Publishable Summary for 17IND09 MetAMCII
Metrology for Airborne Molecular Contaminants II

Overview

Airborne Molecular Contamination (AMC) in the form of chemical vapours or aerosols has an adverse effect on products, processes or instruments. Technological progress is driven by the ability to operate at ever smaller scales and with greater complexity, thus increasing the demand for lower AMC concentration measurement. Real time online monitoring is critical to ensure that corrective action is taken before this impacts on production costs. Therefore, this project focusses on developing underpinning metrology focused on new ultra-sensitive spectroscopic techniques and high accuracy reference materials at extremely low concentrations for key AMCs. The project’s aim is to increase industrial competitiveness, reduce down time and remove barriers to efficient manufacturing.

Need

The European semiconductor industry supports ~200,000 European jobs directly and more than 1,000,000 jobs indirectly. The global turnover of the semiconductor sector was ~€230 billion in 2012, with micro and nano electronic components manufacturing having a turnover of around €1,250 billion in 2012. The manufacture of micro and nano electronics is estimated at 10 % of worldwide GDP (European Semiconductor Industry Association (ESIA) data). Europe currently has 9 % of the world share of the semiconductor manufacturing industry, representing $27 billion, with plans, outlined in a European Leaders Group report, to increase this to 20 % by 2025. In this high value business, the need is clearly demonstrated because a small increase in the yield can lead to savings/profits of hundreds of millions of euros.

Adverse AMC-related effects can occur in electronics production including, for example, the corrosion of metal surfaces on the wafer, and the formation of contamination layers. These AMCs come from sources including process chemicals, filter breakthrough, building and cleanroom construction materials and operating personnel. Regulations and analytical capabilities in this field are much less well developed than in the field of contamination by particles. AMCs generated as part of the production process need to be detectable at very low concentrations as these are detrimental to the product. Prior to this project, there was a need to extend the findings of previous studies to other AMCs (e.g. HCl), to improve detection sensitivity, and to increase the range of dynamic reference standards.

Improved real time measurements of AMC are essential in order to enable corrective actions to be taken before production yields are affected and to demonstrate compliance with ISA Standard S71.04. There are currently no NMI realised standards for HCl with which compliance can be verified. Available instrumentation is often not fit for purpose due to high costs, large size, measurement rate or limited reliability and this issue is specifically raised in the International Technology Roadmap for Semiconductors (ITRS).

Objectives

This project will assess the potential of state of the art optical spectroscopic techniques for traceable AMC monitoring in cleanroom environments and how advanced optical techniques will impact on the detection of smaller AMC quantities. Therefore, this project has the following objectives:

1. To develop ultra-sensitive and real-time spectroscopic methods for the detection of critical airborne molecular contaminants (AMCs) (e.g. NH_3, HCl and water vapour) with target detection values for HCl lower than 1 nmol/mol and in less than 1 minute. In addition, to determine the optimal spectral windows for such techniques based on High Resolution Transmission (HITRAN) calculations and component availability.
2. To develop traceable static and dynamic reference materials for use with real time monitoring for priority AMCs in a nitrogen matrix at less than 1 nmol/mol, specifically static and dynamic references and for HCl at 10 µmol/mol, using methods to produce dilutions higher than 10000:1 for AMCs with a

target accuracy better than 0.5 % relative. In addition to develop instrumentation and novel passivation techniques to optimise the long-term stability of static reference materials for AMCs.

3. To compare and perform field tests of different spectroscopy techniques for real-time AMC detection, including an investigation of typical AMC monitoring scenarios (e.g. monitoring filter breakthrough and confined environments). The target time resolution for the spectroscopy techniques is better than 5 min and with a sensitivity lower than 1 nmol/mol for AMCs.
4. To develop traceable dynamic or static gas transfer standards for AMCs and opto-analytical transfer standards for the validation of measurement techniques commonly used in cleanrooms (e.g. ion-mobility spectrometry), including the use of in-situ calibration techniques.
5. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain (e.g. accredited laboratories and instrument manufacturers), standards developing organisations (e.g. ISO TC 158, CEN TC 264, International Society for Automation (ISA) Standard 71.04-1985 and standards bodies associated with European Waste Incineration Directive 2000/76/EC and the Ambient Air Quality Directive 2008/50/EC) and end users (e.g. the semiconductor and electronics industries).

Progress beyond the state of the art

In this project, sensitive spectroscopic methods developed within the first EMRP “MetAMC” project will be further developed specifically to address HCl and progress towards industrial take-up of the novel technologies being developed – the first project primarily targeted ammonia detection, with some additional work on HF. Prior to the start of this project, there were no NMI realised standards for HCl with which compliance can be verified. Available instrumentation was often not fit-for purpose due to high costs, large size, measurement rate or limited reliability.

1. The consortium will develop ultra-sensitive and real-time spectroscopic methods for the detection of critical airborne molecular contaminants (AMCs) (e.g. NH_3, HCl and water vapour) with target detection values for HCl lower than 1 nmol/mol and in less than 1 minute. Spectroscopic methods to be investigated will include cantilever based photo-acoustics and noise immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS). The project will go beyond the state of the art by extending the range of AMC detection, improving measurement traceability, and improving system robustness and transportability.
2. The consortium will develop traceable static and dynamic reference materials for use with real time monitoring for priority AMCs in a nitrogen matrix at less than 1 nmol/mol.
3. The consortium will compare and perform field tests of our different spectroscopy techniques for real-time AMC detection, including an investigation of typical AMC monitoring scenarios. For example, measurements using NICE OHMS will be compared against a new ultra-sensitive gas sensor that is under development.
4. To develop traceable dynamic or static gas transfer standards for AMCs and opto-analytical transfer standards for the validation of the measurement techniques that are commonly used in cleanrooms (e.g. ion-mobility spectrometry), including the use of in-situ calibration techniques.

Results

1. The consortium has undertaken a review of commercial spectroscopic instruments including a study of the spectral windows available for HCl spectroscopy and detection. A summary of the report prepared by the consortium is available at http://empir.npl.co.uk/metamcii/. The consortium has also tested commercial laser sources for spectroscopic instrumentation, specifically the output wavelength, linewidth, and power to ascertain their suitability. Two participants are developing a new laser source at 1742 nm for the detection of HCl. This is based on the optical fibre amplification of a discrete mode laser signal. The laser source will be combined with different laser sources in a photo acoustic setup developed within the first EMRP project and the overall aim is to measure HCl, NH_3 and HF simultaneously. NPL has evaluated pig-tailed lasers from two commercial suppliers at 1742 nm and compared these to free-space lasers for HCl detection. Laser linewidths were determined via beats between various combinations of lasers and laser drivers to determine the optimum setup. GASERA are continuing to develop a new photoacoustic optical multipass cell which they have partially characterised for enhanced HCl detection sensitivity.

2. The second objective will meet the need for improved reference materials which typically comprise 10 µmol mol^{-1} of an AMC in dry nitrogen. Static reference materials will be prepared in cylinders and their traceability will be provided through gravimetric preparation. The consortium has begun work on static HCl gas standards with the development of an uncertainty budget. Water has been identified as a key contributor and it will be of particular importance to prepare HCl gas standards with a very low water content as the water will react with HCl. The consortium has discussed with the speciality gas industry about (potential) suitable cylinder treatments for HCl at low amount fractions. Different cylinder treatments, including chemically passivated and polymer treated, have been obtained/purchased for testing.

   Material testing is required to optimise the response time and optimise sample concentration stability. Selected materials and coatings are stainless steel (SS) coated with SilcoNert 2000, Dursan, Monal (Nickel alloy) and a polymer, PTFE. Invar has been investigated for use in one of the spectrometers that is under development and it has been shown to be a suitable cavity spacer material. All participants are working on the system design of their spectroscopic instruments, including the testing and development of materials coatings, lasers and electronics.

   Design of the dilution systems at CMI and NPL has been completed. For the dilution system a selection of materials and coatings was made based on their physical and chemical properties and availability.

3. The consortium sent out a questionnaire to find out more about the status and needs for the AMC monitoring in industry. Although the number of responses was limited, the results were clear: AMCs are not a familiar subject for industry and there is a need for more information, emphasising the importance of the project. We will continue to engage with industry via forthcoming events such as CleanZone and are also using LinkedIn to engage with contacts. Participants conducted a literature review of requirements, datasheets, standards and existing monitoring methods. Additionally, during the first stakeholder meeting there was fruitful discussion with stakeholders giving more insight on the present status of AMC monitoring and its need in industry. The consortium is also gathering information from stakeholders on the specifications for field studies and from the participants for laboratory tests. These initial discussions have shown us that there should be a common methodology that is suitable for the assessment and testing of the devices that the project is designing and building in the laboratory. A specification has been developed for the laboratory tests of the consortium's spectroscopic instruments and a summary report is available at http://empir.npl.co.uk/metamcii/

4. Comparisons will be made between well-established techniques, such as photo-acoustic spectroscopy, and more novel heterodyne spectroscopy methods (i.e. NICE-OHMS). The transportability of the more novel instrumentation will be improved so that these devices can also be used in field tests. Field testing is a critical step towards establishing the novel techniques in industrial environments, as identified by the cleanroom and semiconductor manufacturing sectors.

5. Work is continuing to progress on the development of traceable dynamic or static gas transfer standards for AMCs and opto-analytical transfer standards for the validation of the measurement techniques commonly used in cleanrooms (e.g. ion-mobility spectrometry), including the use of in-situ calibration techniques. This will meet the need to develop opto-analytical transfer standards that will allow the transfer of measurement traceability from the standards laboratory to industrial environments where more well-established technology (e.g. ion mobility spectrometry) is currently used. The optical techniques being pursued include direct tuneable diode laser spectroscopy (dTDLAS), photo-acoustic spectroscopy and NICE-OHMS.

6. In April 2019, Paul Brewer (NPL) became the fifth Chair of the CIPM-CCQM Gas Analysis Working Group which oversees the comparability of gas analysis measurements between National Metrology Institutes and Designated Institutes worldwide. An important step in the take up of the technology and measurement infrastructure is the decision expected by the Amount of Substance (CCQM; a committee of the BIPM) to organise a key comparison on HCl in 2021. The final decision is expected to be made in April 2020. The CCQM met in October 2018 at CENAM and input from this project will input into the planning stage and this will develop the capability of the participating institutes.

Impact

To promote the impact generated by this project, we have set up a website at http://empir.npl.co.uk/metamcii/ that details the partners and describes the main aims of the project. The website has been recently updated with abridged versions of the reports produced for D1 & D7; a further report from VSL on “Sampling Lines for HCl” has also been prepared to upload. NPL also hosted a combined project review and stakeholder meeting in January 2019 and feedback received at the meeting will steer the instrument testing planned for later in this project. Further contacts are being made via, for example, LinkedIn.

Impact on industrial and other user communities

Europe has 9 % of the world share of the semiconductor manufacturing industry, representing $27 billion, with plans to increase this to 20 % by 2025. An AMC monitor, providing analysis and feedback within ~1 minute, would enable the timely detection of higher-than-acceptable contamination and determination of the cause, enabling corrective actions that would make a significant impact on industrial competitiveness. AMC is one of the major components affecting product yield in the microscale manufacturing processes of semiconductors and it can lead to increased electronics defects and to higher production costs. This project will create impact by providing improved instrumentation with better sensitivity and a reduced measurement time and also better static and dynamic reference standards. The work on the static gas standards will provide the specialty gas industry with information on the suitability of the tested cylinder treatments for HCl gas standards at low amount fractions. These instruments will be field tested and transfer standards will be improved to enhance traceability from national measurement institutes to industrial environments. To date, the consortium have signed a collaboration agreement with one company that is interested in exploiting the technology being developed within this project.

Impact on the metrology and scientific communities

The partners in this consortium are actively involved in the CCQM Gas Analysis Working Group (GAWG) which met in April and October 2019 and the outputs from this project will be presented to global experts. The development of reference materials for NH_3 and HCl will support future Key Comparisons organised by the GAWG and new calibration and measurement capability claims for amount fraction. Specifically, to date, the CCQM Gas Analysis Working Group is expected to decide on a key comparison on HCl for 2021 and outputs from this project will inform the planning stage and develop the capability of the participating institutes.

Impact on relevant standards

The technical committees targeted by this project are ISO/TC 158 (Gas Analysis) and CEN/TC 264 (Air Quality) and related national standardisation committees in gas analysis. The partners that are members of these committees will ensure that the knowledge developed within the project is fed into the committee meetings. This will ensure that the project’s outputs feed directly into the standardisation activities, and the requirements emerging from the standardisation committees will be used to refine the project in order to maximise its impact.

In static gas mixtures (i.e. cylinders) some loss of HCl is currently unavoidable due to the high reactivity of HCl causing adsorption or reactions with water. The work carried out in the MetAMCII project on this topic is of importance for future revisions of ISO 6142 “Gas analysis – Preparation of calibration gas mixtures” regarding the class of reactive molecules. PTB contributed to a DIN Standards Committee (Materials testing NA 062) which met in November 2018 and the EURAMET TC-MC (Metrology in Chemistry) committee meeting in February 2019.

Longer-term economic, social and environmental impacts

The impact of this project will not be limited to the semiconductor industry; within 5-10 years, other industries that will benefit will include aerospace, pharmaceuticals, medical devices (e.g. breath analysis for health monitoring), food, indoor/outdoor air quality monitoring, healthcare and energy efficiency. These industries will benefit from the improved spectroscopic instrumentation and traceability developed within this project. This could result in, for example, improved production efficiency in the aerospace industry or more reliable diagnoses for some medical conditions. For example, checking for ammonia in breath is used in the diagnosis of renal failure; if our instrumentation were extended to HCN detection, this could be used for the diagnosis of bacterial lung infections. Due to the hazardous nature of the AMC analytes, the long term output of the project will also improve the safety of personnel by quantifying specific analytes more reliably. Other potential application areas include the detection of contaminants in background gases such as hydrogen (for fuel in hydrogen cars) and methane (including bio-methane).

The potential impact on energy efficiency will be huge in the longer-term when the quality of the semiconductor devices produced (light emitting sources (e.g. LEDs) and photovoltaic units) is improved. For example, even small improvements in solar panel efficiency could have a huge impact on global renewable energy production schemes. Simple photovoltaic cells have a conversion efficiency of around or below ~20%. More sophisticated designs use complex structures to obtain better efficiency, but these are more prone to AMC related defects.

As AMC is expected to affect product yield even more in the future, the demand for practical AMC monitoring devices will be high. An effective implementation of AMC monitoring equipment by European industry would give them a competitive edge over global competitors. However, it is expected that every company will adopt AMC monitoring systems when their worth has been proven.

List of publications

None at this time.

<table>
<tr><td colspan="2">Project start date and duration:</td><td>1 May 2018; 36 months</td></tr>
<tr><td colspan="3">Coordinator: Geoffrey Barwood, NPL Tel: +44 208 943 6032 E-mail: geoffrey.barwood@npl.co.uk
Project website address: http://empir.npl.co.uk/metamcii/</td></tr>
<tr><td>Internal Funded Partners:
1. NPL, UK
2. CMI, Czech Republic
3. PTB, Germany
4. VSL, Netherlands
5. VTT, Finland</td><td>External Funded Partners:
6. GASERA, Finland
7. Optoseven, Finland</td><td>Unfunded Partners:
8. POLITO, Italy</td></tr>
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