IEC TS 62607-2-5

Edition 1.0 2022-11

TECHNICAL SPECIFICATION

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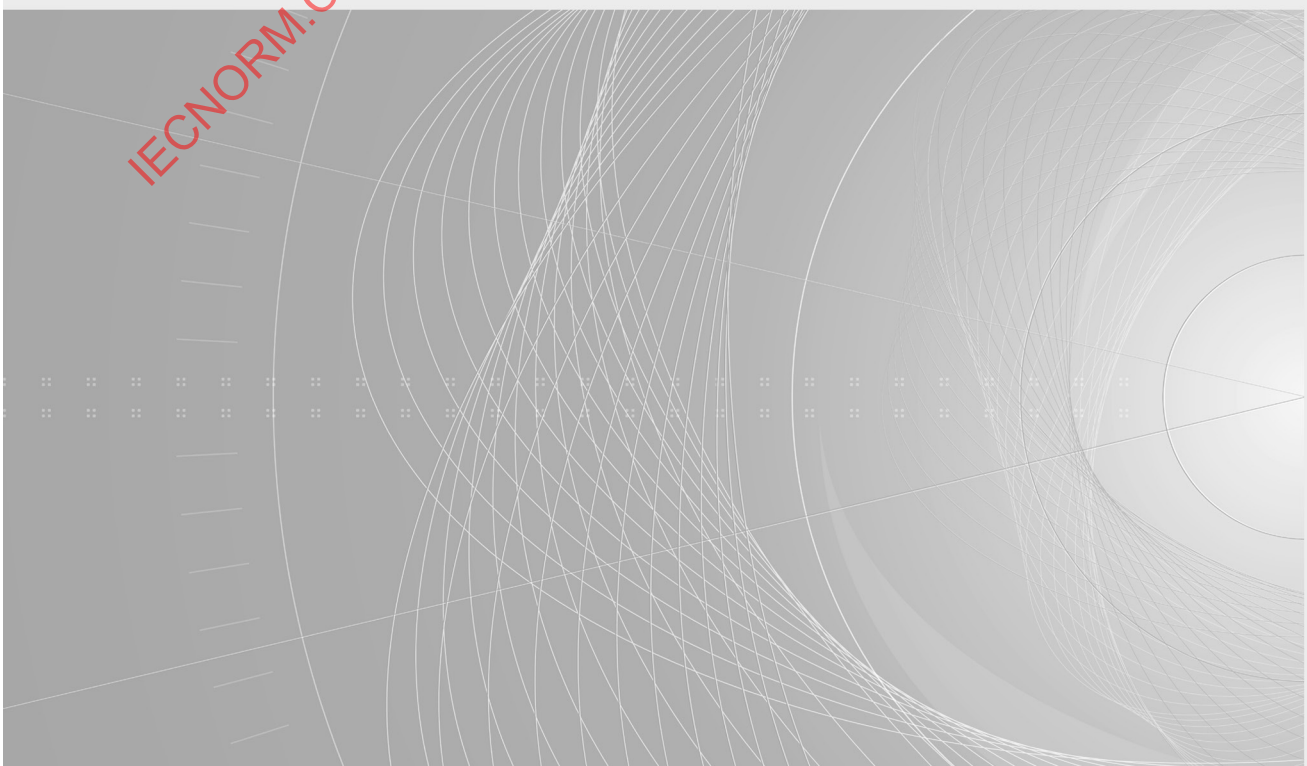
Nanomanufacturing – Key control characteristics –
Part 2-5: Carbon nanotube materials – Mass density of vertically-aligned carbon nanotubes: X-ray absorption method



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Nanomanufacturing – Key control characteristics – Part 2-5: Carbon nanotube materials – Mass density of vertically-aligned carbon nanotubes: X-ray absorption method

INTERNATIONAL ELECTROTECHNICAL COMMISSION

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

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NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 2-5: Carbon nanotube materials – Mass density of vertically-aligned carbon nanotubes: X-ray absorption method

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Draft	Report on voting
113/674/DTS	113/696/RVDTS

Full information on the voting for its approval can be found in the report on voting indicated in the above table.

The language used for the development of this Technical Specification is English.

This document was drafted in accordance with ISO/IEC Directives, Part 2, and developed in accordance with ISO/IEC Directives, Part 1 and ISO/IEC Directives, IEC Supplement, available at www.iec.ch/members_experts/refdocs. The main document types developed by IEC are described in greater detail at www.iec.ch/publications.

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INTRODUCTION

Vertically-aligned carbon nanotubes (VACNTs) are array structures, in which nanotubes are oriented in the perpendicular direction to a substrate surface. VACNTs are useful in many electronic device applications such as field-emission devices, gas and biological sensors, thermal interface materials, supercapacitors, and so on. Chemical vapour deposition (CVD) is one of the common methods for the synthesis of VACNTs, where CNTs can be grown in the presence of metal catalysts, via thermal decomposition of hydrocarbon sources such as methane, ethylene, acetylene, ethanol, and so on.

Physical (electrical, thermal, etc.) properties of VACNT films really depend on their density, which is reflected by distribution and alignment behaviours of individual CNTs. The mass density of nanotubes in VACNT samples was evaluated in various ways. The first choice is measuring the sample mass gain, which is successively divided by the height and the area of the VACNT samples for obtaining density values. However, this mass gain method is a destructive method, and is effective only if the mass of CNTs can be measured with a microbalance, so that the mass density can be estimated from the mass gain during the CVD growth. The second method is counting the number of CNTs in scanning electron microscope (SEM) or transmission electron microscope (TEM) images. However, this counting method is less reliable when the nanotubes are not grown straight on the substrate and the density is low. Liquid-induced compaction can compact the VACNT samples to a maximum density with wetting or drying process of alcohols. However, these methods are destructive analyses (except for SEM) and are not designed for incorporating the wide distribution in size and alignment of nanotubes observed in realistic VACNT samples. Hence, there is strong demand for the development of new reliable methods for evaluating density in VACNTs.

In this context, an X-ray absorption method is proposed as a standard protocol for evaluating density of VACNTs. X-rays can transmit through the film parallel to the substrate surface, and the transmitted X-rays are detected by a high-resolution X-ray imaging apparatus. The observed X-ray projection images can enable the substrate, VACNT film, and air regions to be identified easily. The film density can be calculated from the measured X-ray transmittance of the film. This method is an effective and versatile technique of nondestructive analysis for VACNT film density.

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 2-5: Carbon nanotube materials – Mass density of vertically-aligned carbon nanotubes: X-ray absorption method

1 Scope

This part of IEC 62607 specifies the protocols for determining the mass density of vertically-aligned carbon nanotubes (VACNTs) by X-ray absorption method. This document outlines experimental procedures, data formats, and some case studies. These protocols are applicable to VACNT films with thickness larger than several tens of micrometres. There are no limitations in materials for substrate.

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.

There are no normative references in this document.

3 Terms, definitions, and abbreviated terms

3.1 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

3.1.1
carbon nanotube
CNT
nanotube composed of carbon

[SOURCE: ISO/TS 80004-3:2020 [1], 3.3.3, modified – Note 1 to entry has been deleted.]

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

[SOURCE: ISO/TS 80004-3:2020, 3.3.4, modified – The term "single-wall carbon nanotube" and Note 1 to entry have been deleted.]

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

[SOURCE: ISO/TS 80004-3:2020, 3.3.6, modified – The term "multiwall carbon nanotube" and Note 1 to entry have been deleted.]

3.1.4
vertically-aligned carbon nanotubes
VACNTs
carbon nanotube bundle grown in the perpendicular direction to a substrate surface

3.2 Abbreviated terms

CVD chemical vapour deposition

SEM scanning electron microscope

4 Measurement of mass density of vertically-aligned carbon nanotubes with X-ray absorption method

4.1 General

X-ray is well known for its high penetrating power and has been widely used for nondestructive inspection of various materials. In addition, the absorption (transmission) rate of every element has been extensively studied for a long time and tabulated with very good accuracy. Hence, when the elemental composition of the material is known, the density of the thin film material can be calculated from the measured transmittance of X-rays in a nondestructive way.

4.2 Measurement principle

Figure 1 presents the principle for measuring density of VACNT film by X-ray absorption method. The absorption of X-rays by the VACNT film is expressed as follows: [2][1]

$$I = I_0 \exp\left[-\mu_\rho(E,Z)\rho l\right] \quad (1)$$

where I_0 and I are incident and transmitted X-ray intensity, respectively. μ_ρ is the mass attenuation coefficient of the material , ρ is the mass density of the sample, and l is the path length of X-ray. μ is a physical parameter as a function of the X-ray energy (E) and the elemental composition (Z).

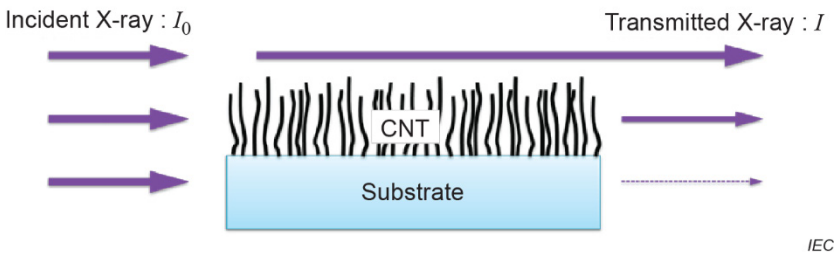


Figure 1 – Measurement principle of X-ray absorption method

[1] Numbers in square brackets refer to the Bibliography.

4.3 Description of measurement equipment and apparatus

In order to measure absorption of the VACNTs, the incident X-ray should be completely parallel to the substrate and the spatial resolution of the measurement should be high enough to detect transmitted X-ray signals separately from substrate, VACNT, and outer surface areas [3]. The spatial resolution of the present method Δ_R is determined by the convolution of beam divergence factor and spatial resolution of the X-ray detector as follows:

$$\Delta_R = \sqrt{\left[\delta_B \left(l + d_{SD}\right)\right]^2 + R^2}\ , \tag{2}$$

where δ_B is the X-ray beam divergence, l is the path length of the sample, d_{SD} the distance from the substrate to the X-ray detector, and R is the spatial resolution of the X-ray detector, as depicted in Figure 2.

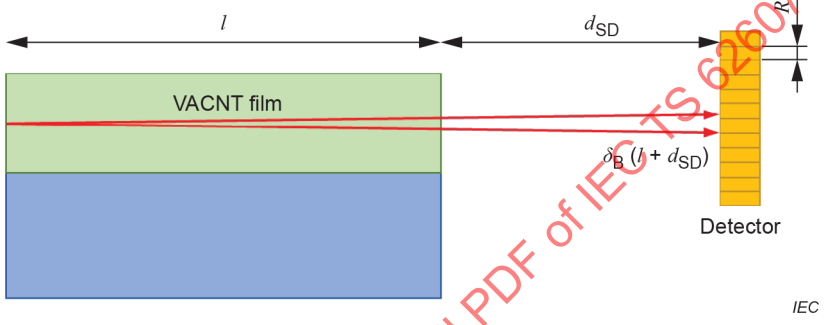


Figure 2 – Parameters determining the spatial resolution of X-ray absorption method

4.4 Sample preparation

VACNT films are usually prepared by using a variety of chemical vapour deposition (CVD) methods such as plasma-enhanced CVD [4], thermal CVD [5], water-assisted CVD [6], and so on. At first, metal catalyst nanoparticles are deposited onto a substrate by physical vapour deposition methods (e.g. sputtering, thermal deposition, and electron-beam deposition) or chemical processes including reduction of metal oxides or oxides solid solutions. After that, the substrate is put into a CVD chamber and heated to a certain CNT growth temperature of several hundred degrees Celsius, followed by the introduction of hydrocarbon sources (e.g. methane, ethylene, acetylene, or alcohols) and process gases (e.g. nitrogen, hydrogen, or ammonia) into the reaction chamber. Then, VACNT films are grown in the presence of metal catalysts via thermal decomposition of hydrocarbon sources. An actual example of VACNT film preparation using CVD is given in Annex A.

4.5 Thickness measurement with X-ray absorption method

Figure 3 shows an X-ray projection image of VACNTs grown on Si substrate, which is a representative result obtained with X-ray absorption method. Three regions can be clearly recognized: substrate, VACNT film, and air. For example, the thickness of the VACNT film presented in Figure 3 can be measured to be approximately 120 μm from the image. Specific stripe patterns can be seen along the air–film interface in Figure 3, which are derived from refraction of X-ray photons near the edge of the film surface due to the difference in X-ray refractive indices between VACNT and air.

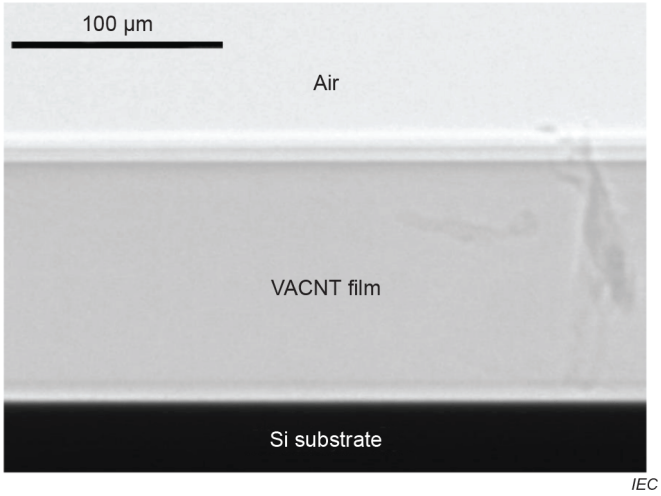


Figure 3 – Example of X-ray projection image of VACNTs grown on Si substrate

4.6 Density measurement with X-ray absorption method

A transmitted X-ray intensity profile obtained from Figure 3 is shown in Figure 4.

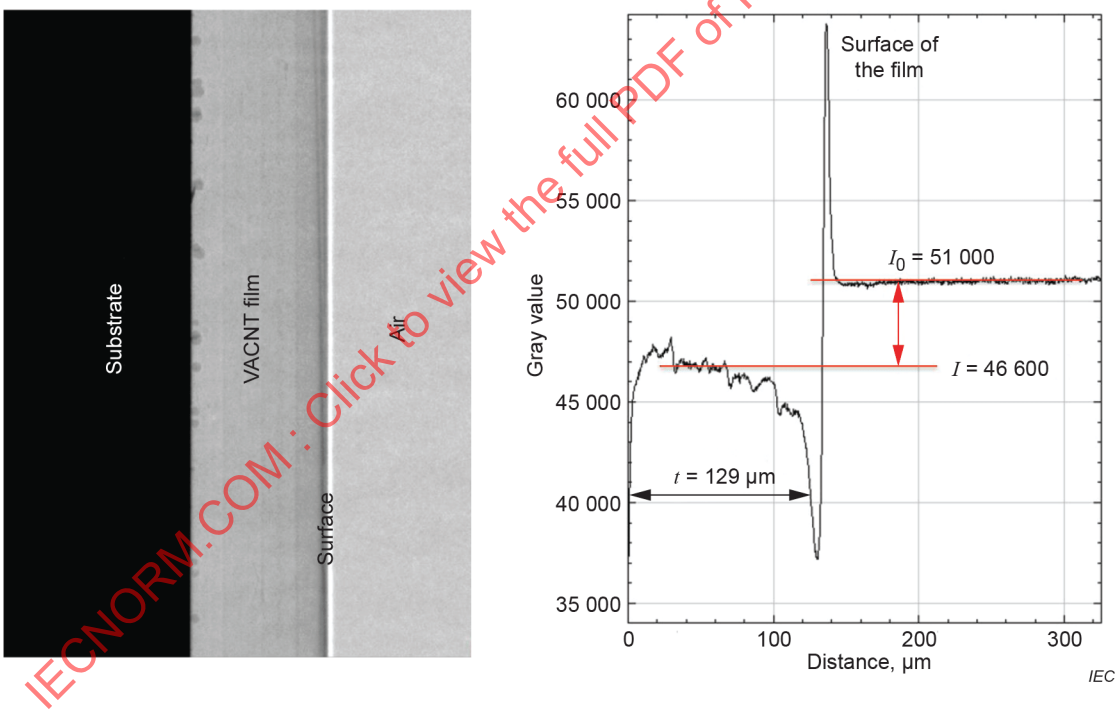


Figure 4 – Example of transmitted X-ray intensity profile for VACNT sample

The absorption of the film can be calculated by comparing between intensities of the incident (I_0) and transmitted X-ray (I). Then, the X-ray absorption amount (x) of the VACNT film can be obtained as follows:

$$x = -\log_e\left(\frac{I}{I_0}\right). \tag{3}$$

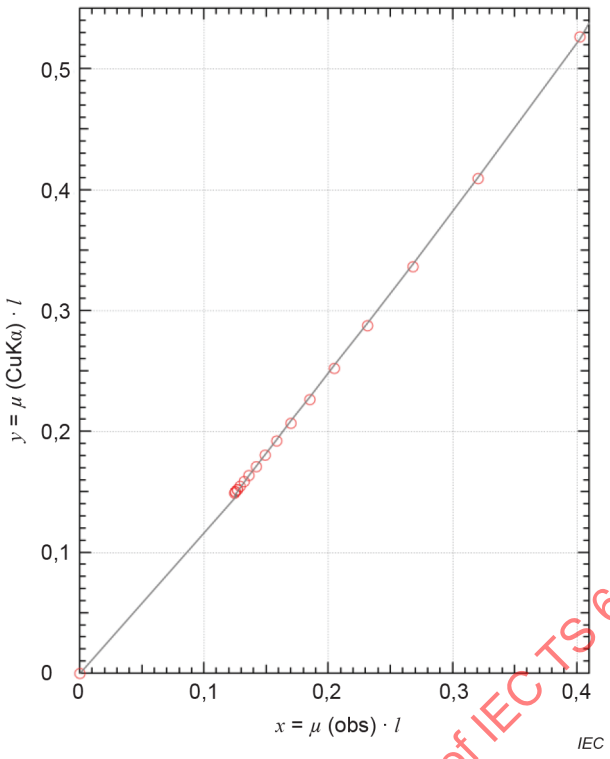


Figure 5 – Example of calibration result for non-monochromatic incident X-ray

When monochromator devices are not used for X-ray source, the incident X-ray beam includes not only characteristic, but continuous radiation. In this case, calibration of the measured absorption signals shall be conducted beforehand, to obtain correct density from X-ray absorption method. Figure 5 shows an example of obtained relation of absorption for a carbon plate measured by the non-monochromatic X-ray (x) and monochromatic characteristic line (e.g. CuKα) (y) with changing the thickness of the carbon plate (the path length of X-ray (l)). Then, the following relation can be obtained for x with respect to y, for pure carbon sample:

$$y = C_1 x + C_2 x^2 , \tag{4}$$

where C_1 and C_2 are the parameters obtained by least-squares fitting. Finally, the film density (ρ) can be evaluated from the x value obtained with Equation (3), namely,

$$\rho = \frac{y}{\mu_\rho \times l} = \frac{C_1 x + C_2 x^2}{\mu_\rho \times l} \tag{5}$$

Here, μ_ρ is the mass attenuation coefficient of carbon against monochromatic X-ray. The carbon mass attenuation coefficient can be found in the International Table of X-Ray Crystallography [7], [8] for the required X-ray energy. For instance, the value of μ_ρ for CuKα radiation is 4,51 cm^2/g. In the case of film density measurements, l is identical to the width of the substrate, which can be easily measured with a good accuracy.

5 Appropriate data formats

An example of possible data format for mass density measurements of VACNT films is given in Table 1. Items regarding measurement and sample conditions and results shall be included in this format. Additionally, X-ray projection images and transmitted X-ray intensity profiles of VACNTs should be shown.

Table 1 – Possible data format to be given together with density of VACNTs obtained with X-ray absorption method

Item	Data
Measurement and sample conditions	X-ray source employed for the measurement: [ ] Calibration of the X-ray source: Yes [ ] No [ ] Preparation method of the VACNT sample: [ ] Material of the substrate: [ ] Thickness of the substrate: [ ] mm
Measurands	Thickness of the VACNT sample [ ] ± [ ] μm Intensity of the incident X-ray: [ ] ± [ ] Intensity of the transmitted X-ray: [ ] ± [ ] Mass density of the VACNT sample: [ ] ± [ ] g/cm^3

Annex A
(informative)

Case study of mass density measurements for vertically-aligned carbon nanotubes

A.1 Overview

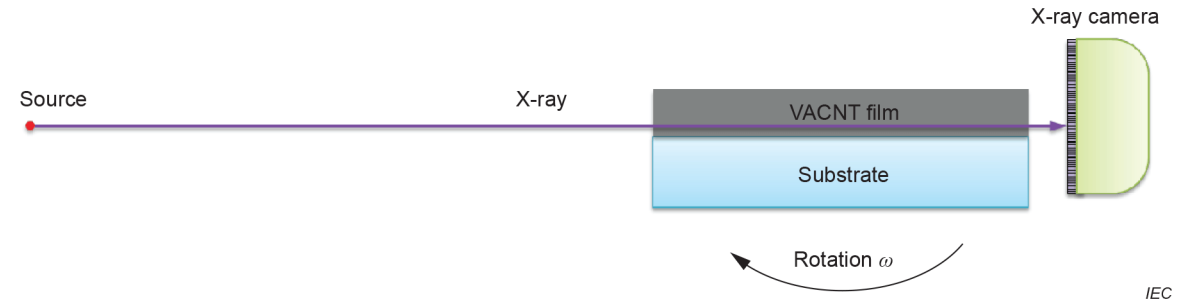
In this Annex A, case studies of measuring mass density of VACNTs grown on Si substrate based on the X-ray absorption method are described. The mass gain measurement and SEM analysis were also performed as complementary assessments for VACNTs. A series of experimental results in this Annex A reveals the effectiveness and versatility of X-ray absorption method as a nondestructive analysis for density of VACNTs [9].

A.2 Sample preparation for VACNTs

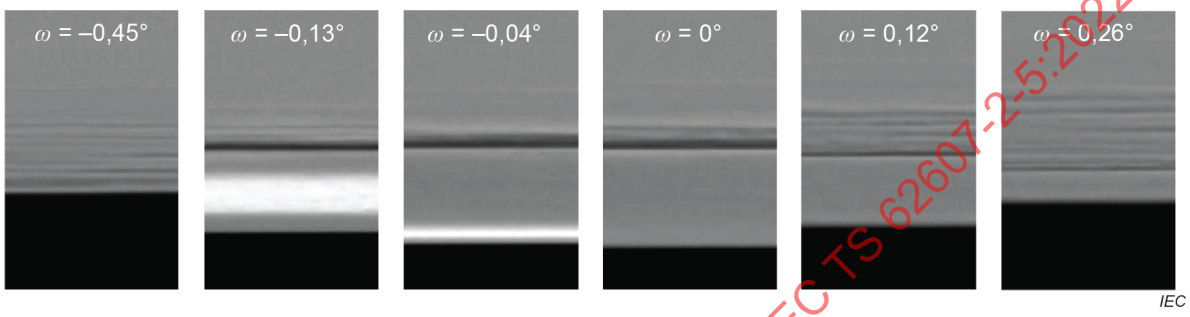
VACNT films were prepared by using chemical vapour deposition (CVD) method. VACNT films were grown from Fe nanoparticles with an ethanol precursor. 1 cm × 1 cm Si wafers coated with 300-nm-thick SiO_2 were employed as substrates without any surface treatment. 20-nm-thick aluminium layers were deposited onto the substrates by radio frequency (rf) sputtering. After air exposure of the substrates, 2-nm-thick Fe films as metal catalysts were deposited by rf sputtering. Then, the Fe-loaded substrates were put into an encapsulated reaction chamber of a mini CVD system. The partial pressures of the nitrogen and ethanol vapours in the reaction chamber were controlled to be 10 kPa and 40 kPa, respectively. Next, the catalyst precursor heating unit using heated filament was switched on in order to generate activated radicals and accelerate CNT growth. Then, the substrate was heated up and maintained at the temperature of the VACNT growth for several minutes. The growth temperature was 700 °C. Two VACNT samples with different thicknesses were prepared and named as Sample A and Sample B.

A.3 Confirmation of X-ray incidence parallel to the substrate surface

Clause A.3 describes how to align the sample surface direction to be parallel to the X-ray beam direction. It can be carried out to collect a certain number of X-ray projection images with changing rotation angle ω of the sample as shown in Figure A.1 a). To make this X-ray measurement feasible, a high spatial resolution X-ray camera with a pixel size of a few hundred nanometres was used. A microfocus high brightness X-ray source was also employed to achieve quasi-parallel X-ray beam with a divergent angle of less than 0,3 mrad. It means that the beam spreads only 3 µm with travelling 10 mm through the film. The images are collected at every 0,01° in step and several typical images are shown in Figure A.1 b). ω = 0° is defined when the surface plane is parallel to the beam direction, and X-ray beam irradiates the sample surface while ω is a minus value. The bright stripe in the images of ω is equal to −0,13° and −0,04°. It is caused by reflection of incident X-rays at the substrate (Si) surface and overlapped on the transmitted X-rays and resultant intensity is increased. When the sample surface is correctly aligned parallel to the beam direction, the thickness of the film on the image shows maximum value (at ω = 0°) and it becomes thinner again when ω is increased.



a) Experimental setup of X-ray absorption measurement for VACNT samples



b) X-ray projection images obtained at various conditions of ω

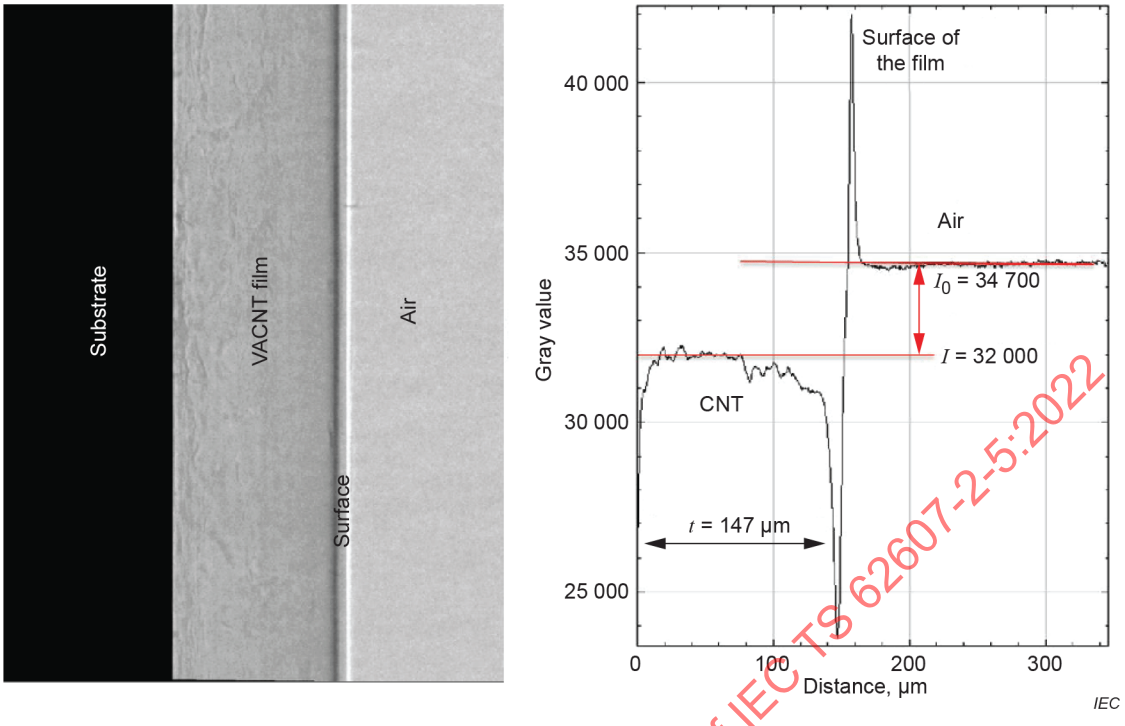
Figure A.1 – Schematic drawings of beam alignment procedures for X-ray absorption measurement

A.4 Thickness and mass density measurements with transmitted X-ray intensity profiles

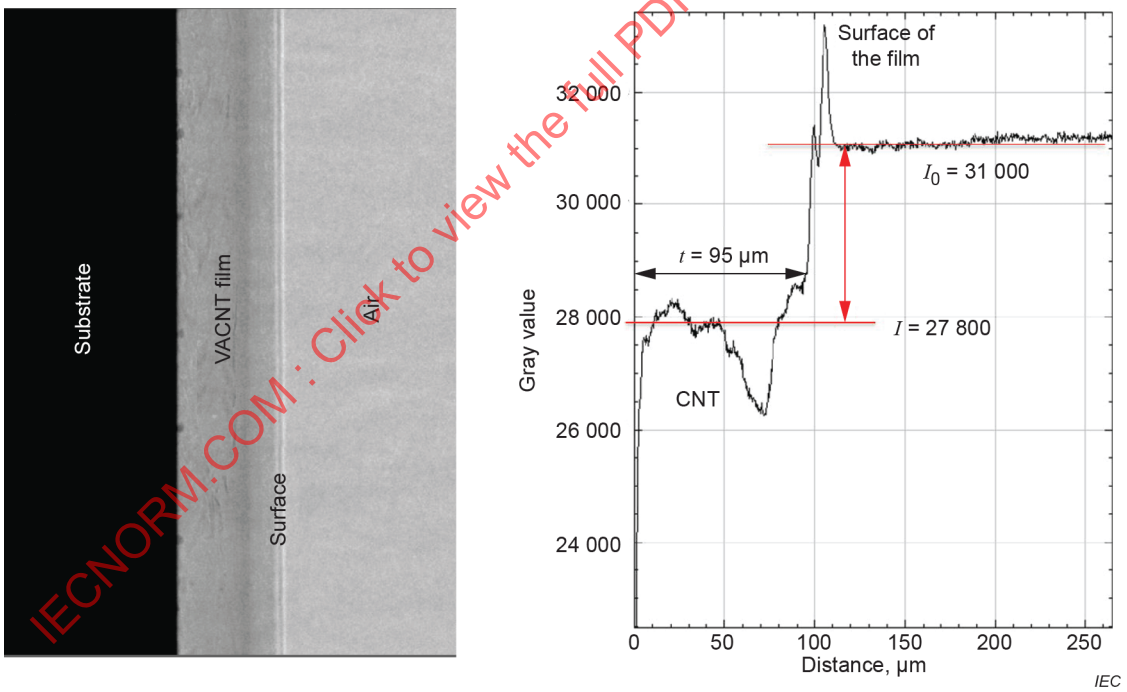
Clause A.4 reports the thickness and density measurements for VACNT samples with transmitted X-ray profiles.

Figure A.2 shows X-ray projection images and transmitted X-ray intensity profiles for both Sample A and Sample B. The thickness of the VACNT parts can be evaluated from the width of the CNT region in the transmitted X-ray intensity profiles. The obtained thickness for Sample A was 147 µm and for Sample B was 95 µm, which are comparable to the values (140 µm and 93 µm) measured from the cross-sectional SEM images shown in Figure A.3. The X-ray absorption amounts (x) of these samples were calculated by using Equation (2) and the transmitted X-ray intensity values shown in Figure A.2. The calculated x value for Sample A was 0,081 0 and for Sample B was 0,109 0. Then, the VACNT film density was evaluated by using Equation (3) with the experimentally determined parameters listed in Table A.1. Finally, the VACNT density was determined to be 0,021 5 g/cm^3 for Sample A and 0,029 2 g/cm^3 for Sample B.

Additionally, the VACNT density of Sample A and Sample B was evaluated with the conventional (destructive) mass gain method after the completion of the X-ray absorption measurements, resulting in the density of 0,028 8 g/cm^3 for Sample A and 0,033 0 g/cm^3 for Sample B. Thus, the present X-ray absorption method is quite promising as a nondestructive method for measuring thickness and mass density of VACNT films.

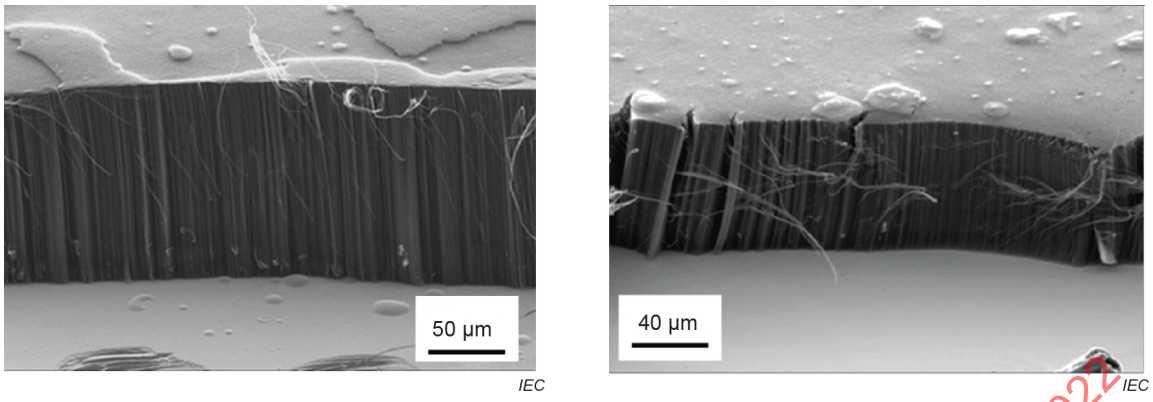


a) **Measurement results for Sample A**



b) **Measurement results for Sample B**

Figure A.2 – X-ray projection images and transmitted X-ray intensity profiles observed for two VACNT samples



a) Sample A b) Sample B

Figure A.3 – Cross-sectional scanning electron microscope images of two VACNT samples

Table A.1 – Parameters obtained from the transmitted X-ray intensity profiles for two VACNT samples

Sample	Thickness (µm)	Transmittance, T	$x = -\log(T)$	y	l (cm)	ρ (g/cm^3)
A	147	0,922	0,081 0	0,096 0	0,987	0,021 5
B	95	0,897	0,109 0	0,130 0	0,986	0,029 2

A.5 Measurement results for a VACNT film with a thickness of several hundred micrometres

Clause A.5 reports the thickness and density measurement for another VACNT sample with a thickness of several hundred micrometres.

Another VACNT film was also prepared by using CVD method. Many of the preparation conditions are similar to those explained in Clause A.2. The different points are growth time and temperature. Here, after the catalyst precursor heating unit was switched on, the substrate was heated up to the growth temperature of 750 °C and maintained at 750 °C for 10 minutes. After that, only the catalyst precursor heating unit was switched off, and the substrate temperature was further annealed at 750 °C for 30 minutes. The sample prepared in this manner was named as Sample C.

Figure A.4 shows an X-ray projection image and transmitted X-ray intensity profiles for Sample C. The thickness of the VACNT parts can be evaluated from the width of the CNT region in the transmitted X-ray intensity profiles. The obtained thickness for Sample C was 360 µm, which is comparable to the value (340 µm) measured from the SEM imaging shown in Figure A.5. The X-ray absorption amount (x) of this sample was calculated by using Equation (2) and the transmitted X-ray intensity value shown in Figure A.4. The calculated x value for Sample C was 0,052 4. Then, the VACNT film density was evaluated by using Equation (3) with the experimentally determined parameters listed in Table A.2. Finally, the VACNT density for Sample C was determined to be 0,013 3 g/cm^3, which is lower than that of thinner Sample A (0,028 8 g/cm^3) and Sample B (0,033 0 g/cm^3). Although the annealing process of the sample is effective for increasing the thickness of VACNTs, higher temperature can simultaneously cause deterioration of metal (Fe) catalysts and decrease the growth rate of carbon nanotubes gradually. This phenomenon can result in the lower VACNT density as observed for Sample C in this case study.

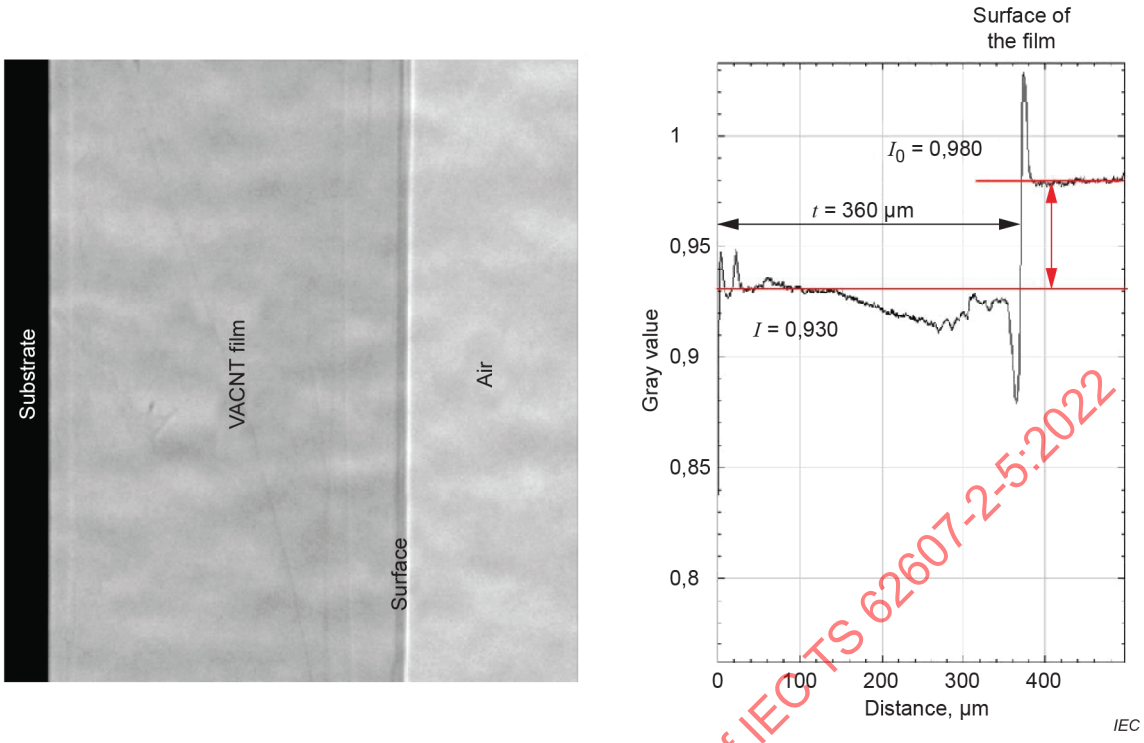


Figure A.4 – X-ray projection image and transmitted X-ray intensity profile observed for a thicker VACNT film

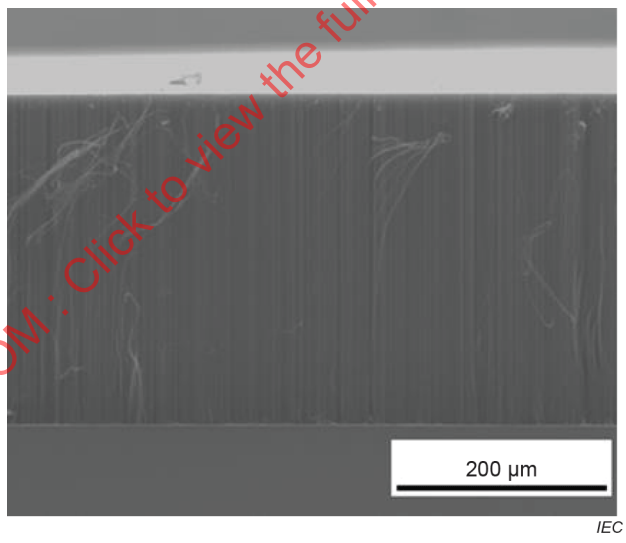


Figure A.5 – Cross-sectional scanning electron microscope image of a thicker VACNT film

Table A.2 – Parameters obtained from the transmitted X-ray intensity profile for a thicker VACNT film

Sample	Thickness (µm)	Transmittance, T	$x = -\log(T)$	y	l (cm)	ρ (g/cm^3)
C	360	0,949	0,052 4	0,061 3	1,020	0,013 3