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Study on Accelerating Voltage of SEM in Observation of Carbon Nanotube Surface

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Abstract: Carbon nanotubes (CNTs) have attracted increasing attention due to their superior physical and chemical properties such as their high electrical and thermal conductivity, great specific area, etc. Scanning electron microscopy on commercial CNTs was optimized. Based of Rayleigh level, the resolution of optical system was induced by substituting parameters of thermoelectric emission scanning electron microscope. The size of interaction range of electron-CNTs is evaluated by substituting parameters of CNTs into the equation evaluating size of Kanaya-Okayama range. Based on theoretical analytical results, the high voltage range is defined in fine structure observation of CNTs surface by thermoelectric emission scanning electron microscope. We selected the spot size as 1.5nm, the working distance as 4.3mm, and did the SEM measurement experiment changing the accelerating voltage. The effects of energy of the incident electron on the size of the electron-CNTs interaction range and the resolution of SEM were theoretically investigated. As a result, in case of microstructure observation of CNTs surface by using thermoelectric SEM, the most proper accelerating voltage was within 5~10kV. Through the experiments based on it, we found that the accelerating voltage of 7.5kV enables us to get the sharpest image of the microstructure of CNT surface. Then we compared theoretical results and experimental results. Theoretical results and experimental results were agreed well.

Keywords: Scanning Electron Microscopy, Carbon Nanotube, Surface, Fine Structure, Accelerating Voltage

1. Introduction

Carbon nanotubes (CNTs) have attracted increasing attention due to their superior physical and chemical properties such as their high electrical and thermal conductivity, great specific area, etc. [10, 11, 17, 18]. Particularly, various applications of CNT-metal nanocomposites, such as energy storage, sensors, catalyzers and portable electronics, are being focused on [10, 11, 16]. Here the microstructure of CNT surface plays an important role [16]. Recently, delicate observation of the microstructures within the range of nm has become more important for the achievement of the better CNT surface properties [2, 3, 15, 16].

Electron-matter interactions are essential in SEM imaging. Generally, SEM imaging is conducted in the accelerating voltage of 0.5~30kV, often in more than 10kV, because the higher the accelerating voltage is the more the electron beam is condensed, the brighter electron beam can be obtained, the higher the resolution of the image is, and because the accelerating voltage of more than 10kV is needed for generation of the characteristic X-ray for many elements in element analysis [21, 22]. When the accelerating voltages increase, the theoretical resolution of SEM increases, but the interaction range of electron-matter can be expanded resulting decreased spatial resolution, so some of the information of surface microstructure of the matter can be omitted [1, 20, 22, 23]. In many of the previous work the observation of nm-microstructure of material surface in the ultra-low accelerating voltages (0.1~1kV) and the low accelerating voltages (1~10kV) by using the ordinary SEM [7, 8, 11-14, 19-23]. By using in-lens detector of SEM, in ultra-low accelerating voltage of less than 1kV, they obtained clear pictures of thin oxide film of thickness of 10nm formed on steel plate and fine grain, which could not be seen in the secondary electron images [14, 21-23], and the secondary electron images without charge storage for an uncoated non-conductive sample were taken [4-6, 14, 20]. Also by using FE (field emission)-SEM, in ultra-low accelerating voltages, structures of the aligned mesoporous silica were directly observed [19].

However, although there are many advantages in SEM measurement methods of ultra-low and low accelerating voltages, it is very important to select the proper accelerating voltage in wide range from ultra-low accelerating voltage to high one (30kV) according to the purpose of observation of the samples [19-21, 23]. And there are field emission scanning electron microscope (FE SEM) and thermoelectric emission scanning electron microscope (SEM) in a sort of SEM, and the measurement conditions of different samples are different. So the study for the selection of measurement condition is essential. Especially, by using FE-SEM with in-lens detector within 0.3~5kV of accelerating voltages, studies on imaging of CNTs in CNTs/polymers have been done, but here no study on the microstructure of CNTs surface have been done [9]. No studies on the observation of the surface microstructure of CNTs were conducted by using the SEM equipped with the standard second electron detectors. Recently, as the study for noble material development is intensified, the requirements on microstructure morphology of CNTs surface is intended in their application.

In this paper, we performed theoretical analysis on the observation of the microstructure of CNT surface and through the observation of the image of microstructure of CNT surface by Quanta 200 SEM, we selected a proper accelerating voltage.

2. Experiment Equipment, Sample and Method

We observed the CNTs using a Quanta 200 SEM. The samples were MWCNTs (multi-wall carbon nanotube) fabricated by CVD. The sample was prepared through 3 stages including fixing the conductive band on Al tab, fastening and sputter coating. In sample fastening, it is attached sample on conductive band of Al tab and then excess sample is blown away by air ball. By SCD 005 sputter coater, the sample was coated with Pt. The sputter coating condition is the duration of 90s, the current of 40mA, and the working distance (between the anticathode and the surface of the sample) of 40mm. The anticathode was Pt plate of which purity is more than 99.9%.

Theoretical analysis on the observation of the microstructure of CNT surface was conducted, the experiments of the observation of them in various accelerating voltages, and the voltage in which the image is the clearest was set. The microstructure of the sample surface was observed in the same region of the sample by variating the accelerating voltage by 2.5kV within the range of 5~25kV, in 20,000 magnifications.

3. Theoretical Analysis and Experiments

3.1. Theoretical Analysis

Here, considering the theoretical resolution of Quanta 200 SEM and the size of electron -CNTs interaction range according to acceleration voltage, we studied theoretically on the selection of proper accelerating voltage.

The resolution of the optical system, d, is expressed as follows by Rayleigh level [8].

$$d=0.61\frac{\lambda}{\alpha}\text{, nm} \tag{1}$$

where α is the light convergence half angle and λ is the wavelength of electron. The wavelength of electron, λ, is expressed as [7].

$$\lambda=\frac{1.24}{\sqrt{U}}\text{, nm} \tag{2}$$

Substituting Eq. (2) to Eq. (1), then the resolution, d, is expressed as

$$d=\frac{0.7564}{\alpha\sqrt{U}}\text{, nm} \tag{3}$$

Because the diameter of final lens aperture is 500 ㎛, work distance (distance from final lens to sample observation area) is 4mm, substituting $\alpha\approx\tan\alpha=0.0625$ [8], equation (3) is converted into

$$d=\frac{12.1}{\sqrt{U}}\text{, nm} \tag{4}$$

Graph of this equation is drawn as following.

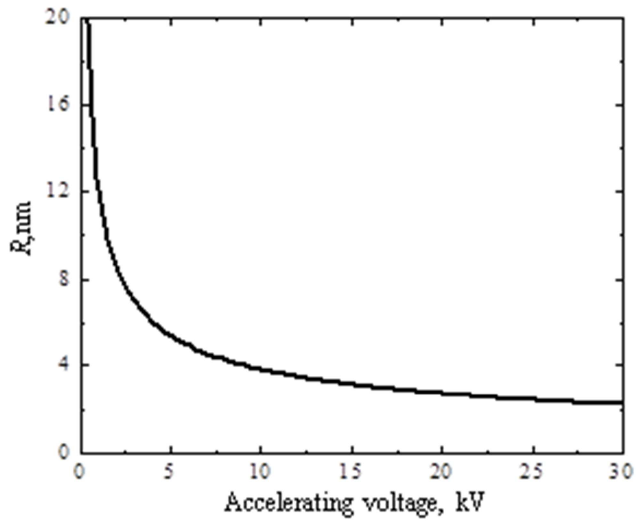

Figure 1. *SEM resolution according to accelerating voltages.*

As shown this Figure 1, as the accelerating voltage increases, the theoretical resolution of SEM, d, decreases drastically until the voltage reaches approximately 5kV, gently when it is within 5kV~10kV, very gently when it is over 10kV.

As the resolution of SEM decreases, the smaller surface structure is able to observe. There are theoretical resolution and spatial resolution in SEM. In real measurement the measurement limit is decided by the spatial resolution. The spatial resolution is effected by many factors such as measurement condition, sample and environment. Many studies for the resolution of SEM were done, but the method which is decided the smallest distance between 2 subjects in the measurement image of standard sample are the exact method. As the accelerating voltage increases, the theoretical resolution of SEM, d, decreases, inversely electron beam-matter interaction range is increased and real resolution can be lowed.

We evaluated the size of electron-CNTs interaction range as the Kanaya-Okayama range more approximated to the actual value. Kanaya-Okayama range is evaluated as a radius of the square which fitted its center on the surface at the electron stroke point surrounding limited area of interaction range [7]. The Kanaya-Okayama range [7] is evaluated by

$$R = \frac{0.0276\,AE^{1.67}}{Z^{0.89}\rho} \quad (\mu\text{m}) \tag{5}$$

where E is the incident electron energy, KeV; A is the atom weight of sample, g/mol; ρ is the density of sample, g/cm^3; and Z is the atom number of sample. The property values of CNTs are A=12, Z=6, and ρ=1.35g/cm^3, respectively. By introducing these into equation (5), the following equation turns out to

$$R=0.05E^{1.67}, \ (\mu\text{m}) \tag{6}$$

The following graph represents this equation.

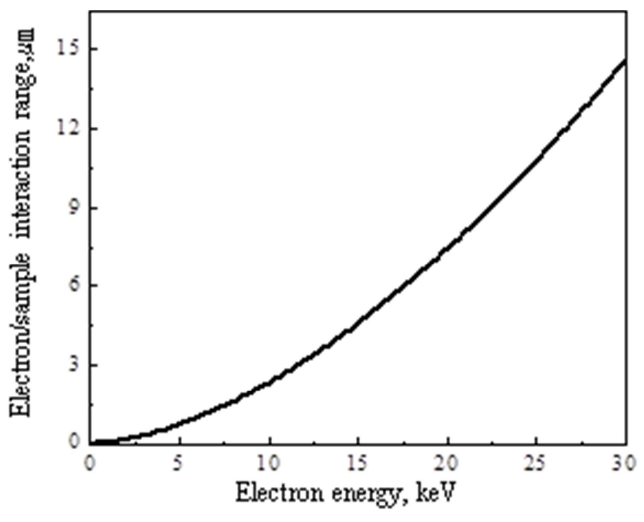

Figure 2. *Electron/sample interaction range according to electron energy.*

As shown this Figure 2, if the interaction range is large, partial practical fine structure of sample surface cannot be revealed. Thus in order to observe the microstructure of the material surface clearly, we must decrease the size of the interaction range. On the other hand, as shown in Figure 2, the size of interaction ranges of electron -CNTs exponentially increases as the energy of the incident electron increases. So we must decrease the energy of incident electron, that is, the accelerating voltage as much as possible to decrease the size of the interaction range. Considering equation (4) we can conclude theoretically that the most proper accelerating voltage is within 5kV~10kV in the observation by Quanta 200Basis of change the theoretical resolution and the size of electron-CNTs interaction range as the accelerating voltage increases.

3.2. SEM Imaging According to the Accelerating Voltages and Image Analysis

Here we performed SEM imaging of CNTs according to various accelerating voltages. Spot size was selected as 1.5nm, work distance was selected as 4.0mm and accelerating voltages was changed into 5.0kV, 7.5kV, 10.0kV, 12.5kV, 15.0kV, 17.5kV, 20.0kV, 22.5kV, 25.0kV, while the image was measured. SEM images of CNTs taken at different accelerating voltages are presented in Figure 3.

In Figure 3, each of the SEM images were obtained for the same sample in the same region. In all the images, CNTs of different diameters are observed. CNTs with different diameters were observed from each image. The diameter size of CNT bunches are 20~40nm. In center part of image, smaller CNTs are observed and their size are 24~30nm. In low part of image, large CNTs are observed and their size are 66~100nm. In the right upper corner is observed aggregation, which is seen as the tip of CNTs in the white square. But if we observe all the images in detail, even if they are images of same yield, they are different each other. However, closer observations of all the images reveal that they are different from each other despite being measured in the same field, especially the surface morphologies in the white square in the image being observed differently. Especially, in area which is labeled as white square, surface morphologies are observed differently each other. In the left upper corner of all images, there are extended images for area which is labeled as white square.

They show that the tips of CNTs are clearly observed as aggregation in inset images g), h) and i) measured at accelerating voltages of 20.0kV, 22.5kV and 25.0kV, as well as in inset images e) and f) measured at accelerating voltages of 15kV and 17.5kV. In e), f) inset images of Figure 3 measured in accelerating voltages of 15kV, 17.5kV, tip of CNTs is observed as an aggregation. While in inset image d) of Figure 3 measured in accelerating voltages of 12.5kV, tip of CNTs is observed as a aggregation or a bundle. However, in inset image d) measured at accelerating voltage of 12.5kV, the tip of CNTs is observed either as aggregation or a bundle, the result of which makes it hard to clearly observe the microstructure of the aggregation. As such this image observation, the fine structure of aggregation is not clearly observed. In a), b), and c) images of Figure, 3 measured in accelerating voltages of 5.0kV, 7.5kV, 10kV, tip of CNTs is observed as a bundle. This shows to be observed exacter fine structure of surface, when CNTs is measured at low accelerating voltages below 10kV, since the size of interaction area between the incident electron and the sample is smaller. If SEM image of the sample is measured in low accelerating voltages below 10kV, because the size of interaction area between incident electron and sample is small, finer structure of surface can be exacter observed. The bundle structure of the CNTs tip in the right upper corner of SEM image measured at accelerating voltage of 7.5kV reflects most accurately the real structure of the sample. If the accelerating voltage is very low, the yield of second electrons is few and so image quality can be poor. These results agree remarkably well with the previous theoretical results.

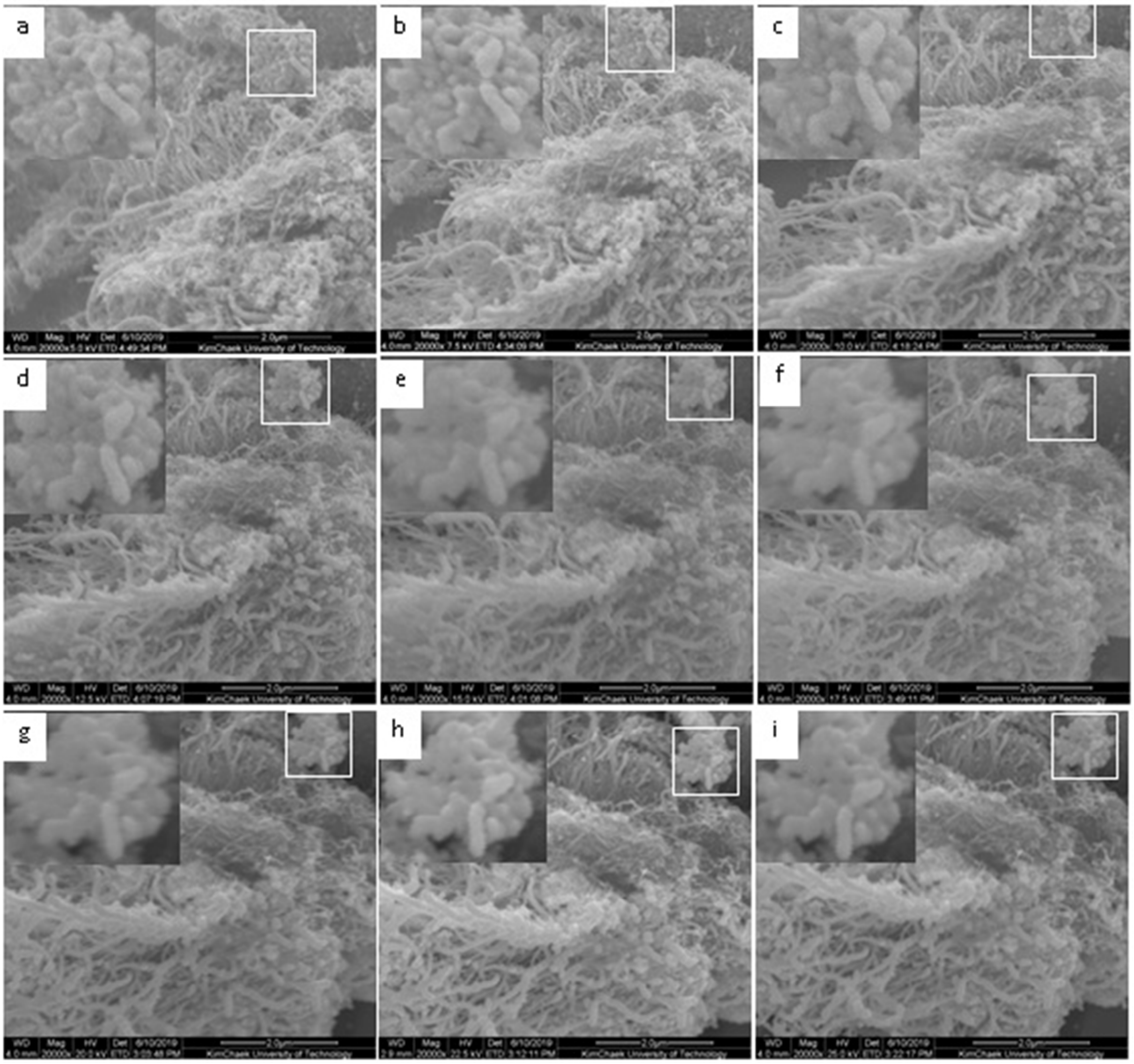

Figure 3. *SEM images of CNTs at different accelerating voltages. (The scale bar is 2.0 μm and the magnification is 20000×) (a-5.0kV, b-7.5kV, c-10.0kV, d-12.5kV, e-15.0kV, f-17.5kV, g-20.0kV, h-22.5kV, i-25.0kV).*

4. Conclusion

The effects of energy of the incident electron on the size of the electron-CNTs interaction range and the resolution of SEM were theoretically investigated. As a result, in case of microstructure observation of CNTs surface by using thermoelectric SEM, the most proper accelerating voltage was within 5~10kV. Through the experiments based on it, we found that the accelerating voltage of 7.5kV enables us to get the sharpest image of the microstructure of CNT surface. Theoretical results and experimental results were agreed well.

This methodology can be used in the observation of several kinds of materials.

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