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ABSTRACT
In this study, we report a simple alignment method to align silver nanowires (Ag NWs) using a dip-coating technique while controlling the temperature of glass substrate and Ag NW dispersion. It is found that the structural anisotropy and transmittance characteristics of the substrate lined with the Ag NWs depend on the temperature of the dispersion and substrate and the withdrawal velocity. The maximum structural anisotropy of the aligned Ag NWs was 0.947 at a withdrawal velocity of 1.0 mm/s and a temperature of 80 °C. In addition, a glass substrate with the aligned Ag NWs shows a high transmittance of 96.7% at the sheet resistance of 22 Ω/sq.

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The development of transparent electrodes had led to a wide range of applications, such as transparent displays, touch panels, and organic photovoltaics (OPVs), among others. For transparent electrodes, low resistance is an important factor in transparent electrodes, though transmittance is also a very important factor. At present, indium tin oxide (ITO) is widely used in industrial areas, but it has critical drawbacks, including its high cost and the fact that it is a rare earth metal.1 As an alternative to ITO, silver nanowire (Ag NW), given their high transmittance and low sheet resistance, is a good candidate. In general, Ag NW transparent electrodes are prepared by roll-to-roll,2 spray coating,3 and dip-coating processes. However, randomly networked Ag NWs are easily formed by these processes, leading to a relatively low transmittance compared to that of the aligned Ag NWs.

To align Ag NWs, various approaches have been attempted, such as capillary printing using a fabricated nano-channel,1 the Langmuir–Blodgett technique using a water bath,1 a stirring-assisted assembly method,1 and substrate stretching, among others. However, these methods are complex and difficult to apply to large-scale display devices. To overcome these issues, we suggest a heat-assisted dip-coating method that allows for large-scale coating and accurate alignment of the Ag NWs. Heating of the substrate and an Ag NW dispersed solution (hereafter, dispersion) is helpful to increase the alignment of the Ag NWs, thus improving the transmittance.

A schematic diagram of the heat-assisted dip-coating procedure for the alignment of the Ag NWs while controlling the temperature of the substrate and the dispersion is shown in Fig. 1(a). An electro-thermal plate is attached onto the backside of a 500-μm-thick glass substrate to elevate temperature. The Ag NW dispersion is heated using a hotplate. The temperature of the substrate and the dispersion is set to be identical, and it varies in the range of 20–80 °C. An auto dip coater (Dao Technology, Korea) controls the withdrawal velocity of the substrate, of which the velocity range is 0.1–30 mm/s. First, 0.1 wt. % of Ag NWs (Ditto Technology, Korea) is dispersed in isopropyl alcohol (99.9% IPA, OCI Company Ltd.). As shown in Fig. 1(a), the withdrawal velocity, meaning the moving direction and speed of the glass substrate, affects the capillarity to draw Ag NWs toward the top side of the substrate. Moreover, the evaporation rate of the dispersion can be controlled by the temperature of the glass substrate and Ag NW dispersion. Five samples were fabricated for each experimental condition, and the average values obtained from the samples were described and plotted in this paper.
FIG. 1. (a) Schematic of the dip-coating procedure for the alignment of the Ag NWs by using a heat-assisted dip-coating system. The dispersion and the substrate are heated to the same temperature simultaneously. (b) Pinning of an Ag NW. (c) Vertical aligning of the Ag NW. (d) Contour plot of the simulated minimal film thickness ($h_0$) of the solvent with different temperatures and withdrawal velocities.

The alignment mechanism of the Ag NWs during the heat-assisted dip-coating process is illustrated in Figs. 1(b) and 1(c). When the Ag NW dispersion is drawn up to the substrate by capillary force, the top part of an Ag NW came out first of the dispersion front. The dispersion solution existing around the top part is relatively quickly dried so that the top part is partially immobilized. However, the other part, dipped into the dispersion, is still movable. As the dispersion dries, a type of meniscus that occurs at the left and right sides of the Ag NWs exerts force onto the Ag NWs, causing them to be vertically aligned. We call this phenomena pinning and waggling. The theoretical calculation of the thickness of the dispersion film raised by capillary action was performed using Eq. (1) from Faustini et al., who also used a dip-coating method. This equation considers that the minimal thickness of dispersion film ($h_0$) is determined by the withdrawal velocity ($u$), the solution evaporation rate ($E$), the substrate width ($L$), and the global constant ($D$), which is the IPA value. Figure 1(d) shows the contour plot of the minimal thickness, during the variation of the dispersion film ($h_0$), caused by the withdrawal velocity (0.01–10 mm/s) and the dispersion temperature (20–80°C). Figure 1(d) indicates that the minimal film thickness decreases as the temperature increases and the withdrawal velocity decreases,

$$h_0 = \frac{E}{Lu} + Du^{2/3}.$$  
(1)

Figures 2(a)–2(f) present the SEM images of the Ag NWs coated onto glass substrates with the following withdrawal velocities at a temperature of 80°C: (a) 0.1 mm/s, (b) 0.5 mm/s, (c) 1.0 mm/s, (d) 5.0 mm/s, (e) 10.0 mm/s, and (f) 20.0 mm/s. The alignment of the Ag NWs can be determined by the structural anisotropy ($S$) defined as the average tilting angle of the Ag NWs from the withdrawal direction as follows:

$$S = \frac{\sum_{i=1}^{N} \cos \theta_i}{N}.$$  
(2)

Here, $\theta_i$ denotes the tilting angle of the Ag NWs from the withdrawal direction, as shown in the inset of Fig. 2(g), and $N$ is the number of Ag NWs. The structural anisotropy ($S$) of the aligned Ag NWs according to the withdrawal velocity (0.1–30 mm/s) and temperature (20–80°C) is shown in Fig. 2(g). There is a tendency for the structural anisotropy to increase as the temperature increases and the withdrawal velocity decreases at the withdrawal velocity higher than 1 mm/s. Temperature and withdrawal velocity for high structural anisotropy are identical to those for a low $h_0$. In this study, however, the highest $S$ did not occur at the lowest withdrawal velocity (0.1 mm/s). The highest structural anisotropy was 0.947 at the withdrawal velocity of 1.0 mm/s at 80°C. If the minimal thickness of the dispersion film is too thin, sufficient waggling time of the Ag NWs is not possible. On the other hand, if the minimal thickness of the dispersion film is too thick, firm pinning of the Ag NWs is challenging. Therefore, a moderate $h_0$ is required to improve the alignment of the Ag NWs.

As shown in Fig. 2(g), the temperature and the withdrawal velocity are both important for the structural anisotropy of the Ag NWs. The higher the temperature, the better the structural anisotropy becomes. It is considered that the high temperature induces rapid evaporation of the dispersion solution compared to that at a low temperature. This rapid evaporation reduces $h_0$ on the dispersion front, benefiting the concrete pinning of the Ag NWs. There is a tendency for the structural anisotropy to increase as the withdrawal velocity decreases, as noted above. However,
FIG. 2. SEM images of the Ag NWs attached onto glass substrates with different withdrawal velocities at 80 °C: (a) 0.1 mm/s, (b) 1.0 mm/s, (c) 5.0 mm/s, (d) 10.0 mm/s, (e) 20.0 mm/s, and (f) 30.0 mm/s. All scale bars are identical at 10 μm. (g) Structural anisotropy for each temperature according to the withdrawal velocity. Degree distribution of the Ag NWs against the withdrawal direction with temperature (h) and the withdrawal velocity (i).

The structural anisotropy does not increase at withdrawal velocities lower than 1.0 mm/s. The highest structural anisotropy for each temperature condition was found at the withdrawal velocity of 1.0 mm/s. For the temperatures of 40 °C, 60 °C, and 80 °C, the structural anisotropy could be divided into two regions: a slow decrease and a rapid decrease. The critical withdrawal velocity dividing the two regions increases as the temperature increases [see the vertical arrow marks that divide the slow decrease and fast decrease in Fig. 2(g)]. In general, the minimal thickness of the dispersion film increases as the withdrawal velocity increases. The higher temperature helps us to decrease the minimal thickness of the dispersion, causing the critical withdrawal velocity to increase as the temperature increases.

The degree (θ) distribution of the aligned Ag NWs from the withdrawal direction can be explained by the full-width at half maximum (FWHM) using a Gaussian function. The quantity of the Ag NWs inclined toward the withdrawal direction has an inverse relationship to the FWHM, indicating deviation of the alignment. Figure 2(h) shows the degree distribution of the Ag NWs with an increase in the temperature, leading to a decrease in the FWHM value. Figure 2(i), showing the FWHM, indicates that increasing the withdrawal velocity of the substrate leads to a large degree deviation...
of the Ag NWs toward the alignment direction. The FWHM shows the best alignment condition at a velocity of 1.0 mm/s and has the lowest degree deviation of the Ag NWs. However, the Ag NWs are relatively randomly arranged at a high withdrawal velocity because the minimal thickness of the dispersion is too thick for pinning of the Ag NWs.

The transmittance and sheet resistance can be controlled by the coating cycle. Figure 3 shows the SEM images of the Ag NWs aligned on glass substrates with different coating cycles, in this case five times (a) and twenty times (b), at 80 °C with a withdrawal velocity of 1.0 mm/s. The sheet resistance measured from the samples for which twenty coating cycles were used was 22 Ω/sq on
average. Figure 3(c) shows the transmittance difference according to the coating time under the fixed condition of a withdrawal velocity of 1.0 mm/s and a temperature of 80 °C. The average measured transmittance of the samples with twenty coating cycles in the visible wavelength (400–750 nm) was 96.7%. The average transmittance based on the data sheet information of conventional ITO (20 Ω/sq) is 85.3%. Figure 3(d) shows the transmittance difference according to the withdrawal velocity in fixed condition with five coating cycles at 80 °C. The measured transmittances of the samples with withdrawal velocities of 1.0 mm/s and 20.0 mm/s were 98.0% and 96.1%, respectively. As the transmittance is mainly affected by the density of Ag NWs, the graphs in Figs. 3(c) and 3(d) indicate that more coating time and high withdrawal velocities are disadvantageous to transmittance. As the withdrawal velocity increases, the minimal thickness of the dispersion increases, resulting in an increase in coated Ag NWs.

Figure 3(e) shows the calculated transmittance spectra of the Ag thin film with different film thicknesses at an incident light wavelength of 550 nm along with their figure of merit (FoM, $\sigma_{\text{dC}}/\sigma_{\text{opt}}$) values, defined as shown below, where the values of sheet resistance ($R_s$) and transmittance ($T$) at a wavelength of 550 nm are used,

$$T = \left(1 + \frac{Z_0}{2R_s}\sigma_{\text{opt}}\right)^{-2}.$$

Here, the constant value of $Z_0$ is the characteristic impedance of free space. Equation (3) implies that the transmittance ($T$) mainly affects the FoM as compared to the sheet resistance. Figure 3(e) clearly shows that a sharp decrease in the transmittance directly leads to a rapid decrease in the FoM. Silver itself has a low specific resistance, implying that it does not show a sharp increase in its resistance as its film thickness decreases, whereas transmittance shows a sharp decline owing to its high refractive index.

Figure 3(f) compares the FoM value of our sample (22 Ω/sq, 96.7%) to the outcomes of other studies, in this case studies involving a-ITO film on PET (50 Ω/sq, 91%), spray-deposited Ag NWs (50 Ω/sq, 90%), dip-coated Ag NWs (15 Ω/sq, 85%), capillary printing with nanochannels (19.5 Ω/sq, 96.7%), the Langmuir–Blodgett technique (11.4 Ω/sq, 89.9%), a hybrid film of graphene–Ag NWs (33 Ω/sq, 94%), long Ag NWs (23 Ω/sq, 95%), spray-coated Ag NWs (20 Ω/sq, 92.1%) and a transfer method of Ag NW films (10 Ω/sq, 85%). Our heat-assisted dip-coating method shows a higher FoM value by 3.5 times relative to the conventional dip-coating method (Ref. 4) and a slightly lower than that with a capillary printing method using nanochannels (Ref. 5), which resulted in the highest FoM among the aforementioned methods. For the heat-assisted dip-coating system, a simple heating device is added to the conventional dip-coating system. The suggested coating method provides several advantages, such as a low-cost equipment setup, a simple coating procedure, and the capability of large-area coating. This coating method is thus suitable for industrial applications.

We suggested a heat-assisted dip-coating method, adding only a heating device to the conventional dip-coating system, to enhance the alignment of the Ag NWs. The alignment of the Ag NWs increases as the temperature increases and the withdrawal velocity decreases. The critical withdrawal velocity increases as the temperature increases. Applied heat activates the evaporation of the dispersion, benefiting the alignment of the Ag NWs. In this study, we found that the highest alignment of the Ag NWs occurred at a withdrawal velocity of 1.0 mm/s and a temperature of 80 °C. Under this condition, a glass substrate with the aligned Ag NWs showed the transmittance of 96.7% at a sheet resistance of 22 Ω/sq. The simple and precise alignment method of the Ag NWs with low resistance and high transmittance has considerable potential in future large-scale and mass-production systems for transparent display and panel applications.

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