphene's exceptional thermal properties will be carried out with the aim of improving thermal transfer in nanoscale high-speed circuits. Explore the potential of large-scale graphene-based electronics.

Exploitation/Spin-Offs
NPL already has a proven track record in the commercialisation of quantum electrical standards and their associated instrumentation. If a highly accurate quantum Hall effect can be demonstrated at elevated temperatures than a portable tabletop quantum standard could be realized. Epitaxial grown graphene opens many opportunities for novel electronic and spintronic devices which could be incorporated into standard CMOS architecture.

Project Partners
Manchester U. (exfoliated graphene), Imperial College (graphene oxide large area films), Surrey U., Graphtronics consortium, INMETRO

Co-funding

Our FP7 proposal Graphtronics aiming to develop largescale production technology for high quality graphene based nanostructures and to understand the fundamentals of charge and spin transport has passdc the first stage review with flying colours. Graphtronics will co-fund this proposal to the tune of £345k if successful.

Summary of Technical Work

We have recently demonstrated that epitaxial grown graphene produces a QHE which is better than that in exfoliated graphene and comparable to that observed in standard GaAs. Although the mobility in epitaxial graphene is not yet as good as exfoliated graphene. We do not yet understand why this is the case and a detailed characterisation and comparison of both material is essential. We propose to use a number of well-developed techniques within NPL to do this (Raman, AFM, STM, thermal transport). One of the key objectives is to understand the interaction of epitaxial graphene with the substrate and its defects.

The epitaxial graphene allows us to perform a very detailed study of the QHE as a function a several key parameters (sample size, carrier type and density, mobility and temperature). This will be of interest to both physicists and metrologists with the aim of proving the universality of the QHE.

Having fully characterised graphene next we want to move to device fabrication. Fabrication of gated and ebeam patterned graphene nanoribbons (GNRs) as planar device prototypes for initial studies of their band gap engineering possibilities and fine-tuning of electronic, magnetic and spin properties. Utilize a range of gate and contact materials to improve the performance of graphene devices, e.g. high-k dielectrics, ferromagnetic contacts, etc. Development of quantum dots and wires on graphene with the aim of producing the first electron pump. Compare results with suspended graphene.

The last logical step is the development of large scale integrated circuits based on graphene in combination with other materials.

Synergy with Other Projects

The study of graphene involves a number of techniques which have been developed in the other quantum detection projects. On the flip side graphene offers a number of novel applications to these projects. These projects are Quantum Current Standard, Nanomagnetism and NEMS.

Risk

Graphene science is a highly competitive area of research and several renowned research institutes and metrology laboratories are perusing the same goals. Others could get there first. We have to ensure that adequate manpower is available for this project and that NPL can fully exploit its recently acquired leading position in this field.

Knowledge Transfer Plan

We aim to publish high-quality papers in leading scientific journals. Give presentations at international conferences. Disseminate our metrological results through the CC and TC working groups to other metrology laboratories. Build collaborations with international partners and industry.

Deliverables

1	**Start: 01/04/10**	**End: 30/03/11**
Demonstration of a system capable of a comparison between graphene and GaAs quantum Hall samples with an accuracy of 1x10^10		
Evidence: Demonstrate (or not...) universality of the QHE by comparison with QHE in GaAs.		
2	**Start: 01/04/11**	**End: 30/03/12**
Demonstrate a combined Raman and transport measurement to support the understand of quality and edge structure issues impacting on future graphene applications		
Evidence: Understanding of graphene properties and role of the substrate published		
3	**Start: 01/04/12**	**End: 30/03/13**
Demonstration of an electro-statically tuneable quantum dot devices in epitaxial graphene		
Evidence: Fabricate graphene devices with optimized properties for studying dimensionality effects, spin/charge effects and thermal effects.		
4	**Start: 01/10/2010**	**End: 31/03/2013**
COFUNDING: Cofunding for FP7 Graphtronics.		
Evidence: results are published		

Project No.	TS003409	Price to NMO	£800,000
Project Title	Cofunding for EMRP 17e Traceable Radiometry for Remote Measurement of Climate Parameters project (optical element)	Co-funding target	£760,000 (in place)
Lead Scientist	Dr Nigel Fox	Stage Start Date	OCT-2011
Scientist Team	Dr Andrew Levick, Dr Emma Woolliams, Dr Theo Theocharous, Agnieszka Bialek, Ruth Montgomery	Stage End Date	SEP-2014
		Est Final Stage End Date	2014
Sector	Climate Change Targets	Activity	NMS infrastructure / Challenge Driven

Summary

Under the framework of the European Metrology Research Programme Joint Research Project (JRP) ENV04 'European Metrology for Earth Observation and Climate (MetEOC)', this project will establish greater coordination and focus more effort on the underpinning metrology, to realise practical, efficient, cost effective, "fit for purpose" traceability for the European EO community. Particularly:

• Satellites require improved uncertainty and traceability through all stages of data production: pre-flight and post-launch calibration and validation and all the intermediate processing steps,

• Data interoperability across the full electro-magnetic spectrum; maintaining and improving the uncertainty available from primary standards and facilities.

• Evolution of laboratory-based metrology, field metrology, and space metrology.

This project is co-funded by the European Metrology Research Programme Joint Research Project (JRP) ENV04 'European Metrology for Earth Observation and Climate (MetEOC)'.

The Need

Remote monitoring of the Earth system is crucial to enable better stewardship of the environment to provide the information to policy makers developing appropriate mitigation strategies for climate change. Global observations can only be made from space, and although such observations are being made, the harsh and challenging environment of space limits the uncertainty currently attainable. In the specific case of climate this is often a factor of 10 larger than required by the community. The drive for reduced uncertainty and the need to combine data from a variety of sources has placed "traceability" at the top of space agencies and GEO (Group on Earth Observation) community's agenda. The goal of GEO to establish a Global Earth Observation System of Systems (GEOSS) by 2015 is recognition that no single nation or region has the resources provide a full global earth observing system with the accuracy needed for climate.

The Solution

This project will establish greater coordination and focus more effort on the underpinning metrology, to realise practical, efficient, cost effective, fit for purpose traceability for the European EO community. Particularly;

• Satellites require improved uncertainty and traceability through all stages of data production: pre-flight and post-launch calibration and validation and all the intermediate processing steps,

• Data interoperability across the full electro-magnetic spectrum; maintaining and improving the uncertainty available from primary standards and facilities.

• Evolution of laboratory-based metrology, field metrology, and space metrology.

Project Description (including summary of technical work)

Within the framework of the EMRP JRP ENV04, this project will establish new transfer standards and methods to improve accuracy and traceability (by factors between 2 to 10) for:

• Laboratory based (air and vacuum) pre-flight calibration of optical and microwave imaging cameras

• In-flight (on-board) calibration for optical imagers and atmospheric limb sounders

• Surface based "test-sites" for the post-launch calibration and validation of land and ocean imaging radiometers

• Models and algorithms to improve performance and traceability of level 2 (L2) land products

• Prototyping techniques to establish an "SI traceable benchmark measurements from space". This will underpin the upgrade of current sensors, and enable a global climate observing system

Impact and Benefits

Although this project focuses on the remote sensing community and the needs of climate, this JRP will identify detailed requirements for the future and build partnerships to ensure full use is made of all relevant European metrological expertise. This will include organisations not eligible for funding under the current EMRP, co-aligning where possible with other related projects within Europe and elsewhere.

To build a long-term evolving and sustainable set of capabilities, infrastructure and expertise with minimal duplication requires a "European centre of excellence", and a subsequent goal from this JRP is the establishment of a virtual European Metrology Centre for Earth Observation and Climate (EMCEOC). If this were established it would encompass the metrological aspects of all Earth Observation application domains and provide a "one-stop-shop" to support the needs of those in industry and academia engaged in the calibration and validation of Earth Observation instrumentation and associated products.

Support for Programme Challenge, Roadmaps, Government Strategies

Extend scope to establish SI traceability for Oceans; Faster uptake of outputs through establishment of prototype services as international demonstrators; Commence work on validation of models/algorithms used to process sensor signals into real bio/geo-physical parameters. Quality assurance of evidence to support environmental monitoring and enables collection of climate quality data to inform Government strategies.

Synergies with other projects / programmes

QI at pixel of image linked to project 2.2 and also existing and likely future SSfM programme. CSAR will provide the international reference standard for photovoltaic efficiency- project 4.4. Ocean colour traceability will build on transfers standards under development in Project 2.2. Operational land imager test site use and adapt mathematical models developed in Project 2.2. Microwave metrology requirements are addressed under a separate, but linked project 4.10.

Risks

Many of the target outputs from this programme are highly challenging and full success will depend on contributions from collaborators. However, traceability in this field is so immature that even incremental gains in accuracy or even improved confidence in the processes through the robust analysis that will occur within this project will be seen as a success by the EO community.

Knowledge Transfer and Exploitation

The results of this JRP will be widely disseminated through peer-reviewed papers, trade journals, news articles, conference presentations, Good Practice Guides and 3 case studies (covering validation of "forest carbon" estimates and uncertainty analysis) that will be used to provide training on how to evaluate uncertainties in EO systems. The JRP will also provide metrological advice for EO applications and climate via a helpline, and provide advice and technical input to standards organisations, including supporting the evolution and implementation of international EO specific standards such as QA4EO. Additionally Stakeholder workshops will be held to establish roadmaps of priority metrology need for the EO sector. All activities will be promoted on the JRP website.

Co-funding and Collaborators

Matching co-funding funding provided by EMRP under ENV04 'European Metrology for Earth Observation and Climate (MetEOC)'. Funded JRP consortium members include PTB, INRIM, JRC, LNE, AALTO, MIKES & WRC-PMOD. Unfunded JRP consortium members include Bergische Universität Wuppertal (BUW Germany), Deutsches Zentrum f. Luft- und Raumfahrt e.V. (DLR Germany), Forschungszentrum Juelich GmbH (FZJ Germany), and Geodeettinen Laitos (FGI Finland).

Deliverables

1	**Start: 01/10/2011**	**End: 30/09/2014**	

Deliverable title: Management, coordination and completion of EMRP JRP ENV04 MetEOC

Evidence: Management, coordination and completion of deliverables EMRP JRP ENV04 MetEOC as detailed in JRP contract.

Project No.	MAT\2011\21	**Price to NMO**	£800k
Project Title	Grains to Structures	**Co-funding target**	£640k
Lead Scientist	Mark Gee / Alan Turnbull	**Stage Start Date**	July 2011
Scientist Team	Ken Mingard, Bryan Roebuck, Nigel Jennett, Jerry Lord, Tony Fry	**Stage End Date**	June 2014
		Est Final Stage End Date	June 2017
Sector	Advanced Manufacturing and Services	**Activity**	Methodology for New Capabilities
Project Champion	Rachel Thomson		

Summary

This project launches the Materials Division in a new underpinning activity to develop and integrate measurement and modelling tools to characterise and generate fundamental understanding of mechanical properties and material characteristics at the sub-grain level. This bottom-up approach, focussed on 3D structural, compositional and mechanical characterisation, coupled with mathematical modelling and macroscopic property and performance measurement in complementary projects will provide the springboard for the development of materials with engineered properties and for prediction of material performance in service from fundamental principles.

The Need

The major drivers in our society include (though not exclusively) energy security, sustainability, reduced impact on environment, improved quality of life, competitive manufacturing and job creation, potable water availability, and information technology/communications. Underpinning the future requirements of all of these is the need to develop novel materials with tailored properties, to make radical advances in materials processing, to optimise manufacturing and engineering through knowledge-based design, and to establish innovative tools for predicting and characterising performance. Characterisation of processes at an increasingly localised scale is recognised as the basis for predicting, rationalising and manipulating macroscopic behaviour. Specifically, 3D sub-grain microstructural characterisation coupled with local mechanical property measurement and supported by multiscale modelling is required. Current capability for microstructural characterisation at NPL and elsewhere is largely based on 2D techniques. There is evolving work on 3D FIB/SEM at a small number of UK universities such as Manchester and Loughborough and centres for microscale X-ray tomography at Manchester and Southampton. Nanoscale mechanical property measurement can be made with nanoindentation and AFM systems but there has also been work on the use of FIB to produce localised small scale pillar and cantilever samples (Steve Roberts, Oxford) for mechanical property measurement. However, these varied studies are at an academic research level and need to be developed on a sound metrological basis with the focus on application to industry.

The Solution

Adopting a progressive long-term strategic approach, measurement and modelling tools will be established to enable understanding of material behaviour at length scales smaller than the grain size with a capability for integrating information to prediction of macro-scale properties and performance. Specifically, 3D characterisation of material microstructure, microchemistry, strain and stress distribution, and mechanical properties will be demonstrated and linked to modelling of crystal plasticity to provide the necessary physical insight. The information generated at this local level will then be correlated with macroscopic measurements undertaken in satellite projects; for example, on wear and environment induced cracking.

Project Description

Phase I, for which funding is sought in this round, is geared primarily to establishing the efficacy and reliability of using focused ion beam machining combined with scanning electron microscopy - energy dispersive X-ray spectroscopy and electron back-scattered diffraction to characterise the near-surface microstructure and microchemistry in three dimensions and its dependence on material history. Such 3D characterisation is still in it embryonic stage and a key output will be a good practice guide on the effective utilisation of the approach and potential uncertainties in measurement. Particular attention will be given to issues such as the accuracy and resolution of the processes used to determine the 3D information, control of ion beam damage to samples, and the integration of information from the multitude of analysis and imaging sources that are available.

Complementing this activity, established nano-mechanical techniques will be used to determine mechanical properties on a sub-grain and grain to grain basis by high resolution mapping. Some work will also be carried out to explore the feasibility of making mechanical property measurements in-situ in the dual beam instrument using the ion beam machining of nanoscale compression pillars or cantilever beams, or in-situ nanoindentation of specific areas revealed during ion machining. This will enable direct correlation of mechanical properties with microstructure. Furthermore, sub-grain measurements of residual stress is being developed in a separate satellite project and the methodology will be applied to evaluate local variations in residual stress for direct correlation with other property data.

Two systems will be studied with these techniques. In the first instance, WC/Co hardmetals will be investigated, for which there is substantial property measurement data available at NPL. The second system will be a corrosion resistant alloy commonly used in the oil and gas industry, the stress corrosion cracking resistance of which is being investigated in a parallel project.

Crystal plasticity modelling of the strain distribution in single grains and in multiple grains will be initiated in order to provide the fundamental physical insight necessary to rationalise the measurement data, while at the same time the latter provides a test of predictions. An important element of this work will be to ensure that the constraint that comes from small size of distinct phases in the materials is taken into account. This modelling work will be undertaken in collaboration with Imperial College through a post-doctoral fellowship with a view to developing an in-house capability in the long term.

Impact and Benefits

- Knowledge-based design of materials microstructure to give best and predictable long-term performance;
- Increased lifetime of components and structure and more efficient deployment of materials in the mining, mineral extraction, manufacturing, automobile, aerospace, rail, and power generation sectors;
- The project will provide UK industry with an integrated approach to prediction of materials performance based on a sound foundation of microstructural characterisation and mechanical property evaluation with sub-grain resolution. This will be aimed at supporting materials and component development and durability, extending in-service performance, and contributing to the validation of finite element models, structural integrity codes and material performance models.

This project will place NPL at the leading edge of international research in the area of materials characterisation, and long-term prediction of materials performance.

Support for Programme Challenge, Roadmaps, Government Strategies

This project fits with the NMO and NPL strategic aims for measurements and modelling to characterise atoms, molecules, bio-systems and materials, and science to support sustainable technologies in the areas of energy generation and usage, and high value manufacture, including life assessment. It also aligns with the TSB strategies for advanced materials and high value manufacturing.

Synergies with other projects / programmes

The project:

- Builds on projects A20 In-situ techniques for measuring stress and strain, AM09 Low friction coatings, P18 Traceable Microstructural Measurements, and T11 Monitoring the degradation of surfaces subject to wear
- Supports project on stress corrosion cracking of corrosion resistant alloys (P13)
- Underpins proposed Materials 2011 short crack growth project
- Links to proposed Materials 2011 micro-relaxation techniques for residual stress project

This project has a 6 to 9 year vision, so the work described in this proposal has detailed deliverables for the first three years only. In future work, increasing engagement with industrial partners is envisaged as the evolving capability is progressively shifted from the development phase to extended application.

Risks

The main risk is associated with significant technical challenges in achieving traceable 3D nanoscale characterisation of materials with dual beam FIB/SEM technology including registration of information, 3D reconstruction, and integration of the different sources of information in the instrument. There are also risks with the in-situ mechanical testing and modelling aspects of the project such as the derivation of mechanical property information to describe the behaviour of specific phases from simple tests with the high spatial resolution that will be required. All these risks will be mitigated by working in collaboration with established experts in the different field to ensure success.

Knowledge Transfer and Exploitation

A key output will be a draft Guide to Good Practice in 3D Characterisation of Materials Microstructure and Microchemistry developed in collaboration with leading researchers in the field. Application of the methodology will be highlighted in 6 scientific papers and 2 conference papers. Industrial sectors targeted will be mineral extraction, power generation, aerospace, materials supply and oil and gas sectors.

Co-funding and Collaborators

Phase 1 of this project is designed to be underpinning but in collaboration with major firms in the relevant industries, such as BP, Alstom, EoN, Airbus, BAe, Tata Steel, and Tata Group (Jaguar-Landrover). Collaboration with leading science base institution such as Oxford, Manchester, Bristol and Loughborough Universities will be key to the success to the project.

Industrial steer and early reporting of results will be gained from participation in relevant Industrial Advisory Groups including the Power, Surface Technology, and Oil and Gas IAGs. NPL will also participate in and promote the activities of user groups for 3D microstructural characterisation.

This project will support a NPL/EPSRC PDRA at Manchester University with £500k funding from EPSRC on the application of FIB to the 3D characterisation of materials. It is also planned to have a post doctoral research fellow with Imperial College to work on the modelling of 3D microstructures with one year of guaranteed funding from NPL with funding sought for the subsequent 2 years from EPSRC.

Deliverables

1	**Start: July 2011**	**End: June 2014**	
FIB - 3D characterisation of material chemistry, and structure. Good Practice Guide			
2	**Start: July 2012**	**End: June 2014**	
Correlating mechanical properties and material characteristics at the sub-grain scale with application to rationalising the performance of hardmetals and corrosion resistant alloys - scientific paper			
3	**Start: July 2012**	**End: June 2014**	
Modelling crystal plasticity and its validation using sub-grain material property measurement – conference paper			

Pathfinder Project	TS0040402		Price to NMO	£829k
Project Title	**Solid-State Quantum Technologies**		Co-funding Target	
			Start Date	01/04/2010
			End Date	30/06/2013
Lead Scientist	**Alexander Tzalenchuk**			

Vision

This project aims to develop measurement capabilities enabling scalable technologies for creating, interlinking, cooling, operating and measuring electric circuits down to the quantum limits.

Impact & Benefits

The most notable application of the engineered quantum systems would be in quantum computing. The practical significance of building a successful large scale quantum computer is tremendous: It will provide a powerful tool for *encryption in national security*; will be used to solve highly complex (many-body) problems in a reasonable amount of time for the *climate modelling, chemical and biological sciences*; provide rapid *search engines* to help navigate through the information age; allow *efficient simulation* of larg quantum systems. Superconducting quantum integrated circuits satisfy DiVicenzo criteria for the implementation of quantum computation. External need in metrology support for quantum computing was a clear message of a recent Seminar On Quantum Measurement and Metrology with Solid State Devices organised by PTB with very strong international attendance. AT gave an invited talk.

Support for Programme Challenge

This proposal is precisely aligned with the strategy set by the "Quantum information processing and communications" priority theme of the Pathfinder Programme: *Using quantum properties as a unique resource in computation, communications and measurement science to perform functions which are intrinsically inaccessible to technologies based on macroscopic devices ruled by the laws of classical physics*.

Support for Government Strategies

This project directly supports: the NMS strategy for the DIUS National Laboratory to "maintain NPL's leading international status" "shaping (and leading) European priorities for metrology research".

The Need

Quantum computing requires *scalable technologies*, based on methods of coupling quantum circuits at will without loss of coherence and architectures, which can be integrated/interfaced with conventional electronics. Longer coherence times are required for individual quantum circuits. Fast, lossless and tuneable interconnecting elements are required as well as innovative interfacing solutions.

Current State of the Art (NMI and elsewhere)

The capability to design, build, operate, measure and understand solid-state quantum circuits becomes increasingly important for the credibility of NMI's. NIST has a big programme on quantum computing using Josephson junction circuits integrated with superconducting resonators. PTB and VTT were involved in FP6 projects on quantum computing with superconducting circuits, and now lobby to include this topic in one of the next EMRP calls.

In particular, great effort of late has seen the decoherence times improved dramatically from a few nanoseconds to an order of microsecond mostly through exclusion of extrinsic noise. Use of interlinking microwave buses, which the group have advocated for years, has become widespread.
Unique NPL expertise, proven by publications (see e.g., T. Lindström et al., PRB 80, 132501 (2009)), is in dielectric-free superconducting devices, low-loss tuneable superconducting resonators and ultra-sensitive dielectric loss measurements.

The Solution

Superconducting materials are well protected from decoherence by the superconducting gap. Intrinsic losses are primarily attributed to dielectric materials – junction barriers, substrates and oxides on the surface of the superconductor – at high frequencies. Further improvement of decoherence time can only be achieved through understanding the nature of fluctuating atomic defects in dielectric materials, better materials with improved bonding of atoms (such as grown by atomic layer deposition, ALD) and novel architectures, which avoid dielectrics altogether. Higher complexity of microwave quantum circuitry, including switches, frequency-tuning elements, microwave splitters, etc., which do not compromise the decoherence time, can only be realized by introduction of novel on-chip quantum circuits.

Metrology Capability to be Delivered

NPL expertise will be extended to novel materials, ultralow temperatures and single-photon levels. Quantum measurements on electrical circuits, presently unavailable at NPL, will be demonstrated.

Project Description

1. Understanding decoherence mechanisms in superconducting quantum circuits. The group shall perform measurement of microwave dielectric losses in novel low-loss dielectrics (e.g., ALD dielectrics), at mK temperatures and extremely low microwave power down to a single microwave photon level. Potential of alternative, dielectric-free devices (QPS and Andreev qubits), will also be assessed.
2. Development of tuneable superconducting buses interlinking quantum circuits. The project will address the crucial issue of multiplexed readout and fast tuneable coupling of quantum circuits. These will be achieved through already tested magnetic control of superconducting lines and also through introduction of novel superconducting (e.g., on-chip "hybrid ring") and nano-electromechanical coupling elements.

Exploitation/Spin-Offs

There is documented interest from academia (e.g., DigiQub) and industry (e.g., NTT) in NPL expertise in the enabling solid-state quantum technologies, such as dielectric-free superconducting devices by FIB, tuneable superconducting resonators, NEMS, ultra-sensitive measurement of dielectric losses.

Results of the project will be exploited *internally* as the new major expertise and capability to perform quantum measurement on electrical circuits and *externally* through licensing out IP on individual quantum components and circuits. A patent has recently been filed by NTT and NPL to protect a microwave dielectric loss probe based on lumped element resonators.

Project Partners

Royal Holloway, Birmingham, NTT, DigiQub consortium.

Co-funding

FP7 proposal DigiQub in collaboration with 10 NMIs, universities and companies was unsuccessful. There is a strong intention to submit a follow-on proposal aiming to realize the concept of scalable quantum-classical circuits through development of superconducting quantum bits with longer coherence time and integration with RSFQ logic. An EPSRC/NPL funded post-doc (Tobias Lindstrom) is already working on frequency multiplexing, which utilizes superconducting buses.

Summary of Technical Work

<u>Understanding decoherence mechanisms in superconducting quantum circuits</u>

- Design and fabrication of a microwave resonator dielectric loss probe
- Development of a technology for localised deposition of thin-film dielectric samples on the probe
- Measurement on thin film dielectrics, such as ALD films of $Al2O3$ or $Hf2O3$
- Modelling of the probe response to the dielectric material
- Comparison of losses in dielectric materials used in quantum circuits; pinpointing the defects responsible for dielectric losses.

<u>Development of tuneable superconducting buses interlinking quantum circuits.</u>

- Design and fabrication of on-chip microwave components, such as frequency shifters, splitters, and tuneable couplers
- Functionality tests using superconducting waveguides and resonators comprising the designed components
- Integration of superconducting qubits produced by the project partners with the microwave circuitry
- Operation of coupled quantum circuits

One of the most striking scientific advancements in recent years has been the development of solid state two-level systems (qubits) to the point where they can used in many experiments that are analogues to well known experiments in atomic physics and optics. In order for this field to progress there is a need for on-chip microwave circuit elements that are equivalent to elements typically used in quantum optics: beam splitters, phase shifters, adjustable couplers etc. These components do not in a form suitable for on-chip use at very low powers and at mK temperatures. In this part of the project we will build on the expertise obtained in our previous work to design and test microwave circuit elements, in particular hybrids, couplers and phase shifters, in the form suitable for quantum information processing.

Synergy with Other Projects

Development of nanomechanical coupling elements will benefit from the results of Project 4 Theme 2.

Risk

The effort to develop scalable solid-state quantum circuits is massive worldwide, hence the risk of being undercut by competition. Nevertheless, our proven ability to design, model, fabricate and measure superconducting devices with metrological accuracy gives us an important niche.

Knowledge Transfer Plan

Conventional routes: publication of high-quality papers in leading scientific journals, presentations at international conferences. Involve our wide international network of collaborators, in particular in industry, such as NTT.

Deliverables

1	**Start: 01/04/10**	**End: 31/03/11**
	Prepare four superconducting resonator samples, test and compare the results with state-of-the-art dielectric loss models	
	Evidence: Centre frequency, coupling strength and intrinsic losses of fabricated resonators correspond to the model	
2	**Start: 01/04/11**	**End: 31/03/12**
	Measurements of dielectric loss factors at temperatures between 50mK-4K and at powers down to -140 dBm, with a sensitivity better than 10^-6	
	Evidence: Dielectric losses (nd2 factors) of thermally evaporated and ALD films compared and published	
3	**Start: 01/04/2012**	**End: 30/06/2013**
	Design, modelling and fabrication of on-chip microwave components for superconducting resonators	
	Evidence: Parameters (additional losses, frequency tunability, power splitting, etc.) correspond to the model	

Project No.	CB/2012/CF17	Price to NMO	£496k
Project Title	Traceable characterisation of nanostructured devices (TReND) (NPL)	Co-funding target	£317k from EMRP
Lead Scientist	Ian Gilmore	Stage Start Date	01/06/2012
Scientist Team	Rasmus Havelund, Martin Seah, Alex Shard	Stage End Date	31/05/2015
		Est Final Stage End Date	2020
Sector	Advanced Manufacturing & Services: High-value manufacturing and bioproducts	Activity	Methodology for new capabilities

Summary

The work proposed contributes to a wider body of research in the European Metrology Research Programme (EMRP) New Technologies "Traceable characterisation of nanostructured devices (TReND; JRP-NEW01)" project. It will develop traceable measurement and characterisation of physical and chemical properties of the next generation of integrated nanostructured semiconductor devices using novel 3D architectures. Specifically, NPL's contribution will focus on developing the essential metrology for 3D-Secondary Ion Mass Spectrometry (3D-SIMS) using argon cluster sputtering.

The Need

The micro and nanoelectronic world is experiencing a revolution in tackling the new challenges in terms of miniaturization, power consumption, power density and processing speed. Novel inorganic semiconductor materials (for example, Ge, InGaAs, GaN, SiC, etc.) and new 3D-architectures (e.g. multiple gate field effect transistors [FETs], nanowire tunnelling-FETs, etc.) with feature sizes < 30 nm are replacing traditional silicon devices. There is now a critical need for metrology to give traceable and quantitative chemical composition measurement of new materials in complex spatial arrangements with buried interfaces and with nm depth resolution. Concurrent with these developments is the emergence of electronics based on organic semiconductors, made of single molecules in highly ordered assemblies and polymeric semiconductors in thin films. This is an important new knowledge-based high innovation sector for the EU. The combined market for organic logic, batteries, sensors and conductors will be €9bn by 2019 and for integrated systems €47bn. Unfortunately, the techniques developed for the inorganic semiconductor industry do not directly apply and there is an urgent need for methods to give 3D nanoscale chemical and electrical imaging. In the current state of the art, 3D SIMS with C_{60} sputtering fails completely for organic electronic materials and there are no existing methods for 3D nanoscale electrical measurements. The challenge here is for metrology at the nanoscale and it is clear that no single technique can provide all the answers required by industry.

The Solution

To address the stated needs above, the project will:

- Develop methods for 3D nanochemical analysis of nanostructured organic electronic materials, (i.e. 3D chemical characterisation of nanolayers and interfaces with depth resolutions of better than 10 nm at depths of up to 400 nm and with spatial resolution to better than 100 nm.). By dramatically reducing the incident energy per atom from 333 eV/atom (typical for C_{60}) to 1.5 eV/atom, it has been shown that large Ar_{2000} clusters radically reduce damage and fragmentation during sputtering and allow successful depth profiles through molecular multilayers material with better than 5 nm depth resolution at a depth of 100 nm.
- Develop methods for 3D nanoelectrical characterisation of nanostructured organic electronic materials (i.e. the conductivity and charge mobility) of materials inside thin films with nanoscale resolution (better than 30 nm).

Project Description (including summary of technical work)

As part of the EMRP TReND project, NPL's contribution will focus on:

- Developing the essential metrology to enable 3D nanoscale chemical imaging of organic electronic materials using new massive argon cluster sputtering combined with SIMS for 3D chemical analysis of nanostructured organic electronic materials. This will be done by (i) provision of the fundamental metrology infrastructure for super-resolution 3D chemical imaging of organic nanolayers using massive argon cluster SIMS, (ii) quantification and depth distribution of impurities and additives in an organic nanolayer and (iii) metrology for 3D nanoscale chemical imaging of organic electronic and organic photovoltaic devices.
- Developing a novel method for 3D nanoelectrical characterisation of organic semiconductor nanostructures and nanostructured self-assembled reference materials for the metrological studies of the techniques. Develop novel measurement of electrical and opto-electrical properties of the surface and subsurface of organic thin films and combined analysis of a selected organic photovoltaic (OPV) device. This will be done by combining AFM nanoindentation and dc electrical measurements for electrical measurement and photoconductive atomic force microscopy (PC-AFM) measurements and modelling for optoelectronic measurement.

Impact and Benefits

The semiconductor and nanoelectronic industry constitutes a vast global market, its size being about $265bn. The market for equipment and materials can be estimated, on average, at $35bn for equipment and $32bn for materials. On top of this, the sector is directly stimulating a much larger electronics applications industry totalling $1,500bn. The UK is an international leader in the innovation and development of organic electronics which is a rapidly growing sector. The combined market for organic logic, batteries, sensors and conductors will be €49bn by 2019. For all these markets there is an urgent requirement for 3D chemical and opto-electrial measurement at the nanoscale to improve device efficiency, lifetime and manufacturing processes.

Support for Programme Challenge, Roadmaps, Government Strategies

This project is aligned with the NMS Strategy 2011 – 2015, the ChemBio Surface Analysis priority theme and roadmap (Organic depth profiling using SIMS with cluster sputtering), a VAMAS TWA 37 survey of needs for the organic electronics industry, the Organic Electronics Association Roadmap for Organic and Printed Electronics (2009) , Strategic Research Agenda Organic & Large Area Electronics, 'Towards Green Electronics in Europe', UK Technology Strategy Board Electronics Photonics Electrical Systems technology pillar (2008), Plastic Electronics: A UK Strategy for Success (BIS; 2009), and The Current and Future Role of Technology and Innovation Centres in the UK (The Hauser Report; 2010).

Synergies with other projects / programmes

The work builds on developments made in previous ChemBio projects (e.g. SA1). Specifically, 3D SIMS using sputtering by argon cluster ions builds on a strong metrology foundation in SIMS at NPL and develops the capability which is a high priority measurement requirement in many industries including semiconductor, medical devices, printing, coatings, speciality chemicals and agrochemicals. The project is also synergistic with EMRP JRP-HLT04 project, (project proposal CB/2012/CF18), which is investigating the quantitative analysis of biomolecular interfaces relevant to the needs of diagnostic device manufacturers.

Risks

Argon clusters may not be able to successfully profile organic electronic materials for OPVs, which would stop the analysis of real world devices. NPL is one of only two laboratories with nitric oxide (NO) radical scavenging facilities to prevent cross-linking of polymers during sputtering. The NO gas can be used in the project. Alternative polymer materials can be used if required.

Knowledge Transfer and Exploitation

Dissemination of the project's outputs will be through the following routes: Publications (reports, articles in trade journals and scientific papers); oral presentations at leading international conferences; a project website, e-forum and online network; and provision of training to industry e.g. NPL will offer 5-days of dedicated instrument time and analysis for 3D chemical imaging of organic nanolayers to European enterprises to showcase the power of the techniques developed in the project with the requirement that case-studies are made public. Further dissemination will be through the development of international standards in SIMS for organic and nano-objects through ISO TC 201 working group and NPL's chairing of VAMAS TWA 2 on Surface chemical analysis.

Co-funding and Collaborators

This project comprises NPL's input into the EMRP New Technologies TReND project (£317K from EMRP). The project is led by NPL with funded partners including PTB (Germany), BAM (Germany), CEA (France), CMI (Czech Republic) and INRIM (Italy) and also ION-TOF working as an unfunded partner. Associated postdoctorate positions will be held at LETI and IMEC. Collaborators include Detech, Dipartimento di Scienze dell' Ambient e della Vita(East Piemonte University), Istituto Italiano Di Techologia, Sigma Aldrich, EMPA, FEI, MEMC, Eight19, Samsung, Rigaku, OEA, KTN-ESP, Asylum Research UK, Fraunhofer Institute for Photonic Microsystems, ST microelectronics, Universite Catholique de Louvain, PANalytical BV, Oxford Instruments.

Deliverables

1	**Start: 01/06/12**	**End: 31/05/15**	

Deliverable title: Cofunding for EMRP project "Traceable characterisation of nanostructured devices (JRP-NEW01)"

Project No.	**NS002SA1a**	**Price to NMO**	£960k
Project Title	Surface and nanoanalysis of surfaces and particles	**Co-funding target**	Cash co-funding only
Lead Scientist	Ian Gilmore/Alex Shard	**Stage Start Date**	01/04/10
Scientist Team		**Stage End Date**	31/03/13
		Est Final Stage End Date	
Sector	Use lexicon	**Activity**	Methodology for new capabilities

Summary

This multi-technique project will develop the key metrology for the chemical analysis of surfaces and particles using:

- Surface and nanoanalysis of micro and nanoparticles for innovation and environment, health and safety
- G-Tip innovation and cluster ion metrology
- Organic depth profiling in SIMS and XPS.

The Need

Nanoparticles are front-runner nanotechnologies key to high innovation products such as biodiagnostics, drug delivery, medical imaging (contrast agents), cosmetics and sunscreens through to catalysts. The surface chemistry is a critical parameter for nanoparticles used in innovation. The international toxicology community is making significant progress in identifying which parameters of nanoparticles have the strongest effect on mammalian cell toxicity. In general, three key parameters have been identified that can give reliable predications of toxicity; particle size distribution (also aspect ratio), specific particle surface area and surface chemistry/charge. The characterisation of the surface and bulk chemistry of nanoparticles is therefore an underpinning requirement for innovation and environment health and safety aspects. In particular, the UK has been tasked to characterise zinc oxide and cerium oxide for a large international study for the OECD. This multi-technique project is proposed to develop the essential underpinning metrology for the chemical characterisation of nanoparticle to PM10 particles that are relevant to innovation (e.g. the pharmaceutical and catalyst industry) as well as toxicology. This is currently a major challenge and no robust methodologies exist for valid measurements.

The Solution

There is a strong requirement for the analysis of organic surfaces including identification and localisation of molecules, for which G-SIMS with G-Tip technology is excellent. For example, in the identification of complex biomolecules, mass spectra are often insufficient and molecular structure is needed, as the mass alone cannot give unique identification. SIMS contains latent information about molecular structure within the spectra from the fragmentation of molecular ions. G-SIMS related Fragmentation Pathway Mapping (G-SIMS-FPM) and SMILES have been shown to make a powerful method to easily access this information and evaluate the molecular structure of complex molecules at surfaces. So far, G-SIMS-FPM and SMILES have been evaluated for a range of small organics using both positive and negative spectra. This has shown to be very powerful but needs extending to important industrial materials such as pharmaceuticals and other molecules relevant to biotechnology.

The composition and structure of organic films are important for many novel, high added value products, such as the areas of organic electronics, medical devices and drug delivery systems. Innovative advances crucially rely upon achieving the correct spatial and in-depth distribution of components. With increasing complexity in organic film formulation, for example requirements to create multilayered, spatially patterned films or films with specified concentration gradients, problems associated with misalignment, intermixing, diffusion, phase separation, migration and contamination of components become difficult to diagnose without an effective measurement tool. It is therefore important that appropriate, validated techniques are developed to identify and localise chemical components in organic films, as well as to obtain quantitative measurements of their concentration. Organic depth profiling is highly promising for the investigation of compositions in organic coatings, with depth resolutions on the scale of ~10 nm and ability to be combined with imaging spectroscopies to allow high resolution, 3D visualisation of the distribution of organic and bio-materials. However, many challenges and unresolved issues are currently preventing its routine uptake in industry, including a lack of knowledge on the sputtering, damage and roughening mechanisms.

Project Description A method and procedure will be developed for the mounting of micro and nanoparticles for analysis by SIMS, XPS and AFM, as well as FIB sectioning methods for preparing samples for STEM+EELS. A fundamental study will be carried out to evaluate the sputtering yield of model nanoparticles for both atomic and cluster primary beams. A method and procedure will be developed for the practical SIMS compositional depth profiling of inorganic nanoparticles, using model materials with different core and surface chemistries. This work will utilise the reference data for sputtering yields, allowing depth resolution, detection limits and practical guidance to be given to analysts. Taking the G-Tip innovation to the next level for ease of use for analysts will involve the implementation of a new configuration to enable real-time G-SIMS using pulse-by-pulse modes and scan-by-scan modes. The effectiveness of this new innovation will be evaluated on a range of different chemically patterned reference materials. So far the G-Tip is available on the ION-TOF instrument, we will collaborate with IONOPTIKA (UK) and other instrument manufacturers to allow their ion beams to be G-Tip enabled. We will use the fragmentation cascades observed for G-SIMS using cluster and atomic primary ions to further understand the fragmentation and processes involved in the thermal spike process and secondly evaluate if it may be possible to use cluster ion beams for G-SIMS in some conditions. G-SIMS FPM and SMILES will also be developed to provide an automated system for interpreting molecular structure from mass spectra.

NPL organic delta-layer reference samples will be developed and made available to analysts, and the results of an interlaboratory study using these reference materials will be evaluated to establish the reproducibility of organic depth profiling and provide guidance to analysts for optimising experimental parameters. We will develop methods for quantitative depth profiling of organic thin films, investigating matrix effects on the quantitative determination of analyte concentrations. We will develop quantitative measurements for key parameters in organic depth profiling, such as depth resolution, roughness, damage and variations in sputter yield. Using the expertise gained with SIMS, we will determine the suitability of XPS as a complementary analytical tool for organic depth profiling, using an appropriate reference material. Finally, we will collaborate with Prof J. Matsuo (Kyoto University, Japan) who has pioneered the use of massive argon clusters Ar_{2000} to investigate the potential of massive argon clusters as a sputtering source using appropriate standard samples and compare with theory.

Impact and Benefits

Results from this project will impact innovation and measurement capability in wide range of industries by:

- Developing underpinning nanometrology, characterisation and standardisation for nanoparticles as highlighted as a key innovation requirement by UK Government. The metrology will be extended to industrially relevant particles up to PM10.
- Clear reference materials, procedures and quantification of key profile parameters will provide the foundation for possible future development of an ISO standard or guide on quantitative organic depth profiling. These reference materials will be made available to the broader community.
- Finally, by adopting a forward looking approach and exploring the promising new technique of massive cluster ion sputtering, for which a secondment of Joanna Lee to Kyoto University will demonstrate impact, we maximise the potential for this new technology to radically expand analytical capability in the UK and enable the UK to stay at the forefront of international competition.

Support for Programme Challenge, Roadmaps, Government Strategies

Key reports by the Defra funded REFNANO project, the Nanotechnologies Research Coordination Group (NRCG) and the OECD (Organisation for Economic Cooperation and Development) Working Party on Manufactured Nanomaterials have highlighted the need for the characterisation of nanoparticle surface chemistry.

Synergies with other projects / programmes

A large part of this work has been used to cofund an FP7 project called PROSPEcT (see NS002CF8).

Risks

The project has relatively some technical risk which is mitigated by the range extensive expertise within the group.

Knowledge Transfer and Exploitation

Knowledge gained from this project will be used to develop internationally recognised standards and handling protocols which will have a wide influence across academia, industry and standards bodies. There will also be several peer reviewed publications.

Co-funding and Collaborators

A large part of this work has been used to cofund an FP7 project called PROSPEcT (see NS002CF8).

Deliverables

1	**Start: 01/04/10**	**End: 31/03/13**	

Deliverable: Surface and Nanoanalysis of surfaces and particles

National Measurement System

The National Measurement System delivers world-class measurement for science and technology through these organisations

The National Measurement System is the UK’s national infrastructure of measurement Laboratories, which deliver world-class measurement science and technology through four National Measurement Institutes (NMIs): LGC, NPL the National Physical Laboratory, TUV NEL The former National Engineering Laboratory, and the National Measurement Office (NMO).