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Different methods to alter surface morphology of high aspect ratio structures

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Abstract

In various applications such as neural prostheses or solar cells, there is a need to alter the surface morphology of high aspect ratio structures so that the real surface area is greater than geometrical area. The change in surface morphology enhances the devices functionality. One of the applications of altering the surface morphology is of neural implants such as the Utah electrode array (UEA) that communicate with single neurons by charge injection induced stimulation or by recording electrical neural signals. For high selectivity between single cells of the nervous system, the electrode surface area is required to be as small as possible, while the impedance is required to be as low as possible for good signal to noise ratios (SNR) during neural recording. For stimulation, high charge injection and charge transfer capacities of the electrodes are required, which increase with the electrode surface. Traditionally, researchers have worked with either increasing the roughness of the existing metallization (Platinum grey, black) or other materials such as Iridium Oxide and PEDOT. All of these previously investigated methods lead to more complicated metal deposition processes that are difficult to control and often have a critical impact on the mechanical properties of the metal films. Therefore, a modification of the surface underneath the electrode's coating will increase its surface area while maintaining the standard and well controlled metal deposition process. In this work, the surfaces of the Silicon micro-needles were engineered by creating a defined microstructure on the electrodes surface using several methods such as Laser ablation, focused ion beam, sputter etching, reactive ion etching (RIE) and deep reactive ion etching (DRIE). The surface modification processes were optimized for the high aspect ratio Silicon structures of the UEA. The increase in real surface area while maintaining the geometrical surface area was verified using scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). The best results were obtained by DRIE induced surface morphology. Decreases in impedance values of electrodes up to 76 % indicate the successful surface engineering of the high aspect ratio Silicon structures.

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Keywords

Surface Modification; Dry Etching; Laser Ablation; Focused Ion Beam; Rough Surfaces; Interface Impedance; Reactive Ion Etching (RIE); Deep Reactive Ion Etching (DRIE)

Introduction

The surface modification of Silicon to create a structure of defined roughness is desirable in many applications. Especially in the development of solar cells, rough Silicon surfaces minimize reflection losses by several reflection and absorption processes [1,2,3]. Besides further applications such as high capacity battery anodes [4], terahertz radiation emitters [5], and water repelling surfaces [6], rough Silicon surfaces are widely used in biosensors [7] and biomedical systems. Miniaturized capillary electrochromatography structures make use of surface engineered Silicon surfaces with a defined roughness for miniaturized total analysis systems (μ TAS) used in drug screening and development [8]. Furthermore, a well-defined roughness on Silicon surfaces can be used for control and increase of cell adhesion and viability [9], but can also exhibit bactericidal effects [10]. Whereas most of the applications require very fine nano-porous surfaces, this work aims for a less dense surface roughness in order to decrease the electrodes impedance by increasing the real surface area while avoiding the pore resistance effect [11]. The pore resistance effect occurs for narrow and deep pores, where only parts of the electrode's surface can be accessed by the current due to higher time constants. Depending on the desired roughness for the various applications, different methods are currently known and reported in literature. The different methods range from wet chemical processes such as stain etching using Hydrofluoric acid (HF) and Nitric acid [12], electrochemical HF etching [13] over dry etching techniques such as reactive ion etching [14] to laser induced surface roughness using femtosecond [15,16,17] laser systems.

One of the applications for changing the surface morphology of high aspect ratio structures is in biomedical devices such as neural implants. This paper e.g. resulted from a National Institutes of Health funded project to improve the electrochemical performance of neural implants. These implants are basically microelectrodes that are used in the study and diagnostics of neurological disorders such as epilepsy and chronic depression [18,19]. Furthermore, neural implants play a crucial role for the development of neural prostheses which can restore lost motor or sensory functions of the body. Two of the most important characteristics for these microelectrodes are selectivity (ability to interact with a limited number of neurons) and sensitivity (ability to interact with neurons which are far from the electrodes). Selectivity increases with decreasing surface area of the electrode. In contrast, sensitivity increases with increasing surface area of the electrode. Hence, there is a trade-off between selectivity and sensitivity. One of the ways to overcome this design trade-off of having selectivity and sensitivity is to keep the geometrical surface area constant while increasing the real surface area by altering the surface morphology of the high aspect ratio Utah array electrodes.

In this paper, various methods and processes were investigated and optimized to engineer the surface of high aspect ratio (15:1) penetrating Utah electrode arrays (UEA). The UEA consists of a 10×10 square grid of 1.5 mm long electrodes with 400 µm spacing. 100 Pt/TiW/Pt bond pads are deposited on the back surface of the array. The tip of each electrode is usually metalized with Pt or sputtered Iridium Oxide (SIROF) to facilitate electronic to ionic transduction. The entire array, with the exception of the tip of each electrode, is insulated with a biocompatible Parylene-C layer (**Error! Reference source not found.**). A detailed fabrication procedure of the UEA is given elsewhere [20].

The modification of the electrode surface leads to an increase of the real surface area (RSA) of the UEA electrodes while keeping their geometric surface area (GSA) constant, hence mitigating the trade-off between selectivity and sensitivity. There are multiple advantages for having surface roughness compared to smooth surface. The roughened UEA will not only increase the SNR, but also decrease the necessary voltage which has to be applied to the electrode to deliver a certain amount of charge by increasing the double layer capacitance at the electrode/electrolyte interface [21]. Furthermore, studies have shown that surface roughness can have a significant impact on cell adhesion [9], leading to enhanced cell growth on the implants and to increased stability of the device in chronic applications. In order to roughen the surface of the electrode tips of the UEA, two main approaches are possible. The first approach is to deposit a material which has superior electrochemical properties and chronic stability. In literature, there are many materials that are added to the electrode tips such as nano-cluster platinum (NCPT) films [22], sputtered iridium oxide film (SIROF) [23,24], fractal Titanium Nitride (TiN) [11,21], Poly(3,4-ethylenedioxythiophene) (PEDOT) [25,26], or conducting polymer/biomolecule blends [27]. The second approach is to roughen the metal/electrode contact material by removing material using etching processes or laser ablation to increase the electrochemical properties. The electrode in contact with the biological tissue usually consists of a Silicon substrate which is coated with a biocompatible material exhibiting better electrochemical characteristics than Silicon. Hence, the patterning of electrode surfaces can either be carried out on the underlying Silicon substrate or directly on the biocompatible coating. This work focusses on dry etching methods to modify the surface of high aspect ratio neural implants. In literature, reactive ion etching (RIE) has been used for surface engineering however it is limited to planar substrates only [28] or turned out to be irreproducible [29].

To the authors best knowledge, publications about surface roughening of neural implants are limited to the previously mentioned deposition of porous materials or the etching of planar Silicon electrodes without a coating for increased biocompatibility and electrochemical properties. Not only does this paper describe the roughening of high aspect ratio 3D structures, but also presents, compares, and discusses different accurate surface modification techniques.

In this paper, a Platinum layer was chosen as coating material, since the roughness was created by dry etching, milling and ablation techniques. As opposed to complicated coating processes, such as reactive ion sputtering for SIROF or electroplating for Platinum black, the deposition of a sputtered Platinum thin film benefits from the simplicity and high

reproducibility of the deposition process. Furthermore, Pt is considered gold standard in the field of neural implants due to its long term stability and electrochemical properties [11].

Experimental

Different processes such as laser ablation, ion milling, sputter etching, RIE and DRIE were investigated as methods for the creation of a micro-structure on the electrodes surfaces. In order to ensure the bio-compatibility of the UEA, the electrodes were coated with a biocompatible Platinum layer. Depending on the surface modification process, the UEAs were Platinum coated prior to the surface modification (sputter etching) or after the surface modification (laser ablation of Si, ion milling, RIE, DRIE).

The Ti/Pt coating was sputtered on the arrays using a TMV Super system. First, a 10 nm thin adhesive Ti layer was deposited in Ar ambient (150 sccm flow rate) at a chamber pressure of 10 mTorr and a sputtering power of 50 W for 4 min. The sputtering parameters were optimized for a low stress Ti film. Afterwards, a 500 nm Pt layer was sputtered on the adhesive Ti film with an Ar flow rate of 150 sccm, a chamber pressure of 11 mTorr and a sputtering power of 50 W for 42 min. DC sputtering at a base pressure of less than 2×10^{-7} Torr was used for both deposition steps. After the sputtering, the deposited Ti/Pt stack between the electrodes was removed by laser ablation (Optec Micromaster KrF) in order to electrically insulate one electrode from another. After the metal deposition and the electrical insulation of the electrodes one from another, the arrays were coated with a 3 μm thick Parylene-C layer using chemical vapor deposition (CVD) with a Paratech 3000 labtop system. The active electrode tips (50 μm) were exposed by selectively etching the Parylene-C in oxygen plasma [30]. The impedance of the modified electrodes was measured using electrochemical impedance spectroscopy (EIS) with a Gamry Instruments PC4 Potentiostat.

Laser ablation

The irradiation of a Silicon surface with excimer laser pulses, leads to the formation of a rough surface topography. The evolution of the surface topography, which is studied elsewhere [31], strongly depends on the number of pulses.

The approach of creating a rough surface structure on the tips of the UEA by laser ablation has been investigated. The UEA was tilted at an angle of 24 degrees by placing it in a specially manufactured array holder, in order to allow a scan with the laser beam along the shaft of the electrodes. The laser processing was carried out on an Optec Micromaster KrF excimer laser system ($\lambda = 248.35 \text{ nm}$). Different parameters such as scan-speed, pulse frequency and radiation power were investigated. The different patterns on the electrodes surface created during the laser processing were analyzed with a FEI Quanta 600F secondary electron scanning microscope (SEM). The best results leading to a maximum roughness of the electrodes surface were obtained with the values listed in **Error!**

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Sputter etching

Sputter etching is a dry etching process, where inert ions have sufficient energy (between 200 eV and 1000 eV [32]) to remove material from the substrate. Due to the high

acceleration of the ions, the process yields high anisotropy. Since the material is physically etched by collisions of inert ions, the selectivity of the process is very low.

The UEA is commonly coated with Platinum or SIROF as biocompatible layers with satisfying electrochemical characteristics such as high charge injection capacitance [11,29]. As a purely physical etching method which also removes noble metals such as Pt, sputter etching represents a possibility of roughening the electrode after the tip metallization. This has the major advantage of not losing some of the microstructure's roughness due to the metal filling pores or closing pockets. The sputter etching was carried out in an RIE/DRIE Oxford Plasmalab System 100. The arrays were mounted using thermal grease on an Aluminum chuck. The grease was only applied on the side walls of the arrays in order to ensure an electrical contact between the bond pads on the backside of the UEAs and the Al chuck. Hence, due to the bias voltage resulting from the etching process, the Argon ions were increasingly accelerated towards the tips of the UEAs where the electric field is strongest [33].

Focused ion beam milling

A focused ion beam (FIB) instrument uses a liquid metal ion source to generate the ion beam. Typically Ga ions are being used to create the ion beam. This is due to the low melting point of Ga and the possibility of focusing Ga ion beam on a very small area (< 10 nm) [34]. FIB processes are commonly used to prepare thin samples for transmission electron microscopy (TEM) [34]. However, since the FIB technique presents a very accurate method of removing material, it is hereafter analyzed as a method of milling the tips of the UEA in order to increase its surface area.

With a FEI Helios NanoLab 650 system, a beam of Ga ions was focused on the Silicon electrode tips. Although the process is known to not be material selective, it was carried out on the bare Silicon UEA. A Ti/Pt coating as described above would increase the drilling time. Furthermore, ion beam milling through a metallized array would reveal Silicon, which will need to be coated again by a biocompatible Pt layer.

As shown in **Error! Reference source not found.**, a pattern of 7 rings which were centered on the electrode tip was etched into the silicon UEA. The diameters of the two circles defining each ring had a difference of $1\text{ }\mu\text{m}$ respectively. The current of the ion beam was 2.5 nA and the depth of the pattern was varied from $0.5\text{ }\mu\text{m}$ to $1\text{ }\mu\text{m}$.

RIE/DRIE—Reactive ion etching (RIE) and deep reactive ion etching (DRIE) processes were examined as methods to engineer the electrode substrate (silicon in Utah array) itself.

RIE is a combination of physical and chemical dry etching. The plasma for the etching process is either created with reactive gases or a combination of inert and reactive gases. DRIE is a variation of RIE for etching very deep structures with a high aspect ratio. The so called Bosch process consists of alternating an etching step with the reactive gas and the passivating gas which covers the etched structure from the previous step. The following etching step removes the passivation layer on the bottom of the etched structure with accelerated chemically inert ions. Only the passivation at the side walls of the structure

remains and one can achieve very deep and vertical structures with typical aspect ratios of 20-30:1 [35].

The process was investigated on both etching systems STS ICP ASE and Oxford Plasmalab System 100. The surface modified electrodes were coated with metal using the sputter system TMV Super. An extensive study on the variation of the etching parameters such as time, RF power, ICP (Inductive Coupled Plasma) power, pressure, and gas flow rate was done to achieve the desired surface roughness. In order to further increase the depth of the rough microstructure, we combined various etching cycles which create the microstructure with a Bosch process of alternating etching and passivating which results in a higher aspect ratio. Based on previous publications [29,36], where RIE was used to increase the RSA of the UEA, the influence of the different process parameters on the formation and the texture of the microstructure was analyzed. Additionally, a further increase of the RSA was targeted by combining RIE with DRIE processes.

STS ICP ASE—An extensive study of the microstructure on UEAs by varying the process parameters time, RF power, ICP power, pressure, and gas flow rate was done on the DRIE system STS ICP ASE. The different tested parameter combinations are listed in Table. In a first step, process parameters were chosen in a way, that only one parameter varied while all other were held constant. This allowed the study of the influence of single parameters such as pressure or platen power on the etching characteristics and the texture of the microstructure on the array tips.

Oxford Plasmalab System 100

DRIE processes for the surface roughening of the UEA were investigated on the Oxford Plasmalab System 100. One of the usually undesired effects during DRIE is the formation of black silicon also known as silicon grass. For standard DRIE processes where smooth high aspect ratio side walls are targeted, black silicon represents an undesired phenomenon. Nevertheless, black silicon has also shown to be useful for several applications such as bio-sensors [7], bactericidal surfaces [10], solar energy applications [37] or the increase in active surface area of silicon-based fuel cells [38]. The different methods of the black silicon fabrication such as electrochemical etching, stain etching, metal assisted chemical etching, reactive ion etching laser treatment and the FFC-Cambridge process were described by Liu et al. [37]. The DRIE approach in particular, is described by Xiao et al. [39]. In this work, black silicon has been studied in order to increase the RSA of the UEA electrodes. The black silicon method described by Jansen et al. [14] was applied on the UEA. During several RIE runs, the etching parameters were adjusted until the shiny and grey color of the silicon arrays turned into a dark almost black color.

Results and Discussion

Laser Ablation

The laser processed roughened electrode tip is shown in **Error! Reference source not found.** The roughness of the electrode's surface is maximal at the tip and decreases when moving down the shaft from the tip. This decrease is due to the geometry of the UEA

causing the electrode to move out of focus while the laser beam scans down the shaft. Given the small dimensions of the electrodes of the UEA and the limitations of the laser system, the reproducibility in roughness and material removal from one electrode to another was poor. Another downside of this technique is the extensive processing time, since every single electrode has to be processed separately. Due to the damage caused to the electrodes, the poor reproducibility and the long processing time, laser ablation does not represent an attractive and promising method to roughen the electrodes surface.

The EIS measurements didn't show any significant impact on the electrode's impedances. Despite the average decrease in impedance at 1 kHz of the modified electrodes by a relative difference of 1.2 %, the coefficient of variation (COV) is 4.45 % for the modified electrodes and 4.78 % for the neighboring unmodified reference electrodes. The COV was calculated as the standard deviation over the mean value of the measured impedances. The impedance at 1 kHz for an exposed surface area of $1.27 \times 10^{-2} \text{ mm}^2$ was 25.86 k.

Sputter etching

The impacting Ar ions led to the creation of a rough microstructure on the electrode tips as shown in **Error! Reference source not found.**. Since the sputter yield strongly depends on the angle of impacting Ar ions, the unique geometry of the UEA causes inhomogeneity in the etching rate along the shaft of the electrodes. Re-deposition of etched material, faceting and trenching [40] also contribute to the distinguished etching profile. Despite the very promising texture of the surface and the decrease in impedance at 1 kHz by 50 % of modified electrodes to unmodified reference electrodes, the method was not further investigated due to several disadvantages. Regarding the purely physical etching process by ion bombardment, very high process power values are necessary, leading to a strong warming of the array. Despite the use of thermal vacuum grease, Helium cooling of the chuck and the Aluminum chuck as heat sink, the temperature increase damaged the bond pads on the back-side of the array.

Furthermore, the sputter etching at such high powers also caused damage to the RIE/DRIE Oxford Plasmalab System 100. Especially the Aluminum clamps for the attachment of the wafer were etched, resulting in a strong contamination of the etching chamber by re-deposition of Aluminum particles. The Aluminum contamination was also observed on the etched arrays, which leads to the loss of their bio-compatible characteristics.

Focused ion beam milling

With the increasing depth of the etching process, the ring shaped structure evolved in a stronger formation of trenches, resulting in geometries of hollow cylinders around the tip (**Error! Reference source not found.**). The adapted current of 2.5 nA rendered smooth cuts into the Silicon substrate.

The major disadvantages of the focused ion beam method to pattern the electrode tips are the long processing times and the resulting costs of operation. The etching procedure for 7 rings on one tip does not take longer than 10 minutes. The time consuming part of the procedure is the focusing and alignment of the electron and ion beams on the desired area.

With a tip exposure of 141 μm resulting in an exposed surface area of 1.27×10^{-2} , mm^2 , the impedance at 1 kHz was 22.63 k (COV = 16.08 %). A distinct difference to unmodified neighboring electrodes could not be identified.

RIE/DRIE

STS ICP ASE: As expected, the time was found to mainly influence the depth and the pore size of the created micro-structure. **Error! Reference source not found.** shows the emerging microstructure after 45 seconds of etching. The comparable although more defined micro-structure displays a higher porosity and depth after 90 seconds of etching.

As seen on **Error! Reference source not found.**, the study of the pressure and RF power shows a strong impact of these two parameters on the micro-structure. While the electrodes etched at 5 mTorr chamber pressure remained almost smooth, the surface roughness increased significantly for the higher pressure values of 20 mTorr and 35 mTorr. The increased roughness is most likely due to the increased etching rate, which increases with the chamber pressure within the lower pressure range for RIE processes. On the sample which was etched at 250 W and 5 mTorr, one can distinguish the early formation of a micro-structure. Given the low pressure values however, the electrode is not sufficiently etched to exhibit a deeper texture. **Error! Reference source not found.** clearly shows the formation of a micro-structure on the electrodes for the lower pressure value of 5 mTorr. The surface modification seen in **Error! Reference source not found.** differs from **Error! Reference source not found.** by a lower ICP power and a lower SF₆ flow rate. The electrodes for pressure values of 10 mTorr and 15 mTorr are highly over-etched, which is indicated by the loose porous scaffold enclosing the remaining bulk silicon part of the electrodes. Furthermore, one can detect a decrease in pore size with increasing pressure.

By comparing the different RF power values (**Error! Reference source not found.**), one can distinguish the expected increase of the etching rate with increasing power. Higher power values accelerate the formation of a roughened surface structure. However, the texture appears to exhibit less density and depth for higher RF power values. This characteristic can be explained by the increased vertical etching rate due to the stronger acceleration of the reactive ions towards the substrate for higher RF power values.

The ICP power significantly increases the etching rate. Hence, higher ICP power values render the etching process extremely time critical in order to avoid over-etching. Furthermore, the etching process gains more of an isotropic character with increasing ICP power. The best results were obtained for ICP power values of 200 W. The formation of a porous microstructure seems to depend on the correct proportion of RF and ICP power and hence, on the correct proportion of anisotropic and isotropic etching mechanisms.

The SF₆ flow rate for the studied range (5 sccm – 50 sccm) significantly influenced the etching rate, which increase with the flow rate. The pore size and texture of the micro-structure however, seemed to not be affected by changes of the flow rate.

As seen on **Error! Reference source not found.** (C, E), static RIE with constant parameters leads quickly to an over-etched electrode enveloped by a fuzzy mechanically weak structure.

Although this scaffold exhibits a high porosity, it is not suitable for insertion. In order to create a porous and deep but mechanically stable micro-structure, the RIE process was combined with a DRIE process. The idea was to define a shallow microstructure such as seen on **Error! Reference source not found.** (A, B) and subsequently use a DRIE process to add depth to the existing pattern.

An example of a promising structure obtained by the use of both RIE and DRIE processes on the UEA with the STS ICP ASE is displayed in **Error! Reference source not found.**

The process parameters of the RIE step resulting in the microstructure displayed in **Error! Reference source not found.** were 5 sccm SF₆ flow rate, 5 mTorr chamber pressure, 275 W RF power and 200 W ICP power for 1 min etching time. For the DRIE process, a Bosch process was applied, where an etching step and passivation step were alternated for 15 cycles. The parameters for the etching and the passivation steps are listed in **Error! Reference source not found.**

With a tip exposure of 160.90 μm and an exposed electrode area of $1.79 \times 10^{-2} \text{ mm}^2$ the impedance at 1 kHz was 21.25 k Ω .

Oxford Plasmalab System 100

Especially the ratio of SF₆ flow rate to O₂ flow rate showed a significant impact on the formation of the black silicon. Whereas other parameters such as pressure, RF and ICP power also influenced the formation of the microstructure, their effect on the etching rate was significantly higher. SEM studies of the etched arrays showed the formation of a silicon micro-structure. Furthermore, a passivating mesh of Oxyfluoride which enveloped the electrodes was observed (**Error! Reference source not found.**).

The perforated Oxyfluoride layer can be used as masking layer for a subsequent DRIE process which will increase the depth of the Silicon microstructure. Hence, the surface roughening of the UEA tips is a two-step etching process. The first step consists of defining a superficial microstructure covered by a passivating perforated Oxyfluoride layer. The second step consists in adding depth to the existing microstructure using a DRIE Bosch process through the masking Oxyfluoride mesh. It was found that the surface topography can be very well controlled by varying the etching time of the two steps, while keeping the other process parameters constant. The first step showed to increase the pore size with increasing etching time up to 2 min. A saturation of this effect however occurs for etching times above 2 min, where the microstructure remains the same while the overall volume of the electrode decreases due to isotropic etching. For shorter etching times than 1 min, the Oxyfluoride layer is too thin, which will lead to less texture of the microstructure on the electrode tips (**Error! Reference source not found.** A, B). The subsequent DRIE Bosch-process consisted in multiple alternating etching and passivating steps. Hereafter, a sequence of an etching with a subsequent passivating step will be referred to as one cycle. It is critical to find the ideal balance between the two steps. **Error! Reference source not found.** A, C show strongly over-etched electrode tips caused by too many DRIE cycles. One can observe the volume decrease of these electrodes by their thinner and sharper shape compared to the electrodes etched with fewer cycles shown in **Error! Reference source not found.** B, D.

Less DRIE cycles prevent the electrodes from being over-etched. However, the first etching step has to be at least 1 min in order to create an Oxyfluoride layer, which is thick enough to serve as mask for the DRIE step. **Error! Reference source not found.** B displays the case of too short first step times. The Oxyfluoride layer was too thin and was etched away by the subsequent Bosch process, leading to a very shallow micro-structure without depth.

The optimized balance of the two etching steps is seen in **Error! Reference source not found.** D. The electrode is not over-etched by excessive DRIE cycles, neither by a long first step. However, the first etching step was long enough to predefine the micro-structure and create an Oxyfluoride mesh, which served as mask during the subsequent Bosch process to add depth and porosity to the micro-structure.

The electrodes in **Error! Reference source not found.** were coated with Ti and Pt as previously described. Since the Oxyfluoride is not biocompatible and electrically insulating, it has to be removed after the RIE/DRIE process. Different methods such as sonication, solvent baths and acids have been investigated. Although sonication removed the Oxyfluoride layer, the created Silicon micro-structure was damaged during this process. Even after several days, solvent baths didn't prove to be useful to remove the passivating layer. Finally, dipping the arrays for 35 s in 5:1 Buffered Oxide Etch (BOE) freed the electrodes from any residual Oxyfluoride. Longer BOE etching times however, did also damage the Silicon micro-structure.

The dry etching process showed an increased formation of microstructure around the tips of the electrodes. **Error! Reference source not found.** shows increased etching at the tips of the electrodes during RIE. This effect could be either due to the concentration of the electric field at the sharp tips of the conductive Silicon needles during etching or resulting from the unique high aspect ratio geometry of the needles. At the bases and the lower area of the shaft almost no microstructure can be detected. The FIB cross section of a modified UEA tip, as seen in **Error! Reference source not found.**, shows that the created microstructure exhibits depths up to 4.4 μm .

As seen in **Error! Reference source not found.** the impedance of the modified UEA decreased by 76% at 1 kHz. Along with the decrease in impedance, the shift of the modified array's phase curve compared to the unmodified array's curve indicates an increase in RSA of the electrode tips. For a tip exposure of 50 μm and a resulting surface area of $2 \times 10^{-3} \text{ mm}^2$ the impedance of a modified electrode was 31.3 k ($\text{COV} = 17.02 \%$) compared to 131.9 k ($\text{COV} = 21.55 \%$) of an unmodified electrode.

Conclusion

Different methods of increasing the RSA of Silicon micro-needles were investigated. The laser induced surface modification due to ablation didn't show any significant decrease in impedance. Furthermore, the laser machining is not a batch process leading to long processing times for devices such as the UEA with 100 electrodes. Also, since the laser beam has to be focused manually on the tip of every electrode needle, the surface modification is highly operator dependent. Sputter etching of the high aspect ratio needles of

the UEA rendered very nice and reproducible surface roughness. Unfortunately, the poor selectivity and high power values of the process damaged the Aluminum clamps of the tool and contaminated the electrodes with the re-deposition of Aluminum particles. Similar to the laser processing, the use of a focused ion beam to increase the RSA of the UEA electrode tips is a very time consuming and expensive procedure. Furthermore, the procedure didn't result in significant decrease of impedance. The use of RIE and DRIE processes proved to be the most promising approach for a precise and reproducible method of increasing the surface roughness of the high aspect ratio Silicon needles of the UEA. Compared to unmodified UEAs from the same batch, the impedance decreased by 76 % indicating an increase in RSA of the electrodes. Another advantage of the dry etching is its high controllability of the roughness of the microstructure as well as its batch process compatibility. The microstructure which forms only at the tips of the Silicon needles seems to be a unique effect caused by the high aspect ratio geometry of the electrodes.

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References

- [1]. Koynov S, Brandt MS, Stutzmann M. Black nonreflecting silicon surfaces for solar cells. *Appl. Phys. Lett.* 2006; 88:203107. doi:10.1063/1.2204573.
- [2]. Branz HM, Yost VE, Ward S, Jones KM, To B, Stradins P. Nanostructured black silicon and the optical reflectance of graded-density surfaces. *Appl. Phys. Lett.* 2009; 94:231121. doi: 10.1063/1.3152244.
- [3]. Oh J, Yuan H-C, Branz HM. An 18.2%-efficient black-silicon solar cell achieved through control of carrier recombination in nanostructures. *Nat. Nanotechnol.* 2012; 7:743–8. doi:10.1038/nnano.2012.166. [PubMed: 23023643]
- [4]. Szczech JR, Jin S. Nanostructured silicon for high capacity lithium battery anodes. *Energy Environ. Sci.* 2011; 4:56–72. doi:10.1039/C0EE00281J.
- [5]. Hoyer P, Theuer M, Beigang R, Kley E-B. Terahertz emission from black silicon. *Appl. Phys. Lett.* 2008; 93:091106. doi:10.1063/1.2978096.
- [6]. Barberoglou M, Zorba V, Pagozidis A, Fotakis C, Stratakis E. Electrowetting properties of micro/nanostructured black silicon. *Langmuir.* 2010; 26:13007–14. doi:10.1021/la101138u. [PubMed: 20593795]
- [7]. Jane A, Dronov R, Hodges A, Voelcker NH. Porous silicon biosensors on the advance. *Trends Biotechnol.* 2009; 27:230–9. doi:10.1016/j.tibtech.2008.12.004. [PubMed: 19251329]
- [8]. Fintschenko Y, van den Berg A. Silicon microtechnology and microstructures in separation science. *J. Chromatogr. A.* 1998; 819:3–12. doi:10.1016/S0021-9673(98)00544-5.
- [9]. Fan YW, Cui FZ, Hou SP, Xu QY, Chen LN, Lee I-S. Culture of neural cells on silicon wafers with nano-scale surface topograph. *J. Neurosci. Methods.* 2002; 120:17–23. [PubMed: 12351203]
- [10]. Ivanova EP, Hasan J, Webb HK, Gervinskas G, Juodkazis S, Truong VK, et al. Bactericidal activity of black silicon. *Nat. Commun.* 2013; 4:2838. doi:10.1038/ncomms3838. [PubMed: 24281410]

- [11]. Cogan SF. Neural stimulation and recording electrodes. *Annu. Rev. Biomed. Eng.* 2008; 10:275–309. doi:10.1146/annurev.bioeng.10.061807.160518. [PubMed: 18429704]
- [12]. Moxon K, Kalkhoran N. Nanostructured porous silicon scaffolds for improved biocompatibility of thin film microelectrodes. *Proc. 25th Annu. Int. Conf. IEEE Eng. Med. Biol. Soc.* 2003; 4:3698–3699.
- [13]. Kleimann P, Linnros J, Juhasz R. Formation of three-dimensional microstructures by electrochemical etching of silicon. *Appl. Phys. Lett.* 2001; 79:1727. doi:10.1063/1.1401792.
- [14]. Jansen H, De Boer M. The black silicon method: a universal method for determining the parameter setting of a fluorine-based reactive ion etcher in deep silicon trench etching with profile. *J. Micromechanics Microengineering.* 1995; 5:115–120.
- [15]. Straub M, Afshar M, Feili D, Seidel H, König K. Efficient Nanostructure Formation on Silicon Surfaces and in Indium Tin Oxide thin Films by sub-15 fs pulsed near-infrared Laser Light. *Phys. Procedia.* 2011; 12:16–23. doi:10.1016/j.phpro.2011.03.100.
- [16]. Schüle M, Afshar M, Feili D, Seidel H, König K, Straub M. Incubation and nanostructure formation on n- and p-type Si(100) and Si(111) at various doping levels induced by sub-nanojoule femto- and picosecond near-infrared laser pulses. *Appl. Surf. Sci.* 2014; 314:21–29. doi:10.1016/j.apsusc.2014.06.140.
- [17]. Vorobyev AY, Guo C. Direct femtosecond laser surface nano/microstructuring and its applications. *Laser Photon. Rev.* 2013; 7:385–407. doi:10.1002/lpor.201200017.
- [18]. Normann, R. a Technology insight: future neuroprosthetic therapies for disorders of the nervous system. *Nat. Clin. Pract. Neurol.* 2007; 3:444–52. doi:10.1038/ncpneuro0556. [PubMed: 17671522]
- [19]. Hochberg LR, Serruya MD, Friehs GM, Mukand JA, Saleh M, Caplan AH, et al. Neuronal ensemble control of prosthetic devices by a human with tetraplegia. *Nature.* 2006; 442:164–71. doi:10.1038/nature04970. [PubMed: 16838014]
- [20]. Campbell PK, Jones KE, Huber RJ, Horch KW, Normann R. a. A silicon-based, three-dimensional neural interface: manufacturing processes for an intracortical electrode array. *IEEE Trans. Biomed. Eng.* 1991; 38:758–68. doi:10.1109/10.83588. [PubMed: 1937509]
- [21]. Aryan, NP.; Kaim, H.; Rothermel, A. *Stimulation and Recording Electrodes for Neural Prostheses.* Springer; 2014.
- [22]. Shah, K.; Tolosa, V.; Tooker, AC.; Felix, SH.; Pannu, SS. Improved chronic neural stimulation using high surface area platinum electrodes; *Annu. Int. Conf. IEEE Eng. Med. Biol. Soc.*; 2013; p. 1546-1549.
- [23]. Negi S, Bhandari R, Rieth L, Solzbacher F. In vitro comparison of sputtered iridium oxide and platinum-coated neural implantable microelectrode arrays. *Biomed. Mater.* 2010; 5:15007. doi: 10.1088/1748-6041/5/1/015007. [PubMed: 20124668]
- [24]. Weiland J, Anderson DJ, Humayun MS. In vitro electrical properties for iridium oxide versus titanium nitride stimulating electrodes. *IEEE Trans. Biomed. Eng.* 2002; 49:1574–1579. [PubMed: 12549739]
- [25]. Abidian MR, Martin DC. Experimental and theoretical characterization of implantable neural microelectrodes modified with conducting polymer nanotubes. *Biomaterials.* 2008; 29:1273–83. doi:10.1016/j.biomaterials.2007.11.022. [PubMed: 18093644]
- [26]. Abidian MR, Ludwig K. a. Marzullo TC, Martin DC, Kipke DR. Interfacing Conducting Polymer Nanotubes with the Central Nervous System: Chronic Neural Recording using Poly(3,4-ethylenedioxythiophene) Nanotubes. *Adv. Mater.* 2009; 21:3764–3770. doi:10.1002/adma.200900887. [PubMed: 26345408]
- [27]. Cui X, Lee VA, Raphael Y, Wiler JA, Hetke JF, Anderson DJ, et al. Surface modification of neural recording electrodes with conducting polymer/biomolecule blends. *J. Biomed. Mater. Res.* 2001; 56:261–272. [PubMed: 11340598]
- [28]. Cheung K, Choi Y, Kubow T, Lee L. Nanostructured electrodes for improved neural recording. *MRS Proc.* 2002; 729
- [29]. Negi S, Bhandari R, Solzbacher F. A novel technique for increasing charge injection capacity of neural electrodes for efficacious and safe neural stimulation. *Conf. Proc. IEEE Eng. Med. Biol. Soc.* 2012; 2012:5142–5. doi:10.1109/EMBC.2012.6347151. [PubMed: 23367086]

- [30]. Hsu J, Rieth L, Normann RA, Tathireddy P, Solzbacher F. Encapsulation of an integrated neural interface device with Parylene C. *IEEE Trans Biomed Eng.* 2009; 56:23–29. [PubMed: 19224715]
- [31]. Conde JC, Lusquinos F, Gonzalez P, Serra J, Leon B, Cultrera L, et al. Laser ablation of silicon and copper targets. Experimental and finite elements studies. *Appl. Phys. A.* 2004; 79:1105–1110. doi:10.1007/s00339-004-2656-4.
- [32]. Madou, MJ. *Fundamentals of Microfabrication and Nanotechnology, Third Edition, Volume Two: Manufacturing Techniques for Microfabrication and Nanotechnology.* 3rd. CRC Press; 2011. p. 163-164.
- [33]. Leber, M.; Shandhi, MMH.; Bhandari, R.; Negi, S. Maskless method to selectively etch Parylene-C from high aspect ratio neural devices; 2015 Transducers - 2015 18th Int. Conf. Solid-State Sensors, Actuators Microsystems, IEEE; 2015; p. 1303-1306. doi:10.1109/TRANSDUCERS.2015.7181170
- [34]. Giannuzzi, L. a.; Stevie, F. a. A review of focused ion beam milling techniques for TEM specimen preparation. *Micron.* 1999; 30:197–204. doi:10.1016/S0968-4328(99)00005-0.
- [35]. Madou, MJ. *Fundamentals of Microfabrication and Nanotechnology, Third Edition, Volume Two: Manufacturing Techniques for Microfabrication and Nanotechnology.* 3rd. CRC Press; 2011. p. 197
- [36]. Bhandari R, Negi S, Solzbacher F. A novel surface modification method to achieve low impedance neural microelectrode arrays. *Solid-State Sensors, Actuators Microsystems Conf.* 2011:2196–2199.
- [37]. Liu X, Coxon PR, Peters M, Hoex B, Cole JM, Fray DJ. Black silicon: fabrication methods, properties and solar energy applications. *Energy Environ. Sci.* 2014; 7:3223–3263. doi:10.1039/C4EE01152J.
- [38]. Feng C, Xiao Z, Chan PCH, Hsing I-M. Lithography-free silicon micro-pillars as catalyst supports for microfabricated fuel cell applications. *Electrochem. Commun.* 2006; 8:1235–1238. doi:10.1016/j.elecom.2006.05.020.
- [39]. Xiao Z, Feng C, Chan P, Hsing I. Formation of Silicon Nanopores and Nanopillars by a Maskless Deep Reactive Ion Etching Process. *Solid-State Sensors, Actuators Microsystems Conf.* 2007:89–92.
- [40]. Madou, MJ. *Fundamentals of Microfabrication and Nanotechnology, Third Edition, Volume Two: Manufacturing Techniques for Microfabrication and Nanotechnology.* 3rd. CRC Press; 2011. p. 175-177.

Highlights

Multiple roughening techniques for high aspect ratio devices were investigated.

Modification of surface morphology of high aspect ratio Silicon devices (1:15).

Decrease of 76% in impedance proves significant increase in surface area.

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Fig. 1. Scanning electron micrographs (SEM) of an entire UEA (A) and of a single electrode, where the active site is formed by the exposed Pt coated tip.

Fig. 2.
Scanning electron micrograph of FIB pattern of 7 rings centered on the tip of the UEA electrode

Fig. 3.
Scanning electron micrograph of roughened electrode tip after laser processing and Platinum coating.

Fig. 4. Scanning electron micrograph of roughened electrode tip after metallization and after sputter etching with Ar ions. The electrodes are coated with a 1.1 μm Platinum layer.

Fig. 5. Scanning electron micrograph of ring shaped pattern resulting from etching the silicon tips of the UEA using FIB technology.

Fig. 6. Scanning electron micrograph showing the influence of the etching time is clearly seen in microstructure on the silicon tips of the UEA. The etching time for the left picture (A) is 45 seconds and for the right (B) 90 seconds, while all other parameters were held constant. Pressure: 20 mTorr; RF power: 275 W; SF₆ flow rate: 10 sccm; ICP power: 200 W.

Fig. 7.

Scanning electron micrograph illustrating the influence of RF power and pressure on the micro-structure created by RIE process. The etching rate increases with the pressure and the RF power. Higher RF power values lead to deeper but smoother textures.

Fig. 8. Scanning electron micrograph illustrating the influence of pressure on the micro-structure created by RIE. Etching rare increases and pore size decreases with increasing pressure.

Fig. 9. Scanning electron micrograph of porous UEA electrode obtained by RIE. The roughened surface is coated with a 500 nm thick sputtered Pt layer.

Fig. 10. Scanning electron micrograph of Silicon UEA electrode etched with the black Silicon method. A white mesh of Oxyfluoride envelopes the roughened electrode.

Fig. 11.

Scanning electron micrograph showing the formation of different microstructures depending on process times of the two etching steps. The electrode tips were coated with a 500 nm Pt layer after etching. The combination of 2 min static etching time and 6 DRIE cycles renders a microstructure exhibiting a high porosity.

Fig. 12.

Scanning electron micrograph showing the increased formation of microstructure at tips of UEA electrodes during RIE.

Fig. 13.

FIB cross section of the modified UEA tip. The depth of the Platinum coated microstructure reaches values up to 4.4 μm .

Fig. 14.

Bode plots of a modified UEA as shown in **Error! Reference source not found.** D and of an unmodified control sample. The curves show the mean values of impedance and phase from 25 measured electrodes on each array. The decrease of the impedance by 76% at 1 kHz and the shift of the phase Bode-plot indicate a significant increase in surface area of the electrode tips.

Table 1

Parameters for Laser induced surface modification of the UEA electrode tips.

Wavelength	248.35 nm
Demagnification	11
Mask	5
Transmission	95%
Pulse frequency	250 Hz
Scan-speed	10 $\mu\text{m/s}$
Spot-size (diameter)	27 μm
Fluence	6130 mJ/cm^2

Table 2

Overview of the different RIE process parameter combinations investigated and their influence on the texture of the microstructure on the UEA tips. X marks the investigated process parameter combination.

	Pressure [mT]							SF6 [scm]						Platen Power [W]								ICP Power [W]					Time [s]				
	5	10	15	20	35	45	70	5	10	15	20	50	150	200	225	250	275	300	50	100	200	300	600	20	30	45	60	90	180		
Pressure [mT]	5																														
	10																														
	15																														
	20																														
	35																														
	45																														
	70																														
SF6 [scm]	5	X	X																												
	10	X		X																											
	15	X	X	X																											
	20	X		X	X		X						X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
	50				X		X					X				X															
	150				X		X				X	X																			
	200	X			X						X																				
Plate Power [W]	225	X			X						X																				
	250	X			X		X				X																				
	275	X	X	X	X	X	X		X	X	X								X	X	X	X	X	X	X	X	X	X	X	X	
	300				X		X				X																				
	50				X						X																				
	100				X						X																				
	200		X	X	X		X				X																				
ICP Power [W]	300			X							X																				
	50										X																				
	100										X																				
	200		X	X	X	X	X				X																				
	300				X						X																				
	600	X			X	X	X				X	X	X	X	X	X	X	X													
	20																														
Time [s]	30	X								X									X	X	X	X	X	X	X	X	X	X	X	X	
	45	X	X							X	X																				

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		Pressure [mT]					SF6 [sccm]					Platen Power [W]					ICP Power [W]					Time [s]													
		5	10	15	20	35	45	70	5	10	15	20	50	150	200	225	250	275	300	50	100	200	300	600	20	30	45	60	90	180					
		X		X					X	X	X						X			X	X	X													
	60	X			X				X	X	X						X			X	X	X													
	90	X			X				X	X	X						X																		
		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X																
	180	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X																

Table 3

DRIE Bosch-process parameters for the creation of a deep and porous micro-structure on the STS ICP ASE.

Parameter	Etch	Passivate
Step duration	9 s	6 s
Pressure	3 mTorr	3 mTorr
SF6 flow rate	130 sccm	0 sccm
O2 flow rate	13 sccm	0 sccm
C4F8 flow rate	0 sccm	80 sccm
RF power	6 W	0 W
ICP power	300 W	300 W