NITINOL THIN FILM THREE-DIMENSIONAL DEVICES – FABRICATION AND APPLICATIONS

Vikas Gupta, A. D. Johnson, V. Martynov, L. Menchaca
TiNi Alloy Company, 1619 Neptune Drive, San Leandro, CA 94577
Tel: (510) 483-9676, Fax: (510) 483-1309, Email: vgupta@tinialloy.com

ABSTRACT

A method has been developed in which three-dimensional structures of nitinol thin film are fabricated using a sequence of processes that involve alternating sputter deposition of multiple layers and Micro-Electro-Mechanical-Systems (MEMS) photolithographic steps. The multiple-layered nitinol parts are transformed into integral three-dimensional shapes by "shape-setting" annealing process using steel mandrels. This method eliminates the difficulties of joining, welding or bonding of nitinol films. Stent-like-devices such as cylinders, cones and hemispheres of few microns thick TiNi thin film have been fabricated and characterized. Micron-scale fenestration patterns fabricated using MEMS techniques enable to design and fabricate wide spectrum of nitinol thin film devices for medical industries and others.

Keywords: Shape memory alloy, Nitinol, Thin film, Sputtering, Three-dimensional, Structures, Stents

INTRODUCTION

Today's TiNi stents are made using bulk nitinol tubes. Stents made from such drawn tubes are relatively large and are too inflexible to be delivered by intravascular catheters to brain lesions. (although recently a thin nitinol neurovascular stent has been developed at SMART Therapeutics, now an entity of Boston Scientific Corp. which is being used in an occlusion system for aneurysms in brain.) Nitinol tubes with wall thickness as small as 50 microns have been achieved by etching and electro polishing techniques. However such techniques aren't suitable to achieve wall thickness smaller than 50 microns. Sputter-deposition techniques can produce TiNi film as thin as 1 micron or more. There is a growing demand for smaller and thinner stents that can be surgically implanted or delivered via catheter, into small diameter, highly tortuous blood vessels. There is also a need to develop specially designed medical devices such as blood clot retrievers or a filter device, which can be delivered through a very small diameter blood vessel in the brain.

Using thin film shape memory alloys one can make such three-dimensional devices. Several methods of fabricating three-dimensional thin film shapes were explored, namely: 1) Rolling and welding of planar film, 2) cylindrical sputtering and sputtering onto a rotating three-dimensional substrate, and 3) multiple layer planar sputter deposition method. The results from each method, with their merits and shortfalls, are presented.

In the first method, planar TiNi film was rolled into cylindrical and conical shapes and the rolled-up edges were welded together. However, the film around the weld spots had been severely damaged that made the bonded film brittle and easy to tear.

In the second method, the problems of welding were solved by sputtering TiNi on three-dimensional substrates. Deposition from a cylindrical sputtering source onto glass cones and cylinders seemed a logical approach; however, it resulted in problems such as overheating of substrates and undesirable alloy composition – again resulting with poor material. In another method, TiNi film was sputter-deposited from a planar TiNi target on the glass cones and cylinders. Patterning of thin film on three-dimensional substrate using photoresist was challenging. Thin film structures were separated from the three-dimensional substrates by chemically etching the underlying sacrificial layer. TiNi film formed by this method wa shown to have good shape memory and superelastic properties; however, it is too slow a process to be considered for production. This paper presents the difficulties encountered with sputter deposition on three-dimensional surfaces.

The third, and the most successful, method has been developed to produce three-dimensional structures of sputter-deposited TiNi thin film. Three-dimensional TiNi thin film structures are produced by a sequence of processes which involves sputter deposition of multiple layers of thin film material on a silicon wafer and standard Micro-Electro-Mechanical-Systems (MEMS) based etching processes. The multiple-layered nitinol parts are transformed into integral three-dimensional shapes by "shape-setting" annealing process. This method eliminates the difficulties of joining, welding or bonding of nitinol. Composition and heat treatment affect the phase transition temperature of the alloy, which in turn determines whether it exhibits shape memory or superelastic properties [2]. For implantable medical devices, thin film is superelastic at body temperature.

The method of producing three-dimensional TiNi thin film structures using multiple layers has opened a window of opportunity for making a wide range of small and implantable medical devices and others. Some of the medical devices in which this method of fabricating is directly applicable are briefly mentioned in this paper.

FABRICATION OF THREE DIMENSIONAL STRUCTURES OF TiNi THIN FILM

METHOD 1: FROM PLANAR TiNi THIN FILM

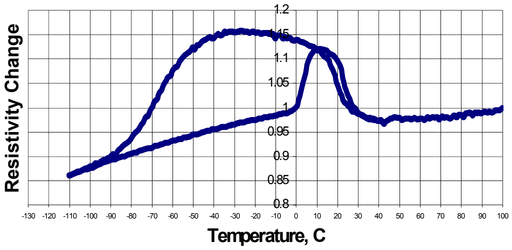
Planar TiNi Thin Film Preparation

TiNi film in planar form is formed by sputter deposition from a flat TiNi target onto a smooth flat substrate, usually an oxidized silicon wafer. Silicon oxide surface has two advantages: it provides a good adhesion with TiNi, and also acts as a barrier layer to prevent any diffusion of TiNi atoms into silicon. Silicon wafer is loaded into a sputter deposition chamber, which is pumped down to low 10-7 Torr pressure range. Argon gas is introduced into the chamber at a pressure of about 2 milliTorr. At high DC power (2 kWatts) argon gas is ignited to create dense plasma, which initiates the sputtering of TiNi material from the TiNi target. A magnetron system is used to control the direction of the TiNi material being sputtered and also to enhance the sputter rate. The sputtered TiNi material gets deposited on a silicon wafer that is being rotated under the target. TiNi film with thickness from a few angstroms to few tens of microns can be sputter deposited. The sputtered TiNi film is an amorphous material therefore it exhibits no shape memory or superelastic properties. To obtain these properties from this material, TiNi film on the silicon wafer is annealed (crystallized) at 500^{o}C in an oxygen-free environment (vacuum in 10-6 Torr range is adequate).

TiNi thin film can be separated from the silicon substrate using a sequence of process which involves putting down an intermediate sacrificial layer between TiNi and silicon substrate and then chemically etching it away after the TiNi film has been annealed. A thin chromium layer (about 500 Angstroms thick) is sputter deposited (RF sputtering technique) prior to the deposition of TiNi. After the TiNi has been deposited and annealed, the underlying chromium layer is chemically etched away in a commercially available chromium etchant. Chromium makes an excellent sacrificial material for several reasons: 1) Chromium does not diffuse into TiNi during the high temperature annealing process resulting with no change in composition of TiNi alloy, 2) The etchant for chromium does not effect TiNi or the silicon substrate and, similarly, the etchant for TiNi does not effect Chromium, and 3) Chromium and TiNi both can be sputter deposited in the same sputtering chamber.

The mechanical properties of a planar TiNi thin film were characterized using two measurement techniques: 1) Four-probe resistivity measurement to determine phase transformation of the material, and 2) Stress-strain measurement to determine the mechanical strength. To measure transformation temperature, each thin film sample was heated and cooled while changes in voltage were measured and recorded using a 4-probe constant-current technique to produce temperature versus resistivity data (see Figure 1).

In stress-strain measurements, film samples 20mm x 2mm x 5 microns in size were used. The deformation fixture used allowed the deformation at a constant temperature in the temperature range from -50^{o}C to $+90^{o}$C by immersion in an alcohol or water bath. The force applied to the sample and the sample elongation was measured respectively by a strain gage and an LVDT connected to a computer (see Figure 2). LABVIEW™ software was used for collecting the data and plotting the stress-strain and resistivity graphs.



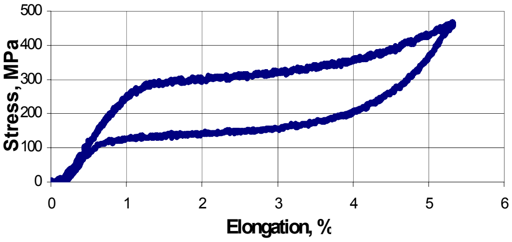


Figure 1: Resistivity data of TiNi thin film

Figure 2: Stress-strain measurement of TiNi film

Released TiNi film was rolled up into the conical and cylindrical shapes and joined using welding techniques.

Welding and Brazing of TiNi Film

Two different technologies were used: resistance welding and laser welding. Resistance welding and brazing were studied using a commercial conventional welder. Even at the lowest power, the heating was concentrated in small areas, tending to burn holes in the films rather than melt them together (see Figure 3a and 3b). Welds produced were strong enough to tear the film. But the film was locally damaged so that it was no longer strong and supple. A brazing material layer was deposited on the film surface in an attempt to provide union of the two films without melting. Burn-through holes to the TiNi film occurred persistently.

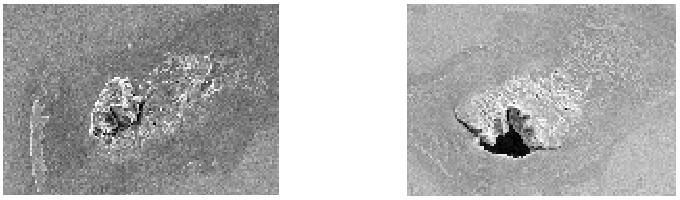

(a) (b)

Figure 3: SEM shows two welded TiNi thin film after they were easily torn apart (a) a welded piece of TiNi thin film still attached but leaves a hole, as in (b), in the other film caused due to weakened film

A small set of sample welds from Nd:YAG laser welding was made, using varying power and pulse duration. These welds were analyzed in the scanning electron microscope (SEM), with the finding that the pulses used were not consistently controlled with enough precision: some spots were burned through, while adjacent spots were clearly not melted.

Welding was not found to be a successful method of joining Nitinol thin film. Holes were very likely to be created. It is hypothesized that the surface oxide layer (native) on the Nitinol film may have prevented formation of metal-to-metal bonds. The combinations of force, time, and energy were either insufficient to overcome the oxide layer (producing no welds) or were strong enough to overcome the oxide layer but too strong to preserve the integrity of the Nitinol film.

METHOD 2 – SPUTTER DEPOSITION ON 3D SUBSTRATES AND ITS DIFFICULTIES

Sputtering onto three-dimensional substrates was proposed. A cylindrical sputtering source with a cylindrical DC magnetron in which the material is removed from the inside surface of a hollow cylinder of target material and is deposited on the exterior surface of the substrate. In this case, a target was formed by rolling a TiNi sheet into a cylinder two inches in diameter and 6 inches in length. Glass cones and cylinders were the substrates and were inserted along the axis of the cylindrical TiNi target.

After sputter deposition of TiNi, substrates were analyzed and inspected. SEM analysis showed that even though titanium and nickel were present in the sputtered film, the composition was significantly different from the composition of the target material. Also the surface of the thin film was very rough and contained pits or cracks (see Figure 4c). We believe that these defects in the film were caused by over-heating of the substrate during sputter deposition. We also found that even a brief period of sputter deposition of TiNi (a few minutes) caused an over-heating of the substrate – making it impossible to produce reasonably thick, good quality TiNi film. Furthermore, the film produced in these experiments was brittle due to the columnar crystal structure in the film (see Figures 4a and 4b).

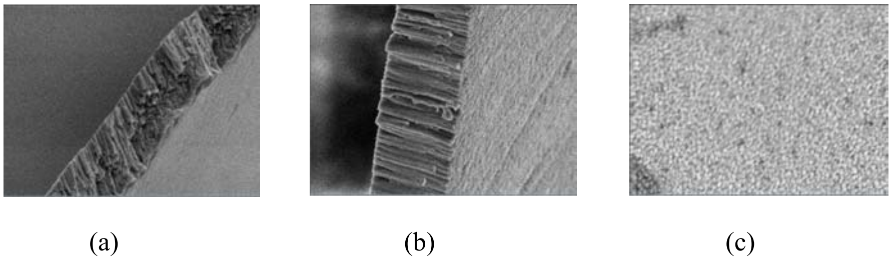

(a) (b) (c)

Figure 4: SEM image showing (a) and (b) columnar crystal structure of the TiNi film resulting in brittleness, (c) Pits on the TiNi film surface obtained from cylindrical sputtering source

Another method was introduced in which TiNi film was instead sputtered from the regular 8-inch diameter flat sputtering source onto three-dimensional substrates. Good quality glass rods were found to be reasonably suitable substrates. Glass rods were also heat-softened using a propane gas flame to create other shapes such as cones and hemispheres. Using controlled and steady rotation and controlled stretching of the glass rod, cones of reasonably uniform size and shape were formed. A liquid polyimide PI 2611(manufactured by HD Microsystems) layer was spin-coated on to the rod to fill up the pits and to smoothen the sharp edges on the glass rod surface. The polyimide was cured at 500^{o}C in the oven. A fully cured polyimide coating is an extremely stable material and is inert to most of the aggressive chemicals used in photolithography. The coated glass rod was loaded into the sputtering chamber via a small load chamber, separated from the main sputtering chamber by a load lock valve. Inside the sputtering chamber, the substrate was kept at a fixed distance of about 2 inches from the TiNi target. A shutter mask with a narrow opening, made of aluminum, was used between the substrate and the TiNi sputtering source to prevent sputter deposition on the sidewalls of the cylindrical substrate. An externally attached electrical motor was used for rotating the substrate during the sputter deposition at a speed of 0.4 rpm. The Perkin Elmer 4450 sputtering system was used for the sputter deposition of chromium and TiNi layers.

A thin layer of chromium was sputter deposited on the polyimide-coated surface of the rotating glass rod in the sputtering chamber after which the substrate was moved to the TiNi source for TiNi sputter deposition. A layer of TiNi was sputter deposited on top of the chromium layer from an 8-inch diameter DC magnetron target. The substrate was rotated on its axis during the sputter deposition of both layers. A second layer of chromium was sputter deposited on top of the TiNi layer, which was used as a mask material for patterning the underlying TiNi layer. The glass rod with sputter-deposited layers of TiNi and chromium was then heat treated at 500^{o}C in a vacuum in order to crystallize the TiNi film. The rod was cooled to room temperature in the vacuum to prevent from oxidizing.

Some changes were made to the photolithography techniques to perform the photoresist processing on three-dimensional substrate. Photoresist OCG 825 is spin-coated using a custom designed chuck, baked in an oven, exposed through the mask using ultra violet light and developed in a photoresist developer. Chromium and TiNi layers were etched in appropriate etchants and the photo-resist layer is dissolved away in a solvent. TiNi cylinder and cone were released from the substrate surface by chemically etching the underlying chromium layer as shown in Figure 5a and 5b.

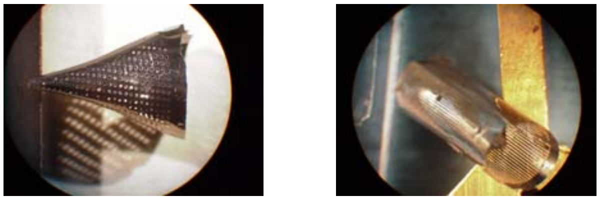

(a) (b)

Figure 5: TiNi thin film (a) cone and (b) cylinder with fenestrations released from glass substrates

TiNi film formed by this method was shown to have good shape memory and superelastic properties. Ductility was demonstrated by bending and heat recovery. However, this method produced one device at a time. The sputter rate was reduced considerably by the introduction of the shutter mask making it even less favorable for production.

METHOD 3 – MULTI-LAYER SPUTTER DEPOSITION IN THE PLANAR FORM

A third and new method of making three-dimensional shaped objects has been developed which permits the forming of a wide variety of TiNi film structures without the need to weld or bond. In this method, TiNi film is sputtered in the planar form, which eliminates the problems associated with sputtering on three-dimensional substrates. Fabrication of three-dimensional TiNi thin film structures is accomplished by the deposition of two (or more) layers of TiNi interspersed with layers of sacrificial material (chromium), part of which is removed to form bonds between the two TiNi layers at selected locations, producing structures that can be opened to produce cones, cylinders, and other shapes.

The processing steps to fabricate three-dimensional TiNi film structures from this method are shown in Figure 6.

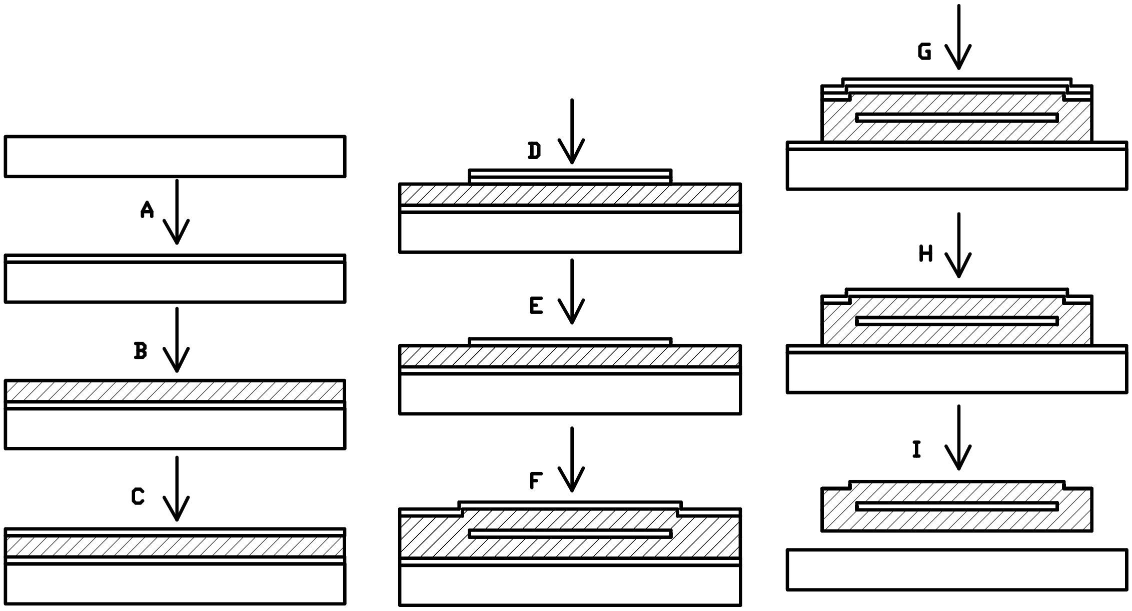


Figure 6: Process steps for the fabrication of three-dimension structures from multi-layer sputter deposition method.

To fabricate three-dimensional shapes of thin film from this method, multiple layers of TiNi thin film and sacrificial material are sputter deposited sequentially on a flat substrate surface in the process chamber. Chromium was used as a sacrificial material. Polished and oxidized silicon wafers are used as substrates.

The silicon substrate is loaded into the Perkin Elmer 4450 sputtering chamber, which is brought to a high vacuum (low 10-7 Torr) using a cryo pump. The PE 4450 sputtering chamber has a TiNi alloy DC magnetron target and a chromium RF target, each 8 inches in diameter. The silicon wafers are rotated during the sputter deposition to obtain film of uniform thickness and alloy composition. In step A of Figure 6, a thin layer of chromium is sputter deposited on the oxidized silicon wafer using RF sputtering at argon pressure of about 2 milliTorr. Thickness of the deposited chromium film is about 500 Angstroms. A layer of TiNi is sputter deposited on top of the chromium using DC magnetron sputtering at an argon pressure of about 2 milliTorr (Figure 6, step B). Thickness of the deposited TiNi layer is from 1 micron to 40 microns. A second layer of chromium (500 Angstroms thick) is sputter deposited on top of the TiNi layer (Figure 6, step C). The top chromium layer serves two purposes: 1) as a masking layer for patterning the underlying TiNi layer in subsequent process, and 2) also as an intermediate sacrificial layer which in the final steps of fabrication is chemically etched away.

To make three-dimensional thin film structures, a minimum of two photomask plates (here called mask#1 and mask#2) with appropriate pattern designs are prepared. Mask#1 contains the design which is used to pattern the second chromium layer on the wafer and mask#2 contains the design to pattern the TiNi layers in the final stage. The designs on these masks determine the size and shape of the final device. The designs for the masks were prepared using AutoCAD and were then printed on to mask plates.

Standard MEMS techniques were used to pattern the TiNi and chromium layers. A layer of a liquid photoresist OCG 825 is spin-coated on the top chromium layer on the wafer at about 4000 rpm and baked at 90^{o}C in a clean convection oven. In a mask aligner, the wafer with baked photoresist and mask#1 are brought in proximity contact (about a couple of microns gap) and the photoresist layer is UV exposed though the photomask plate which transfers the patterns from the mask#1 on to the photoresist layer. The exposed wafer is immersed in the photoresist developer solution, which selectively removes the exposed regions of the photoresist and leaves the unexposed photoresist – creating a pattern of openings in the photoresist layer. When immersed in the chromium etchant, the openings in the photoresist allow for the selective etching of the chromium layer as shown in Figure 6, step D after which the photoresist layer is chemically dissolved in a solvent (Figure 6, step E).

The above wafer with the selectively etched chromium layer is loaded back into the sputtering chamber, which is brought to high vacuum. In the chamber, the substrate surface is sputter-etched to remove any contamination layer. Highly energetic argon ions when operated in sputter-etch mode also remove the undesired thin native oxide layer on the TiNi film surface that may have formed during the lithography process. A second layer of TiNi film is sputter deposited followed by a third layer of chromium (Figure 6, step F). Thickness of these layers is kept the same as previously in steps B and C.

The sputtered TiNi layers are heat-treated at 500^{o}C in a vacuum to obtain shape memory and superelastic properties. The wafer from above is mounted on a hot plate in a vacuum chamber. At a vacuum of about 10-6 torr range, the power to the hot plate is turned on to heat it up to about 500^{o}C. The temperature is monitored at the bottom and top side of the wafer using thermocouples to ensure for the complete crystallization of the TiNi film.

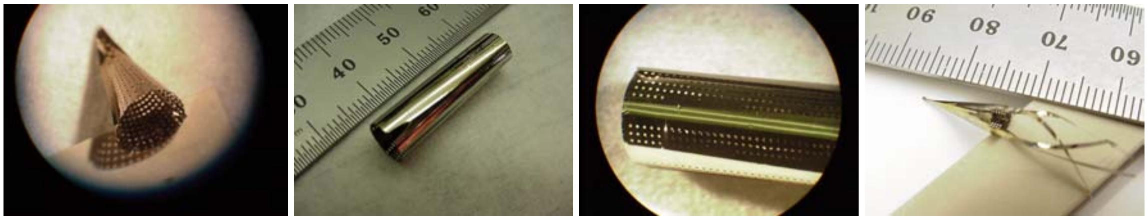
The same photolithography steps are followed to pattern the top layer of chromium with the designs in mask#2. The underlying TiNi layers are chemically etched in the TiNi etchant as shown in Figure 6, step G. This is followed by the complete removal of the photoresist layer in a solvent (Figure 6, step H). To separate the multi-layered TiNi thin film structures from the surface of the substrate, the wafer is immersed in the chromium etchant to completely dissolve all the chromium layers which includes the first, second and the third layers as shown in Figure 6, step I. The final etching of chromium not only separates the multi-layered TiNi thin film structures from the silicon wafer but also creates a pocket between the first and second TiNi layer.

The released multi-layered thin film structures from above are in planar form and are of various sizes and shapes: triangular, rectangular, semicircular, etc. These multi-layered thin film structures are then transformed into their corresponding three-dimensional shapes (cone, cylinder and hemisphere) by inserting a close-fit stainless steel mandrel shaped in cone, cylinder and hemisphere into the pocket between the two TiNi layers and followed by another heat treatment at 500^{o}C in vacuum. The shape of the mandrel during this heat treatment process determines the final shape of the thin film structures. Figure 7 contains computer-generated drawings (not to scale) to illustrate the transformation of the multi-layered planar thin film structures into thin film cone and cylinder.

(a) (b)

Figure 7: Computer-generated drawings to illustrate the transformation of planar multi-layer TiNi film into 3D structures (a) cylinder, and (b) cone after re-annealing with steel mandrel

Fenestration designs of any size and shape can also be added in the TiNi layer. Using photolithography techniques, fenestrations of micron size and with excellent edge quality can be achieved. Fenestration designs are included into the AutoCAD design for the mask#2. The basic process sequence to fabricate thin film devices with fenestration patterns remains the same as in Figure 6. Magnified images of actual released and fenestrated Nitinol thin film cone and cylinder resulting from this multi-layer method are shown in Figures 8a and 8b. Round fenestrations, about 25 microns in diameter, on TiNi thin film cylinder are shown at higher magnification in Figure 8c. Figure 9d shows an image of a released and fenestrated TiNi thin film cone with strings as integral parts of the cone using the multi-layer method.



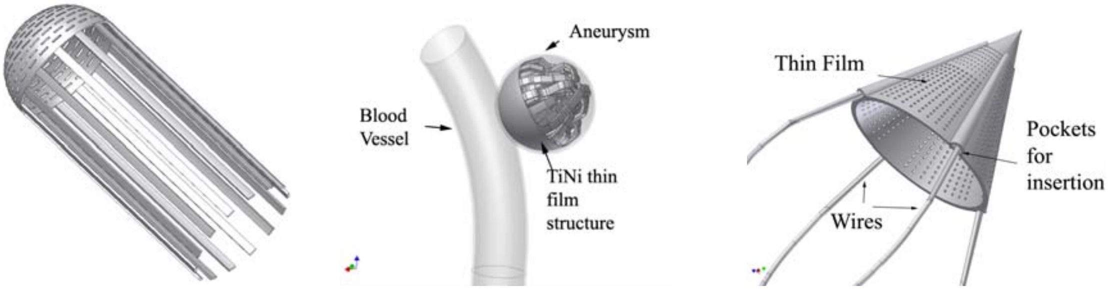
(a) (b) (c) (d)

Figure 8: (a) TiNi thin film cone, (b) cylinder fabricated using multi- layer sputter deposition method (c) Magnified optical image to illustrate micron-scale fenestration patterns on TiNi structures (d) Image of a TiNi cone structure with strings as integral parts made from multi-layer method

APPLICATIONS

Nitinol's thin film shape memory characteristics make it particularly useful for implantable devices such as intravascular stents. The hemispherical shaped thin film device with tentacles structures as shown in Figure 9a can be folded, loaded into a microcatheter, inserted through small and tortuous blood vessels in the brain and deployed in an aneurysm such that the hemispherical shape closes the aneurysm at its neck and the tentacles fill the aneurysm as shown in Figure 9b. This will stop the blood flow into the aneurysm thus preventing rupturing of the aneurysm and ultimately a stroke. The cone shaped thin film device with fenestrations as shown in Figure 9c is intended to be used as a blood clot retriever device to filter/capture/remove blood clots in small blood vessels. The microcatheter loaded with the device will be traversed through the blood vessel to the site where the device will be deployed to capture and remove a blood clot. Once inside and warmed to body temperature, the TiNi device expands to its original shape and exhibits considerable resistance to deformation, damage, or kink after implantation. Sieves and clot retrievers are other potential applications for nitinol thin film, especially in areas of the body distal from the heart where vessels are smaller, stiffer and more muscular, as in the case of intracranial arteries and veins. Stents fabricated from thin film process can be from 1 to 40 microns thick and fenestration feature size can be as small as a micron.

The multi-layer method can also be used for making TiNi structures with more than two layers without much change to the fabrication steps described above. Figure 9c shows a picture of a four-layer TiNi structure in which pockets in the outer layers were formed to insert wire or other object as a means to attach the thin film device with an external skeleton or support structure.



(a) (b) (c)

Figure 9: Conceptual drawings of (a) hemispherical thin film structures, (b) Hemispherical structure with folded tentacles inside an aneurysm, and (c) Conical thin film structure with pockets in the film for insertion of a wire as an attachment mechanism.

CONCLUSIONS

Using a multi-layer planar sputter deposition method, three-dimensional structures of thin TiNi film have been fabricated. Since in this method TiNi film is sputtered in the planar form, it exhibits excellent shape memory and superelastic properties. Like in the microelectronics industry, this planar method will also allow the batch fabrication of thin film devices resulting with high throughput and low cost devices. This method of producing three-dimensional structures of TiNi thin film is particularly applicable for the development of a wide range of medical devices for deployment in small blood vessels.

ACKNOWLEDGEMENTS

National Institute of Health (NIH) and SMART Therapeutics, Inc. (now an entity of Boston Scientific Corp.) for providing funding for this development work.

REFERENCES

1. V. Gupta, A. D. Johnson, V. Martynov, Actuator 2002, pp. 355 – 358.
2. T. W. Duerig and D. E. Tolomeo, SMST 2000, pp. 585 – 604.
3. D. Stockel, SMST 2000, pp. 531 – 542.
4. A. D. Johnson et. al., NanoSpace 2000 – Micro/Nano Technology Conference, Jan 2000.
5. V. Martynov, A. D. Johnson, V. Gupta, and V. Galhorta J. Phys. IV France 11 (2001).
6. I. Roch, L. Buchaillot, X. Wallart, SMST 2000, pp 217 – 224.
7. P. Krulevitch, et. al., J. MEMS, vol. 5. No. 4, December 1996.
8. Frank, W. Xu, A. Cuschieri, SMST 2000, pp. 549 – 560.