PART I

Nanostructure Fabrication

CHAPTER 1

Nanofabrication Techniques

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1.1 INTRODUCTION

Interest in the study and production of nanoscaled structures is increasing. The incredibly small sizes of nanoscaled devices and functionality of nanoscaled materials allow them to potentially change every aspect of human life. This technology is used to build the semiconductors in our computers; nanoscaled materials are studied for drug delivery, DNA analysis, use in cardiac stents, and other medical purposes. Layers of molecules can be placed on machine parts to protect them from wear or aid in lubrication; monolayers of molecules can be added to windows to eliminate glare. Although we are already greatly affected by this technology, new advances in nanofabrication are still being made.

Microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) have the potential to perform tasks and study the human body (BioMEMS and BioNEMS) at the molecular level. BioMEMS have existed for decades and were first used in neuroscience. In the 1970s, Otto Prohaska developed the first planar microarray sensor to measure extracellular nerve activity [1]. Prohaska and his group developed probes used for research in nerve cell interactions and pathological cell activities in the cortical section of the brain [1]. In the future, NEMS and other nanoscaled structures may be able to perform more advanced tasks. This technology may allow us to cure diseases or heal tissues at the molecular level. Computers may be even more powerful, while taking up less space.

Many of the fabrication methods for nanoscaled devices used today are actually based on previously conceived methods. Others take advantage of new technologies to make nanoscaled structures. Still others combine several

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different methods to produce new technologies. This section will describe several technologies commonly used in nanofabrication. These methods produce a large variety of structures from fibers, to columns, to layers of materials that are a single molecule thick.

1.2 PHOTOLITHOGRAPHY

Originally, lithography was a printing method invented in 1798 by Alois Senefelder in Germany. At that time, there were only two printing techniques: relief printing and intaglio printing [2]. In relief printing, a raised surface is inked and an image is taken from this surface by placing it in contact with paper or cloth. The intaglio process relies on marks engraved onto a plate to retain the ink [2]. Lithography is based on the immiscibility of oil and water. Designs are drawn or painted with an oil-based substance (greasy ink or crayons) on specially prepared limestone. The stone is moistened with water, which the stone accepts in areas not covered by the crayon. An oily ink, applied with a roller, adheres only to the drawing and is repelled by the wet parts of the stone. The print is then made by pressing paper against the inked drawing.

Optical lithography began in the early 1970s when Rick Dill developed a set of mathematical equations to describe the process of lithography [3]. These equations published in the "Dill papers" marked the first time that lithography was described as a science and not an art. The first lithography modeling program SAMPLE was developed in 1979 by Andy Neureuther (who worked for a year with Rick Dill) and Bill Oldman [3].

Photolithography is a technique used to transfer shapes and designs onto a surface of photoresist materials. Over the years, this process has been refined and miniaturized; microlithography is currently used to produce items such as semiconductors for computers and an array of different biosensors. To date, photolithography has become one of the most successful technologies in the field of microfabrication [4]. It has been used regularly in the semiconductor industry since the late 1950s; a great deal of integrated circuits have been manufactured by this technology [4]. Photolithography involves several generalized steps, cleaning of the substrate, application of the photoresist material, soft baking, exposure, developing, and hard baking [5]. Each step will be explained briefly below.

1.2.1 Cleaning of the Substrate

During substrate preparation, the material onto which the pattern will be developed is cleaned to remove anything that could interfere with the lithography process including particulate matter and impurities. After cleaning, the substrate is dried, usually in an oven, to remove all water [3].

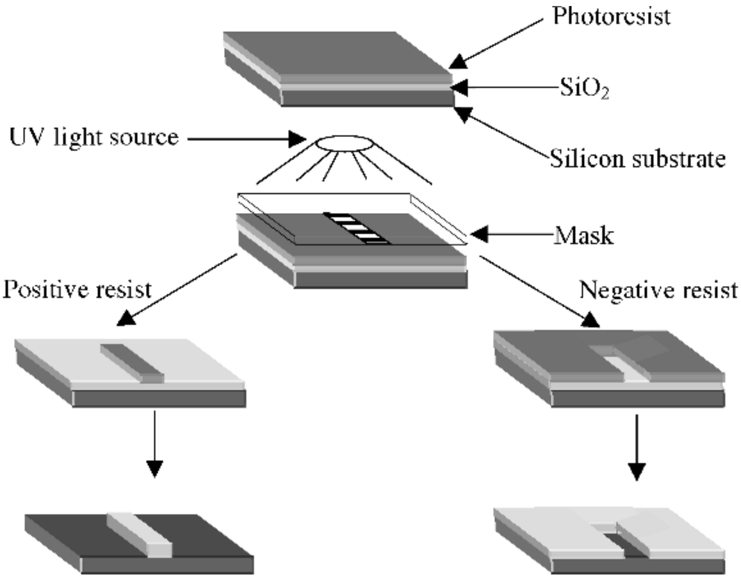

FIGURE 1.1 Steps in photolithography using positive and negative photoresists.

1.2.2 Application of the Photoresist Material

There are two types of photoresist materials, positive and negative. Positive photoresists become more soluble when they are exposed to UV light (Fig. 1.1). So in photolithography, when the mask is laid down onto the positive photoresist, the exposed areas (those not covered by the mask) will be removed by the developing solution leaving only the shape of the mask and the underlying substrate (Fig. 1.1) [5].

Negative photoresist materials work in the opposite manner (Fig. 1.1). These photoresist materials polymerize with exposure to UV light, making them less soluble after exposure. Once the mask has been lifted and the material has been washed with developing solution, the photoresist covered by the mask is washed away (Fig. 1.1). Therefore, using a negative photoresist creates the photographic negative of your mask [5].

Photoresists commonly used in the production of microelectronics include ethylene glycol, monoethyl ether propylene glycol and methyl ether acetate [6].

1.2.3 Soft Baking

The soft baking step is used to remove the solvents from the photoresist coating. Soft baking also makes the coating photosensitive [3].

1.2.4 Exposure

In this step, the mask is placed onto or over the substrate so that the pattern can be placed onto the surface of the substrate (Fig. 1.1). There are three different techniques used to position the mask prior to exposing the photoresist to UV light; these techniques are contact printing, proximity printing, and projection printing [5].

1.2.4.1 Contact Printing During contact printing, the substrate surface is covered with the photoresist and the mask physically touches the surface. The substrate is exposed to UV light while it is in contact with the mask. The contact between the mask and the substrate makes micron resolution possible. Unfortunately, if debris is trapped between the mask and the substrate, it can damage the mask and cause defects in the pattern [5].

1.2.4.2 Proximity Printing In proximity printing, the mask and the substrate are separated by a small distance (10–25 μm) before exposure to UV light. This technique protects the mask and the pattern from some debris damage that could occur during contact printing. The distance between the mask and the substrate lowers the resolution to 2–4 μm [5].

1.2.4.3 Projection Printing In projection printing, an image of the mask is projected onto the substrate after it is covered with the photoresist. This method can produce patterns with high resolution (1 μm) by projecting a small section of the mask at a time. Once the mask is in the correct position, the photoresist is exposed to high intensity UV light through the pattern in the mask [5].

1.2.5 Developing

Through developing, the photoresist becomes more soluble (positive photoresists) or less soluble (negative photoresists). When using a positive photoresist, an increase in energy causes an increase in the solubility of the resist until the threshold energy is reached. At this energy, all of the resist is soluble. In negative photoresists, the material becomes less and less soluble with increased energy. At the threshold energy, the material is even less soluble; as the energy is raised above the threshold energy, more of the photoresist is insoluble and more of it will remain after developing. The amount of time and energy necessary to complete the developing step depends on a variety of factors such as the prebaking conditions, amount of photoresist material, and developing chemistry. After the developing, a solvent is used to wash the sample [5].

1.2.6 Hard Baking

This is the final step of photolithography. Hard baking is used to harden the photoresist and improve bonding between the photoresist layer and the substrate underneath [5].

1.2.7 Limitations of Photolithography

Current photolithography techniques used in microelectronics manufacturing use a projection printing system (known as a stepper). In this system, the image of the mask is reduced and projected, via a high numerical aperture lens system, onto a thin film of photoresist that has been spin coated onto a wafer [4]. The resolution that the stepper is capable of is based on optical diffraction limits set in the Rayleigh equation (Eq. 1.1).

$$R = k_1 \lambda / \mathrm{NA} \tag{1.1}$$

In the Rayleigh equation, k_1 is a constant that is dependent on the photoresist, λ is the wavelength of the light source, and NA is the numerical aperture of the lens.

The minimum feature size that can be achieved with this technique is approximately the wavelength of the light used, λ; although theoretically, the lower limit is $\lambda/2$. So, in order to produce micro- or nanoscaled patterns and structures, light sources with shorter wavelengths must be used. This also makes manufacturing more difficult and expensive [4].

1.3 SPECIALIZED LITHOGRAPHY TECHNIQUES

In order to produce patterns at the nanometer scale, which is necessary for the fabrication of semiconductor integrated circuits, nanoelectromechanical systems, or lab-on-a-chip applications, specialized lithography techniques are used. Some of these techniques involve steps similar to those seen in photolithography; the differences lie in the use of energy sources with smaller wavelengths and smaller masks (both changes are used to produce nanoscaled patterns and structures). Such specialized lithography techniques include electron beam lithography, nanosphere lithography, and focused ion beam lithography (FIB). Other specialized techniques are more reminiscent of original lithography in that they transfer the pattern of molecules directly onto the substrate as a print. These techniques include types of soft lithography (such as microcontact printing, replica molding, microtransfer molding, and solvent-assisted micromolding), nanoimprint lithography, and dip pen lithography (a type of scanning probe lithography) [4, 7]. Other techniques, such as LIGA, combine elements from both categories. A few of these techniques will be briefly discussed below.

1.3.1 Electron Beam Lithography

Electron beam lithography has been used in the production of semiconductors and the patterning of masks for other types of lithography (such as X-ray and optical lithography). In electron beam lithography, the exposed substrate is modified by the energy from a stream of electrons.

1.3.2 Nanosphere Lithography

Nanosphere lithography is similar to other types of lithography. In this type of lithography, the mask is replaced with a layer of nanospheres. After exposure and developing, the uncovered resin is washed away leaving behind nanoscale vertical columns.

1.3.3 Soft Lithography

Soft lithography is called "soft" because an elastomeric stamp or mold is the part that transfers patterns to the substrate and this method uses flexible organic molecules and materials rather than the rigid inorganic materials commonly used during the fabrication of microelectronic systems [4]. This process, developed by George Whitesides, does not depend on a resist layer to transfer a pattern onto the substrate. Soft lithography can produce micropatterns of self-assembled monolayers (SAMs) through contact printing or form microstructures in materials through imprinting (embossing) or replica molding [4].

In this process, a self-assembled monolayer is stamped onto the substrate [4]. The molecular impressions left by the monolayer can be used to seed crystal growth or bind strands of DNA for bioanalysis. Soft lithography techniques are not subject to the limitations set by optical diffraction, as discussed earlier (the edge definition is set by van der Waals interactions and the properties of the materials used) [4]. They offer procedurally simple, less expensive alternatives to the production of nanoscaled structures through photolithography.

1.3.4 Dip Pen Lithography

Dip pen lithography is a type of scanning probe lithography. In this lithographic technique, the tip of an atomic force microscope (AFM) is used to create micro- and nanoscaled structures by depositing material onto a substrate. The AFM tip delivers the molecules to the substrate surface using a solvent meniscus that forms in ambient atmospheres. Structures with features ranging from several hundreds of nanometers to sub-50 nm can be generated using this technique [7].

Dip pen lithography is a direct-write method that yields high resolution and has been used to create microscale and nanoscale patterns with a variety of "inks" (such as biomolecules, organic molecules, polymers, and inorganic molecules) on a number of substrates. The AFM tip was first used to form patterns of octadecanethiols in ethanol on the mica surfaces [8]. The technology can now be used to construct protein arrays for proteomics, pharmaceutical screening processes, and panel immunoassays [9].

Dip pen lithography involves several steps. The first is substrate preparation: the substrate is cleaned and rinsed to remove all impurities and produce a

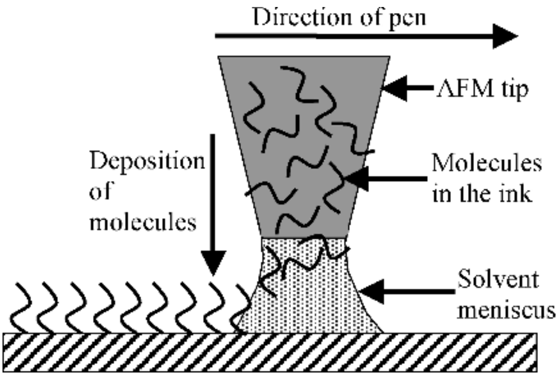

FIGURE 1.2 Dip pen lithography, transferring the molecules from the pen to the substrate surface.

flawless surface. In order to aid in adhesion of the material being deposited, a self-assembled monolayer may be added to the surface. The AFM tip is then coated with the "ink" to be deposited onto the substrate. Finally, the tip is used to produce the desired pattern (Fig. 1.2) [7].

The formation, structure, and stability of the deposited material depend on several different variables. The formation and stability of the structure are subject to the strength of the adhesion between the substrate and the deposited material and the amount of adhesion between the material being deposited and the AFM tip [9]. One source of this adhesion is surface charge. The static interaction between a charged substrate surface and oppositely charged nanospecies will lead to the successful deposition onto the substrate surface [7].

If the adhesion between the material and the AFM tip is too strong, it may prevent material deposition; if it is too weak, the material will not stay on the tip long enough to be deposited onto the substrate and the amount on the tip may not be enough to produce the structure. The deposition of material from the tip to the substrate is also influenced by the cohesion between the material already deposited and the material on the tip [8].

Temperature is also an important factor in dip pen lithography. When working with biomolecules and organic molecules, temperature affects the solubility and diffusion rate of the molecules, which influences the size of the nanopatterns. The solvent used is also a factor in stability. The amount of solvent in the material can influence the shape of the deposit. As the solvent evaporates from the material after deposition, the deposits could harden [8]. Temperature can also influence solvent evaporation rates.

The speed of tip can change the dimensions of the pattern. Increasing speed causes a decrease in pattern size. Humidity can also affect this process. The proper humidity is necessary for the transfer of the material to the substrate [7].

Progress has been made in using dip pen lithography in nanopatterning biomolecules and organic molecules by modulating interactions between target surfaces and the molecules being deposited [8]. Very few inorganic materials have been successfully patterned with this technique; successes include pure metals and metal oxides [7].

1.3.5 LIGA

LIGA is a German acronym for Lithographie, Galvanoformung, Abformung. This process for creating three-dimensional microstructures was developed in the 1980s by W. Ehrfeld [10, 11]. It is an early technique for producing micro- and nanoscaled structures and involves lithography, electroforming, and plastic molding. LIGA was one of the first techniques used to create microstructures with high aspect ratios and depths of hundreds of nanometers [10, 11]. LIGA is a valuable tool for the production of micro- or nanoscaled molds; these molds can aid in the mass production of micromachine parts. The basic steps of LIGA (Fig. 1.3) are explained below [10–12].

1.3.5.1 Deep X-Ray Lithography In LIGA, a several hundred microns thick radiation sensitive polymer layer is applied to a substrate (a metallic base plate or a silicon wafer). This layer is either glued to the substrate or polymerized onto it; polymethyl methacrylate (PMMA) is an example of a polymer that can

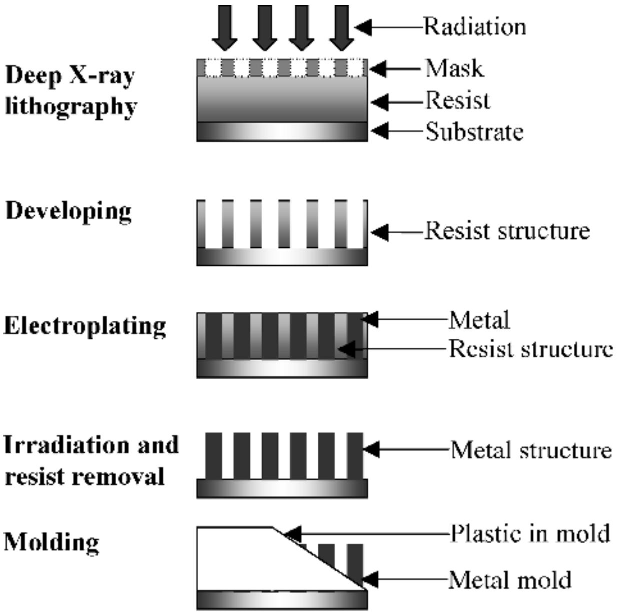

FIGURE 1.3 Diagram of the LIGA technique.

be bonded to the substrate. A mask is placed over the polymer layer and the mask pattern is then transferred onto the polymer layer using deep X-ray exposure with wavelengths from 0.2 to 0.6 nm (using Synchtron radiation) [11].

1.3.5.2 Electroplating After irradiation, the exposed polymer is removed by solvent during development leaving behind the polymer micro- or nanostructures with high aspect ratios. The cavities between three-dimensional structures are typically filled in with metals such as gold, copper, or nickel by electroplating. Alloys, such as nickel–iron or nickel–cobalt, can also be used to fill in the cavities left after development [8].

1.3.5.3 Molding The structure is exposed to X-ray radiation a second time (without the mask) and the remaining polymer (from the structures with the high aspect ratio) is removed with solvent or developer. This step creates metal micro- or nanostructures with a high aspect ratio. These metal structures are used as a mold for plastic parts using injection molding, hot embossing, or resin casting [8].

1.4 THIN FILM DEPOSITION

Thin film deposition techniques allow one to deposit a thin layer of material onto a surface or a substrate. Typically, the thicknesses of these thin films are in the nanometer scale. Some techniques even allow the addition of single atom layers of a material to the substrate. These techniques are used to create a wide variety of devices including coatings for optics components, conductors, semiconductors, and insulators for electronic devices, and films for packaging. Although thin film deposition includes a broad range of technologies and methodologies, a generalized process can be described in three steps: (1) creation of the flux of condensable species, this includes either neutral atoms or ions, (2) transportation of the created species to the substrate, and (3) growth of the film onto the substrate. Thin film deposition has a wide variety of applications including the manufacture of reflective coatings for optics, the manufacture of electronics, and the purification of metals such as copper through electroplating. Electronics is perhaps the most well-known field that requires thin film deposition. The technology is continually allowing the electronics industry to create smaller and smaller electronic components including insulators, semiconductors, and integrated circuits, allowing developers to increase the speed and efficiency of their products without increasing the product size. Thin film deposition can be divided into two broad categories: physical deposition and chemical deposition. Only a few thin film deposition techniques do not fit completely into these categories; they will be described later. Many methods of thin film deposition do not rely on one technology to attain their goals; often a combination of techniques and technologies are used.

Physical deposition, as the name implies, involves thin film deposition techniques that use physics, typically in terms of mechanical or thermodynamic means, to deposit the desired film onto the substrate. Physical deposition includes three primary classes: evaporation, sputtering, and ion beam. Evaporation thin film deposition employs the ability to evaporate the material to be deposited by physical heating to create the flux of material. The species created through the heating process is then transported to the substrate to be deposited onto the surface. Although rather simple in concept, many different methods to heat the materials have been used, including resistance heating, electron beam heating, arc evaporation, induction heating, and flash evaporation.

An example of arc evaporation is cathodic arc plasma deposition (CAPD). This technique utilizes vacuum arcs to produce the condensable species. The source material to be deposited is created from the cathode in the arc discharge circuit. The condensable species is created from the source material through flash evaporation as the arc spots move along the surface of the target. The arc spots are sustained by the plasma being formed by the arc itself [13].

The second class of physical thin film deposition is the sputtering technique. This process involves the synthesis of the condensation species by bombardment of the source (target) with positive ions of an inert gas. The collisions cause the atoms on the target to be knocked off through momentum transfer and result in the creation of ions on the target as well. This technique is typically called plasma-assisted (enhanced) deposition, which encourages the atoms to be knocked off and collected onto substrates [13]. The sputtering technique has an advantage over the aforementioned evaporation technique because it can occur at lower temperatures (heating is not required) and because the process is independent of the evaporation rate of the material.

Another class of physical thin film deposition utilizes ion beam technology. These techniques employ the use of an ion beam to ionize the material to be deposited. An example is gas cluster ion beam technology (GCIB). Neutral gas clusters are produced by the expansion of atoms or molecules at high pressure through a room temperature nozzle into a vacuum. The neutral gas cluster is ionized by the bombardment of electrons and is accelerated by a high voltage to impact a substrate. The impact causes all of the atoms to nearly interact simultaneously and deposit a very high energy density into a small volume of the target material [14].

The second large category of thin film deposition techniques is chemical deposition. As the name implies, chemical deposition causes a chemical change of the fluid material that results in the deposition. Chemical vapor deposition (CVD) is a class of chemical deposition where the condensable species is formed from gases or vapors that are, without energy input, not condensable. The substrates are heated at high temperature to cause the gases to decompose resulting in deposition. Plasma-enhanced chemical vapor deposition (PECVD) utilizes plasma that is created through the action of an electric field. Ionization, dissociation, and gas phase reactions occur as the reactant gases are passed through the low pressure plasma. The addition of plasma to the technique allows the process to occur at much lower temperatures, not entirely relying on the reactions to be driven thermally [13]. This method will be discussed in more depth later in Section 1.7.

Plating is another class of chemical deposition used to produce thin films. The plating technique distinguishes itself because of its use of liquid precursors. The material to be deposited is initially dissolved in an aqueous solution. Although the process can be driven entirely by the reagents within the solution, usually an electric current or ion beam is used to drive the reaction to form the layer of desired material.

The final two techniques of thin film deposition to be discussed are molecular beam epitaxy (MBE) and reactive sputtering. MBE and reactive sputtering do not entirely fit into either chemical or physical deposition categories, being more of a combination of chemical and physical. During MBE, ultrapure elements are heated until they begin to slowly evaporate. The evaporated elements do not react with one another until they condense onto the substrate. The process occurs in a high vacuum, which allows a slow deposition rate. The slow deposition rate allows the material to grow epitaxially, meaning instead of many randomly arranged grains being formed, as in higher deposition rates, the material tends to grow in larger grains with a more uniform orientation. The slow deposition rate also allows the element to be deposited one layer at a time [15].

The last technique to be discussed is reactive sputtering. In reactive sputtering, a small amount of non-noble gas (such as oxygen or nitrogen) is mixed with the plasma forming gas. The material is then sputtered from the target to the substrate reacting with the gas. The result is the deposition of a different material. If the gas used is either oxygen or nitrogen, an oxide or nitride can be formed. The method is not limited to oxygen or nitrogen; a wide variety of compounds can be created via this method [16].

1.5 ELECTROSPINNING

Electrospinning is a technique used to create polymeric fibers with diameters in the nanometer range. This process involves the ejection of a charged polymer fluid onto an oppositely charged surface. One of the first investigations into the flow of conducting liquid through a charged tube with a counterelectrode some distance away was conducted by Zeleny [17]. A great deal of these experiments used aqueous electrolyte solutions with high electrical conductivity and low viscosity. The addition of a charge to this solution caused it to form a fine spray of charged droplets that were attracted to the counterelectrode. These droplets quickly evaporated in the air; this process was later called electrospraying.

Electrospinning is very similar to electrospraying; a charge is applied to a polymer solution or melt and ejected toward an oppositely charged target (Fig. 1.4). A typical electrospinning experimental setup is shown in Fig. 1.4.

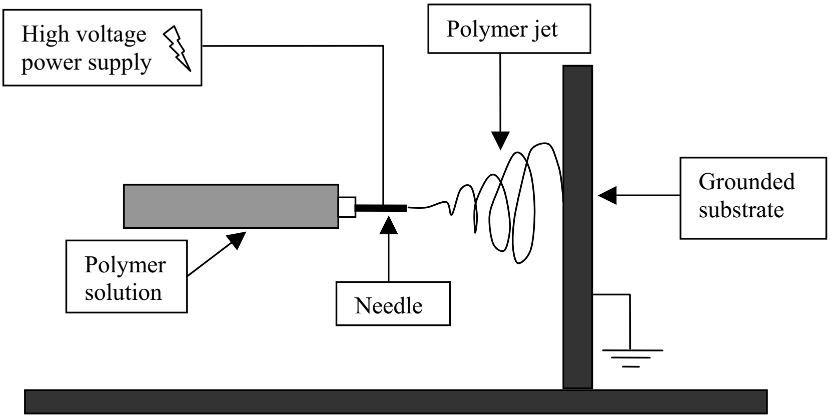

FIGURE 1.4 A typical electrospinning setup.

In both processes, the surface tension and viscoelastic forces of the polymer solution cause drops at the tip of the syringe to retain their hemispherical shape. The charge induced by the electric field causes the droplet to deform into a "Taylor cone" at the tip of the tube [18]. When the applied voltage is increased beyond a threshold value, the electric forces in the droplet overcome the opposing surface tension forces and a narrow charged jet is ejected from the tip of the Taylor cone. In electrospraying, the strength of the electric field and low viscosity of a solution cause droplets to separate from the cone and spray onto the target. In electrospinning, the concentration of the solution, viscosity of the solution, and the entanglement of the polymer chains cause a fiber to be extruded from the tip of the cone. The polymer jet begins as a nearly straight line because of the stabilization from the longitudinal stress of the external electrical field on the charge carried by the jet. However, the polymer jet quickly becomes unstable because of the repulsive forces from the opposite charges in the polymer jet. The jet experiences electrically driven bending instabilities and the jet is whipped around in a spiral, as demonstrated by Reneker et al., using high speed videography [19]. The polymer jet is stretched while it bends and travels through the spiral causing a significant decrease in fiber diameter and rapid evaporation of the solvent resulting in the formation of nanoscale thin fibers. These fibers land randomly onto the grounded target forming a nonwoven fiber mat (Fig. 1.5).

Electrospinning produces fibers with submicron diameters [19]. The diameter of the fibers can be adjusted by altering the distance between the polymer source and the target, the polymer concentration, and the voltage. The orientation of the fibers onto the target can be changed by employing various external mechanical or electrostatic forces [20]. The mechanical properties of the fiber mat can be altered by changing the diameter and orientation of the fibers.

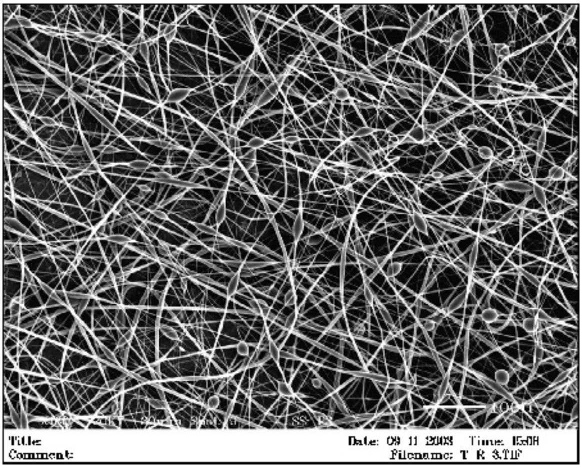

FIGURE 1.5 Electrospun polylactic acid-co-glycolic acid nanofibers.

Cellulose acetate was one of the first solutions electrospun; Formhals was given a U.S. patent for this process in 1934 [21]. In another early study, molten wax was observed to form threads when subjected to high electrical field [17]. Presently, a wide variety of polymers have been electrospun from natural polymers such as type I collagen or elastin to synthetic polymers such as polyphosphazenes.

Several parameters affect the electrospinning process. These parameters can be split into different groups, polymer solution properties, processing parameters, and environmental parameters. Polymer solution properties include solution viscosity, polymer molecular weight, polymer concentration, surface tension, solution conductivity, and dielectric effect of the solvent [22–24]. Processing parameters that affect electrospinning include voltage, distance from needle to collector, flow rate, needle/orifice diameter, and type of collector [22, 23, 25, 26]. The environmental parameters that can affect electrospinning of nanofibers include humidity, pressure, and type of atmosphere [22, 25].

1.6 NANOSPHERES

Nanosphere technology revolves around the creation of polymeric spheres that are hundreds of nanometers in diameter. Their tiny size and ability to absorb or bind to (through surface chemistry) drugs or growth factors make them ideal vehicles for drug or growth factor delivery.

Polymeric nanospheres can be created by emulsion solvent diffusion. The polymer is dissolved into a volatile organic solvent (such as chloroform, ethyl acetate, or methylene chloride). This solution is then poured into an aqueous phase with a surfactant or stabilizer and agitated usually with a sonicator. The nanospheres are then collected by evaporating the solvent (this may be done with mixing) or dilution with water.

Drugs and growth factors may be added to the organic or aqueous phase in order to incorporate them into the nanospheres. Scanning electron microscopy is used for nanosphere characterization. The size and density of the spheres can be altered by changing the amount of polymer added to the surfactant or stabilizer solution and the speed with which the solution is agitated.

1.7 CARBON NANOTUBES

Carbon is the building block for all organic life. It is found in a variety of structures that display vastly different properties. In nature, pure carbon is found in a variety of forms from the soft, flexible, and conductive graphite to the hard, inflexible insulating diamond. The properties of these materials stem from the arrangement of their carbon atoms. In graphite, the carbon atoms are arranged into sheets of honeycomb-shaped matrices; these matrices are held together by covalent bonds between the carbon atoms. The sheets are held to one another by weak van der Waals forces; this allows graphite to flake off into layers (sheets of carbon atoms slide over one another when force is applied) making graphite a good lubricant. In contrast, the carbon atoms in a diamond are arranged into a tetrahedral pattern. This arrangement makes diamonds hard and prevents them from flaking like graphite. Similarly, it is the arrangement of their atoms and their nanoscale size that give carbon nanotubes their mechanical, chemical, and electrical properties.

Carbon nanotubes (CNTs) are fullerenes that are structurally similar to long rolls of graphite. Fullerenes are molecules composed entirely of carbon that exist as hollow objects (spheres, ellipsoids, or tubes); they are named after Buckminster Fuller, an American architect, designer, and author known for his work on geodesic domes.

CNTs are created as single-walled nanotubes (SWNTs) or multiwalled nanotubes (MWNTs). SWNTs have only one wall whereas MWNTs have many walls formed around one another. The walls of MWNTs are held to one another by van der Waals forces. The properties of CNTs depend on their length, diameter, and chirality (the direction in which the graphite sheet is rolled up).

Carbon filaments were first noticed under gaseous conditions in the presence of metal catalysts in the 1950s after the development of the electron microscope. Carbon filaments up to several hundred nanometers long were noticed extending from catalytic particles of transition metals [27]. Tibbetts was the first to document these structures and speculate about their growth mechanism [27]. In the 1990s, Iijima observed the formation of MWNTs through the electric arc discharge method and later documented the synthesis of SWNTs via laser ablation [28].

SWNTs are very strong and very stiff because of the strength of the carbon–carbon bond and the seamless structure of the nanotube; the modulus of an SWNT has been calculated as 0.64 TPa with an ultimate tensile stress of approximately 37 GPa [29]. The electrical properties of SWNTs can range from metallic to semiconducting with various band gaps depending on the chirality and diameter of the tube [29]. CNTs have been used in a variety of applications including increasing mechanical properties of polymers through composite reinforcement, use in nanosensing devices, and in bioimaging.

CNTs have been made using a variety of fabrication methods; some of the more common methods will be mentioned in this section. These methods include electric arc discharge, laser ablation of carbon, and chemical vapor deposition, techniques that are also used to create thin films, as mentioned in an earlier section.

1.7.1 Electric Arc Discharge

The electric arc discharge method was one of the first methods used to fabricate CNTs [30]. An electric arc is a discharge of current that occurs when a current jumps between two electrodes or a gap in a circuit; to form CNTs, high purity carbon electrodes are used. During this process, the anode, the source of the carbon, is consumed throughout the process. As the nanotubes are formed from the material in the anode, they are deposited onto the cathode. The composition of the electrodes affects the type of CNTs produced. MWNTs are produced when pure carbon electrodes are used. To produce SWNTs, a small hole is drilled into the anode and filled with metallic catalyst particles and graphite powder. Mixtures of Ni and Y have been shown to produce high quality SWNTs [31].

1.7.2 Laser Ablation

Ablation is the melting or vaporizing of a substance; in laser ablation for the fabrication of CNTs, a graphite target is subjected to a laser at high temperatures. The graphite target is ablated with a powerful laser in the presence of an inert gas. The gas collects the ablated carbon powder and deposits it onto a cooled substrate. The powder consists of CNTs and onion-like structures [30]. Similar to the electric arc discharge method, MWNTs are produced when pure carbon (graphite) is used and SWNTs are produced when the target is mixed with catalyst metals ($<1\%$) such as Co–Ni powder [30].

1.7.3 Chemical Vapor Deposition

Unlike the previously mentioned techniques for CNT production (electric arc discharge and laser ablation), chemical vapor deposition allows the user to deposit the CNTs directly onto a substrate. Chemical vapor deposition is commonly used in the manufacturing of metals and ceramics [27]. This technique can produce CNTs at a continuous rate and is easily scalable to produce large amounts of CNTs for commercial distribution [30]. By changing growth conditions such as growth temperature, carbon source, catalyst, catalyst-to-carbon ratio, and type of substrate, CNTs can grow in a variety of ways, including randomly oriented and aligned.

There are several ways to perform chemical vapor deposition, including hot-wall chemical vapor deposition, cold-wall chemical vapor deposition, high pressure CO conversion (HiPCO) chemical vapor deposition, and laser-assisted chemical vapor deposition; both hot-wall and cold-wall chemical vapor deposition are forms of thermal chemical vapor deposition. In hot-wall chemical vapor deposition processes, such as thermal chemical vapor deposition, the process takes place in a high temperature tube furnace. The substrate that the CNTs will be deposited on is placed inside of the tube and the entire tube is heated (heating the substrate to the growth temperature). A hydrocarbon source, such as benzene, xylene, or hexane, is also introduced into the tube. Once in the tube, it decomposes and deposits onto the substrate. In cold-wall chemical vapor deposition processes, including plasma-enhanced chemical vapor deposition, the temperature of the sample holder is raised and the rest of the system is left at a lower temperature. In HiPCO chemical vapor deposition, high pressure carbon monoxide is fed into the system and used as the carbon source.

Laser-assisted chemical vapor deposition is a technique that is used for thin film deposition and can be adopted to produce films of CNTs. In laser-assisted chemical vapor deposition, the global energy source that warms the furnace is replaced by a localized energy source, the laser. In this method, the source of the energy on the substrate is localized, so the growth of the CNTs can be limited to the area over which the laser passes.

Laser-assisted chemical vapor deposition is controlled by two mechanisms: photolytic laser-assisted chemical vapor deposition and pyrolytic laser-assisted chemical vapor deposition. Depending on the conditions, such as temperature and position of the laser beam, both mechanisms can take place simultaneously. In such cases, one mechanism for CNT deposition may dominate the other. Only the photolytic process can occur at low temperatures, but at high temperatures both the photolytic and pyrolytic processes can occur simultaneously [32]. Pyrolytic or photolytic reactions are caused by the laser radiation wavelength, precursor compounds used, and chosen substrate material [33].

1.7.4 Photolytic Laser-Assisted Chemical Vapor Deposition

Photolytic laser-assisted chemical vapor deposition can be performed at low wavelengths and with short pulse durations. This combination of conditions creates a low temperature during processing, eliminating damage that can be caused by thermal reactions with the substrate, such as recrystallization, oxidation, and crack formation. This allows for exact processing of materials for use in microelectronics [34]. Since it does not produce high temperatures, photolytic laser-assisted chemical vapor deposition is used in conjunction with temperature-sensitive substrates. Lasers or lamps can be used as a source for photons, but the increased power densities of lasers lead to a 100-fold increase in growth rate when compared to lamps [35].

Resonant absorption of the laser radiation by the precursor causes bonds in the precursor molecules to break freeing them for deposition onto the substrate [30]. In photolytic laser-assisted chemical vapor deposition, the laser beam is parallel to the substrate and passes just above it. The photons from the laser are absorbed by the gas phase starting the reaction [36]. This arrangement allows for the control of the substrate temperature independent from the laser radiation [30]. Photolytic laser-assisted chemical vapor deposition may also occur in a perpendicular laser–substrate arrangement, but this geometry also introduces pyrolytic laser-assisted chemical vapor deposition [33].

1.7.5 Pyrolytic Laser-Assisted Chemical Vapor Deposition

In pyrolytic laser-assisted chemical vapor deposition, the thermal energy produced by the laser causes molecules of the reagent to disassociate and deposit as CNTs on the substrate. The laser beam strikes the substrate at perpendicular incidence and the chemical reaction is driven thermally by the local heating of the substrate by the laser radiation. If the substrate is moved throughout the process, single-step patterns can be made. If the substrate is stationary, this process can produce three-dimensional structures [33]. Since this method is essentially a type of thermal chemical vapor deposition, the same conditions used for thermal chemical vapor deposition can be used with pyrolytic chemical vapor deposition. The major difference is the heat source; the use of a localized heat source (the laser) changes the reaction kinetics. This improves the deposition rate and allows three-dimensional objects to be produced [37].

Pyrolytic laser-assisted chemical vapor deposition was first performed by Lydtin in 1972 [33] using an IR laser to deposit carbon onto aluminum substrates. Now any commercially available laser can be used as a radiation source for this technique. Typically, argon and krypton lasers are used for submicron-sized patterns (necessary for nanofabrication and microelectronics) [30]. Otherwise, other types of lasers, such as CO_2 lasers, can be used since most gases do not absorb the infrared or visible wavelengths emitted.

Pyrolytic laser-assisted chemical vapor deposition can also be performed with an IR laser through vibration excitation. In this technique, the gas phase is excited through collisional and vibrational relaxation processes. This heats up the gas phase and the substrate, leading to the deposition of the film. Examples of laser and gas phase systems used in this technique include CO_2 lasers and BCl_3, SiH_4, or NH_3 gas [33].

1.7.6 Substrate-Site-Selective Growth

There are other techniques that can deposit CNTs into precise shapes and patterns. One of these techniques is substrate-site-selective growth. This procedure combines lithography with chemical vapor deposition to achieve targeted nanotube deposition for pattern production. In this process, a pattern is placed onto the substrate using lithography; Wei and colleagues developed a pattern of SiO_2 on top of a silicon substrate [30]. After the pattern has been laid down, the nanotubes are deposited using a chemical vapor deposition technique. In previous work, Wei and colleagues used a conventional tube furnace with ferrocene ($Fe(C_5H_5)_2$) as the nanotube nucleation initiator and xylene as the carbon source [30]. The furnace was gradually heated to 800 °C and the ferrocene–xylene solution was fed into the reactor at 150 °C. The choice of precursors is extremely important because it dictates the length of the nanotubes deposited onto the substrate. The combination of ferrocene and xylene produced vertically aligned MWCNTs that were 20–30 mm in length onto the SiO_2 pattern; there was no CNT deposition on the silicon surface [30]. This technique has great potential for the design of mesoscale systems similar to those in MEMS [30].

1.8 SELF-ASSEMBLED NANOSTRUCTURES

The self-assembly of molecules into structures is a phenomena seen frequently in nature; type I collagen molecules are examples of molecules that can orient and arrange themselves to form two-dimensional and three-dimensional structures. Among the nanofabrication methods discussed in this chapter, self-assembly of molecules is one of the most promising ways to form a large variety of nanostructures [38]. This technique relies on the noncovalent interactions between molecules (electrostatic, van der Waals, hydrogen bonding, π–π interactions, and capillary force) to organize groups of molecules into larger, regular structures [38].

Self-assembled monolayers are among the most commonly studied self-assembled structures. SAMs are surfaces covered by a thin film consisting of a single layer of molecules. Typically, they are formed when surfactant molecules are absorbed onto a substrate as a monomolecular layer. Among the most common and widely studied SAM systems are gold–alkylthiolate ($CH_3(CH_2)_nS$) and silicon oxide–alkylsilane monolayer systems (Fig. 1.6).

In typical SAM fabrication, a group with a strong attraction to a particular substrate is attached to the head of a long molecule, an alkane chain with about 10–20 methylene units. The head group absorbs easily onto the substrate surface, creating a monolayer with the tails pointing away from the substrate surface [39]. An example of this is the gold–thiol SAM; thiol (S–H) head groups in solution absorb readily onto gold. In work with methyl-terminated thiols, Krishnan and colleagues first cleaned the substrate, silicon wafers, in hot 1:4 H_2O_2 (30%)/ H_2SO_4 and then rinsed them in distilled–deionized water and absolute alcohol. Next, a layer of gold was added in order to allow the thiol groups to bind. The wafers were covered in gold using vapor deposition of chromium and gold from heated tungsten boats in a cryogenically pumped deposition chamber [39].

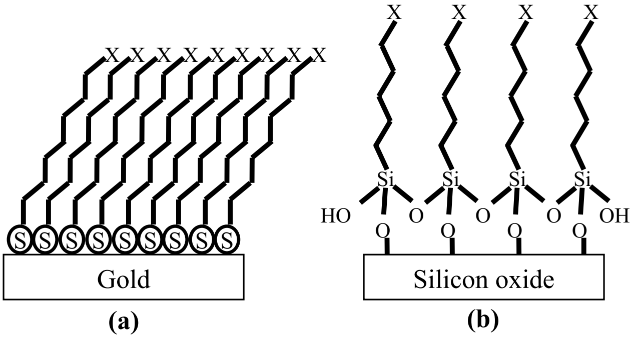

FIGURE 1.6 A diagram of (a) gold–alkylthiolate and (b) silicon oxide–alkylsilane SAMs.

The layer of chromium was deposited before the layer of gold to enhance adhesion to the substrate. The gold-coated samples were removed and placed into 1 mM solutions of 1-hexadecanethiol in ethanol, contained at ambient temperature, for 3 days. Afterward, the wafers were placed into the thiol solution. Before experimental use, they were rinsed with ethanol and air dried [39]. In this method, the thiol heads form a dense layer (1 molecule thick) on the gold surface whereas the tails of the molecules point outward forming another layer covering the substrate surface.

By changing the group attached to the tail of the absorbed molecules (or using different molecules), you can tailor the functionality of the new surface. Functionality can also be added to that tail groups after the SAM is formed. The tail groups and molecules can be selected to form SAMs for specific applications. Adding short oligomers of ethylene glycol groups to the tail decreases protein adhesion [40]. Methyl-terminated groups can increase plasma and protein binding [39], which could increase the biocompatibility of the substrate. Creating a monolayer of fluoroalkylsilane (FAS) onto silicon surfaces reduces neural cell growth [41]. The use of 1-octadecanethiol, 1-dodecanethiol, and 1-hexanethiol groups protects copper from corrosion [42]. Absorbing a layer of octadecyltrichlorosilane (OTS) increases wear resistance of polysilicon, a technique that may increase the durability of MEMS or NEMS [43].

1.9 CONCLUSIONS

Nanotechnology is an exciting field that has seen tremendous growth and has advanced into the biomedical and electronics arena. Nanotechnology has become an integrated part of our everyday lives. From medicine, to clothing, to electronics, breakthroughs in nanofabrication have lead to new products. There are a plethora of techniques for creating nanoscaled devices for biomedical engineering. Many of these, such as lithography-based techniques, are applications of older techniques with more modern and powerful equipment. All of these techniques produce patterns, structures, and surface morphologies at the nanoscale that lead to devices and materials with unique surface properties and functionality. These techniques impart unique chemical, mechanical, electrical, and optical properties to materials for use in electronics, materials science, and medicine. Nanofabrication has lead to major advances in these fields and holds promise for the creation of new technologies.

REFERENCES

1. Urban GA, Prohaska O, Olcaytug F. In: Urban GA, editor. BioMEMS. Dordrecht, The Netherlands: Springer; 2006. p 1–14.
2. Henshaw M. First impressions: the early history of lithography–a comparative survey. Artonview 2003;(33):33–38.
3. Mack CA. Optical lithography modeling. In: Sheats JR, Smith BW, editors. Microlithography Science and Technology. New York: Marcel Dekker, Inc.; 2006. 109–170.
4. Xia YN and Whitesides GM. Soft lithography. Annu Rev Mater Sci 1998;28: 158–184.
5. Madou MJ. Fundamentals of Microfabrication: The Science of Miniaturization. Boca Raton, FL: CRC Press LLC; 2002.
6. Atkinson GA and Ounaies Z. Polymer systems: materials and fabrication. In: Gad-el-Hak M, editor. MEMS Design and Fabrication. Boca Raton, FL: Taylor & Francis;2006. p 9-1–9-39.
7. Ding L, Li Y, Chu HB, Li XM, Liu J. Creation of cadmium sulfide nanostructures using AFM dip-pen nanolithography. J Phys Chem B 2005;109:22337–22340.
8. Jaschke M and Butt HJ. Deposition of organic material by the tip of a scanning force microscope. Langmuir 1995;11:1061–1064.
9. Lee KB, Lim JH, Mirkin CA. Protein nanostructures formed via direct-write dip-pen nanolithography. J Am Chem Soc 2003;125:5588–5589.
10. Becker EW, Ehrfeld W, Hagmann P, Maner A, Münchmeyer D. Fabrication of microstructures with high aspect ratios and great structural heights by synchrotron radiation lithography, galvanoforming, and plastic moulding (LIGA process). Microelectron Eng 1986;4:35–36.
11. Kathuria YP. L^3: laser, LIGA and lithography in microstructuring. Indian Inst Sci J 2004;84:77–87.
12. Menz W, Mohr J, Paul O. The LIGA process. In: Menz W, Mohr J, Paul O, editors. Microsystem Technology. Wiley-VCH; 2001. p 285–350.
13. Randhawa H. Review of plasma-assisted deposition processes. Thin Solid Films 1991;196:329–349.
14. Yamada I and Toyoda N. Recent advances in R&D of gas cluster ion beam processes and equipment. Nucl Instrum Methods Phys Res B: Beam Interact Mater Atoms 2005;241:589–593.
15. Ota Y. Silicon molecular beam epitaxy. Thin Solid Films 1983;106:1–136.

16. Brodsky MH. Plasma preparations of amorphous silicon films. Thin Solid Films 1978;50:57–67.
17. Zeleny J. Electric discharge from points. Phys Rev 1917;9:562–563.
18. Yarin AL, Koombhongse S, Reneker DH. Taylor cone and jetting from liquid droplets in electrospinning of nanofibers. J Appl Phys 2001;90:4836–4846.
19. Reneker DH, Yarin AL, Fong H, Koombhongse S. Bending instability of electrically charged liquid jets of polymer solutions in electrospinning. J Appl Phys 2000;87:4531–4547.
20. Huang ZM, Zhang YZ, Koraki M, Ramakrishna S. A review on polymer nanofibers by electrospinning and their applications in nanocomposites. Composites Sci Technol 2003;63:2223–2253.
21. Formhals A. Apparatus for producing artificial filaments from material such as cellulose acetate. US patent 1,975,504. 1934.
22. Ramakrishna S, Fujihara K, Teo W, Lim T, Ma Z. An introduction to electrospinning and nanofibers. Singapore: World Scientific Publishing Co.
23. Buchko CJ, Chen LC, Shen Y, Martin DC. Processing and microstructural characterization of porous biocompatible protein polymer thin films. In: 1999. p 7397–7407.
24. Fong H and Reneker DH. Elastomeric nanofibers of styrene-butadiene-styrene triblock copolymer. Journal of polymer science. Part B-Polymer Physics 1999;37:3488–3493.
25. Baumgarten PK. Electrostatic spinning of acrylic microfibers. Journal of colloid and interface science 1971;36:71–79.
26. Deitzel JM, Kleinmeyer J, Harris D, Tan NCB. The effect of processing variables on the morphology of electrospun nanofibers and textiles. Polymer. 2001;42:261–272.
27. Tibbetts GG. Why are carbon filaments tubular. J Crystal Growth 1984;66:632–638.
28. Iijima S. Helical microtubules of graphitic carbon. Nature 1991;354:56–58.
29. Baughman RH, Zakhidov AA, de Heer WA. Carbon nanotubes–the route toward applications. Science 2002;297:787–792.
30. Wei B, Vajtai R, Ajayan PM. Synthetic approaches for carbon nanotubes. In: Kumar CSSR, Hormes J, Leuschner C, editors. Nanofabrication Towards Biomedical Application Techniques, Tools, Applications and Impact. Weinheim: Wiley-VCH; 2005. p 33–55.
31. Journet C, et al. Nature 1997;388:756–758.
32. Mogyorosi P and Carlsson JO. Growth characteristics of photolytic laser-induced chemical vapor-deposition of tungsten from WF6. J Vac Sci Technol A: Vac Surf Films 1992;10:3131–3135.
33. Conde O and Silvestre AJ. Laser-assisted deposition of thin films from photoexcited vapour phases. App Phys A: Mater Sci Process 2004;79:489–497.
34. Jantunen H. Electronics materials, packing and reliability techniques (EMPART). INFOTECH OULU Annual Report; 2005. p 16–24.
35. Gonzales P, et al. Photo-induced chemical vapour deposition of silicon oxide thin films. Thin Solid films 1992;218:170–181.

36. Heszler P, Landstrom L, Lindstam M, Carlsson JO. Light emission from tungsten nanoparticles during laser-assisted chemical vapor deposition of tungsten. J Appl Phys 2001;89:3967−3970.
37. Lehmann O and Stuke M. 3-Dimensional laser direct writing of electrically conducting and isolating microstructures. Mater Lett 1994;21:131−136.
38. Wei B, Vajtai R, Ajayan PM. Molecular Biomimetics: Building Materials Nature's Way, One Molecule at a time. In: Kumar CSSR, Hormes J, Leuschner C, editors. Nanofabrication Towards Biomedical Applications Techniques, Tools, Applications, and Impact. Weinheim: Wiley-VCH; 2005, p 119−134.
39. Krishnan A, Cha P, Liu YH, Allara D, Vogler EA. Interfacial energetics of blood plasma and serum adsorption to a hydrophobic self-assembled monolayer surface. Biomaterials 2006;27:3187−3194.
40. Senaratne W, Andruzzi L, Ober CK. Self-assembled monolayers and polymer brushes in biotechnology: current applications and future perspectives. Biomacromolecules 2005;6:2427−2448.
41. Patel KR, et al. Evaluation of polymer and self-assembled monolayer-coated silicone surfaces to reduce neural cell growth. Biomaterials 2006;27:1519−1526.
42. Li G, Ma H, Jiao Y, Chen S. An impedance investigation of corrosion protection of copper by self-assembled monolayers of alkanethiols in aqueous solution. J Serb Chem Soc 2004;69:791−805.
43. Baker MA and Li J. The influence of an OTS self-assembled monolayer on the wear-resistant properties of polysilicon based MEMS. Surf Interface Anal 2006;38:863−867.