Voltage Contrast in Scanning Electron Microscopy to Distinguish Conducting Ag Nanowire Networks from Nonconducting Ag Nanowire Networks

Kouji Suemori,* Yuichi Watanabe, Nobuko Fukuda, and Sei Uemura

Cite This: ACS Omega 2020, 5, 12692−12697

ABSTRACT: A study of the electrical properties of metallic nanowires requires a clear analysis of conductive networks. In this study, we demonstrated that the conducting networks of Ag nanowires (AgNW) could be visually observed by examination of the voltage contrast of the scanning electron microscopy (SEM) images, which was caused by the differences in the degrees of charging of AgNWs. When AgNWs dispersed on a quartz glass were irradiated by primary electrons, the substrate became negatively charged. This induced positive charges on the AgNWs in contact with the electrodes. As a result, AgNW networks connected to electrodes appeared dark in the SEM image, while the isolated AgNWs appeared brighter. By varying the acceleration voltage of the primary electrons, the extent of charging could be controlled, which, in turn, enabled the observation of the voltage contrast of AgNWs. Using the voltage contrast of SEM images, we could visually distinguish the AgNW networks having an electrical connection with the electrode from the ones that were not connected to the electrode.

INTRODUCTION

Nanowires with electrical conductivity can be used for various applications such as transparent electrodes,1−3 optoelectronic devices,4−9 and energy conversion devices.9−12 The electrical conduction in nanowires occurs through conductive networks formed by obeying the percolation theory.2 At lower concentrations, the relationship between the density of conducting nanowires and the electrical conductivity has a threshold value, which is known as the percolation threshold.13 For two-dimensional widthless sticks of length, L, the number density of the sticks at the percolation threshold (Nt) is given by14

\[ NtL^2 = 5.637 \times 26 \]  

(1)

When sticks are added to a film at the percolation threshold, additional connections are formed between the sticks and the conducting path; this leads to a reduction in the electrical resistance of the network.

Metallic nanowires with concentration slightly higher than the percolation threshold are promising materials for transparent electrodes with flexibility.1−3,15,16 Among many metallic nanowires, Ag nanowire (AgNW) is the most widely investigated metallic nanowire due to the high electrical conductivity of Ag and relatively easier synthetic process.15 Metallic nanowires need to possess both high optical transparency and high electrical conductivity if they are to be used as transparent electrodes. Thus, the efficient formation of a conducting network using low concentrations of metallic nanowires is indispensable. A lot of studies have been conducted to analyze the network formation of nanowires using theoretical calculation of percolation.17−19 The theoretical calculation clarified various types of valuable knowledge. For example, it was evident from the theoretical calculations that the conductive network formation becomes easier by increasing the aspect ratio of nanowires.19 However, in practical conditions, it is necessary to consider the variations in different parameters that may not have considered in theoretical calculations. For instance, Tokuno et al. reported that the residual insulating polymer used for synthesizing the AgNWs suppressed the electrical conductivity of the transparent electrode made from AgNWs.16 The amount of such residual impurities in the transparent electrodes made up of AgNWs depends on the synthetic process for the preparation of AgNWs and conditions of formation of the conductive networks. Thus, it can be seen that a precise estimation of the effect of these impurities on the electrical conductivity may be difficult by theoretical calculations. This may become pronounced in the case of nanowires with concentrations close to the percolation threshold because only a small number

Received: December 10, 2019
Accepted: April 13, 2020
Published: May 26, 2020
of conductive paths dominate the overall electrical conductivity of the material. Therefore, the development of an experimental method that allows visualization of the formation of a conductive network is required.

A scanning electron microscopy (SEM) is one of the most widely used equipments for the direct observation of the nanostructure of various materials, including conductive nanowires. The contrast of SEM images depends on the emissivity of secondary electrons (SEs), which is determined by various parameters including the shape of the materials and voltage at the material surface. The contrast in a SEM image caused by a difference in the surface voltage of the material is called “voltage contrast.” and it can be used for the estimation of the difference in the degree of charging of the material surface caused by charge carrier doping. SEM measurement causes the charging of the material surface due to the irradiation of primary electrons (PEs). Thus, the difference in the charging of the material surface caused by PE irradiation can be estimated by the voltage contrast. For example, Song et al. observed a voltage contrast in AgNWs partially coated with poly(vinylpyrrolidone) (PVP), caused by the irradiation of PEs during SEM measurement. The study has also shown that the PVP-coated part of the AgNWs could be distinguished using the voltage contrast.

The voltage contrast is also used to observe other nanowire materials such as Si nanowires and insulating polymers.

In the case of metallic nanowires with concentrations close to the percolation threshold, the degree of charging of nanowires by irradiation of PEs may differ for the isolated nanowires and nanowires in contact with the conductive network. Thus, the voltage contrast analysis in SEM images potentially becomes an effective method for the observation of conductive networks. In this study, we report the use of voltage contrast SEM to observe the conductive network of AgNWs.

**RESULTS AND DISCUSSION**

Figure 1 shows the schematic representation of the device structure used in this study. AgNW networks were fabricated on the quartz glass substrate by spin-coating the solution of AgNWs dispersed in isopropanol. The length and diameter of the AgNWs used in this study were 10 ± 5 µm and 60 ± 10 nm, respectively. The values of number density per unit area (D) of AgNWs in the devices were 2.14, 3.85, 4.31, 5.51, 7.98, 11.7, and 13.2 × 10^6 cm^-2. These D values corresponded to the areal mass density (D_M) values of 6.34, 11.4, 12.8, 16.3, 23.7, 34.8, and 39.1 mg/m^2, respectively.

Figure 2a shows the current–voltage characteristics of the device. The device with D_M values of 6.34, 11.4, and 16.3 mg/m^2 did not exhibit current flow, whereas the other device showed a linear relationship between current and voltage. Figure 2b shows the electrical conductance of the device calculated from the slopes of the lines in Figure 2a. The conductance increased from approximately 15 mg/m^2, which indicates the percolation threshold of AgNWs used in this study. The electrical conduction of AgNW films near the percolation threshold is dominated by only a small number of conducting paths. In this case, the fluctuation in the number of conducting paths in each device significantly influences the electrical conductivity of the devices. Consequently, the devices with the D_M of 12.8 mg/m^2 show electrical conduction, while those with the D_M of 16.3 mg/m^2 do not.

The use of AgNWs at the percolation threshold may be suitable for observing conductive and nonconductive AgNW networks using SEM images. However, obtaining the exact density at the percolation threshold from experiments, such as the one shown in Figure 2b, is difficult. Therefore, we instead measured the SEM images using AgNWs with slightly lower (D_M = 11.4 mg/m^2) and higher (D_M = 23.7 and 34.8 mg/m^2) densities than that at the percolation threshold.

Figure 3a shows the SEM image of the device with an areal mass density of AgNWs of 11.4 mg/m^2. We carried out a continuous scan of the same area up to four times (Figure 3a–d). The change in the contrast with an increase in the scan time was observed. This indicates that the charging of device surfaces by irradiation of PEs enhanced with the scan time. The contrast change was almost saturated at the third scan. The Ag nanowires that were in contact with the electrodes appeared darker than those that were not in contact with the electrodes (Figure 3a–d).

The SEM images of the negatively charged sample surfaces look generally brighter than the positively charged sample surfaces. This is because negative surface charges facilitate the SE emission due to electrostatic repulsion, while positive surface charges suppress the SE emission due to electrostatic attraction. The charges generated by PE irradiation on AgNWs in contact with the electrodes flow to the sample stage of the SEM equipment via the electrodes during the analysis because the Au electrodes are connected to the sample stage. On the other hand, the charges get accumulated on the AgNWs isolated from the electrodes. This leads to the differences in the degrees of charging of the AgNWs in contact with the electrodes and of AgNWs isolated from the electrodes. As a result, a voltage contrast is observed. The darker image ofAgNWs in contact with the electrodes compared to that of the

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Schematic representation of the device structure used in this study.
isolated AgNWs indicates that these AgNWs are charged positively.

Figure 4 shows the SEM images captured by applying different acceleration voltages for the device whose $D_M$ of AgNWs is 39.1 mg/m². The SEM image with an acceleration voltage of 1 kV did not show a significant difference in the contrast between AgNWs (Figure 4a). A clear contrast between AgNWs was observed when the acceleration voltage was 2 kV, and the contrast increased with an increase in the acceleration voltage (Figure 4b–f). This indicates that by controlling the acceleration voltage the extent of charging could be varied, which, in turn, enabled the observation of the voltage contrast of AgNWs. The quartz glass substrate became brighter with an increase in the acceleration voltage (Figure 4a–f), suggesting that the accumulation of negative charges on the surface of the quartz glass substrate increased with an increase in the acceleration voltage. This is a commonly observed phenomenon in the SEM analysis occurring due to
lowering of emissivity of SEs of material surfaces with an increase in the acceleration voltage. On the contrary, AgNWs on the quartz glass substrate became darker with an increase in the acceleration voltage, which indicated that these nanowires became positively charged as the acceleration voltage increased. The darkening of the contrast of AgNWs is only observed on the quartz glass substrate and not observed on the Au electrodes, which indicated that the AgNWs placed on the quartz glass substrate only got positively charged. The device surface charges, i.e., the origin of the voltage contrast, as observed during SEM imaging are depicted in Figure 5. The positive charges on the AgNWs placed on the quartz glass substrate indicate that the negative charge on the surface of the quartz glass substrate should be the origin of the positive charges on AgNWs. This is consistent with the following facts. (1) The Au electrodes are connected to the sample stage of the SEM equipment; hence, they do not get charged. As a result, AgNWs on the Au electrodes also do not get charged. (2) The accumulation of positive charges in AgNWs suggests the flow of electrons to the electrode from the AgNWs, which would take place only if the AgNWs were in contact with the electrode.

The number of darkened AgNWs were observed to increase as the acceleration voltage increased; further, the darkened AgNWs became darker and wider (Figure 4), which indicated that the positive charge in the AgNWs was augmented with the increase in the acceleration voltage. The number of darkened AgNWs increased with an increase of up to 4 kV in the acceleration voltage. This indicates that at the acceleration voltage of 4 kV the positive charge in the AgNWs reached an amount that was sufficient to cause the voltage contrast. At acceleration voltages of 2 and 3 kV, some of the AgNWs showed an intermediate contrast, indicating that these AgNWs were under charging.

The widths of the darkened AgNWs seem to span across several hundred nanometers (Figure 4d). This indicates that the capturing of secondary electrons, which resulted from the electric field formed by the positive charges in the AgNWs, occurs within several hundred nanometers from the AgNWs. Furthermore, this may limit the spatial resolution of the voltage contrast.

Figure 6a–c shows the SEM images of the device with the \( D_M \) values of AgNWs of 11.4, 23.7, and 39.1 mg/m². It was observed that the conductive networks connecting both the electrodes (Figure 6b). However, due to the insufficient \( D_M \) of AgNWs, a lot of AgNWs seemed electrically disconnected from the electrodes. (Such AgNWs can be seen in the areas enclosed by the dotted line in Figure 6b.) On the contrary, most of the AgNWs seemed to have a connection with the electrodes in the device with the \( D_M \) of AgNWs of 39.1 mg/m² (Figure 6c). The difference in the amount of AgNWs without any connection with the electrodes, as shown in Figure 6b,c, was consistent with the electric characteristics of the device (Figure 2b). Namely, the electrical conductivity of the device with the \( D_M \) of AgNWs of 23.4 mg/m² was significantly smaller compared to that of the devices with the \( D_M \) of AgNWs of 39.1 mg/m². The device with the \( D_M \) of AgNWs of 39.1 mg/m² had a firm conductive network. However, some of the AgNWs, e.g., the AgNWs enclosed by the white dotted line in Figure 6c, were bright, which indicated that these AgNWs did not have a strong electrical connection with the electrode. The electrical conduction in AgNW networks depended not only on the electrical conductivity of individual AgNW but also on the contact resistance between AgNWs. The contact resistance increased with an increase in the distance between AgNWs at the contact, and the electron tunneling at the contact almost
disappeared when the distance between AgNWs at the contact is over several nanometers. Although AgNWs seemed to connect to the electrode via AgNW networks in the top view of SEM images, the electrical connection between the electrode and some of AgNWs would be weak owing to the distance between AgNWs at the contact exceeding the tunneling length of electrons. Tokuno et al. have actually observed such weakly bonded contacts of AgNWs. The bright AgNWs in the SEM image of Figure 6c indicated that regions with a weaker electrical connection between electrodes and AgNW networks could be detected by the voltage contrast of the SEM image. The effective AgNW ratio, the ratio of the number of AgNWs that are electrically connected to the electrode and the total number of AgNWs placed between the electrodes, can be estimated by counting the darkened AgNWs and bright AgNWs in the voltage contrast image. For example, in the case of the device with the $D_M$ of 39.1 mg/m$^2$, approximately 81% of AgNWs were electrically connected to the electrodes.

Figure 7 shows the SEM image of the device with the $D_M$ of 23.7 mg/m$^2$ fabricated on a poly(ethylene naphthalate) (PEN) film substrate. The observed voltage contrast indicates that the voltage contrast measurement can be used when the insulating polymer film is used as a substrate.

Based on the results of this study, we concluded that the voltage contrast in SEM analysis is effective for the observation of the network formation of metallic nanowires. Thermography-based measurements, such as lock-in mode thermography, of nanowires may yield results that are similar to those of the voltage contrast measurement carried out in this study. The application of the external electric field to conductive nanowires induces an increase in the temperature of the nanowires through Joule heating. A sufficiently high spatial resolution that would allow for the thermographic measurement of individual AgNWs was obtained in the previous study. In the case of thermography-based measurements, the results are affected by the contact area between AgNWs and the substrate, which generally varies among individual AgNWs. The voltage contrast measurement may be useful when the dispersion of heat from AgNWs to the substrate fluctuates between each measurement point during the thermographic measurement.

### CONCLUSIONS

We demonstrated that the voltage contrast of AgNWs in the SEM analysis is effective to analyze the electrically conducting networks of AgNWs. The AgNW networks having a connection with the electrode appeared dark in the SEM image due to PE-irradiation-induced negative charging of the quartz glass substrate, which in turn induced positive charges on the AgNW networks connecting to the electrode. By controlling the acceleration voltage of PEs, the extent of charging of AgNWs could be controlled, which, in turn, enabled the observation of the voltage contrast of AgNWs. Using the voltage contrast of the SEM images, we visually distinguished between the conducting and nonconducting AgNW networks.

### EXPERIMENTAL SECTION

Au electrodes of the devices with a thickness of approximately 30 nm were fabricated by vacuum evaporation on a quartz glass substrate. We purchased the solution of AgNWs dispersed in isopropanol (Sigma-Aldrich, product number 739421). We then prepared the AgNW-dispersed solutions with concentrations of 0.06, 0.125, 0.17, 0.2, 0.25, 0.34, and 0.5 wt % by adding isopropanol to the purchased AgNW-dispersed solution. The AgNW layer in the device was fabricated by spin-coating the AgNW-dispersed solution at 2000 rpm for 30 s. The $D_M$ values of AgNWs in the devices were 6.34, 11.4, 12.8, 16.3, 23.7, 34.8, and 39.1 mg/m$^2$. A source measure unit (Agilent, model 2902) was used to measure the current–voltage characteristics of the device. For imaging, a field-emission SEM system (Hitachi High Technologies, S-4800) with a secondary electron detector was used. Each of the two electrodes was connected to the sample stage of the SEM equipment using Ag paste and Cu tape. The working distance during SEM observation was set at approximately 8 mm. We used the acquisition mode of "slow 3", which requires approximately 10 s per scan.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04222.

- SEM image of the device with a short channel length;
- SEM image of the device obtained using an acceleration voltage of 1 kV; and SEM image of the device obtained using an acceleration voltage of 4 kV

### AUTHOR INFORMATION

**Corresponding Author**

Kouji Suemori — Sensing System Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8565, Japan; orcid.org/0000-0002-5523-1282; Email: kouji-suemori@aist.go.jp

**Authors**

Yuichi Watanabe — Sensing System Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8565, Japan; orcid.org/0000-0002-7013-3613
Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b04222

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
We thank K. Kimura for her assistance in fabricating the device and evaluating the electrical characteristics. A part of this study was carried out at the AIST Nano-Processing Facility, supported by the “Nanotechnology Platform Program” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. The authors gratefully acknowledge the financial support from the New Energy and Industrial Technology Development Organization (NEDO).

REFERENCES
(1) Lee, J.-Y.; Connor, S. T.; Cui, Y.; Peumans, P. Solution-processed metal nanowire mesh transparent electrodes. Nano Lett. 2008, 8, 689−692.
(2) Sannicolo, T.; Lagrange, M.; Cabos, A.; Celle, C.; Simonato, J.-P.; Bellet, D. Metallic nanowire-based transparent electrodes for next generation flexible devices: a Review. Small 2016, 12, 6052−6075.
(3) Zhang, D.; Wang, B.; Ren, W.; Men, W.; Weng, D.; Cui, X.; Sun, J.; Li, H.; Lu, Y. Synthesis of ultralong copper nanowires for high-performance transparent transparent electrodes. J. Am. Chem. Soc. 2012, 134, 14283−14286.
(4) Qiu, C.; Zhang, Z.; Xiao, M.; Yang, Y.; Zhong, D.; Peng, L.-M. Scaling carbon nanotube complementary transistors to S-nm gate lengths. Science 2017, 355, 271−276.
(5) Sekiguchi, A.; Tanaka, F.; Saito, T.; Kuwahara, Y.; Sakurai, S.; Futaba, D. N.; Yamada, T.; Hata, K. Robust and soft elastomeric electronics tolerant to our daily lives. Nano Lett. 2015, 15, 5716−5723.
(6) Battoli, E. N.; Wan, Q.; Guo, W.; Chen, Y.; Pan, X.; Lu, W. Fully transparent thin-film transistor devices based on SnO2 nanowires. Nano Lett. 2007, 7, 2463−2469.
(7) Cao, L.; White, J. S.; Park, J.-S.; Schuller, J. A.; Clemens, B. M.; Brongersma, M. L. Engineering light absorption in semiconductor nanowire devices. Nat. Mater. 2009, 8, 643−647.
(8) Shen, G.; Chen, P.-C.; Ryu, K.; Zhou, C. Devices and chemical sensing applications of metal oxide nanowires. J. Mater. Chem. 2009, 19, 828−839.
(9) Hochbaum, A. I.; Chen, R.; Delgado, R. D.; Liang, W.; Gametti, E. C.; Najarian, M.; Majumdar, A.; Yang, P. Enhanced thermoelectric performance of rough silicon nanowires. Nature 2008, 451, 163−167.
(10) Suemori, K.; Hoshino, S.; Kamata, T. Flexible and lightweight thermoelectric generators composed of carbon nanotube−polystyrene composites printed on film substrate. Appl. Phys. Lett. 2013, 103, No. 153902.
(11) Tsakalakos, L.; Balch, J.; Fronheiser, J.; Korevaar, B. A.; Sulima, O.; Rand, J. Silicon nanowire solar cells. Appl. Phys. Lett. 2007, 91, No. 233117.
(12) Hochbaum, A. I.; Yang, P. Semiconductor nanowires for energy conversion. Chem. Rev. 2010, 110, 527−546.
(13) Mohiuddin, M.; Hoa, S. V. Estimation of contact resistance and its effect on electrical conductivity of CNT/PEEK composites. Compos. Sci. Technol. 2013, 79, 42−48.
(14) Li, J.; Zhang, S.-L. Finite-size scaling in stick percolation. Phys. Rev. E 2009, 80, No. 040104.
(15) Langley, D.; Giusti, G.; Mayousse, C.; Celle, C.; Bellet, D.; Simonato, J.-P. Flexible transparent conductive materials based on silver nanowire networks: a review. Nanotechnology 2013, 24, No. 452001.
(16) Tokuno, T.; Nogi, M.; Karakawa, M.; Jiu, J.; Nge, T. T.; Aso, Y.; Suganuma, K. Fabrication of silver nanowire transparent electrodes at room temperature. Nano Res. 2011, 4, 1215−1222.
(17) Mutisio, R. M.; Sherrott, M. C.; Rathmell, A. R.; Wiley, B. J.; Winey, K. I. Integrating simulations and experiments to predict sheet resistance and optical transmittance in nanowire films for transparent conductors. ACS Nano 2013, 7, 7654−7663.
(18) White, S. I.; Mutisio, R. M.; Vora, P. M.; Jahnke, D.; Hsu, S.; Kikkawa, J. M.; Li, J.; Fischer, J. E.; Winey, K. I. Electrical percolation behavior in silver nanowire−polystyrene composites: simulation and experiment. Adv. Funct. Mater. 2010, 20, 2709−2716.
(19) Foygel, M.; Morris, R. D.; Anez, D.; French, S.; Sobolev, V. L. Theoretical and computational studies of carbon nanotube composites and suspensions: Electrical and thermal conductivity. Phys. Rev. B 2005, 71, No. 104201.
(20) Perovic, D. D.; Castell, M. R.; Howie, A.; Lavoie, C.; Tiedje, T.; Cole, J. S. W. Field-emission SEM imaging of compositional and doping layer semiconductor superlattices. Ultramicroscopy 1995, 58, 104−113.
(21) Venables, D.; Jain, H.; Collins, D. C. Secondary imaging as a two-dimensional dopant profiling technique: Review and update. J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct. 1998, 16, 362−366.
(22) Kazemian, P.; Twitchett, A. C.; Humphreys, C. J.; Rodenburg, C. Site-specific dopant profiling in a scanning electron microscope using focused ion beam prepared specimens. Appl. Phys. Lett. 2006, 88, No. 212110.
(23) Song, J.; Chen, M.; Olesen, M. B.; Wang, C.; Havelund, R.; Li, Q.; Xie, E.; Yang, R.; Beggild, P.; Wang, C.; Besenbacher, F.; Dong, D. Direct electrospinning of Ag/polyvinylpyrrolidone nanocables. Nanoscale 2011, 3, 4966−4971.
(24) Verma, A.; Connaughton, S.; Stamenov, P. Multiple contacts investigation of single silicon nanowires with the active voltage contrast scanning electron microscopy technique. Meas. Sci. Technol. 2019, 30, No. 017002.
(25) Loos, J.; Aleexeev, A.; Grossiard, N.; Koning, C. E.; Regev, O. Visualization of single-wall carbon nanotube (SWNT) networks in conductive polystyrene nanocomposites by charge contrast imaging. Ultramicroscopy 2005, 104, 160−167.
(26) Zhao, M.; Ming, B.; Kim, J.-W.; Gibbons, L. J.; Gu, X.; Nguyen, T.; Park, C.; Lillehei, P. T.; Villarrubia, J. S.; Vladar, A. E.; Liddle, J. A. New insights into subsurface imaging of carbon nanotubes in polymer composites via scanning electron microscopy. Nanotechnology 2015, 26, No. 085703.
(27) Langley, D. P.; Lagrange, M.; Giusti, G.; Jiménez, C.; Bréchet, Y.; Nguyen, N. D.; Bellet, D. Metallic nanowire networks: effects of thermal annealing on electrical resistance. Nanoscale 2014, 6, 13535−13543.
(28) Sannicolo, T.; Muñoz-Rojas, D.; Nguyen, D. D.; Moreau, S.; Celle, C.; Simonato, J.-P.; Brechot, Y.; Bellet, D. Direct imaging of the onset of electrical conduction in silver nanowire networks by infrared thermography: evidence of geometrical quantized percolation. Nano. Lett. 2016, 16, 7046−7053.
(29) Maize, K.; Das, S. R.; Sadeque, S.; Mohammed, A. M. S.; Shakouri, A.; Janes, D. B.; Alam, M. A. Super-Joule heating in graphene and silver nanowire network. Appl. Phys. Lett. 2015, 106, No. 143104.
(30) Estrada, D.; Pop, E. Imaging dissipation and hot spots in carbon nanotube network transistors. Appl. Phys. Lett. 2011, 98, No. 073102.