IEC TS 62607-6-3

Edition 1.0 2020-10

TECHNICAL SPECIFICATION

colour inside

Nanomanufacturing – Key control characteristics –
Part 6-3: Graphene-based material – Domain size: substrate oxidation

IEC TS 62607-6-3:2020-10(en)

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NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

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FOREWORD

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Technical Specifications are subject to review within three years of publication to decide whether they can be transformed into International Standards.

IEC TS 62607-6-3, which is a Technical Specification, has been prepared by technical committee 113, Nanotechnology for electrotechnical products and systems.

The text of this Technical Specification is based on the following documents:

Enquiry draft	Report on voting
113/496/DTS	113/549/RVDTS

Full information on the voting for the approval of this Technical Specification can be found in the report on voting indicated in the above table.

This document has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts in the IEC TS 62607 series, published under the general title *Nanomanufacturing – Key control characteristics*, can be found on the IEC website.

The committee has decided that the contents of this document will remain unchanged until the stability date indicated on the IEC website under "http://webstore.iec.ch" in the data related to the specific document. At this date, the document will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

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INTRODUCTION

Graphene with two-dimensional honeycomb structures of carbon atoms is known to have exceptional electrical, thermal, and mechanical properties. Because of these properties, graphene is considered for applications in high speed, flexible and transparent devices. Figure 1 shows the images of graphene field effect transistor, flexible touch screen in display, and transparent electrode in solar cell. These applications of graphene are promising candidates for nanoelectronics and optoelectronics. Graphene has been widely investigated by researchers from academic institutions, research institutes, and industries.

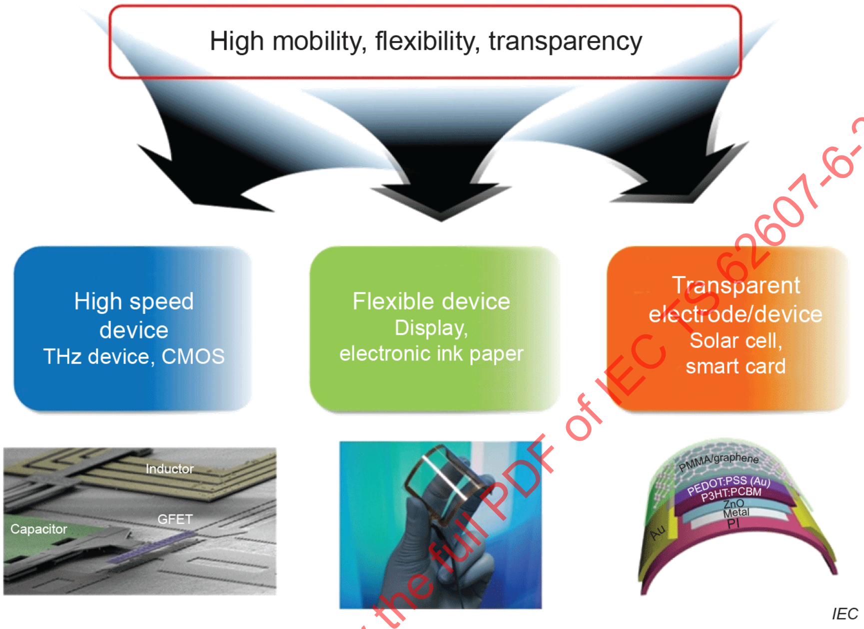


Figure 1 – Applications of graphene

Graphene synthesized on Cu or Ni substrate by chemical vapour deposition (CVD) is composed of graphene domains formed during the nucleation and initial growth stage. Graphene defects, such as pinholes, domain boundaries, and cracks, can be formed during the CVD growth or the transfer process.

Properties of graphene are related to the size and distribution of graphene domains and defects. As graphene domain size is increased and graphene defects are reduced, electrical and thermal properties of graphene are improved.

Graphene domains and defects are usually observed by atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and scanning tunnelling microscopy (STM). These analysis methods may cause inconvenience in preparing a sample for analysis and require very expensive equipment that provides only local information of several micrometres and below.

Facile, fast, reliable methods of evaluating graphene domains have not yet been established and urgently need to be developed.

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 6-3: Graphene-based material – Domain size: substrate oxidation

1 Scope

This part of IEC TS 62607 establishes a standardized method to determine the structural key control characteristic

– domain size

for films consisting of graphene grown by chemical vapour deposition (CVD) on copper by

– substrate oxidation.

It provides a fast, facile and reliable method to evaluate graphene domains formed on copper foil or copper film for understanding the effect of the graphene domain size on properties of graphene and enhancing the performance of high speed, flexible, and transparent devices using CVD graphene.

– The domain size determined in accordance with this document will be listed as a key control characteristic in the blank detail specification for graphene IEC 62565-3-1. Domain density is an equivalent measure.
– The domain size as derived by this method is defined as the mean value of size of the domains in the observed area specified by supplier in terms of cm^2 or $μm^2$.
– The method is applicable for graphene grown on copper by CVD. The characterization is done on the copper foil before transfer to the final substrate.
– As the method is destructive, the samples cannot be re-launched into the fabrication process.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ASTM E1951-14, *Standard Guide for Calibrating Reticles and Light Microscope Magnification*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

3.1 General terms

3.1.1
blank detail specification
BDS
structured generic specification of the set of key control characteristics which are needed to describe a specific nano-enabled product without assigning specific values and/or attributes

Note 1 to entry: The templates defined in a blank detail specification list the key control characteristics for the nano-enabled material or product without assigning specific values to it.

Note 2 to entry: Examples of nano-enabled products are: nanomaterials, nanocomposites and nano-subassemblies.

Note 3 to entry: Blank detail specifications are intended to be used by industrial users to prepare their detail specifications used in bilateral procurement contracts. A blank detail specification facilitates the comparison and benchmarking of different materials. Furthermore, a standardized format makes procurement more efficient and more error robust.

3.1.2
sectional blank detail specification
SBDS
specification based on a blank detail specification adapted for a subgroup of the nano-enabled product

Note 1 to entry: In general, the sectional blank detail specification contains a subset of those key control characteristics listed in the blank detail specification. In addition, sectional specific key control characteristics can be added if they are not listed in the blank detail specification.

Note 2 to entry: The templates defined in the sectional blank detail specification can contain key control characteristics with and without assigned values and attributes.

Note 3 to entry: The section can be defined by application, manufacturing method or general material properties.

3.1.3
detail specification
DS
specification based on a blank detail specification with assigned values and attributes

Note 1 to entry: The properties listed in the detail specification are usually a subset of the key control characteristics listed in the relevant blank detail specification. The industrial partners define only those properties which are required for the intended application.

Note 2 to entry: Detail specifications are defined by the industrial partners. SDOs will be involved only if there is a general need for a detail specification in an industrial sector.

Note 3 to entry: The industrial partners can define additional key control characteristics if they are not listed in the blank detail specification.

3.2 Graphene related terms

3.2.1
domain
single crystal of graphene, which might or might not contain defects

Note 1 to entry: The domain is surrounded by the domain boundary, a line discontinuation of crystal structure.

3.2.2
domain boundary
in-plane interface between two or more crystalline domains of a 2D material where the crystallographic direction of the lattice changes

3.2.3
graphene
graphene layer
single-layer graphene
monolayer graphene
single layer of carbon atoms with each atom bound to three neighbours in a honeycomb structure

Note 1 to entry: It is an important building block of many carbon nano-objects.

Note 2 to entry: As graphene is a single layer, it is also sometimes called monolayer graphene or single-layer graphene and abbreviated as 1LG to distinguish it from bilayer graphene (2LG) and few-layered graphene (FLG).

Note 3 to entry: Graphene has edges and can have defects and grain boundaries where the bonding is disrupted.

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.1]

3.2.4
graphene-based material
GBM
graphene material
grouping of carbon-based 2D materials that include one or more of graphene, bilayer graphene, few-layer graphene, graphene nanoplate, and functionalized variations thereof as well as graphene oxide and reduced graphene oxide

Note 1 to entry: "Graphene material" is a short name for graphene-based material.

3.3 Key control characteristics measured in accordance with this document

3.3.1
key control characteristic
KCC
key performance indicator
material property or intermediate product characteristic which can affect safety or compliance with regulations, fit, function, performance, quality, reliability or subsequent processing of the final product

Note 1 to entry: The measurement of a key control characteristic is described in a standardized measurement procedure with known accuracy and precision.

Note 2 to entry: It is possible to define more than one measurement method for a key control characteristic if the correlation of the results is well-defined and known.

3.3.2
domain size
mean value of size of the domains in the observed area specified by the supplier

Note 1 to entry: The unit of domain size is cm^2 or μm^2.

4 General

4.1 Measurement principle

Domain boundary is the good pathway for active oxygen species while active oxygen species are blocked by graphene within domain. Oxygen species pass through the domain boundary and oxidize Cu substrate. Copper oxide can be easily observed by microscope. An optical microscope or scanning electron microscope image is analysed using a software program such as Image J.[1]

———————

[1] ImageJ is a public domain, Java-based image processing program developed at the U.S. National Institutes of Health. This information is given for the convenience of users of this document and does not constitute an endorsement by IEC of this product.

NOTE Under special circumstances other methods can be suitable to gather additional information. Examples are given in Annex B.

4.2 Sample preparation method

To apply the method described in this document, the test sample shall be removed from the production process. The sample was placed in the oxidation chamber with humidity control and Hg lamp. As the method is destructive, the test samples cannot be re-launched into the production process. Even though the sample was oxidized and tested by optical microscope, the measurement process does not generate additional defects such as wrinkles. The oxidation procedure does not change the domain size.

Graphene formed on Cu substrate or Cu film using chemical vapour deposition shall be exposed to ultraviolet light under moisture-rich ambient condition for tens of minutes.

As shown in Figure 2, this approach is based on the robust oxidation of copper foil at room temperature via the selective diffusion of oxygen radicals through O and OH-functionalized defects in the graphene domain boundaries. These radicals are generated using ultraviolet irradiation under moisture-rich ambient condition. To accelerate the oxidation reaction, the sample is heated on hot plate. The temperature is lower than 200 °C. The humidity of an environment where the water vapour is formed may be 25 % to 80 %.

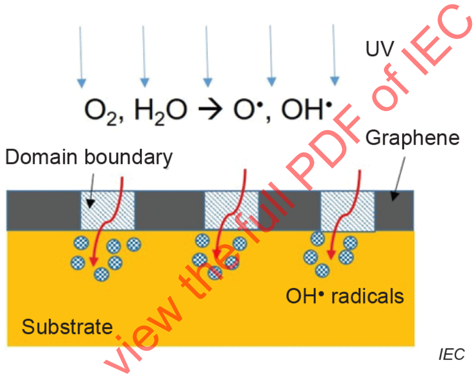


Figure 2 – Schematics for oxidation of copper foil through the graphene boundaries

Oxidation of the copper takes place at the Cu substrate beneath domain boundaries and defects within domain due to the selective diffusion of O and OH radicals. Oxidation may be carried out using hot plate in the air.

Typical oxidation conditions are the following.

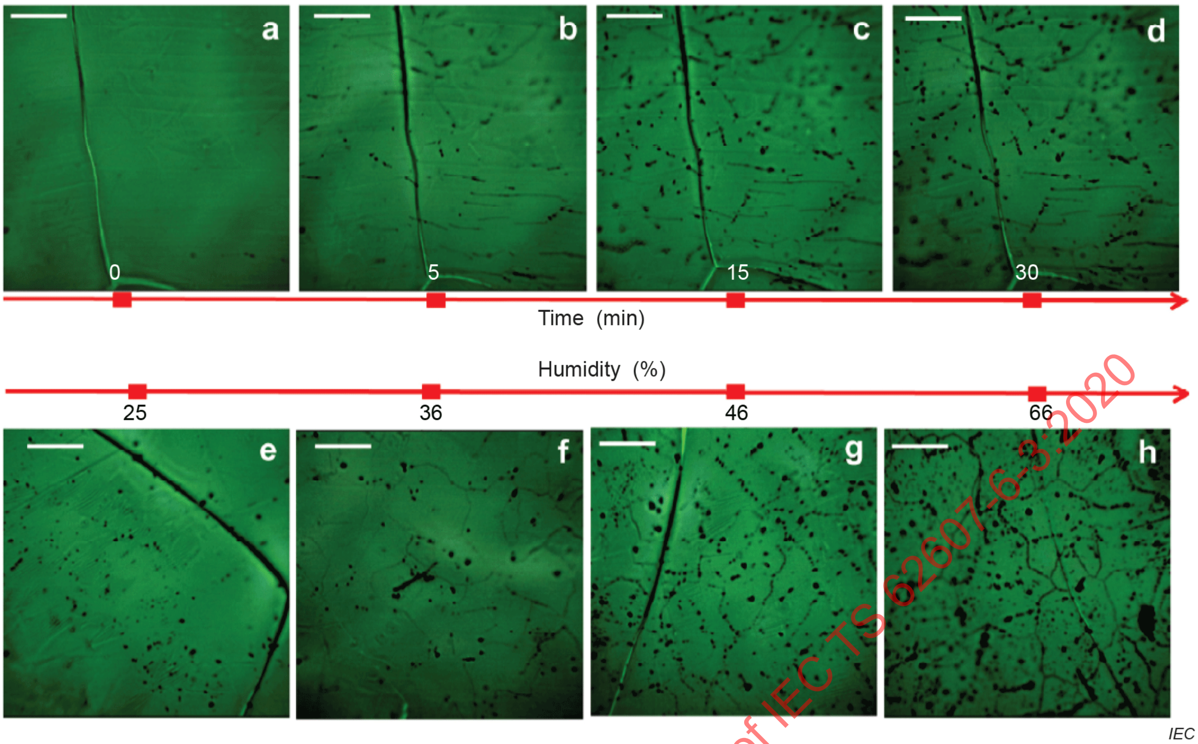
– Humidity: 25 % to 80 %.

– UV light intensity: 20 mW/cm^2 to 70 mW/cm^2.

– Oxidation time: 5 min < t < 60 min.

– If hot plate is used to accelerate oxidation, temperature of hot plate: 100 °C < T < 200 °C.

Optical images from samples oxidized under different conditions are shown in Figure 3.



NOTE Graphene on Cu foil was oxidized under different conditions: (a-d) Graphene/Cu foil was oxidized for different times at humidity of 25 % at room temperature. (e-h) Graphene/Cu foil was oxidized under different humidities for 10 min at room temperature. The scale bar is 10 µm. The intensity of the illumination of the Hg lamp was 20 mW/cm^2.

Figure 3 – Optical image of the graphene domains on Cu foil

4.3 Measurement system

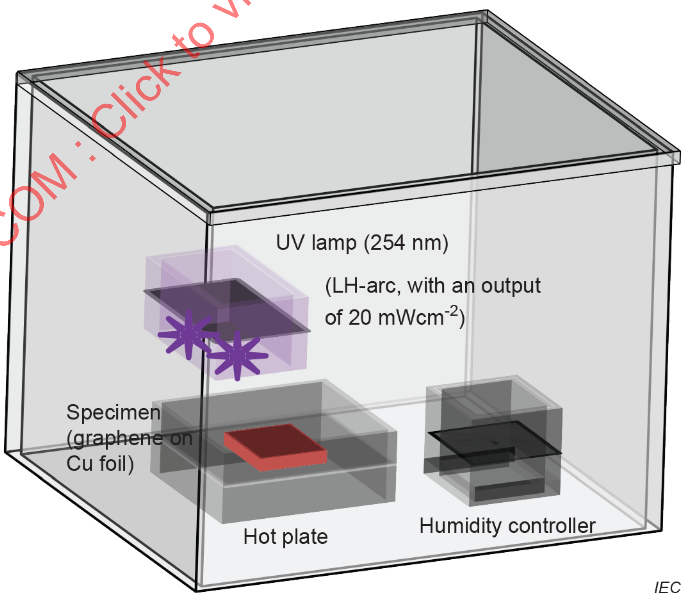


Figure 4 – Schematic view of oxidation system

Figure 4 shows a schematic view of the oxidation system, consisting of UV lamp, humidity controller, and hot plate

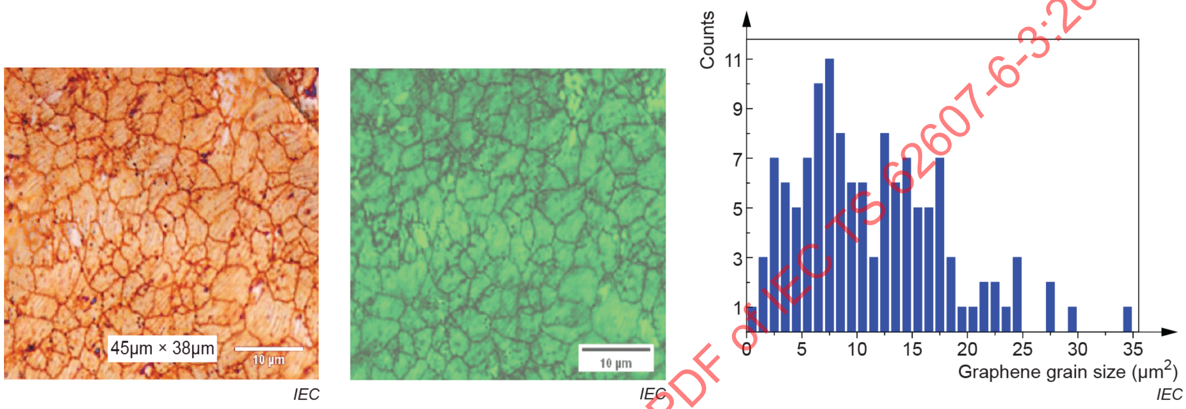
4.4 Description of measurement equipment/apparatus

Conventional optical microscope or SEM is the measurement equipment.

Optical microscope or SEM with scale bar can be used for taking a fluorescent image of sample.

An image analysis program such as ImageJ can be used for measuring the size of the graphene domain where the number of pixels in domain was counted first and it was converted into size of domain in area scale (cm^2 or μm^2) by multiplying the number of pixels in domain by size of pixel.

Figure 5 shows the example of domain size of the graphene/Cu foil using ImageJ.



a) optical images of graphene/Cu after oxidation | b) measuring graphene grain size by using Image J | c) grain size distribution and average grain size of graphene

NOTE Experimental condition: UV exposure (254 nm) and heat treatment (200 °C) for 1 h, humidity 85 %.

Figure 5 – Optical images of graphene/Cu after oxidation and analysed grain size distribution

4.5 Calibration standards

No specific standard is required.

4.6 Ambient conditions during measurement

Room temperature and atmospheric condition during measurement.

5 Measurement procedure

5.1 Calibration of measurement equipment

– Use a stage micrometer to determine the true linear magnification for each objective, eyepiece and bellows, or zoom setting to be used within ±2 %.

– Use a ruler with a millimetre scale to determine the actual length of straight test lines or the diameter of test circles used as grids.

– Calibration shall be carried out in accordance with ASTM E1951-14.

5.2 Detailed protocol of the measurement procedure

5.2.1 General

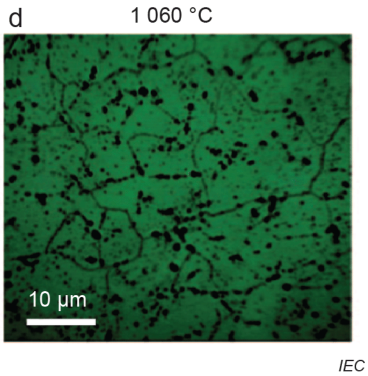
– Take the image of the sample using an optical microscope or scanning electron microscope.

– Use a software program such as ImageJ and make the image clearer using various options provided by software program.

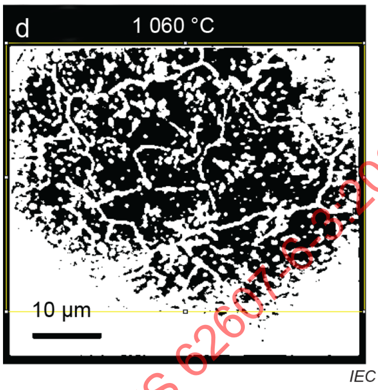
– Measure the domain size and distribution of domain size.

5.2.2 Example

The test sample was prepared. Graphene was formed on Cu foil at 1 060 °C for 5 min. Graphene/Cu was oxidized at 65 % of ambient humidity for 10 min. An SEM image was taken and domain size was analysed using ImageJ. The results are shown in Figure 6.



Before adjust



After adjust

NOTE Graphene was formed on Cu foil at 1 060 °C and graphene/Cu was oxidized at 65 % ambient humidity for 10 min.

Figure 6 – Example of domain size analysis

Domain boundaries were visualized and black dots were observed. Because of black dots, analysis was not easy nor correct. To obtain good results, graphene with fewer defects was formed and the oxidation condition was optimized depending on the sample.

6 Results to be reported

6.1 General

The results of the measurement shall be documented in a measurement report, including the date and time of the measurement as well as the name and signature of the person responsible for the accuracy of the report. Guidelines for the reporting are given in Annex A "Worked example".

6.2 Product/sample identification

The report shall contain all information to identify the test sample and trace back the history of the sample:

– General procurement information.
– General material description, including a technical drawing:
  - top view, indicating the inspected area and location of the measurement positions;
  - cross section, showing the layer structure.

NOTE This information will be included in the future blank detail specification for graphene (IEC 62565-3-1).

6.3 Test conditions

The laboratory ambient conditions during the test:

– atmosphere;
– temperature;

– range of relative humidity.

To measure the domain area (hundreds of nanometres), SEM with high magnification is recommended.

6.4 Measurement specific information

- Oxidation method: exposure of sample to UV illumination at ambient humidity at different hot plate temperatures.
- Oxidation condition:

  Range of relative humidity: 25 % < RH < 90 %.

  Oxidation time: 10 min < t < 60 min.

  Hot plate temperature: room temperature < T < 200 °C.

6.5 Test results

- Coordinate system used in the measurement setup in absolute positions with a definition of the origin so that the measurement locations can be related to the technical drawing of the sample.
- Table of mean values and standard deviation of the KCC measured in accordance with this document at the positions defined by the sampling plan.
- Colour maps for KCC measured in accordance with this document. The colour map shall be scaled in absolute positions in respect of the origin of the coordinate system. The colour code should be calibrated in absolute values of the measured KCC.

Annex A
(informative)

Worked example

A.1 Example

Figure A.1 to Figure A.5 show the example of characterization of domain size. Graphene was grown on Cu foil as substrate at 1 050 °C using CVD with CH_4. Size of the sample is 7 × 7 cm. Measurement of domain size was performed in accordance with the sample plan as specified in Figure A.6.

Dimensions in centimetres

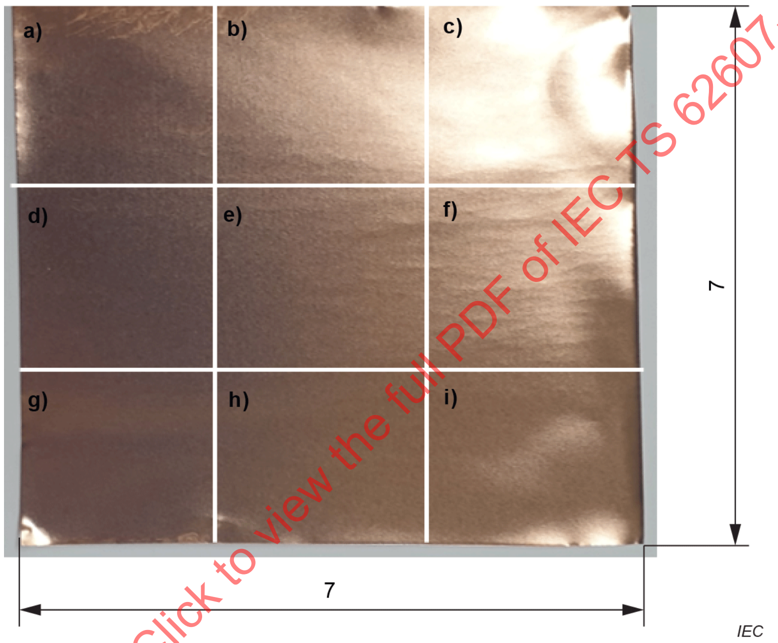


Figure A.1 – Photograph of graphene/Cu foil (7cm × 7 cm) for graphene grown at 1 050 °C by CVD with CH_4

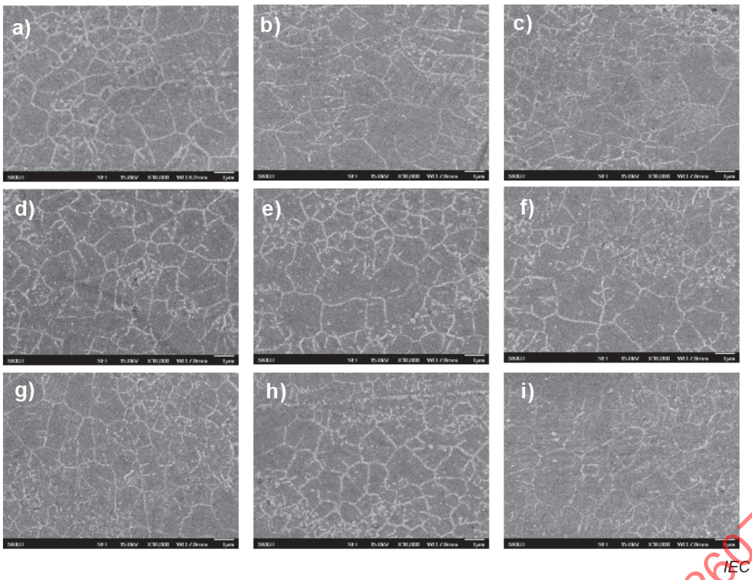


Figure A.2 – SEM image of graphene/Cu after oxidation at the points as specified in Figure A.6

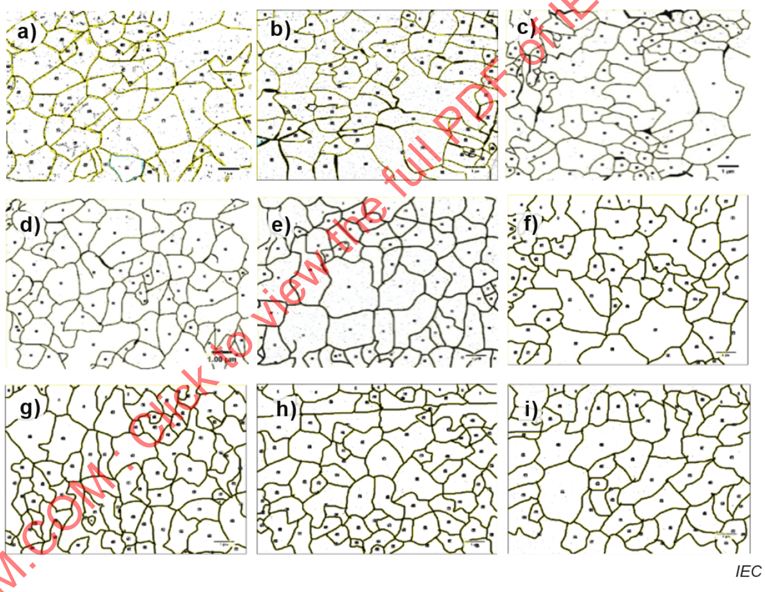


Figure A.3 – Measuring graphene domain size of Figure A.2 using Image J

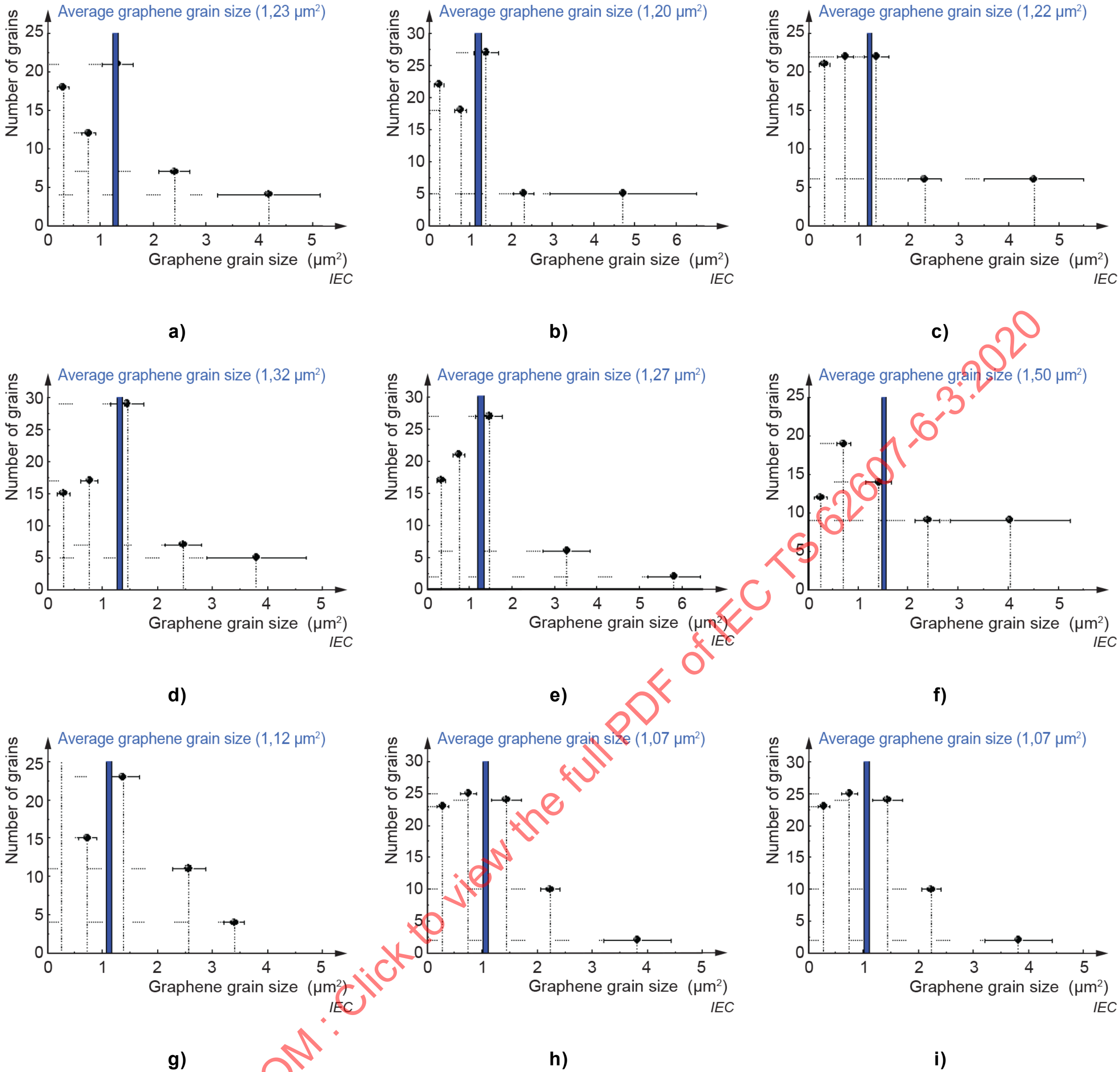


Figure A.4 –Domain size distribution and average domain size of graphene shown in Figure A.2

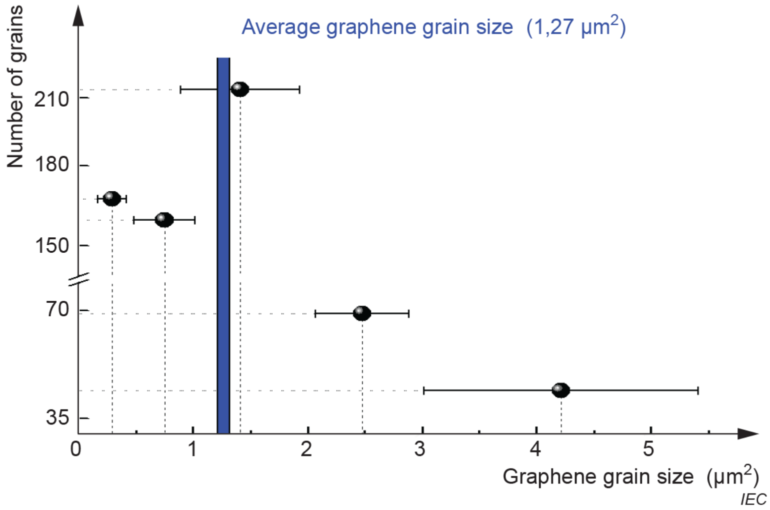
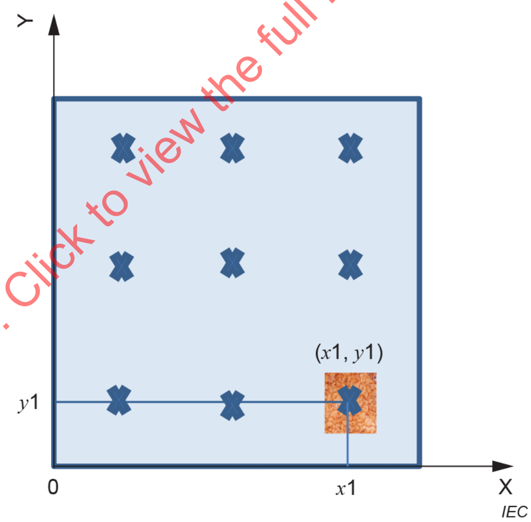


Figure A.5 – Accumulative domain size distribution shown in Figure A.4 and average domain size of graphene measured at 9 points shown in Figure A.6

A.2 Sampling plan

Figure A.6 shows the location of the analysed area on the sample. The origin (0, 0) is placed at the left bottom corner of the sample. As shown in Figure A.6, nine areas including the centre of the sample are measured.



Origin: The origin of the coordinate system shall be defined in a way that the measurement positions can be reproduced reliably. The best way is to have a mark on the substrate.

Usable area: Due to the manufacturing process, not the whole substrate surface might be usable. The supplier shall define the usable area of the substrate in which the specifications are guaranteed (blue coloured area in the figure).

Measurement locations: Measurement locations (Example: blue cross located on the substrate) shall be provided in absolute coordinates ($x1;y1$). If requested by the standard, the reported value of the KCC might be averaged over a defined area (blue coloured area in the figure) around the measurement position, $[x1 - \Delta x/2{:}x1 + \Delta x/2];[y1 - \Delta y/2{:}y1 + \Delta y/2]$.

Positions of colour maps and pictures shall be given in absolute coordinates.

Figure A.6 – Location of the analysed area on the sample