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Electrodeposition of Platinum-Iridium Alloy Nanowires for Hermetic Packaging of Microelectronics

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Abstract— **An electrodeposition technique was applied for fabrication of dense platinum-iridium alloy nanowires as interconnect structures in hermetic microelectronic packaging to be used in implantable devices. Vertically aligned arrays of platinum-iridium alloy nanowires with controllable length and a diameter of about 200 nm were fabricated using a cyclic potential technique from a novel electrodeposition bath in nanoporous aluminum oxide templates. Ti/Au thin films were sputter deposited on one side of the alumina membranes to form a base material for electrodeposition. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) were used to characterize the morphology and the chemical composition of the nanowires, respectively. SEM micrographs revealed that the electrodeposited nanowires have dense and compact structures. EDS analysis showed a 60:40% platinum-iridium nanowire composition. Deposition rates were estimated by determining nanowire length as a function of deposition time. High Resolution Transmission Electron Microscopy (HRTEM) images revealed that the nanowires have a nanocrystalline structure with grain sizes ranging from 3 nm to 5 nm. Helium leak tests performed using a helium leak detector showed leak rates as low as 1 x 10^{-11} mbar L s^{-1} indicating that dense nanowires were electrodeposited inside the nanoporous membranes. Comparison of electrical measurements on platinum and platinum-iridium nanowires revealed that platinum-iridium nanowires have improved electrical conductivity.**

I. INTRODUCTION

The use of implantable devices for treatment of medical disorders such as movement disorders, deafness and urinary incontinence has drastically increased [1]. Such devices include microelectronics that is embedded in protective biocompatible cases. Microelectronic components such as integrated circuits in implantable devices need to be protected inside a hermetic packaging in order to prevent the penetration of water and mobile ions such as K^+, Na^+ and Cl^- in body fluid. However, in order to stimulate tissue, the hermetic package must conduct stimulation current from the electronics inside the package to the tissue outside the package. These conducting paths connecting the encapsulated microchip to the outside of the hermetic case are called feed-through or interconnect. Humidity has been one of the major factors causing failure of the microelectronics [2, 3].

Earlier developed implantable electronic devices such as cardiac pacemakers have few relatively large electrical interconnects, while newer devices such as cochlear implants contain nearly 20 interconnects. Brain machine interfaces and visual prostheses will require hundreds of interconnects to make a parallel connection with the brain. Advanced interconnect technology for implantable microelectronics can be achieved by applying proper fabrication processes.

Several research groups have been trying to overcome the existing issues on the fabrication of hermetic packages for implantable microelectronics [4, 5, 6, 7]. Since these implanted devices are to remain hermetic for the lifetime of the patients (several decades) many important factors should be considered in hermeticity of the fabricated packages. These include the use of an advanced and proper interconnect fabrication technology.

A novel fabrication process using an electrochemical deposition method has been applied for the fabrication of platinum-iridium feed-throughs. The electrodeposition fabrication method for nanowires is an alternative to existing conventional processing methods with many advantages over complex and costly nanowire fabrication routes. Advantages include the cost effectiveness and simplicity of the process which makes it a more applicable method in industrial applications. In comparison with most of the existing nanofabrication techniques at high temperatures, the electrodeposition baths are operated at low-temperatures, usually below 80°C. Also non-equilibrium phases can be produced by electrodeposition which cannot be achieved by thermal processing techniques [8].

To date, no studies have been reported on the fabrication of ultra-high-density platinum-iridium nanowires using electrodeposition methods. Using this technology, ultra-high density interconnect arrays could be fabricated.

This study focuses on the fabrication and evaluation of platinum-iridium dense nanowires with improved electrical and mechanical properties to be used as feed-through technology in hermetically packaged implantable microelectronics. In this study, an electrochemical deposition method for the fabrication of platinum-iridium thin films was used [9] and the effects of the pH of the solutions and the electroplating potential range on the chemical composition of

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the alloy surface structure and the hermeticity of the fabricated nanowires were comprehensively investigated.

II. Experimental approach

Platinum-Iridium Nanowire Electrodeposition

Nanowires were fabricated using an electrochemical deposition technique into nanoporous anodized aluminum oxide (AAO) membranes with a pore size of 200 nm in diameter. Ti thin films as adhesion layer with a thickness of 40nm and Au thin films with a thickness of 80 nm were sputter-deposited on the side of the AAO membranes with smaller pore size to make the membranes the working electrode (cathode). Nanowires were electrodeposited starting at the cathode, using a three-electrode electrochemical cell.

The Ti/Au coated alumina template was put on a copper plate on its coated side. An Ag/AgCl electrode was used as the reference electrode and a spiral platinum wire with 1 mm diameter was used as counter electrode. The electrodeposition potential range was selected similar to the results from electrodeposition of platinum-iridium alloy thin films [9] except that the deposition was performed on titanium thin films instead of gold substrates). Platinum-iridium nanowires were electrodeposited within different potential ranges in which different atomic percentage of iridium was measured.

Parallel platinum-iridium nanowires were fabricated using a potential cycling technique within potential range of 0.2 V to -0.2 V vs. Ag/AgCl using AAO templates.. The solution preparation the electrodeposition conditions were similar to those previously described [9].

Nanowires were isolated for further analysis. Ti/Au thin layers were etched using Ti and Au etchants, respectively and the electrodeposited AAO template was immersed in an aqueous solution of NaOH in a vial. In this process, AAO was totally dissolved and individual nanowires were floating. A certain amount of time was allowed for individual nanowires to sink. Then the solution was pipetted off and DI water was added to the vial to rinse the nanowires. This process was repeated three more times until a neutral solution was achieved.

SEM Characterization

SEM images were used to characterize the surface morphology, structure and size of the electrodeposited platinum and platinum-iridium nanowires using a field emission scanning electron microscope (ZEISS 1550VP) with an accelerating voltage of 4 kV. Individual platinum-iridium nanowires were distributed on the surface of SEM aluminum flat stubs and gently dried with nitrogen gas prior to SEM imaging.

TEM Characterization

Isolated platinum-iridium nanowires were distributed on carbon coated copper grids with 300 mesh size (Ted Pella Inc.). Copper grids with platinum and platinum-iridium nanowires were then separately loaded in TEM (JEOL 2100, Japan) to acquire images and diffraction patterns. Images were taken on the thinner edges of the nanowires with smaller branches of 20 nm for transmission of the electron beam through the samples, in dark and bright field modes.

Diffraction patterns were taken on the isolated platinum and platinum-iridium nanowires using beam widths smaller than the width of the nanowires. Several wires were characterized by diffraction patterns.

Electrical Testing

For comparison purposes, electrical testing was performed on single platinum and single platinum-iridium nanowires. In this process, randomly oriented single nanowires between two Ti/Au contact pads were trapped in order to measure the conductivity through the length of the single nanowires. Platinum and platinum-iridium nanowires were soaked into methanol in separate vials. Diluted amounts of each set of nanowires were dispersed on the Si/SiO_2 substrates. After the desired nanowire density was achieved, photolithography was applied to pattern the surface of the SiO_2 substrates. Using e-beam evaporation, a thin layer of Ti/Au with a thickness of about 5/50nm was deposited on top of the substrates. Using a metal lift-off technique, the excess of deposited metal was removed from the surface. After device fabrication, a voltage bias was applied cross the nanowires and the current was measured.

The electrical conductivity of the nanowires was measured across the contact pads on the fabricated device. The electron transport measurements of the single nanowires were performed using an Agilent 4156B semiconductor parameter analyzer.

Helium Leak Testing

Helium leak tests were performed using an ASM 182-TD (Alcatel, Inc.), helium leak detector with capability of detecting helium leak rates down to 5×10^{-12} mbar L s^{-1}. A custom sample mounting fixture was designed for NIA sample testing. The fixture with a flat and ultra-fine surface was mounted to the inlet aperture of the leak detector using a standard vacuum seal and clamp. A small circular inlet was considered in the center of this fixture in order to vacuum the He gas.

Measurements were taken after the flow rate was below 1×10^{-11} mbar L s^{-1} and a stable flow was read. A continuous small dose of He was sprayed on the top side of the sample exposed to ambient air. He gas was sprayed from nearly 10 cm from the sample surface with a pressure of 20 lbs for 10 seconds.

After helium exposure, the highest observed leak rates were measured and recorded. Leak rate measurements were repeated three times for each sample. After each measurement, time delay was given in order to return the leak rate to below 1×10^{-11} mbar L s^{-1}.

III. Results and Discussion

Platinum-Iridium Nanowire Electrodeposition

In this electrochemical fabrication method, platinum and iridium ions dissolved in the electrodeposition solution were reduced to platinum-iridium alloy inside the porous channels of the AAO substrate.

The potential range for electrodeposition of the nanowires was first identified by cycling the applied potential over various 200 mV ranges vs. Ag/AgCl until 60:40% platinum-iridium nanowires were electrodeposited. An important effecting factor in the electrodeposition of the nanowires was found to be the pH of the electrodeposition bath. Alumina templates showed surface wear and destruction of the pores due to the high pH of the electroplating bath.

SEM Characterization

The size and surface structure of Platinum-iridium nanowires were characterized using scanning electron microscopy (SEM). Figure 1 represents the profile of the nanowires formed in the AAO nano-pores, indicating the parallel formation and growth of the nanowires.

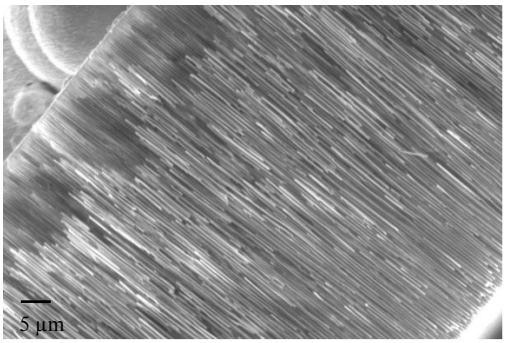

Figure 1 SEM micrograph of the cross section of platinum-iridium nanowires grown in AAO pores.

SEM micrographs revealed that the pH of the electrodeposition bath directly affected the morphology of the nanowires. Several sets of nanowire samples were prepared using electrodeposition baths with different pH levels until platinum-iridium nanowires with the desired surface structures were achieved.

Nanowires deposited in electrodeposition baths with pH levels of 5 and higher appeared to be brittle with discontinuities (Figure 2), while nanowires deposited

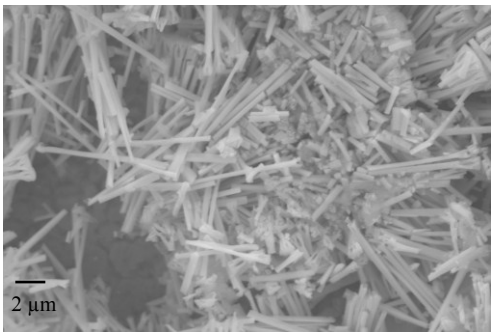

Figure 2 SEM micrograph of isolated nanowires with brittle structures electrodeposited at higher pH.

with pH between 1.5 to 2.5 appeared to be short in length because of suppression of the deposition process due to the wear on the surface of the templates during stirring the electrodeposition solution which caused the pores to fill up with partially dissolved floating AAO particles in the electroplating solution (not shown here). Satisfactory results were obtained using electrodeposition baths with pH of nearly 3.5. Samples prepared using this electrodeposition bath were formed to be dense and long nanowires without discontinuity (Figure 3).

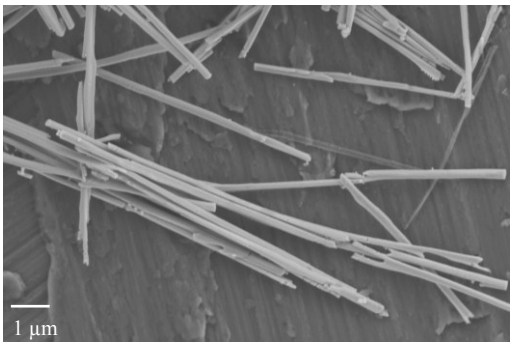

Figure 3 SEM micrograph of isolated dense nanowires electrodeposited at pH = 3.1.

Conductivity Measurements

The conductivity measurements of the platinum and platinum-iridium nanowires were carried out by applying electrical potential across single nanowires. Figure 4 shows the scanning electron micrograph of the fabricated devices for platinum-iridium nanowire, where two thin film Ti/Au stripes were sputter-deposited on top of dispersed nanowires as contact pads. The distance of the gap between the two parallel source and drain electrodes is 2 µm.

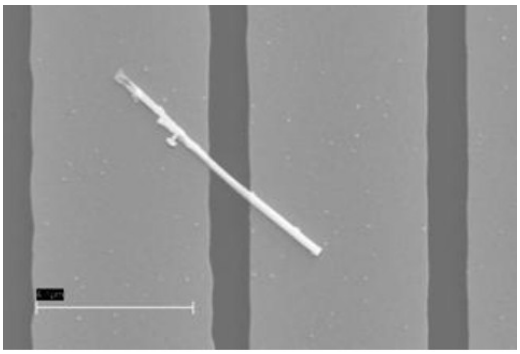

Figure 4 SEM micrograph of the testing device used for electrical conductivity measurement of single platinum and platinum-iridium nanowires.

The representative current-voltage plots (Figure 5) show the conductivity measured across the length of the platinum and platinum-iridium nanowires. The ratio of the average measured currents of platinum-iridium nanowires to that of platinum revealed approximately 2 times higher conductivity for the platinum-iridium nanowires.

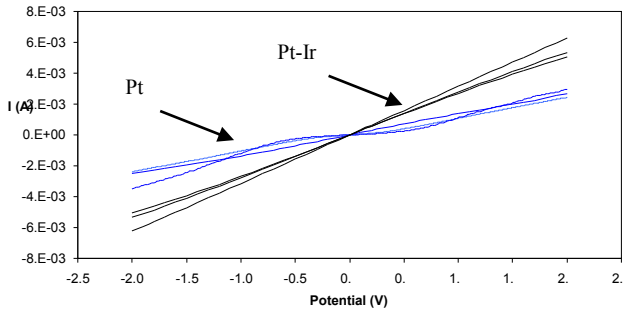

Figure 5 Current vs. voltage plots demonstrating the improved conductivity of platinum-iridium nanowires.

Helium Leak Testing

Helium leak testing performed on the electrodeposited platinum-iridium nanowires using the template fabrication technique showed hermetic characteristics. The results suggest that fabrication of hermetic interconnect structures with desirable platinum-iridium composition is possible. Helium test measurements using helium leak detector showed leak rates as low as 1 x 10^{-11} mbar L s^{-1} indicating that dense nanowires were synthesized inside of the nanoporous membranes. Measured helium leak rates for platinum-iridium nanowires showed that hermeticity was achieved by lowering the electrodeposition bath pH from neutral to nearly 3. Although further investigation is required, the results demonstrated that hermetic platinum-iridium alloy interconnect arrays can be fabricated using this nanowire interconnect construct.

IV. Conclusions

Platinum-iridium alloy nanowires were fabricated using an electrodeposition method with a solution containing platinum and iridium salts [9] in nanoporous aluminum oxide templates. Hermeticity tests results indicated that the fabricated platinum-iridium nanowires were continuous with the desired density to provide hermetic interconnects. This study also showed some advantages of platinum-iridium nanowires over conventional platinum nanowires. In a previous study, mechanical characterizations using nanoindentation tests on platinum-iridium alloys thin films revealed that the measured hardness was increased nearly100% compared to pure platinum control sample [9]. Electrical measurements on single platinum and platinum-iridium nanowires revealed increased conductivity of platinum-iridium nanowires. This result will have a great impact on the efficiency of implantable microelectronics by reducing the device power consumption with improved resolution of the transferred data between the device and the biological cells.

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