Whitepaper on The Role of Nanowire webs

Introduction.

Nanowires and nanotubes, slender structures that are only a few billionths of a meter in diameter but many thousands or millions of times longer, have become hot materials in recent years. They exist in many forms — made of metals, semiconductors, insulators and organic compounds — and are being studied for use in electronics, energy conversion, optics and chemical sensing, among other fields.

The discovery of carbon nanotubes is generally credited to the Japanese physicist Sumio Ijima, although some forms of carbon nanotubes had been observed earlier but weren't perhaps identified as such. Almost immediately, there was an explosion of interest in this exotic form of a commonplace material. Nanowires, being solid rather than hollow, gained similar prominence a few years later. Due to their extreme slenderness, both nanotubes and nanowires are essentially one-dimensional. They are quasi-one-dimensional materials. Two of their dimensions are essentially on the nanometer scale, and this one-dimensionality confers distinctive electrical and optical properties.

Nanotubes, wires and webs are becoming increasingly important in a number of engineering applications, and research in them is being taken up by individuals, companies, and academic institutions.

<u>Overview of Nanowire Technology</u>

The term"nanotechnology" is used to describe the process and manipulation of matter on an atomic level, and encompasses the work in technical fields as diverse as surface science and molecular biology. It describes the micro-fabrication of structures and devices on a scale normally measured in nanometres (10^{-9} metres) and has led to breakthroughs in materials such as carbon nanotubes. Nanotechnology has evolved into the engineering of materials for mechanical and electrical purposes, creating fully-functioning systems and devices on an atomic level. Much of the work that has been applied to the subject focuses on the manufacture of the basic building blocks that help make nanostructures so enduring.

Of these new structures nanowires are of special importance as they can fulfil a number of roles from static devices to various states of electrical conductor, and have the potential to take electronic devices to the next generation. It has been observed [1] that nanowires made from well known, materials can differ significantly in properties when reduced to a nanoscale. Examples of this include:

- Gold: - Known for its exceptional electrical and thermal conductivity in bulk material, when reduced to nanoscales, gold takes on the properties of a semi-conductor.
- Aluminium: - This is a soft, ductile metal with no magnetic properties on a macro scale but becomes magnetic in small clusters at a nanoscale.
- Carbon: - Soft and a noted conductor in bulk form, carbon nanotubes can be made to form semiconductors if manufactured in one way and vastly stronger than steel if manufactured in a different way.

Nanowires can be manufactured by a number of means and are typically tens of nanometres thick and may be constructed in lengths of a ratio of 1000 times their thickness. This makes them useful for constructing complex 1d forms such as networks or webs. This, allied to the abilities of the materials to behave in different electrical ways, gives rise to the possibility of making complex structures that may have both structural and electrical or optical properties.

Over the years of research and development into nanowires, much has been made of the difficulties in manufacturing them in commercial quantities and with repeatable reliability. While advances have been made in the area, it still remains only partially resolved. The realisation of reliable methods of controlled assembly of nanowires has become essential since the potentials of the materials are obvious and an impasse has been reached where those potentials will remain unfulfilled until manufacturing issues are overcome.

Nanowebs are a logical progression from single fibers and comprise a mass of single fibers. The term "nonwoven" means that the multitude of randomly distributed fibers that may or may not be interconnected. The fibers can be bonded to each other in a matrix or can remain unbonded. The fibers can be staple fibers or continuous fibers. The fibers can comprise a single material or a multitude of materials, either as a combination of different fibers or as a combination of similar fibers each comprised of different materials. Nanofibre webs offer a whole raft of possibilities as they are generally easier to construct and only marginally less strong than woven nanofibres, giving rise to cheap, lightweight, but hugely strong structural materials

There is currently much research into fabricating usable lengths of nanofibres and whole nanowebs suspended from specially constructed nanoarchitecture. This process is now one of the main areas of investigation from a manufacture point of view. This is discussed in further detail in section iii.

Applications of Nanowire webs

Nanowire webs are currently being considered for three main areas of application:

- Micro-electronics.
- Micro-structures.
- Optoelectronics

Micro-electronics is the most promising field for nanowires and webs. Because the materials exhibit properties that differ from their bulk counterparts, and are able to be manipulated to match the intended requirements, the possibilities are endless.

The current generation of capacitive touchscreens rely on a thin indium-tin oxide layer to facilitate the transfer of touch to action. Unfortunately ITO is renowned for being brittle and subject to fracture which can lead to local inoperable areas. As these failing areas build up in number on the surface layer, the touchscreen becomes less responsive and prone to mis-selection. In addition, ITO is expensive to manufacture because of the relative costs of its component materials and has to be applied to a glass surface using vapour deposition process which is costly in itself. The possibility of adding nanofilaments or nanowebs to an ink which may be applied to a surface has the potential for a relatively cheap and durable conductive surface that can be applied to complex shapes, leading to a variety of touch-sensitive shapes and applications.

The use of nanowebs to construct nanoelecronic components has long been considered as the next logical step in the evolution of computers to produce so called "quantum computers" which pass information at near light speed and suffer none of the resistivity found within the current design of micro-electronics. Added to this, because current is supplied at almost zero resistivity, quantum computers using nanoweb technologies do not produce the same excess heat found in micro-circuits leading to greater efficiencies in the overall device.

By creating components and devices on a nanoscale, the possibilities of manufacturing assemblies of the next level up become realities with power supplies and mechanical components being only marginally bigger than the nanofilaments and webs used to construct diminutive assemblies and nanorobotic systems.

Nanowebs are also being considered for two very high-use applications in the form of piezoelectric components and photoelectric cells. Piezoelectric devices turn kinetic energy in electrical energy and vice-versa but tend to be relatively bulky. Nanowebs offer the potential for a cheap and effective way of producing the same effect on a nanoscale and would follow the same principle where physical manipulation of the web would result in a corresponding electrical charge. Because of the tiny size of the webs, practical applications are still being considered, but with the principle proven, engineers will find everyday uses.

Both the theory and the application already exist when considering nanowebs as practical components of photo-electric cells. Also known as solar cells, the current design of device uses sunlight falling on semiconductor device to create a potential difference and thus and electric charge, which is passed along and collected. Scientists are considering the possibility of using nanowire webs held within a support medium to carry out a similar task. While there is much interest in so called nanoflakes have been constructed and tested and found to convert up to 30% of received sunlight into electricity, research continues into the viability of using nanowebs to accomplish a similar effect. The advantage of using nanowebs is that once mounted in a suitable medium, they have the potential be flexible or manufactured in odd shapes which may match a light-receiving structure in a more acceptable way than their flat and inflexible silicon counterparts.

As well as the construction of specific electrical components, there is much potential for nanowebs to be used as constructional and anchoring devices to retain other nanoelectrical components. The beauty of considering this method is that, depending on the method of manufacture, the web can be effectively grown around the component that it is securing and holding it in place with greater force and efficiency than any screwed or bolted system currently being used. Because of the subtle modifications to base material that can be found at nanotechnology levels, an apparent conducting material such as carbon can be made to be a very strong semi-conducting material that not only anchors but forms part of an electrical device.

One area where nanowebs are becoming increasingly important is in that of optoelectronics where electronic devices control and generate light in all wavelengths. There is much research continuing into the investigation of the optical properties of nanofilaments wires and nanowebs. The current field of research is focusing on three main areas that have been found as common properties of nanowebs. These are:

- Antireflection.
- Light Adsorption

- Directional light emission

Antireflection deals with the phenomenon of the change in direction of a beam of light as it arrives at the interface between two different media. In this case, almost all of the light may be reflected at large angles normal to the interface. This method can be used to increase the amount of light that falls onto a light detector increasing its efficiency. In order to achieve this, nanowebs are constructed in conical shapes and placed over a semiconductor to create a gradual angle of incidence and therefore reducing reflection over a broad range of the received spectrum. This in turn increases the efficiency of the detector.

While the actual volume density of a nanoweb array is quite low, they adsorb light extremely efficiently as the relative low density of the material produces only a minor contrast ratio between it and the air and therefore minimises losses due to reflection. Investigations have shown that nanowires mounted in a substrate of the same material adsorb nearly 98% of incident light. The actual mechanism of adsorption is a product of the diameter of the nanowire with thicker wires absorbing longer wavelengths so it is possible to engineer a nanoweb that will adsorb light in one particular wavelength only while ignoring all others. This property is being investigated with a view to manufacturing a new generation of smart photovoltaic applications.

It has been observed that nanowebs and arrays are also able to influence the actual direction of light they can be made to emit. If arranged in particular ways, nanowebs can be made to modify the dispersion characteristics of the light and determine direction of emission. It is these properties that mark nanowebs out as increasingly important in the field of optoelectrics

<u>**Manufacture of Nanowire Webs**</u>

Many of the properties of nanowebs are a direct consequence of their size and structure, with even small differences when measuring properties between webs. This means that the structures need to be manufactured to exhaustive tolerances in order to achieve consistent results and places the focus back on the manufacturing route.

Nanowires and webs can be manufactured by two distinct methods; top-down and bottom-up. The top-down method takes a block of the bulk material and removes material until only the nanofilament is left. This is akin to the conventional methods of machining using tools such as lathes and mills, but on a much reduced scale. In reality, one of the most efficient ways of making nanofilaments using the top-down approach is not to remove material but to realign it under the action of applied heat to allow the atoms to flow. This might be done be taking a larger rod of the desired material and to apply a load while heat is applied to a section which will allow elongation and realignment of the atoms. Done with patience and care over several applications, the material becomes elongated into a nanofilament.

This is a good and repeatable process for producing lengths – though even these are still a long way from what would be considered to be mass-production – nanowebs need to be produced using the alternative method of bottom-up production. This method quite literally grows the structure from a substrate and allows building at almost one atom at a time. While normally carried out by Chemical Vapour Deposition (CVD) methods, there have been recent development s in the ability to 'print' nanofilament structures onto an appropriate substrate [2]. Having electrically carved the silicon substrate wafer with the shape of the structure they hoped to build, the Swiss research team then pressed the wafer against a synthetic rubber to produce a mold. They then drew a liquid rich in gold nanoparticles across the mould and produced a 'print of the structure in nanoscale. Further investigation showed that their process could be carried out constantly, creating the semblance of mass-production.

As mentioned in section i. advances are being made in the use of nano-architecture as a base to support nanofibres and webs as they are being manufactured. This is now being investigated as a credible method of mass-producing these artefacts.

A distinct mixture of both bottom-up and top-down manufacturing, the key to doing this effectively is to produce a structure that will support the fibres while they are forming, and this can be achieved by a number of ways. Much research has been carried out into the creation of a series of conical supports which are then doped to form the start of the nanowire [3]. The cones are themselves made by selective dry-etching the substrate. The edges of the needles are protected by a self-masking phenomenon that is a by-product of the gaseous reaction producing a passivation effect. By following a series of etching and passivation cycles the needles are erected. With those in place, the deposition of the silicon nanowires can commence.

The Vapor-Liquid-Solid (VLS) process is a well-documented and practised method of growing silicon nanofibres. It is basically a chemical vapour deposition method that is driven in the presence of a catalyst that accelerates the rate of the reaction but does not take any part in the reaction itself. Catalysts are generally a thin film of a transition metal such as iron, cobalt, or nickel, or a noble metal such as gold. The process breaks down into distinct steps;

- A catalyst in the form of a thin film is deposited on the substrate via thermal evaporation or sputter deposition. This forms a point for the subsequent nucleation and growth of the nanowire.
- More droplets are applied to the thin film with the diameter of the droplet size being manipulated by lithography.
- The nanowire can then be advanced by using a physical vapour deposition process operated in a vacuum.

This process is demonstrated in figure 1, below.

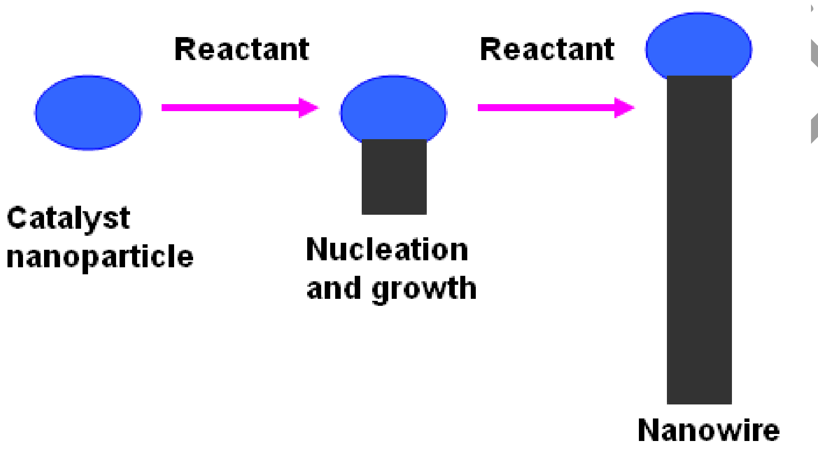

Figure 1: VLS process.

This process has certain requirements for the catalyst particles (4). These include:

- The catalyst must be able to form a liquid solution with the base material at the nanowire growth temperature.
- The solubility of it needs to be low solid and liquid phases of the substrate.
- The catalyst should ideally be inert to any reaction products.

By using the VLS method, the nanowire can be made to bridge the gaps between the points of the suspension architecture, thus forming usable lengths. By having a block of substrate points to join onto, it is possible to quickly manufacture a network of nanofilaments that grow to become a web.

The VLS method has a number of distinct advantages over other bottom-up means of growing nanofibres. The process has a much lowered reaction energy compared to the more usual vapour-growth methods and the nanofilaments only grow where the catalyst allows activation. In addition, this method tends to produce highly anisotropic arrays, and can be carried out using several different materials.

Variations of this support principle have been demonstrated by other research teams with much work being carried out by a team from Berkley[4]. The team led by Paulo grew silicon nanowires horizontally across an etched and passivized silicon substrate using a similar method to the above. Though rather than creating a series of peaks, the team decided on a trench in the silicon substrate, which has the potential for ease of harvesting the completed nanofibres.

Future Applications.

While current research has identified a huge number of potential applications for nanowebs and nanofilaments, there is still much research into future applications based on the properties of what we can already observe in these structures. One of the most exciting applications at the moment is in the field of energy solutions where a team is working on how a small nanoweb structure might assist with clean energy production [5].

Initial research and results have shown that nanowebs constructed from gallium sulphid nanofilaments which have the ability to deconstruct water to liberate hydrogen from water using sunlight. This startling advancement has enormous ramifications for green and sustainable energy.

The energy is produced by splitting hydrogen from water resulting in a potential energy that is completely clean and effectively has no carbon footprint. While the technology plainly exists and is proven, it is the mass-production of the process that will prove to be the main challenge. It is hoped that this type of application will become an important component in the so-called "terawatt challenge" to meet the Earth's growing energy needs, but is unlikely to produce major contributions to that pool for at least ten years.

Nanowebs are also becoming increasingly important in biofuel cells, with work examining the use of a network or web of carbon nanotubes being the energising element in biofuel cells capable of utilizing non-toxic, non-flammable and renewable fuel substrates. Previously, biofuel cells have been hampered by low efficiencies compared to inorganic cells due to torturous reaction pathways, but the possibility of using an array of carbon nanotubes has given these green energy cells new hope of competing.

Outside the sphere of energy production, nanowebs offer huge potential applications in terms of both vehicular and personal armor for the military. With the joint advantages of being lightweight and immensely strong, it is seen that these materials could easily take the place of the already lightweight and durable carbon-fiber applications by offering a solution that is lighter and less bulky than even these.

As the world's population continues to grow and disease picks up in centers of population, nanowebs offer a solution to the filtration of both airborne and liquid-immersed infection and may provide complete protection against any element requiring flirtation. Creating massed filters from nanowebs is guaranteed to prevent the ingress of unwanted particles from bacterial to spores and ensuring a free flow of air.

Nanowebs have become a topic of huge interest and offer huge possibilities in a number of diverse fields from green energy production through quantum computing and on to structural applications. While many of these fields have been proven on a small scale, with the exception of nanoelectronics they nearly all require stable and commercial available methods of production to proceed to the next level.

References:

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