Compact Sub Micro-resolution X-ray Microscope Based on Carbon Nanotube FE-SEM* 

Masaru Irita†
Department of Quantum Engineering, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan and Venture Business Laboratory, Nagoya University, Nagoya 464-8603, Japan

Hitoshi Nakahara and Yahachi Saito
Department of Quantum Engineering, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
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Generally, nano-resolution X-ray imaging has been achieved using synchrotron radiation facility. The spatial resolution (below 100 nm) achieved with a Fresnel zone plate for focusing the X-ray in SPring-8 lately. We have developed a compact composite of field emission-scanning electron microscope (FE-SEM) with a single isolated multi-walled carbon nanotube (CNT) electron source in our previous study. The spatial resolution of SEM image was estimated as ≃ 10 nm. This result indicates that the electron source we developed is suitable for a point-like X-ray source. We developed two kinds of X-ray microscope: projection-type X-ray microscope (PXM) and transmission-type X-ray microscope (TXM) in this study. The X-ray microscope based on the CNT-FE-SEM was constructed with a metal target for the X-ray source. Developing our X-ray microscope has been miniaturized to a compact size so that it can be placed on a desk. Moreover, the spatial resolution of 400 nm achieved the theoretical resolution limit. Because there is resolution limit by the acceleration voltage of 17 kV for the focused electron beam spot, the spatial resolution is an order of the electron penetration depth. The present study shows a potential that the CNT-based X-ray microscope would be applied to various field studies including the scene of an archaeological site excavation and future planet search. [DOI: 10.1380/ejssnt.2018.84]

Keywords: Carbon nanotube; Field emission; Scanning electron microscopy (SEM); X-ray emission

I. INTRODUCTION

Carbon nanotube (CNT) possesses various benefits as a field electron emitter [1]. Multi-walled CNT (MWNT) exhibits high brightness and sustains stable field emission (FE) even under poor ultrahigh-vacuum condition 10^{-6}–10^{-7} Pa without ion pumping [2]. Furthermore, CNT field emitters possess excellent properties such as a small virtual source size of 2–3 nm and high brightness of 10^9–10^{10} A/cm^2 sr [3, 4]. These properties are unique advantages of CNT electron source in comparison to conventional electron sources. However, the application of CNT emitter has not been in practical use yet in 2017. In the field of electron source, thermionic electron sources have been used for electron microscopes. In some of high-resolution electron microscopes, FE is used. Tungsten (W) field emitters are commonly used. Yabushita et al. tried to develop a compact scanning electron microscope (SEM) equipped with a MWNT bundle FE electron source and a ballast resistance [5]. They demonstrated the performance of MWNT bundle FE-SEM and showed SEM images taken under the poor vacuum condition at room temperature. Next, Yabushita et al. developed a transmission-type X-ray microscope with a MWNT bundle FE electron source [6]. An X-ray generated from a target in vacuum chamber and is ejected into air through a beryllium window. A sample is set in air and is observed by their transmission-type X-ray microscope. They estimated the resolution of SEM images as 50 nm and observed X-ray images with resolution higher than 700 nm. CNT field emitter has been intensively studied in applications to microscopes.

In our previous study, we had experimentally manufactured a compact composite of FE-SEM and X-ray microscope with a single isolated MWNT FE electron source [7]. The CNT emitter operated stably without any ballast resistance. Insertion of a ballast resistance is not desirable, because the electron beam spot becomes broad. The spatial resolution of SEM image was estimated as ≃ 10 nm [7]. This result indicates that the electron source we developed is suitable for a point-like X-ray source.

Generally, nano-resolution transmission-type X-ray imaging has been achieved using synchrotron radiation facility [8, 9]. The spatial resolution was estimated to be 70 nm from a line profile at an edge of a gate pattern using 3D nano-ESCA in SPring-8 [9]. The 3D nano-ESCA is constructed with a Fresnel zone plate for focusing the X-ray. Synchrotron radiation facility has an advantage of wavelength tunable light source. In this study, we tried to develop a portable compact nano-resolution of X-ray microscope.

II. EXPERIMENTAL

We considered that developing two kinds of X-ray microscope: transmission-type X-ray microscope (TXM) and projection-type X-ray microscope (PXM). The X-ray microscope based on the CNT-FE-SEM was constructed with a metal target for the X-ray source. Our compact X-ray microscope has been miniaturized to a compact size so that it can be placed on a desk. The MWNT electron source was installed in the gun chamber, which was evacuated with a turbo-molecular pump down to 10^{-7} Pa. The

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† Corresponding author: irita.masaru@d.mbox.nagoya-u.ac.jp
FIG. 1. (a) Schematic diagram of PXM apparatus. The double arrow shows the distance $b$ of 135 mm. (b) SEM image of a target for X-ray source and a sample of W needle. The target for X-ray source was Zr. A piece of Au mesh is also set for X-ray source as shown in (b). The double arrow shows the distance $a$ of $\simeq 450 \mu m$ between X-ray source and the sample. (c) PXM image of the W needle was acquired using focused beam current $I_{foc} \simeq 1 \times 10^{-9}$ A by 10-min exposure at acceleration voltage $V_{acc} \simeq 16$ kV. The X-ray target made of Zr was used. The yellow square in (b) shows a side view of the sample (W needle).

First, we explain about PXM. Figure 1 shows a schematic diagram of the PXM apparatus used in this study. The electron beam axis is fixed by the PXM design and thus, the distance $b$ is a constant value of 135 mm. The distance $a$ could be directly observed by SEM as shown in Fig. 1(b). Therefore, the magnification is determined precisely. PXM is one of X-ray imaging methods, the principle is similar to shadow play. The SEM and PXM images of sample are different in an angle of observation.

Next, we explain about TXM. Figure 2 shows a schematic diagram of the TXM apparatus. A SiN film (50 nm thick) was used as a base of target for X-ray source. The base was deposited with an Au film (10 or 50 nm thick) by electron beam physical vapor deposition. An X-ray generate from controlled thickness of Au metal film. Because the X-ray generated along the electron beam axis as shown in Fig. 2(a), the distances $a$ and $b$ could not be directly observed in TXM method. Furthermore, the distances $a$ and $b$ are dependent on the electron beam focusing point. Therefore, it is necessary to observe a specific sample for the calibration of magnification. The SEM and TXM images of sample could be observed in a same angle. TXM method is preferably used in previous research. Our TXM is characterized as setting X-ray target and sample in the vacuum chamber.

FIG. 2. (a) Schematic diagram of TXM apparatus. (b) SEM image of a sample of W needle. (c) TXM image of the W needle was acquired using $I_{foc} \simeq 2 \times 10^{-10}$ A by 10-min exposure at $V_{acc} \simeq 17$ kV. The X-ray target made of Au was used.

FIG. 3. (a) PXM and (b) conventional SEM image of W needle.

III. RESULTS AND DISCUSSION

We observed PXM images as shown in Figs. 1(c) and 3(a). Figures 1(c) and 3(a) are same PXM image. After PXM observation, the sample of the W needle was observed by conventional SEM, and the shape was investigated. Observed PXM and conventional SEM images of the W needle are same magnification of $\simeq x300$ as shown in Fig. 3. The PXM image of the W needle apex [Fig. 3(a)] is transparent, as revealed by comparison with the corresponding SEM image [Fig. 3(b)]. X-ray is transmitted through the thin part of the needle around less than $10 \mu m$ thick. Thus, it is necessary a thickness of more than $10 \mu m$ of the sample for X-ray observation.

Figure 4(a) shows an MWNT electron source used for SEM and PXM operation. The length of MWNT was...
The X-ray target mode of Zr and Au are different in a critical excitation voltage. The critical excitation voltage
is \( V_{c} \simeq 15.7 \) kV (\( K_{\alpha 1,2} \)) for Zr and a wavelength of X-ray is \( \lambda \simeq 0.08 \) nm. On other hand, the critical excitation voltage is \( V_{c} \simeq 9.7 \) kV (\( L_{\alpha 1} \)) for Au and a wavelength of X-ray is \( \lambda \simeq 0.13 \) nm. In this study, the acceleration voltage of 16 and 17 kV were used for the critical excitation voltage, respectively. The electron penetration depth in the energy range 5 to 15 kV is expressed as \( R_{e} = kV_{acc}^{1.5} (\mu m) \), where \( k \) is a parameter dependent on material [10]. The X-ray source size is expressed as \( \delta_{X} = 0.033(V_{acc}^{1.7} - V_{c}^{1.7})/\rho \), where \( V_{acc} \) (kV) is acceleration voltage, \( V_{c} \) (kV) is critical excitation voltage, \( A \) is atomic weight, \( Z \) is atomic number and \( \rho \) (g/cm\(^3\)) is density of material [11]. This is called Castaing’s equation. The electron penetration depth and X-ray source size depend on the density of material. The calculated quantities for each material are listed in Table I. We found \( \delta_{X} \simeq 35 \) nm for Zr was obviously small as compared with \( \delta_{X} \simeq 270 \) nm for Au at \( V_{acc} = 16 \) kV. We investigated the possibility of using Zr as X-ray target. Figure 5 shows EDX spectrum of the X-ray target mode of Zr and Au. The EDX spectrum of Au-L\( \alpha 1 \) was detected, although the EDX spectrum of Zr-\( K_{\alpha 1,2} \) was not detected. The X-ray almost did not generate from the X-ray target mode of Zr. Thus, the Zr is not suitable for the X-ray source. Though the PXM image was observed using the X-ray target mode of Zr as shown in Figs. 1(c) and 3(a), the focussed beam current \( I_{loc} \simeq 1 \times 10^{-8} \) A was higher than other measurements. In this case, the electron source suffered damage and the operation was unstable. The best PXM image was observed using the X-ray target mode of Au with \( I_{loc} \simeq 7 \times 10^{-10} \) A as shown in Fig. 4(b).

Let us compare the spatial resolution with theoretical predictions. The theoretical spatial resolution is expressed as \( \delta = \sqrt{\delta_{Zr}^{2} + \delta_{F}^{2} + \delta_{X}^{2}} \), where \( \delta_{Zr} \) is an electron beam spot size and \( \delta_{F} \) is Smearing due to Fresnel diffraction. In previous study, the electron beam spot size \( \delta_{Zr} \) size \( \delta_{X} \) for two acceleration voltages of 16 kV and 17 kV.

![FIG. 4. (a) SEM image of a CNT emitter used for PXM operation. (b) PXM image of Au mesh was acquired using \( I_{loc} \simeq 7 \times 10^{-10} \) A by 30-min exposure at \( V_{acc} \simeq 17 \) kV. The X-ray target mode of Au was used. Inset, low-magnification image of the mesh was acquired by 10-min exposure. Scale bar, 100 \( \mu m \). (c) Line profiles of the PXM image (b) obtained along a line indicated in the image. The solid black curve is the result of fitting.](image)

![FIG. 5. EDX spectrum of the X-ray target mode of Zr and Au. The X-ray target was the same as shown in Fig. 1(b). The EDX spectrum was observed by conventional SEM equipment. The X-ray target mode of Zr and Au were observed at the same time. The acceleration voltages was 17 kV and a collecting time was \( \simeq 4 \) min. The red arrows show the characteristic X-ray peak.](image)

| Material | \( 0\)16 kV | \( 0\)17 kV |
|----------|-----------|-----------|
| \( R_{e} \) (nm) | \( \delta_{X} \) (nm) | \( R_{e} \) (nm) | \( \delta_{X} \) (nm) |
| Au       | 290       | 270       | 320       | 320       |
| Zr       | 660\(^{a}\) | 35        | 720\(^{a}\) | 170       |

\(^{a}\) The electron penetration depth is calculated using density of Cu. The density of Zr \( (Z = 40) \) is 6.52 g/cm\(^3\), which is close to 8.94 g/cm\(^3\) of Cu \( (Z = 29) \).
was estimated to be $\simeq 10$ nm [7]. Smearing due to Fresnel diffraction is expressed as $\delta_F \simeq \sqrt{a\lambda}$, where $\lambda$ is wavelength of X-ray. In the case of Fig. 4, the distance $a \simeq 0.17$ mm was determined, then $\delta_F \simeq 147$ nm. The theoretical spatial resolution is $\delta \simeq 360$ nm for the Au target at $V_{\text{acc}} = 17$ kV. Therefore, the theoretical result agrees well the experimental result.

We assumed that the X-ray source size might be controlled by a thickness of metal film as a target in the TXM. For better resolution below 100 nm, we tried to develop the TXM. We observed TXM images of sample with the Au film thickness of 10 and 50 nm as shown in Fig. 6. The magnification was calibrated with the specific sample. In the case of an Au film thickness of 10 nm, a bright spot appears at the center as shown in Fig. 6(a). We could not find the sample because the electrons are almost transmitted through the Au film. With an Au film thickness of 50 nm, W needle sample was observed, although the image was affected by transmitted electron as shown in Fig. 6(b). Observed all TXM images showed a bright spot at the center. We assumed that the electron beam penetrated through the thin Au film because of $R_z \simeq 320$ nm for Au at $V_{\text{acc}} = 17$ kV. The X-ray source size could be controlled by the deposition, although the transmitted electron could not be restricted by TXM method. To solve this problem, the X-ray detector should be installed tilting from the electron beam axis. As one of solutions of this problem, an X-ray generated from the target in vacuum chamber and is ejected into air in previous research [6].

IV. CONCLUSION

The present study has demonstrated the best performance of PXM housed in the CNT based compact FE-SEM. Because there is resolution limit by the acceleration voltage of 17 kV for the focused electron beam spot, the spatial resolution is an order of the electron penetration depth. The spatial resolution of 400 nm achieved the theoretical resolution limit. In the TXM, the X-ray source size may be controlled by the deposition, although there are still problems regarding the transmitted electron. Developing our X-ray microscope is portable and compact. Moreover, the spatial resolution is about synchrotron radiation facility. The technique of this research would be beneficial for the application in the near future.

[1] Y. Saito, K. Hamaguchi, K. Hata, K. Uchida, Y. Tasaka, F. Ikazaki, M. Yumura, A. Kasuya, and Y. Nishina, Nature 389, 554 (1997).
[2] H. Nakahara, S. Ichikawa, T. Ochiai, Y. Kusano, and Y. Saito, e-J. Surf. Sci. Nanotech. 9, 400 (2011).
[3] K. Hata, A. Takakura, A. Ohshita, and Y. Saito, Surf. Interface Anal. 36, 506 (2004).
[4] H. Nakahara, Y. Kusano, T. Kono, and Y. Saito, Appl. Surf. Sci. 256, 1214 (2009).
[5] R. Yabushita, K. Hata, H. Sat0, and Y. Saito, J. Vac. Sci. Technol. B 25, 640 (2007).
[6] R. Yabushita and K. Hata, J. Vac. Sci. Technol. B 26, 702 (2008).
[7] M. Irita, S. Yamazaki, H. Nakahara, and Y. Saito, IOP Conf. Ser.: Mater. Sci. Eng. 304, 012006 (2018).
[8] A. L. D. Kilcoyne, T. Tyliszczak, W. F. Steele, S. Fakra, P. Hitchcock, K. Franck, E. Anderson, B. Harteneck, E. G. Rightor, G. E. Mitchell, A. P. Hitchcock, L. Yang, T. Warwick, and H. Ade, J. Synchrotron Rad. 10, 125 (2003).
[9] K. Horiba, Y. Nakamura, N. Nagamura, S. Toyoda, H. Kumigashira, M. Oshima, K. Amemiya, Y. Senba, and H. Ohashi, Rev. Sci. Instrum. 82, 1 (2011).
[10] V. E. Cosslett and R. N. Thomas, Br. J. Appl. Phys. 15, 1283 (1964).
[11] R. Castaing, Ph. D. Thesis, Univ. Paris (1951).