Flexible cost-effective transparent conducting electrodes (TCE) are critically important components for next-generation technologies ranging from consumer electronics to clean energy. In addition to replacing expensive mechanically brittle rare earth oxides such as indium tin oxide (ITO), flexible TCE have the potential to be compatible with large-volume manufacturing techniques such as roll-to-roll processing. Electrically conducting nanomaterials serve as a cornerstone for many ITO alternatives. A variety of nanomaterial compositions have been pursued in many laboratories including silver nanowires (AgNW), carbon nanotubes, graphene, and copper. Polymer-nanoparticle composites can increase the conductivity without impacting transmittance in TCE. Hybrid metallic-polymer composites have also been explored in the context of highly ordered grid structures. Active efforts focus on maximizing optical transmittance while maintaining sufficient electrical conductivity. These two key properties can be condensed...
into lumped parameters to simplify optimization strategies.[13] The optimal values for these two figures of merit are both (1) application-specific (2) and predictably dependent upon a combination of the material composition and the processing conditions employed in fabricating the film. General guidelines involve careful selection of the characteristic dimensions of the colloidal system. In the specific case of AgNW, the length distribution impacts percolation thresholds while the thickness influences the intrinsic conductivity of AgNW.[14]

TCE based on metallic nanomaterials can be processed by employing a number of solution-based techniques. Alternative fabrication methods include chemical vapor deposition,[16] electrospinning,[17] or layer-by-layer assembly.[18] The desired manufacturing method must also consider the scale of the amount of devices fabricated. Solution-based manufacturing techniques are amenable to large area format processing. One specific embodiment of this general approach is the use of hydrodynamic focusing using microfluidics.[19] Microfluidic processing has the potential to fabricate AgNW arrays into large areas rapidly with the added benefit of simultaneous electrical characterization.[20] Microfluidics and thermal gradients have been used more recently as a technique to fabricate high throughput arrays for rapid characterization of organic semiconductors[21, 22] in an approach that is analogous to high through-put screening in biotechnology.[23–25] When used in combination with well-defined thermal gradients, microfluidics can be used as a reliable tool to rapidly identify nanomaterial compositions and processing conditions that yield optimal combinations of maximum transmittance and minimum sheet resistance as determined by the intended application. We hypothesize that microfluidic processing of TCE based on AgNW using microfluidics in combination with thermal annealing gradients can be used to screen processing conditions to simultaneously optimize transmittance and electrical conductivity. Furthermore, the properties of AgNW devices fabricated using high throughput arrays with unique processing conditions can be rapidly measured using several available approaches. Taken together, high throughput microfluidic arrays with coordinated electrical and optical measurements of AgNW devices can be used to expedite the design and fabrication of solution processable TCE.

TCE have a broad range of applications ranging from displays in consumer electronics to photovoltaics. The trade-off between sheet resistance and transmittance is heavily dependent upon the intended application. The mutual consideration of these two figures of merit has been previously described by the construction of lumped parameters. For example, one such parameter is defined as follows where $\sigma$ and $\alpha$ are the electrical conductivity and visible absorption coefficient, respectively, $R_s$ is the sheet resistance, $T$ is the total visible transmission, and $R$ is the total visible reflectance.[26–29]

$$\frac{\sigma}{\alpha} = - \frac{R_s \ln (T+R)^{-1}}$$

Additional parameters have been constructed in order to incorporate other emerging and important considerations such as the mechanical robustness of the film.[13, 28] The implementation of microfluidics in combination with thermal annealing gradients can be used to identify the optimal processing conditions given the intended application. The monolithic device arrays described herein can produce over 900 AgNW devices, each of which is processed with a distinct combination of AgNW concentration and annealing temperature (Scheme 1). The concentrations and surface temperatures in AgNW arrays ranged from 3.0 to 5.9 mg-mL$^{-1}$ and 112 to 252 °C, respectively. Simultaneous variation of both the AgNW concentration and the thermal annealing temperature in a monolithic device can lead to rapid determination of the relevant figures of merit.
Increasing the density of AgNW monotonically reduces both sheet resistance and transmittance (Fig. 1). AgNW arrays annealed at 220 °C produce values of $R_s$ that range from 10.26 to 441.8 $\Omega \Box$ and transmittances ($\lambda = 500$ nm) that range from 75.4% to 88.3%. All of the AgNW concentrations (3.0 to 5.9 mg-mL$^{-1}$) used in microfluidic device arrays produce percolating networks. Device arrays using sub-percolation thresholds yield sheet resistances several orders of magnitude higher as expected (Supporting Information). The critical concentration was measured to be between 0.9 and 1.77 mg-mL$^{-1}$. This observed range of experimental values is much larger than the previously reported value of 0.21 mg-mL$^{-1}$.[30] This increased value can be attributed to the anisotropy in AgNW that evolves during flow processing (Supporting Information). Increasing the surface temperature during annealing yields a non-monotonic variation in $R_s$. This trend can be explained by recognizing that there are essentially three thermal annealing regimes. The different conditions are defined by two key thermal annealing temperatures; $T_{\text{min-fuse}}$ and $T_{\text{melt}}$. These two temperatures define the minimum temperature required for AgNW fusion and the melting point of AgNW, respectively. At temperatures below $T_{\text{min-fuse}}$, AgNW fusion is limited and the dominant network resistance occurs at the AgNW junctions. At temperatures above $T_{\text{melt}}$, the geometry of the AgNW is impacted, which can reduce the probability of percolation. Surface temperatures between $T_{\text{min-fuse}}$ and $T_{\text{melt}}$ promote fusion without melting and thus lead to the observed global minimum in sheet resistance for a given concentration of AgNW. The overall sheet resistance of individual devices in high throughput AgNW arrays could be further reduced through several techniques. For example, HCl vapor treatment can eliminate highly resistive oxide layers in AgNW.[31] It will likely be possible to achieve the benchmark values of $R_s \sim 100$ $\Omega \Box$ at $T = 90\%$ if appropriate post-processing strategies are employed.

There is not one single surface temperature that leads to a minimum $R_s$ across all AgNW concentrations. Rather, the optimal temperature fluctuates between 221 and 235 °C as the AgNW concentration is increased from 3.0 and 5.9 mg-mL$^{-1}$ (Fig. 1a). These variations can be attributed to the application of microfluidics in device fabrication. For example, slight non-uniformities in AgNW networks can form during solvent removal. Furthermore, increased alignment of AgNW can result due to hydrodynamic focusing of one-dimensional AgNW in solution during microfluidic processing. The relatively small absolute dimensions of AgNW devices fabricated using microfluidics arrays can also serve as a source of error in $R_s$ measurements as well. However, this technique is intended to serve primarily as a sensitivity analysis technique and a method to rapidly identify the regions of interest. The fabrication and precise characterization of devices with larger physical dimensions and increased sample sizes are appropriate next steps.

The typical bottleneck that limits the utility of high throughput approaches is the relatively slow analysis of the many samples generated. This limitation is particularly relevant in high throughput techniques for biotechnology and biomedical applications in which biological assays are essential. Rapid characterization of AgNW arrays fabricated using high throughput techniques could be achieved using automated probe techniques. A more potent approach could be the application of optical methods to rapidly characterize the statistics of AgNW networks. In general, the $R_s$ and, to a lesser extent, the $T$ of AgNW films are highly dependent upon network topology. A precise measurement of AgNW network characteristics can potentially provide a more accurate assessment of device performance. Representative optical micrographs of AgNW networks can be used to estimate network topology by applying image analysis algorithms. The detected AgNW can then be used to extract network statistics such as distributions of nanowire geometry and orientation (Fig. 3). For example, a critical parameter in determining $R_s$ is the length distribution of AgNW, which is plotted for representative samples. These data could be used to create deterministic models for predicting the performance of TCE. Prospective methods for rapid optical non-

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contact electrical characterization of AgNW arrays could be used as a future tool for real-time monitoring of the reliability and uniformity of solution processable AgNW. In general, high throughput arrays in combination with non-contact optical characterization could lead to accurate and rapid mapping of processing conditions to film properties in solution processable TCE materials. These methods may also be compatible with real-time characterization of film properties processed in roll-to-roll formats.

The devices and methods described herein could be applied to a variety of solution processable materials for TCE including graphene and carbon nanotubes. Similarly, microfluidic processing of solution processable polymers and colloidal metals could be extended to identify optimal processing conditions for other types of conducting networks as well. Taken together, the high throughput fabrication and characterization techniques described here will accelerate progress in TCE for expanded use in a variety of applications in clean energy and consumer electronics.

Experimental

Preparation of Ag Nanowire Device Arrays Using Microfluidics

Microfluidic channels with a height of 100 µm were fabricated using soft lithography as previously described. Briefly, SU-8 masters were fabricated using photolithography. Replica-molded poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning, Midland, MI USA) microfluidic networks were formed through curing at 70 °C for 24 h. PDMS channels were reversibly laminated to either silicon-silicon oxide wafers or glass substrates and affixed using a custom device. The inlet and outlet ports were exposed using a 1.0 mm biopsy punch (Miltex, York, PA USA). The completed device was perfused using a syringe pump (KDS-210, KD Scientific, Holliston, MA USA) using AgNW solutions of 5.9 mg-mL\(^{-1}\) and 3.0 mg-mL\(^{-1}\) that were prepared from stock solutions (NanoGap, San Francisco, CA USA) in isopropyl alcohol. AgNW solutions were dispersed and purified through sonication and centrifugation to remove large AgNW aggregates. Solutions were flowed into two inlet ports at 15 µL-min\(^{-1}\). The solvent was removed under reduced pressure for 24 h. AgNW device arrays on silicon-silicon oxide substrates were annealed in a temperature gradient using convective cooling using a hot plate source at 340 °C for 20 min and cooled thereafter at a rate of 3 °C-min\(^{-1}\). The surface temperature was measured at multiple distances from the heat source using a type-k surface temperature probe (Control Company, Friendswood, TX USA). AgNW device arrays on glass were thermally annealed at pre-defined temperatures in an oven with digital temperature control. Individual AgNW devices were defined by thermal evaporation of gold electrodes through a shadow mask. Briefly, gold films 50 nm in thickness were deposited at a rate of 0.5 Å-s\(^{-1}\) (NexDep, Angstrom Engineering, Kitchener, ON Canada). The resulting devices were nominally 2 mm in length with a channel length of 100 µm.

Electrical and Optical Characterization of Ag Nanowire Arrays

Sheet resistances were measured in two configurations. Characterization of AgNW device arrays was performed using either two-point or four-point probe measurements with an Agilent 34401A DMM (Agilent Technologies, Santa Clara, CA USA) and a Wentworth MP-926 probe station (Wentworth Laboratories, Santa Clara, CA USA) with gold microwire contacts (Surepure Chemetals, Florham Park, NJ USA). All resistance values are reported as mean ± std dev. Brightfield images of AgNW arrays for statistical network calculations were taken using an Olympus BH2 microscope equipped with a PL-A686C camera and PixeLink OEM Software (PixeLink, Ottawa, ON Canada). Scanning electron microscopy as performed using a Philips XL30 FEG (Eindhoven, Netherlands). Optical transmission spectra of the AgNW arrays fabricated on a silica substrate were recorded using a OL-770
UV-vis spectroradiometer equipped with OL 700-71 6” integrating sphere and OL 700-73 solid transmittance accessories (Optronic Laboratories, Orlando, FL, USA). AFM images were acquired in tapping mode using an aluminum reflex coated silicon probe tip (Nano and More USA, Lady’s Island, SC USA) on a Veeco Dimension 3100 SPM system at a rate of 1.25 Hz equipped with Nanoscope 6.13 software (Veeco, Plainville, NY USA).

Optical Characterization of Nanowire Networks

The population statistics and quantification of AgNW networks were carried out by applying a fully automated image analysis algorithm to the field of views of optical images. The algorithm includes a sequential execution of four estimation-inference steps. In the first step, the likelihood of pixels belonging to silver nanowires were estimated and their rough orientation computed by filtering the original image with a bank of simulated wire templates that differed in rotation and scale. The best response from the filters in conjunction with the original intensity of the optical image were used to construct a nanowire likelihood (or enhanced) image. In the second step, a binary clustering algorithm based on previous methods was applied to the nanowire likelihood image to obtain a binary image split into nanowire and non-nanowire pixels. This step detected a band of probable nanowire pixels around the true centerlines of the nanowires that have a thin but finite spread. The third step applied a particle thinning procedure based on diffusion of the nanowire pixels obtained from the second step towards their corresponding centerlines. The diffusion was based on the constrained movement of the nanowire pixels roughly orthogonal to the local orientation of the nanowires suggested by step one, with an aim to converge the particles on the likelihood maxima, simultaneously minimizing the interparticle distance in each particle neighborhood. At the end of the third step, a set of particles that were locally one-dimensional is estimated and stored in a converged particle set. The final step iteratively chose optimal AgNW segments as suggested by the converged particles from step three as follows: At every iteration, the straight line segment with the highest concentration of converged particles around the segment (from step three) was determined to be the representative nanowire segment for that portion of the image and added to a list of optimal nanowire segments. The corresponding particles surrounding the optimal nanowire segment was deleted from the converged particle set. The algorithm iterated until the converged particle set was empty. The algorithm then returned a list of optimal nanowire segments that were used for subsequent network analysis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Funding provided by the following organizations: the Berkman Foundation; the American Chemical Society Petroleum Research Fund (ACS PRF #51980-DNI7); the Proctor & Gamble Education Grant Program; and the Carnegie Mellon University School of Engineering. S.B. and G.K.R acknowledge support from NIH grant GM090033.

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Small. Author manuscript; available in PMC 2013 December 21.

Small. Author manuscript; available in PMC 2013 December 21.


Figure 1.
(a, b) The sheet resistance of high throughput arrays of AgNW networks is shown. The sheet resistance is reduced monotonically as the AgNW concentration increases. Conversely, a global minimum in sheet resistance is observed between surface temperatures of 220—230 °C. This minimum corresponds to the optimal temperature to maximize AgNW fusion while minimizing melting and dewetting. (c) Transmittance spectra for AgNW prepared across different concentrations but annealed at one temperature (220 °C). Transmittance values of these networks begin to approach 90% for concentrations of AgNW of 3.0 mg-mL$^{-1}$. 

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Figure 2.
High throughput fabrication techniques produce AgNW arrays that vary two important processing conditions on orthogonal axes; AgNW concentration and surface temperature. Increasing the AgNW concentration reduces sheet resistance and optical transmittance both monotonically and in concert. Increasing the annealing temperature may further reduce sheet resistance by virtue of nanowire fusion. However, the sheet resistance is expected to rapidly increase as the annealing temperature approaches the melting point of AgNW. This is primarily due to melting and subsequent dewetting of AgNW. The expected trends are depicted (a) schematically in cartoons (b) and in SEM images of AgNW processed by high throughput microfluidic arrays. Note the observable vertical anisotropy of AgNW networks.
is due to flow alignment during solution processing. The flow direction is vertically oriented in all panels. Scale bars represent 5 µm.
Figure 3.
Rapid characterization of AgNW network topology can be performed by image analysis of optical micrographs. High magnification optical images can be used to measure network morphology. A representative image of AgNW networks processed from a 4.4 mg-mL$^{-1}$ solution and annealed at 225 °C is shown (optical) with an overlay of the AgNW detection (analysis). Network statistics can be analyzed by producing histograms for nanowire geometry and orientation. A population of eighty nanowires with an average length of 14.9 µm is detected in this sample image. A histogram of AgNW orientation is determined by measuring the angle between each AgNW and the horizontal. These data indicate a strong bias in AgNW orientation, which can be attributed to hydrodynamic alignment in the direction of flow (horizontal). This general method will serve as a convenient method to rapidly characterize network topology and ultimately estimate the physical properties of AgNW networks prepared using high throughput fabrication techniques. Scale bar represents 10 µm.
Scheme 1.
Fabrication of high throughput AgNW arrays. (a) PDMS microfluidic devices are fabricated using replica-molding. (i) Negative molds composed of photoresist are used to (ii) cure (iii) patterned PDMS devices. (iv) PDMS microchannels are reversibly applied to silicon substrates with 300 nm thermal oxide followed by deposition of AgNW from solution. (v) The PDMS mold is removed and AgNW networks are annealed on a (b) thermal gradient. (vi) Electrical contacts are deposited via thermal evaporation of gold through a shadow mask. (c) Representative optical micrographs of the network demonstrate typical morphology of AgNW networks of (i) several devices and (ii) a single device. Scale bars represent 200 µm in (c-i) and 20 µm in (c-ii).