Nanostructured Porous Silicon Scaffolds for Biofuel Cells

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***Abstract*—An Enzymatic biofuel cell is a specific type of fuel cell which uses enzymes as catalysts to oxidize its fuel. They pose as a great promise in terms of their relatively inexpensive components and fuels, as well as a potential power source for bionic implants. Here, we present the use of dry-etched nanotextured porous silicon scaffolds to increase the contact surface area of silicon with surrounding biofuel to enhance the process of harvesting of energy, and consequently, the efficiency of the cell.**

Keywords-nanotechnology; porous silicon; biofuel cell

I. INTRODUCTION

Recent advances in micro and nanotechnologies allow the development of implantable, portable, and miniature devices for a broad range of applications, including biomedical fields. Powering implantable medical devices necessitates the development of lightweight, non-toxic and stable sources of energy with long life spans. In fact, the number of battery charging cycles in micro-energy harvesting methods is a major source of limitation [1]. Several micro-energy harvesting sources have been already identified in previous research, namely, low and high frequency electromagnetic Radio Frequency (RF) signal harvesting, conversion of vibration into energy, thermal and pressure gradients energy harvesting in addition to the latest attempts towards organic energy generation directly within the human body using fuel cells [2, 3].

Harvesting energy using ambient vibration has been the focus of various projects [4-6]. Devices made for this purpose are mechanically modeled with a base excitation of an elastically mounted seismic mass moving past a coil. Optimal architecture for maximal power generation under different operating conditions has also been shown [7]. Various applications of this principle have manifested in systems integrated in footwear to harvest energy from walking [8], while in other designs piezoelectric and electromagnetic generators convert pressure variations into electricity [9]. The power generated using these methods ranges from tens to hundreds of milliwatts [3, 6, 7]. On the other hand, several studies have focused on energy harvesting from low frequency vibrations [6, 10]. This concept was made viable by creating a generator that converts low-frequency environmental vibrations to a higher frequency by employing the frequency up conversion technique [11, 12]. One major limitation of this technology is encountered with patients that are not able to perform any physical activities in order to power the generator and, hence, produce the necessary charging current.

Energy harvesting using RF inductive coupling is a very promising technology, particularly in the presence of such a wide variety of RF signals in our everyday environment. Additionally, this technology can also be used to send data back to a base station, thus creating a two-way link. The system consists of a power generating circuit linked to a receiving antenna in order to capture the RF signal and convert it to a DC voltage [13]. The main challenge in this technology is in the receiver's capacity to read various frequencies, as well as the use of efficient power rectifiers. Several interesting studies have reported either the use of multiple energy harvesting antennas in one area [14], which has shown that an increase of 83% in area results in 300% increase in power, or the design of a high efficiency, ultra-low voltage active rectifiers [15].

This article covers the use of porous silicon scaffolds for biofuel cells. The next section presents and compares different types of biofuel cells. Section III introduces porous silicon technology. Section IV discusses existing porous silicon fabrication techniques. Section V details the fabrication process of the porous silicon scaffolds using XeF_2.

II. BIOFUEL CELLS

The first enzyme based glucose/O_2 fuel cell to generate electricity was introduced in 1964 by Yahiro et al., aiming at using this concept to power an artificial heart [16]. While the field of fuel cell research has flourished in various industrial and environmental arenas, biomedical applications started making use of the technology only after 2001, with recent successes in micro fuel cell technology [17-19]. The two most dominant classifications of fuel cells are enzymatic, illustrated in Fig. 1, and microbial, based on the catalyst used to oxidize or reduce the fuel used in the design [20]. While microbial catalysts offer more longevity to the fuel cell, microbial fuel cells require a barrier between the cathode and the anode and between the fuel cell and its surrounding environment [21]. Such a design increases its size and decreases the current density since the fuel cell lacks direct contact with the fuel. Most importantly, when it comes to the use of microbial fuel cell for implantable devices, long term infections, thrombosis and other types of complications raise serious concerns [22, 23]. Therefore, it is natural that the use

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of microbial fuel cells was limited to few studies, one of them suggesting its use within the intestinal environment inside the transverse colon [24]. On the other hand, enzymatic fuel cells have lower stability and shorter lifespan because the longevity of enzymes is in the range of 10 days [25]. This has driven research in enzymatic fuel cells towards short term uses such as glucose sensors, post-op temperature measurement or as a power supply for pressure sensors indicating blockage of fluid flow in the nervous system [22]. However, since enzymes are selective in nature, the design of enzymatic fuel cells can be made into microscopic sizes without the need for a separating membrane to regulate the flow of the fluid and enzymes used in its design, thus achieving higher power densities due to the direct contact between the probes and the fuel [25]. Continuous attempts to increase the lifetime of the enzymes exist using immobilization techniques or using magnetic iron nanoparticles that shield the enzymes from getting oxidized or self-digested [26].

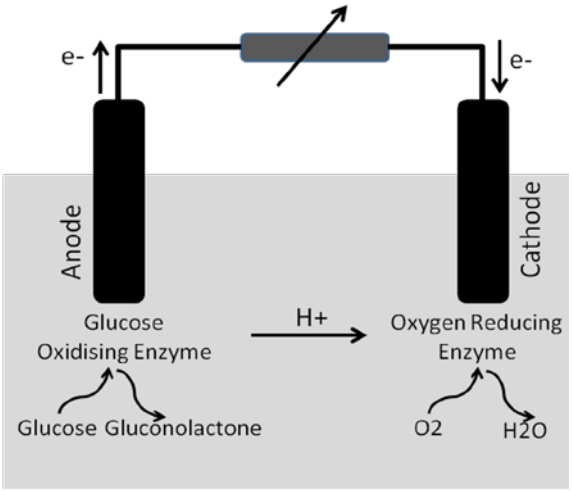

Figure 1: Illustration of an enzymatic biofuel cell using Glucose and Oxygen.

Another important factor in the design of the fuel cell is the target fuel. Although most implantable fuel cell studies have focused so far on the use of blood stream glucose, some studies have considered other alternatives such as the use of white blood cells based on their ability to generate electron current across their cellular membrane [27-29].

Most importantly, the complex environment inside the human body, such as the amount of glucose and oxygen available in addition to the neo-vascular build up that can hinder the exposure of the fuel cell to body fluids, represent important obstacles that any fuel cell design have to overcome in order for it to become a viable one [28]. Based on the first in-vivo study conducted by Cinquin et al., an enzymatic fuel cell was built by adjusting the types of enzymes used in order to account for the specific HP concentration and the effect of urea presence on the fuel cell [30]. This was implanted inside the peritoneal cavity of a rat, and has proven to provide a stable power of more than 7.52 μW/mL for a period of 3 months [30].

Here, we are interested in increasing the efficiency of energy harvesting in enzymatic fuel cells by increasing the contact surface area between the harvesting probes and the surrounding fuel. This can be achieved by using a porous interface which provides a large surface to volume ratio. Doped porous silicon represents a good candidate due to the fact that it combines both biocompatibility and electrical conductivity [31, 32].

III. POROUS SILCION TECHNOLOGY

Implantable biomedical devices built from bulk silicon have been available for biosensing and actuating applications for several years. However, this form of silicon is not biocompatible and so far this has prevented its use in vivo. Bulk silicon-based devices need coating or packaging in a biocompatible material, if they are to be used in and linked to living tissues [31, 32]. The majority of today's medical devices are coated with materials such as Polyvinylchloride (PVC), polypropylene, polycarbonate, fluorinated plastics and stainless steel. These materials are tolerated by the human body and are described as bioinert. An effective biomaterial, however, must bond to living tissue and is known as bioactive.

Nanostructured porous silicon (PS), whose particular texture can be described as a network of pores interconnected by solid nanocrystalline silicon, has properties that make it a very promising bioactive biomaterial [33, 34], in particular for devices that need to be linked to the biological system such as implantable devices [35]. Porous silicon material is useful and attractive for a wide variety of applications to develop biological sensors [35-37] and biomedical devices [38, 39]. This has significantly increased the interest in using porous silicon in biofuel cells.

An essential requirement for fabricating porous silicon in different applications is to have the ability to vary the size and configuration of the pores by choosing the appropriate fabrication parameters and conditions. For instance, for photonic bandgap filters, the pores are designed to the on the order of the wavelength of the light to retain and tune the optical reflectivity of the porous silicon [40, 41]. For biological sample filters, the pore size has to be large enough to allow the desired biomolecules to be filtered and cross through the pores freely [42].

IV. FABRICATION OF POROUS SILCON

Many previous reports have shown that porous silicon can be prepared through a galvanostatic, chemical, or photochemical etching procedures in the presence of hydrofluoric (HF) acid solutions or through stain etching [43-45]. Other methods such as pulsed anodic etching [46] and magnetic-field assisted anodization [47] were also employed for porous silicon preparation. In these techniques, the pore characteristics such as diameter, geometric shape and direction of the pores not only depend on the composition of the etching solution, but they also depend on temperature, current density, crystal orientation, dopant and doping density of the silicon substrate [43, 45, 48]. Moreover, porous silicon produced on large surface areas

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along with high porosity and/or thickness leads to a systematic cracking of the layer during the evaporation of the etching solvent. The origin of the cracking is the large capillary stress associated with evaporation from the pores. During the evaporation process, a pressure drop occurs across the gas/liquid interface that forms inside the pores [49].

In this paper, we employ a novel and simple fabrication technique which employs Xenon Difluoride (XeF_2)-based dry isotropic etching to selectively form porous silicon in bulk single crystal silicon wafers [50]. XeF_2 is plasma-less etching technique and is based on the reaction of the fluorine ions, which represents the main etchant, with the solid silicon to produce – at room temperature – the volatile gas SiF_4. In a XeF_2-based etching process, a standard hard baked layer of photoresist can serve as a masking layer. In addition to its etching process simplicity, XeF_2 has a high etch selectivity to silicon. It reacts readily with silicon, but is relatively inert to photoresistance, silicon dioxide, silicon nitride and aluminum, which allows this technique to be used in the presence of CMOS integrated circuits as a post processing step. This is not the case when HF-based etching is used, as this latter will etch or damage the circuitry without a very hard mask followed by complex post-processing to remove the mask.

V. METHODS

We utilized XeF_2 dry etching to create porous silicon surfaces on single crystalline silicon wafers. We used 3 inch diameter, 381± 20 μm thick <100> boron-doped (5–10 ohm cm) silicon wafers. The wafer was cut into 1.3 X 1.3 cm^2 that were then loaded in the XeF_2 etching chamber. The XeF_2 etching process does not depend on the silicon crystal orientation or its dopant content.

The fabrication process is achieved in a sequence of steps. First, undissociated gaseous XeF_2 is adsorbed onto the exposed areas of bulk silicon. The adsorbed gas is then dissociated into xenon and fluorine, after which the fluorine ions react with silicon to produce SiF_4 gas. Dissociation of the gas phase at room temperature leaves behind a porous silicon surface. In this process, increasing the etching process time increases the overall size of the pores and the thickness of the porous silicon film. The chemical reaction for the etching of silicon by XeF_2 is: $Si + 2XeF_2 \rightarrow SiF_4 + 2Xe$. As a dry etching technique, there is no post-fabrication drying step required, thus reducing the risk of damage to the newly formed porous surface.

XeF_2 leaves behind porous silicon surfaces on top of the remaining bulk silicon with porous silicon layer thickness on the order of several hundreds of nanometers (600 to 700 nm). The obtained porosity depends on the etching time. Fig. 2 shows a representative Scanning Electron Microscope image of porous silicon sample prepared using XeF_2. “”

VI. CONCLUSION AND FUTURE WORK

Nanostructured doped porous silicon is a promising material for Biofuel cells. It offers several advantages including the use of silicon in microelectronics, biocompatibility, and simplicity in tailoring porosity and conductivity. Future work will focus on testing porous silicon samples in complete enzymatic fuel cell setup.

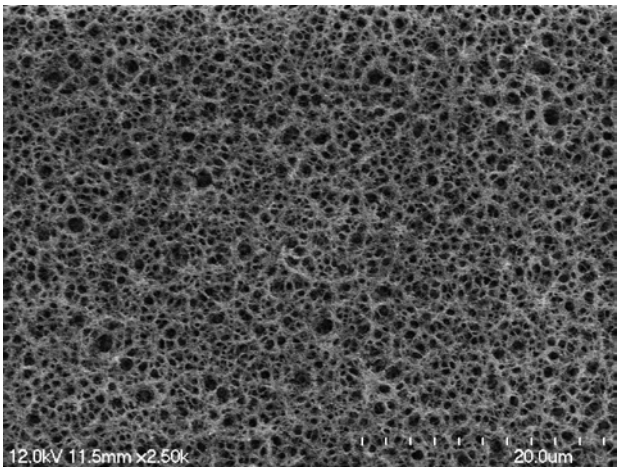

Figure 2: Scanning electron micrograph of a nanostructured porous silicon etched with XeF2.

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