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Short communication

Substantial power density from a discrete nano-scalable biofuel cell

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ABSTRACT

A direct electron transfer biofuel cell consisting of a pair of single walled carbon nanotubes and enzymes on a single plane is reported, which allows for extremely close spacing of electrodes. The discrete device has a measured power and current density of 18 mW/cm^2 and 90 mA/cm^2, respectively, into 200 TΩ. Analysis of measurements from up to 3 million devices in parallel shows that the performance will improve by at least 2 orders of magnitude at peak power.

1. Introduction

A well-established path for increasing the efficiency of fuel cells is to decrease the spacing between the cathode and anode, which effectively decreases the internal resistance [1–3]. For fuel cells that require membranes, the thickness of the membrane limits the cathode/anode spacing. There are enzymatic biofuel cell systems that do not require membranes [4–6]. Carbon nanotube (CNT) versions have been demonstrated in vivo [7,8]. However, for macroscale planar electrodes, the performance can decrease if the spacing between electrode plates is on the same order as the Nernst diffusion layer thickness (<100 μm) due to concentration gradients limiting fuel to the electrodes [1]. Our solution is a single-planar architecture of pillars of cathodes interdigitated with closely spaced anodes using nanofabrication techniques, which limits concentration gradients to those imposed by packaging.

CNTs functionalized with glucose oxidase (GOx) and laccase have been used as electrodes in glucose/oxygen fueled enzymatic biofuel cells without membranes or mediator molecules [5,9]. The direct electron transfer mechanism is not fully resolved [10]. A method to deposit individual vertically oriented single wall CNTs (SWCNT) at predefined locations on metal interconnects that are masked by an insulating film has been reported [11]. We report the fabrication of a single-planar biofuel cell using single SWCNTs functionalized with GOx and laccase as electrodes spaced 2 μm apart. Initial measurements indicate that this architecture is capable of achieving current and power densities greater than 1 A/cm^2 and 1 W/cm^2, respectively.

2. Experimental

2.1. Wafer processing and packaging

Two biofuel cell designs are shown in Fig. 1. The single-cell device (Fig. 1a and b) consists of individual cathode/anode pairs of functionalized SWCNTs. It has 14 windows to electrodes arranged as pairs spaced 2 μm apart. The mega-cell device consists of up to 3,020,800 pairs of biofuel cells wired in parallel using a spiral interconnect pattern (Fig. 1c, d, e) with 50 μm electrical leads that branch out into interdigitated anode and cathode micro-rails (see Fig. 1d) with nanoscale windows where nanotubes will be deposited (Fig. 1e). Chips were fabricated on silicon wafers with a 1 μm film of SiO_2. Ti electrodes were patterned using photolithography and e-beam evaporation. 75 nm of low stress SiN_x was then deposited and 30–40 nm holes were patterned and etched in this layer using e-beam lithography. Chips were mounted and wirebonded in a 14-pin dual inline package, which was subsequently capped with silicone while leaving the area around the devices exposed.

2.2. Carbon nanotube deposition

SWCNTs in an aqueous suspension were assembled on the Ti metal at the base of the nitride windows using electrophoresis deposition (EPD) [11]. For < 40 nm diameter windows that are 75 nm deep, there is a high probability that there will be only one nanotube deposited [11]. A SEM of an EPD result is shown in Fig. 1f. Micro-Raman

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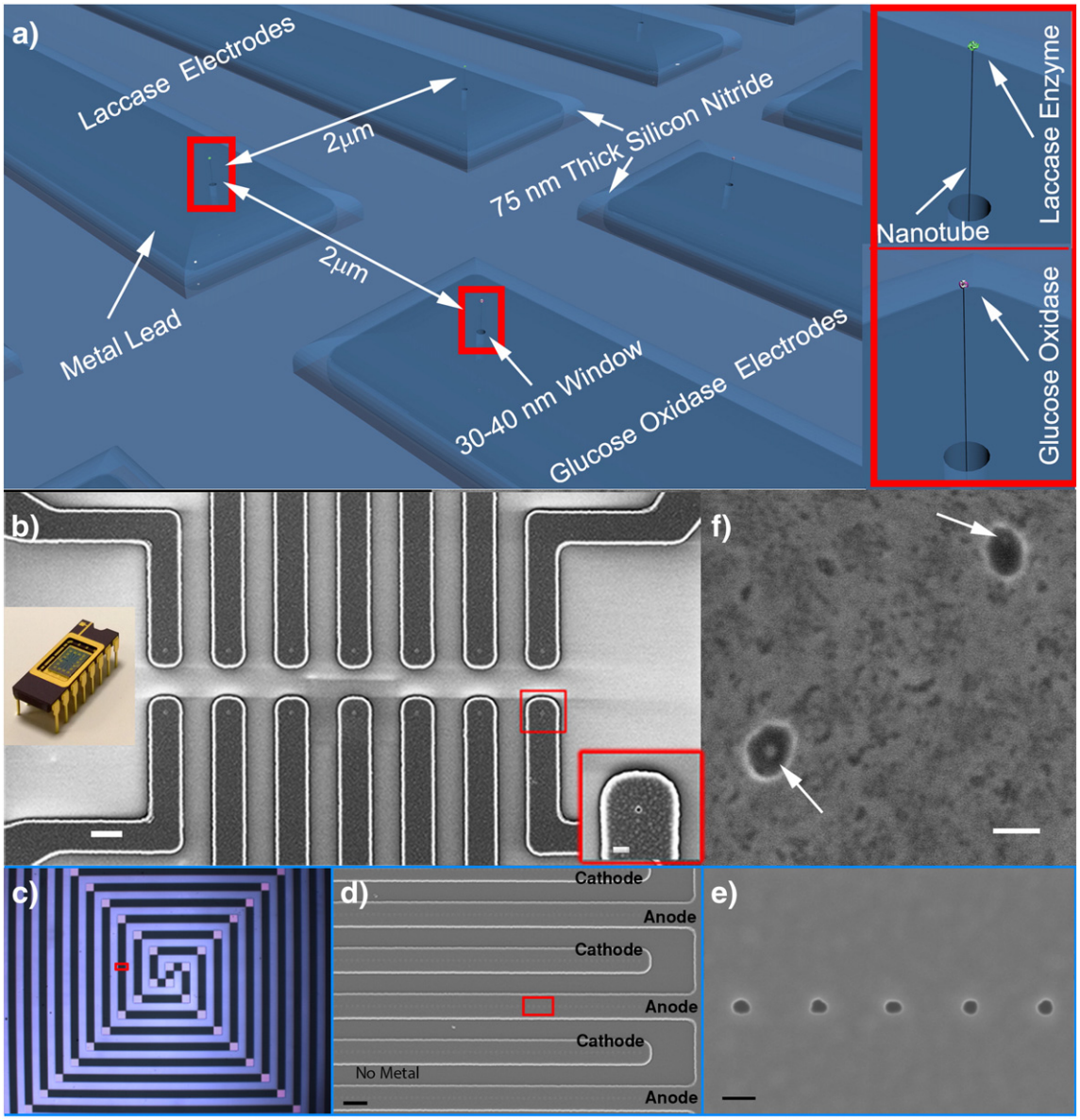

Fig. 1. a) Schematic of single-cell biofuel cell. Insert shows the zoomed view of the nanotubes and enzymes. b) SEM image of the electrodes with the 30–40 nm windows leading down to the metal (1 μm scale bar). Right insert shows a single electrode with the nanoscale window (200 nm scale bar). A packaged device is shown to the left. c) Optical image of the mega-cell architecture. d) SEM image of some of the microrails in the red box in c (1 μm scale bar). e) SEM image of a set of windows in a microrail highlighted by the red box in d (100 nm scale bar). f) SEM image of nanotubes deposited into the windows along a microrail (40 nm scale bar). Nanotubes are only present in the windows (see arrows).

spectroscopy was also used to verify that SWCNTs were deposited [5,11] along with IV measurements before and after EPD (reported separately) to establish that the SWCNTs are in electrical contact with the Ti at the base of the windows.

2.3. Enzyme attachment to carbon nanotubes

Electrochemical functionalization of the SWCNTs with enzymes was accomplished and monitored using cyclic voltammetry (CV) [5]. Half of the nanoscale windows (with Ti at the base) were used as working electrodes in a three-electrode cell with a Pt counter electrode and an Ag/AgCl reference electrode in a solution of laccase in phosphate buffer (1 mg/ml for single-cell and 10 mg/ml for mega-cell). CV scans were recorded at various speeds for several cycles. The samples were rinsed and the procedure repeated with the remaining Ti shorted together and used as the working electrode for GOx functionalization using the same concentration.

2.4. Biofuel cell measurements

The output voltage between pairs of GOx/laccase functionalized SWCNTs (single-cell) was measured after 30–40 μl drops of fuel (20 mM of glucose in pH 7 phosphate buffer) was placed on the chip. Voltage was measured at room temperature using a Keithley 6517A electrometer with an internal resistance of 200 TΩ, which (considering the device) is not an open circuit measurement. The mega-cell chips were immersed in a relatively large bath of the glucose/buffer solution for the measurements while air was bubbled into the solution. For the mega-cell, voltages were measured across loads ranging from 10 KΩ to 100 MΩ.

3. Results and discussion

Example CV plots are shown in Fig. 2 at 0.1 V/s. The separation between the cathodic and anodic peaks ($\Delta E > 0.8$ V) indicates that the