With consumer electronics transitioning toward flexible products, there is a growing need for high-performance, mechanically robust, and inexpensive transparent conductors (TCs) for optoelectronic device integration. Herein, we report the scalable fabrication of highly conductive poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) thin films via solution shearing. Specific control over deposition conditions allows for tunable phase separation and preferential PEDOT backbone alignment, resulting in record-high electrical conductivities of 4,600 ± 100 S/cm while maintaining high optical transparency. High-performance solution-sheared TC PEDOT:PSS films were used as patterned electrodes in capacitive touch sensors and organic photovoltaics to demonstrate practical viability in optoelectronic applications.

Transparent conductor | solution shearing | PEDOT:PSS

Conductive films of high optical transparency are required in a myriad of applications, including electromagnetic shielding, antistatic layers, lighting displays, touch sensors, and as electrodes for photovoltaics (1, 2). As flexible, lightweight displays for televisions and portable consumer electronics become closer to reality, emerging transparent conductors (TCs) need to be mechanically robust (3). An ideal TC, therefore, should have a sheet resistance <100 Ω, transmissivity greater than 0.90, and be inherently flexible, all while remaining inexpensive to process on a mass scale (4).

Indium tin oxide (ITO) is the most widely used TC material due to the combination of low sheet resistance and high transparency when grown on a variety of substrates. Although common to use, ITO is an expensive material due to the requirement for vacuum deposition and a number of postprocessing steps (5). For example, in organic photovoltaic (OPV) modules ITO was estimated to represent 24% of the module cost (6). However, alternative transparent conductor materials, such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) are estimated to comprise only ∼1% of an OPV module cost. Additionally, ITO is not compatible with flexible applications, because small applied strains of as little as 4.5% lead to an order of magnitude increase in the resistance (7).

In recent years there have been a number of emerging TC materials studied in the literature ranging from metal nanowires (Au, Ag, Cu) (8–11), conducting carbon allotropes (graphene, carbon nanotubes) (12–15), conducting polymers (16, 17), and other hybrid approaches (18). Recent attempts using metal nanotrenches by Wu et al. have resulted in superior optoelectronic properties with a sheet resistance of 2 Ω at 90% transmission (19). The use of metal mesoscale grids further enhanced the properties of metal nanowires electrodes to a sheet resistance of 0.36 Ω at 92% transmission (20). Although metal nanowires combine low resistance and high transparency, they have inferior flexibility and stretchability compared with polymer-based TCs (3).

PEDOT:PSS consists of insoluble PEDOT that is charge stabilized by PSS (Fig. 1A), which affords good solubility in aqueous formulations. Within these solutions, PEDOT:PSS forms micelles where hydrophilic PSS is in contact with water and hydrophobic PEDOT is located in the micelle core (21). Upon spin-coating from solution, the micelles are deposited as a film and can have conductivities on the order of ∼1 S/cm (22). Subsequent annealing, treatment with cosolvents, and postprocessing steps can increase the conductivity of films to over 3,000 S/cm (23, 24). High-performing spin-cast PEDOT:PSS TCs have reached a sheet resistance of 46 Ω at 90% transmission (25, 26). Furthermore, it is compatible with flexible electronics as films can withstand over 90% applied strain without electrical breakdown (7).

There is a wide variety of solution processing techniques used to deposit uniform, low-roughness films (27). Spin-casting is a popular laboratory-scale deposition technique due to its simplicity and ability to deposit high-quality films with a variety of materials. However, it is a batch process that is difficult to implement on a continuous mass production scale. Furthermore, it is difficult to use elevated substrate temperatures during spin-coating, a parameter that may play a role in the final film characteristics. Contrarily, scalable fabrication through solution shearing allows for tunable deposition conditions which enable enhanced kinetic control resulting in large impacts on the electrical performance of organic electronics (28–30).

In this work we use solution shearing to fabricate high-performance TC PEDOT:PSS films (Fig. 1A). Tunable control of PEDOT backbone orientation, local ordering, and phase separation is demonstrated via precise control of the deposition parameters. Record-high PEDOT:PSS conductivities of 4,600 ± 100 S/cm are obtained and reach a sheet resistance of 17 ± 1 Ω at 97.2 ± 0.4% transmission. A patterning method (Fig. 1C) is also developed which enables the use of high-conductivity PEDOT:PSS as a flexible film.


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transparent conductive films in capacitive pressure sensors and OPV devices.

Results and Discussion

Properties of Solution-Sheared PEDOT:PSS Transparent Conductors.

The effects of shearing speed and temperature on the electronic properties of PEDOT:PSS films are shown in Fig. 2A. At 65 °C there is a sharp increase in the sheet resistance of films with faster shearing speeds. This is consistent with depositing thinner films at higher shearing speeds, resulting in higher resistances. However, when the substrate temperature is increased to 85 °C, there is a near-flat response between increasing shearing speed and sheet resistance. PEDOT:PSS film thickness decreases from 95 ± 2 nm to 41 ± 2 nm when increasing the shearing speed from 0.5 to 1.5 mm/s. The film thickness then begins to increase at 2 mm/s (53 ± 2 nm), signaling the PEDOT:PSS processing changes from the evaporative to the Landau–Levich regime (31). Fig. 2B illustrates the effect of shearing speed on the transmissivity at 550 nm of PEDOT:PSS films at 65 and 85 °C. The film transmission ranges from 83.5 ± 0.2% to 97.1 ± 0.2% for increasing shearing speed from 0.5 to 1.5 mm/s. Because the film thickness begins to increase at 2 mm/s, the corresponding film transparency also begins to decrease to 96.5 ± 0.3%. Tuning the temperature and shearing speed allows for optimization of film thickness, as well as the resulting sheet resistance and transparency.

Recently there have been a number of methods reported to improve the transparent conductor properties of PEDOT:PSS. Fig. 2C illustrates some of the highest performance PEDOT:PSS transparent conductor films using a Zonyl fluorosurfactant (light blue open diamonds) (16), posttreatment with methanol (green open squares) (22), and sulfuric acid (brown open triangles) (23). Repeating spin-coated PEDOT:PSS films and posttreatment with methanol (purple open squares) yields similar performance as the previously reported literature (22). However, sheared PEDOT:PSS films at both 65 °C (blue solid squares) and 85 °C (red solid circles) outperform spin-coated films (all methanol treated), combining a beneficial decrease in sheet resistance with improved transparency. Sheared PEDOT:PSS films at 85 °C have superior performance and lead to more reliable deposition of films, as evident in the tighter clustering of data points. Fig. 2D plots the effect of shearing speed on film conductivity deposited at 85 °C. Single-layer conductivity peaks at 0.75 mm/s, but when the thickness is increased by depositing a second layer of PEDOT:PSS, the optimal conductivity occurs at a shearing speed of 3 mm/s. For double-layered films, the drop in conductivity with further increasing or decreasing the shearing speed is minimal compared with single-layered films.

The figure of merit (FoM) for transparent conductors is defined as the ratio of direct current conductivity (σ_{dc}) to optical conductivity (σ_{op}):

\[
\text{FoM} = \frac{\sigma_{dc}}{\sigma_{op}(\lambda)} = \frac{188.5 \ \Omega}{R_{\text{sheet}}(T(\lambda)^{1/2} - 1)}
\]

where \( R_{\text{sheet}} \) is the sheet resistance and \( T \) is the transmittance at \( \lambda = 550 \text{ nm} \). Typically an FoM greater than 35 is a minimum benchmark indicating commercial viability of transparent conductors (4). This constitutes a sheet resistance ≤100 Ω/□ and transparency ≥90%. The FoM for single- and double-layered sheared PEDOT:PSS films are shown in Fig. 2D. The FoM for all sheared films was in excess of 35 and reached 286 for double-layered}

Fig. 1. Schematic of solution shearing process. (A) Chemical structure of PEDOT:PSS. (B) Schematic of the solution shearing design and (C) patterning PEDOT:PSS via selective patterning of solvent wetting and dewetting regions.

Fig. 2. PEDOT:PSS as a transparent conductor. The effect of coating speed on the sheet resistance (A) and transmittance (B) of PEDOT:PSS films on glass substrates sheared at 65 °C and 85 °C. (C) The sheet resistance and transmittance of PEDOT:PSS films sheared and spin-cast compared with literature reports of PEDOT:PSS treated with methanol (22), H_2SO_4 (23), and a Zonyl fluorosurfactant (16). (D) The conductivity and σ_{dc}/σ_{op} ratio of single- and double-layered PEDOT:PSS films sheared at 85 °C and treated with MeOH.
PEDOT:PSS films sheared at 3 mm/s (Supporting Information). This dramatically surpasses the previous highest FoM for PEDOT:PSS transparent conductors which had an FoM of 72 for \( H_2SO_4 \) treated films \( R_{sheet} = 46 \Omega \text{\square} \) and \( T = 0.90 \) (23). PEDOT:PSS solution sheared at 2.5 mm/s and treated with methanol results in films with \( R_{sheet} = 38 \Omega \text{\square} \) at 96% transmission for an FoM of 232. Spin-coated PEDOT:PSS films treated with methanol have \( R_{sheet} = 112 \Omega \text{\square} \) with 92% transmission, a conductivity of 891 S/cm, and FoM = 39. Shearing PEDOT:PSS greatly improves the optical transparency while also decreasing the sheet resistance, enabling films to surpass the FoM of typical alternative transparent conductors.

Characterization of PEDOT:PSS Films. To decipher the different effects the deposition techniques have on the film morphology, we prepared a series of spin-cast and sheared films on Si and imaged them using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM and AFM images in Fig. 3 show that spin-cast films treated with methanol show very small spherical particles somewhat assembled into ill-defined short nanofibers. However, sheared films show more prominent well-defined fibers which become elongated with faster shearing speeds. Whereas the sheared nanofibers do not appear to have any preferential arrangement in the direction of shearing according to these images, the fibrous networks form an interconnected mesh network which may enable superior charge transport.

Treatment of PEDOT:PSS spin-cast films with methanol has shown to increase phase segregation between PEDOT and PSS domains and reduce excess PSS content as evidenced through X-ray photoelectron spectroscopy (XPS) surface scans (22). Although surface XPS acquisitions can provide valuable information, being able to probe the chemical composition through the bulk of the film can reveal whether vertical compositional gradients are present. High-resolution XPS of the S 2p region of PEDOT:PSS comprises two peaks: the sulfonate moiety from PSS occurs at higher binding energy and the thiophene in PEDOT appears at lower binding energy (Supporting Information) (32).

XPS depth profiles in Fig. 4A and B show different vertical phase gradients between the two deposition techniques (example spectra can be seen in Supporting Information). The yellow boxes on the plots highlight the areas of significant difference in the vertical composition of films. Spin-coated films are PSS-rich but quickly change to a near 1:1 ratio of PSS:PEDOT throughout the bulk of the film (Fig. 4A). For sheared films, the top half is dominated by PSS, whereas the bottom half is dominated by PEDOT (Fig. 4B). Sheared films exhibit a greater extent of phase separation, where the PSS surface has segregated from the PEDOT-rich layer beneath.
highest ratio. This speed corresponds with the optimized conditions for maximized double-layer FoM.

To help elucidate the mechanism of increased conduction via solution shearing and MeOH postprocessing treatment, temperature-dependent conductivity was measured. As seen in Fig. 6, treatment with MeOH increases conductivity in both samples by over 2 orders of magnitude, with the solution-sheared films continuing to exhibit higher overall conductivity. Additionally, two slopes are clearly observed above/below 160 K in MeOH-treated solution-sheared films, indicating a switching of the dominant hole scattering process below that temperature. The change is more clearly seen in the Arrhenius plot (Fig. 6, Inset). It has recently been shown that solvent-treated films can increase the ordering and shorten interpolymer distances (35). Whereas the MeOH treatment is having similar effects on the PEDOT:PSS films, the increased ordering provided by the solution shearing process gives way to the further enhanced electrical transport properties.

**Applied Devices and Patterning.** The high conductivity of the solution-sheared PEDOT:PSS film renders it a viable material as a transparent conductor in various devices. Specifically, the high-quality interface it can provide was demonstrated in OPV devices. Highly conductive sheared PEDOT:PSS films was applied as the anode in OPV devices, where the device architecture contained a poly(3-hexylthiophene) (P3HT): [6,6]-phenyl-C_{61}-butyric acid methyl ester (PC_{61}BM) photoactive layer and LiF/Al cathode. The current density–voltage (J–V) plots are shown in Fig. 7A and photovoltaic characteristics in Supporting Information.

Sheared PEDOT:PSS electrodes obtained a power conversion efficiency (PCE) of 2.87%, which was similar to using ITO TCs (2.86%). The ITO electrodes had higher open-circuit voltages (V_{OC}) and short-circuit current densities (J_{SC}), but a lower fill factor (FF). High fill factors for sheared PEDOT:PSS devices can be attributed to the low sheet resistance of TC films, and potentially improved bulk heterojunction morphology in the photoactive layer. Spin-cast PEDOT:PSS films had a PCE of 2.20% with lower J_{SC} and FF compared with sheared films. The reduction in these photovoltaic parameters is the result of high sheet resistance and lower transparency of spin-cast PEDOT:PSS TCs. The similar photovoltaic performance of sheared PEDOT:PSS and ITO transparent electrodes indicates that solution-sheared PEDOT:PSS electrodes could be a cost-effective alternative to ITO in OPV devices.

Whereas some applications require conformal coatings, lateral patterning of electrodes is important for fabricating some device structures, such as circuits and sensors. Here, a simple technique was developed to deposit the PEDOT:PSS films into patterns, preventing the need for postdeposition lithographic processes that can damage the film. Before shearing, defined patterns of hydrophillic and hydrophobic areas (see Materials and Methods for details) are prepared on the substrate surface (36). As the PEDOT:PSS solution is sheared, the meniscus is confined and pinned within the hydrophillic region, resulting in selective film deposition. Fig. 7B is an optical image of patterned PEDOT:PSS film. Line width and spacing as small as 2 μm are achievable with this methodology.
One possible application of patterned electrodes is two-dimensional position pressure sensing. To demonstrate this concept, 10 electrodes were patterned in parallel on polyethylene terephthalate (PET) with width and spacing of 5 mm. A polydimethylsiloxane (PDMS) spacer separated two coated PET substrates aligned perpendicular to each other (Fig. 7D, Top). The middle pixel (5, 5) was then pressed at a pressure of 50 kPa, and the change in capacitance was measured for all of the arrays. Fig. 7C is a contour map showing the change in capacitance over the entire array. Fig. 7D contains a plot of change in capacitance versus time at various pixels away from the pixel being pressed at a pressure of 50 kPa. The change in capacitance is the highest at the pixel being pressed. This simple example demonstrates the feasibility of using flexible, patterned electrodes in similar architectures such as active-matrix organic light-emitting diode displays and radio-frequency identification tags.

In conclusion, we have used a scalable deposition technique for the fabrication of high-performance polymer transparent conductors. Control of the solution shearing parameters results in record-high PEDOT:PSS conductivity of 4.600 ± 100 S/cm with a sheet resistance of 17 ± 1 Ω/□ at 97.2 ± 0.4% transmission. Tuning the shearing conditions allows for kinetic control over film deposition morphology, composition, and anisotropy. Solution-sheared films outperform spin-coated films in all aspects of FoM and applied device performance. Additionally, solution shearing allows for patterned deposition, with a demonstrated resolution of 2 µm. This patterning of TCs allows use in a variety of applications including capacitive touch sensors, transistors, and OPVs. This study established PEDOT:PSS as a low-cost and mechanically robust alternative to ITO transparent conductors.

Materials and Methods

Materials. PEDOT:PSS formulations: PH1000 and PVP AI 4083 were purchased from Heraeus. P3HT P200 was obtained from Rieke Metals and PC$_6$BM was acquired from nano-C. Methanol, 2-propanol, 1,2-dichlorobenzene, and lithium fluoride were used as received from Sigma-Aldrich.

Solution Shearing PEDOT:PSS Films. PEDOT:PSS films were sheared on glass, Si, Si/SiO$_2$, and PET substrates. Substrates were rinsed with 2-propanol and exposed to a 5-min O$_2$ plasma (1 min for PET substrates) at 150 W with 200 mtorr of O$_2$ pressure. Films were deposited at 65 °C and 85 °C on a temperature-controlled shearing stage. The Si shearing blade was functionalized with a highly crystal-line monolayer of octadecyl(trichlorosilane according to our previously published methods (37). The shearing blade was orientated completely parallel to the substrate. A gap height of 100 µm was used between the substrate and shearing blade. PEDOT:PSS was coated at speeds of 0.02-4 mm/s, producing films with a range of thickness from 20 nm to over 250 nm. Films were then placed on a hotplate at 130 °C and methanol dropped on top, covering the PEDOT:PSS film. The film was annealed for 10 min, cooled to room temperature, and rinsed with methanol. Once again, the substrate was annealed for 10 min at 130 °C. For double-layered films, methanol treatment was performed after the first deposited layer before shearing the second layer on top (and subsequent methanol treating).

Spin-Cast PEDOT:PSS Films. Spin-cast PEDOT:PSS was performed on the same substrates as sheared films. PEDOT:PSS was filtered with a 0.2-µm mixed cellulose acetate filter directly onto substrates and spin-coated at 1,000-4,000 rpm for 60 s. Films had the same methanol treatment procedure as sheared films.

Instrumental. AFM images were recorded in tapping mode using a Veeco Multimode AFM. The resistance of films was measured using four-point probe with collinear probes of 0.5-cm spacing, and tested using a Keithley 2400 source meter. The resistance of sheared films was measured perpendicular to the shearing direction, unless otherwise noted. SEM was performed with an FEI Magellan 400 XHR SEM with an acceleration voltage of 700 V. UV-vis absorption was taken with a Cary 6000i spectrophotometer. An aperture measuring 1.3 × 0.4 cm was used for all measurements. Transmission values throughout the paper were recorded at 550 nm. Film thicknesses were measured using a contact probe Dektak 150 profilometer. All thickness values were the average of at least three measurements in different areas of the film. Typically depth profiling XPS uses an Ar ion sputtering gun which is destructive in organic films often losing valuable chemical information. Spin-cast and sheared films on Si were analyzed with a C$_{60}$ ion sputtering gun.
which allows for considerably gentler spattering while often preserving chemical information in organic films. XPS was performed with a PHI VersaProbe Scanning Auger Probe with a 1.486-eV Al Kα photon source with a 100-μm spot size (100 W, 20 kV). Sputtering was performed at 10 kV and 20 mA over a spot size of 2 × 2 mm. Grazing incidence wide angle X-ray spectroscopy (GIWAXS) was performed at Stanford Synchrotron Radiation Lightsource at beamline 11–3. Analysis and integration of diffraction data were analyzed using WiffDiff (38).

Six 50-nm-thick patterned Au electrodes were thermally deposited on Si/SiO2 (300-nm oxide thickness) substrates with a width of 7,500 μm and length of 500 μm, and PEDOT:PSS was spin-coated or sheared on top. To account for contact resistance, the four-probe method was used. The conductivity was calculated for each electrode measurement according to the following calculation:

\[ \sigma = \frac{\text{I}}{\text{V} \times \text{R} \times \text{L} \times \text{T} \times \alpha} \]

where \( T \) is the film thickness.

Patterning of PEDOT:PSS Films and Transiton Fabrication. To generate small line features of PEDOT:PSS film, photolithography was used to generate strips of photoreist on a silicon substrate. The surface was then treated with O2 plasma for 30 s at 150 W to activate the SiO2 surface. The substrate was then placed in a desiccator with a vial filled with 50 μL of tridecafluoro-1,1,2,2-tetrahydrooctyl trimethoxysilane (fluorosilane) for 3 h (39). Thereafter, the photoreist was removed by soaking the substrate in acetone under sonication for 1 h. The substrate was then taken out of acetone, washed with isopropyl alcohol, and dried with nitrogen gas. To generate larger features of PEDOT:PSS film, a substrate (glass, PET, or silicon) was firstly treated with O2 plasma and fluorosilane, as described above. Then a metallic shadow mask with desired features was placed on top of the substrate, and the substrate was treated briefly with O2 plasma for 10 s at 150 W. The fluorosilane was removed where there was an opening, resulting in patterned hydrophobic and hydrophilic regions.

Device Fabrication. Position pressure sensors were fabricated by shearing PEDOT:PSS film on PET substrates with an array of 10 hydrophilic lines in parallel. The line width and spacing were 5 mm. Two PET substrates were then placed on top of each other with the PEDOT:PSS films facing inward, and with the electrode arrays oriented perpendicular to each other. PDMs 2 μm in diameter and 1 mm thick were placed between every other pixel. The electrodes were wired out using copper tape.

OPV devices were fabricated on sheared PEDOT:PSS (with and without methyl alcohol treatment), spin-coated PEDOT:PSS, and ITO substrates. For ITO substrates, PEDOT:PSS (AI PVP 4083) was filtered with a 0.2-μm mixed cellulose acetate filter directly on the substrate and was spin-coated at 3,000 rpm for 1 min. The film was then annealed at 140 °C for 10 min. The photographic layer solution was prepared from a 1:1 mass ratio of P3HT and PCBM at a total weight concentration of 50 mg/mL in o-dichlorobenzene and stirred overnight at 40 °C. The photographic blend solution was spin-coated in air on top of the appropriate TC substrate at 600 rpm for 1 min and placed in a covered Petri dish to dry for 20 min in air. Substrates were then loaded into a thermal evaporator and top contacts were deposited at a pressure <1×10−3 torr; 0.4 nm of LiF at 0.1 Å/s, and 50 nm of Al at 1–4 Å/s were deposited defining an area of 0.04 cm2. Devices were removed from the evaporator, exposed to air, and tested under AM1.5 simulated solar conditions in a glove box. The Newport solar simulator had a photon flux of 100 mW/cm² and was calibrated using a certified KG-S filtered silicon reference cell. Source voltage and measured current was conducted using a Keithley 2400 source meter.

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