

Fabrication of Microelectrode Arrays Having High-Aspect-Ratio Microwires

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A method is described for the fabrication of arrays of conducting, high-aspect-ratio microelectrodes. The microelectrode arrays are fabricated by electrochemical deposition of metals, including Ni, Pt, and Rh, in microchannel glass templates having parallel, uniform, hollow channels. The metals completely fill the hollow channels, yielding highly uniform, 5.5- μm -diameter microelectrodes with aspect ratios up to 500. The microelectrodes are electrically insulated from one another by the glass template and the surface area of each array is $>1\text{ cm}^2$. The surface of the electrode arrays can be polished to provide an array of disk electrodes or it can be etched with acid to remove the glass surrounding the electrodes, exposing an array of bare, solid wires. The high-aspect-ratio microelectrode arrays were fabricated to provide the electrical interface with an intraocular retinal prosthesis. The properties of the solid wire, metal microelectrode arrays are also well-suited for use in electrochemical trace analysis and implantable neuro-prosthetic devices.

Introduction

The fabrication and use of microelectrode arrays is of current interest in a number of fields, including electrochemical analysis (environmental and medical) and in basic neuroscience and neurobiology research. Low-aspect-ratio microelectrode arrays are fabricated using conventional silicon-based microfabrication techniques. These techniques utilize standard silicon processing methods such as photolithography to yield arrays of thin films of metallic or carbon electrodes¹ on a silicon substrate. Thin film, microfabricated microelectrode arrays often have limited stability and useful lifetime as a result of defects present in the various layers of the array.^{2–4} These defects lead to poor resistance to corrosion and subsequent swelling and delamination of the layers. Microfabricated arrays typically are fragile and cannot be cleaned using conventional cleaning methods and materials (polishing, solvents, and sonication), but must be cleaned using methods such as reactive ion etching. It has been reported⁵ that even after cleaning with an oxygen plasma, the electrodes of a microelectrode array, fabricated using a photoresist, were still contaminated with small quantities of the photoresist and that the traces of photoresist were responsible for the observed elec-

trochemical characteristics of the array. In effect, the microelectrodes were unavoidably modified as a result of the fabrication procedures.

Arrays of high-aspect-ratio, conducting microelectrodes have been of interest in neurobiology. These microelectrode arrays are designed to penetrate brain tissue to permit highly localized electrical stimulation and/or recording of signals from neural tissue. Silicon micromachining,^{6,7} silicon microfabrication,⁸ and techniques involving bundling of multiple solid wires⁹ have been used to fabricate arrays of electrodes that are capable of penetrating neural tissue. There are advantages and disadvantages associated with each approach. The micromachined electrodes^{6,7} (Utah Electrode Array) are coated with a layer of platinum at the tip. These platinum coatings can crack due to mechanical stress or corrosion. Cracks can lead to contamination problems, delamination, and the appearance of non-ohmic interfaces, causing degradation in the performance of the electrodes. Although solid wire electrode arrays⁶ do not delaminate and will not exhibit non-ohmic interfaces, they typically have only a handful of electrodes. The Utah Electrode Array contains 100 electrodes. High-aspect-ratio microelectrode arrays are also of interest for their use as an electrical interface in an intraocular retinal prosthesis (IRP).^{10,11} An IRP is a device that is attached directly to the retina and that is intended to electrically stimulate the retina in an effort to restore vision to patients with impaired vision. An array of high-

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aspect-ratio microelectrodes is necessary to conduct the electrical stimulation from a flat microelectronic circuit to the curved surface of the retina.

In this paper we describe the fabrication of regular arrays of high-aspect-ratio, solid wire microelectrodes. The microelectrodes are fabricated by electrodeposition of metal within the high-aspect-ratio, hollow channels of microchannel glass templates. The metals completely fill the hollow channels of the microchannel glass.

Electrodeposition of metallic nanowires throughout the void spaces of porous, nanostructured templates has been reported previously. Porous, anodically etched alumina,^{12,13} polycarbonate track-etched filters,¹⁴ and porous nanochannel glass¹⁵ have been used as templates for the electrodeposition of nanowire arrays. The diameter of the pores in these templates was on the order of tens of nanometers and the density of the nanowires ranged up to values as high as $10^9/\text{cm}^2$. Electrodeposition of metal nanowires in nanostructured templates has yielded novel nanocomposite materials having unique optical and magnetic properties.

Alumina and polycarbonate membranes result in arrays limited to a thickness of tens of micrometers. Although variation of the fabrication conditions can control the average pore density, a distribution of pore spacings and diameters still results. The resulting arrays are either flexible (polycarbonate) or brittle (alumina). The distribution of pore sizes, spacing, parallelism, and regularity of the electrode pattern cannot be controlled to the degree possible using microchannel glass. No other method has been reported of fabricating all-glass arrays similar to those we describe here.¹⁶

Experimental Section

Conducting microelectrode arrays having high-aspect-ratio microwires were fabricated using electrodeposition methods similar to those used in the fabrication of the nanocomposite materials described above. The fabrication of microwires having both larger diameter and higher aspect ratio presented new challenges both in the preparation and in the use of the porous microchannel glass templates and in the electrodeposition procedures. Each task in the fabrication of a microelectrode array is described in detail below. The tasks, broadly, are as follows: (1) preparation of a porous, microchannel glass template; (2) electrodeposition of metal within the hollow channels of the glass template; and (3) final preparation of the array following electrodeposition.

The porous templates used in this work were etched wafers of microchannel plate glass. Microchannel glass boules, ~ 25 cm in length and 3 cm in diameter, were purchased from Litton EOS (Garland, TX). The glass had circular, hexagonally close packed, acid-etchable elements that were $5.5\ \mu\text{m}$ in diameter.

The center-to-center pitch between the acid-etchable elements was $8\ \mu\text{m}$. The boule was cut into wafers, ranging in thickness from 0.25 to 2.5 mm, using a diamond saw. Both surfaces of the wafer were ground and polished. The microstructured region of the polished wafer was ~ 27 mm from flat to flat, the surface area was about $5\ \text{cm}^2$, and the channel density was $>10^9/\text{cm}^2$. It is important to note that $>40\%$ of the surface area of an etched, microchannel plate glass is void space (occupied by channels). Because of this, the etched wafers are highly stressed and often distort to a nonplanar shape to the point of fracture upon drying. Although it is generally not possible to reduce the stress in the etched wafers without breaking them, the stress can be significantly reduced by annealing the wafers before they are etched. The unetched wafers were heated to $500\ ^\circ\text{C}$ at a rate of $5\ ^\circ\text{C}/\text{min}$, held at $500\ ^\circ\text{C}$ for 1 h, and then cooled to ambient temperature at $2\ ^\circ\text{C}/\text{min}$.

The thermally annealed, unetched, microchannel glass wafers were etched by tumbling in 1% (by volume) acetic acid solution. The etching solution, of volume $\sim 100\ \text{mL}$, was changed after 2–3 h and the etching continued overnight, for a total etch time of 16–24 h. The etched wafers were then rinsed (tumbled again) once or twice with deionized water for half an hour each. Etching of thick wafers of microchannel glass (~ 1 -mm thick and up) occasionally leads to fracture of the glass in a plane parallel to the top and bottom surface of the wafer, near the center of the wafer. Etching thick wafers of microchannel glass also can lead to noncylindrically shaped channels. Although the matrix glass of microchannel glass is referred to as an acid-inert glass, this terminology is relative to the etching rate of the etchable glass. In fact, the matrix glass does etch in acid, but at a lower rate. When the channel glass is in the etching solution for long durations, the matrix glass surfaces inside the hollow channels will etch, forming hourglass-shaped channels. Thus, the upper limit of the aspect ratio of the channels in the glass and, by extension, of the microwires in the microelectrode array, is determined by the glass properties and the specific glass-etching procedures, not by the metal deposition procedure. Microchannel glass templates having aspect ratios in the range of 100–500 were readily prepared and used in this work. The hollow channels in the glass were uniformly circular, perpendicular to the surface, and parallel to one another (no overlapping channels).

To electrodeposit metal throughout the channels of the microchannel glass, the templates were mounted on metal-coated glass substrates, typically metal-coated microscope slides. The slides provided support for the microchannel glass templates while immersed in the electrodeposition solutions, and the metal coating on the slides provided the electrical connection needed to drive the electrodeposition. The templates and the glass substrates were carefully cleaned prior to each being coated with metal to ensure good adherence of the metal coating. Failure to properly clean the glass resulted in the loss of adhesion of the metal films, which resulted in loss of electrical contact between the channel glass template and the glass substrate during electrodeposition. The cleaning procedure consisted of washing the glass pieces by hand in detergent and water. Next, the pieces were sonicated for 15 min in detergent and water. The detergent was free of insoluble particulates that could clog the channels of the template. The pieces were then sonicated in three successive rinse baths of distilled water. Last, the pieces were dried by holding them in the warm vapor above a beaker of boiling 2-propanol.

The templates were coated on one side with 100-nm-thick films of titanium and platinum, sputtered sequentially in a vacuum at an incident angle of 45° with respect to the plane of the wafer. The wafers were rotated about an axis normal to the wafer surface during the sputtering. This permitted the metal to deposit uniformly on the edges of the channels as well as a short distance into the channels. The metallic coatings adhered well to the glass and provided a surface from which the electrodeposited metal could grow. Ideally, the metal film should completely occlude the channel ends, providing a continuous conducting surface in the channel from which wire growth can be initiated. This provides the most advantageous situation for the growth of uniform wires by electrodeposition.

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Table 1. Deposition Conditions for Metals Studied

material	voltage (V)	current density (mA/cm ²)	temp (K)	growth rate (μm/h)	current efficiency
Ag	0.2	2	295	~4	0.5
Au	1.8	0.5	315	~1.7	0.9
Cu	~1	10	315	~12	0.9
Ni	1.7	5	295	~4	0.65
Pt (black)	2.3	3	315	~3	
Pt (silver)	1.8	1–2	315	~0.5	0.3
Rh	1.5	4	315	~3	0.7

Larger diameter channels ($>1\ \mu\text{m}$) could not, however, be effectively occluded by sputtering layers of metal. It was found that metal films tens of micrometers thick could pinch off these larger diameter channels, but these films did not adhere to the glass and electrodeposition of metal in the channels was not successful. Electrodeposition throughout the $5.5\text{-}\mu\text{m}$ -diameter channels of microchannel glass was performed by coating one surface of the template with the thin titanium and platinum films. No attempt was made to occlude the channels.

The glass substrates that support the channel glass during electrodeposition were also coated with similar titanium and platinum films. When the substrate was a microscope slide, a titanium/platinum strip, $\sim 5/8\ \text{in.} \times \sim 2\frac{1}{4}\ \text{in.}$, was deposited onto the slide at normal incidence.

After sputtering, the hollow, channel glass templates were mounted on the metal-coated, glass substrates. The Ti/Pt strip on the substrate provided an electrical connection from the wafer to a connector and then to the deposition power supply. The etched, circular channel glass templates were typically broken into four equal quarters. Each quarter-wafer template was bonded to the Ti/Pt strip using 5-min epoxy applied around the periphery. A light downward force was applied to the center of the template during epoxying and curing to ensure that the Ti/Pt-coated template maintained good contact with the Ti/Pt strip on the substrate. Epoxy was applied to all of the remaining exposed metal on the slide that was to be immersed in the electroplating solution to provide electrical isolation. A portion of the Ti/Pt strip on the slide, which was subsequently kept above the electroplating solution, was not covered with epoxy to permit electrical contact with the external circuitry. While common "5-min" epoxy is a convenient electrical insulator, its adhesion at elevated temperature (above $40\ ^\circ\text{C}$) is not optimal. Electrodeposition is often enhanced at elevated temperature and the solutions are frequently quite acidic or otherwise chemically harsh. A hard, inert epoxy (Epoxi-Patch 1C White, Dexter Corp.) is better suited to withstand harsh conditions and was used for deposition at elevated temperature.

Porous microchannel glass templates prepared following the procedures described above were used for the electrodeposition of microelectrode arrays using a wide range of metals. Several conducting metals, including platinum, palladium, gold, silver, copper, nickel, rhodium, and iridium, were investigated and were deposited throughout the microchannel glass templates. In this paper the deposition of three of these metals, nickel, platinum, and rhodium, are discussed.

Table 1 summarizes the deposition conditions and results for the materials used in this study. The current density is the maximum value attained during the growth of the wires and usually was sustained for the last 50–70% of the growth. The growth rate is averaged over the entire deposition. The efficiency given is very approximate and is determined by dividing the observed length with that calculated assuming 100% efficiency and a metal density equal to the literature value. Since the density of the porous black platinum varies greatly with deposition conditions and is not tabulated, its efficiency was not calculated.

While the detailed electrodeposition procedures vary somewhat for each metal, the methods are generally similar. For example, the maximum current density was different for each electroplating solution and was determined each time a

different metal was deposited. The specific procedure for the electrodeposition of rhodium is described below in some detail.

Electrodeposition of rhodium was performed using a commercially available electroplating solution, Techni Rhodium "S-less", available from Technic Inc., (Cranston, RI). The solution is primarily $\text{Rh}_2(\text{SO}_4)_3$ in $\sim 0.5\ \text{M}\ \text{H}_2\text{SO}_4$. The solution was purchased in the "heavy" formulation with a concentration equivalent to 10 g of rhodium/L of solution. The solution was used as-received. The depositions were carried out at $\sim 40\ ^\circ\text{C}$, although room temperature was also adequate. The samples were mounted using the hard "white" epoxy.

Electrodeposition was performed at constant current density. The maximum current density throughout most of the deposition was $5\ \text{mA/cm}^2$ of deposited material. The current density was controlled to ensure that hydrogen bubbling did not occur. Electrochemical generation of hydrogen bubbles is well-known to result in pitted deposits and can produce porous, nonuniform wires. The counter electrode (anode) was a strip of platinum foil with a surface area several times larger than the $\sim 1.5\text{-cm}^2$ channel glass template. The quality of the deposition was optimized by setting the initial current density during the first few hours of deposition to a low value of $\sim 0.1\ \text{mA/cm}^2$. The voltage remained stable during deposition with only smooth gradual changes observed when the current density was changed. Rapidly fluctuating voltages, usually indicative of bubble formation due to the electrolysis of water, were avoided. Limiting the current density during the initial few hours, and limiting the maximum voltage thereafter to about 1.8 V, usually prevented such voltage fluctuations. After the first few hours, the deposition was carried out at a constant current density of $1\text{--}5\ \text{mA/cm}^2$. The high conductance of the deposition solutions, the use of a large area counter electrode, and the small separation between the electrodes ($\sim 3\ \text{cm}$) were sufficient to make the use of a reference electrode unnecessary. It should be noted that, even without bubble formation, higher current density can result in lower quality deposition. Although the voltage was allowed to freely range below 1.8 V, it was typically observed to be quite steady in the $1.5\text{--}1.8\text{-V}$ range. Deposition rates were approximately $1\ \mu\text{m}$ per mA/cm^2 per h. After deposition was completed, the rhodium microelectrode array was removed from the white epoxy seal by boiling in dimethylformamide for about 15 min. The array was then cleaned and polished on both sides. Samples that survived all the processing steps to this point were typically fairly robust. They could be heated to autoclaving temperatures without adverse effect on the structural integrity.

Final sample preparation depended on the type of electrode array that was required. Arrays of microelectrode disks were fabricated by simply grinding and polishing flat the surfaces of the array. Alternatively, the array surface was first polished flat, and then the glass matrix was etched away from the surface with a solution of 5% hydrofluoric acid (HF) in water. This produced arrays of bare, high-aspect-ratio rhodium microwire stubs. The etch rate was initially about $10\ \mu\text{m/min}$ but was observed to decrease as the etch depth increased. The HF solution appeared to have no effect on the metal.

Electrodeposition of other metals was similarly performed using commercially available electroplating solutions. Nickel was deposited using "Techni Nickel S" (Technic Inc.) nickel sulfamate solution. The solution was purchased in the RTU (ready to use) form, with no dilution with water necessary. When used as-received, wire deposition was observed, but the bulk-deposited nickel had a brownish cast, and although dense and hard was somewhat coarse or grainy in appearance. Two additives, "HN5", a surfactant, and "semibright additive", were subsequently employed with this solution, significantly improving the appearance of the deposited nickel. Both additives were also purchased from Technic. The surfactant most likely ensured that the high-aspect-ratio, hollow channels were completely wetted by the solution.

Platinum was deposited using two different solutions. Technic "Platinum TP" concentrate was diluted with water to a concentration of $\sim 15\ \text{g}$ of platinum/L. This solution was used to make smooth, hard, shiny, silver-colored platinum wires. Technic "Platinum AP" solution with a concentration of $\sim 3\ \text{g}$

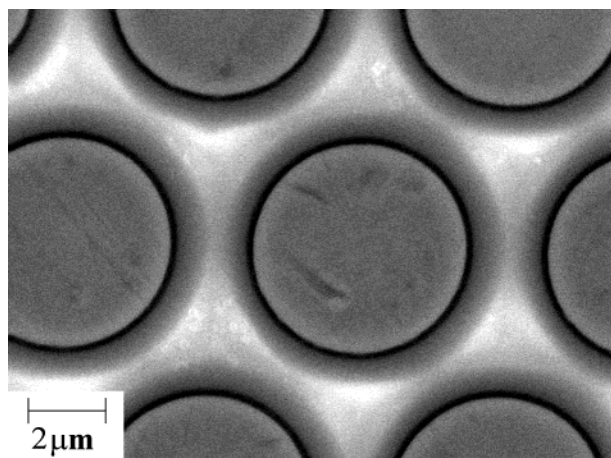


Figure 1. SEM micrograph of the end of a polished electrode array with nickel electrodes. The circular nickel elements are $5.5\ \mu\text{m}$ in diameter.

of platinum/L was used as-received. This solution was used to deposit porous, spongy, rough "black" platinum wires.

All solutions were used both at room temperature and at the recommended elevated temperature, usually $40\text{--}50\ ^\circ\text{C}$. No effect was observed on the quality of the deposition, but the deposition voltage was lowered by about $0.1\ \text{V}$ at the elevated temperature.

Results and Discussion

Electrodeposition is a method that is particularly well-suited for depositing materials in high-aspect-ratio channels. This is because the deposition begins at the metal surface at the bottom of the channels and continues uniformly up the channels toward the open ends of the channels. Electrodeposition of nickel, platinum, and rhodium by direct current, under constant current conditions, resulted in highly uniform filling of the porous microchannel glass templates with various metals.

Nickel has been successfully deposited in previous studies of electrodeposition in nanostructured templates.^{13–15} Nickel is a ferromagnetic metal that is fairly hard and rigid and has electrical resistivity lower than that of platinum. However, nickel is not as resistant to corrosion and is much more electrochemically active than platinum. For this reason nickel microelectrodes, in contrast to platinum electrodes, are not appropriate in applications that require biological compatibility with living tissue. Despite this, since nickel electrodeposition is relatively straightforward in bulk electroplating applications, nickel was chosen for study to facilitate the determination of optimal parameters for electrodeposition of solid wires in the microchannel glass templates. Using the procedures and solutions described above, it was found that nickel electrodeposition throughout the microchannels was relatively straightforward. Attempts to gravimetrically measure electrochemical deposition efficiencies resulted in values of $\sim 65\text{--}95\%$ in terms of atoms deposited per pair of electrons passed, when using a nickel counter electrode. The density of the nickel wires, determined by measuring the length, diameter, and total mass of the deposited wires, agreed with that of bulk nickel. Figure 1 is a SEM micrograph of the surface of the nickel array after polishing. The nickel in the channels appears dense and uniform and the

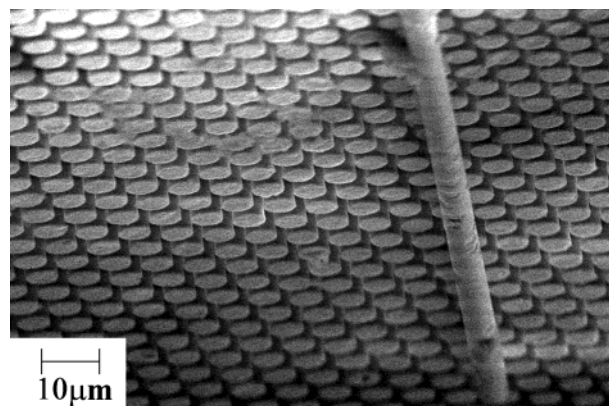


Figure 2. SEM micrograph of the end of a HF-etched electrode array. The nickel elements are $5.5\ \mu\text{m}$ in diameter.

interfaces between the nickel wires and the glass channels show no evidence of void spaces. Since the nickel is softer than the glass, it is assumed that the nickel wires have been undercut by the polishing and that depressions are present at each wire. These depressions may be acceptable or even advantageous for some disk microelectrode applications, that is, when minimization of convection to the sample is desirable.¹⁷ For other applications in which an increased electrode surface area is advantageous, the characteristics of the high-aspect-ratio, solid metal wires can be exploited. The exposed surface area of the microwires was increased by removing a $70\text{-}\mu\text{m}$ -thick layer of glass at the microelectrode array surface by etching the array in 5% HF solution for 10 min. The etched surface subsequently exhibited a dense, regular array of uniform, aligned, bare nickel microwires. The etched surface of the nickel microelectrode array, with aligned nickel wires extending beyond the surface, is shown in the SEM micrograph of Figure 2. The array was completely immersed in the HF solution when etched. A single free nickel wire is present on the surface of the array. Wires are released from channels at the edge of the array during etching. They can usually be rinsed away, but this one still adheres to the surface, most likely due to magnetic attraction to the wires of the array. Figure 3 shows a SEM micrograph of an etched nickel microelectrode array after it had been scored and broken. The array was $\sim 350\text{-}\mu\text{m}$ thick and the SEM micrograph reveals that the nickel wires were solid and extended throughout the entire length of the template. The figure also shows some debris from the etched glass that was caught between the protruding, bare nickel wires. No effort was made to remove this debris. Several free nickel wires are also evident in Figure 3.

Slight etching (a few micrometers) of the surface of a microelectrode array can significantly increase the surface area of an array of disk microelectrodes while maintaining a fairly low aspect ratio. The increased surface area of the wires can have a significant effect on the electrical properties, such as the impedance, of the array. This would be important, for example, to facilitate the electrical stimulation of retinal tissue by a retinal prosthesis by reducing the current density and power required for stimulation. Deeper etching of the

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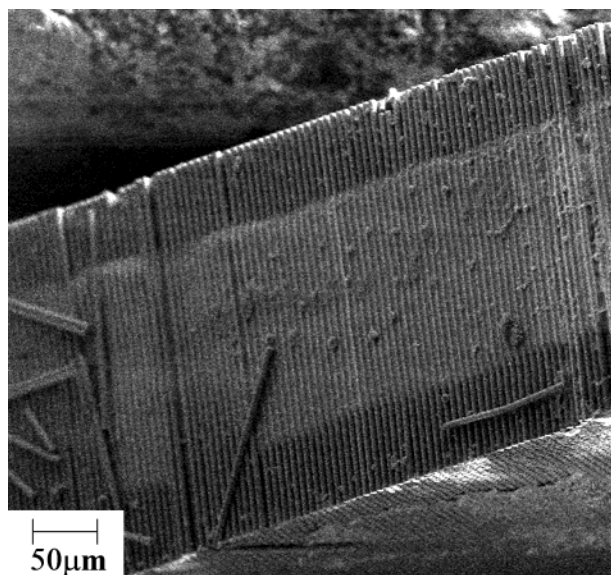


Figure 3. SEM micrograph of the side of a HF-etched electrode array. The nickel elements are $5.5\ \mu\text{m}$ in diameter and $\sim 310\ \mu\text{m}$ in length.

glass can provide arrays of solid, high-aspect-ratio microelectrodes up to 1 mm in length.

Platinum is a widely used material for many microelectrode applications, particularly for neurobiology applications that involve electrical stimulation of neural tissue. Metal electrodes used for neural stimulation must be able to facilitate the change in charge carriers at the metal/tissue interface without creating new chemical species (maintain reversibility). Platinum can accommodate a relatively large charge density before electrolysis occurs. Platinum is also more resistant than many metals to electrochemical dissolution that poisons neural tissue. Alloys of platinum and iridium (Pt:30% Ir) have also been used because of the greater mechanical strength of the alloy. The rigidity moduli of platinum and iridium are 61 and 210 GPa, respectively, while the hardness (M Ω scale) values are 3.5–4.3 for platinum and 6–6.5 for iridium.

Platinum was deposited into the glass with mixed results. Shiny platinum without voids or pits could be deposited using the “Platinum TP formulation”. The resulting wires (not shown) were identical in quality to the previously shown nickel wires. However, the growth rate was extremely slow ($<0.5\ \mu\text{m}/\text{h}$) since the current density had to be kept very low to avoid bubbling. Ultimately, the prolonged exposure to the acidic deposition solution resulted in the glass cracking before the $350\text{-}\mu\text{m}$ -deep channels could be completely filled. Nonetheless, wires of length up to $50\ \mu\text{m}$ were deposited. Electrodeposition of short lengths of platinum on top of longer rhodium or nickel wires can provide “capped” wires that will have the biocompatibility and most of the electrical advantages of a solid platinum wire.

Porous, black platinum wires were also grown using the “Platinum AP” formulation. A SEM micrograph of electrodeposited black platinum wires is shown in Figure 4. The wires are $\sim 250\text{-}\mu\text{m}$ long. The wires completely occupy the channels from top to bottom, but are quite porous. The depositions were typically performed in the recommended voltage range of 2–3 V. This resulted in the evolution of bubbles, which con-

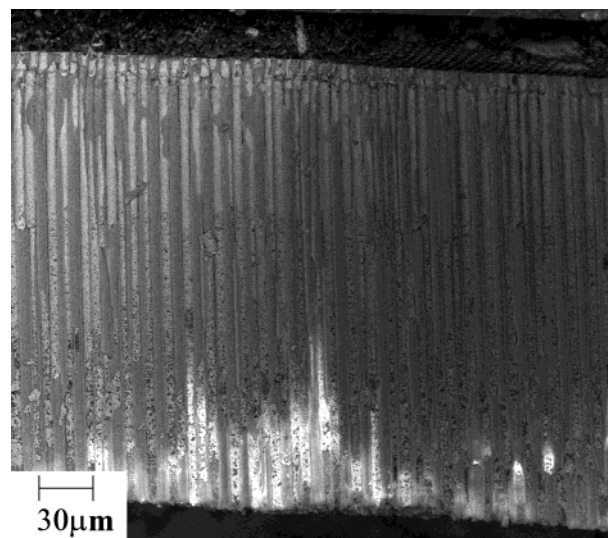


Figure 4. SEM micrograph of the side of an electrode array with “black” platinum elements. The porous platinum wires are $\sim 5.5\ \mu\text{m}$ in diameter and $\sim 250\ \mu\text{m}$ in length.

tributed to the porous deposits. The growth rate was up to $5\ \mu\text{m}/\text{h}$. Any attempt to reduce the voltage to avoid bubbling resulted in vanishingly small growth rates below $0.1\ \mu\text{m}/\text{h}$. The black platinum adhered well to the glass (it could not be wiped away with a tissue). Black platinum-capped microelectrodes may be desirable due to the superior behavior of black platinum as a neural stimulus electrode.¹⁸

The difficulty in depositing nonporous platinum wires with appreciable length led us to investigate the electrodeposition of other electrochemically inert metals that could be used for neural electrode applications (recording and stimulation). High-aspect-ratio arrays of rhodium were successfully deposited into porous microchannel glass templates. Rhodium is a precious metal that has a number of advantages, compared to platinum, for microelectrode array applications. Rhodium has excellent resistance to corrosion and has excellent mechanical strength. The rigidity modulus of rhodium is 150 GPa, 2.5 times that of platinum. Rhodium is harder than platinum (M Ω scale = 6) and more resistant to abrasion than platinum. The electrical conductivity of rhodium is more than twice that of platinum. Even though rhodium is harder and more rigid than platinum, its density is less than half that of platinum. The reduced weight, enhanced conductivity, and excellent corrosion resistance of the rhodium microelectrode arrays are all attractive features that would be advantageous in many electrode applications, including, in particular, use as an intraocular retinal prosthesis.

Dense, high-quality rhodium microwires were found to deposit readily using the procedure described above, in contrast to platinum. The deposition rate, $\sim 1\text{--}3\ \mu\text{m}/\text{h}$, with a current density of $\sim 2\text{--}4\ \text{mA}/\text{cm}^2$, was comparable to that for nickel. Rhodium is notable for having high deposition efficiency with a platinum anode. We measured gravimetric deposition efficiencies of $\sim 70\text{--}90\%$ for the deposition of rhodium. Figure 5 shows a SEM micrograph of the polished surface of an array of rhodium wires. The average wire diameter at the

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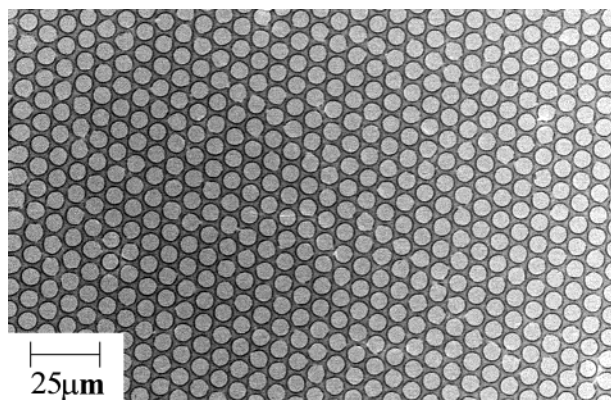


Figure 5. SEM micrograph of the end of a polished electrode array with rhodium electrodes. The rhodium electrodes are $5.5\ \mu\text{m}$ in diameter.

surface was $\sim 5.5\ \mu\text{m}$. The total surface area of the array was $\sim 1.5\ \text{cm}^2$. The rest of the sample had the same highly uniform, high-quality appearance as the small area illustrated in Figure 5. The individual wires shown in Figure 5 appear uniformly dense across their diameter. It is possible under certain deposition conditions to form wires that are less dense in the center, and in extreme cases a void can form in the interior. The average diameter of the wires is the same as that of the original empty channels, within the error of measurement. From this it can be inferred that the diameter of the hollow channels remains unchanged and uniform despite the approximately 1-week immersion of the template in the acidic rhodium deposition solution. From this we conclude that negligible etching of the exposed channels occurs in this solution on this time scale. Every channel appears to have been filled, there are no voids evident, and no channels are apparent that are less than completely filled. Examination of templates in which the electrodeposition was suspended midway up the channels revealed that the growth rate was nearly equal, to within $\sim 5\%$ of the mean, for all of the channels.

The top and bottom surfaces of the rhodium microelectrode arrays were given a light polish before SEM characterization. After polishing, the arrays were sonicated in water for a few seconds to remove the polishing compound. Some residual polishing compound is still evident in the SEM micrographs. The rhodium microelectrode arrays are fairly robust, as arrays have been sonicated for up to an hour and heated to $300\ ^\circ\text{C}$ without damage. The rhodium microelectrode arrays can be heated to this, and higher temperatures, without mishap because of the excellent match in thermal expansion coefficients between the rhodium and the matrix glass. The thermal expansion coefficients for rhodium and the matrix glass are 8×10^{-6} and $9 \times 10^{-6}\ ^\circ\text{C}^{-1}$, respectively.

Figure 6 is an SEM micrograph of the side of a rhodium-filled array. The inset to Figure 6 shows a close-up view of the bottom end of the broken wire that sticks up out of the surface in the center of the array. The length of the wires, and the thickness of the array, is about $365\ \mu\text{m}$. The surface of the array had been polished because near the end of the electrodeposition period the metal had begun to "mushroom" out of the filled channels and spread over the surface. It is

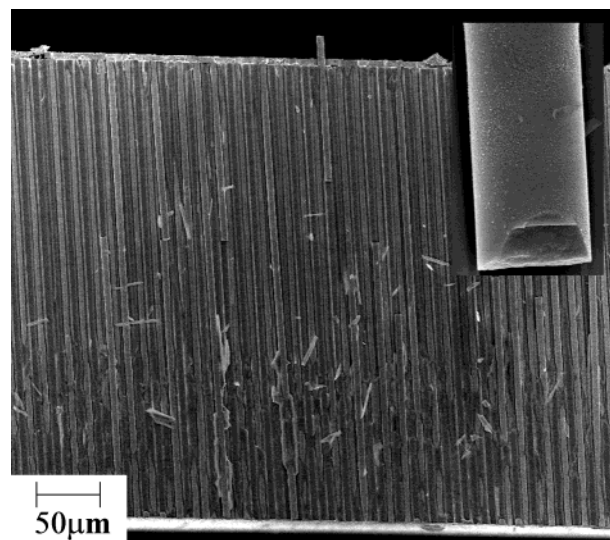


Figure 6. SEM micrograph of the side of an electrode array with rhodium electrodes. The inset shows a close-up of the lower end of the electrode that protrudes from the top surface. The electrodes are $5.5\ \mu\text{m}$ in diameter and $\sim 365\ \mu\text{m}$ in length.

apparent from Figure 6 that the wires are parallel and are all of equal diameter and that the diameter is uniform across the length of the wire. The close-up shows that the metal is dense and uniform, with no voids or pitting. This array was prepared for SEM study by scoring the surface of the metal-filled template with a diamond scribe and then snapping the template along the scribe line. This results in some obvious glass debris seen in the picture, as well as the breakage of a few wires. Sample sonication to remove the debris after snapping was not performed since many of the wires near the surface would be released, and they are the very ones that are observed in the SEM. The fact that the wires break, rather than bend, when the array is snapped is due to the high rigidity of rhodium. Arrays fabricated using other metals were observed to produce a large number of bent wires in the region where the arrays were snapped. This is not unexpected since rhodium has a rigidity modulus of $150\ \text{GPa}$, double that of nickel, 2.5 times that of platinum, 3 times that of copper, and 5 times that of silver and gold. This stiffness can be desirable for etched arrays containing exposed wires. Wires that can easily bend could short circuit each other. This could occur if the array is pushed into contact with another surface such as neural tissue. It should be noted that the single wire shown in close-up in the inset of Figure 6 became separated from its channel as a result of breaking the array. No wire in the interior of any array has ever been observed to have separated from the channel except at the point of breakage.

A test to estimate the stability of the arrays in physiological solutions was conducted. An etched wafer, and arrays filled with nickel and rhodium, were all soaked in physiological saline ($0.9\% \text{ NaCl}$ in water, B. Braun Medical Inc., Irvine, CA) at an elevated temperature of $60\ ^\circ\text{C}$ for 1 week. The results are summarized in Figure 7, which shows SEM micrographs of an etched wafer before and after soaking and a rhodium-filled array after soaking. No residue from the etching is observed. It is interesting to note that an unetched wafer (not shown) with the "acid-etchable" core glass

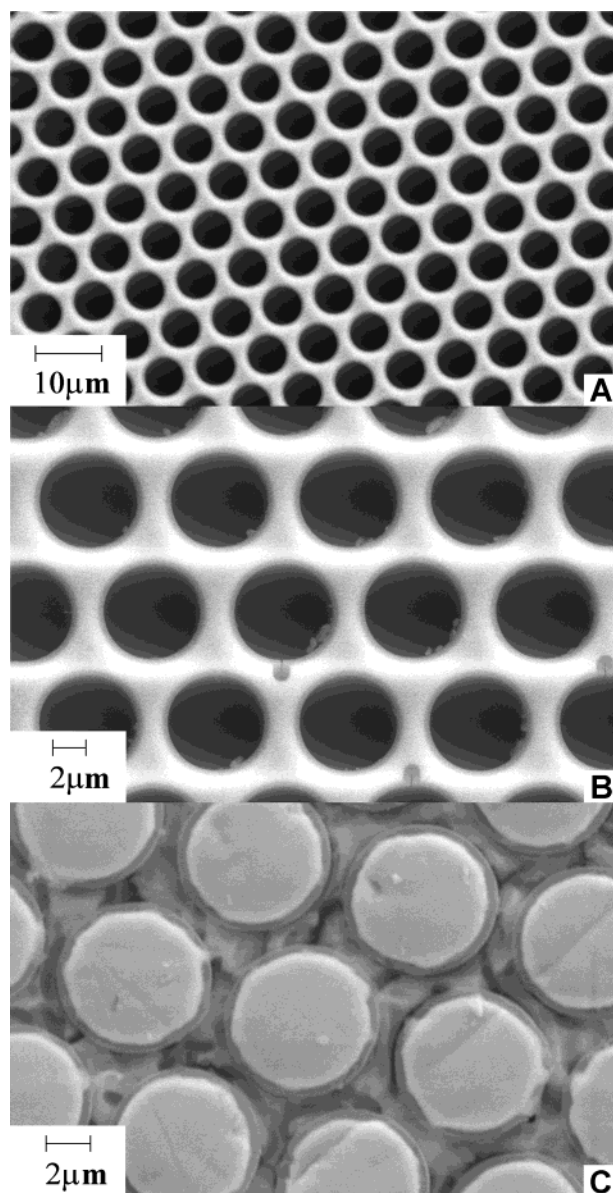


Figure 7. SEM micrograph of the surface of microchannel glass substrates: (A) etched but unfilled, (B) etched but unfilled after soaking in 1% saline at 60 °C for 1 week, and (C) a Rh-filled array after soaking in 1% saline at 60 °C for 1 week.

still intact showed slight ($\sim 10\ \mu\text{m}$ normal to the surface in 1 week) etching of the core glass in the neutral pH saline solution at 60 °C.

Figure 7a shows an etched wafer that has not been soaked. The $5.5\text{-}\mu\text{m}$ channels show no defects induced by etching out the core glass.

Figure 7b shows an etched wafer following soaking at 60 °C for 1 week. Residual NaCl crystals from the saline solution are evident, although the glass was rinsed and dried prior to the SEM photo. The glass shows small hairline fractures of some of the channel walls at the wafer surface. The fractures do not appear

to extend from one channel to the next. For that reason, it is probable that the cracks do not extend deeply down the channel either. The soaked glass is qualitatively still as strong as the unsoaked etched glass and can still survive sonication without breaking apart. It should be emphasized that a piece soaked at room temperature does not show any damage.

Figure 7c shows a rhodium-filled wafer following soaking at 60 °C for 1 week. In this view of the surface, a small amount of cracking of the surface glass surrounding the metal electrodes can be seen. However, the metal itself is unchanged, and the surface damage is superficial and does not extend into the piece. In summary, the matrix glass was found to sustain slight cracking at the surface with no damage apparent down inside the channels. The metal wires were unaffected by soaking.

The microelectrode arrays discussed in this paper were fabricated using commercially available, porous microchannel glass templates. The composition and characteristics of the glass were determined by the manufacturer and could not be adapted or optimized. It is fortuitous that the size and geometry of the microelectrode arrays ($\sim 5.5\text{-}\mu\text{m}$ -diameter electrodes, $8\text{-}\mu\text{m}$ pitch, and hexagonal close-packed geometry) are adequately suited for electrical stimulation of the retina. However, this geometry is not well-suited for other applications. For example, for electrochemical analysis, it is necessary to space electrodes at least 10 diameters apart to avoid overlapping diffusion hemispheres. For intracortical implant applications, smaller numbers of larger diameter, longer length electrodes, spaced farther apart, are desirable. The biocompatibility of the microchannel glass composition is an important consideration for applications in which the glass must be in contact with living tissue. The glass used in the manufacture of microchannel glass (Corning 8161) contains lead. It has been observed that the lead readily leaches out of the 8161 glass during the acid etch, particularly in channel glasses with submicrometer diameter channels.¹⁹ Since lead is a neurotoxin, for neurobiology and neuroscience applications, use of a glass host that does not contain lead, or any other toxic material, is desirable. Commercial channel glasses are not available with a wide range of channel diameter, channel pitch, channel geometry, or glass composition. Novel channel glasses having optimized channel geometry and glass composition and that will serve as exemplary templates for the electrodeposition of metal microelectrodes are currently being fabricated at our laboratory. This work will be reported in a future paper.

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