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ARTICLE

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We demonstrate a scalable method to create metallic nanowire arrays and meshes over square-centimeter-areas with tunable sub-100 nm dimensions and geometries using the shear alignment of block copolymers. We use the block copolymer poly(styrene)-*b*-poly(2-vinyl pyridine) (PS-P2VP) since the P2VP block complexes with metal salts like Na_2PtCl_4, thereby enabling us to directly pattern nanoscale platinum features. We investigate what shear alignment processing parameters are necessary to attain high quality and well-ordered nanowire arrays and quantify how the block copolymer's molecular weight affects the resulting Pt nanowires' dimensions and defect densities. Through systematic studies of processing parameters and scanning transmission electron microscopy (STEM) tomography, we determine that the equivalent of 2-3 monolayers of PS-P2VP are required to produce a single layer of well-aligned nanowires. Resulting nanowires' widths and heights can be tuned between 11-27 nm and 9-50 nm, respectively, and have periodicites varying between 37 and 63 nm, depending on the choice of block copolymer molecular weight. We observe that the height-to-width ratio of the nanowires also increases with molecular weight, reaching a value of almost 2 with the largest dimensions fabricated. Furthermore, we demonstrate that an additional layer of Pt nanowires can be orthogonally aligned on top of and without disturbing an underlying layer, thereby enabling the fabrication of Pt nanowire meshes with tunable sub-100 nm dimensions and geometries over a cm^2-area.

Introduction

Ordered metal arrays and meshes with sub-100 nm linewidths and sub-micron periodicities have promising uses in a number of optical and electronic applications, including UV-polarizers, optical metamaterials, and, most notably, visibly transparent electrodes.[1-6] However, realizing these applications requires a cost-effective means of fabricating such metallic nanostructures over large, device-relevant areas. Traditional top-down nanofabrication approaches, such as electron beam lithography, focused ion beam milling, and extreme UV lithography, are at present each lacking in either size-scalability or cost-effectiveness.[7-9] For such applications, block copolymer lithography is poised to offer a scalable, low-cost bottom-up solution.

Block copolymers (BCPs) are composed of two or more covalently linked but chemically dissimilar polymers (i.e., blocks) that microphase separate to form nanometer-scale patterns. The pattern's geometry (hexagonally packed spheres, cylinders, lamellae, or gyroids) and dimensions (*ca.* 10-100 nm) can be tuned by proper selection of the relative volume ratio of the two polymer blocks and the overall degree of polymerization or molecular weight of the BCP.[7, 10] While none of the patterns that BCPs naturally self-assemble into resemble nanowire arrays and meshes as desired for the optical and electronic applications previously described, researchers have shown that applying shear stress to cylinder-, sphere-, or lamellae-forming BCP thin films causes them to reorder into striped, nanowire-like patterns with long-range ordering.[1, 6, 11-14]

With BCPs adopting such a pattern, metal nanowires can then be templated – either by selectively removing one phase of the BCP and using the remaining polymer as a mask during metal deposition[15] or by using a block copolymer where one phase directly complexes with metal salts, namely poly(styrene)-*b*-poly(2-vinyl pyridine) (PS-P2VP).[6, 13, 14] Majewski *et al.* recently used a technique known as soft-shear laser zone annealing (SS-LZA) to demonstrate this concept and create metal nanowire arrays and meshes.[6, 16] This SS-LZA technique requires the BCP to be deposited atop a light-absorbing substrate with a silicone pad placed atop the BCP film; as a laser rasters across the sample, the light is absorbed by and heats the substrate, inducing large thermal gradients that result in local thermal expansion of the silicone pad and shear stress in the PS-P2VP film.[16] This method produces impressive nanowire meshes with low defect densities, but requires use of a light-absorbing substrate and the processing time increases linearly with sample area.[6]

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In this work, we create metal nanowire meshes over large areas using a scalable method to induce BCP alignment. Specifically, we apply an approach first demonstrated by Angelescu *et al.*[11] where a BCP thin film is heated and shear stress is applied by slowly moving a contacting silicone pad across the film surface via an external mechanical force. Since the shear force is applied uniformly across the entire sample ather than locally, the processing time is independent of sample size. Additionally, this method is suitable for direct use on a wide range of substrates, including glass or transparent plastics. As the quality of the resulting nanowire array is highly dependent on the shear alignment parameters,[11, 16-26] we investigate these parameters and develop guidelines for processing PS-P2VP to form well-ordered Pt nanowire arrays. Using various molecular weights of PS-P2VP, we demonstrate that nanowire arrays with a range of dimensions can be achieved, and furthermore, these arrays can be stacked atop one another to create Pt nanowire meshes over at least cm^2-areas with features on the order of 10 nm.

Results and Discussion

We fabricate Pt nanowire arrays by shear aligning thin films of PS-P2VP, which are then used to directly pattern metal nanowires through selective metal salt infiltration of the P2VP domain, as outlined in Figure 1. Specifically, PS-P2VP is spin coated onto silicon substrates to produce thin films with targeted thicknesses between 35 and 125 nm. Spin coated films are smooth (R_s = 1.5 nm over 200 μm^2) regardless of the film thickness within this range. Atomic force microscopy (AFM) of as-cast samples shows that they adopt a hexagonally close-packed sphere morphology, as shown in Figure 1b. After spin coating, shear force is applied to the films, which are heated above the BCP's glass transition temperature, for a specified amount of time using a simple hotplate and pulley system similar to that described by Angelescu *et al.*[11] The shearing procedure transforms the hexagonally close-packed spheres into aligned cylindrical polymer domains that are parallel to the substrate and the direction of applied shear (Fig. 1c). To convert the resulting block copolymer pattern into metal nanowire arrays, the aligned polymer film is soaked in a Pt salt solution, which selectively complexes with the P2VP phase (Fig. 1d).[13, 14] An oxygen plasma etching treatment then removes the PS-P2VP and reduces the metal, as demonstrated by Chai *et al.*,[14] resulting in Pt nanowire arrays (Fig. 1e). Metal meshes can be achieved by aligning a second layer of nanowires atop the first in the orthogonal direction (Fig. 1f).

To tune the nanowire dimensions (i.e., height, width, and periodicity), we used four PS-P2VP block copolymers having different molecular weights with similar dispersities and P2VP weight fractions so that the equilibrium morphology remained the same across all the polymers studied.[27] The PS-P2VPs that we explored have number-averaged molecular weights of 48-b-14.5 kg/mol, 68.5-b-26 kg/mol, 79-b-36.5 kg/mol, and 110-b-52 kg/mol and are henceforth abbreviated as 48-14, 68-26, 79-36, and 110-52, respectively (Table 1).

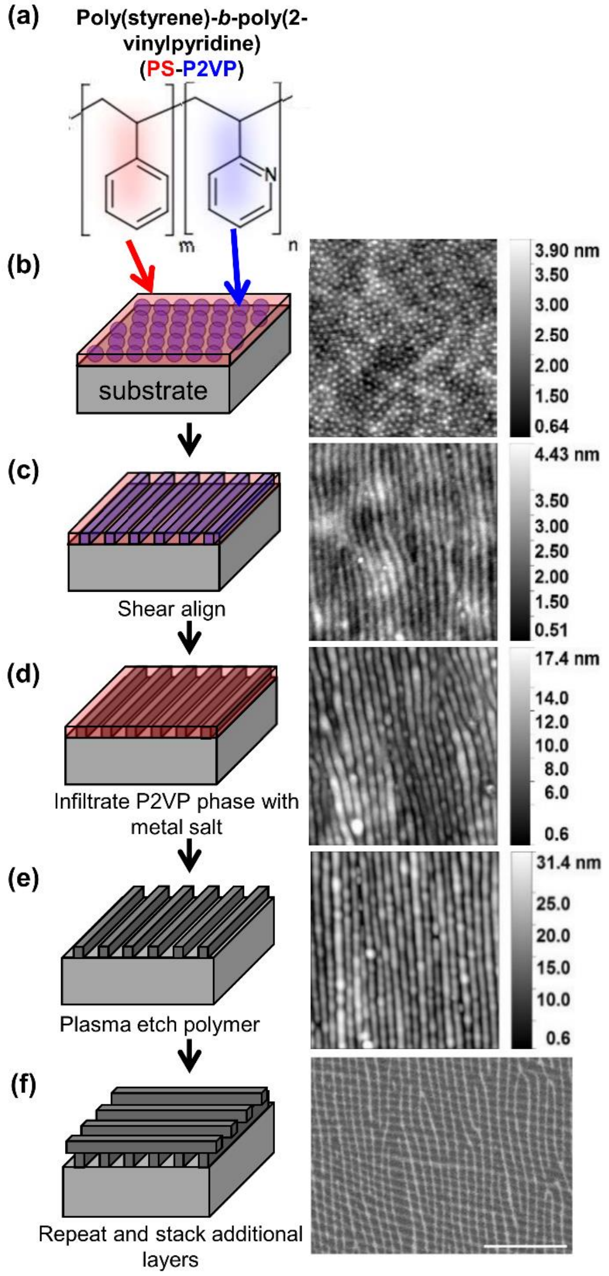

Figure 1. (a) Chemical structure of diblock copolymer poly(styrene)-b-poly(2-vinyl pyridine) (PS-P2VP). (b-e) Schematic of the procedure to fabricate ordered platinum nanowire arrays by shear-aligning PS-P2VP (left column) with representative AFM images of the surface morphology across a 1μm^2-area at each step (right column). Films in (b) and (c) were briefly annealed with toluene-vapor (selective solvent for PS) prior to imaging to enhance contrast between the two polymer phases. (f) A second layer can be aligned on top in the orthogonal direction, resulting in a metal mesh. Scalebar is 500 nm.

We first explored the effects of the shearing conditions to derive processing guidelines for aligning the different molecular weight PS-P2VPs. To quantify the quality of the nanowire arrays, we measured: (1) the normalized defect density, or the number of nanowire terminations and junctions within a given area defined by the square of the BCP periodicity, and (2) Hermans orientation parameter, which indicates how well the wires are oriented with respect to a defined axis (see SI for details). We roughly found that the magnitude of shear stress applied did not have a significant effect on the PS-P2VP alignment quality

Table 1. Details of polymers studied.

PS-*b*-P2VP Abbreviation	w_{PS}	M_n (kg/mol)	Total M_n (kg/mol)	Dispersity Index	Periodicity (nm)
48-14	0.77	48.5-b-14.5	63.0	1.07	37±3
68-26	0.73	68.5-b-26.0	94.5	1.10	43±2
79-36	0.68	79.0-b-36.5	115.5	1.05	47±3
110-52	0.68	110.0-b-52.0	162.0	1.10	63±4

as long as it was above a minimum threshold of ca. 33 kPa. This observation agrees with reports in the literature concerning other sphere- and cylinder- forming diblock copolymers, where the alignment quality increases and then plateaus with increasing shear stress.[11, 17-19, 22]

To determine the effect of film thickness on alignment quality, we created a series of samples with increasing film thickness for each molecular weight of PS-P2VP. For the 68-26, 79-36, and 110-52 PS-P2VPs, we observed a 10-30 nm window in film thickness in which well-aligned, continuous nanowires are obtained and the defect density and orientation parameter are at a minimum and maximum, respectively (see Fig. S2). From this observation, we conclude that PS-P2VP does not appear to be as sensitive to film thickness as other shear-aligned BCPs reported in literature, such as PS-PEP, which experiences significant degradation in alignment quality if the film thickness is more than 2 nm above or below a monolayer.[11] At thicknesses outside the 10-30 nm window, the alignment quality of PS-P2VP significantly worsens: discontinuous wires or sparse metal features occur in thinner films while nanowires branch significantly in thicker films, possibly due to a second layer of wires beginning to form above the first (see Fig. S3). Interestingly, unlike the other PS-P2VPs, shear-aligned films of the lowest molecular weight PS-P2VP, 48-14, demonstrate multiple maxima in alignment quality with increasing film thickness, though the origin for this behavior remains unclear.

Figure 2a shows the minimum PS-P2VP film thickness, *d*, required for good alignment (defined as a maximization of orientation and minimization of defect density; see Fig. S2) as a function of the sheared BCP's periodicity, *p* (which in turn correlates with the BCP's number-average molecular weight; periodicity was measured from the nanowire arrays). The minimum film thickness was defined as the first point in our series at which the defect density is at a minimum and the orientation parameter is at a maximum. The minimum film thickness appears to be linearly correlated with periodicity as $d \propto 2.2p$. Previous studies have reported that a monolayer corresponds to the optimal film thickness required for good alignment,[11] which is proportional to $(\sqrt{6}/3)p$ for hexagonally packed spheres - a factor significantly lower than our observations. PS-P2VP is known to form a brush layer with the substrate, as the P2VP phase preferentially wets silicon, which has previously been cited as the reason for required PS-P2VP film thicknesses that are thicker than a monolayer when shear aligning.[3] However, three-dimensional scanning transmission electron microscopy (STEM) tomography of the Pt infiltrated as-cast 68-26 PS-P2VP (Fig. 2b-e; Pt allows for sufficient contrast in electron density) shows that the PS-P2VP film at the optimal thickness (i.e. the thickness at which defect density is minimized and orientation is maximized) forms multiple layers of hexagonally close-packed spheres. This morphology suggests that multiple PS-P2VP layers are required to achieve good alignment in PS-P2VP, which is consistent with our increased scaling factor. Interestingly, tomography of the aligned polymer film at the same thickness shows that only a single layer of nanowires is formed (Fig. 2f-h) even though multiple layers of hexagonally close-packed spheres are present in the unaligned PS-P2VP film. The volume fractions of the Pt phases in the as-cast and shear aligned films (which is proportional to the

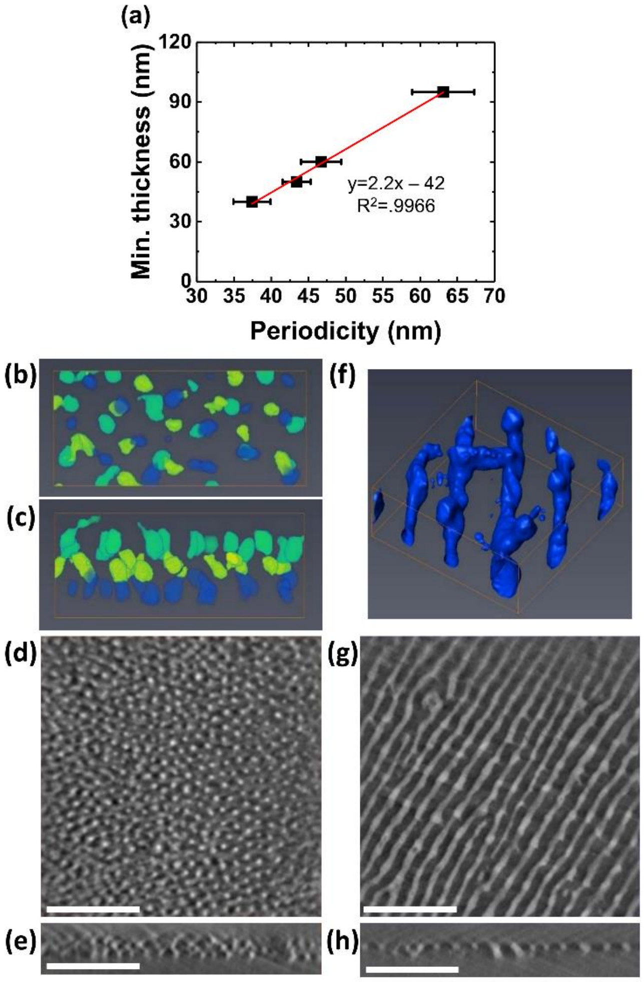

Figure 2. The minimum polymer film thickness required for good alignment, defined as a maximization of orientation and minimization of defect density, as a function of the block copolymer's periodicity (which scales with the block copolymer's molecular weight). The red line represents a linear fit of the data. (b)-(h) 3D STEM tomography of a 68-26 PS-P2VP film (55 nm thick) after Pt-salt infiltration of the P2VP phase to provide electron contrast. All scalebars are 300 nm. (b) Top-down and (c) side views of 3D reconstructed image of as-cast PS-P2VP, which forms approximately three layers of hexagonally packed spheroids. Each layer is a different color for clarity. Bounding box is 242 x 111 x 93 nm. (d) Top-down slice of the as-cast PS-P2VP film reconstruction (5.5 nm from the bottom of the film). (e) Side-view slice of as-cast PS-P2VP film reconstruction of as-cast PS-P2VP film. (f) 3D reconstructed image of shear-aligned PS-P2VP, which forms a single layer of nanowires. Bounding box is 221 x 221 x 89 nm. (g) Top-down slice of the shear-aligned PS-P2VP film reconstruction (15.5 nm from the bottom of the film). (h) Side-view slice of shear-aligned PS-P2VP film reconstruction.

volume fraction of the P2VP phases), based on tomography, are approximately 0.094±0.02 and 0.101±0.02, respectively, indicating that the spheres coalesce into larger cylinders, since volume is conserved. These fractions are lower than one might expect based on the P2VP weight fractions of the block copolymer, which may be due to incomplete metal salt complexation with P2VP or potentially the presence of a P2VP wetting layer (which is difficult to capture from the tomography due to limitations in imaging angles).

Having determined the optimal film thickness for shear-aligning each molecular weight PS-P2VP, we also explored varying the shearing time to examine its effect on the quality of nanowire arrays (see Fig. S5). We find that at short shearing times, alignment quality is low, presumably because the polymer chains have not had sufficient time to rearrange. The nanowire array quality increases with time until an optimum is reached, which scales with PS-P2VP molecular weight and ranges between 2-3.5 hours for the BCPs we studied. Past this optimal shearing time, the alignment quality worsens. Similarly, Majewski *et al.* observed a decrease in alignment quality at long effective annealing times when using SS-LZA.[6] The origin for this non-monotonic relationship between alignment quality and shearing time is unclear, but it is consistent with the aligned configuration being a transient state.

Using the different molecular weight BCPs along with the derived optimal shearing conditions, we fabricated Pt nanowire arrays with a range of dimensions. Figures 3a-d show representative topologies of Pt wires made from the 48-14, 68-26, 79-36, and 110-52 PS-P2VPs, and Figure 3e summarizes the dimensions of the resulting arrays. After etching, the wires have heights that range between approximately 9-50 nm, widths between 11-27 nm, and periodicities between 37-63 nm, which scale with the molecular weight of the block copolymer. The periodicities of the sheared arrays are comparable to those of the unsheared BCPs within a standard deviation (see Table S1). The heights of nanowires fabricated from 48-14 and 68-26 PS-P2VP are similar to their widths, indicating that the nanowires have a near-circular cross-section, but interestingly, nanowires fabricated from 79-36 and 110-52 PS-P2VP are approximately 1.5 to 2 times taller than they are wide, suggesting that these nanowires have an ellipsoidal cross-section. Independent of the choice of PS-P2VP molecular weight, the dimensions of nanowires can be decreased after fabrication by sintering, as shown in Figure 3e with the filled symbols. Sintering reduces the nanowires' heights and widths by an average of 65% and 50%, respectively, indicating that the post-etching (i.e., pre-sintering) wire density is lower than bulk Pt. Sintering enables the fabrication of Pt nanowires with heights and widths as small as 3.4 nm and 7.4 nm, respectively, with the lowest molecular weight PS-P2VP we explored, 48-14. One could potentially achieve any width or height between the etched and sintered values by changing the sintering temperature or time, granting another dimension of tunability. However, sintering is expected to change the electrical properties of the Pt wires due to the increase in density. Alternatively, they can be used as a template for depositing additional metal, such as through pattern transfer or electroless deposition.

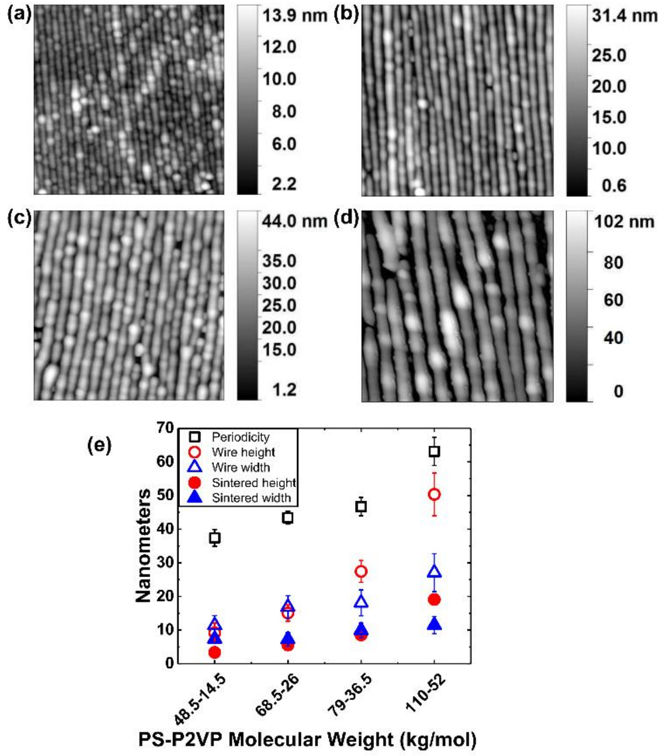

Figure 3. (a-d) AFM images of optimized Pt nanowire arrays fabricated by shear-aligning thin films of the following PS-P2VPs: (a) 48-14, (b) 68-26, (c) 79-36, and (d) 110-52. All AFM images are 1 μm x 1 μm. (e) Nanowires' average periodicity, height, and width both before (open symbols) and after (filled symbols) sintering as a function of the PS-P2VP molecular weight.

To achieve the mesh geometries suitable for transparent electrode and metamaterial applications, we aligned multiple BCP layers in orthogonal directions atop each other. Before a second layer can be stacked, the first layer must be immobilized so that it is not affected by shearing of the second layer. This immobilization can be done through either: (1) etching away the aligned polymer after metal salt infiltration and repeating the shear alignment process over the nanowire arrays,[6] or (2) exposing the first BCP layer to UV light to induce crosslinking (and therefore immobility) in the polystyrene phase, prior to adding the second layer.[15] Using both methods for stacking nanowire arrays, we aligned multiple layers of BCPs and fabricated Pt nanowire meshes of various dimensions, shown in Figure 4. The dimensions of each layer can be independently

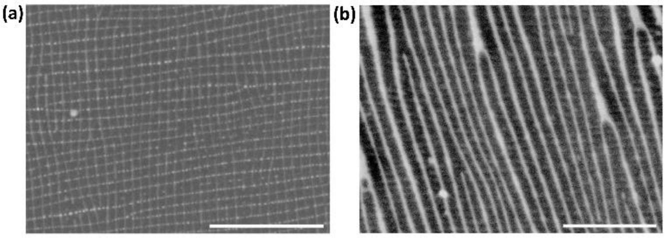

Figure 4. Platinum nanowire meshes templated by orthogonally shear aligning two layers of PS-P2VP having either (a) the same molecular weight and yielding an isotropic pattern or (b) having differing molecular weights, yielding an anisotropic pattern. Scalebars are 500 nm.

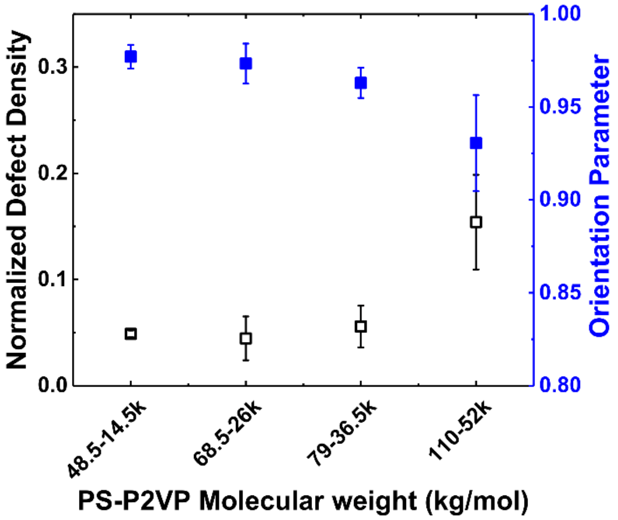

Figure 5. The average normalized defect densities (left axis, black open squares) and orientation parameters (right axis, blue open squares) of the best Pt nanowire arrays created with optimal film thickness and duration of shearing for each molecular weight PS-P2VP.

tuned by using different molecular weight polymers, as shown in Figure 4b. This layer-by-layer control may enable tailorable electrical and optical anisotropy for potential electrode and metamaterials applications.

Figure 5 compares the defect densities and orientation parameters of the Pt nanowire arrays created with the optimal shearing conditions for each molecular weight PS-P2VP. The alignment quality decreases with increasing molecular weight, presumably due to slower polymer dynamics.[16] Our lowest molecular weight PS-P2VP, 48-14, yields nanowire arrays with a unitless normalized defect density of 0.049 and the highest molecular weight PS-P2VP, 110-52, yields nanowire arrays with a defect density three times higher at 0.154. Though these defect densities are between 4 to 25 times higher than the best shear-aligned thin films of other block copolymers,[25] we expect that they may be suitable for transparent electrode applications, since, when two layers are stacked atop one another to form a mesh, significant conductive redundancy is added to the network.[5] For example, our previous simulations predicted that while random networks of silver nanowires commonly require lengths in excess of 50 µm to attain comparable performance to indium tin oxide (ITO), this threshold decreases significantly to only ca. 300 nm when the nanowires are ordered into a rectangular mesh. While our meshes form an ordered network with sufficient connectivity, efforts to improve nanowire conductivity merit further exploration, as previous reports have shown that it is significantly lower than bulk material,[6, 14] possibly due to the wires having a multi-grained structure.

Conclusions

In summary, we demonstrated the scalable fabrication over device-relevant areas (ca. 1 cm^2) of metal nanowire meshes with tunable sub-100 nm dimensions via the shear-alignment of the block copolymer PS-P2VP. To fabricate these materials, we developed processing guidelines for shear-aligning PS-P2VP across a range molecular weights. Well-aligned, continuous metal nanowires can be achieved when films have a minimum thickness equivalent to approximately 2-3 monolayers – well over the monolayer previously thought to be needed. 3D STEM tomography, possible because of the electron contrast provided by metal-infiltration of the P2VP phase, confirms that indeed multiple layers of spheres present in as-spuncast PS-P2VP thin films transform into a single layer of well-aligned, continuous cylindrical domains. This fabrication method is especially well-suited for creating nanowires with sub-10 nm dimensions since the defect densities are actually lowest for the smallest structures – a trend opposite to more traditional top-down based techniques where fabricating increasingly smaller features is more difficult and defect-prone. We believe that this ability to create ordered metal nanowire arrays with sub-10 nm features over cm^2-areas will be of interest for a variety of optoelectronic applications requiring such structures but lacking cost-effective and scalable means of producing them.

Methods:

Materials and Preparation

All PS-P2VP were obtained from Polymer Source, Inc. (Montreal, Canada). Details of the polymers studied are in Table 1. Substrates were 0.5 mm-thick boron-doped (100) silicon p-type wafers with either a native ~2 nm or 300 nm oxide layer from Addison Engineering, Inc. (San Jose, USA). The substrates were cleaved into approximately 1.2 cm x 1.2 cm pieces and rinsed with isopropyl alcohol. Polydimethylsiloxane (PDMS) pads were made from Dow Corning Sylgard 184, mixed in a 5:1 ratio of base to curing agent. The silicone was cast, degassed under vacuum for 10 min, and cured at 60°C for 24 hr, yielding a film with a thickness of approximately 0.7 mm.

Film Formation & Shear Alignment

PS-P2VP was dissolved in toluene in concentrations ranging from 1 wt% to 2.1 wt% and spin-coated at either 1600 or 2000 rpm to generate films with targeted thicknesses between 35-125 nm. Samples' film thicknesses were determined by ellipsometry using a J. A. Woollam VASE VB-400. PS-P2VP films were shear-aligned using a setup similar to that reported in Angelescu, *et al.*[11] A PDMS stamp approximately 1 cm x 1 cm in area was pre-stamped on a separate silicon wafer to remove excess uncured oligomers and then placed on top of the PS-P2VP film. The assemblage was then heated to 150°C on a hot plate. A metal block weighing approximately 0.9 kg was attached to a pulley and placed on top of the assembly. Shear stress was applied (33 kPa for 48-14 PS-P2VP, 45 kPa for all other molecular weight PS-P2VPs) by attaching a weight to the pulley. Shear stress was calculated from the pulley weight and alignment area. After a specified time, heating was turned off, and the sample cooled to room temperature while shear force was maintained. After reaching approximately room temperature (typically 1 hr), the PDMS stamp was removed from the sample.

Metallization

The aligned polymer film was soaked in an aqueous solution of 20 mM Na_2PtCl_4, (Strem Chemicals Inc., Newburyport, USA) with 0.5 M HCl for 20 min, as no significant improvement in wire quality was observed with increasing soaking time. The polymer was then removed via oxygen plasma etching using a Plasma Equipment Technical Services (Livermore, USA) system with etching conditions of 5 sccm O_2 at 52 W for 5 min. Sintering was performed in a tube furnace under an atmosphere of 4% H_2/96% Ar at 800°C for 5 min with a ramp rate of approximately 9.75°C/min.

UV Crosslinking

To stack polymer layers, aligned, Pt-infiltrated PS-P2VP was crosslinked under UV light for 50 sec with a Uvitron International Intelli-ray 600 with a power of 297.6 mW at 254 nm and 121.2 mW at 365 nm, as measured by a Thorlabs PM100D sensor.

Microscopy

Samples were characterized through AFM and/or SEM. AFM images were taken using tapping mode on a Bruker Dimension Fastscan under ambient conditions with a Fastscan B tip and a scan rate of 4 Hz. Images were taken with a 512 x 512 pixel resolution. SEM was performed using a Jeol 7401F with an accelerating voltage of 3 kV. Nanowire height and periodicity measurements were taken from AFM images. Since lateral AFM measurements of nano-features are affected by the AFM tip radius, wire width measurements were taken from SEM images. A minimum of 3 images were analyzed per sample for nanowire array defect and orientation quantification.

3D STEM Tomography

Metal-infiltrated PS-PVP films were deposited on silicon with a 300 nm-thick sacrificial oxide; the films were floated onto a TEM grid using 20wt% hydrofluoric acid to etch away the sacrificial oxide. Tomography measurements were performed in a Titan™ TEM 80-300 instrument at a 300kV accelerating voltage. Scanning transmission electron microscopy (STEM) images were collected with an annular dark-field detector with the tilt range from ±70°, every 2°, with a 2 µm field-of-view (FOV). Images were aligned using Inspect3D™ (FEI) with cross-correlation loops running 4 times. Manual tilt-alignment was performed to minimize artifacts followed by the final reconstruction using the simultaneous iterative reconstruction technique (SIRT) with 30 iterations with a final field-of-view of 1 µm. Visualization was done through Avizo 9.4 using an anisotropic smoothing filter followed by an isosurface (global threshold).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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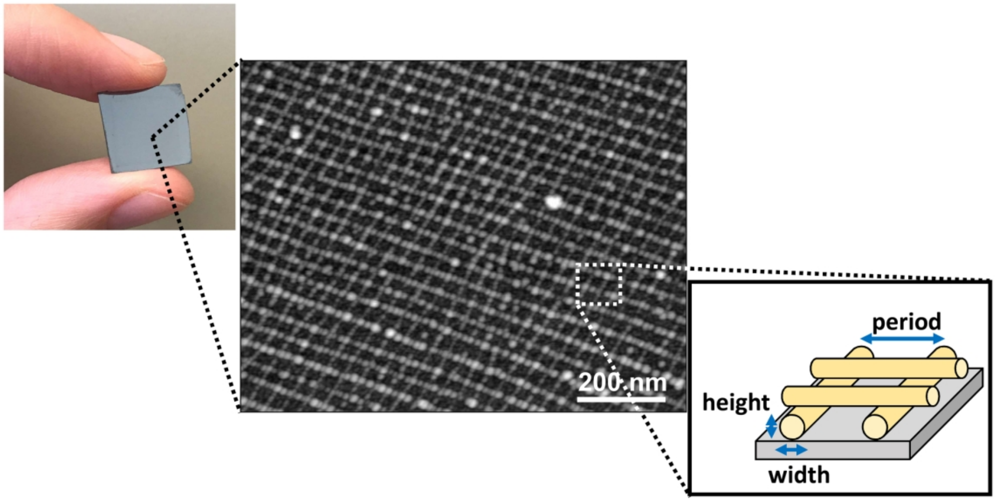

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