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. These developments are urgently needed in order to improve manufacturing processes and to control contamination. The 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.

Progress in advanced technology requires operation at an ever smaller scale with increased complexity. 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 concentrations below 1 nmol/mol as these are detrimental to the product. There is therefore 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. This is substantiated in the International Technology Roadmap for Semiconductors (ITRS), which states ‘There is clearly a need for better AMC monitoring instrumentation in the cleanroom to measure AMC at the part-per trillion level (by volume) in real time’.

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

The methods used for AMC monitoring can be divided into online and offline analysis methods. Offline methods are commonly based on thermal desorption followed by gas chromatography and/or mass spectrometry analysis. Thermal desorption can reach pmol/mol sensitivities with commercial instrumentation, but sampling and measurement times are long (~10 minutes or longer) and measurements can be labour intensive when samples need to be taken manually. Real time methods allow for timely intervention, but they generally have lower sensitivities as the contaminants are not accumulated. Examples include ion mobility spectroscopy, chemiluminescence for nitrogen oxides, and laser cavity ring down spectroscopy and photo-acoustics for ammonia.

In this project, the sensitive spectroscopic methods developed as part of EMRP JRP IND63 MetAMC will be further developed. This will include technologies such as cantilever based photo-acoustics and noise immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS). These techniques have great potential for use in online monitoring. In this follow on project, the consortium will go beyond the state of the art with the emphasis being on extending the range of AMC detection, improving measurement traceability, and improving system robustness and transportability. This project will emphasise the importance of HCl, ammonia, and water vapour to the cleanroom industry. Of these molecules, HCl is the AMC currently requiring the most research effort and it will therefore be the main focus of this project. The work on ammonia will follow-on from the previously funded developments. To facilitate the take-up of new technology by industry, measurements using NICE OHMS will be compared with a new ultra-sensitive gas sensor that is under development. This sensor will be developed, as part of this project, on a commercial gas sensor platform and it will be compared against the output from a novel gas dilution system yielding samples of trace AMC down to 0.1 nmol/mol. Improvements to system robustness will also be required for future industrial use. To initiate the process of technology transfer, measurements will be performed against the NMIs in house standards and then in industrial settings to determine ambient AMC levels.

Results

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.*

This project will develop and apply novel spectroscopic methods to the problem of developing improved instrumentation and improved gas metrology of AMCs at low amount fractions (<1 nmol/mol) and at faster measurement timescales (< 1 minute) than is currently possible in order to meet industrial requirements. The primary focus of this project will be on the development of techniques for HCl detection; the consortium will improve the technology that was developed in EMRP JRP IND63 MetAMC to measure ammonia and the capability of one of the measurement methods will be extended to include water vapour detection. Water is not an AMC, but its presence can influence the results produced by spectroscopic devices and this will be investigated. Different spectroscopic solutions will be pursued by the partners within this consortium. Improved reliable AMC monitoring has been identified as a key requirement, particularly within the cleanroom and semiconductor manufacturing industries.

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.*

Objective 1 focuses on meeting the need for improved instrumentation, whilst objective 2 will meet the need for improved reference materials, currently, a typical static reference material comprises 10 µmol mol^{-1} in dry nitrogen. Static reference materials will be prepared in cylinders and their traceability will be provided through their gravimetric preparation methods. Work will be undertaken to improve the passivation technology available for these cylinders which will improve the stability of the reference materials over time (typically >1 year, even for reactive AMCs such as HCl). These static standards will then be used in dynamic mixing techniques to produce a range of concentrations down to 1 nmol mol^{-1}. These low concentrations will be of most interest to the cleanroom and semiconductor manufacturing industries.

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.*

Objective 1 outlines the plan for the development of the different spectroscopic techniques. Objective 3 will compare the results from these different techniques; i.e. in establishing measurement reproducibility it is critically important that the results from different measurement techniques agree. 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.

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.*

Objective 4 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.

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).*

This final objective is targeted towards the take-up of the results of this project by the manufacturing supply chain. Following the field tests in the previous objective, the aim is to demonstrate the improved traceability, reliability and measurement sensitivity of our technology by directly addressing industrial needs. The output from this project, together with the output from our previous EMRP study, specifically targets ammonia and HCl. Work will also be undertaken that shows the robustness of our instrumentation when measuring one AMC in the presence of water. The improved measurement methodologies and reference materials will allow more robust standards to be adopted by industry, leading to reduced manufacturing down-time, lower manufacturing costs and less wastage.

Impact

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 (objective 1) and also better static and dynamic reference standards (objective 2). These instruments will be field tested (objective 3) and transfer standards will be improved to enhance traceability from national measurement institutes to industrial environments (objective 4). The consortium is well connected with the advanced manufacturing community and as a result, the project's outputs will have a direct impact on industrial research.

The infrastructure developed in this project will create impact as there will be fewer product failures and less downtime of facilities, and this will increase the competitiveness of European industry. Impact will also be created by the dissemination of documentary standards under ISO/TC158 on Gas Analysis and CENTC/264 on Air Quality to the industrial and other user communities.

Impact on the metrology and scientific communities

The partners in this consortium are actively involved in the CCQM Gas Analysis Working Group (GAWG) 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.

The outputs from this project relate to both improved instrumentation (objective 1), comparison between different instrument technologies in the field (objective 3) and improved standards. These improved standards include both static and dynamic references (objective 2) and also transfer standards such as those based on opto-analytical methods (objective 4). This combination of improved reference standards and instrumentation together with comparisons between the different technologies being developed within European NMIs and instrumentation companies will provide impact through significantly improved confidence in the measurement traceability of airborne molecular contaminants.

Impact on relevant standards

The technical committees targeted by this project are ISO/TC 158 (Gas Analysis) and CEN/TC 264 (Air Quality) and the related national standardisation committees in gas analysis. This is where the work performed in this project will be the most relevant and where it will have the most impact. 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. The knowledge gained from the development of dynamic capabilities for HCl and NH_3 will be provided to ISO/TC158 (Gas Analysis) to help with the preparation of future revisions of ISO6142 (Preparation of calibration gas mixtures – Gravimetric method) and ISO6145 (Preparation of calibration gas mixtures using dynamic methods). The project's objectives will create impact leading to the take-up of these standards by industry (objective 5).

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.

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.

Project start date and duration:	1 May 2018; 3 years duration	
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