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An image analysis algorithm to measure the diameters of carbon nanotubes

***Abstract**. Carbon nanotubes (CNTs) have excellent properties, and wide application fields are expected. The diameters of the tubes influence the physical properties of CNTs. This paper proposes an image analysis algorithm to measure the diameters of CNTs to automate human measurement work. We have confirmed that the mean value of the diameters measured by our algorithm was close to that obtained by human measurement work. We also measured the diameters of the CNTs after laser annealing, and demonstrated the changes of the mean values of the diameters.*

***Streszczenie.** Nanorurki węglowe (CNT) mają doskonałe właściwości i potencjalnie szeroki zakres zastosowań. Średnice nanorurek zależą od fizycznych właściwości CNT. W pracy zaproponowano zautomatyzowany, bazujący na analizie obrazu, algorytm pomiaru średnic CNT. Potwierdzono, że średnie wartości zmierzonych za pomocą zaproponowanego algorytmu średnic nanorurek węglowych mają wartości bliskie otrzymanym za pomocą pomiaru manualnego. Stwierdzono wpływ wyżarzania laserowego na zmiany średnich wartości średnic CNT. (**Algorytm pomiaru średnic nanorurek węglowych bazujący na analizie obrazu**)*

Keywords: carbon nanotubes, scanning electron microscopy, image processing, diameter measurement of CNTs
Słowa kluczowe: nanorurki węglowe, elektronowy mikroskop skaningowy, przetwarzanie obrazu, pomiary średnicy nanorurek.

Introduction

Since the discovery of carbon nanotubes (CNTs) [1], numerous researchers have investigated single-walled nanotubes (SWNTs), multi-walled nanotubes (MWNTs), their growth methods, geometrical characteristics, physical properties, alignment mechanism, applications, etc. In Przegląd Elektrotechniczny (Electrical Review), researches on CNTs have been reported [2, 3]. We have also investigated several characteristics of CNTs [4-6].

The diameters of CNTs have a huge effect on their physical properties. It is also very important to evaluate the uniformity of the diameters of CNTs in order to increase the uniformity of the geometrical and physical characteristics of CNTs for their applications. The diameters of CNTs are generally estimate manually using the image taken by scanning electron microscopy (SEM) or transmission electron microscopy (TEM). Such human visual works are extremely inefficient.

The most popular methods to estimate the diameters of CNTs are to use Raman spectroscopy [7-9]. However, the methods estimate only the diameters in the region of the Raman laser irradiation. Therefore, these methods cannot provide the variations of numerous diameters, and also cannot estimate the uniformity of diameters in a wide measurement area.

Recently, a few methods to measure the geometrical characteristics of CNTs using image processing have been proposed [10-12]. A measurement method for the characteristics of MWNTs has been proposed [10]. This method provides outer radius, inner radius, and a physical characteristic of MWNTs. However, the selected areas to measure MWNTs are restricted by the image segmentation procedures. Therefore, it is not effective to evaluate the uniformity of the diameters of CNTs in a wide area. To analyse the SEM and TEM images and to get the distribution of the diameters, an image processing technique has been proposed [11]. However, this image processing method is semi-automated not automated, and its algorithm is not described in detail. Another image processing algorithm has been proposed to analyse the chirality of a carbon nanotube [12]. However, this method cannot be used to measure the diameters of CNTs.

In this paper, we propose a diameter measurement algorithm using image processing for wide areas of CNTs SEM images. Proposed algorithm provides the numerous values of diameters detected by x-direction and y-direction scans in the binary images.

The diameter measurement was carried out for the MWNTs SEM images by the proposed algorithm. We confirmed that the mean value of the diameters measured by using our algorithm approximated that measured by human visual work. We also measured the diameters of the CNTs before and after laser annealing by using our algorithm, and demonstrated the changes of statistical values of the diameters.

Proposed algorithm to measure the diameters of CNTs

Fig. 1 shows a MWNTs image taken by SEM. First of all, two kinds of pre-processing are done. First pre-processing is to reverse the gray levels of the original image. Second pre-processing is to add the white color frame to the outer circumference of CNTs image. The second pre-processing is necessary to detect CNTs regions located in the circumference of the image frame.

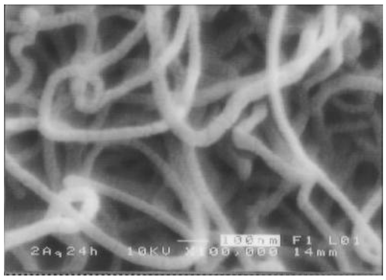

Fig. 1. A MWNTs original image taken by SEM

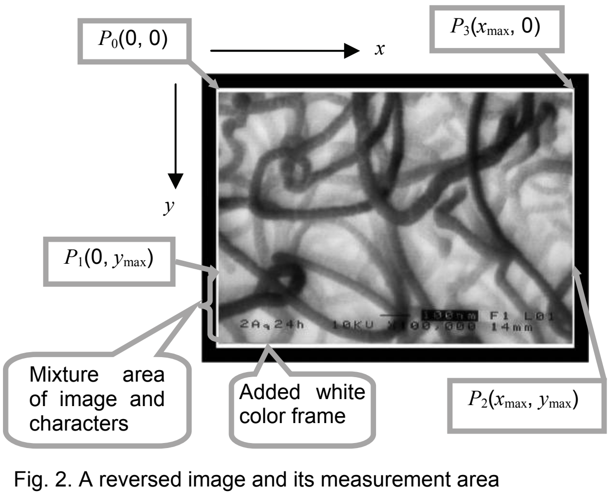

Fig. 2. A reversed image and its measurement area

The proposed program measures the diameters of CNTs in the rectangle surrounded by four points P_0-P_3 as shown in Fig. 2. The mixture area of image and characters is not measured because each pixel cannot be distinguished between image and character. Fig. 2 also shows x and y coordinates.

The program is mainly composed from the image processing and the measurement of the diameters of CNTs as shown in Fig. 3.

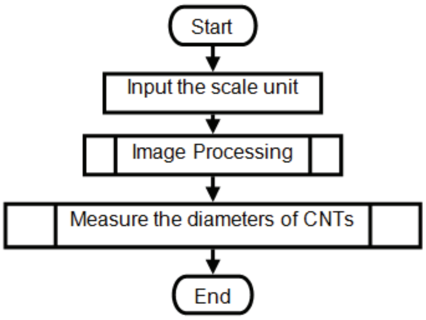

Fig. 3. Main program of the diameter measurement

After the start of the image processing, the scale unit should be inputted. The both ends of the scale bar are pointed with a mouse, and the unit value is inputted as shown in Fig. 4. The input data are used to convert the numbers of pixels into the real lengths. Fig. 5 exhibits the flow chart and the explanation of the image processing. The 24-bit color image is converted to 8-bit grayscale image, and the histogram equalization is carried out to emphasize the contrast. Then, the noise is reduced by the median filter. After that, the automatic binarization is performed using Otsu's method [13]. We have confirmed that the Otsu's method is effective for the binarization of CNTs images.

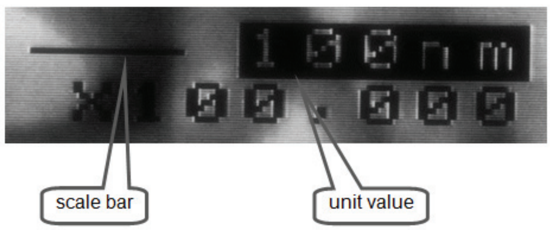

Fig. 4. Scale area in a CNTs SEM image

Original images obtained by SEM have many scanning noise due to the mechanism of SEM. The noise is still remained after image binarization. So, it is important to reduce the noise in binary images. Opening and closing operations are generally used to reduce noise in binary images. Although the iteration of opening and closing operations reduce the noise, the shapes of tubes in binary images are changed. One-time opening and closing operations do not change the shapes of tubes in binary images. However, they do not reduce the noise. Therefore, we examined that the number of iteration of opening and closing operations is effective to reduce the noise without the influence for the shapes of tubes. The result showed that three times of the iteration is best.

After the CNTs binary image is created, the measurement of diameters of the CNTs is performed. The flow chart of the measurement program is shown in Fig. 6. In this program, x-direction and y-direction scans are executed to search CNTs, and measure the diameters. The procedure how to measure the diameters is explained in Fig. 7 using x-direction scan.

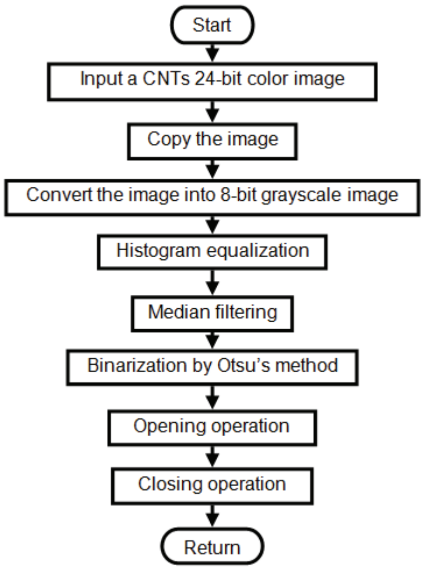

Fig. 5. Program of the image processing

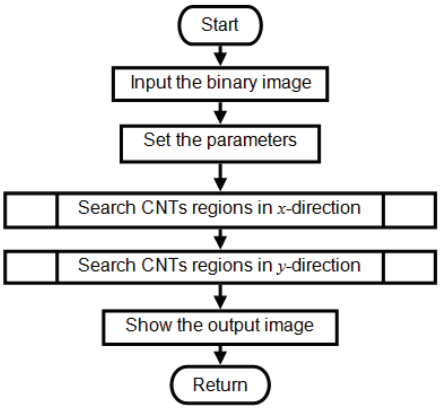

Fig. 6. Flow chart of measuring the diameters of CNTs

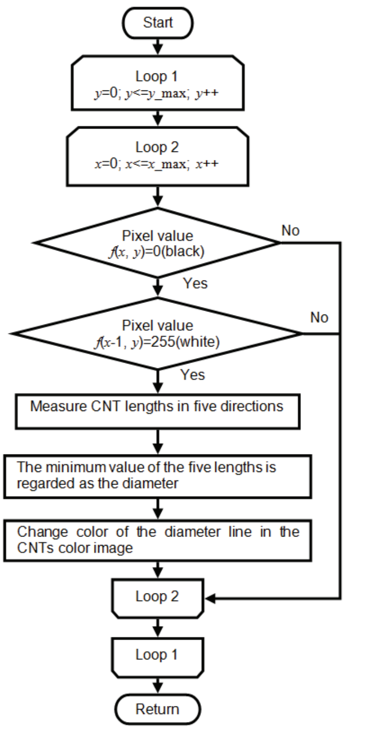

Fig. 7. Flow chart of searching CNTs regions in x-direction

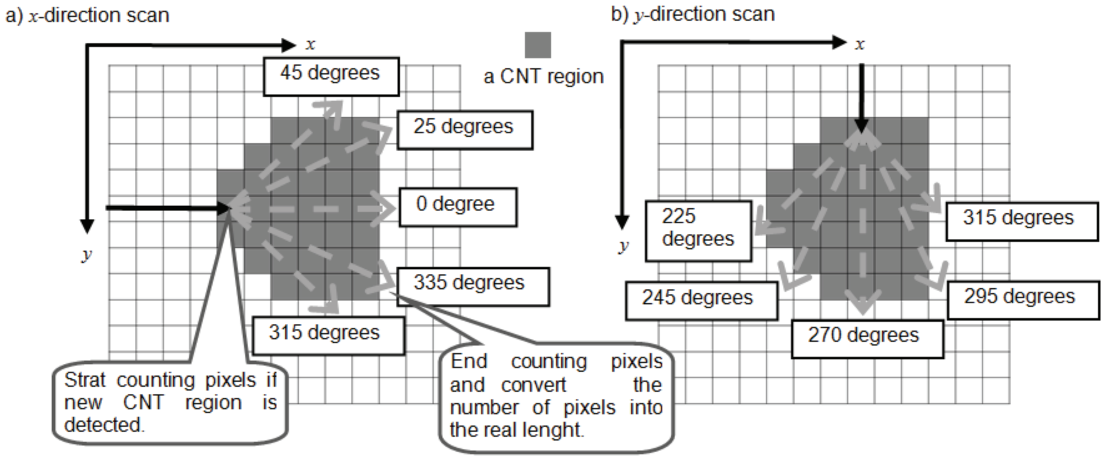

Fig. 8. Explanation of the procedure for searching CNTs regions in x-direction scan and y-direction scan

At first, the y axis is fixed, and x-direction scan starts. If the pixel value at x is 0 (black) and the pixel value at the x-1 is 255 (white), the program recognizes that the x position is the edge of a CNT, and starts counting black pixels in five directions of 0, 25, 45, 315 and 335 degrees shown in Fig. 8a). The minimum length in the 5 measured lengths is regarded as the diameter. The length of a square pixel is changed depending on the direction. As shown in Table 1, the length of a pixel is corrected by using the unit length for each direction on the basis that the side length of square pixel is one. To convert the counted pixels into the real length, the algorithm uses the real length of one pixel which is measured and computed just after the start of the image processing. The diameter d of CNT is calculated by:

$$d = \min(n_{p0} \cdot L_{p0}, n_{p25} \cdot L_{p25}, n_{p45} \cdot L_{p45}, n_{p315} \cdot L_{p315}, n_{p335} \cdot L_{p335}) \cdot L_r \quad (1)$$

where n_{p0}, n_{p25}, n_{p45}, n_{p315} and n_{p335} show the numbers of pixels which are obtained by scanning in five directions: 0, 25, 45, 315 and 335 degrees; L_{p0}, L_{p25}, L_{p45}, L_{p315} and L_{p335} show the unit lengths in five directions shown in Table 1; and L_r shows the real length for the side length of one square pixel. This process is repeated by increasing y positions.

After x-direction scan, the scan direction is changed, and y-direction scan is executed like the x-direction scan. In y-direction scan, five directions of 225, 245, 270, 295 and 315 are used as shown in Fig. 8 b).

Table 1. Unit length for each direction

Degree	Unit length for each direction
0	1
25, 245, 295, 335	1.10338
45, 225, 315	1.41421

Our algorithm detects also remained noise and other parts except diameter regions. Therefore, the upper and lower limits to be considered as the diameters must be decided. We measured the diameters of CNTs without the upper and lower limits, and obtained the distribution of the diameters. Fig. 9 shows the distribution of the diameters for the image as shown in Fig. 1. We can consider that the distribution of diameters approximates a normal distribution. So, appearance of the valley in Fig. 9 shows the contamination of noise and other parts except the diameters. Therefore, the lower limit is decided at the valley of lower diameter side of the distribution. Then, we created again the distribution excluding the part of the data lower than the valley. We assumed this distribution as a normal distribution, and computed the mean value μ and the standard deviation σ. We decided that the upper limit is the value of μ + 1.96σ.

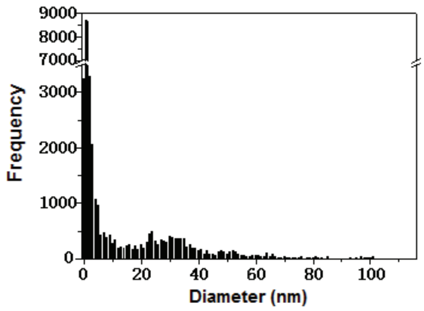

Fig. 9. Distribution of measured diameters

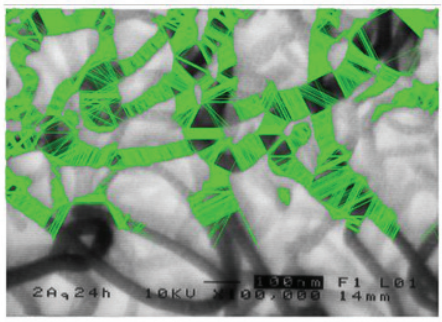

Fig. 10. Diameter detection result

CNTs image measurement experiment and its result

We have developed our algorithm with Visual C++ 2008 and computer vision library OpenCV [14]. In this experiment, we decided that the scanned vertical length between P_0 and P_1 in Fig. 2 was set to 70 % of the height of the image.

We have applied above mentioned statistical method to the processing of CNTs image shown in Fig.1, and obtained that the lower and upper limits are 19 nm and 70 nm respectively. The obtained range approximates the ranges shown in many literatures. The size of the image shown in Fig. 1 is 4,400 X 3,200 pixels.

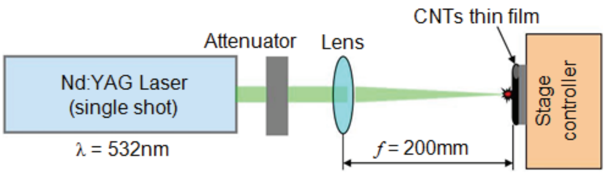

Fig. 11. Laser anneal apparatus

Table 2. Irradiation conditions

Laser energy density	33.82-247.51 mJ/cm^2
Irradiation frequency	1 shot
Gas	N_2, Air

Table 3. Results of laser anneal experiments in N_2 atmosphere

Laser energy density	Before annealing	146.78 mJ/cm^2	188.51 mJ/cm^2	247.51 mJ/cm^2
Number of detection in both x- and y-direction scans	44,800	51,101	41,636	31,235
Mean value of diameters	21.9 nm	21.7 nm	25.1 nm	25.8 nm
Standard deviation of diameters	9.34 nm	10.06 nm	10.28 nm	10.70 nm

Table 4. Results of laser anneal experiments in air atmosphere

Laser energy density	Before annealing	33.82 mJ/cm^2	151.10 mJ/cm^2	217.29 mJ/cm^2
Number of detection in both x- and y-direction scans	44,800	48,579	47,527	38,784
Mean value of diameters	21.9 nm	24.1 nm	21.4 Nm	28.4 nm
Standard deviation of diameters	9.34 nm	8.93 nm	10.43 nm	12.17 nm

Fig. 10 shows the diameter detection result for the CNTs image shown in Fig. 1 in which detected diameters are displayed in green. We can see that the proposed algorithm detects well the parts of diameters in the wide area. In x-direction scan, 12,599 diameters were detected and their mean value was 35 nm. In y-direction scan, 12,655 diameters were detected and their mean value was 34 nm. We confirmed that both scan results were close to each other. Moreover, we measured 100 diameters by human visual work, and the mean value of the 100 diameters was 36 nm. The results using our algorithm approximated to the result by human visual work. In the human visual work, we took about one minute to measure one diameter. It is very difficult to measure a lot of diameters within a CNTs image by such human visual work. Therefore, the accuracy and effectiveness of our algorithm have been verified.

Laser anneal experiments and their results

The pulse laser light was irradiated to CNTs with the experimental apparatus shown in Fig. 11, and the CNTs were laser annealed. Table 2 shows the irradiation conditions.

We measured the diameters of CNTs before and after laser annealing by using our algorithm. Tables 3 and 4 show the diameter measurement results of CNTs before and after laser annealing in N_2 and air atmospheres, respectively. Figs. 12 and 13 show the diameter detection results for CNTs images before and after laser annealing in N_2 and air atmospheres, respectively. The tendency that the diameters of CNTs grew as the laser energy density larger was seen from the results.

Conclusion

In this paper, we proposed an image analysis algorithm to measure the diameters of CNTs to automate the human visual work. The developed program could detect the diameters of CNTs, and calculate precisely the statistics such as the mean values and the standard deviations of the diameters.

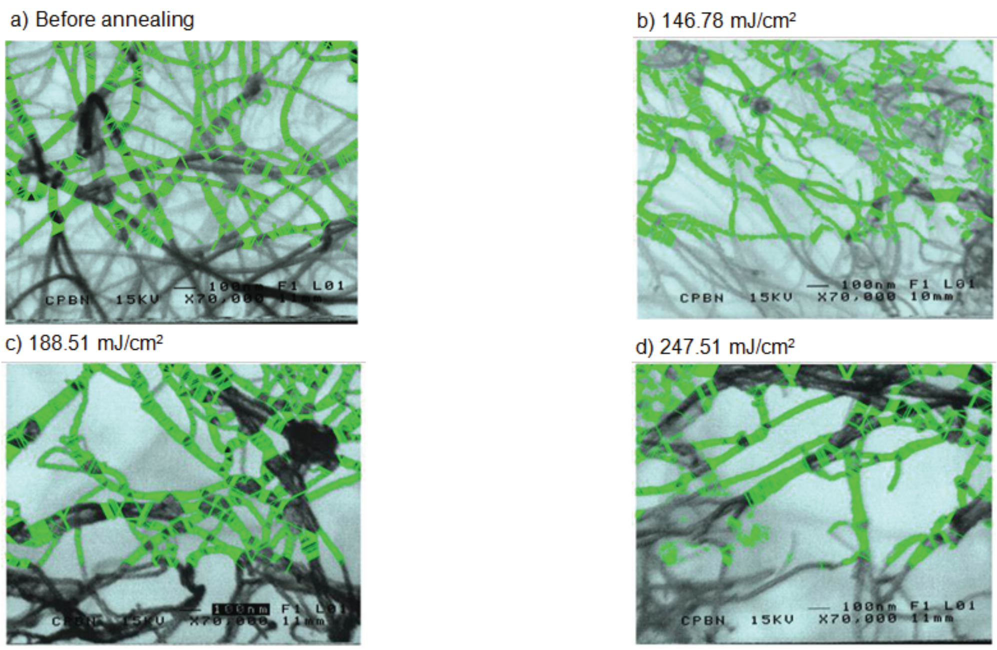

Fig. 12. Diameter detection results for CNTs images before and after laser annealing in N_2 atmosphere

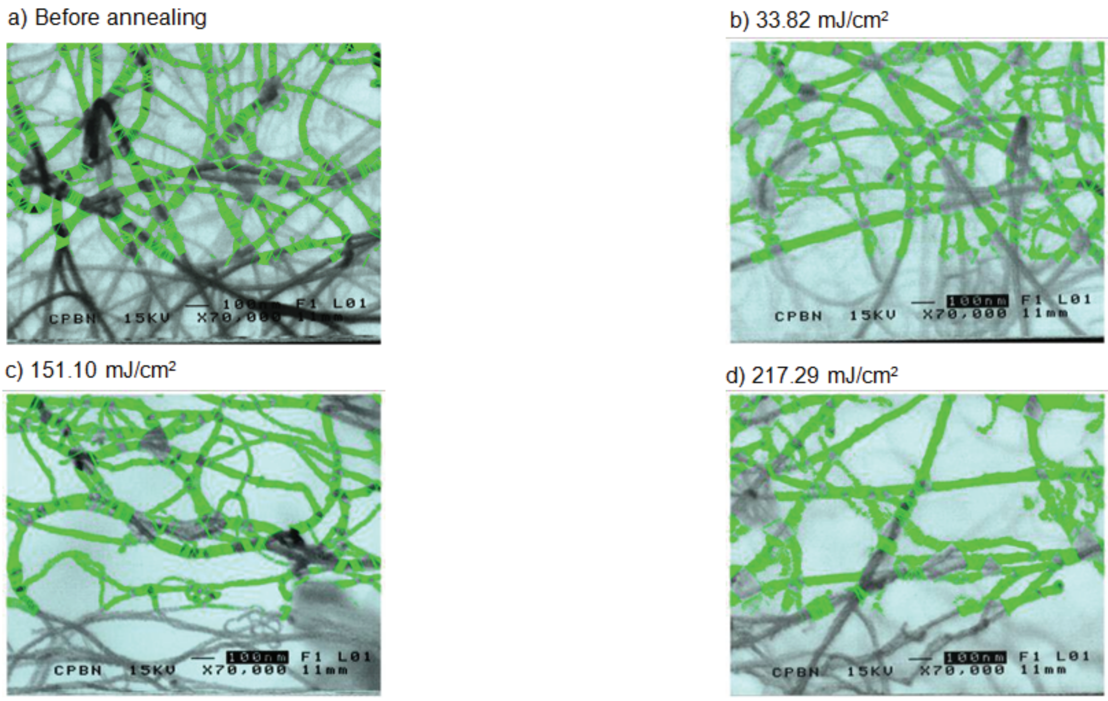

Fig. 13. Diameter measurement results for CNTs images before and after laser annealing in air atmosphere

We also measured the diameters of the CNTs before and after laser annealing by using our algorithm, and demonstrated the changes of statistical values of the diameters. We will research the principle that the diameters of CNTs grew as the laser energy density larger.

We suppose that this algorithm is useful to evaluate the diameters of the CNTs not only for the management of the CNTs products but also for the optimization of CNTs preparation processes.

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