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Title: Literature Review of Nanosprings

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Literature Review of Nanosprings

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Nanosprings are helical structures grown on the nanoscale. Numerous choices exist for composition and coating which give them a wide range of possible uses. They compare favorably in some aspects to other nanostructures and unfavorably in other aspects. This paper reviews the available literature, discusses techniques for formation and coating, and explores a variety of potential applications that may be developed in the near future.

Introduction

The quest for innovative nanostructures began with graphene and carbon nanotubes and has led to a plethora of structures, such as nanoframes[2], nanostars[3], and nanohorns[4]. In addition to a wide variety of structures, numerous different compositions and coatings have been used. The result of this research is a staggering number of combinations for structure, composition, and coating.

Nanosprings or nanospring like structures have been observed since 1955[5], but it has not been until recently that they have been investigated as a potentially useful tool in research and industry. Like other nanostructures, nanosprings are a very simple building block on the nanoscale that has remarkable material properties on the macroscale. They are most commonly grown through a Chemical Vapor Deposition (CVD) process using the Vapor Liquid Solid (VLS) method[6]. Like many other nanostructures, they have a very high surface area of up to 400 square meters per gram[7], but unlike other nanostructures they also possess a very low resistance to flowing liquid or gases[8]. The mechanical properties of a macroscale spring also translate to the nanoscale. Schilke was able to use Atomic Force Microscopy (AFM) cantilevers to pull the springs apart and observed no deformation within the spring even when elongated up to 50% of its resting length[8]. Besides having great elasticity, the springs can also withstand water flow rates of up to 85 centimeters per second[8] without being torn off their substrate or degraded. The structure of nanosprings is not affected by large differences in temperature. Thus the their maximum operating temperature that they can be exposed to is determined by the melting points of the material they are composed of or coated in.

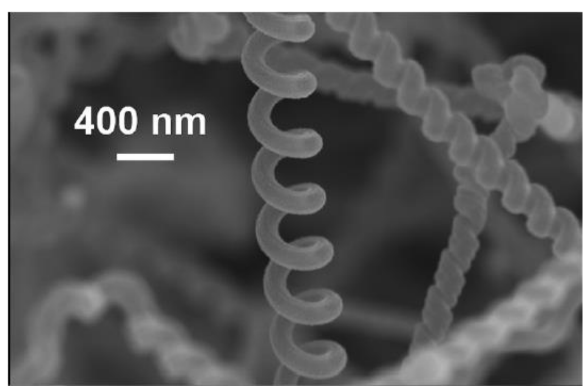

Figure 1. SEM image of silica nanosprings[7].

Formation Processes

Nanosprings are usually grown with CVD via the VLS growth process, which has the advantages of being simple, fast, and occurring at standard pressure. Metal is deposited on a substrate by any standard coating technique. The sample is heated to at least the eutectic point of the metal and the substrate, which causes the metal and substrate to form drops of eutectic or liquid. A precursor vapor gas is directed into the chamber. The vapor is adsorbed into the liquid drops of metal and substrate. These drops very quickly supersaturate with vapor components, which cause them to be deposited at the interface between substrate and droplet. This pushes the metal and substrate droplet upwards away from the substrate and forms a solid "whisker" of some component of the vapor. As more vapor is supplied to the chamber, the droplet continues to build itself upward on top of the already deposited column.

Figure 2 shows an example of the process where gold is deposited on a silicon substrate. The sample is heated to the eutectic point of the gold and silicon liquid alloy, which depends on the concentrations of both components but at a minimum is about 360 °C. Silicon tetrachloride and hydrogen gas flow over the sample. The gases are adsorbed into the liquid alloy droplet and react to produce silicon, which is deposited at the interface between the droplet and the substrate, and hydrogen chloride, which is removed as waste.

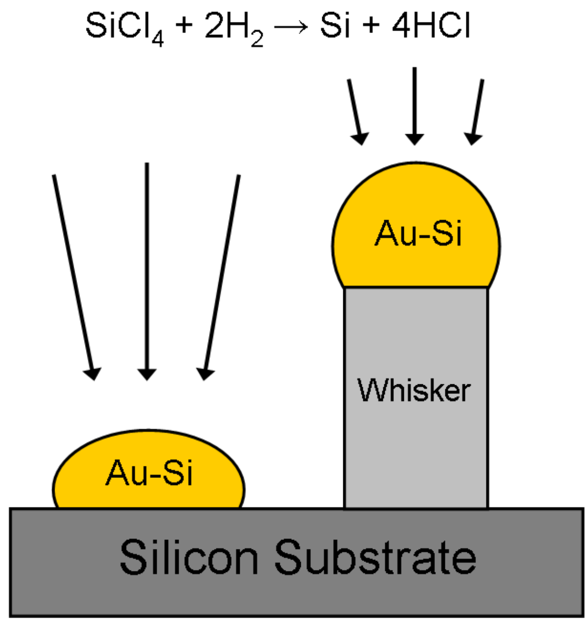

Figure 2[12]. Silicon tetrachloride and hydrogen gas adsorb into the gold silicon droplet, which quickly saturates. More adsorption results in silicon being deposited between the substrate and the droplet and forming a column or "whisker."

The VLS process is very flexible and a multitude of precursor vapors can be chosen to create nanosprings with the desired composition. The choice of catalyst metal determines most features of the nanosprings, including the dimensions of the spring itself[9]. The growth rate of the springs is determined by the rate of adsorption of the vapor into the catalyst droplet. Almost any material can be used as a substrate so long as it is stable at the temperatures required for the eutectic droplets to form. Authors have used glass, sapphire, silicon, aluminum foil, and polymers with high glass transition temperature, to name a few[9].

There are two different growth mechanisms that introduce asymmetry into the growth and cause the whiskers to form springs. The first for single nanowires is contact angle anisotropy at the interface between the eutectic droplet and nanowire[6]. The second, for bundles of nanowires growing together to form larger nanosprings, is differing growth rates between each nanowire[11], which are caused by slightly different rates of vapor adsorbing into each catalyst drop in a nanowire.

Nanosprings can be grown as individual whiskers or as thick bundles of multiple whiskers twined together. The precise reason why a process results in single wires or bundles is not fully understood. A possible explanation is that at low formation temperatures, the metal catalyst may not become liquid but remains as a solid and retains distinct facets[11]. Single nanowires then grow off of each facet, and their close proximity causes them to twine together. For a gold coating with a silicon substrate, which has a minimum eutectic point of about 363 C, a choice of formation temperature at or only a few tens of degrees above the eutectic point would facilitate the growth of nanospring bundles.

Under normal growth conditions, the final product is a dense mat of nanosprings of a random orientation. Depending on the process conditions, a mat can also contain a large percentage of nanowires grown in a straight or random direction. The percentage of mat that is nanosprings is the yield achieved, and can range from zero to close to one hundred[11]. The nanosprings can also be grown to be an oriented mat, as shown in Figure 3[13]. As can be seen in the figure, the uniformity of the orientation is not total. The authors intended to use these uniformly oriented nanosprings in a biosensor based on alternating current impedance spectroscopy. Briefly, the theory behind the device is a voltage is applied to the nanosprings, the nanosprings are exposed to a solution, and the resulting changes to amplitude and phase shift of the current or voltage are monitored and matched to known solutions.

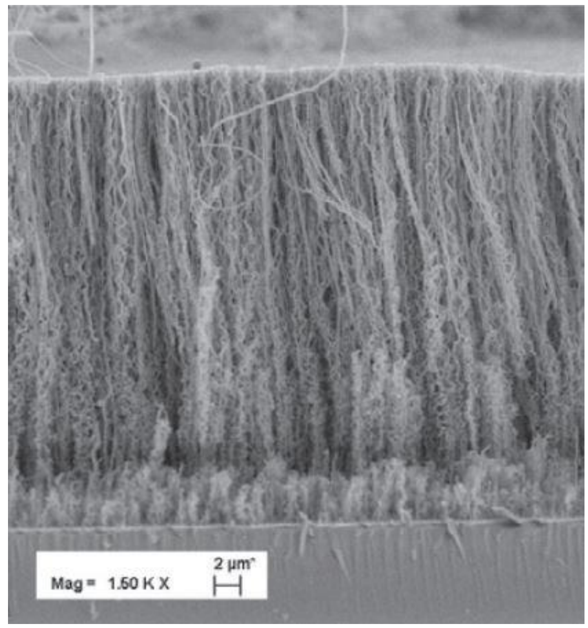

Figure 3. Vertically oriented nanospring mat grown to act as a biosensor[13].

Coatings

Nanosprings are durable enough to be coated with many different materials using standard coating methods. For catalytic applications, palladium or platinum can be coated with electroplating or sputtering[14]. To function as electrodes, they can be coated with copper, nickel, or any other low resistance metal. Hydrogen storage can be achieved by coating with palladium[14].

With the right coatings and techniques, more exotic applications are possible.

Dobrokhotov et al coated a sample with zinc oxide and palladium nanoparticles using Atomic Layer Deposition (ALD)[15]. Electrodes were attached to the sample and vapors of known composition were directed to the sample. The vapors caused a change in the conductance of the sample, and a current signal that passed through the sample had a distinct deviation that could be recognized using the Linear Discriminant Analysis (LDA) method. This nanospring "nose" was sensitive to concentration levels of parts per billion, had a very quick relaxation time of 20 to 40 seconds, which after exposure to chemicals is the amount of time it requires that it must be exposed to a "neutral" environment before it is capable of accurately detecting the presence of chemicals again, and was able to successfully detect chemicals associated with explosives, such as trinitrotoluene and triacetone triperoxide.

Nanosprings may also be coated with biological structures. Schilke prepared a nanospring mat coated with thiol groups[8]. This was submerged in a phosphate-citrate (PC) buffer that contained the enzyme β-galactosidase, which had been previously chemically modified to introduce thiol-reactive groups. After being allowed to sit overnight, many of the enzymes had been immobilized on the nanosprings. The unbound enzymes were removed by extensively washing with a PC buffer. The enzymes were strongly bound to the nanosprings and able to withstand high rates of flow of up to 85 cm / sec of water with very low resistance to that flow. The author dubbed this a microreactor, showed that its performance exceeded that of batch assays of enzymes, and discussed the possibilities of using this technology for biosensors or lab-on-chip devices. The range of biological agents that can be attached is limited only by the requirement that the biological agent must be able to be modified to contain thiol-reactive groups or possess them naturally.

Advantages Over Other Nanostructures

Many different nanostructures are now available to researchers. Depending on the application, nanosprings can be preferable to other options. For example, although they have lower surface area than carbon nanotubes since carbon nanotubes can be coated both on the exterior and interior surfaces, the interior surface of carbon nanotubes can only be accessed by a lengthy diffusion process. Thus the nanosprings, which possess inverse porosity and have all their functionalized surface area immediately accessible, are much faster to react and preferable for any application that calls for speed, such as a catalytic reaction. An additional advantage nanosprings enjoy is their low resistance to flow, which was measured by Schilke et al to have a Darcy permeability of about 3×10^{-6} square centimeters[8]. Finally, through the VLS technique nanosprings can be very quickly and easily made, and their durability allows them to be coated with almost any standard coating technique.

Alternative Growing Process

Authors have begun to investigate growing nanosprings by techniques other than the VLS process. Liu et al filled open columns of an anodic aluminum oxide template with copper and palladium metal ions and deposited them with electrodeposition as shown in Figure 4[16]. The copper and palladium formed rods that coiled around each other in a helical fashion. The template and copper were chemically etched away to leave pure palladium nanosprings, which the authors theorized were created through spring dislocation. Furthermore, the physical dimensions of the nanosprings were able to be tuned by altering the diameter of the template to change the diameter of the nanospring and altering the amount of charge transported during electrodeposition to change the length of the nanospring. These nanosprings have potential applications as nanomachines, sensors, and nanoinductors.

Figure 4. A diagram of the process that Liu et al used to create pure palladium nanosprings[16].

Another alternative to VLS is to create a structure that will self-assemble into nanosprings. This was done by Bell et al through molecular beam epitaxy as shown in Figure 5[17]. Three layers were deposited on a substrate. Part of the top deposited layers are etched away to expose the sacrificial bottom layer, which is then attacked by a gaseous etch that does not chemically interact with the top layers. The top layers peel away as the bottom layer is removed, and curl together as a result of their internal stresses to form nanosprings. The authors' AFM and SEM measurements demonstrated the nanosprings possess a very low initial stiffness and a high range of strain capabilities, indicating a potential application as high-resolution force sensors.

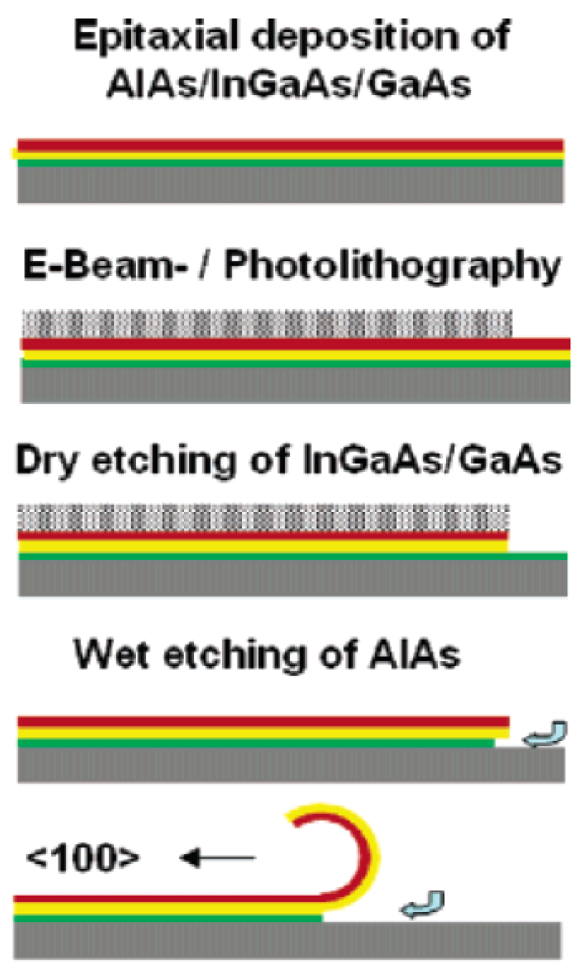

Figure 5[17]. A diagram of the process that Bell et al used to create nanosprings made of InGaAs and GaAs. In the first step molecular epitaxy is used to deposit layers of AlAs, InGaAs, and GaAs, represented by green, yellow, and red, respectively. In the second photoresist is laid down and then removed with lithography. In the third a gaseous etch is used to remove the exposed layers of InGaAs and GaAs. In the fourth a chemical etch is used to remove the layer of AlAs. The final step shows how as AlAs underneath the top layers is removed, the top layers curl onto each other and create a nanospring.

A third possibility is the use of wet chemical synthesis, stirring, and centrifugation. Briefly, Mendoza-Crúz et al mixed copper dichloride, octadecylamine, glucose, and tetrachloroaurate trihydrate[18]. This solution was heated, stirred, and centrifuged for several minutes. This resulted in nanosprings formed through precipitation and self-assembly as seen in Figure 6. The nanowires composing the nanosprings had an average diameter of 1.8 ± 0.3 nanometers, which is much thinner than nanowires formed with the traditional VLS method, and were several micrometers in length, which is more typical of the VLS method.

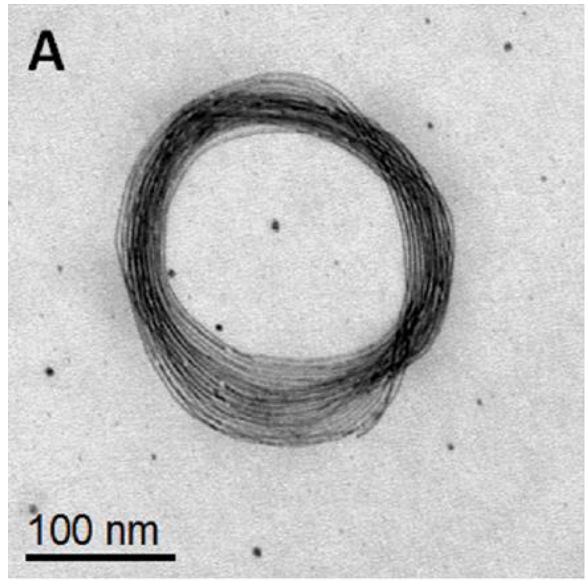

Figure 6[18]. Thin nanosprings formed through wet chemical synthesis, centrifugation, and precipitation.

Conclusion

Nanosprings are a helical nanostructure that is most commonly made through the VLS technique. They are potentially revolutionizing and have applications in diverse areas of physics, chemistry, engineering, and biology. Their primary strengths lie in their simplicity, versatility, and durability. The great number of choices for composition and coatings mean they can be tuned to fit the demands of many different applications in many different environments. Although research into them is still in its infancy, they have great potential. Three alternative growth methods exist to form nanosprings were discussed. These involved the techniques of electroplating, wet chemical etching, photolithography, dry chemical etching, self-assembly, centrifugation, and precipitation.

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