Printable Transparent Microelectrodes toward Mechanically and Visually Imperceptible Electronics

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Flexible and transparent electrodes are highly useful in wearable optoelectronic systems for healthcare and biosensing applications for conducting multimodal assessments with electrophysiological and optical measures. In such systems, the electrodes should exhibit a low sheet resistance, high visible transmittance, and small feature size, for reliable electrical sensing, optical observation of attached objects, and integration of devices for mapping local biology events, respectively. Herein, fine-printed, flexible, and transparent microelectrodes that allow biosensing and device integration are reported. The microelectrodes containing cross-aligned silver nanowire (AgNW) networks are patterned via a selective wetting deposition technique on a 1 μm-thick polymer substrate. A low sheet resistance of 25 Ω sq⁻¹ and a visible transmittance of 96%–99% are achieved with a small pattern width of 25 μm. The biosensing application is demonstrated by detecting the leaf electric potential; the leaf cells under the microelectrodes are observed because of visible transparency. Furthermore, device integration is demonstrated by electronic circuits with ultrathin and transparent organic transistors. The transistors exhibit white-light illumination stability and mechanical stability to bending stress. These demonstrations provide a basis for developing ultraimperceptible wearable sensor systems with ultrathinness and high visible transmittance.

1. Introduction

Flexible and transparent electronics could be extremely important for the development of wearable optoelectronic devices and systems for healthcare and biosensing.[11–13] A remarkable function of such electronics is that they can allow for multimodal assessments with electrophysiological and optical measures to monitor physiological or biological events in detail.[4–6] However, there are challenges in applying this function to versatile sensing purposes. For example, the high mechanical flexibility is desirable to conform various shapes of biology, and the high optoelectric performance (i.e., high visible transparency and low sheet resistance) is required for reliable electrical sensing and the optical observation of attached objects. In addition, the low-cost fabrication of the electronics in a solution process is desirable for the mass production and easy prototyping of sensors. Solution-processable 1D nanomaterials satisfy the above requirements, and thus, they have attracted attention in recent years.[7] The networks of metal nanowires (NWs),[8] carbon nanotubes,[9] and metal-oxide NWs[10] play an important role as transparent electrodes and semiconductors in flexible and transparent applications such as light-emitting diodes (LEDs),[11] thin-film transistors (TFTs),[12,13] and wearable sensors.[14,15] Among them, silver nanowire (AgNW)-network-based transparent electrodes are considered as promising fundamental components to create flexible and transparent electronics because of a high visible transmittance of ≈99%,[16] a low sheet resistance of ≈10 Ω sq⁻¹,[17] and a mechanical durability of down to ≈100% strain.[18] AgNW networks are easily constructed utilizing the gold-standard solution processes of spin coating, drop casting, and spray coating.[7,8] Such low-cost production in the solution process is essential for fabricating flexible and transparent electronics. However, solution processes frequently lead to random
networks of NWs, which cause the inhomogeneity of electrical properties over the area of networks.\textsuperscript{19} In addition, the random networks are difficult to retain the electrical paths at the micropatterns with few-tens μm resolution, owing to the lower probability of 1D nanomaterials’ connections (i.e., a high percolation threshold).\textsuperscript{20} Thus, the high-resolution patterning of functional networks with homogeneous electrical properties is still challenging. However, this is required for future applications such as flexible sensor systems combined with microelectrodes and the active components of LEDs and TFTs\textsuperscript{21} to probe electrophysiological signals from a single cell/neuron and groups of cells/neurons (20–100 μm).\textsuperscript{2,24}

The alignment of AgNWs is a promising approach for creating high-performance, flexible, and transparent electrodes with homogeneous electrical properties even in micropatterns because the percolation threshold can be reduced by controlling the alignment degree and angle of NWs.\textsuperscript{20,25,26} In recent years, researchers have developed several alignment-control techniques such as the Langmuir–Blodgett method\textsuperscript{27} brush coating,\textsuperscript{28} solution shearing,\textsuperscript{29} capillary printing,\textsuperscript{30} and meniscus dragging.\textsuperscript{31} These approaches can provide highly aligned networks despite simple solution processes. Among these, one of the most attractive approaches for achieving homogeneous electrical properties is cross alignment, which involves conducting alignment multiple times\textsuperscript{26,31,33} and ionic electrostatic charge repulsion.\textsuperscript{17} It is noteworthy that, in substrates with a large area (>20 × 20 cm\textsuperscript{2}), cross-aligned AgNW conductive networks exhibit high homogeneity at a sheet resistance of 21 Ω sq\textsuperscript{−1} and a visible transmittance of 95%.\textsuperscript{13} In addition, a previous study\textsuperscript{20} showed that the cross-aligned AgNW networks can make more effective percolation pathways on a microscale pattern, compared with the random AgNW networks. This was done by implementing the theoretical calculations and the experiments.\textsuperscript{20} However, it is difficult to create microscale patterns in cross-aligned networks without using etching technologies\textsuperscript{20} as the advantages (low material consumption, large-area fabrication, etc.) of the solution process would be lost.

In this work, we developed a high-resolution printing technique for cross-aligned AgNW networks utilizing a selective wetting deposition technique to create an ultraimperceptible sensor sheet with ultrathinness and high visible transmittance (Figure 1). The feature sizes (widths) of the AgNW patterns (or spacing between them) were down to 20 μm. In addition, the AgNW pattern exhibited a sheet resistance of ≈25 Ω sq\textsuperscript{−1} and a high visible transmittance of 96–99% at a narrow pattern width of 25 μm (average 68 Ω sq\textsuperscript{−1} in 11 samples). The sheet resistance of the AgNW patterns was comparable with that of large-area cross-aligned AgNW conductive networks (10–70 Ω sq\textsuperscript{−1}).\textsuperscript{17,20,31,33} In this printing, rod coating was applied to a hydrophilic–/hydrophobic-patterned surface prepared on an ultratin (1 μm) polymer substrate,\textsuperscript{34} as shown in Figure 1b. In a previous study, we reported a fine-printing method for AgNW electrodes based on the hydrophilic-/hydrophobic-patterned surface with a fast rod coating speed of ≈3.6 mm s\textsuperscript{−1}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{a) Conceptual diagram of an ultraimperceptible sensor sheet system with fine-printed and cross-aligned AgNW electrodes. b) Schematic of the printing technique of rod coating onto hydrophobic (blue)- and hydrophilic (red)-patterned surfaces. Below: SEM image of AgNWs with a thickness of 39 nm and a length of 13 μm and dark-field optical micrographs of 20 μm-width line patterns of AgNWs in 20 μm-width spacings. c) Biosensor application of cross-aligned AgNW electrodes. d) Electronic circuit application of ultrathin and transparent OFETs with cross-aligned AgNW electrodes.}
\end{figure}
method results in the accumulation of AgNWs on the pattern periphery, leading to a lower sheet resistance because of the coffee-stain effect.\(^{[14]}\) However, due to the faster rod coating, the narrow spacings (50–100 \(\mu m\) width) between the AgNW electrode patterns were filled because of the meniscus pinning on the patterned hydrophilic areas. In the present study, we have used a slower rod coating speed of 0.4 mm s\(^{-1}\) to ensure that the meniscus follows the rod, without pinning (Movie S1, Supporting Information). This resulted in high-resolution patterns with spacings down to 20 \(\mu m\). Furthermore, instead of the coffee-stain effect, the cross alignment of AgNW networks\(^{[17,20,31–33]}\) was introduced as an approach for lower sheet resistance, which can be achieved by implementing rod coating in different directions. The sheet resistance of cross-aligned networks was consequently ten times lower than that of parallel-aligned networks. The feature size (or spacing) of the patterns was independent of the coating direction. Furthermore, due to the scalability of rod coating, we could extend the patterning of transparent electrodes with a width of a few tens of micrometers to polymer substrates with an area of 6 \(\times\) 6 \(cm^2\). We demonstrated the feasibility of the printing technique using two applications toward ultraimperceptible electronics (Figure 1c,d). First, we implemented the AgNW electrodes in biosensing applications to detect the electrophysiological signal from plants (Egeria densa in this work). Second, we developed flexible and transparent electronic circuits with ultrathin transparent organic field-effect transistors (OFETs) fabricated with the AgNW electrodes printed as the source, drain, and gate electrodes. Remarkably, the mobility of the OFETs fabricated using cross-aligned AgNWs was ten times higher than that of the OFETs fabricated using parallel-aligned AgNWs due to the low sheet resistance of AgNWs and low contact resistance between AgNWs and organic semiconductors. These applications suggest that the printing technique can provide a basis for manufacturing ultraimperceptible sensor sheet systems with low material consumption (Figure 1a).

2. Results

2.1. Patterning Technique of AgNWs

We patterned AgNWs by sweeping AgNW dispersion over the hydrophilic-/hydrophobic-patterned surface of a 1 \(\mu m\)-thick parylene layer using a glass rod (Figure 1b and Figure S1, Supporting Information). In this process, first, a hydrophobic surface was prepared on a 1 \(\mu m\)-thick parylene layer via the spin coating of a fluorocarbon agent. To pattern the hydrophilic areas, the hydrophobic surface was covered with a photomask and exposed to vacuum ultraviolet (VUV) light from an excimer lamp.\(^{[34,35]}\) The hydrophilicity was because of the removal of the coated fluorocarbon by VUV light exposure, which was confirmed via X-ray spectroscopy (XPS) (Figure S2, Supporting Information). Then, the AgNW dispersion was swept on the surface, resulting in selective wetting just on the hydrophilic areas (Movie S1, Supporting Information). This process enabled us to fabricate AgNW patterns of various geometries with feature sizes down to 20 \(\mu m\), as shown in Figure 1b, Figure S3a–f, and Figure S4a, b, Supporting Information.

The cross-aligned networks were created by rod coating in a direction perpendicular to the long axis. The feature sizes of the patterned AgNWs were independent of the sweeping direction of the glass rod (Figure 2a-d and Figure S4a,b, Supporting Information). Such cross alignment can help reduce the percolation threshold and provide high-performance transparent AgNW electrodes.\(^{[17,20,31–33]}\) Figure 2c,d shows the color-coded images of AgNWs with a width of 50 \(\mu m\), indicating the local orientation of the NWs relative to the long axis. The AgNWs patterned by parallel sweeping are aligned around 0° (long axis, light blue), whereas the AgNWs patterned by perpendicular sweeping are aligned around 0° (long axis, light blue) and ±90° (red). We extracted the angular distributions from the color-coded images for further analysis, as shown in Figure 2e. In the angular distribution for perpendicular sweeping, two peaks are

![Figure 2. Cross alignment of AgNWs. a,b) Schematic of printing in (a) parallel (∥) sweeping and (b) perpendicular (⊥) sweeping directions. c,d) Color-coded optical micrographs of AgNWs prepared with (c) ∥ sweeping and (d) ⊥ sweeping. The color scale based on angles is shown on the right (scale bar: 20 \(\mu m\)). e) Angular distribution of the images shown in (c) and (d) relative to long axis (0°).](image-url)
clearly observed around 0° and ±90°. This indicates that AgNWs are cross aligned. In contrast, in the case of parallel sweeping, there is only one peak around 0°. This indicates that AgNWs are aligned to only the long axis. The mechanism of cross alignment by perpendicular sweeping could be shear force, similar to previous reports on cross-aligned AgNWs.[20,32,33] However, in this work, AgNWs are simultaneously patterned and cross aligned owing to selective wetting on the hydrophilic patterns via rod coating. This provides unprecedented advantages of low material consumption and process simplicity over previous reports (Table S1, Supporting Information).

2.2. Accuracy of AgNW Patterning

We focused on the contact angles of the AgNW dispersion on the hydrophilic and hydrophobic surfaces to pattern AgNWs with a high accuracy and high resolution. A key condition for high accuracy is a large difference between the contact angles on the hydrophilic and hydrophobic surfaces. Therefore, we aimed to prepare AgNW dispersion with a large difference between the contact angles.[36,37] We prepared AgNW dispersion with different isopropanol (IPA) addition ratios for this purpose. Then, we measured the contact angles and observed the patterned AgNWs using an optical microscope. Figure S5a, Supporting Information, shows the contact angles on the hydrophilic and hydrophobic surfaces as a function of the IPA addition ratio. The difference between the contact angles increases with the IPA addition ratio. This implies that a high IPA addition ratio may lead to high accuracy. We evaluated patterning accuracy using several optical micrographs, which are shown in Figure S5b-i, Supporting Information. A low IPA addition ratio (0, 33 wt%) caused AgNW aggregation in certain parts, whereas a high IPA addition ratio (50, 67 wt%) enhanced the uniformity of AgNWs. These results suggest that a high IPA addition ratio increased the difference between the contact angles and improved the uniformity of AgNW patterning. This trend is in agreement with a previous report.[36] For the further investigation of patterning accuracy, we calculated the root-mean-square (RMS) error in the channel length between source and drain patterns (design spacing of 50 µm) using the following equation

\[
\text{RMS error} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (L_d - L_m)^2}
\]

where \(n\) is the number of measured samples, \(L_d\) is the designed length (50 µm), and \(L_m\) is the measured length of the samples. The RMS error (≈2 µm) decreased as the IPA addition ratio increased from 0 to 50 wt%, as shown in Figure 3a. However, the RMS error doubled (≈4 µm) at an IPA addition ratio of 67 wt%, even though there was a large difference between the contact angles. This may imply that patterning accuracy is determined not only by the difference between the contact angles but also by other factors such as the volatility of dispersion and the sweeping rate of the glass rod. These factors should be investigated in future. We used an IPA addition ratio of 50 wt% to minimize the RMS error. Thus, a close agreement was obtained between actual patterns and designs (in photomask) in the patterning of AgNW electrodes with widths and spacings down to 20 µm each, as shown in Figure 3.
Figure 3b,c. An almost linear relationship was obtained between pattern widths and design widths with $R^2 \approx 0.99$ with near-unity slopes (1.01 for line, 0.94 for spacings) and near-zero intercepts (2.12 for line, 0.96 for spacings). In addition to the above-described feature sizes (20–250 μm), the AgNW patterns with <20 μm and >250 μm width may also be available (Figure S3g and Figure S6b, Supporting Information). Such high-accuracy and high-resolution patterning is sufficient for applying the electrodes to flexible transistors and microsensors.[23,24–26]

2.3. Characteristics of AgNW Electrodes

We tested the resistance of the AgNW electrodes with different widths prepared using different sweeping directions to evaluate their electrical performance. Figure 4a shows the sheet resistance of the AgNW electrodes as a function of pattern width. Sheet resistance decreased by 3–12 times in perpendicular sweeping (25–1340 Ω sq$^{-1}$) compared with parallel sweeping (633–3885 Ω sq$^{-1}$). It is noteworthy that in perpendicular sweeping, the sheet resistance of the patterns with a width of less than 100 μm was 25–170 Ω sq$^{-1}$ This range is suitable for transparent electronics applications.[38] This improvement in sheet resistance may be due to the lower percolation threshold in cross alignment.[20,25–26] The improvement is less likely to be due to the area covered by AgNWs on a single pattern, as explained later.

Figure 4b shows the visible transmittance (at a wavelength of 550 nm) of the AgNW electrodes with different widths prepared using different sweeping directions. We used microspectroscopy to evaluate the optical characteristics of the area of a single electrode pattern. A high visible transmittance of 96%–99% was obtained for all pattern widths in both sweeping directions. This suggests that the area covered by AgNWs on a single pattern is similar for both sweeping directions.[39] Thus, the improvement in sheet resistance should be ascribed to the lower percolation threshold in cross alignment, as shown by previous reports.[17,20,25,26]

As shown earlier, the developed printing method provides a low sheet resistance of 25–170 Ω sq$^{-1}$ and a high visible transmittance 96–99% in fine-patterned AgNW electrodes with a pattern width of <100 μm. Such high performance in terms of electrical and optical characteristics is similar to the performance of cross-aligned AgNWs reported in previous studies (Table S1, Supporting Information). In addition, in this work, fine patterns are printed with widths down to 20 μm. This provides a higher resolution compared with previous patterning technologies with and without the etching process (Table S1, Supporting Information). These simultaneous achievements by printing should be more suitable for the fabrication of flexible and transparent electronics owing to an advantage of low material consumption without using harsh chemicals and reactive ions.

2.4. Application to Biosensing of Plants

To demonstrate the biosensing applications of the electrodes, we monitored the electrophysiological signal of plants in a dark environment and white-light illumination using the cross-aligned AgNW electrodes. The electrophysiological signal of plants could be correlated with the water status, wounded parts, and photosynthetic activity, which would help producers with the healthcare of plants.[40–43] We used Egeria densa as the target plant because its leaves easily come in contact with a surrounding medium owing to the thin structure (1.9 μm thickness).[44] As the sensors, the cross-aligned AgNW electrodes are patterned with a width of 60 μm. The pattern width is close to the cell width of Egeria densa, showing the potential for sensing local biology events. In addition, organic mixed ionic/electronic conductors of poly(ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) were coated onto the cross-aligned AgNWs using the same patterning method to decrease the contact impedance between the AgNWs and plants (Experimental Section, Text S1 and Figure S6a–c, Supporting Information). PEDOT:PSS is known as a suitable biointerface owing to the lower impedance at the interface with tissue and it allows highly sensitive sensing even when it is patterned with a width of few ten micrometers.[24]

To define the sensing area on the electrodes, an SU-8 encapsulation layer was patterned, as shown in the inset of Figure 5a. Figure 5a,b shows the schematic of the electrical measurement setup and the optical micrographs of the AgNW-based microelectrodes on a leaf. The leaf cells are clearly observed even under the electrodes. This indicates suitable features for the simultaneous assessments of biology with electrophysiological and optical measures. Figure 5c shows the traces of the electric potential

Figure 4. Optoelectric characterization of printed AgNW electrodes. a) Sheet resistance as a function of the pattern width of AgNW electrodes prepared with || sweeping and ⊥ sweeping. b) Transmittance at a wavelength of 550 nm as a function of pattern width.
(EP) of the leaf surface in a dark environment and under white-light illumination, until the potential changes reach a steady state. The EP is in the range of a few hundred millivolts, which is more reasonable compared with the results of a previous report.\textsuperscript{42} The EP trace shows the transient state (before 600 s) and the steady state (after 600 s). The steady-state EPs in the dark environment are lower than those under white light in multiple measurements, as shown in Figure 5c and Figure S6, Supporting Information. In contrast, in the transient state, the EPs in the dark environment are higher than those under white light. This is because the EP is higher immediately following the previous steady state under white light. Steady-state data can provide important information for understanding the state of the plant because changes in the EP according to the plant state appear after a long time (>10 min) after the environment changes.\textsuperscript{40,41,43,44} A previous study\textsuperscript{41} also detected the EP difference and assessed the health of a plant in terms of its water stress conditions and nycthemeral rhythm. However, a complete understanding of the reason behind changes in the EPs of plants has not been realized because it requires the consideration of several factors such as the kinetics of ion transport and photosynthetic activity.\textsuperscript{40,43,44} We believe that the developed flexible and transparent microelectrodes will further this understanding because the microelectrodes can enable multimodal assessments owing to their visible transparency (Figure 5b). Furthermore, owing to their ultrathinness, the microelectrodes can be attached without damaging the plants, which can allow plants to be assessed in their natural state.

2.5. Application to Transparent and Ultrathin OFETs

To demonstrate the feasibility of the proposed patterning process, we fabricated transparent and ultrathin OFETs using the AgNW electrodes as source, drain, and gate electrodes. The detailed description of the fabrication process is provided in the Experimental Section and Figure S7, Supporting Information. The schematic and optical micrograph of OFETs are shown in Figure 6a,b, respectively. The patterns of source, drain, and gate electrodes were consistent with the designs on the photomask (width of 50 μm for the source and drain electrodes and 700 μm for the gate electrode). The channel length between the AgNW electrodes was clearly defined down to 25 μm (Figure S8, Supporting Information). The gate electrodes were patterned on 150 nm-thick parylene dielectrics without losing the functionality of organic semiconductors because the fluorocarbon coating and VUV light exposure modify only the surface of parylene.\textsuperscript{19} The transparent organic semiconductors were prepared by depositing a 30 nm-thick layer of 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT) via vacuum thermal evaporation. C8-BTBT was used because it provided stable operation under visible light illumination owing to its high optical bandgap (3.5 eV).\textsuperscript{45} Parylene layers were used as the substrate, gate dielectrics, and encapsulation layer because of their high transparency and thickness controllability. The thicknesses of the substrate, gate dielectrics, and encapsulation layer were 1, 150–500, and 1 μm, respectively. Thus, the total thickness of the OFETs was 2–3 μm, which can provide high conformability\textsuperscript{22} to the uneven surfaces of a leaf (Figure 7a). Furthermore, the OFETs exhibited a high transmittance of ≈90% in the visible region from 400 to 800 nm (Figure S7h, Supporting Information). This can allow for the optical observation of attached objects.

We investigated the electrical characteristics of two kinds of OFETs. The source and drain electrodes were composed of the cross-aligned AgNW networks in the first type and parallel-aligned AgNW networks in the second type. The transfer and output characteristics of the OFETs are shown in Figure S9, Supporting Information. A low gate-leakage current of ≈100 pA and low hysteresis were obtained in both types of OFETs. This indicates that the AgNW electrodes can be patterned without electrical shorting or damage on gate dielectrics with a thickness of a few hundred nanometers. The field-effect mobility and

![Figure 5](Image 110x492 to 240x591)

**Figure 5.** Biosensing applications of cross-aligned AgNW-based microelectrodes. a) Schematic of the measurement set-down to detect the electrophysiological signal from a leaf of Egeria densa. Inset image shows the representative AgNW-based microelectrode with a width of 60 μm. Dashed lines indicate the boundary of the patterned SU-8 encapsulation. b) Optical micrograph of a leaf covered by the AgNW-based microelectrodes. Dashed lines indicate the boundary of the patterned SU-8 encapsulation. c) Traces of EPs recorded with the AgNW-based microelectrodes in the dark and under white-LED light.
on–off ratio were obtained from the transfer characteristics, as shown in Figure 6c,d, and compared for both types of OFETs. The OFETs with the cross-aligned AgNWs exhibited an average mobility $0.44 \pm 0.07$ cm$^2$ V$^{-1}$ s$^{-1}$ and a high on–off ratio of $\approx 10^5$. These values are comparable with the previously reported values for transparent OFETs (Table S2, Supporting Information). The mobility and on–off ratio of the OFETs with the parallel-aligned AgNWs were approximately one-tenth ($0.05 \pm 0.03$ cm$^2$ V$^{-1}$ s$^{-1}$ and $\approx 10^4$, respectively) of those of the OFETs with the cross-aligned AgNWs.

We implemented four-probe measurements using specific OFET structures with and without cross alignment to further investigate the electrical properties of the printed AgNWs. The fabricated OFETs were composed of AgNWs printed with a thickness of 10 μm, a width of 50 μm, and a channel length of 500 μm. The mobility and on–off ratio of the OFETs were obtained from the transfer characteristics, as shown in Figure 6c,d, and compared for both types of OFETs. The OFETs with the cross-aligned AgNWs exhibited an average mobility $0.44 \pm 0.07$ cm$^2$ V$^{-1}$ s$^{-1}$ and a high on–off ratio of $\approx 10^5$. These values are comparable with the previously reported values for transparent OFETs (Table S2, Supporting Information). The mobility and on–off ratio of the OFETs with the parallel-aligned AgNWs were approximately one-tenth ($0.05 \pm 0.03$ cm$^2$ V$^{-1}$ s$^{-1}$ and $\approx 10^4$, respectively) of those of the OFETs with the cross-aligned AgNWs.
investigate transistor characteristics (Figure S10, Supporting Information). The detailed measurement method is described in Experimental Section. Figure S10d,e, Supporting Information, shows the channel and contact resistances in the OFETs with the parallel-aligned AgNWs and cross-aligned AgNWs, respectively, as a function of gate voltage. The channel resistances of both types of OFETs normalized by channel width were similar at \( \approx 2 \times 10^5 \ \Omega \text{cm} \) in the on state \((V_{GS} = -20 \text{ V})\). This indicated that the performance of C8-BTBT was independent of the geometries of the AgNW networks. In contrast, the total contact resistance, that is, the sum of the contact resistances normalized by the channel width of the source and drain, of the OFETs with the cross-aligned AgNWs \( (0.7 \ \text{M} \Omega \text{cm}) \) was ten times lower than that of the OFETs with the parallel-aligned AgNWs \( (8.5 \ \text{M} \Omega \text{cm}) \). These contact resistances were considerably higher than the resistance \(<20 \ \text{k} \Omega \) of the AgNW electrodes. Thus, the high performance of the OFETs with the cross-aligned AgNWs was caused by the relatively low contact resistance.

For the stability test, we first examined transistor performances under white-LED-light illumination with a high irradiance of 2.3 mW cm\(^{-2}\). Figure 6e shows the transfer characteristics under white-LED-light illumination. The OFETs with C8-BTBT maintained the current modulation with a negligible change in the on–off ratio \( (\approx 10^3) \). OFETs were fabricated using with dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT), which has an optical bandgap of 3.2 eV,\(^{[47]}\) for the purpose of comparison. The on–off ratio of the OFETs with DNTT decreased from 10\(^6\) (dark environment) to <10\(^3\) (under illumination), as shown in Figure S11, Supporting Information. These results indicate that transparent OFETs should be fabricated using materials with a broad bandgap, such as C8-BTBT, to achieve photostable characteristics and high visible transmittance.

Furthermore, the OFETs also should endure mechanical stress for sensing applications. Here, the devices are intended for less-moving organisms such as plant surface, because such organisms would allow for the optical observation simultaneously. When the devices are attached on such organisms, mechanical stress occurs on the devices once. Thus, the OFETs should endure a one-time mechanical stress. For this purpose, the mechanical stability of the OFETs was tested by a single-bending test. Figure 6f and Figure S12, Supporting Information, show the electrical characteristics of the OFETs and the variation in the capacitance of the AgNW–parylene–AgNW structure, respectively, before and after the OFETs were bent with a radius of 0.8 mm. The leakage current remained around \( \approx 100 \text{ pA} \), and the on–off modulation was maintained with negligible changes in the on–off ratio for multiple devices (Figure 6f and Figure S13, Supporting Information). This indicated the high mechanical stability of the ultrathin OFETs. Furthermore, the capacitance remained the same without leakage before and after the OFETs were bent.

2.6. Circuit Applications

We developed inverter circuits composed of transparent and ultrathin OFETs through the fine printing of AgNWs onto a parylene substrate with a large area of \( 6 \times 6 \text{ cm}^2 \) to demonstrate large-area implementation (Figure 7a). An inverter circuit is a fundamental component in logic and analog circuits, and it is applicable to a sensor matrix system.\(^{[48]}\) The inverter circuit configuration comprised a diode-load inverter consisting of two p-type OFETs (inset in Figure 7b), as designed in a previous work.\(^{[49]}\) Figure 7b,c shows the transfer characteristics of the inverter circuits with and without the cross-aligned AgNWs, respectively. The OFETs without cross-aligned AgNWs were operated by applying a driving voltage \((V_{DD})\) of 40 V, resulting in a gain of 1.7 at an input voltage \((V_{IN})\) of 20 V (Figure 7c).

In contrast, a \( V_{DD} \) of 15 V provided a higher gain of 4.1 at \( V_{IN} \approx 12 \text{ V} \) (Figure 7b). The relatively low voltage operation and high gain may be due to the current modulation with the low contact resistance and sheet resistance of cross-aligned AgNWs, as mentioned earlier. Remarkably, the performance of the developed inverters is also comparable with that of an organic circuit for biosignal amplification (driving voltage of 30 V, voltage gain of 3–5),\(^{[23]}\) and thus, they can also be useful for the development of biosensor systems.

3. Discussion and Conclusion

First, we discuss the mechanism of the high printing accuracy achieved in this work. One of the biggest challenges in printed electronics is to improve the resolution and accuracy of patterning. This is particularly difficult in NW-based printed electrodes owing to the length of NWs. To overcome this challenge, we developed a high-resolution printing technique for AgNWs where a feature size (or a spacing) down to 20 \( \mu \text{m} \) could be achieved. The high accuracy of printing, i.e., RMS errors of 2–3 \( \mu \text{m} \), was obtained utilizing an optimized ink formulation for the hydrophilic/hydrophobic-patterned surface. The high resolution and accuracy were achieved by aligning NWs along the edges of patterns and preventing the protrusion of NWs from the edges. Wang et al. have reported that AgNWs are subject to bending and aligning along the liquid–air interface of droplets.\(^{[50]}\) Thus, in our printing technique, where the liquid–air interfaces were defined as hydrophilic/hydrophobic interfaces, AgNWs could be bent and aligned along the boundary lines on the edges of hydrophilic areas. However, few AgNWs remained on the hydrophobic areas (Figure 3c); however, they are unconnected to the AgNW patterns. For future applications such as very-large-scale integration,\(^{[51]}\) the residual AgNWs will have to be removed.

We emphasize that the feature sizes of patterned AgNWs were independent of the sweeping direction. This is useful for the fabrication of various geometries of transparent electrodes via single coating. Furthermore, the technique we developed can be useful in recent AgNW coating technologies; AgNW-based transparent conductive films have been fabricated on >10 in. substrates by roll-to-roll slot-die production.\(^{[52,53]}\) These recent technologies can be utilized to apply the proposed printing technique to an area larger than \( 6 \times 6 \text{ cm}^2 \), which is used as the maximum area in this work. Also, other coating rods with engineered structures, such as the Meyer rod, could help further improve AgNW alignment.\(^{[54,55]}\)

In addition, our printing technique can be used to conduct precise alignment based on photomasks for the fabrication of multilayer devices, particularly OFETs. In recent years, the ink
jet, screen, gravure, and flexographic printing techniques have been explored for creating multilayer optoelectronic devices (Table S1, Supporting Information). However, to the best of our knowledge, transparent ultrathin devices integrated with printed electrodes with widths of a few tens of micrometers have not yet been reported. Thus, we believe that our demonstration of ultrathin and transparent OFET circuits will promote the development of optoelectronic sensor systems with a high performance. However, the proposed printing technique requires some improvements for this. For examples, as shown in Figure 4a, the sheet resistance varies with the pattern width of the AgNW electrodes and the errors in the values of the sheet resistance are still large, compared with conventional technologies that use materials such as indium tin oxide and a large-area AgNW conductive layer.[8] This may be undesirable when designing electric circuits. In the future, a more constant sheet resistance and smaller errors should be achieved by further improving distribution uniformity of conductive paths in the AgNW patterns. This could be done, for example, by combining with other transparent conductive materials such as graphene and using the welding process of AgNW junctions.[8]

In conclusion, we have developed a high-resolution printing technique for cross-aligned AgNW electrodes for flexible and transparent electronics using rod coating on hydrophilic-/hydrophobic-patterned surfaces. The AgNW electrodes exhibit a low sheet resistance of 25 \( \Omega \) sq \(^{-1} \) and a high visible transmittance of 96–99%. The printed electrodes can be used as biosensors to detect the electrophysiological signal from plants. In addition, we have used the electrodes for creating ultraimperceptible, ultrathin (2–3 \( \mu m \)), and transparent OFETs with high visible transmittance (\( \approx 90\% \)), photostability, and mechanical stability. Furthermore, the cross alignment improves transistor characteristics with low contact resistance and low sheet resistance. These applications of fine-printed and cross-aligned AgNW electrodes will allow for the development of various kinds of high-performance printed optoelectronic sensor systems with low material consumption and large-area scalability.

4. Experimental Section

Preparation and Characterization of AgNW Ink: To make the AgNW ink compatible with hydrophilic/hydrophobic patterning, AgNW ink (Showa Denko K.K., JPN) with a AgNW concentration of 0.3 wt% was mixed with IPA (Wako Pure Chemical Industries, Ltd., JPN). The average width and length of AgNWs were 39 nm and 13 \( \mu m \), respectively. Contact angle measurements (Figure S2, Supporting Information) were conducted at least five times at different points using the FAMAS and DM 500 apparatus (Kyowa Interface Science). All contact angles were measured at room temperature around 25 °C 60 s after a droplet with a volume of 2 \( \mu l \) placed on the samples.

Patterning of AgNW Electrodes: The method described in a previous study[10] was used for preparing the hydrophilic/hydrophobic-patterned surface (Figure S1, Supporting Information). The AgNW dispersion was swept over the hydrophilic-/hydrophobic-patterned surface using a glass rod, which was at a distance of \( \approx 250 \mu m \) from the substrate. We used a commercially available glass rod that was hydrophilic and was generally used to mix chemicals and liquids to spread the AgNW dispersion along the rod even on hydrophobic surfaces. The substrate was at room temperature \( \approx 20 \) °C during sweeping. The sweeping rate was maintained at 400 \( \mu m \) s \(^{-1} \) utilizing a custom-made coating system with a stepping motor. The coating direction was changed by rotating the substrate.

We performed sweeping twice to pattern AgNWs. In the parallel-aligned case, sweeping was conducted twice in the same direction. However, different directional sweeping was implemented in the cross-aligned case: the first along the parallel direction and the second along the perpendicular direction. After sweeping, the substrates were heated for 1 h at 120 °C in near vacuum (\( \approx 100 \) Pa) to remove the residual solvents.

For the patterning of PEDOT:PSS layers on the AgNW electrodes, a PEDOT:PSS aqueous dispersion (Organo N-1005; Sigma-Aldrich Co. LLC, USA) was prepared by adding 5 vol% ethylene glycol (Wako Pure Chemical Industries, Ltd., JPN) and 1 vol% (3-glycidoxypropyl)trimethoxysilane (Tokyo Chemical Industry Co., Ltd., JPN). The dispersion was swept after AgNW dispersion and in the same condition as that for the AgNW dispersion. After sweeping, the substrates were heated in the same condition as that for AgNW electrodes. In the samples for electrical measurement, 50 nm-thick layers of Au were deposited on the edge of the AgNW electrodes by vacuum evaporation through a shadow mask.

Measurements of Leaf Surface Potential: The cross-aligned AgNW electrodes overcoated with PEDOT:PSS were prepared as described earlier. Then, 5 \( \mu m \)-thick SU-8 (SU-8 25; KAYAKU Advanced Materials, Inc., USA) layers were patterned over the AgNW electrodes to provide selective openings for sensing on small areas (\( \approx 200 \times 800 \) \( \mu m ^2 \)), according to the manufacturer’s instruction. A wireless module, which we used previously,[3] was utilized to detect the EP. The Ag/Au(C) electrodes (World Precision Instruments., USA) with Ten20 gel pastes (Weaver and Company, USA) were used for the ground electrodes, which were placed on the stem. The reference electrodes were the AgNW electrodes, which were close to the stem on a leaf of Egeria densa, whereas the counter electrodes were close to the tip of the leaf. The detected potentials of the reference and counter electrodes were differentiated. We also confirmed that conventional stainless electrodes can detect similar potential traces as the cross-aligned AgNW electrodes. The measurements were carried out for 20 min each in the dark and white-LED-light illumination (LEDW-R255CP; OPTOCODE CORPORATION, JPN). The detected EPs were low-pass filtered below 10 Hz and smoothed using the moving average in a sampling range of 2 s.

Fabrication of OFETs: The AgNW ink was patterned on a 1 \( \mu m \)-thick parylene film as source and drain electrodes using the hydrophilic/hydrophobic surface patterns. To form contact pads for the AgNW electrodes (source and drain), 50 nm-thick layers of Au were deposited on the edges of AgNW electrode patterns by vacuum evaporation through a shadow mask. About 30 nm-thick layers of the C\(_{60}\)-BTBT organic semiconductor were deposited on the source and drain electrodes at a rate of 0.03 nm s\(^{-1}\) by vacuum sublimation through masked shadow masks. A 150–500 nm-thick layer of parylene (dix-SR: Daisan Kasei Co., Ltd, JPN) was deposited as the gate dielectric by chemical vapor deposition (CVD). The different thickness of parylene dielectrics was employed as follows: 150 nm thickness for Figure 6c,d,f and Figure S9, Figure S12, and Figure S13, Supporting Information, 500 nm thickness for Figure 6e and Figure S7, Figure S8, and Figure S11, Supporting Information, and 250 nm thickness for Figure 7h and Figure S10, Supporting Information. The AgNW ink was patterned again as the gate electrode on the gate dielectric using the hydrophilic/hydrophobic surface pattern (excluding the heating process at 120 °C for 1 h). The contact pads of Au were formed again for electrical access to the AgNW electrodes (gate). Finally, the OFETs were encapsulated with a 1 \( \mu m \)-thick parylene layer by CVD. In the four-probe devices, Au layer was used as the gate electrode and probe electrodes to ensure the reliable comparison of source and drain electrodes in the different alignment conditions of AgNWs.

Characterizations of Patterned AgNW Electrodes and OFETs: The pattern width of the AgNW electrodes and the spacing between the patterns were measured by observing the electrodes in a dark field with an optical microscope (DM4000 M; Leica Microsystems, DEU). The resistance of the AgNW electrodes was measured using a source measurement unit (B2902A; Keysight Technologies, Inc., USA). The values of resistance were normalized into sheet resistance by dividing them with lateral dimensions (\( W_s/\ell_s, \ell_p = 1 \) mm, \( W_p = \) pattern width). Visible transmittance was measured on a single pattern without considering the spacing between patterns utilizing microspectroscopy (MSV-5000; JASCO Corporation, JPN).
and a measurement spot with a width of 20 μm. The orientation analysis of optical images was conducted using Orientation[14] which is a plugin developed for ImageJ software. The coherency and energy in Orientation were set to be 20% and 5%, respectively, to prevent noisy pixels. The characteristics of the OFETs were evaluated in the dark environment or white-LED-light illumination in ambient conditions, using a semiconductor device parameter analyzer (B1500A, Keysight Technologies, Inc., USA). The mobility (μ) of the OFETs was extrapolated from the transfer characteristics in the saturation regime using the following equation.

\[
I_{\text{DS}} = \frac{\mu W C_{\text{i}}}{2L} (V_{\text{GS}} - V_{\text{th}})^2
\]

\(I_{\text{DS}}\) is the current measured between source and drain electrodes, \(L\) and \(W\) are the channel length and width, respectively, \(C_i\) is the capacitance per unit area, and \(V_{\text{GS}}\) and \(V_{\text{th}}\) are the gate-source voltage and the threshold voltage, respectively. The values of \(C_i\) were determined by the capacitance of the metal–insulator–metal structure measured with an LCR (Inductance (L), Capacitance (C), and Resistance (R)) meter (E4980A, Keysight Technologies, Inc., USA).

In four-probe measurements, the channel resistance \(R_{\text{ch}}\) of organic semiconductors was evaluated using the following equation

\[
R_{\text{ch}} = \frac{1}{\frac{1}{R_{\text{S}}} + \frac{1}{R_{\text{D}}}}
\]

\(V_1\) and \(V_2\) are the potentials measured on the probes in the middle of the channel region, and \(L_1\) (200 μm) and \(L_2\) (400 μm) are the distances of the probes from the source, as shown in Figure S10. Supporting Information. The values of contact resistance on the source \(R_S\) and drain \(R_D\) were calculated according to the following equation

\[
R_{\text{S(D)}} = \frac{\Delta V_{\text{S(D)}}}{I_{\text{DS}}}
\]

\(\Delta V_{\text{S(D)}}\) is the potential drop at the source or drain, and it can be obtained through the linear extrapolation\[46\] of the potential diagram, as shown in Figure S10b, Supporting Information.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

alignments, biosensing, organic transistors, silver nanowires, transparent electrodes

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