Electron Holography Study of Secondary Electron Distribution around Charged Epoxy Resin

Takafumi Sato¹, Naoya Tsukida¹,*¹, Mitsuki Higo¹,*², Hideyuki Magara¹, Zentaro Akase¹, Daisuke Shindo¹,²,*³ and Nobuhiko Ohno³,*⁴

¹Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
²RIKEN Center for Emergent Matter Science (CEMS), Wako 351-0198, Japan
³Jichi Medical University, Shimotsuke 329-0498, Japan
⁴National Institute for Physiological Sciences, Okazaki 444-8787, Japan

The accumulation and distribution of electron-induced secondary electrons around epoxy resin are studied using electron holography. The distribution of secondary electrons is determined to be sensitive to the surface conditions of the epoxy resin, particularly to the presence of conductive materials on the surface that are introduced during specimen preparation processes. These results provide a deeper understanding of the charging and discharging mechanisms for epoxy resin, and the behavior of secondary electrons around these materials. This study also provides a new perspective for the visualization of various forms of electron behavior around insulating materials such as epoxy resin through the control of their surface characteristics. [doi:10.2320/matertrans.MI201904]

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1. Introduction

Transmission electron microscopy (TEM) techniques have been widely utilized to study the microstructures of various materials. Among these techniques, electron holography has the unique feature of enabling the visualization of electromagnetic fields at the nanoscale. As such, both electric and magnetic fields have been extensively studied for a variety of materials. However, when insulating materials are examined using TEM, care should be taken with respect to the charging effect because the specimens become positively charged as a result of secondary electron emission. The additional electric field due to the charging effect tends to modify the inherent electromagnetic field of the specimen. Severe charging effects also cause specimen drift and anomalous image contrast. Various fixing and coating techniques with conductive materials have been widely utilized to suppress specimen charging and realize improved observation.

However, the detailed mechanisms of the charging and discharging effect, and the behavior of secondary electrons around the charged specimens have yet to be clarified.

We have recently conducted a systematic investigation on the charging phenomenon for insulating materials using electron holography. With biological specimens, e.g., microfibrils in sciatic nerve tissues, in addition to the electric field, the distribution of secondary electrons around the charged specimens can be observed by the detection of electric field variations due to the motion of secondary electrons. For example, the orbits of secondary electrons around microfibrils were clarified using reconstructed phase and amplitude images obtained with electron holography. The accumulation of secondary electrons in the branched regions of microfibrils was also studied. These studies observed the motion and accumulation of secondary electrons in the upper-edge regions of microfibrils that were far from the supporting film. The reason for this precaution is that charging of insulating materials is strongly affected by the irradiation of secondary electrons from the substrate and/or supporting film, as reported elsewhere. In the present study, particular attention was given to the effect of conductive materials placed on the surfaces of epoxy resin. The electric field fluctuation due to the motion of secondary electrons was then studied in relation to the surface conditions of charged epoxy resin.

2. Experimental

Epoxy resin (EPO–TEK® 375, Epoxy Technology Co., Ltd.) was used as a TEM specimen. A method for the preparation of a shape-controlled epoxy resin specimen is described in the following. Initially, the resin and the curing agent were mixed in a ratio of 10:1. This mixture was heated at a temperature of around 80°C for 90 min to accelerate the reaction and curing process to prepare a bulk epoxy resin specimen. Sectioned flakes were obtained by slicing a bulk specimen with an ultramicrotome (Leihurt Ultracut S, Leica Microsystems) and these were fixed on a thin Cu plate using a conductive epoxy resin. Figure 1 shows an optical microscopy image of the geometrical configuration of a sectioned epoxy resin flake and the Cu plate. The shape and size of the sectioned flake were adjusted using a focused ion beam (FIB) apparatus (JIB-4500, JEOL). Control of the specimen shape and the thinning processes were performed very carefully because the thin specimen rod of epoxy resin was easily deformed and broken during the microfabrication processes.

The electron holography experiment was conducted using an electron microscope (JEM-3000F, JEOL) equipped with a...
thermal field emission gun having a biprism, and another microscope (HF-3000X, Hitachi High-Technologies) equipped with a cold field emission gun having three biprisms in the imaging system. The accelerating voltage used for both the microscopes was 300 kV. The exposure time was set to 6 s and 3 s for observations with the JEM-3000F TEM and HF-3000X TEM, respectively. Holograms were obtained for the reconstructed phase and amplitude images using Fourier transform operation.

Surface contaminants on the TEM specimens were analyzed using an electron probe microanalysis (EPMA; JXA-8530F, JEOL) system with an acceleration voltage of 15.0 kV. Elemental mapping images were obtained for C, Ga and Al elements using the EPMA system.

To simulate the electric potential distribution around the epoxy resin, ELFIN and ELF/MAGIC software (ELF Corporation) were used for the electric field analysis. These simulations were performed on the basis of Maxwell’s equations.

Figure 2 shows a schematic illustration of the experimental conditions to form a hologram using TEM with a biprism. The hologram is obtained by application of a voltage to interfere an object wave with a reference wave. Phase and amplitude information can be extracted by processing these holograms through the Fourier transform operation.31,33)

Reconstructed phase images clarify the electric potential distribution, while reconstructed amplitude images detect the fluctuation of electric field due to the motion of secondary electrons.

3. Results and Discussion

Figure 3 shows a low-magnification TEM image of an epoxy resin specimen shaped by FIB. The Y-shape epoxy resin imitates the shape of the biological specimen observed in the previous study.32,33) Figure 4(a) shows a hologram of the specimen, and Fig. 4(b) shows the reconstructed phase image, where the purple region corresponds to the epoxy resin. A simulation was conducted based on a simplified three-dimensional model whose thickness is uniformly 10 µm, and a shape of top view and a potential distribution on its top surface are shown in Fig. 4(c). The potentials on the side and bottom surface are set at 0.0 V. A three-dimensional electric potential distribution around the model was calculated. A region between ±10 µm from center of the specimen along a beam direction was considered in the simulation. In this simulation, an electric potential caused by secondary electrons distributed around the specimen was not considered. Figure 4(d) shows a phase image simulated with the above model. A modulation of a phase shift of the reference wave was considered in Fig. 4(d). A width of an interference fringes region was assumed to be 4.4 µm. A result of a calculated phase image without consideration of the modulation of the phase shift of the reference wave is shown in Fig. 4(e) for comparison. Contour lines around the specimen in Fig. 4(e) correspond to electrical equipotential lines projected along the incident electron beam direction.

Figure 5(a) shows a reconstructed amplitude image, where the dark regions correspond to fluctuations in electric field due to the motion of secondary electrons.31,33) Color images are presented in Fig. 5(b), where the color scale bar in the lower part indicates the relation between the visibility of the interference fringes and the contrast of the reconstructed amplitude images. Here, the incident electron intensity is homogeneous in the observed area outside the charged specimen. The decrease of visibility of interference fringes results from the electric field fluctuation, which was discussed in previous paper.33) On the other hand, this low
visibility of interference fringes results in lower amplitude in the reconstructed amplitude images. We measured the visibility of interference fringes and the contrast of the reconstructed amplitude image in the same points of various regions. The relationship was obtained in the color scale bar as shown in Fig. 5(b). As indicated by the white arrows, faint red color regions are observed in the lower right and left parts, which correspond to the region of relatively high electric potential in Fig. 4(c). This feature is significantly different from biological specimens, i.e., microfibrils of sciatic nerve tissue, in which secondary electrons tend to accumulate at the top region between two branches. Figures 6(a) and 6(b) show the reconstructed amplitude images around microfibrils of sciatic nerve tissue observed in the previous paper.32) The bright red color regions are considered to correspond to the part where the fluctuation of electric potential due to the motion of the secondary electrons is prominent. This point will be discussed later. It is also noted that the red color regions shift gradually with the passage of time along the inside surfaces of the two branches of microfibrils.32)

To confirm the distribution of secondary electrons around the branched region of the epoxy resin specimen, holograms were observed under different experimental conditions, as shown in Fig. 7. In Fig. 7(a), interference fringes are observed in one part of the two branches. Note that Fresnel fringe contrasts were significantly suppressed in the hologram because the hologram was acquired with the double-biprism interferometry.36) Figure 7(b) shows the reconstructed phase image of the region. Figure 7(g) is a result of a simulation of a phase image using a three-dimensional potential model shown in Fig. 7(f). The width of the interference region was assumed to be 2.8 μm. Figure 7(g) basically represents the asymmetry of the phase distribution along the branch of the epoxy resin in the experimental phase.
image of Fig. 7(b). Note that the electric potential distribution is slightly different from that of Fig. 4(c) due to the specimen conditions, such as illumination intensity and area of the incident electron beam. Figure 7(c) shows the reconstructed amplitude image, and the corresponding color image is presented in Fig. 7(d). It is found that the lower part of the branch indicated by the arrow “L” (8.0 V) shows a faint red color region different from the upper part indicated by the arrow “U” (4.0 V). Figure 7(e) shows the averaged intensity distribution of the reconstructed amplitude image along the direction of the black arrow in the rectangular regions indicated in Fig. 7(c). The amplitude of the lower part is lower than that of the upper part of the branch. These features are consistent with the results in Fig. 5(b).

The difference between the present results and those obtained in previous observations with Y-shaped biological specimens is considered to result from the presence of metallic elements on the surface of the epoxy resin due to the FIB thinning process. To confirm this, EPMA elemental mapping analysis was performed. Figure 8(a) shows a scanning electron microscopy (SEM) image, and Figs. 8(b) to 8(d) show elemental mapping images that for C, Ga and Al. The epoxy resin contains carbon; therefore, the red color, which indicates carbon-rich areas, is reasonable. On the other hand, Figs. 8(c) and 8(d) show that Ga and Al are also present. The Ga is caused by the Ga ion beam used in the FIB thinning process. The presence of Al is considered to be due to redeposition from the Al specimen supporting plate of the FIB system. The presence of these metallic elements on the surface of the Y-shaped epoxy resin is attributed to the small accumulation of secondary electrons at the top edge region.

Note that in the elemental mapping analysis by EPMA systems, the signals obtained strongly depend on the shape of specimens and also geometrical configuration of the specimen and the detector. Thus, from these analyses it is difficult to quantitatively evaluate the distribution of metallic elements. Nevertheless, it is considered that the final thinning process was mainly done at the top edge region between the branches and relatively high density of metallic elements is
expected to form at the top edge region resulting in low electric potential of the surface and thus the low density of secondary electrons around the surface.

To examine the effect of these metallic elements on the surface, the secondary electron distributions were compared for different surface conditions of the epoxy resin specimens, i.e., one specimen prepared by ultramicrotomy and the other by the FIB system. Unlike when the FIB system was used, a clear specimen surface without metallic elements was obtained by ultramicrotomy. Figure 9(a) shows a reconstructed phase image of a thin film of epoxy resin (dark brown region) prepared by ultramicrotomy. In order to estimate the electric potential of a top surface of the specimen, we simulated the phase images by the same method shown in Fig. 4. The thickness of the model was 2.0 µm. The electric potentials on side and bottom surfaces of the model were set at 0.0 V. The width of interference fringes region was assumed to be 2.8 µm. Compared with the simulation results shown in Fig. 9(b), the electric potential of the epoxy resin is estimated to be 1.2 V. This electric potential is relatively low comparing with the side surface of the Y-shaped epoxy specimen (Fig. 4(c)). Although there are no metallic elements on the surface of the specimen prepared by ultramicrotomy, the charging effect is suppressed due to the irradiation of secondary electrons from the specimen support plate near the observed area. The reconstructed amplitude image in Fig. 9(c) shows red color regions around the surface of the epoxy resin, which are considered to correspond to a high density of secondary electrons strongly interacting with the surface of the positively charged specimen. Particularly in the concave region, as indicated by the arrow in Fig. 9(c), a bright red color region is evident, which corresponds to a large fluctuation of the electric field due to the interaction of accumulated secondary electrons with the surface. After observing the hologram of the epoxy resin, both sides of the thin specimen were irradiated with a weak Ga-ion beam. The beam intensity was $0.85 \times 10^{-3}$ mC·m$^{-2}$, which is 200 times smaller than that typically used for polishing specimens. The reconstructed phase image in Fig. 9(d) shows that the electric potential of the specimen becomes 1.0 V by computer simulation (Fig. 9(e)). The electric potential of the specimen before and after was not significantly different due to the weak Ga-ion beam. It should also be noted that the shape of the specimen in Fig. 9(d) is almost the same as in Fig. 9(a), which indicates that the irradiation damage by Ga ions is small. In the reconstructed amplitude image in Fig. 9(f), the colored regions observed in Fig. 9(c) are no longer visible. Thus, the distribution of secondary electrons that interact strongly with the surface of the positively charged epoxy resin is sensitive to the presence of metallic elements on the surface.

Finally, we discuss the fluctuation of electric potential distribution around the charged specimen observed in the reconstructed amplitude images taking account of the systematic studies on the charging effect of insulating materials performed so far. First we note that there exist possible contributions to the cause of the fluctuations of electric potential around the charged specimens, i.e., secondary electron motions and electric potential change of the specimens. The charging effect of insulating materials results from the unbalance of secondary electron emission and supply of electrons, such as irradiation of secondary electrons from the substrate. When the experimental conditions such as irradiation intensity and illumination area of the incident electron beam are constant, the charging state...
of the insulating specimen becomes stationary. In that case, it is considered that drastic changes of the electric potential of the charged insulating specimens do not occur.\textsuperscript{32,33} In the case of microfibrils of sciatic nerve tissue as shown in the reconstructed amplitude images presented in Fig. 6, if there exist considerable fluctuations of electric potential of the specimen, the red color regions are expected to be observed around the specimen monotonously as discussed in the previous paper.\textsuperscript{33} In the observed images, however, the red color regions are observed mainly around the inside surfaces between the two branches of microfibrils. Furthermore, the color regions are localized and shifted gradually along the inside surfaces of the two branches. These features are well explained through the interaction between the secondary electrons and the surfaces of charged specimens as discussed in the previous papers.\textsuperscript{32,33} In the epoxy specimen shown in Fig. 9(c), red color regions are observed around the charged specimen. As noted above, the bright red colored region is prominent in the concave region indicated by an arrow in Fig. 9(c). This tendency is also explained by the interaction between the secondary electrons and the surface of the charged epoxy specimen. Thus, the red color regions around the charged insulating materials observed in the reconstructed amplitude images can be interpreted as the fluctuations of electric potential mainly caused by the motions of secondary electrons around the charged specimen. Accordingly, this interpretation may be applicable to the contrast of amplitude images of Figs. 5(b) and 7(d). On the other hand, as clarified in this study, the existence of metallic elements on the surface of charged specimens drastically reduces the fluctuations of electric potential due to the secondary electron motions. In addition, we should note that the reconstructed amplitude images do not visualize the whole information about the distribution of secondary electrons whose density is relatively low at the region far from the charged specimen and even near the charged specimen with the existence of metallic elements on the surface.

4. Conclusions

In summary, the electric potential of charged epoxy resin was quantitatively evaluated by simulation. The distribution of secondary electrons around the charged epoxy specimen was visualized by the reconstructed amplitude imaging process. The distribution of secondary electrons was determined to be sensitive to the presence of metallic elements on the surface. Therefore, the distribution of secondary electrons can be controlled by adjustment of the surface conditions of the epoxy resin specimen. This study is expected to open a new perspective for electron holographic visualization of various forms of electron behavior around insulating materials by control of the surface conditions.

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REFERENCES