Analysis of transparent conductive AgNw film by dip coating flows

Kwangguk Ahn, Onyu Kim, Dongjae kim, Jaewook Nam*

[1] School of chemical engineering, Sungkyunkwan University, 2066 Seobu-ro, Jangan-gu, Suwon, Gyeonggi-do 440-746, Korea

Presented at the 17th International Coating Science and Technology Symposium
September 7-10, 2014
San Diego, CA, USA

Introduction

Transmittance and conductivity are most important properties of transparent electrode (Barnes et al., 2012). When the silver nanowires are used to produce such electrode, the wire number density, i.e. the number of silver nanowire per unit area, is one of the key factors that determine such opto-electrical properties (De, Sukanta et al., 2010 , Mutiso et al., 2013).

The transmittance is strongly proportional to the wire number density: the more wires the less transparent. Although it is well known that, over the percolation threshold, which is strongly related to the number density, the number of the wires does not contribute to the conductivity, significantly. However, practically important regime for the transparent electrode, i.e. near 90% transparent and 100 ohm/m^2, the number of the wires is still sensitive enough to change the conductivity (Mutiso et al. 2013).

Meanwhile, commercial success of the transparent electrode depends not only on their opto-electrical properties but also the possibility of the roll-to-roll processing of the conductive film. There are numerous candidates for the processing, but liquid coating method is the most promising one: it can create a thin liquid layer of the conductive inks on top of the fast moving substrate and dry out extra solvent(s) to solidify the layer.

For the success of the transparent electrode production by coating process, one needs to understand how to control the wire number density under a given type of coating flow. This microscopic feature of the coated layer can provide another important operating limit indicator, like the upstream meniscus location in the slot coating process (Nam and Carvalho 2010), that can be used to construct an operating window for a given coating method.

In this study, we use a simple coating method, so called dip coating (Scriven 1988), to produce the silver nanowire transparent conductive electrode on the glass substrate. Numerical computation and image analysis of the coated film surface are developed to quantify the how the process parameter, such as the substrate speed, affects the wire number density.

Computational prediction of thickness from dip coating flow

When we assume that the nanowire concentration is constant for a given coating liquid, the wire number density of the coated film is proportional to the thickness of the coated layer.

Therefore, the precise prediction of the wet thickness from the dip coating flow is extremely important.

The dip coating flow is governed by the two equations: Navier-Stokes equation and the continuity equation,

$$\rho \mathbf{v} \cdot \nabla \mathbf{v} = -p\mathbf{I} + \mu \nabla^2 \mathbf{v} + \rho \mathbf{g}$$
$$\nabla \cdot \mathbf{v} = 0,$$

where, ρ, p, μ, $\mathbf{v}$, $\mathbf{g}$ are density of solvent, pressure, viscosity, velocity of flow and gravitational acceleration, respectively. These equations were discretized by finite element method, and solved iteratively using Newton's method (Kistler and Scriven 1984, Romero and Cavalho, 2008). The proposed computational model includes wetting of container wall and confinement effect that arose from the small container size used in the actual dip coating experiment.

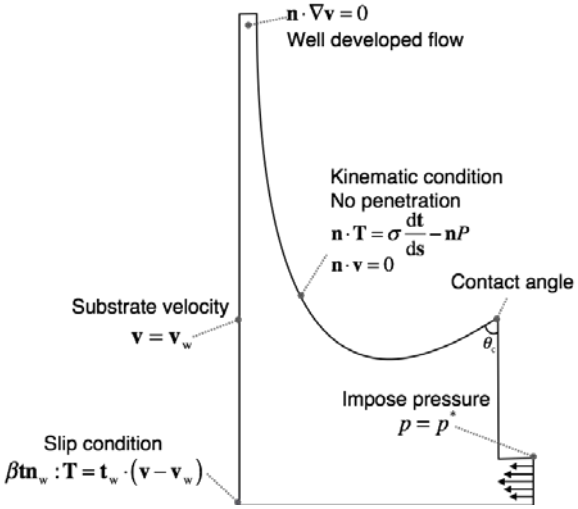

Figure 1 Boundary conditions of the model.

Dip coating experiments

Commercially available silver nanowire solution (Blue Nano, Inc.) is used in the dip coating experiment. When the coating solution is fixed, the thickness is determined solely by the substrate withdrawing speed. Because the container size for the dip coating is small, the distance between the substrate and the container wall less than 2 cm. According to the computational model, in this size, the wall is close enough distorting the gas-liquid interface more than "infinite" pool case. Therefore the most of the simplified thickness prediction model assumed, e.g. Landau-Levich model (Scriven, 1988), does not precisely predict the wet film thickness. Therefore we use the computational model to determine the range of the operating conditions.

For the solvent, iso-propyl alchol (IPA) is used and it wets the surface of the container wall significantly. For the accurate measurement of the contact angle, which is another important parameter for the model, we measure the rising height of IPA liquid inside the dip coating container, which is transparent. Then the solution of Young-Laplace equation including gravity is used to determine the contact angle.

Following Mutiso et al. (2013), we use the area fraction (AF) that is defined as the number density of the nanowires in the film multiplied by the projected area of a nanowire, instead of using the wire number density directly. For the first approximation, we assumed that the nanowire concentration in the coated layer constant over the thickness. When the concentration is fixed, the wire number density is just a linear function of the thickness, or a power-law function of capillary number of the dip coating flow. Once the number density is calculated, the projected area is estimated by product of the density and the average size of the nanowire used in this study (35 nanometer thickness and 20 micron length). Figure 2 (a) shows this estimated area fraction (AF_{EST}) *vs*. the dip-coated wet thickness of the film from the computation.

To check the validity of our assumption, we measure the transmittance using UV spectrometer. Considering the edge effect that is inevitable in the liquid coating method due to capillarity and wetting, we use the spot away from edges of the substrate for measuring the transmittance of the film. As shown in Fig. 2 (b), the area fraction is almost inversely proportional to the measured transmittance.

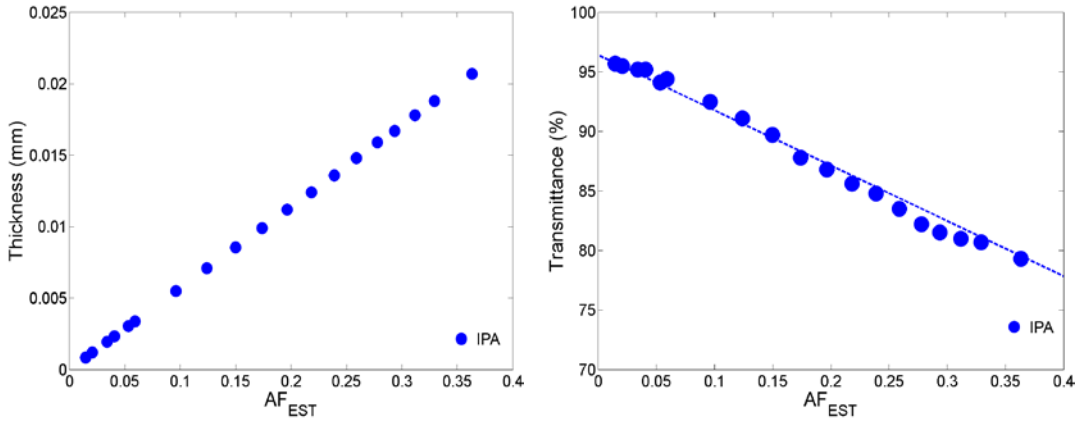

Figure 2 Estimated area fraction versus thickness and transmittance

However, the estimated area fraction may lead to over estimated value. Probably, the constant concentration across the thickness may not be valid for such a small wet thickness (order of ten micron). Note that average length of the wire is about 20 micron. When a gas-liquid surface of the nanowire solution drop is examined with a high-resolution optical microscopy, one can easily found that very few wires can be detected near the surface. Note that the wire is optically visible because of its length. Evidently the wire is hard to penetrate through the gas-liquid interface because of surface tension. Also the wire cannot poke through the rigid substrate as well. Therefore there will be regions near the rigid substrate and the gas-liquid interface, where the center of mass of nanowire is hardly placed or located. We will call these regions as depletion layers, as shown in Fig. 3.

Furthermore, unlike the diameter of wire, which can be precisely controlled during synthesis (Bergin et al. 2012), the length has wide distribution: blindly use of the average wire length may cause additional inaccuracy. Furthermore, some choice of solvent, such as water or ethylene glycol, has a strong surface tension, which may lead to bundles of wires instead of

evenly dispersed wires. Therefore, it is inevitable to check coated film surface in detail by image analysis of microscopic images to check the structure of nanowire networks.

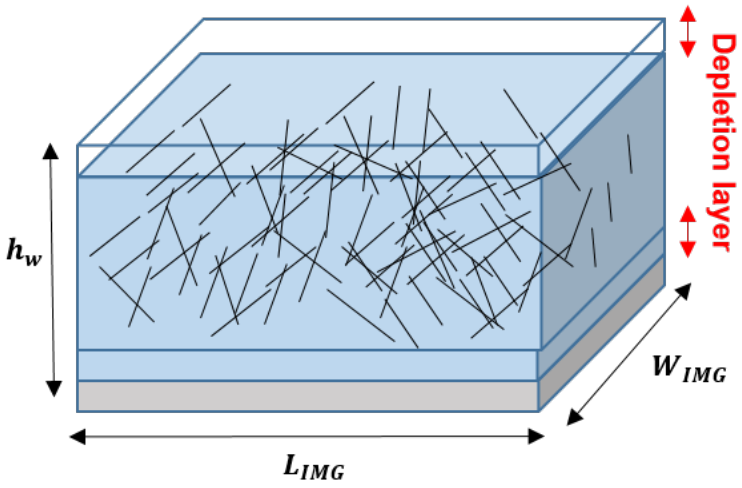

Figure 3 Structure of nanowire films

Image analysis of silver nanowire networks

To precisely counting the number of nanowires, their length and their network connectivity. We performed image analysis method for optical or electrical microscope images. Here, we assumed that nanowire as a cylinder with virtually constant diameter. Note that the metal wire has a polygonal cross-section shape due to its growth mechanism (Ye et al. 2014). Using the analysis, we are attempting to provide a correction factor, which compensates overestimated area fraction, and possibly determine the size of depletion layer.

Pixels of the nanowire network image are classified into 0 (background) and 1 (materials) based on image segmentation method (manuscript in preparation). Here we are exploiting that the nanowire is not damaged inside the coating flow, they are rigid enough to maintain almost straight shape. Then selecting few selected section in the frequency domain of the image data can select the nanowires oriented in a certain direction. However, resulting image of this process may include chopped nanowire sections potentially overlapped with other nanowires. To prevent this, junction and end points of segmented image are extracted and compared with the selected nanowire image segmentation to determine whether they are a single wire or not.

Figure 4 summarized the procedure of selecting nanowire segments oriented in a certain direction using the frequency domain analysis. Figure 4 (a) presents an SEM (JSM-7401F, JEOL, Ltd.) image of a silver nanowire network and (b) shows frequency components of (a) by Fourier transform. Figure 4 (c) shows a window for selecting a certain direction in the frequency domain, and (d) shows the corresponding nanowire segmentations in the image.

At counting step, we filter out trivial or non-wires by using chain code (Freeman and Herbert, 1961). Figure 5 presents results of above procedure.

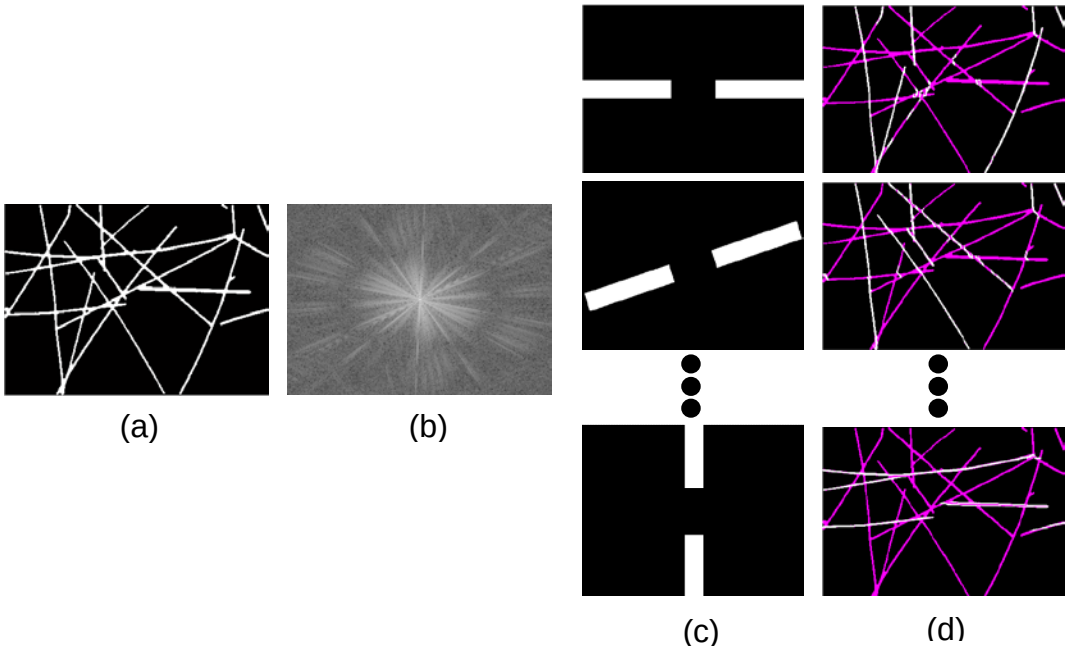

Figure 4 Image analysis procedure for detecting wires

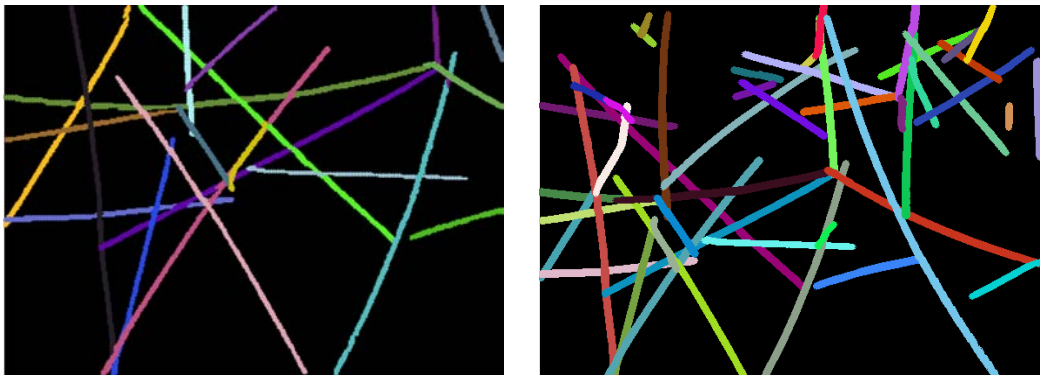

Figure 5 Several results on detecting individual nanowires from SEM image.

Final remarks

In this study, we analyzed the silver nanowire transparent electrode fabricated by the dip coating flow, especially focused on determining the number of nanowires on the substrate. The thickness of the dip-coated film is predicted by solving Navier-Stokes equation considering the wetting and the confinement effect due to the small dip coating container size. The first approximation for the number density estimation, i.e. constant nanowire concentration across the coating layer, produces a reasonable relationship between area fraction and measured transmittance. However, this over-simplified estimation may lead to incorrect area fraction. To correct this, we are developing the nanowire network image analysis method. This method is not only useful in counting number of wires and their length,

but also useful in investigating the network connectivity. This percolation network analysis can be used to analyze yield another important opto-electrical property, i.e. conductivity of the film. Furthermore, combining with experimentally measured conductivity, one can even estimate representative contact resistance of the nanowire networks, which can be affected by choice of processing methods and solvents. We are currently working on this issue.

Reference

Barnes, T. M., Reese, M. O., Bergeson, J. M., Larsen, B.A, Blackburn, J. L, Beard, M. C., Bult, J., and van de Lagemaat, J., 2012, Comparing the fundamental physics and device performance of transparent, conductive nanostructured networks with conventional transparent conducting oxides, *Advanced Energy Materials* **3**, 353-360

De S., King, P. J., Lyon, P. E., Khan, U., Coleman, J. N., 2010, Size effects and the problem with percolation in nanostructured transparent conductors, *Acs Nano* **12**, 7064-7072.

Mutiso R. M., Sherror, M. C., Rathmell, A. R., Wiley, B. J. and Winey, K. I., 2013, Integrating simulations and experiments to predict sheet resistance and optical transmittance in nanowire films for transparent conductors, *ACS nano* **9**, 7654-7663.

Nam. J., Carvalho, M.S., 2010, Flow in tensioned-web-over-slot die coating: Effect of die lip design, *Chemical Engineering Science*, **65**, 3957-3971

Scriven, 1988, Phyics and applications of dip coating and spin coating, Material research society symposium proceeding, **121**, 717-729

Bergin, S. M., Chen Y.-H., Rathmell, A.R., Charbonneau, P., Li, Z.-Y., Wiley, B. J., 2012, The effect of nanowire length and diameter on the properties of transparent, conducting nanowire films, *Nanoscale* **6** ,1996-2004.

Kistler, S. F. and Scriven, L. E., 1984 Coating flow theory by finite element and asymptotic analysis of the Navier-Stokes system, *International Journal of Numerical Methods in Fluids*, **4**, 207–229.

Romero, J. O. and Cavalho, M. S., 2008, Response of slot coating flows to periodic disturbances, *Chemical Engineering Science* **63**, 2161–2173

Ye, S., Chen, Z., Ha Y.-C., and Wiley, B. J., 2014 Real-Time Visualization of Diffusion-Controlled Nanowire Growth in Solution, *Nano Letters*, (article in press).

Freeman, H., 1961, On the encoding of arbitrary geometric configurations, *Electronic Computers, IRE Transactions on* **2**, 260-268.