"Nano Necklace" formed by Electroless Deposition of Metal on Polymer Nanofiber for Flexible Transparent Conducting Films

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Transparent Conducting Electrode

Transparent conducting electrode (TCE) is widely used for the display of electric devices such as liquid crystal displays for mobile phones, cameras, PCs, televisions, or solar cells. The TCE is indispensable as the thin film for optical electronics. Recently, not only "transparency & conductivity" but also flexibility or anti-corrosion characteristics are strongly required[1]. In addition, TCE without using scarce commodity such as **In** is also important concerning limited natural resources. From these point of view, we carried out the electroless deposition on the surface of polymer nanofiber. We reported "nanoweb"[2], very fine polymer nanofiber structure with the diameter of 20-100nm, was fabricated by electrospinning of polyamide-6 (Nylon6). In this study, the surface of the fine nanofiber was coated by **Au** sputtering deposition and electroless deposition of **Ni** and the both characteristics were compared.

Experimental Method

Polyamide-6 nanofiber was fabricated by electrospinning method according to the previous paper[1]. Applied voltage during the fabrication was varied from 15 to 30kV. Tip-to-collector distance (TCD) was varied from 5 to 15cm. Aluminum plates (1.5 mm thickness, 200 mm × 300 mm) was used. Fabrication machine was sealed by acrylic desiccator. The temperature and humidity of the desiccator inside was kept at 28±2℃, 30±2%^{RH}, respectively. The distribution of the diameter and the length of the fabricated fiber was analyzed from SEM images by using the image processing software, Image J. The average diameter and the distribution were obtained from 100 data points. The structural diagram of polyamide-6 was shown in Figure 1.

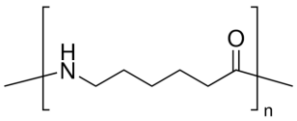

Figure 1 Structural diagram of polyamide-6

Metal Coating on the Nanofiber Surface

Metal coating on the nanofiber surface was carried out by the two methods, one is Au sputtering deposition using a magnetron sputtering (E-1030, Hitachi) and the other is the electroless deposition of Ni. For the substrate of sputtering, the bridge-electrospinning process was carried out.

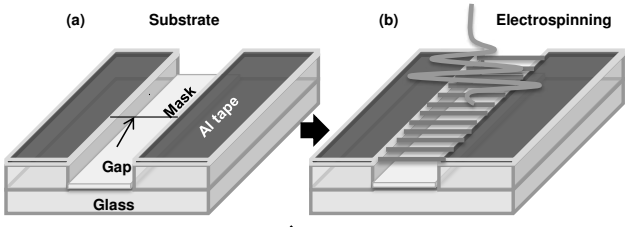

Figure 1 Concept schematics of bridge-electrospinning process, (a) substrate design of bridging collector, (b) bridge-electrospinning, collecting nanofiber as uniaxial array between the gap.

As shown in Figure 2, on the glass substrate of 25mm x 25mm, two sheets of glass substrates were adhered with the various distance of 1.0 mm to 4.0mm. The two glass sheets were covered by Aluminum tape. As for the mask, Aluminum coated polyethylene terephthalate (PET) film was attached on the bottom of the gap. By using this technique, nanofibers were formed over the gap like bridges. We call this method as bridge spinning, hereafter. The density of the nanofibers adhered over the gap was controlled by changing the spinning time. The current during the sputtering was 10mA and the time was 50 to 250s.

For the electroless deposition, the Polyamide-6 nanofibers were fabricated on the PET substrate. The substrate was first put into the $SnCl_2$ solution for the sensitization, then immerse in the HCl solution with $PdCl_2$ for activation. Then the NiP was deposited from an alkaline solution. Ni sulfate as source of ion, sodium citrate as complexing agent, ammonium chloride as buffering agent, and sodium hypophosphite as reducing agent were used for Ni electroless deposition. Deposition time was 4 to 40s. The bath temperature was changed from 40ºC to 65ºC.

Transparency of the film was evaluated by UV-Vis spectroscopy (UVmini-1240, Shimadzu) with the wavelength from 300nm to 1000nm. For the conductivity measurement of Au sputtered film or Ni coated nanofiber sheet, a resistivity meter with 4-pin probe (MCP-T610,Mitsubishi Chemical Analytech) was used. And for the conductivity measurement of nanofibers formed by bridge spinning, multi tester (MCD010, Multi measuring instruments) was used. The measurement was carried out for

5 points with 5 mm interval. The transformation to sheet resistance was carried out by deducting contact resistance from the measured value according to the literature[3].

Results & Discussions

Au sputtered nanofiber

Polyamide-6 nanofibers were successfully formed by the bridge electrospinning. As you see in the SEM images in Figure 3, the nanoweb structure with the diameter of 20nm web type fiber and the diameter of 100 nm straight nanofiber was uniformly formed over the gap of the substrates.

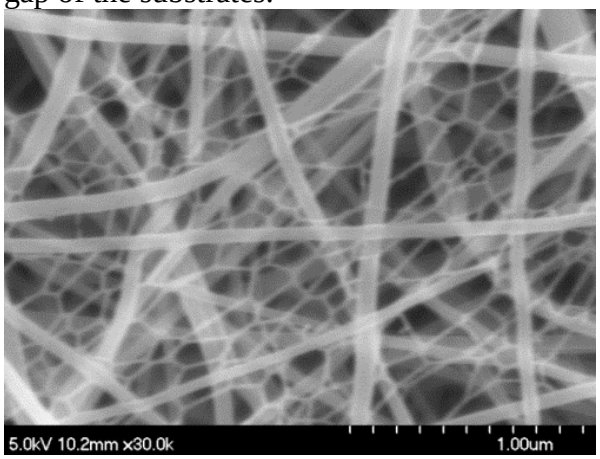

Figure 3. As formed Polyamide-6 nanofibers over the gap

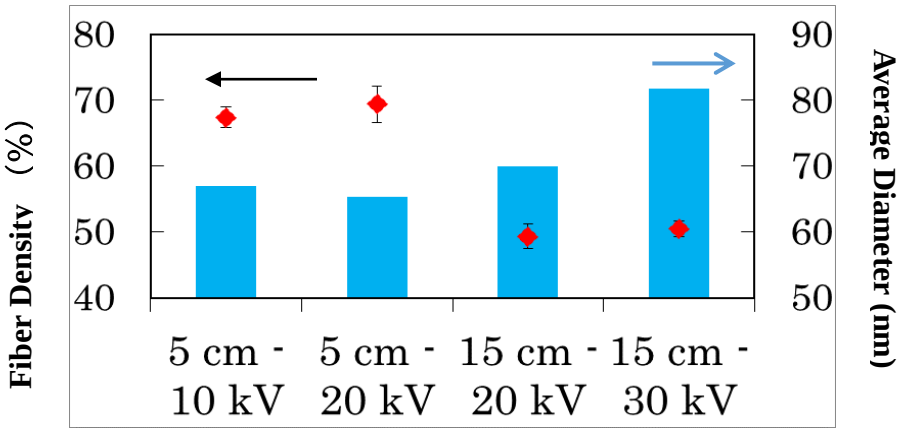

Figure. 2 Fiber density and average diameter of polyamide-6 nanofiber with various Tip-to-Collector Distance and voltage.

For polyamide-6 nanofibers, fiber density and average diameter was controlled by TCD and applied voltage. The results were shown in Figure 4. And also, the fiber density can be controlled by the electro spinning (ES) time. As we can predict, at least up to 600s, the longer the ES time, the higher the fiber density.

Then Au was sputtered on the nanofiber. The sputtering time was changed from 50s to 250s. After the sputtering, the transparency of the film was measured by UV-Vis spectroscopy. The relationship between sputtering time and sheet resistance was shown in

Figure 5. In this figure, we can see the tendency that the sheet resistance was decreased as the increase of sputtering time, however, for the sample fabricated for 250s, the resistivity was higher than that fabricated for 200s. Similar characteristics were observed for the relationship between transmittance and sputtering time. The results are shown in Figure 6. These results indicate that the formed nanofiber of metal coated nanofiber density was not uniform.

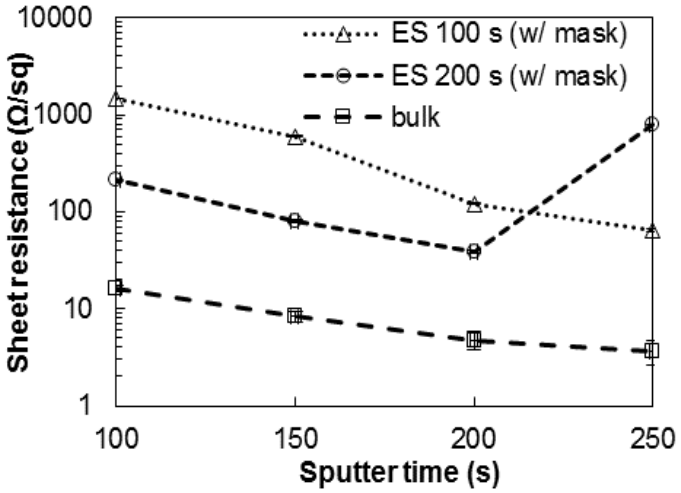

Figure 5. Sheet resistance of sputtered PA6 nanofibers with varying sputter time (with mask)

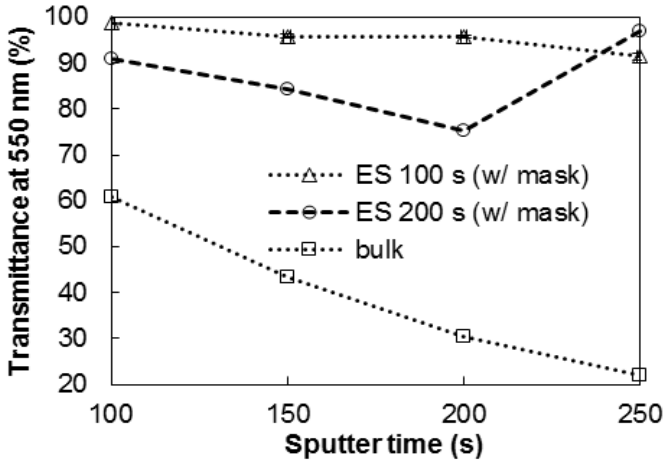

Figure 6. Transmittance at 550 nm wavelength for sputtered nanofibers (with mask).

In order to clarify the reason of the resistivity increase for the nanofiber sheet fabricated for 250s, SEM observations were carried out. The results were shown in Figure 7.
As shown in these SEM images, numerous damages were observed for the nanofiber sheets with sputtering time 250s, however, there was no damage for the sheets with sputtering time 200s.

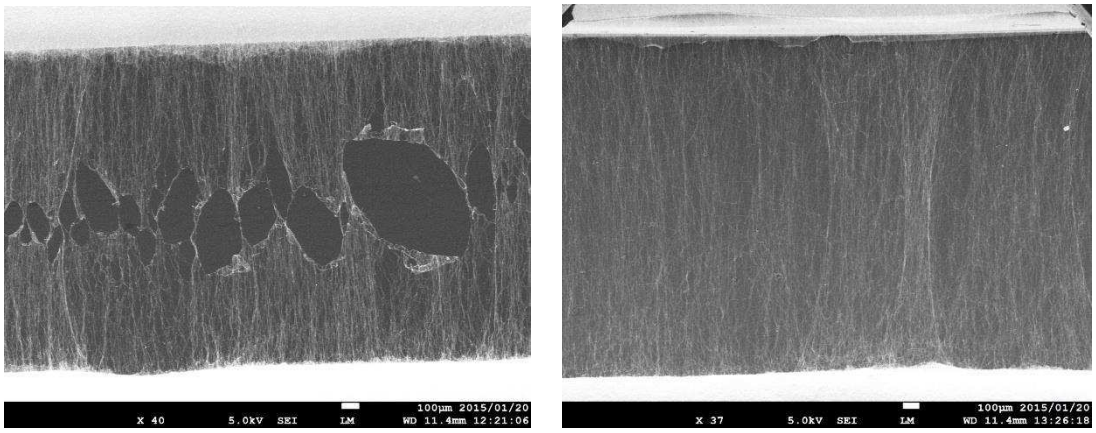

Figure 7. Sputtered PA6 nanofibers with sputtering time (left) 250 s: cracked, (right) 200 s: uniform.

Though the obtaied results as TCE was relatively good value[4]: the transparency was over 91.5% and the sheet resistance was 65 **Ω/sq**, these results demonstrate that Au sputtering is not always suitable for the coating on very fine polymer nanofiber because of the higher damage to the fine fibers caused by the high energy sputtering. Therefore, we started to coat on the fiber by wet, electroless plating method.

Ni electroless deposited nanofiber

NiP deposition test was carried out by changing the solution temperature. In case of 40s deposition time, there was no deposition up to 50 ^{o}C, however, the deposition starts on small spots on the surface from 60 ^{o}C. When the solution temperature was increased up to 65 ^{o}C, large area of deposition was observed by an optical microscope. The result of higher magnification SEM observations was shown in Figure 8.

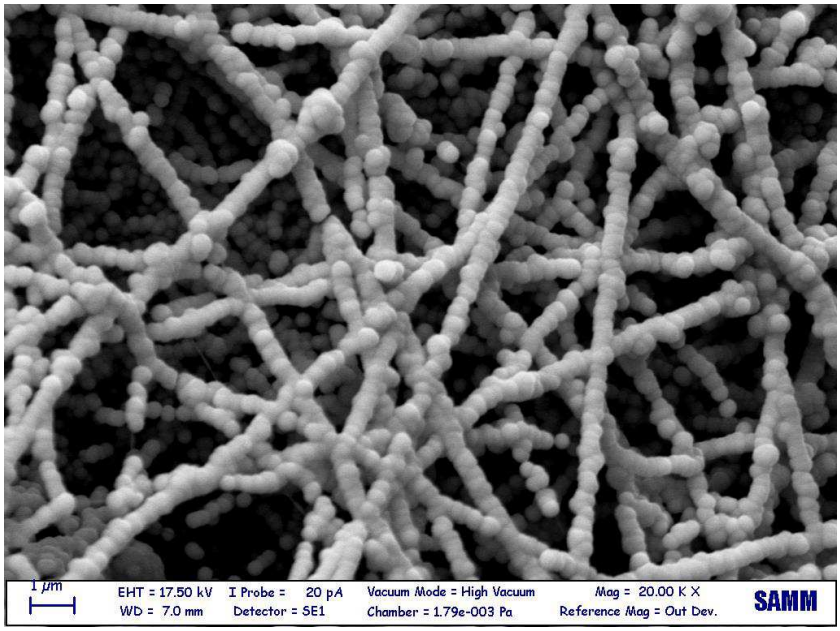

Figure 8. "Nano Necklace" formed by Electroless Deposition of NiP on the surface of Nylon 6 nanofiber

By the SEM observation, it was found that numerous spherical shape of NiP beeds with the diameter of 300nm were tightly connected and arranged on the surface of nylon 6 nanofiber with the diameter of 50nm. It seems that same size of numerous metal beeds were formed just like “Nano Necklace” surrounding the nylon 6 nanofiber.

The sheet resistance was distributed from 2 to 16/Ωsq and all the samples showed good conductivity.

Conclusions

We have developed an electroless deposition for the Nickel metallization of nanofibers obtained via electrospinning. The method is able to give high conductivity and high transparency for the fabrication transparent conductive electrode even in this early stages of development. Compared with the coating by sputtering, fine fiber structure was maintained in the case of the electroless deposition. We considered that the prospective application for such electrodes is a flexible, transparent, wet process electrode will be organic solar cells[5]. The “Nano Necklace” with small, sub-micron diameter can be much more adapt for an ITO replacement.

Acknowledgements

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References

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