Simple assembly of long nanowires through substrate stretching

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Abstract

Although nanowire (NW) alignment has been previously investigated, minimizing limitations such as process complexity and NW breakage, as well as quantifying the quality of alignment, have not been sufficiently addressed. A simple, low cost, large-area, and versatile alignment method is reported that is applicable for NWs either grown on a substrate or synthesized in solution. Metal and semiconductor NWs with average lengths of up to 16 µm are aligned through the stretching of polyvinyl alcohol (PVA) films, which compared to other stretching methods results in superior alignment because of the large stretching ratio of PVA. Poly[oxy(methyl-1,2-ethanediyl)] is employed as lubricant to prevent NW breakage. To quantify NW alignment, a simple and effective image processing method is presented. The alignment process results in an order parameter (S) of NW alignment as high as 0.97.

Keywords: nanowire, alignment, assembly, image processing

1. Introduction

Nanowires (NWs) are a promising material for both interconnects and functional device elements in applications such as optoelectronics [1,2], electronic devices [3,4], sensors [5], and transparent electrodes [6,7]. The development of low cost assembly methods that enable hierarchical organization of NWs over large areas is central to the “bottom-up” approach. Furthermore, aligned NWs are required for applications in optical polarization and nanocomputing [8,9]. Over the past decade, NW alignment has been widely studied and multiple methods have been developed for NW alignment including: microfluidic flow [10], the Langmuir-Blodgett technique [11], electric and magnetic fields [12,13], bubble-blown films [14], and contact printing [15]. While this past work has resulted in successful alignment of NWs, there are significant issues that remain to be addressed. Past methods require either complicated fabrication processes, are not suitable for alignment over large areas, require the NWs to be grown on a substrate (contact printing), or can only be used for a subset of nanowire materials (field alignment methods). An alternative method, where NWs are mixed with a polymer and stretched to align the NWs, was developed to overcome some of these drawbacks [16,17]. However, this method is not applicable for device integration as the NWs are embedded in the polymer and cannot be accessed. Recently, a few reports have deposited NWs on the surface of a plastic substrate, followed by a contraction or stretching of the substrate. This achieves NW alignment by the shear force of
the underlying substrate [18–20]. However, the substrate materials that have been used, polydimethylsiloxane (PDMS) or polyvinylidene fluoride (PVDF) [17], are elastomers with relatively low stretching ratios, with maximum strains employed being limited to 120%. Consequently, (i) the low stretching ratio means that either high alignment cannot be achieved or multiple transfer/stretching cycles are required [18] which complicates the process and (ii) if stretched, these substrates return to the undeformed state without an applied force and thus the NWs must be transferred to another substrate while maintaining the stress on the original substrate. Additionally, breakage of the nanowires during stretching or contracting of the substrate is a severe problem that has not been addressed [21,22]. This latter issue is also problematic for assembly by contact printing and has been addressed by oil lubrication [15]. However, even with lubrication, the assembled NW lengths in that work are still only 50% of their original lengths.

In addition to the aforementioned issues, robust methods to quantify NW alignment are lacking. In many NW assembly papers, the alignment is assessed by measuring the angle of alignment of individual NWs in scanning electron microscopy (SEM) images by hand or through measuring the polarization effect of aligned metal NWs [16,23]. This is not only time consuming and inaccurate, but in the latter case also limited to metal NWs. Furthermore, the metric used to assess alignment varies from one study to another, making it difficult to compare the quality of alignment between different studies. There exist a few studies where image processing tools and standardized metrics are used. Unfortunately, however, they either employ the complicated autocorrelation function or they do not sufficiently explain their method in a way that NW researchers can understand and, subsequently, implement [24,25].

In this paper we demonstrate a simple, low cost, large-area, one-step NW alignment technique with minimal breakage and a high degree of alignment. This method can be utilized for NWs grown on a substrate or in solution, and is not limited to metallic NWs. Polyvinyl alcohol (PVA) films are used as the stretchable substrate. They can be stretched to 450% of the original size and do not shrink back after stretching. A lubricant, poly[oxy(methyl-1,2-ethanediyl)], is employed to nearly eliminate NW breakage while maintaining good alignment. Additionally, the feasibility of large-area NW transfer from PVA to a polyethylene terephthalate (PET) substrate is demonstrated. Lastly, a method for quantifying NW alignment using image processing is presented which uses quantities to describe orientational order consistent with
other ordered elongated structures such as liquid crystalline phases.

2. Experimental

2.1 Nanowire deposition

Silver NWs (AgNWs) dispersed in ethanol were purchased from Blue Nano Inc. (Charlotte, NC). The average AgNW diameters were 35 nm and 90 nm with average lengths of 7 µm and 16 µm, respectively. Ethanol was used to further dilute the as-received solution. Zinc oxide NWs (ZnO NWs) in powder form with average diameters and lengths of 50 nm and 4.6 µm, respectively, were purchased from M K Impex Corp. (Mississauga, Canada). The ZnO NWs were dispersed in isopropyl alcohol (IPA); polyvinylpyrrolidone (PVP) was added to the solution to improve the dispersion. For the purpose of minimizing breakage, a polymer lubricant poly[oxy(methyl-1,2-ethanediyl)] of various amounts was then added to the Ag and ZnO NW solutions. PVA films, obtained from Kuraray Co. (Tokyo, Japan, 70 µm thick) were sonicated in methanol for 30 min and dried in nitrogen. The NW/polymer solutions were then uniformly dispersed on 3 × 5 cm PVA films using Mayer rod coating (figure 1(a), (b)) [26–28].

2.2 Alignment method

The PVA films were immobilized in a vice and slowly stretched to 450% of their original lengths (figure 1(c), (d)). 450% is the manufacturer-specified maximum stretch ratio of the PVA. Larger stretching ratios led to film breakdown and smaller stretching ratios led to inferior alignment [16]. A heat gun set at 140 °C was directed at the substrate to facilitate stretching and prevent shrinkage post-stretching. Higher temperatures could not be used due to a visible breakdown of the film. Films were stretched at a constant strain rate of 0.002 s⁻¹ along the PVA film machine direction (MD) [29]. This rate was chosen since slower stretching rates did not improve alignment and at significantly higher rates the film deformation was partially elastic (i.e. the films shrank in length once the stretching force was released which is not preferred).

2.3 Lubricant removal

The lubricant poly[oxy(methyl-1,2-ethanediyl)] is soluble in ethanol at room temperature [37][38] and can be removed post-alignment if desired. Firstly, to increase adhesion of the nanowires to the PVA surface, the samples were pressed at room temperature using an electric rolling press (MSK-HRP-01, MTI Corporation, Richmond, CA). The samples were then immersed in ethanol for 5 minutes and dried using a heat gun at 85 ºC for 15 s. A fast evaporation time was necessary to prevent distortion of the PVA film. If transfer of the aligned NWs to another substrate such as PET is desired, lubricant removal can be done after the transfer.

2.4 Nanowire transfer

PET films, obtained from Dupont Inc. (Tianjin, China, 127 µm thick), were sonicated for 30 s in IPA then in deionized (DI) water. The PET was subsequently immersed in a 1 mol/L sodium hydroxide (NaOH) solution for 4 hours at room temperature to render the surface hydrophilic (this process can be shortened to 8 min if the NaOH solution temperature is raised to 70 ºC) [30]. The chemically-modified PET was then rinsed with DI water and dried in nitrogen. The aligned NWs on PVA films were pressed against the PET films (figure 2(a)) using the rolling press. The rolling speed was 5 mm/s, the temperature of the rollers was 70 ºC, and the distance between the two rollers was 115 µm.
2.5 Characterization
To investigate alignment and NW lengths before and after stretching, SEM images were taken of the samples, which were coated with a 10 nm thick layer of gold to prevent electron charging.

2.6 Image processing
Image processing is performed using the Python programming language interface to the Open Computer Vision Library (OpenCV) \(^3\) [31]. The image processing method consists of four sequential tasks all implemented using the OpenCV library methods: filtering, thresholding, object detection, and shape fitting.

The filtering task involves removing measurement “noise” from the image, where noise refers to variations of the image brightness localized to one or a few pixels. For example, for the case where there is a single pixel with high brightness in an area of the image where the intensity is otherwise low, the filtering task will reduce the outlier pixel brightness. A raw input gray-scale SEM image (figure 3(a)) is first normalized (0 → 1) and then filtered using a Gaussian filter function or “kernel” with the kernel size chosen to be smaller than the NW diameter to avoid loss of information (figure 3(b)).

The thresholding task involves digitizing the filtered image into the pixel values corresponding to either foreground (NW) or background (substrate). The output of this task is a binary image with pixel values being either foreground (1) or background (0). Global thresholding methods typically fail for images with significant noise or varying background intensity, thus an adaptive thresholding method is used [31].

The method determines a threshold for every pixel in the image based upon a localized calculation, where a Gaussian kernel is used as the localization function. Values above the threshold are assigned a 1, and values below the threshold are assigned a 0.

The object detection task involves using the binary image to determine the presence of objects in the image. Objects are essentially connected areas in the foreground of the binary image, which could include individual NWs, collections of overlapping NWs, or any other connected foreground feature resulting from the thresholding task. These regions are detected through the use of a border-following method [32] to determine a set of contours which enclose each of the objects in the image.

Given a set of candidate NW objects in the form of contour lines determined from the previous tasks, the shape fitting task involves determining which of these candidate objects could be individual nanowires through morphological analysis. A least-squares method [33] is used

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\(^3\) The image processing use in this work is provided in the supplementary information under an open-source license.
to find the minimum size ellipse which encloses each of the candidate NW objects. Then, if the aspect ratio of the ellipse is greater than 7, it is considered a NW. This value of 7 is determined through a convergence analysis of the orientational order parameters for the set of images. The orientation and lengths of the ellipses are used to approximate the alignment vectors and lengths of the NWs, respectively.

2.7 Quantifying Orientation Order

In order to quantify the presence of orientational order, or alignment, of the NWs the use of an alignment metric or set of metrics is needed. In past work [34] the use of an orientational order parameter \( S \), formulated to characterize two-dimensional nematic liquid crystalline phases has been used which ranges from 0 (random alignment) to 1 (perfect alignment),

\[ S = < 2 \cos^2 \theta_i - 1 > \]  

where \( <> \) is the statistical mean, and \( \theta_i \) is the angle between the average orientation vector \( \langle n \rangle \) and the axis of NW \( i \) \( \langle m_i \rangle \).

A simple method to compute both \( S \) and \( n \) simultaneously is presented [35], which involves computing a tensor order parameter,

\[ < Q > = < m_i m_i - \frac{1}{2} > \]  

and then finding \( n \) from the eigenspace associated with the largest eigenvalue \( \lambda_1 \) and \( S = \lambda_1 - \lambda_2 \), where \( \lambda_2 \) is the smaller eigenvalue. This simplified method is used in this work.

3. Results and discussion

3.1 Aligning nanowires

Figure 4(a) is an SEM image of 35 nm AgNWs prior to stretching, and shows that the NWs are randomly oriented. Figure 4(b) and (c) show SEM images of AgNWs on a PVA film stretched to 450%, without and with the addition of the polymer lubricant to the NW solution before deposition, respectively. In either case, it can be seen that almost all the AgNWs were aligned along the stretching direction due to the large shear force from the PVA film [16]. PVA compression in the orthogonal direction improves NW alignment as well [18].

It can clearly be seen that the NWs stretched without the use of the lubricant (figure 4(b)) broke into several short pieces after stretching, which is typically undesirable for device applications. The average NW length is 2.4 µm after stretching, compared to the 6.8 µm average length before stretching. And comparing the histograms in figure 4(b) to that of 4(a), the length distribution is compressed to lower values with nearly all NWs being less than 5 µm. The breakage is caused by too strong of an attachment force between the NWs and the PVA surface, and as the PVA is stretched, the NWs get pulled apart into multiple pieces.
When the polymer lubricant is used, good NW alignment is achieved with minimal NW breakage. In figure 4(c), where a volume ratio of poly[oxy(methyl-1,2-ethanediyl)] to AgNW solution of 1:1300 was used and the nanowire density is 3 NWs/100 μm², the average NW length after stretching was 6.8 μm and the length distribution, as seen in the histogram, appears similar to that before stretching. The polymer reduces friction between the AgNWs and the PVA film as well as acts as a shear force medium.

To achieve good alignment and minimal breakage, the properties of the chosen polymer lubricant is important. Several different polymers were tested. If the polymer viscosity is too low, NW breakage will still occur since the NWs will still have a significant friction force with the substrate surface. If it is too high, the alignment will degrade since the polymer does not flow easily with substrate stretching. Furthermore, because the PVA is stretched at an elevated temperature, the polymer cannot harden or evaporate under heat. It was found that poly[oxy(methyl-1,2-ethanediyl)] has an appropriate level of viscosity and can flow when the substrate underneath is stretched. It does not solidify or evaporate quickly, and can be removed post-alignment with ethanol. Through the use of this lubricant, the NWs do not have a strong attachment force to either the substrate or the lubricant and therefore do not break. They become aligned with the flowing force of the polymer, similar to NW assembly using microfluidics.

Nanowires of various densities were aligned. Figure 5 shows the alignment of nanowires with a density of 20 NWs/100 μm². At this higher density, good alignment is still achieved and the average NW length is 6.6 μm, nearly the same average length as at a density of 3 NWs/100 μm². However, for samples denser than shown in figure 5, more NWs become tangled and alignment is degraded.

To demonstrate the versatility of our alignment method, ZnO NWs were also aligned. Unlike the AgNWs used in this work, which are synthesized in solution [36], the ZnO NWs were grown on a substrate using chemical vapor deposition (after which they were removed from the substrate as a power and dispersed in solution). SEM images of the ZnO NWs before and after alignment are shown in figure 6. The volume ratio of polymer lubricant to ZnO NW solution was 1:600. Similar to the AgNWs, the ZnO NWs were well aligned after PVA stretching, with minimal breakage. The average NW length after alignment was 4.4 μm, only slightly less than the original 4.6 μm average length.

The orientation order parameter, S, quantifies alignment conveniently and objectively, and makes it feasible to compare alignment results between different studies. Otherwise, measuring NW angular distribution by hand (the most common way previous studies used) without any bias is impossible. In our study, S was calculated for both the 35 nm diameter AgNWs and 90 nm diameter AgNWs aligned with various polymer lubricant concentrations (tables 1(a) and 1(b)). The densities of the aligned nanowires was 3 NWs/100 μm² and 1 NW/500 μm² for the 35 nm and 90 nm nanowires, respectively. S was calculated from a minimum of 400 NWs in each case. It can be seen that when the polymer concentration is too low, the average NW length is small. If the polymer concentration is too high, S is lower, indicating poorer alignment. The optimal balance between minimizing breakage and maximizing alignment for the 35 nm diameter NWs occurred at a polymer/AgNW solution volume ratio of 1:1300, and 1:400 for the 90 nm diameter NWs. For the Mayer rod used (#10), it can be calculated that the height of deposited polymer in each of these cases is 35 nm and 114 nm, respectively. Therefore, the thickness of the polymer lubricant in the optimal case is approximately equal to the diameter of the NWs.

To be able to compare our alignment results to studies where S is not used, the angular distribution of the aligned...
Figure 6. SEM images of ZnO NWs (a) before substrate stretching, and (b) after substrate stretching with lubricant (scale bar: 10 µm).

Table 1. (a) Average length and orientational order parameter, $S$, of 35 nm diameter AgNWs aligned using different polymer concentrations

<table>
<thead>
<tr>
<th>Polymer/AgNW solution volume ratio</th>
<th>Average length (µm)</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No polymer, no stretching</td>
<td>6.81</td>
<td>0.15</td>
</tr>
<tr>
<td>No polymer, stretched to 450%</td>
<td>2.40</td>
<td>0.96</td>
</tr>
<tr>
<td>1:7800, stretched to 450%</td>
<td>3.52</td>
<td>0.97</td>
</tr>
<tr>
<td>1:5200, stretched to 450%</td>
<td>3.97</td>
<td>0.95</td>
</tr>
<tr>
<td>1:3900, stretched to 450%</td>
<td>4.18</td>
<td>0.96</td>
</tr>
<tr>
<td>1:2600, stretched to 450%</td>
<td>4.99</td>
<td>0.97</td>
</tr>
<tr>
<td>1:1300, stretched to 450%</td>
<td>6.76</td>
<td>0.93</td>
</tr>
<tr>
<td>1:130, stretched to 450%</td>
<td>6.62</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Table 1. (b) Average length and $S$ of 90 nm diameter AgNWs aligned using different polymer concentrations

<table>
<thead>
<tr>
<th>Polymer/AgNW solution volume ratio</th>
<th>Average length (µm)</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No polymer, no stretching</td>
<td>16.22</td>
<td>0.34</td>
</tr>
<tr>
<td>No polymer, stretched to 450%</td>
<td>9.25</td>
<td>0.95</td>
</tr>
<tr>
<td>1:3000, stretched to 450%</td>
<td>10.31</td>
<td>0.94</td>
</tr>
<tr>
<td>1:400, stretched to 450%</td>
<td>16.14</td>
<td>0.95</td>
</tr>
</tbody>
</table>

NWs was amassed from the image processing data (figure 7). More than 85% of the NWs are aligned within ±10° of the stretching direction.

3.2 Nanowire transfer

Devices can be made using the aligned NWs directly on PVA. Or, if a different substrate is desired such as PET, the aligned NWs can be transferred as described in the experimental section. Figure 2(b) is an SEM image of aligned 90 nm AgNWs after transferring to a PET film. All the AgNWs remained aligned and there wasn’t obvious breakage after the transfer process. In addition, less than 2% of the NWs were found on the PVA films after transfer, indicating that almost all the NWs had been transferred to the PET films.

Figure 7. Angular distribution of 35 nm Ag nanowires aligned using polymer lubricant.

3.3 Comparison to other alignment methods

Very good alignment results can be achieved by many assembly methods such as bubble-blown films and using an electric/magnetic field, but all these methods [12–14] have limitations such as complicated fabrication processes, NW materials, scalability, and/or NW breakage. The alignment method in our study is very simple while achieving good alignment and minimal breakage. In other works where $S$ was used to quantify NW alignment [25,34,39], the highest value obtained was $S = 0.92$. In our work, we achieved an $S$
value as high as 0.97 (table 1(a)), with some breakage, and $S = 0.95$ with very minimal breakage (table 1(b)). In studies where stretching or contraction of a substrate [17,18,20] is employed $S$ was never used, but comparison can be made using the angular distribution data in figure 7. The alignment in this work is superior to all these other works (except for the case where aligned NWs are transferred to another substrate and stretched for a second time, a strategy which could also be used in the current study to improve alignment). The reason is that PVA was used as the stretching substrate rather than PDMS or PVDF, which can support much higher strains than the latter materials.

This method does not have limitations on the type of NW material that can be aligned and is available for NWs in solution or grown on a substrate. In the latter case, the NWs can be sonicated and dispersed in a solution for deposition as was done in this study, or the NWs can be transferred to the PVA through mechanical sliding of the growth substrate across the PVA surface.

4. Conclusions

Aligning NWs by stretching PVA is a simple, low-cost, large-area NW alignment method that can be used for both metallic and semiconductor NWs synthesized either in solution or on a substrate. Because PVA can be stretched 450% and does not retract after stretching, the method is both highly effective and convenient. Using poly[oxy(methyl-1,2-ethanediyl)] as a lubricant significantly reduces NW breakage which solves a persistent problem with shear force-based alignment methods. Image processing was shown to provide an effective and rapid way to analyze NW alignment. In future work, we will apply this alignment method for device integration.

References

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