Fabrication of micro/nanowire fibres, novel fibre devices and their applications

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Fabrication of micro/nanowire fibres, novel fibre devices and their applications

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Summary

The research topic comprises of the fabrication of specialty fibres, fibre-based novel devices and their applications.

The focus of fabrication is to realize novel high-throughput micro and nanostructured fibres through scalable methods, the newly developed planar-fibre nanomanufacturing, which combines the conventional microstructuring techniques with fibre drawing. This hybrid process enables fabrication of high aspect ratio (length-to-width ratio) one-dimensional (1D) nanostructures, such as metallic micro/nanowires and nanoribbon-like chalcogenide semiconductors (e.g. germanium-antimony-telluride, GeSbTe or simply GST) embedded in a glass-clad material of choice.

Based on some fibre-based device designs, functional fibre-based photodetectors are achieved by multilayer coatings and electrode fabrication. The conventional deposition methods behind fibre coating, thermal or electron-beam evaporation and RF sputtering technique, are employed to carry out the desired device fabrication.

As far as applications, we will target fiberized photodetectors, photodiodes, plasmonics and non-linear optics.

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1. Introduction

1.1 Background

A quick review on the background regarding fabrication of micro/nanowire fibres (MNFs) and fibre-based novel devices is introduced. A variety of advanced fabrication techniques of MNFs in planar and fibre configurations are shortly reviewed in the first part and preliminary studies of fibre-based devices such as photodetectors, batteries, supercapacitors and photovoltaic (PV) cells, are gone through briefly in the following part.

1.1.1 Fabrication of Micro/Nanowire Fibres

Nanoscale features or one-dimensional (1D) structures, such as nanowires (nanofibres or whiskers), nanoribbons (nanobelts) and nanotubes as illustrated in Figure 1.1, have been the intense research subject since their realization few decades ago. They exist in various types of materials such as metals, superconductors, dielectrics, organic/inorganic molecules, or semiconductors. Among them, semiconductor and metallic 1D nanostructures have gained huge research investment and effort due to their particular physical properties that can't be found in bulk material structures. Much lower electrical and thermal conductivity due to quantum dissipation and electron scattering from boundaries, extremely high coercivity for high-density data storage, higher and consistent specular and diffusive transmittance and very high aspect ratios for transparent flexible electrodes, are those main properties as compared to their bulk counterparts. Semiconductor nanowires possess a great scope of promising applications [1] in the areas of electronic (FETs, diodes, or logic devices) [2], optoelectronic or photonic (laser, photodetector, LED) [2-5], biological (drug delivery, sensors) [6], energy (thermoelectric generators, batteries, solar cells) [7, 8], and magnetic (memory, spintronic) [9-11] devices.

Along with it, a vast range of their fabrication techniques have been evolved with emerging new active materials and advanced device designs.

Semiconductor nanowires have been realized by a variety of approaches which can be categorized into one of two main paradigms according to their fabrication fashion, top-down or bottom-up. Top-down strategies (lithography techniques combined with etching processes) are carried out by successive cutting or etching structures from a

bulk of material into a nano-sized features, on the other hand, bottom-up strategies (MBE: molecular beam epitaxy, VLS: vapour-liquid-solid mechanism, MOVPE: metalorganic vapour phase epitaxy, soft templating, to name a few) are referred to that where structures are built up from the bottom base: cluster by cluster, molecule by molecule or atom by atom [12].

Figure 1.1: Schematic representation for different 1D nanostructures: (A) Nanowires (whiskers or nanofibres), (B) Nanoribbons (nanobelts), (C) Nanotubes.

By taking both benefits from top-down and bottom-up processes, directed self-assembly (DSA) [13, 14] and superlattice nanowire pattern transfer (SNAP) [15] strategies have been developed for nanowire array fabrication, which presents a number of advantages over other approaches. It provides sub-lithographic resolution through multiplication of patterns, and as such, increasing the feature density by taking out some complex processes such as high-density lithography and double patterning. Additionally, DSA is a relatively economical process yielding high throughput and producing specific device geometries. The SNAP process forms a pattern by selectively etching one of the layers in a superlattice thin film grown from bottom-up, producing large nanowire arrays in the form of metals, insulators, and semiconductors, but is somehow limited with geometries of structures and complexity of process.

In the meantime, various kinds of techniques have been also explored to synthesize metallic nanowires – electrochemical approaches [16-18], nanoimprint lithography [19], synthetic chemical routes [20], and template assisted technique [21], chemical vapor deposition (CVD) [22], and electric arc discharge methods [23]. To overcome

the limitations (cost, efficiency, or mass production) of above-mentioned techniques, electrospinning technique has been proposed [24, 25] and developed recently [26-28] to achieve metallic, polymeric, and ceramic nanowires. Although this technique is relatively simple in terms of set-up and theory, yet there exist several challenges to overcome for smooth and continuous nanowires – precursor optimization, jet instabilities, limited fibre length, and control of microstructure [29]. Despite of their developed fabrication processes, very limited real time applications have been proposed so far due to difficulties encountered in their reliable characterization and integration with other materials and systems. They have found some applications with electrodes for batteries, nano-reinforcement for composite materials, conductive transparent film for photovoltaic (PV) cells, sensors, and key factors for future MEMS and NEMS [29].

Except for those above-mentioned nanowire fabrication methods in planar configurations except for electrospinning, a few other advanced fabrication techniques in optical fibre form have been performed to yield mass production of micro/nanowire fibres (MNFs) from polymers or glasses. Along with it, plenty of their applications have been also investigated in many research areas as shown in the Figure 1.2.

MNFs are normally realized directly from a bulk glass [30] or glass fibre [31-33] via a well-known and commonly used approach – taper drawing with a flame/laser or electrically heated configurations. Under a certain pulling force and heat condition, the fibre is stretched and elongated gradually so that the control of reduced diameter and length of the fibre taper can be reached. Laser-heated taper drawing presents an advantage over the other taper drawing techniques, which is free from H₂O/OH contamination. On the other hand, electrically heated taper drawing gives more flexible shapes into the geometries of MNFs and is much more convenient for drawing MNFs from soft glasses.

At the same time, fabrication of polymer MNFs has been also developed through physical drawing [34, 35]. Inserting a sharp needle tip (a fibre tip or AFM tip) into the polymer melt or solution and then pull out of it, forming and patterning suspended MNFs into useful nanostructures and 3D geometries could be achieved.

Besides taper drawing as a post procedure of optical fibres, two melt-filling methods have been also explored to realize high-purity metallic nanowires in the air channels of

photonic crystal fibres (PCFs) – high temperature pressure filling [36] and splice-fibre pressure filling [37] techniques.

High temperature pressure filling: a piece of gold is placed in a pressure chamber and heated up to 1200°C. Once the gold is molten into a solution, silica PCF is inserted into the solution while applying argon gas with a high pressure into the chamber, as such, the molten gold is pressed into the air cladding of the PCF.

Figure 1.2: A series of potential applications of optical MNFs [32].

Splice-fibre pressure filling: a gold wire (diameter of 50um) is placed at the end of a silica capillary (OD=200um & ID=80um). One capillary end-face is cleaved and cleaned to splice to silica PCF. Careful adjustment of splicing parameters should be taken to keep the splice mechanically strong and hollow channels open. Then, the

spliced fibres are loaded into a pressure chamber and heated up to 1200°C. At the same time, high pressure is applied from the other end of the capillary, inducing the gold melt to run into the air channels of the PCF. It should be noted that the materials have considerable lower melting temperatures than the softening point of the silica to be properly injected into the holes.

Recently, a few of specific polymeric, metallic and chalcogenide semiconductor nanowires have been realized through fibre drawing nanomanufacturing technique [38-40], which has resulted in well-ordered and oriented, ultralong nanowires, excellent controls over structures and dimensions and as well the desired functionality. This fibre drawing nanomanufacturing basically involves two processes – rod-in-tube and draw-cut-stack methods as schematically illustrated in Figure 1.3.

In the first process of rod-in-tube, a chosen material powder or rod (metals or metal alloys) is poured or sleeved into a specific glass tube for the first fibre drawing. Then, the first drawn fibres are cut into equal-length segments and stacked together to form desired-shape of bundles and inserted into a tube again for next drawing. By iterative process of draw-cut-stack with fibre drawing techniques, one could achieve nanoscale features desired while preserving the ordered arrangements.

In case of employing polymers as outer matrices, some chalcogenide semiconductor or metallic rods with comparable thermal properties are inserted into a polymer tube realized from thin-film rolling followed by consolidation process. As same way, iterative draw-cut-stack processes are performed and obtained globally oriented, endless parallel, axially and radially uniform nanowires.

Figure 1.3: Schematic illustration of rod-in-tube and draw-cut-stack methods.

1.1.2 Fibre-based Novel Devices

Wearable, flexible, and portable devices are promising for next-generation photodetectors, solar cells, energy conversion or storage devices. Optical fibres are one of the appropriate options for those applications by taking advantage of their flexible and optical properties.

Recently, fibre-based novel devices are of huge interest and importance due to their flexibility and wearability. Fibre-based photodetectors were realised by a branched double-shell heterojunction nanowire array synthesized radially on a flexible micro-optical fibre with enhanced performance through the piezo-phototronic effect from zinc oxide (ZnO) nanowires [41-43]. Fibre-shaped organic photovoltaic cells [44] and fibre-array thin film solar cells [45] are promising building blocks for practical applications in future high efficiency and cost-effectiveness of solar cell architectures. In addition, a stretchable fibre-based dye-sensitized solar cell (DSSC) with stable electrolyte from hydrophobic ionic liquid-gel has been realized [46]. The developed stable electrolyte based on polymer-ionic liquid gel has been shown enlarged durability and high non-volatility so that it can suffer from high temperatures up to 300°C, which renders the device more compatible to stretching deformations or bending and environmentally adaptive. A new fascinating material, perovskite, has been attracting increasing attention for flexible solar cells possessing enhanced energy conversion efficiencies with respect to organic PV cells. Very recently, a fibre-shaped perovskite solar cell has been fulfilled for the first time [47, 48]. Novel configurations forming PV cells based

on fibres are all-solid-state; moreover, they could be interlaced into well-developed textiles for a huge-scale system [49]. Lastly, fibre-based energy conversion and storage devices [50] like supercapacitors [51, 52] or lithium-ion batteries [53, 54] have been realized in various novel functional materials and configurations. These devices will be considered as next-generation wearable and portable components that can be woven into large piece of textiles.

1.2 Motivation, Objectives and the Major Contribution

Due to the drawbacks and limitations (mass-production, time-consuming and cost-effectiveness for top-down, and reliability or reproducibility for bottom-up methods) of above-mentioned techniques for fabrication of nanostructures, a novel technique has been developed that combines planar fabrication and fibre drawing techniques. It provides ultralong nanostructures (nanowire or nanoribbon) with a single fibre draw by taking an advantage of thin film thermal properties.

Building complex nanostructures with new materials hold the key for several next-generation fibre-based devices, when combined with new simple fabrication methods allow large volume production in a time efficient and cost effective way.

Milestones set by the project of “Fibre-Drawing Nanomanufacturing” are undertaken throughout my study, which includes the nanomanufacturing of functional material in fibre form and novel fibre-based devices with applications in the fields of optoelectronics, plasmonics, or nonlinear optics.

The major contribution of this thesis is the fabrication of functional metallic or semiconductor micro/nanowires through the hybrid method developed by integrating thin-film microstructuring processes and fibre drawing techniques. Ultralong nanowires (up to 3cm) have been realized via this approach in a way of mass-production and less time-consuming, which is relatively remarkable compared to other fabrication methods and has the advantages that it is flexible, easy-to-handle and easy-to-integrate it into other devices or optical telecom systems as it is in fibre form.

1.3 Organization of the Thesis

The thesis is divided into the following chapters, comprising of a series of detailed steps for preparing the fibre preforms, fibre drawings and fibre-based photodetectors along with their applications.

Chapter 1: A brief introduction and background of the fabrication techniques of micro/nanowire fibres are addressed and followed by the motivation and goals based on it.

Chapter 2: A comprehensive guide of preparation of the fibre preforms and fibre drawings is discussed. Every detailed steps of the preform preparation are covered in the first part, which includes cutting and polishing of chosen glass rods, deposition of materials by means of the combination of lithography and conventional deposition techniques including thermal/e-beam evaporation and sputtering process, and fusing the glass rods back forming the final preforms to be ready for the fibre drawing which is described in the second part. Applications of the drawn fibres are briefly explored in the last part.

Chapter 3: A concept of realising all-in-fibre devices is presented by coating multilayer of functional materials around a coreless bare silica fibre, which are working as photodetectors.

Chapter 4: Some future works are proposed in this last chapter regarding fabrication of multimaterial fibres with intriguing structures for multifunctional applications and next-generation fibre-based components (solar cells, photodetectors, energy storage devices, etc.) with novel emerging materials and building structures.

By following all above chapters, a list of references and publications regarding this work are provided. In addition, appendices related to the fabrication of sputtering target (N-LAF7 as an example), a list of fibre draws and fibre draw data are attached.

2. Preparation of Fibre Preforms and Fibre Drawing

The entire processes, starting from preparation of fibre preforms to fibre drawing, have been performed through the action of planar-fibre nanomanufacturing which is a hybrid method we have developed by combining planar micro/nanofabrication technique and fibre drawing technique. This new concept of innovative manufacturing method enables the realization of metallic nanowires embedded in silicate glass fibres by taking advantage of the melting point depression commonly seen in thin films. Furthermore, this method allows an unprecedented ability to combine materials with different thermal properties in a fibre draw tower. As a proof of principle, of the potential of this process, semiconductor nanoribbon-like structure of Germanium Antimony Telluride (GeSbTe or simply GST) that thus far has not been realized in fibre form was drawn with single fibre draw.

2.1 Preparation of Fibre Preforms

The method of planar-fibre nanomanufacturing involves four main steps; glass preparation – cutting glass rods and polishing the facets of half-cut rods, planar patterning and materials deposition, preform fusing, and fibre drawing. Figure 2.1 illustrates the schematic view for the preparation of fibre preforms. Every detailed step is described in the following.

Figure 2.1: Schematic view of each step for preparing fibre preforms as an example of single-line gold nanowire fibres: (A) Commercial Schott glass rod, (B) Half-cut rods along the length, (C) Photoresist or contact mask for photolithography and deposition, (D) Material deposition through e-beam/thermal evaporation or sputtering, (E) Lift-off process, (F) Vacuum fusing the glass rods back.

2.1.1 Cutting/Polishing of Glass Rods

Commercial silicate glass rods, N-SF8 (refractive index $n_{(\lambda=578\text{nm})}=1.69413$ & $n_{(\lambda=546\text{nm})}=1.69413$, softening temperature $T_{10}^{7.6}=678^{\circ}\text{C}$) and N-LAF7 (refractive index $n_{(\lambda=578\text{nm})}=1.7495$ & $n_{(\lambda=546\text{nm})}=1.75459$, softening temperature $T_{10}^{7.6}=669^{\circ}\text{C}$) with 10mm-diameter and 10cm-long, were chosen to support gold (Au) and GST materials ($T_m=600^{\circ}\text{C}$), respectively. The glass rods were cut in half along the length using precision cutting saw having thickness of 0.8mm to create two flat facets as shown in Figure 2.2.

Figure 2.2: (A) Commercial N-SF8 Schott glass rod, (B) Half-cut rod along the length.

Then, lapping and polishing of the facets were followed in sequence to yield a flat and optically smooth surface, which allows the novel introduction of planar fabrication techniques into the process. First lapping was done with $9\mu\text{m-Al}_2\text{O}_3$ for 20 minutes and then followed by another 20 minutes of lapping with $3\mu\text{m-Al}_2\text{O}_3$. About 20min of polishing was then accompanied to have smooth optical surface of facets in order to aid homogenous spinning of photoresist and better surface adhesion of deposited layers. Figure 2.3 displays the machine for lapping and polishing, fitting the half-cut rod into a jig, and the final two facets with smooth optical surface after lapping and polishing.

Figure 2.3: (A) LP50 Precision Lapping and Polishing System, (B) Half-cut rod is attached to a jig ready for lapping and polishing, (C) Polished glass rods with flat and clean facets.

Microscope images of the half-cut facet are illustrated in Figure 2.4 before and after polishing, demonstrating that the surface roughness is much reduced and developed for next action.

Figure 2.4: Microscope images of a half-cut facet (A) before and (B) after polishing.

To attain the maximum process reliability, it's recommended for the polished glass rods to be cleaned and dried prior to applying the resist. The polished glass rods were cleaned through a series of consecutive steps with acetone, isopropanol (IPA), and followed by a deionised (DI) water rinse. After that, the glass rods are dried with nitrogen blow and heated in a 90°C convection oven for 30 minutes to dehydrate the facets for the subsequent action of spin coating of photoresist on the flat facet.

2.1.2 Materials Deposition

This section consists of a chain of sequential processes – spin coating of photoresist on the facet, soft bake, and photolithography, developing, planar deposition and lift-off or etching. These whole processes are summarized in Figure 2.5.

Spin coating: one of the polished and cleaned facets was used to spin coat the required photoresist in order to introduce micro-scale patterns into the preform, which will scale down to nanoscale features during the fibre drawing. Two different photoresists, LOR 30B and positive S1828, were used to realise bi-layer resist stack which accommodate submicron line-width control and thickness, excellent adhesion, and finely tuned undercuts. The recipes for LOR 30B and S1828 resists were at the speed of 5000rpm for 60 seconds, which had the final bilayer, resist thickness around 5µm. The thickness can be varied over a broad range depending on a variety of spin coating conditions

(refer to MicroChem). Figure 2.6 (A) shows the photoresist on the facet before spinning, which attached to a vacuum holder.

Figure 2.5: The entire processes for pattering required material on the facet.

Figure 2.6: (A) Photoresist before spin coating, (B) Photoresist after development, (C) Measured thickness profile.

Soft bake: a pre-exposure bake or soft bake was followed to dry the film and to fix the development and undercut rate after spinning each photoresist. The temperature for soft bake is the crucial factor on undercut rate, although exposure dose of the S1828 resist, developing time, baking time, and choice of developer are also influential. Soft bake is typically carried out on hot plate; 6min of bake on 150°C hot plate and 2min of bake on 100°C hot plate for LOR 30B and S1828 were conducted, respectively. No

intermixing occurred between the two resists, permitting the S1828 resist to be applied and soft-baked directly on top of the LOR 30B resist.

UV exposure: subsequently, any given pattern was introduced by UV exposure through a photomask with Karl-Suss MA6 double-sided mask aligner. The exposure time depends on the resist thickness and optical transparency of the substrate materials. 30 seconds of exposure time was applied for the bilayer stack of resists.

Developing: a development process was followed right after the UV exposure. Both resists are sensitive and designed to offer superb control of undercut process in metal-ion-free developer, Shipley's MF-319. The bilayer stack was developed for around 2-3min, but typically it would take 1min for single layer of resist. Figure 2.6 (B) shows the resist after development in MF-319 for 2min and the measured thickness profile is depicted in Figure 2.6 (C), which was calibrated from KLA Tencor P-16 Stylus Profiler giving the thickness of around 5 μ m.

Thin-film deposition: after development of the resist, conventional thin film deposition methods such as plasma sputtering, CVD, or thermal/ e-beam evaporation techniques were utilized to deposit the desired material on the facet of the pre-patterned preform. Thermal evaporation (Edwards Auto 306)/e-beam evaporation (Edward Auto 500) and sputtering (Kurt J. Lesker Sputter) were used to deposit 1 μ m-thickness of single-line Au film and 2 μ m-thickness of few-line GST film on the facet of N-SF8 and N-LAF7, respectively.

In the case of GST material that is highly reactive functional material and would easily oxidize on the exposure to atmosphere, an optional capping layer made from the same material of the glass rod was deposited to protect the patterned material from oxidation and contamination. A detailed fabrication process of N-LAF7 glass target for sputtering will be found in Appendix A.

Lift-off or etching: lastly, lift-off or etching process has been done to reveal the patterned material on the flat facet by removing the resists. SVC-14 solvent was used to strip off the LOR 30B resist. The preform was immersed into a beaker filled with SVC-14 and put in an ultrasonic wave environment for 5min. As a test example, a patterned 2 μ m-thickness of GST film on glass substrate was released, which is shown in Figure 2.7 with very sharp edges.

Figure 2.7: (A) 2μm-thick GST film resulted from the lift-off, (B) Optical microscope image corresponding to the small red-color box in (A).

Figure 2.8 demonstrates the outcome, an array of micro-scale GST-film lines deposited on half-cut N-LAF7 glass facet, resulted from lift-off process and the measured film thickness, nearly 2μm from the profiler.

Figure 2.8: (A) An array of GST lines patterned on polished N-LAF7 glass facet, resulted from lift-off process, (B) A profile of measured thickness of the GST film.

Along with lift-off process, a similar result could be achieved from dry etching by OPT Plasmalab 80 Plus Reactive Ion Etcher (RIE). An example of GST film from dry etching is shown in Figure 2.9 under the condition with 20 sccm (Standard Cubic Centimeters/Minute)-argon gas flow rate, 100mTorr-chamber pressure, 200V (volts)-forward power, and running time of 1 hour.

Figure 2.9: Microscope images of patterned GST film resulted from RIE etching.

It should be noted that instead of using photolithography technique, the use of patterned shadow/contact mask would also produce similar results, but not sharp as the one from photolithography and with simple design patterns. A brass contact mask with desired pattern having single-line or double-line was machined as shown in Figure 2.10 (A) with required dimensions. This mask was tightly contacted with rod facet and followed by conventional deposition of materials. Figure 2.10 (B) and (C) demonstrate the deposited materials on the facets through contact mask. Like the preceding, the GST film was covered once again with N-LAF7 to prevent it from oxidization and contamination.

Figure 2.10: (A) Designed contact mask, (B) Single-line gold deposited from the mask, (C) GST deposited from the mask.

2.1.3 Fusing of Glass Rods

Finally, the two half-cut glass rods are fused back together in a vacuum furnace. Figure 2.11 (A), (B) and (C) demonstrate the schematic of fusing the rods, putting one rod on the other one prior to fusing in a vacuum furnace and the fused rods forming final

preform for last fibre drawing, respectively. The fusing conditions for N-LAF7 and N-SF8 are listed in the following Figure 2.12 (A) and (B), respectively.

Figure 2.11: (A) Schematic design for fusing the rods, (B) Stacking two rods for being fused in a vacuum furnace, (C) Fused rods form final preform ready for fibre draw.

Figure 2.12: Fusing conditions of the glass rods: (A) N-LAF7, (B) N-SF8.

Alternatively, an alternative with a furnace of nitrogen gas flow condition can also be utilized by controlling the gas flow rate into the chamber. As you might be noticed from the graph, the fusing temperatures are slightly lower than the softening points of the glass rods in atmosphere.

2.2 Fibre Drawing and Physical Characterization

Fabrication of fibres from the above fused glass rods have been performed through the technique of preform-rod drawing. A list of fibre draw runs and an example of run data sheet will be found in Appendix B and C.

A schematic diagram of fibre draw tower comprising of each part as annotated is illustrated in Figure 2.13, which is connected to an inert gas control system and a computer control system.

Figure 2.13: A schematic diagram of the fibre draw tower.

The fused final preform was fed into the preform holder on top of the tower and placed in an appropriate position in the furnace, and the feed speed is managed by preform feed control system. There was a weight attached to the preform to compensate for the higher viscosity that is necessary when caning. Figure 2.14 (A) describes the schematic view of preform positioning in the furnace, the corresponding photograph is shown in Figure 2.14 (B), and the furnace set-up is displayed in Figure 2.14 (C).

The temperature of a susceptor can be tuned from 100°C up to 1500°C through the windings of RF coil induction system as can be seen in Figure 2.14 (C). Stainless steel or carbon (graphite) susceptor was employed as a heat element to heat the fibre preform. Also, susceptors with different sizes in diameters and lengths can be applied depending on the sizes and shapes of preforms. It has been shown from the temperature measurement of the centre of preform (preform temperature) that carbon susceptor has higher temperature than stainless steel susceptor in preform temperature, and the difference was around 100°C when susceptors were inductively heated by a water-cooled RF coil, i.e. the temperature difference between susceptor and preform was

around 200°C and 100°C for stainless steel and carbon susceptors, respectively. Furthermore, the preform temperature is not exactly proportional to the susceptor temperature and normally it is less in preform temperature, i.e. if the susceptor temperature was increased by 10°C then the preform temperature would only increase by around 6°C. If the neck of the preform moved vertically out of the hottest zone of the susceptor this sensitivity was reduced further. Altering the length of the susceptor had a marked effect on the drawing temperature. A shorter susceptor made the hot zone of the furnace narrow and reduced the amount of heated glass; the converse was also true. Hence, the top half of a long susceptor only preheated the glass before it was heated to final drawing temperature in the lower half. It was found that this preheating was a major factor in improving the drawing of fibres, which allowed lower temperature to be used.

Figure 2.14: (A) Schematic view of preform position in the furnace, (B) Preform with a weight attached, (C) Fibre drawing furnace set-up.

Cooling of the preform or the susceptor was accomplished by injecting the inert gas (nitrogen or argon). The preform core and preform skin temperatures were varied according to the different flow rate of the inert gas, which is shown in Figure 2.15.

Figure 2.15: (A) Temperature calibration set-up for preform core, (B) Temperature calibration set-up for preform surface, (C) The measured results of preform core and surface temperature changes depending upon the gas flow rate.

The fibre drawing temperature (preform core temperature) was affected by several parameters. Short preforms drew at lower temperatures as the wires holding an attached mass to them, and them to the preform feed mechanism, would couple with RF coil, introducing additional heating. The diameter of the preform also has a substantial effect on the fibre drawing temperature. The drawing temperature of identical glasses could drop by up to 20°C by replacing from an 8mm to a 10mm diameter preform. The positioning of the preform in the susceptor also had some effect. If it were positioned slightly off from the centre, the initial drawing temperature would be slightly lower than for a centrally positioned preform. This would generally correct itself as the rod softened, and deformed to hang vertically, especially if a large weight was attached. As mentioned in the above, of course, the inert gas flow also significantly had an introduction to the drawing temperature and even in the reduction of preform viscosity as evident on the tension in the fibre during a draw.

The fibre drawing was performed under a variety of initial conditions. The weight attached to the bottom of the preform was varied from 0-180g; the length of the susceptor and the inert gas flow could be varied. The most crucial part of the draw is the initial neck down, when the neck in the preform forms and starts to drop down. When the initial set temperature was too low, and therefore the neck had not appeared after some time, necking often began at a relatively high temperature. The fibre drawn from the neck would then have low tension, indicating that significant overheating was required to initiate necking. It was found that dropping the temperature could alleviate

this problem. For example, if the preform had been held at 900°C (susceptor temperature) for around 20 minutes with no sign of necking, a drop to around 600-700°C (well below the drawing temperature) for ten minutes followed by ramping up to 910°C (ramp rate of 100°C/min) would produce necking whereas a slow increase from 900°C to 910°C would not. This might be due to the heating rate dependence of viscosity or movement of the hot zone with temperature, but it is most likely due to thermally induced stresses. As has been previously seen from Figure 2.13 (C), the surface is the coolest part of the preform which may have given rise to a high viscosity layer around the outside of the preform that prevents the necking. The thermally induced stresses caused by rapid heating of the preform may plasticise this surface layer of the preform, allowing flow to take place at a temperature that would ordinarily leave this layer solid.

Once the neck was started, the manner in which the draw proceeded became critical. The success of the pull was determined by the first minutes after initial necking. With a low temperature and high feed the diameter of the preform reduced slowly making a long cane of preform and a large quantity of the available preform could be wasted. With the temperature too high and the feed too low, the drop rapidly sped up and the neck moved up out of the maximum of the hot zone. This might have two effects. Firstly, the temperature at the neck of the preform dropped off rapidly giving increasingly stiff fibre as the neck moved higher, this could break the fibre. Secondly, as the temperature of the susceptor had a decreasing impact on the temperature of the preform at the neck, the control over the temperature of the draw was reduced. The level of feed required to replace the preform removed from the hot zone depended on the diameter of the fibre and its drop rate, both of which were relatively difficult to gauge in the early and crucial part of the draw.

The diameter and tension of the fibre could be monitored through the diameter monitor system and tensile strength measurement system (or by hand simply), respectively, once the fibre was on the pulling drum. Some adjustments made to keep the tension steady. The procedure is relatively simple; low tension means the drawing temperature is too high and a reducing fibre diameter meant that more preform is being removed from the neck than being added. Pulling a fibre at low tension introduces a fibre with irregular cross section and diameter and at too high tension the fibre would break.

Lastly, the most critical point with this fabrication method is the pulling speed to realize ultra-long (up to cm) of nanowires or other nanoscale composites encased in

protective glass fibres with one single draw. The pulling speed should be fast enough (up to few hundred meters per minute) to reduce the staying time of the preform neck in the furnace and hence be able to achieve continuous ultra-long wires by taking advantage of thin film thermal properties as shown in Figure 2.16. From the measurements, we can see that the N-SF8 preform has its transition temperature around 600°C as marked with orange arrow and 1 μ m-thickness Au film has its melting temperature around 800°C as marked with black arrow, inferring that the softening point of N-SF8 preform is comparable to melting temperature of the Au film.

Figure 2.16: Thermogravimetric/Differential thermal analysis of gold thin film (Thickness=1 μ m, in black), bulk gold (blue) and N-SF8 preform (red), measured by Behrad.

As you can see from the microscope images in Figure 2.17, continuous and ultra-long wires could be realized, but some defects were also present at some points, probably due to the fluctuation of temperature with furnace or preform fusing. By appropriate combination control on the preform feed, pulling speed and temperature one could get nanoscale features required.

Figure 2.17: Microscope images of different parts of fabricated gold nanowire fibres with regions of (A) defects, (B) no defects.

Gold nanowire fibres with different diameters ranging from around 200nm to a few microns were fabricated by means of above mentioned several parameters. The scanning electron microscope (SEM) images of gold nanowire fibres with different wire diameters are shown Figure 2.18, and the drawing conditions of the corresponding fibres in Figure 2.18 are listed in Table 2.1.

Fibres		T_d (°C)	Pull speed (m/min)	Feed (mm/min)	Gas flow (l/min)
Wire ϕ_1	Outer ϕ_2				
230nm	70 μ m	840	20	2	0.5
400nm	90 μ m	840	13	2	0.5
500nm	100 μ m	840	10	1	0.5

Table 2.1: The drawing conditions for gold nanowire fibres with different diameters (ϕ_1 , ϕ_2 : diameters of the gold wires and fibres, T_d : drawing temperature).

Furthermore, releasing gold nanowires from the glass matrix by wet etching using hydrofluoric (HF) acid was performed. The preparation was done by attaching the fibres to a substrate coated with gold on all sides, as shown in Figure 2.19. The sample was slightly tilted and immersed into 10% HF acid solution for different duration to find out the optimal condition.

Figure 2.18: SEM images of fabricated gold nanowire fibres with various wire diameters around (A) 230nm, (B) 410nm, and (C) 510nm.

Figure 2.19: Sample preparation for HF etching.

Figure 2.20 illustrates several SEM images of gold nanowires released from glass matrix by 10% HF acid solution for different etching durations. Figure 2.20 (A) and (B) show some results from 30 minutes of etching, demonstrating that the etching process was not homogeneous and didn't fully etch away the glass clad, which can be seen from the fibres at different positions having thick and thin glass clads. Figure 2.20 (C), (D) and (E) show the fully etched continuous gold nanowires with different diameters released from the glass clad through one hour etching. Figure 2.20 (F) shows a magnified view of the highlighted region in (E), revealing the nanowire's diameter measurements.

Figure 2.20: SEM images of several gold nanowires released from glass matrix using 10% of HF acid solution: (A, B) 30minutes of etching, (C, D, E) one hour of etching, (F) Magnified image of highlighted region in (E).

In order to test the integrity of ultra-long gold nanowires across large distances, conductivity tests were carried out on 3cm pieces of the fibre with different diameters, the results shown in Figure 2.21. The observed current-voltage (I-V) measurement shows a clear difference in conductivity across the various widths of the nanowires.

Figure 2.21: Conductivity test (I-V characteristics) of 3cm gold nanowires of 800nm (blue), 300nm (black) and no wires (red).

Nanoribbon-like structured GST inline fibres were also fabricated through the same way instead of depositing few-line GST films, shown in Figure 2.22 and the drawing conditions are listed in Table 2.2.

Figure 2.22: (A) Optical microscope image of a GST inline fibre, (B) SEM image.

GST-array fibre (OD ϕ_2)	T _d (°C)	Pull speed (m/min)	Feed (mm/min)	Gas flow (l/min)
150 μ m	900	10	3	0.5

Table 2.2: The drawing condition for GST inline fibre

Lastly, the existence of the nanostructure elements within glass-clad enclosure was confirmed by the analysis of energy dispersive X-ray (EDX). Figure 2.23 shows the results for the gold and GST fibres, demonstrating the existence of gold and germanium, antimony, and tellurium elements, respectively. The other elements were from the glass clads, N-SF8 for gold nanowire fibres and N-LAF7 for GST inline fibres.

Figure 2.23: EDX analysis: (Top) Gold nanowire fibre, (Bottom) GST inline fibre.

2.3 Applications of the Drawn Fibres

Gold nanowire fibres will find applications in plasmonics and nonlinear photonics. Through pumping femtosecond laser pulses (100 femtosecond pulse width at 1KHz

repetition rate and average input power of 20mW) axially into the fibre with length around 4cm, a highly collimated output beam was observed as shown in Figure 2.25. In comparison, a highly diverged output beam was investigated with the corresponding coreless bare fibre. Presumably, the physical origin of this behavior is facilitated by the presence of plasmonic modes propagating along the surface of the gold nanowire. Some surface plasmon modes are shown in Figure 2.24 through the numerical calculations (Finite Element Method, FEM) using COMSOL. This confines the energy in a small dielectric silicate area around the nanowire core. Due to the high confinement of light energy within the region, it will exhibit a higher refractive index than the rest of the surrounding dielectric silicate area. Consequently, the fibre will switch from a super multimode bare silicate fibre to a few-mode graded index fibre. The higher the input intensity, the higher the refractive index in the dielectric area containing plasmonic modes. Hence, the fibre will become more mono-mode, and more energy will be distributed again into the collimated fundamental mode from higher order modes. Furthermore, another factor leading to few-mode behavior of the fibre will be the amplification of lower-order modes by higher-order modes due to nonlinear spatio-spectro-temporal dynamics such as self-focusing, occurring in the hybrid plasmonic-dielectric mode. This fibre provides a new type of highly confined and collimated optical source that could easily be integrated within existing fibre system to supply broadband optical radiation in compact sensors and telecom devices.

Figure 2.24: A few of low modes of Surface plasmon polaritons (SPPs) around gold nanowire with diameter of around 400nm.

Figure 2.27: I-V measurement from 1.3cm-long GST inline fibre device.

Figure 2.28: I-V measurement from 4mm-long GST inline fibre device.

Furthermore, similar results were achieved for in-line injection, i.e. pumping the light source axially along the fibre. For the device fabrication, 1cm-long GST-inline fibre was employed with semi-transparent electrodes (30nm-thick gold thin-film, deposited through thermal evaporation) around the two ends of fibre tips. Then, silver liquid was coated around the gold thin-film to realize the final electrodes (refer to the schematic figure below). Figure 2.29 illustrates the schematic of designed fibre device along with

the photocurrent measurement system, experimental set-up and the measured I-V results upon different input light powers.

Figure 2.29: (a) Schematic view of the built GST-inline photodetector device, (b) Experimental set-up, (c) Measured I-V curves at different light input powers.

Inspected from above experimental results based on GST-inline fibres, the active material, GST, could play a photocurrent effects in fibre-embedded form upon different light intensities. Higher intensity of light corresponds to higher number of photons interacting with the active materials, and thus releasing more free electrons from the bonding states in GST structures. In consequence, it will excite better photocurrent efficiencies. Although the photo-sensitivities are not as high as those photodetectors based on other materials, it possesses a very interesting advantage that it could be a robust, easy-handling and flexible fibre photodetector component for the future devices.

3. Fibre-based Devices

The fibre-based devices, fibre photodetectors and photodiode structures, were realized by means of coating multilayer of novel functional materials using the conventional deposition techniques on coreless silica fibres (FG125LA from Thorlabs: diameter of 125 μ m). Since the optical signal will leak into the active layer while propagating along the bare fibre, a photoconductive signal will be generated.

For the novel functional materials, chalcogenide semiconducting material of GeSbTe (GST) and organic semiconducting material of P3HT, were employed to realize the device structures by taking advantages of these materials properties; GST has low bandgap so that it will have a broad range of sensitive spectrum for photodetector devices; it could also have various properties depending on their different phase state (amorphous or crystal phase) which can be engineered relatively easy. On the other hand, P3HT is an organic semiconductor material that is less-cost, flexible and easy for processing.

3.1 Fibre-based Photodetector Structures

Firstly, a simply designed photodetector was manufactured by coating GST on a coreless bare silica fibre followed by coating gold as contacts using a shadow mask. Figure 3.1 illustrates the schematics of thermal evaporator and sputtering system (Oerlikon UNIVEX 250 Thin Film Deposition System) and smooth and continuous GST film surface after coating from sputtering.

Figure 3.1: (Left) Schematic view of high-vacuum thermal evaporation and sputtering system, (Right) SEM images of GST surface sputtered on a bare silica fibre.

Figure 3.2 describes the schematics of the device design and the experimental set-up for I-V measurement. The inset of Figure 3.2 (A) illustrates a photo and an optical microscope image of the device displaying a fibre coated with GST (black) and gold (yellow) films and the gap between two gold electrodes is around 1mm.

Figure 3.2: (A) Schematic view of a fibre photodetector component achieved by coating bilayer of GST and gold, (B) Experimental set-up for I-V measurement.

The I-V performance of the device were characterized in two ways as annotated with number 1 and 2 in Figure 3.2 (B), one with the input light launched along the fibre and the other with vertical pumping from top of the fibre. Figure 3.3 displays the I-V curves measured with these two ways under the white light source with intensity of around 200mW/cm^2 . As could be seen from the Figure below, there was no photocurrent effect when the light was coupled along the fibre and a little effect when light exposure from top. This can be improved by using high power light source instead of white light source and through other advanced structures.

Figure 3.3: I-V characteristics of the fibre photodetector when incident light was launched (Left) along the fibre, (Right) vertically shined from the top as shown in insets.

Another photodetector was made based on an active organic semiconductor material, Poly (3-hexylthiophene-2, 5-diyl) (P3HT). A thin layer of P3HT (1 μm) was uniformly

coated around a coreless silica fibre by spin coating, and followed by deposition of two gold electrodes with distance of 0.1mm by thermal evaporation. Figure 3.4 shows the schematic of the building device structure and measured I-V curves depending on different input intensity of the light (CW green laser with wavelength of 532nm).

Figure 3.4: (Left) Schematic view of a P3HT-based photodetector, (Right) I-V characteristics at two different light intensities.

3.2 Fibre-based Photodiode Structure

Based on the photovoltaic structure, a simple in-line fibre photodiode structure was realized by depositing multilayer of functional materials on coreless bare silica fibre. An n-type of indium tin oxide (ITO) film (optically transparent and electrically conductive) working also as a back electrode, p-type of GST film as an active layer and silver (Ag) as top electrode also acting as a back mirror were deposited with 100nm thickness in a sequence to realize the p-n junction with contacts, which is schematically displayed in Figure 3.5.

Figure 3.5: A schematic of the proposed fibre photodiode structure, experimental setup, and I-V measurement result.

It also shows the experimental set-up for axial injecting the CW green laser light (wavelength of 532nm with input power around 4mW) into the fibre end face and the measured photo-effect I-V curve.

As a starting point on fibre-based novel devices, although all those above-proposed fibre-based photodetector structures have taken the advantages of the new materials, it needs more improvements to have stable contacts, higher sensitivities, and sophisticated device building structures or set-up, which could be considered as future recommendations.

4. Conclusions and Future Work

As well as aiming towards milestones set by the ‘Fibre-Drawing Nanomanufacturing’ project, conclusions of the work and a brief summary of other future work planned to tend towards will be described in the following.

4.1 Conclusions

Firstly, metallic and chalcogenide semiconductor nanostructures encased in silicate glass fibre were manufactured through the method called ‘planar-fibre nanomanufacturing’ which was newly developed by combining the conventional microstructuring techniques and fibre drawing process. As a first trial for the process, gold nanowires and GST nanoribbon-like structures have been realized in fibre configuration with ultra-long (up to 3cm long) and mass-production in more effective way.

Secondly, fibre-based photodetector devices have been realized by simply coating multilayers of novel material films on bare silica fibres. Functional materials such as ITO, GST, P3HT and metals (Au or Ag) were used to fabricate the devices through thin-film deposition techniques. By taking advantages of the chosen functional materials, the devices will act as novel components for next-generation portable and flexible devices.

Lastly, some applications of the drawn fibres in fiberized photodetectors, plasmonics, and non-linear optics have been discussed shortly.

4.2 Future Work

Multimaterial fibres and novel fibre-based devices are promising and intriguing optoelectronic components for future multifunctional devices or systems in the intense research subjects of optics, electronics, mechanics, bio-chemistry, sensing, and etc.

On the fabrication of specialty fibres, functional multimaterial fibres incorporating metallic, semiconducting or dielectric (insulator) materials are promising all-in-fibre devices with multiple and simultaneous functionalities for optical, electrical, mechanical, and chemical interrogation [32]. It will be a good practice and base for further research topics with different materials and structures, which will be done in COFT.

Furthermore, fabrication of metamaterials in fibre form with mass production using the fibre drawing method were developed and realized, which has plasma frequency from THz up to Mid IR [33]. The metamaterials fibres have been realized through the iterative draw-cut-stack method by embedding metal (indium) into polymer (PMMA) that both have comparable low melting temperatures.

Arrays of metallic wires encased in glass matrices are going to be explored by the same draw-cut-stack method in fibre drawing tower to realize metamaterial fibres. Furthermore, by aligning metallic fibres with different structures will also be investigated to realize metamaterial effects.

On the part of fibre-based novel devices, further considerations would be recommended – wavelength, intensity and incident angle of the input light, thickness of the functional thin-film materials, building structures and so on. Also other device structures could be considered depending on other fibre substrates or active materials for respective applications.

5. Bibliography

1. S. Barth, F. Hernandez-Ramirez, J. D. Holmes, A. Romano-Rodriguez, "Synthesis and applications of one-dimensional semiconductors", *Progress in Materials Science*, 55(6), pp. 563-627 (2010).
2. C. M. Lieber and Z. L. Wang, "Functional Nanowires", *MRS Bulletin*, 32, pp. 99-108 (2007).
3. O. Hayden, R. Agarwal and C. M. Lieber, "Nanoscale avalanche photodiodes for highly sensitive and spatially resolved photon detection", *Nature Materials*, 5, pp. 352-356 (2006).
4. Z. Fan, J. C. Ho, Z. A. Jacobson, H. Razavi, and A. Javey, "Large-scale, heterogeneous integration of nanowire arrays for image sensor circuitry", *Proceedings of the National Academy of Sciences of the USA*, 105(32), pp. 11066-11070 (2008).
5. C. Soci, A. Zhang, X. Y. Bao, H. Kim, Y. Lo, and D. Wang, "Nanowire Photodetectors", *Journal of Nanoscience and Nanotechnology*, 10(3), pp. 1430-1449 (2010).
6. K. E. Fischer, B. J. Aleman, S. L. Tao, R. H. Daniels, E. M. Li, M. D. Bunger, G. Nagaraj, P. Singh, A. Zettl and T. A. Desai, "Biomimetic Nanowire Coatings for Next Generation Adhesive Drug Delivery Systems", *Nano Letters*, 9(2), pp. 716-720 (2009).
7. G. J. Snyder and E. S. Toberer, "Complex thermoelectric materials", *Nature Materials*, 7, pp. 105-114 (2008).
8. C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins and Y. Cui, "High-performance lithium battery anodes using silicon nanowires", *Nature Nanotechnology*, 3, pp. 31-35 (2008).
9. E. S. Liu, J. Nah, K. M. Varahramyan and E. Tutuc, "Lateral Spin Injection in Germanium Nanowires", *Nano Letters*, 10(9), pp. 3297-3301 (2010).
10. D. D. Awschalom and M. E. Flatte, "Challenges for semiconductor spintronics", *Nature Physics*, 3, pp. 153-159 (2007).
11. C. Gould, K. Pappert, G. Schmidt and L. W. Molenkamp, "Magnetic Anisotropies and (Ga, Mn) As-based Spintronic Devices", *Advanced Materials*, 19(3), pp. 323-340 (2007).
12. R. G. Hobbs, N. Petkov, and J. D. Holms, "Semiconductor Nanowire Fabrication by Bottom-Up and Top-Down Paradigms", *Chemistry of Materials*, 24(11), pp. 1975-1991 (2012).
13. S. B. Darling, "Directing the self-assembly of block copolymers", *Progress in Polymer Science*, 32(10), pp. 1152-1204 (2007).

14. Daniel J. C. Herr, "Directed block copolymer self-assembly for nanoelectronics fabrication", *Journal of Materials Research*, 26(2), pp. 122-139 **(2011)**.
15. J. R. Heath, "Superlattice Nanowire Pattern Transfer (SNAP)", *Accounts of Chemical Research*, 41(12), pp. 1609-1617 **(2008)**.
16. M Yun, N. V. Myung, R. P. Vasquez, C. Lee, E. Menke, and R. M. Penner, "Electrochemically Grown Wires for Individually Addressable Sensor Arrays", *Nano Letters*, 4(3), pp. 419-422 **(2004)**.
17. G. S. Lotey, S. Kumar, and N. K. Verma, "Fabrication and electrical characterization of highly ordered copper nanowires", *Applied Nanoscience*, 2(1), pp. 7-13 **(2012)**.
18. R. P. Chauhan and D. Gehlawat, "Effect of Experimental Conditions on Preferred Orientation of Crystal Planes in Zn Nanowires", *Science of Advanced Materials*, 4(1), pp. 151-155 **(2012)**.
19. J. H. Lee, K. Y. Yang, S. H. Hong, H. Lee, and K. W. Choi, "Fabrication of 70nm narrow metal nanowire structure on flexible PET film by nanoimprint lithography", *Microelectronic Engineering*, 85(4), pp. 710-713 **(2008)**.
20. J. Y. Lee, S. T. Connor, Y. Cui, and P. Peumans, "Solution-Processed Metal Nanowire Mesh Transparent Electrodes", *Nano Letters*, 8(2), pp. 689-692 **(2008)**.
21. C. F. Monson and A.T. Woolley, "DNA-Templated Construction of Copper Nanowires", *Nano Letters*, 3(3), pp. 359-363 **(2003)**.
22. S. K. Lim, M. J. Tambe, M. M. Brewster and S. Gradecak, "Controlled Growth of Ternary Alloy Nanowires Using Metalorganic Chemical Vapor Deposition", *Nano Letters*, 8(5), pp. 1386-1392 **(2008)**.
23. Y. Zhou, S. H. Yu, X. P. Cui, C. Y. Wang, and Z. Y. Chen, "Formation of Silver Nanowires by a Novel Solid-Liquid Phase Arc Discharge Method", *Chemistry of Materials*, 11(3), pp. 545-546 **(1999)**.
24. W. J. Morton, "Method of dispersing fluids", US Patent, 705, 691 **(1902)**.
25. A. Formhals, "Process and apparatus for preparing artificial threads", US Patent 1, 975, 504 **(1934)**.
26. N. A. M. Barakat, B. Kim and H. Y. Kim, "Production of Smooth and Pure Nickel Metal Nanofibers by the Electrospinning Technique: Nanofibers Possess Splendid Magnetic Properties", *Journal of Physical Chemistry C*, 113(2), pp. 531-536 **(2009)**.
27. H. Wu, L. Hu, M.W. Rowell, D. Kong, J. J. Cha, J. R. McDonough, J. Zhu, Y. Yang, M. D. McGehee, and Y. Cui, "Electrospun Metal Nanofiber Webs as High-Performance Transparent Electrode", *Nano Letters*, 10(10), pp. 4242-4248 **(2010)**.
28. N. S. Hansen, D. Cho and Y. L. Joo, "Metal Nanofibers with Highly Tunable Electrical and Magnetic Properties via Highly Loaded Water-Based Electrospinning", *Small*, 8(10), pp. 1510-1514 **(2012)**.

29. A. Khalil, B. S. Lalia, R. Hashaikh and M. Khraisheh, "Electrospun metallic nanowires: Synthesis, characterization, and applications", *Journal of Applied Physics*, 114(17), pp. 171301 **(2013)**.
30. L. Tong, L. Hu, J. Zhang, J. Qiu, Q. Yang, J. Lou, Y. Shen, J. He, and Z. Ye, "Photonic nanowires directly drawn from bulk glasses", *Optics Express*, 14(1), pp. 82-87 **(2006)**.
31. L. Tong, R. R. Gattass, J. B. Ashcom, S. He, J. Lou, M. Shen, I. Maxwell and E. Mazur, "Subwavelength-diameter silica wires for low-loss optical wave guiding", *Nature*, 426, pp. 816-819 **(2003)**.
32. G. Brambilla, "Optical fibre nanowires and microwires: a review", *Journal of Optics*, 12(4), pp. 043001 **(2010)**.
33. X. Wu and L. Tong, "Optical microfibers and nanofibers", *Nanophotonics*, 2(5-6), pp. 407-428 **(2013)**.
34. S. A. Harfenist, S. D. Cambron, E. W. Nelson, S. M. Berry, A. W. Isham, M. M. Crain, K. M. Walsh, R. S. Keynton, and R. W. Cohn, "Direct Drawing of Suspended Filamentary Micro- and Nanostructures from Liquid Polymers", *Nano Letters*, 4(10), pp. 1931-1937 **(2004)**.
35. P. Wang, Z. Li, L. Zhang, and L. Tong, "Electron-beam-activated light-emitting polymer nanofibers", *Optics Letters*, 38(7), pp. 1040-1042 **(2013)**.
36. H. W. Lee, M. A. Schmidt, H. K. Tyagi, L. P. Sempere and P. S. J. Russell, "Polarization-dependent coupling to plasmon modes on submicron gold wire in photonic crystal fiber", *Applied Physics Letters*, 93(11), pp. 111102(1-3) **(2008)**.
37. H. W. Lee, M. A. Schmidt, R. F. Russell, N. Y. Joly, H. K. Tyagi, P. Uebel, and P. S. J. Russell, "Pressure-assisted melt-filling and optical characterization of Au nanowires in microstructured fibers", *Optics Express*, 19(13), pp. 12180-12189 **(2011)**.
38. H. K. Tyagi, H. W. Lee, P. Uebel, M. A. Schmidt, N. Joly, M. Scharrer, and P. S. J. Russell, "Plasmon resonances on gold nanowires directly drawn in a step-index fiber", *Optics Letters*, 35(15), pp. 2573-2575 **(2010)**.
39. X. Zhang, Z. Ma, Z. Y. Yuan, and M. Su, "Mass-Production of Vertically Aligned Extremely Long Metallic Micro/Nanowires Using Fiber Drawing Nanomanufacturing", *Advanced Materials*, 2008, 20(7), pp 1310-1314.
40. M. Yaman, T. Khudiyev, E. Ozgur, M. Kanik, O. Aktas, E. O. Ozgur, H. Deniz, E. Korkut and M. Bayindir, "Arrays of indefinitely long uniform nanowires and nanotubes", *Nature Materials*, 10, pp. 494-501 **(2011)**.
41. F. Zhang, Y. Ding, Y. Zhang, X. Zhang, and Z. L. Wang, "Piezo-Phototronic Effect Enhanced Visible and Ultraviolet Photodetection Using a ZnO-CdS Core-Shell Micro/nanowire", *ACS Nano*, 6(10), pp. 9229-9236 **(2012)**.

42. F. Zhang, S. Niu, W. Guo, G. Zhu, Y. Liu, X. Zhang, and Z. L. Wang, "Piezo-phototronic Effect Enhanced Visible/UV Photodetector of a Carbon-Fiber/ZnO-CdS Double-Shell Microwire", *ACS Nano*, 7(5), pp. 4537-4544 **(2013)**.
43. Z. Wang, R. Yu, C. Pan, Y. Liu, Y. Ding, Z. L. Wang, "Piezo-Phototronic UV/Visible Photosensing with Optical-Fiber-Nanowire Hybridized Structures", *Advanced Materials*, 27(9), pp. 1553-1560 **(2015)**.
44. Y. Li, W. Nie, J. Liu, A. Partridge, and D. J. Carroll, "The Optics of Organic Photovoltaics: Fiber-Based Devices", *IEEE Journal of Selected Topics in Quantum Electronics*, 16(6), pp. 1827-1837 **(2010)**.
45. M. Mariano, F. J. Rodriguez, P. Romero-Gomez, G. Kozyreff & J. Martorell, "Light coupling into the Whispering Gallery Modes of a fiber array thin film solar cell for fixed partial Sun tracking", *Scientific Reports*, 4, pp. 4959 **(2014)**.
46. H. Li, J. Guo, H. Sun, X. Fang, D. Wang, and H. Peng, "Stable Hydrophobic Ionic Liquid Gel Electrolyte for Stretchable Fiber-Shaped Dye-Sensitized Solar Cell", *ChemNanoMat*, 1(6), pp. 399-402 **(2015)**.
47. L. Qiu, J. Deng, X. Lu, Z. Yang, and H. Peng, "Integrating Perovskite Solar Cells into a Flexible Fiber", *Angewandte Chemie International Edition*, 53(39), pp. 10425-10428 **(2014)**.
48. J. Deng, L. Qiu, X. Lu, Z. Yang, G. Guan, Z. Zhang and H. Peng, "Elastic perovskite solar cells", *Journal of Materials Chemistry A*, 3, pp. 21070-21076 **(2015)**.
49. S. He, L. Qiu, X. Fang, G. Guan, P. Chen, Z. Zhang and H. Peng, "Radically grown obelisk-like ZnO arrays for perovskite solar cell fibers and fabrics through a mild solution process", *Journal of Materials Chemistry A*, 3(18), pp. 9406-9410 **(2015)**.
50. Y. Xue, Y. Ding, J. Niu, Z. Xia, A. Roy, H. Chen, J. Qu, Z. L. Wang, L. Dai, "Rationally designed graphene-nanotube 3D architectures with a seamless nodal junction for efficient energy conversion and storage", *Science Advances*, 1(8), pp. 1400198 **(2015)**.
51. Z. Zhang, J. Deng, X. Li, Z. Yang, S. He, X. Chen, G. Guan, J. Ren, and H. Peng, "Superelastic Supercapacitors with High Performances during Stretching", *Advanced Materials*, 27(2), pp. 356-362 **(2014)**.
52. B. Wang, X. Fang, H. Sun, S. He, J. Ren, Y. Zhang, and H. Peng, "Fabricating Continuous Supercapacitor Fibers with High Performances by Integrating All Building Materials and Steps into One Process", *Advanced Materials*, 27(47), pp. 7854-7860 **(2015)**.
53. H. Lin, W. Weng, J. Ren, L. Qiu, Z. Zhang, P. Chen, X. Chen, J. Deng, Y. Wang and H. Peng, "Twisted Aligned Carbon Nanotube/Silicon Composite Fiber Anode for Flexible Wire-Shaped Lithium-Ion Battery", *Advanced Materials*, 26(8), pp. 1217-1222 **(2014)**.

54. Y. Luo, Y. Zhang, Y. Zhao, X. Fang, J. Ren, W. Weng, Y. Jiang, H. Sun, B. Wang, X. Cheng and H. Peng, "Aligned carbon nanotube/molybdenum disulphide hybrids for effective fibrous supercapacitors and lithium ion batteries", *Journal of Materials Chemistry A*, 3(34), pp. 17553-17557 **(2015)**.
55. A. Canales, X. Jia, U. P. Froriep, R. A. Koppes, C. M. Tringides, J. Selvidge, C. Lu, C. Hou, L. Wei, Y. Fink and P. Anikeeva, "Multifunctional fibers for simultaneous optical, electrical and chemical interrogation of neural circuits in vivo", *Nature Biotechnology*, 33(3), pp. 277-284 **(2015)**.
56. O. T. Naman, M. R. New-Tolley, R. Lwin, A. Tuniz, A. Hadi Al-Janabi, I. Karatchevtseva, S. C. Fleming, B. T. Kuhlmei, and A. Argyros, "Indefinite Media Based on Wire Array Metamaterials for the THz and Mid-IR", *Advanced Optical Materials*, 1(12), pp. 971-977 **(2013)**.

6. Publications

1. A. Tittl, A. U. Michel, M. Schaferling, X. Yin, B. Gholipour, *L. Cui*, M. Wuttig, T. Taubner, F. Neubrech, and H. Giessen, “A Switchable Mid-Infrared Plasmonic Perfect Absorber with Multispectral Thermal Imaging Capability”, *Advanced Materials*, 27(31), pp. 4597-4603 **(2015)**.
2. *Long Cui*, Behrad Gholipour, Paul Bastock, Khouler Khan, Chris Craig, Dan Hewak and Cesare Soci, “Planar-fibre Nanomanufacturing”, ICMAT & IUMRS-ICA, Oral Invited **(2015)**.
3. *Long Cui*, Behrad Gholipour, Paul Bastock, Khouler Khan, Chris Craig, Dan Hewak and Cesare Soci, “Planar fabrication assisted fiber nanowire manufacturing”, CLEO/Europe-EQEC Conference, Oral **(2015)**.
4. D. M. Nguyen, Z. Wang, *L. Cui* and C. Soci, “P3HT-coated coreless silica fiber for in-line photodetection”, CLEO/Europe-EQEC Conference, **(2015)**.
5. Duc-Minh Nguyen, Behrad Gholipour, *Long Cui* and Cesare Soci, “Single Mode, Multimode Infrared Optical Switching based on Phase Change Materials Cored Optical Fibers”, CLEO/Europe-EQEC Conference, **(2015)**.
6. B. Gholipour, D. M. Nguyen, *L. Cui*, V. Nalla, K. Wu, H. Wenchao, P. Bastock, K. Khan, C. Craig, D. Hewak, N. Zheludev, and C. Soci, “Beyond the crunch with specialty fibers”, Communication networks beyond the capacity crunch – further discussion, The Royal Society, Chicheley Hall, London (Talk), May 13-14, **(2015)**.
7. Duc-Minh Nguyen, Behrad Gholipour, *Long Cui* and Cesare Soci, “Ultra-Fast Spatial Mode Modulator Using Phase Change Material Cored Optical Fibers”, ICMAT & IUMRS-ICA, **(2015)**.
8. Duc Minh Nguyen, Behrad Gholipour, *Long Cui*, Venkatram Nalla, Daniel Hewak, Nikolay Zheludev and Cesare Soci, “Plasmonic nanowire-cored silicate fiber spaser”, 5th International Topical Meeting on Nanophotonics and Metamaterials (NANO META), **(2015)**.
9. B. Gholipour, V. Nalla, D. M. Nguyen, *C. Long*, P. Bastock, K. Khan, C. Craig, D. W. Hewak, N. I. Zheludev and C. Soci, “Multimaterial Fiber Nanomanufacturing: from Photodetectors to Nonlinear Light Sources”, *Photonics North*, **(2014)**.

7. Appendices

A: Preparing N-LAF7 Glass Sputtering Target

The sputtering target was manufactured through glass melt and casting. First, commercial N-LAF7 glass rods (10mm in diameter and 10cm length) were crushed into small pieces or powder by means of Ball Mill technique at the condition of 250rpm for 30 minutes. Then, the glass pieces or powder were placed in an aluminium oxide crucible and melted (see figure below showing the recipe of glass melt).

Figure Appendix A-1: Recipe of melting N-LAF7 glass.

After melting for few hours, an immediate air quenching were followed and poured the melt in a casting mould (see figure A below) for 6 hours annealing a little below the glass transition temperature to release the strains caused in quenching process.

Figure Appendix A-2: (A) N-LAF7 glass powder after ball-mill, (B) Casting mould and aluminium oxide crucible, (C) N-LAF7 glass sputtering target.

Finally, the glass sputtering target (see figure above B) was achieved by consecutive casting and polishing.

B: Summary of Fibre Draws to Date

Date	Contents
22/05/2013	GST Nano-ring array around oxide glass (N-SF8) with oxide glass clad
06/06/2013	Oxide glass practice draw
10/07/2013	GLS glass fibre
30/08/2013	Ge ₃₀ As ₁₃ Se ₃₂ Te ₂₅ glass fibre
13/09/2013	As ₄₀ Se ₆₀
27/09/2013	Au nanowire in oxide glass
03/10/2013	Oxide glass (N-SF8) with CIGS & ZnS
15/10/2013	Oxide glass (N-SF8) with GST
12/11/2013	Oxide glass (N-LAF7) with GeSe & Bi ₂ Te ₃
02/12/2013	Polyethylenimine (PEI) tube draw
25/02/2014	Polyethylenimine (PEI) fibre draw
16/03/2014	As ₄₀ Se ₆₀ fibre draw

02/04/2014 – 04/04/2014	As ₄₀ Se ₆₀ fibre incorporated into PEI tube
09/04/2014	Oxide glass (N-SF8) with Au+GST+Au structure (no success)

Table A: Fibres drawn in ORC, University of Southampton

Date	Contents
20/06/2015	NBK7 rod (10mm-diameter, 150mm-length) as first trial in Soft-Glass Tower
08/10/2015	Furnace and preform temperature check in Soft-Glass Tower
12/10/2015	Soft glass – DURAN tube (9mm outer diameter & 1mm inner diameter) draw in Soft-Glass Tower
22/10/2015	Polymer (PEI) tube (2.3mm outer diameter & 0.9mm inner diameter) fibre draw in Soft-Glass Tower
29/10/2015	As ₄₀ Se ₆₀ glass fibre draw Polymer (PEI) tube (2.3mm outer diameter & 0.9mm inner diameter) fibre draw in Soft-Glass Tower: rod-in-tube method
10/11/2015	Soft glass fibre tapering (N-SF8 fibre): 150um fibre tapering down to 30um fibre
17/11/2015	Metallic-core (tin: Sn) fibre tapering: 150um fibre tapering down to 30um fibre
23/12/2015	DURAN tube (9mm outer diameter & 1mm inner diameter) + Copper wire (1mm diameter): wire-in-tube (Taylor wire process) fibre draw in Cane-Draw Tower → bulge in preform: melting point of the wire is higher than softening point of the glass

14/01/2016	DURAN tube (9mm outer diameter & 1mm inner diameter) + Silver wire (1mm diameter): wire-in-tube (Taylor wire process) fibre draw in Cane-Draw Tower → bulge in preform: melting point of the wire is higher than softening point of the glass
20/01/2015	DURAN tube (6mm outer diameter & 2mm inner diameter) + Tin wire (1mm diameter): wire-in-tube (Taylor wire process) fibre draw in Cane-Draw Tower → very good results
27/01/2015	DURAN tube (9mm outer diameter & 1mm inner diameter) + Tin wire (1mm diameter): wire-in-tube (Taylor wire process) fibre draw in Cane-Draw Tower → continuous metallic core along the fibre

Table B: Fibres drawn in COFT, EEE, NTU

C: Example of a Fibre Drawing Data and Run Sheet

Example of fibre drawing data:

<u>Date:</u> 12 th May 2014	<u>Run No:</u> 243	<u>Operator(s):</u> Cui Long	
<u>Glass Codes/Material:</u> N-SF8 + Gold		<u>Glass Composition:</u>	
<u>Purpose:</u> Gold deposited structure within an N-SF8 preform to be drawn to nanowire fibres			
<u>Properties of Glasses:</u>			
<u>Glass</u>	<u>T_g, °C</u>	<u>T₁₃, °C</u>	<u>T_{7.6}, °C</u>
N-SF8	567	564	678

Other Important Glass Properties:

Gas Flow:

4 litre/min of argon to the carbon susceptor.

0.5 litre/min argon to preform

Preparation:

10x100mm N-SF8 preform was cut in half longitudinally using high precision saw. A gold structure was then deposited onto the flat face using thermal evaporator. The preform was fused back together in a furnace at 675oC with a 30minute dwell. 10oC/min ramp up. 20oC/min ramp down.

Conclusions, Thoughts & Sketches

Fast drawing will be needed.

Example of Run Sheet:

	Temperature (°C)				Gas Flow (litre/min)			Feed Rate (mm/min)	Drum Speed (m/min)	Desired Fibre OD (μm)	Fibre OD (μm)	Fibre Length (m)	Notes
	Time	Set	Control	Monitor	N ₂	Ar	O ₂						
1	0.00	0/800	19			0.5							
2	5.38	800				0.5							start to neck down very slowly
3		810				0.5							
4		820				0.5							a little bit tight with drawing
5						0.5							
6						0.5							
7		840				0.5		1	10		100		
8								2	15		80		
9									20		70		
10									25		65		
11									30		60		
12													
13													
14													
15		830						2	5		150		
16		820						2	2		180		
17													
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