GLADIATOR

grant number 604000

Large scale Integrating Collaborative Project

Deliverable Report

Work Package Leader	CEA
Deliverable Number	D4.5
Title	Determination of exposure level during CVD production.
Name of Author	Ismo K. Koponen, Marcus Levin
Contributing Project Partners of Deliverable	DTU, AIX-Ltd.
Due Date	30.4.2016
Document status	Final
Dissemination Level (PU, PP, RE, or CO)	PU
Version Number	1.0

Deliverable achieved on time?	Yes
Quality assurance	Beatrice Beyer, James Whitby
Deliverable quality satisfactory?	Yes

0.1. Quality Assurance

1st revision	29.04.16 – Beatrice Beyer, James Whitby

0.2. List of Abbreviations

AMCOR-K	AMCOR Flexibles Kreuzlingen AG
AMCOR-S	AMCOR Flexibles Singen GmbH
AUTh	Aristotelio PanepistimioThessalonikis
AIX-Ltd	AIXTRON Ltd
AIX-SE	AIXTRON-SE
AMAN	Amanuensis GmbH
CEA	Commissariat à l' Energie Atomique et aux Energies Alternatives
COM	Fraunhofer COMEDD
CVD	Chemical vapour deposition
DTU	Danmarks Tekniske Universitet
GRA	Graphenea S.A.
HJY	Horiba Jobin Yvon S.A.S
IOM	Leibniz IOM
NRCWE	Det Nationale Forskningscenter For Arbejdsmiljo
OET	Organic Electronic Technologies P.C.
SGE	Sgenia Soluciones SL
SUR	Suragus GmbH
R_{Sh}	Sheet resistance
T	transmission

1 Summary

The Gladiator project aims to enable the production of cheaper and better graphene. It is important that when new technologies are developed health and safety should not be neglected. We have, therefore, measured the potential exposure to particle emissions during specific work processes involving small scale production of graphene (at **DTU**) and at one large scale production site (at AIXTRON Ltd.). Small scale measurements at **DTU** were done in a clean room and at **AIX** in the normal industrial environment. We used a so called first tier[1] approach where assessment is based on total number concentration of emitted airborne particles and EM micrographs to verify the origin of potential emission. We observed only low levels of particles (under 10 cm^{-3} and 2000 cm^{-3} number concentration in near-field with CPC and DiscMini at **DTU** and **AIX-Ltd**, respectively). At **AIX-Ltd** measurements were not done in a clean room and therefore general particle concentrations in the room are higher. Data from the on-line measurements confirms that particle emissions are low. Later the micrographs will reveal if these low particle numbers are from the process or if they are just particles from the background.

In future work, we will determine the dustiness of selected graphene materials using a standardized dustiness test (CEN51015). Based on the measured exposure levels, **NRCWE** will evaluate the risk of exposure to nanomaterials during specific processes such as opening of CVD chambers and transfer of the grapheme sheets. This data will be presented in D4.6 "In vitro and in vivo testing of graphene completed" due in project month M36 (October 2016).

[1] See e.g. "Guidance on information requirements and chemical safety assessment" Chapter R.14 Occupation Exposure Estimation. European Chemicals Agency (2012) https://echa.europa.eu/documents/10162/13632/information_requirements_r14_en.pdf

2 Deliverable scope and context to the project

We have conducted measurements to assess exposure levels of particle emissions during specific work processes of small scale production (**DTU**) and at a larger scale production site at **AIX-Ltd**. Measurements were conducted successfully. **DTU** and **AIX-Ltd** were extremely helpful and made it possible to get the necessary information and provided all the help we needed. Based on the measured exposure levels **NRCWE** will evaluate the risk from exposure to nanomaterials during specific processes such as opening of CVD chambers and transfer of the graphene sheets.

Data analysis of the on-line data has been conducted and measurement set-up parameters for the future deliverable 4.6 have been determined.

3 Scientific and technological achievements

Particle number concentrations at **DTU** and **AIX-Ltd.** were measured using a Condensation Particle Counter (CPC,TSI 3007), a DiSCmini (matter aerosol, Testo) and collected on TEM-grids using Miniature Particle Samplers. This was done in both the near field (close to process,) and the far field (background), see Figures 1a and 1b for the details.

3.1 Site descriptions

3.1.1 DTU Danchip

DTU Danchip is the national centre for micro- and nanofabrication. **DTU** operates and maintain state-of-the-art processing equipment within our 1350 m^2 cleanroom facilities. **DTU** Danchip is the National Centre for Micro- and Nanofabrication in Denmark and is owned by and located at the Technical University of Denmark (**DTU**). **DTU** Danchip operates and maintains advanced processing equipment within 1350 m^2, class 10-100, ISO 9001-certified, open access, pay-per-use cleanroom facilities.

Measurements were made in the cleanroom using commercial Black magic (AIXTRON). Black Magic Chemical Vapour Deposition (CVD) system can handle substrates ranging from single chips up to 4”. The system can run processes up to 1100 °C with high speed ramping up to 5 K/s and active cooling for faster processing. A multitude of carbon materials can be deposited in the Black Magic system. These range from single- and multi-walled carbon nanotubes (SWT, MWT), amorphous carbon films (aC, aC:H), diamond-like films (DLC) to single layer graphene.

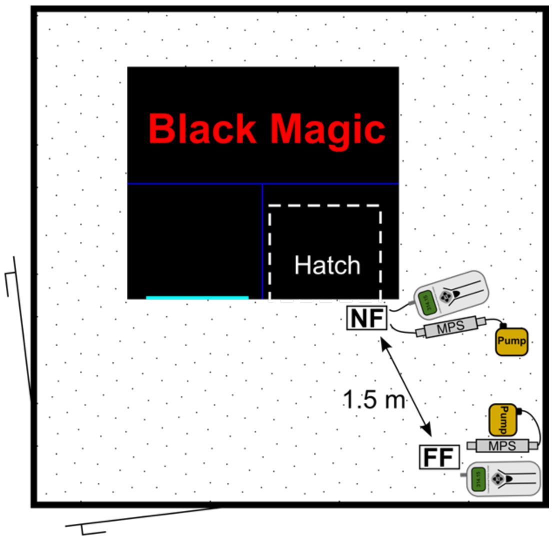
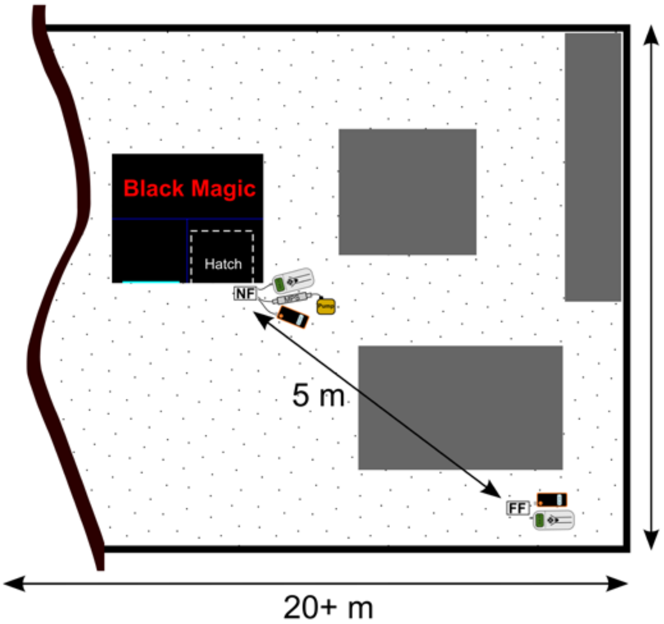


Figure 1a. Measurements at DTU. Instrumentation (Near field + Far field), CPC 3007 - Particle number concentration, DiSCmini - Particle number concentration and size, MPS - Particle sampling on TEM-grids.

3.1.2 AIXTRON



a) **Figure 1b. MEasurements at Aix-Ltd. Instrumentation (Near field + Far field), CPC 3007 - Particle number concentration, DiSCmini - Particle number concentration and size, MPS - Particle sampling on TEM-grids.**

3.2 Results

3.2.1 DTU

Figure 2 shows the concentration measurements made in the **DTU** clean room while a graphene CVD process is running. During the measurement period, several process related activities were carried out and during those activities microscope samples were taken (see Figure 2). Figure 2 shows that opening the reactor at the beginning of the process does not cause any measurable emissions. Same applies when reactor is turned on. After the process was completed, the reactor was opened and the internal atmosphere sampled **-** it showed a very low (< 10 cm^{-3}) concentration of particles; DiscMini could not detect anything. Cleaning of the instrument was done after the process and the particle concentration then rose to15 cm^{-3}. EM micrographs will in due course tell us the nature of these particles.

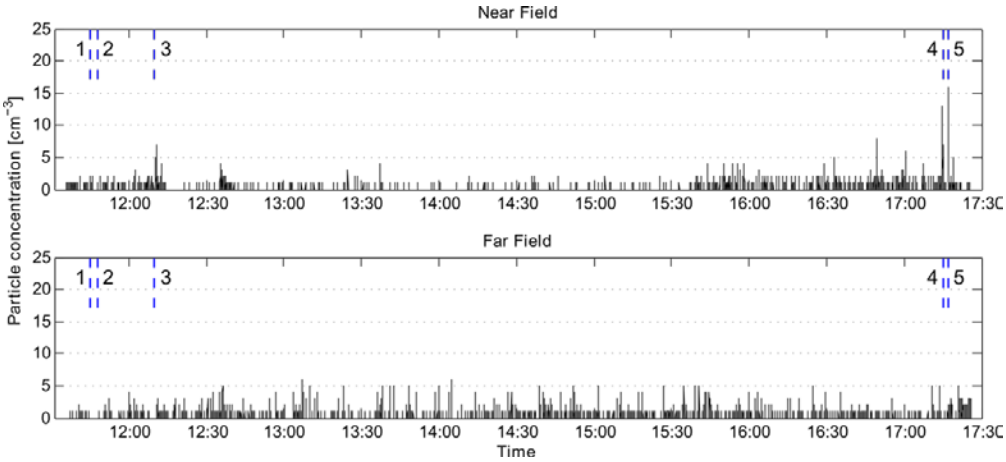
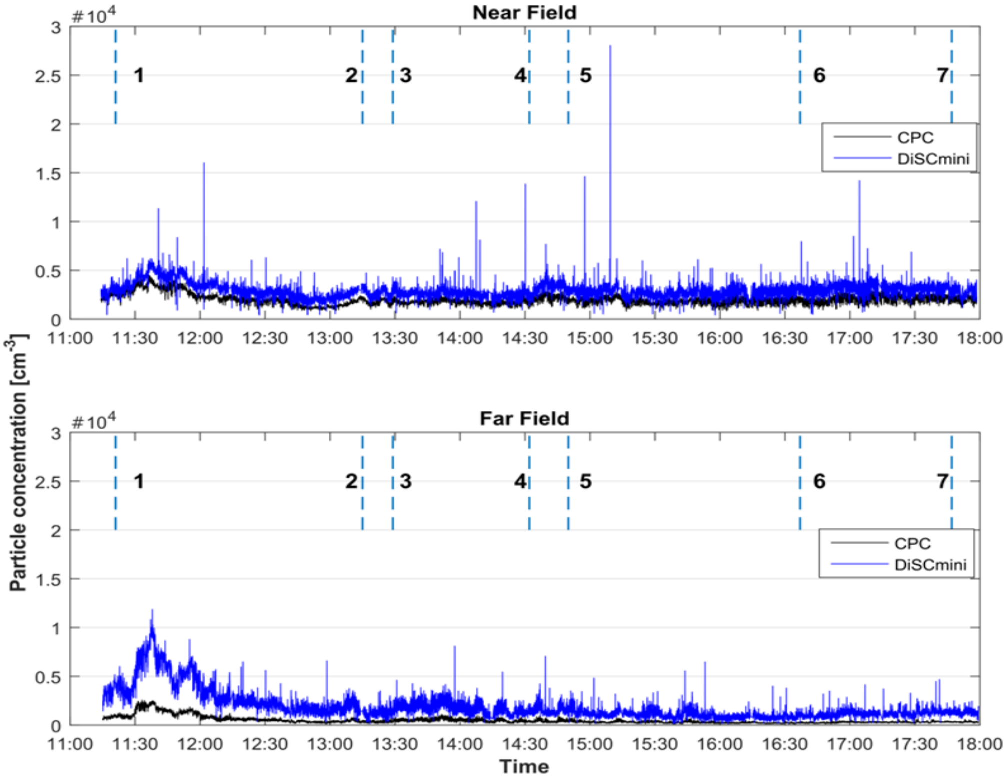


Figure 2: 1-Open BM reactor, 2-Close BM reactor 3-Initiate growth recipe, 4-Open BM reactor and 5-Dry wiping of quartz cylinder.

3.2.2 AIXTRON

Figure 3 shows total number concentrations measured from **AIX-Ltd.** during a graphene CVD process, also conducted with a BlackMagic reactor. The **AIX** site differs from that of **DTU** in not being a clean room location; this makes it more complicated to estimate possible emissions during CVD run (because of the low emission and higher background).

Generally, both near field and far field concentrations are have same trends, near field being bit higher. The CVD process related activities did not have a significant effect on the aeosol number concentrations. During the measurements different kind of process related events were carried out, and during some of those activities microscope samples were taken.In Figure 3 we can see short peaks in the Discmini data which do not appear in the CPC data. In this case these are most propably instrument related peaks (i.e. measurement artefacts). These apparent sudden concentration peaks in the Discmini data underline also the importance of using multiple measurement techniques. At **AIX-Ltd.** where the CVD process is not conducted in the clean room environment and has several particle sources, it will be vital to analyze the electron microscope samples before reporting if the reactor is a source of graphene particles or other process related emissions.



b) Figure 3. 1-Reactor Warm-up, 2-Open reactor, 3-Initiate growth recipe, 4-Open CNT chamber, 5-Open reactor–Wafer out, 6-Open reactor–Wafer out and 7-Open reactor – Wafer out.

4 Deviations from the DoW and Challenges

NRCWE have not yet received the EM micrographs from the **DTU** sampling and the dustiness tests are not completed yet (because of issues with the dustiness system). The dustiness test is now planned for May 2016. In addition, data from hazard experiments are needed for exposure assessment, therefore, we have decided to add this data to deliverable D4.6.

5 Conclusions, expected impact and use of Deliverable

We have measured potential exposure levels of particle emissions during specific work processes of small scale production of graphene (at **DTU**) and at a larger scale production sites (at **AIX**). Small scale measurements at **DTU** were done in a cleanroom and at **AIX** in a normal industrial environment. We used a first tier approach in which assessment is based (conservatively) on the total concentration number of emitted airborne particles and microscopicity to verify the emissions' origin. We measured low levels of 10 cm^{-3} and 2000 cm^{-3} number concentration in the near-field with CPC and DiscMini at **DTU** and **AIX-Ltd**, respectively. At **AIX-Ltd**. the online measurements showed really low emission levels. Later the micrographs will reveal if these low numbers are originating from the process or are they particles from the background.