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TECHNICAL SPECIFICATION

colour inside

Nanomanufacturing – Key control characteristics – Part 2-4: Carbon nanotube materials – Test methods for determination of resistance of individual carbon nanotubes

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

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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 62607-2-4, which is a Technical Specification, has been prepared by IEC technical committee 113: Nanotechnology for electrotechnical products and systems.

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

DTS	Report on voting
113/492/DTS	113/509/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 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 publication will remain unchanged until the stability date indicated on the IEC website under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

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- withdrawn,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

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INTRODUCTION

Carbon nanotubes (CNTs) are one-dimensional conductors that exhibit a rich variety of low-dimensional electric transport phenomena. Ballistic conduction is the typical nano-enabled characteristic that possesses the largest potential for industrial application. In the field of nanoelectronics, for example, CNT-based interconnects are a promising alternative to conventional Cu interconnects. However, even in the academic research society, the resistive characteristics have not yet been systematically investigated. This is because these characteristics are very sensitive to the protocol and the measurement conditions. Furthermore, since the individual CNT reaches the nanometre dimension, the contact resistance has a larger relative impact on the measurement. These bottlenecks impede not only the above-mentioned interconnect application but also developments of various electrotechnical applications, such as thermoelectric devices in which the electrical resistance is required to evaluate the figure of merit.

This document offers the accurate and reproducible test method for determining the resistance of CNT and the dependability of the measurement.

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 2-4: Carbon nanotube materials – Test methods for determination of resistance of individual carbon nanotubes

1 Scope

This part of IEC 62607 specifies the test method for determining the resistivity and the contact resistance of an individual CNT and the dependability of the measurement.

This document includes:

– outlines of the experimental procedures used to measure resistance of carbon nanotubes,
– methods of interpretation of results and discussion of data analysis, and
– case studies.

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.

IEC 62624, *Test methods for measurement of electrical properties of carbon nanotubes*

ISO/TS 80004-1, *Nanotechnologies – Vocabulary – Part 1: Core terms*

NOTE IEC 62624 describes the general procedures for characterization of CNT. For example, no environmental condition is specifically required. On the other hand, this document focuses not only on the characterization of the individual CNT but also the reproducibility. To obtain the intrinsic nano-originated result and to measure up to the dependable measurement, in-vacuum non-destructive measurements are indispensable, and therefore this document (IEC TS 62607-2-4) is required.

3 Terms, definitions, and abbreviated terms

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 80004-1 and the following 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

3.1.1
carbon nanotube
CNT
nanotube composed of carbon

[SOURCE: ISO/TS 80004-3:2010, 4.3]

3.1.2
single-wall carbon nanotube
SWCNT
single-walled carbon nanotube
carbon nanotube consisting of a single cylindrical graphene layer

Note 1 to entry: The structure can be visualized as a graphene sheet rolled into a cylindrical honeycomb structure.

[SOURCE: ISO/TS 80004-3:2010, 4.4]

3.1.3
multiwall carbon nanotube
MWCNT
multi-walled carbon nanotube
carbon nanotube composed of nested, concentric or near-concentric graphene sheets with interlayer distances similar to those of graphite

Note 1 to entry: The structure is normally considered to be many single-wall carbon nanotubes (3.1.2) nesting each other, and would be cylindrical for small diameters but tends to have a polygonal cross-section as the diameter increases.

[SOURCE: ISO/TS 80004-3:2010, 4.6]

3.1.4
device under test
DUT
sample attached to an apparatus for evaluation of a specific physical property such as electrical resistance or I-V behaviour

3.1.5
***I*-*V* characterization**
measurement of the current-voltage characteristic

Note 1 to entry: In 4-probe measurement, V is the voltage drop between two inner probes.

3.1.6
4-probe measurement
method to measure the resistance of a material with large sample dimensions whose measured value is independent on the probe resistance

Note 1 to entry: This is different from four-point probe measurement. With 4-probe measurement, the length of the DUT can be varied without causing damage to the CNT under measurement by changing the distance of the inner two probes.

[SOURCE: IEC 62607-2-1:2010, 2.1.6, modified – In the definition, "with large sample dimensions" has been added.]

3.1.7
nanoscale contact resistance
electrical resistance associated with a nanoscale contact

[SOURCE: IEC TS 80004-9:2017, 3.1.9]

3.1.8
scanning electron microscope
SEM
intermediate type of microscopic morphology observation instrument between transmitted electron microscope and light microscope which uses a focused beam of high-energy electrons to generate a variety of physical information signals

[SOURCE: ISO 17751-2:2016, 2.2]

3.2 Abbreviated terms

CVD chemical vapour deposition

EBAC electron beam absorbed current

SMU source measure unit

4 Measurement of resistance

4.1 General

The accurate and reproducible test protocol of resistance measurement, together with the confirmation of the dependability, is standardized.

4.2 Method for processing and fabrication of DUT

Fabrication process information of DUT is to be reported, such as the method of dispersion and the method to apply it onto a substrate.

Fabrication process information of CNT is to be reported [CVD, laser ablation, electric arc, etc.], along with descriptions of any postgrowth treatments, such as a chemical purification, a disaggregation, a structural sorting, and a surface modification.

In order to avoid resistance measurement artefacts, the substrate with the higher electric resistance and the flat surface in nanometre scale, such as a thermally oxidized Si substrate with the insulating SiO_2 layer and a glass substrate, should be utilized as the substrate of DUT. In order to avoid resistance measurement artefacts, the electric resistance of the substrate (R_{sub}) should be higher than that of DUT (R_{dut}). The parallel current path in the substrate becomes smaller with the ratio of R_{dut}/R_{sub}. This value should be smaller than the error bar of the data. The surface of the substrate should be flat in nanometre scale, such as a thermally oxidized Si substrate with the insulating SiO_2 layer.

4.3 4-probe measurement

Experimental procedures and measurement conditions.

- 4-probe measurement of CNT is performed with a probing system in a SEM chamber, as shown in Figure 1.
- Firstly, a suitable probe type is chosen based on the diameter of the CNT to be measured.
- Before measurement, it is important to check the vacuum condition and SEM condition of the probing system in order to confirm the equipment condition for measurement.

  Technical specification: The vacuum level should be lower than 10^{-5} Pa.

  Technical specification: Check to see there is no measurable electromagnetic interference.
- For assuring high quality contact of probe onto CNT, the probe tip condition is confirmed under SEM observation. A probe with bent tip or contamination should be replaced.
- After loading the sample, the vacuum condition and SEM condition should be checked again to guarantee the qualified measuring condition.
- A fast SEM image is useful to search for proper CNT to measure. Straight isolated CNT with length long enough is preferred as it is easy to touch down probes with varying probe-to-probe distance.
- 4 probes are touched down onto CNT one by one.
- It is necessary to check the contact condition between probe and CNT before every measurement. In order to verify the contact condition, the current is measured while voltage is applied between the outer (or inner) two probes.
- The compliance current is set to protect CNT.

- Finally, 4-probe measurement of selected CNT is performed by applying voltage and observing current at the outer two probes while measuring voltage at the inner two probes.

  Technical specification: I-V curves with at least 4 different lengths of the selected CNT.

NOTE 1 Hereinafter, outer probes may also be referred to as current probes and inner probes as voltage probes.

NOTE 2 One of the practical candidates to measure the vacuum level is an ionization gauge.

NOTE 3 One of the practical candidates to evaluate the electromagnetic interference is the SEM image.

The current compliance should be settled in order to avoid the breakdown. The example is shown in Figure A.9.

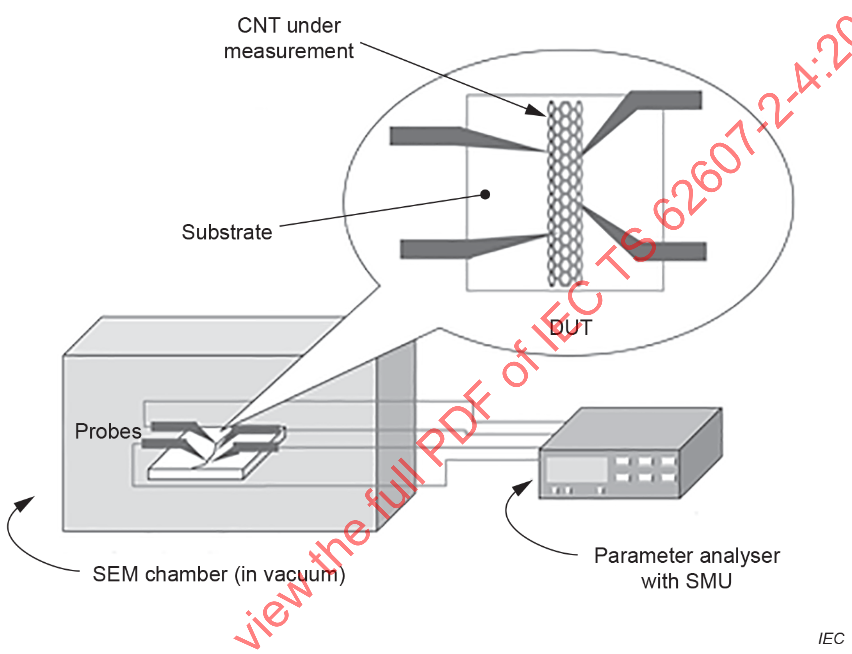


Figure 1 – 4-probe measurement in a SEM chamber

5 Reporting data

- Vacuum condition (before measurement)
- Vacuum condition (after loading sample)
- Material of the probe used
- I (as the I-V relationship with 2- and 4-probe measurements)
- V (as the I-V relationship with 2- and 4-probe measurements)
- CNT length in contact with the probes
- CNT length dependence of the resistance
- Resistance with the unit length and the error in the fitting analyses
- CNT diameter
- Substrate (material, thickness, electric property)
- Conditions of the SEM observation (acceleration voltage, magnification)

NOTE These sets of reporting data are shown in any manner, depending on the practical purpose.

6 Data analysis / interpretation of results (Annex A)

6.1 General

The measured raw current is plotted as a function of voltage. Then a linear fitting as $y = K1 \times x$ with the least-squares method is performed to estimate the resistance value, which is calculated as follows:

$$R = 1 / K1,$$

where R is the resistance and $K1$ is the slope calculated by the least-squares method.

Linear fitting equation is $y = K0 + k1 \times x$. $K0$ is fixed as a constant value of 0, then the line passes through the origin.

6.2 Measurement error

Example 1.

Using crooked or curved CNT may result in measurement error, which in turn significantly affects the accuracy of the result. As shown in Figure 2, for example, when measuring voltage over a relatively straight section of such CNT (across the voltage probes V1 and V2, in this case), the linear distance, d, between V1 and V2 is substantially equal to the length of DUT or the length of CNT in contact with the inner probes, and the measurement error is therefore negligible. When placing the voltage probes over a crooked/curved portion of CNT, however, the linear distance, d', between V1 and V2′ is considerably less than the length of DUT, presenting a measurement error that cannot be ignored. It is thus strongly recommended that a straight CNT be chosen for the measurement.

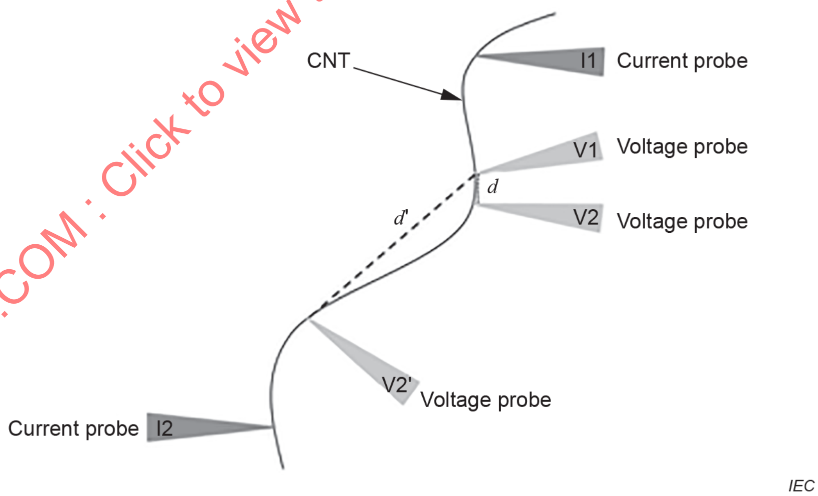
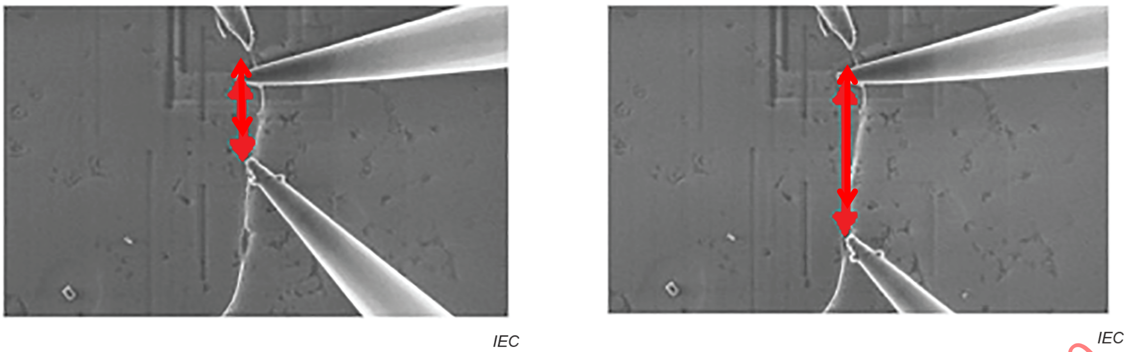


Figure 2 – A crooked/curved CNT under measurement

As shown in Figure 3, when the CNT under measurement is sufficiently straight, the inter-probe distance can be regarded as the length of CNT in contact with the probes. The inter-probe distance for (a) and (b) are 1 106 nm and 2 102 nm, respectively.



(a) (b)

Figure 3 – *I*-*V* measurement of a sufficiently straight CNT

6.3 Need to prepare the proper electric probing circuit

The resistance changes drastically depending on the length and the diameter of CNT. Proper electric probing circuit is necessary to obtain the intrinsic result.

6.4 Need to prepare the proper substrate and electric contact

The resistance changes depending on the substrate holding the individual CNT and how to contact with the probe.

6.5 Dynamic range

In order to obtain the intrinsic result of *I*-*V* measurement, the dynamic range of the probing circuit should be larger than the resistance change of CNT.

6.6 Current density

The resistance changes depending on the current density. In order to obtain the proper result from measurement, the estimated uncertainty of the condition should be provided in the test report.

6.7 Voltage bias of the substrate

The resistance changes depending on the voltage bias of the substrate. In order to obtain the proper result from measurement, the estimated uncertainty of the condition should be provided in the test report.

6.8 Measurement in vacuum

The resistance changes depending on the circumstances, such as the existence of oxygen. The measurement in vacuum is recommended.

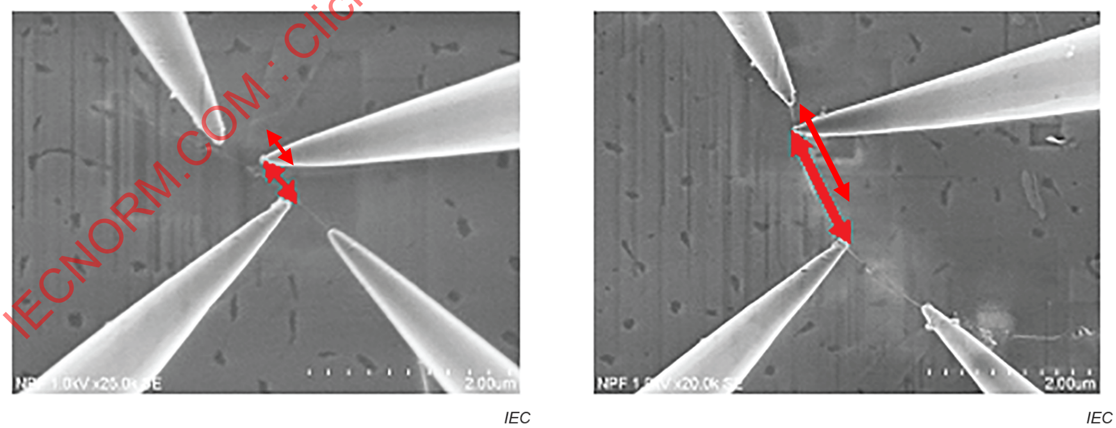
Annex A
(informative)

Case study

A.1 4-probe measurement of MWCNT

A.1.1 *I-V* measurements of MWCNT

- 4-probe measurement of MWCNT is performed with a probing system in a SEM chamber, as shown in Figure A.1.
- Firstly, a suitable probe type is chosen based on the diameter of the CNT to be measured.
- Before measurement, it is important to check the vacuum condition and the SEM condition in order to confirm the equipment condition for measurement.
- For assuring high quality contact of probe onto CNT, the probe tip condition is confirmed under SEM observation. A probe with bent tip or contamination should be replaced.
- After loading the sample, the vacuum condition and SEM condition should be checked again to guarantee the qualified measuring condition.
- A fast SEM image is useful to search for proper CNT to measure. Straight isolated CNT with length long enough is preferred as it is easy to touch down probes with varying probe-to-probe distance.
- 4 probes are touched down onto the CNT one by one under piezoelectric force.
- It is necessary to check contact condition between probe and CNT before every measurement. In order to verify the contact condition, the current is measured while voltage is applied between the outer (or inner) two probes, as shown in Figure A.2 and Figure A.3.
- The compliance current is set to protect CNT.
- Finally, 4-probe measurement of selected MWCNT is performed by applying voltage and observing current at the outer two probes while measuring voltage at the inner two probes, as shown in Figure A.4.



(a) L = 364 nm (L_1) (b) L = 1 443 nm (L_2)

Figure A.1 – *I-V* measurements of a CNT with different lengths, *L*

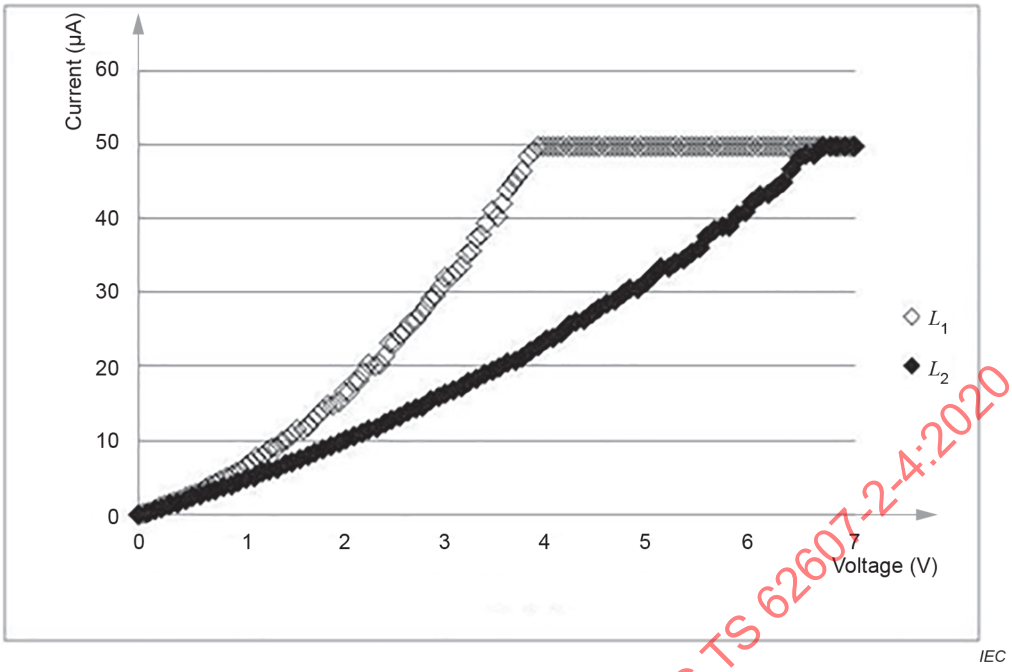


Figure A.2 – *I*-*V* relationships for different CNT lengths – 2-probe measurement

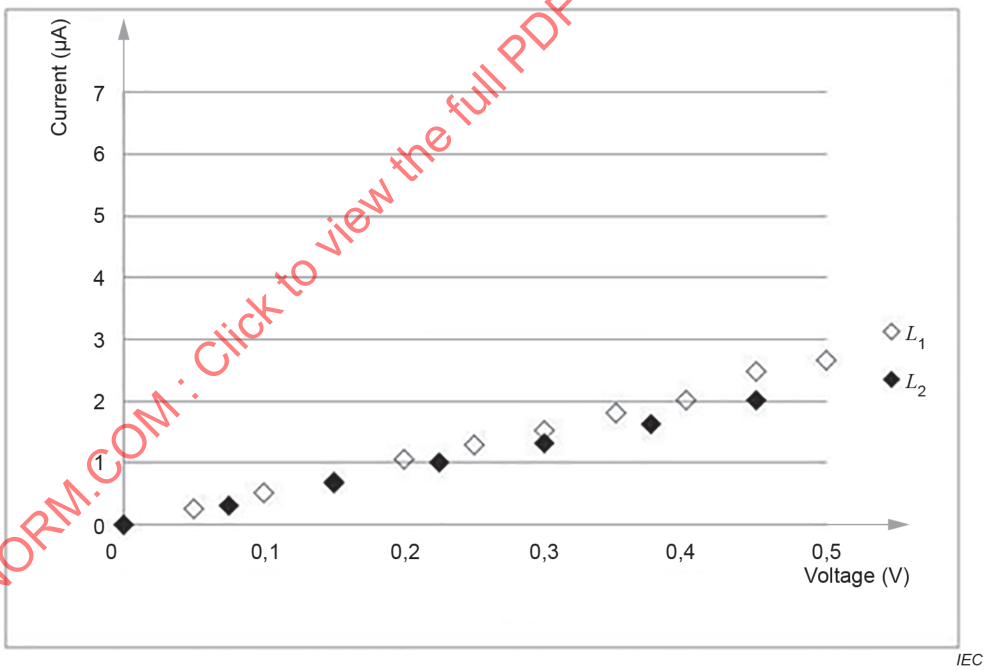


Figure A.3 – *I*-*V* relationships for different CNT lengths – 2-probe measurement (0 to 0,5 V)

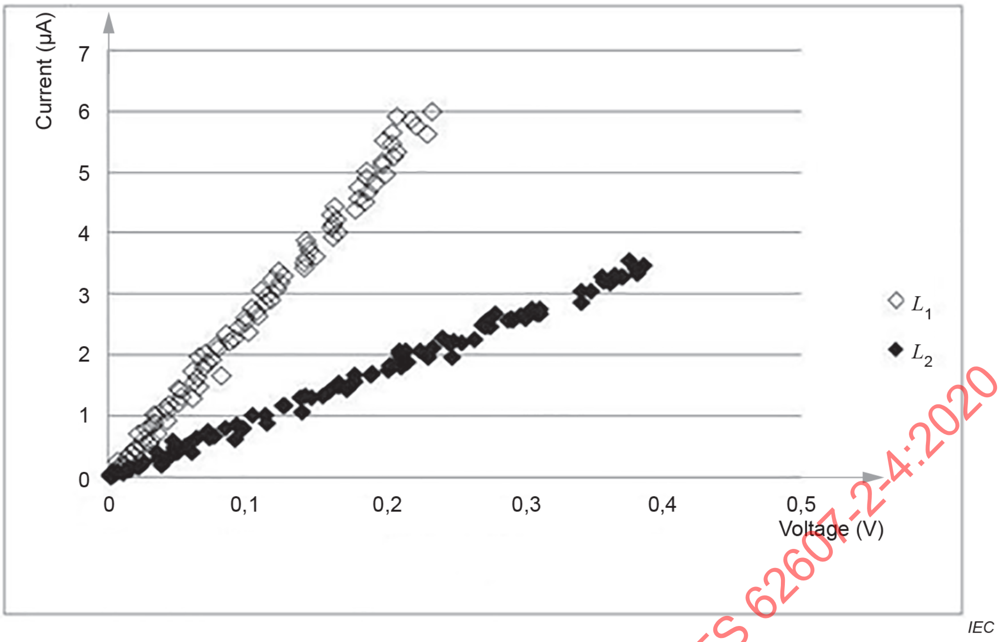


Figure A.4 – *I*-*V* relationships for different CNT lengths – 4-probe measurement

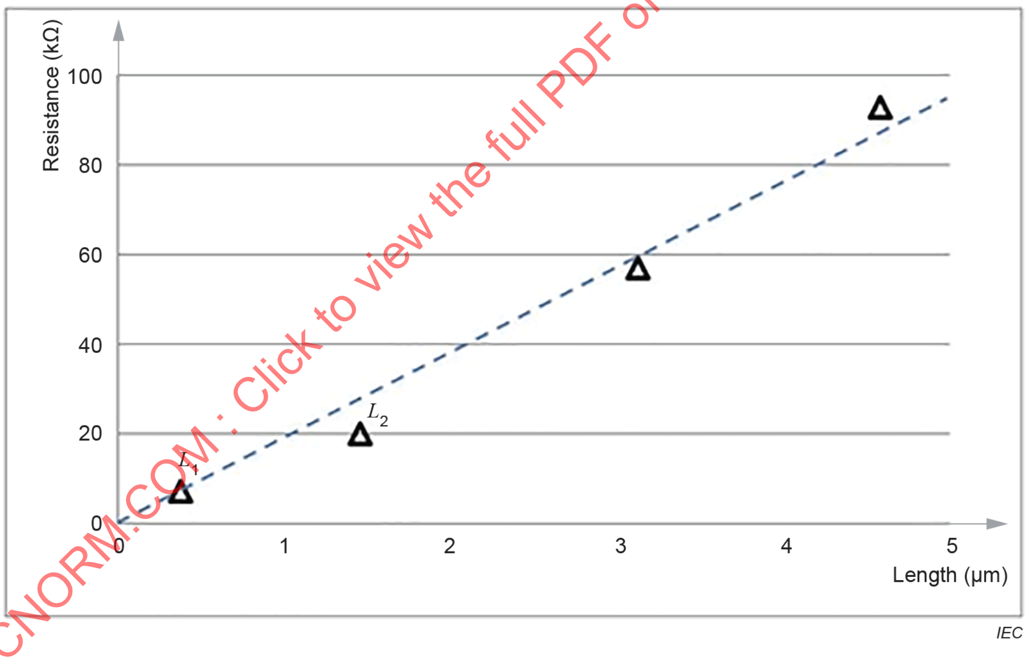


Figure A.5 – Resistance vs. CNT length

For the fitting line in Figure A.5, R (kΩ) = 19,292 × L (µm). The error calculated by residual sum of squares was 92,454 37 (kΩ^2), and the coefficient of determination, r^2, was 0,854 206.

NOTE 1 In the case that the linear condition is shown, the diffusive conduction is considered to be confirmed.

NOTE 2 The contact resistance can be estimated together with the resistance of CNT.

NOTE 3 The small error indicates the accuracy and the repeatability of test methods.

A.1.2 Fabrication process information of MWCNT and DUT

Fabrication method of MWCNT: CVD.

Postgrowth treatment: Thermal annealing of 2 000 °C in an inert atmosphere.

Dispersion: Ultrasonic dispersion in surfactant solutions in H_2O and organic solvent (AK-225).

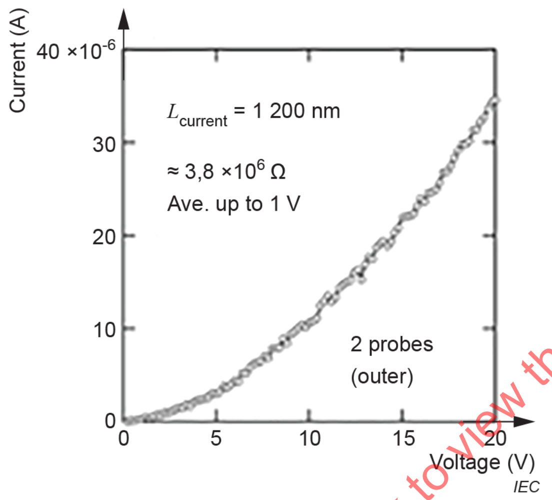
Method to apply onto a substrate: DIP coating onto a glass substrate.

A.2 4-probe measurement of SWCNT

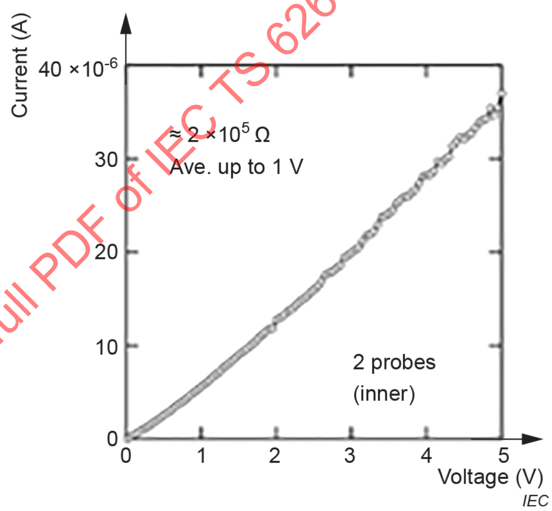
A.2.1 *I-V* measurements of SWCNT

4-probe measurement of SWCNT is performed with a probing system in a SEM chamber.

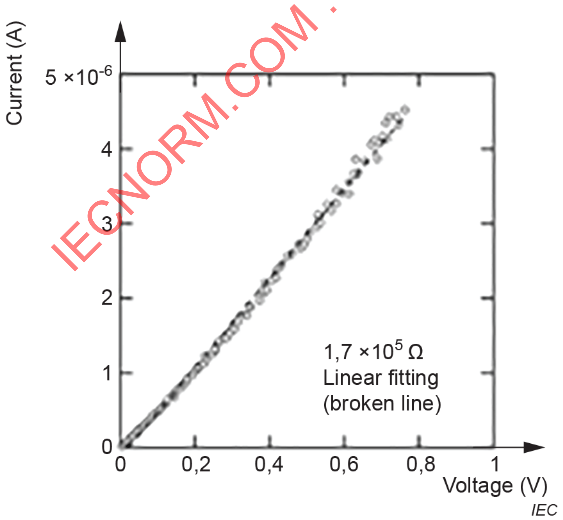
The protocol of the measurement was the same as in Clause A.1. The *I-V* relationship of 2-probe and 4-probe measurements and the SEM image are shown in Figure A.6. Figure A.7 shows the length dependence of resistance.



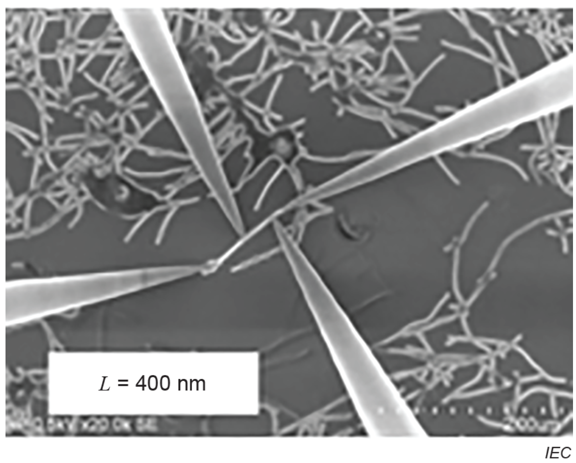
a) relationship of two outer probes with the interval of 1 200 nm



b) relationship of two inner probes with the interval of 400 nm

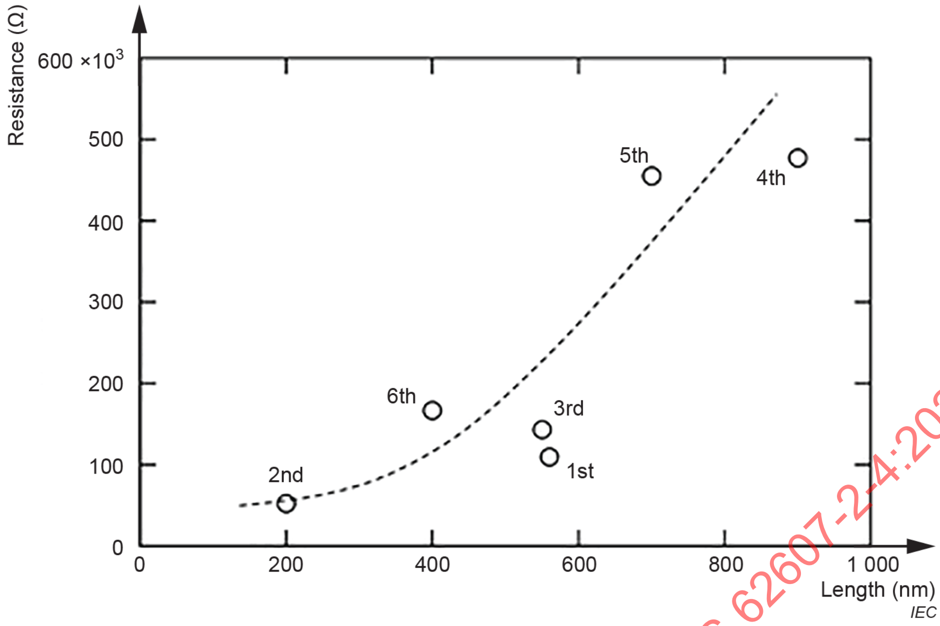


c) relationship of 4-probe measurement



d) SEM image of the DUT

Figure A.6 – *I-V* relationships of SWCNT



1st, 2nd, 3rd, etc. indicate the order of the *I*-*V* measurements.

Figure A.7 – Resistance vs. SWCNT length

NOTE The accuracy and the repeatability of test methods are specified by showing the relationship between the resistance and the length of CNTs. The value of the resistance and the tendency of the length-dependence are similar to those previously reported [P.J. de Pablo et al. (2002), see Bibliography].

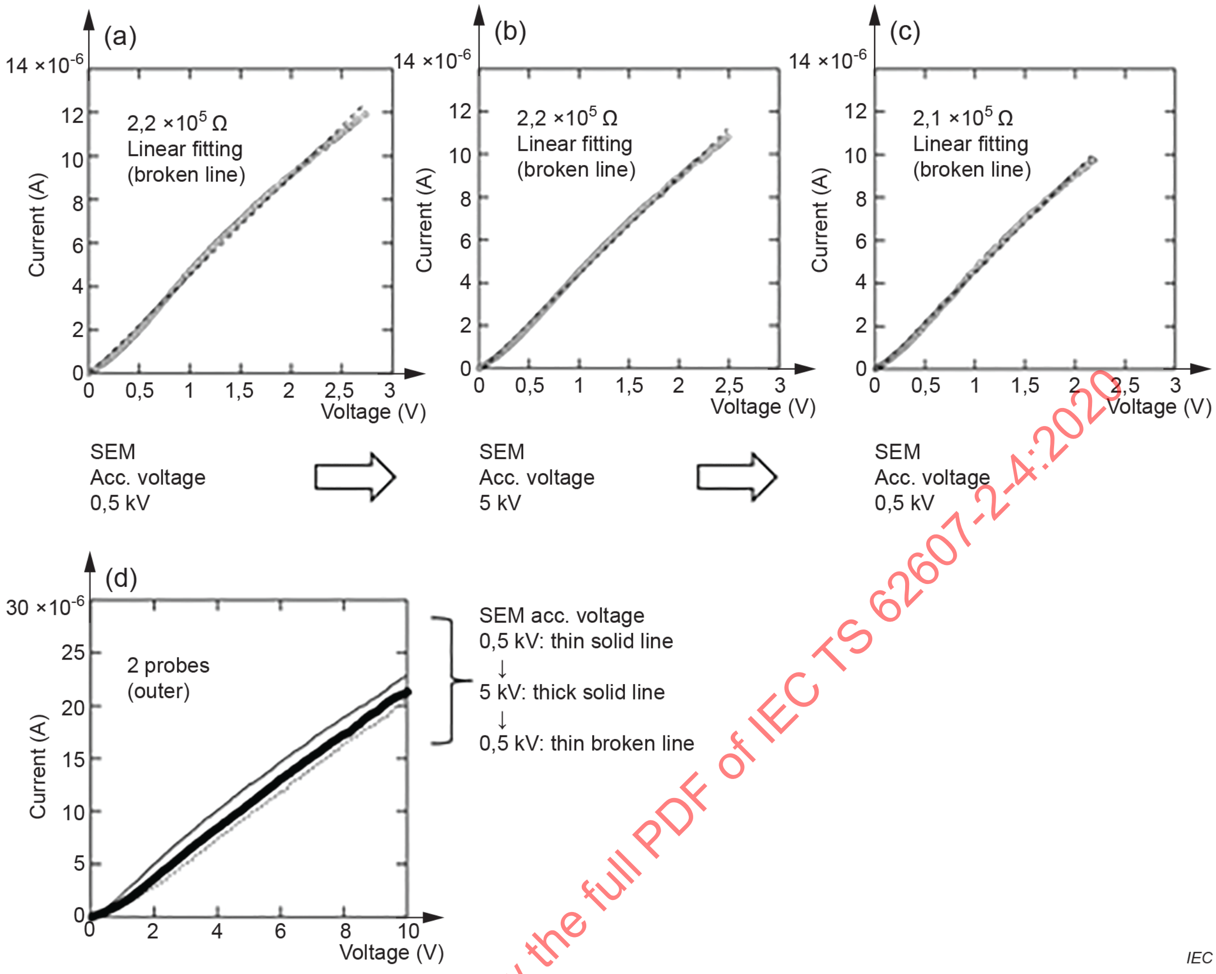


Figure A.8 – *I*-*V* relationships of SWCNT under the electron-beam exposure

In 4-probe measurements, almost no change by the electron-beam exposure has been observed [a) to c)], whereas the change did appear in 2-probe measurements [d)], as shown in Figure A.8.