DEVELOPMENT OF SUSPENDED 2D CARBON NANOSTRUCTURES: NANOWIRES TO NANOMESHES

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ABSTRACT

We report on the development of monolithic suspended glassy carbon nanostructures inclusive of nanowires and nanomeshes fabricated using only two simple batch processes consisting of UV lithography and the polymer pyrolysis. Owing to the volume shrinkage during pyrolysis process, the micros-sized photoresist structures are converted to the nanoscale glassy carbon structures. The suspended glassy carbon structures can be patterned in various geometries such as mesh depending on the photomask patterns. The suspended glassy carbon nanostructures show good electrical and electrochemical behaviors, and perfect ohmic contact due to monolithic structure. The feasibility of the suspended glassy carbon nanostructures for sensing platforms was confirmed by electrochemical current characterization.

KEYWORDS

Glassy carbon, carbon-MEMS, suspended nanowire, suspended nanomeshes

INTRODUCTION

Distinct properties of various types of carbon allotropes ranging from graphene, carbon nanotube (CNT), diamond-like carbon (DLC), to glassy carbon have attracted research interests for the development of nanostructure devices. Among these carbon materials, the glassy carbon can be stressed because of its advantages inclusive of wide electrochemical stability window, excellent biocompatibility, thermal and chemical stability[1-4]; these good properties drove the development of solar cell systems, thin film transistors, batteries, optical memory device and electrochemical sensing platforms.

As compared with the other carbon materials, the glassy carbon can be pattered in various morphologies in accordance with the shapes of the polymeric precursors because the morphology and chain configuration of the polymer are maintained during the polymer pyrolysis. Typical polymer precursors for the glass carbon nanowire fabrication are poly furfuryl alcohol (PFA) [1] and photo-sensitive polymers [2-4]. Carbon nanowires could be pyrolyzed from of which pore size determined the nanowire size. Although nanoscale glassy carbon wires can be made easily, e.g. pyrolyzing PFA in a anodized aluminum oxide template, difficult positioning of glassy carbon nanowires at the desired sites of pre-existing structures for completing micro/nano scale devices and high contact resistance between the nanowire and the contact pads limit the extension of the nanowire applications. These limitations can be overcome by pyrolyizing pre-patterned micro/nano polymer structures in desired shapes patterned using e-beam lithography[2], electo-spining[3] and photolithography[4]. This simple batch process is called carbon-MEMS. The pyrolysis process induces a dramatic volume reduction up to 90% so that microscale photoresist structures can be converted into nanoscale carbon structures; this dramatic volume shrinkage enables conventional photolithography to batch-fabricate carbon nanostructures. And the carbon structures resemble the polymer precursor structure so that the nanowires can be connected to microstructure with perfect ohmic contact.

In this study, we present novel monolithic suspended glassy carbon nanostructures including nanowire and nanomeshes that were patterned using photolithography and polymer pyrolysis. The suspended morphology of the carbon nanostructures prevents detrimental effects from the substrates such as surface contamination, temperature variance, and stagnant layer. It also improves the mass transfer of target molecules to the suspended carbon nanostructures resulting in enhanced sensitivity in sensor applications. Owing to the simple and accurate alignment in photolithography process, it is easier to position and pattern variety of carbon nanostructures in a designed manner compared to electro-spinning that can also fabricate suspended carbon nanowires[3].

EXPERIMENTAL

Fabrication

Figure 1 shows the fabrication steps of suspended glassy carbon nanostructure. First, an insulation layer of SiO_2 was deposited on a 6-inch silicon wafer. Then, a 30 μm thick SU-8 photoresist layer was spin-coated on the SiO_2/Si substrate. An UV exposure onto the thick photoresist was executed to create tall contact pads supporting suspended photoresist microscale structures. And single wires or mesh patterns were printed on the shallow region of the photoresist using low energy UV exposure. The suspended patterns were released in a development process. Finally the monolithic polymer structures inclusive of the suspended micropatterns and the polymer contact pads were converted into a monolithic carbon structures including suspended carbon nanostructures in the polymer pyrolysis process.

The polymer pyrolysis process consists of a pre-baking step for effective outgassing and major volume reduction, and a carbonization step for making solid glassy carbon materials in vacuum condition.

Characterization

To characterize the conductivity-temperature relationship of the suspended carbon nanowire, the resistance of the suspended single carbon wire was measured while varying the temperature.

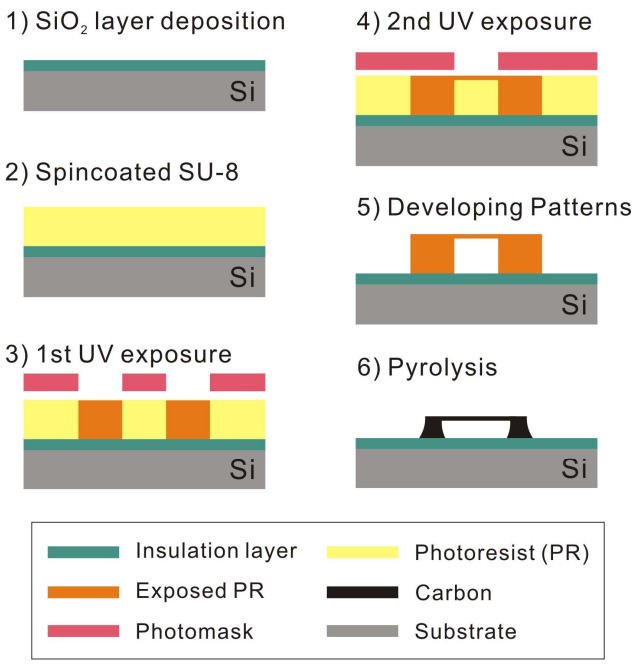

Figure 1: Fabrication steps of a suspended carbon nanostructure.

Electrochemical behavior of the suspended carbon nanowire was characterized using cyclic voltammetry (CV) and simulation. In the both studies, 10 mM $K_4Fe(CN)_6$ in 0.5 M KCl solution was used. The applied voltage was scanned from 0.0 V to 0.6 V at a scan rate of 0.05 V/s against a pseudo Ag/AgCl reference electrode and a Pt wire was used as a counter electrode. The simulation calculating diffusion-limited current was performed for a suspended structure and a surface-bound structure to demonstrate the advantage of suspended morphology.

The microstructure and composition of the pyrolyzed structure were studied using high resolution transmission electron microscopy (HRTEM) and Raman spectroscopy.

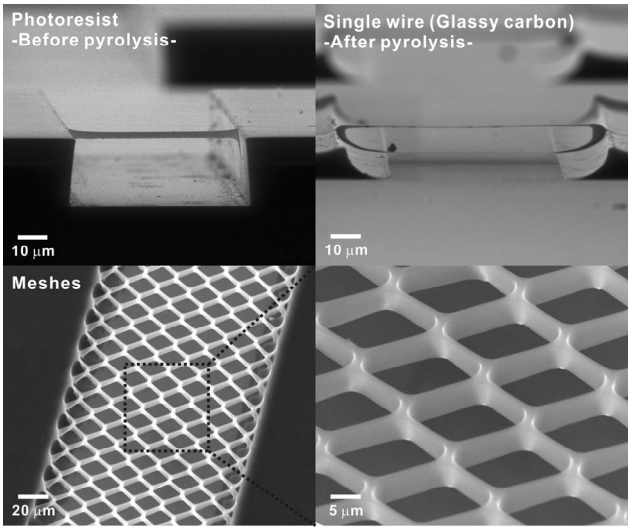

Figure 2: SEM images of suspend structures; (Top-left) suspended photoresist structure (width: 1 μm, thickness: 2.2 μm, length: 60 μm), (Top-right) suspended glassy carbon structure (width: 260 nm, thickness: 440 nm, length: 88.8 μm), (Bottom) high aspect ratio nanomesh structure (width: 310 nm, thickness: 2.3 μm)

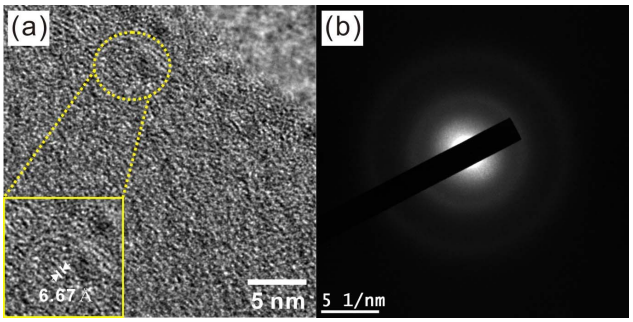

Figure 3: (a) HRTEM images and (b) diffraction patterns of a suspended glassy carbon single nanowire.

RESULTS

Figure 2 shows the SEM images of a suspended single polymer microscale wire and a corresponding suspended glassy carbon nanowire. In the case of the polymer microstructure, the width of the suspended wire is determined by the size of the photomask but the wire thickness depends on the dose of the UV exposure and the width of the photomask pattern. The smallest polymer microscale wire of 1 μm width and 2.2 μm thickness was converted into a 260 nm wide and 440 nm thick in the carbon nanowire. During the pyrolysis process, the tall polymer posts also shrink and thus the suspended polymer wire are pulled by the post; this render the suspended carbon nanowire not droop down to the substrate during the polymer pyrolysis.

Figure 3 shows a HRTEM image of the suspended single glassy carbon nanostructure and the corresponding diffraction pattern image. Suspended glassy carbon nanostructure is mainly disordered but partially some short -range crystal structure is also found in the nanowire. This microstructure of the nanowire was also confirmed in ring patterns of the diffraction pattern image of the wire.

Composition change of the SU-8 photoresist after the polymer pyrolysis was measured using Raman spectroscopy as shown in Figure 4. The raman spectrum of a polymer precursor structure does not show any clear peak found in carbon materials but that of a glassy carbon pattern shows D-band and G-band. The D-band indicated disordered carbon materials at 1350 cm^{-1} and the G-band is representative of sp^2 hybridized graphitic materials at 1590 cm^{-1} [5]. This result of the raman spectrum also matches with the result from HRTEM.

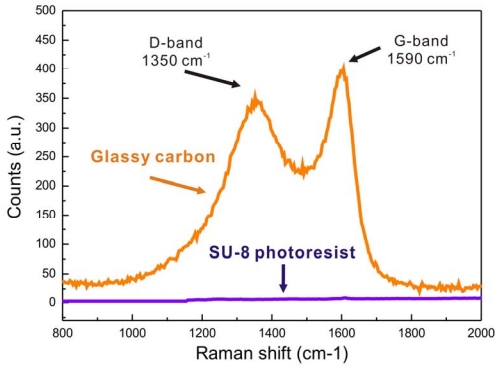

Figure 4: Raman spectrums of glassy carbon (orange line)

and SU-8 photoresist (violet line).

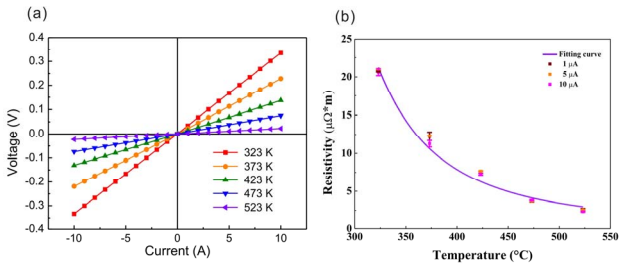

Figure 5: (a) Voltage versus current curve from suspended single nanowire in various temperature conditions, (b) Resistivity to temperature curve of the suspended carbon nanowire.

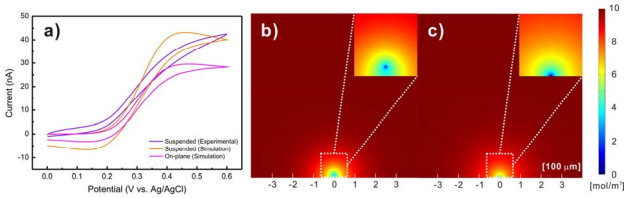

Figure 6: (a) Cyclic voltammograms of a single suspended carbon nanowire (orange line: simulation result from a suspended nanowire, pink line: simulation result from an on-plane structure, violet line: experimental results from a suspended nanowire). Simulated concentration profiles from (b) a suspended structure and (c) an on-plane structure.

The slopes of the lines in Figure 5 (a) indicate the resistance of the suspended single carbon nanowire at various temperature conditions. The resistance of the nanowire is reduced in accordance with temperature increase. This semiconductor-like electrical behavior is more clearly demonstrated in the curve shown in Figure 5 (b).

The current from a single suspended carbon nanowire in CV reached to ~ 42.6 nA at 0.6 V as shown in Figure 6 (a). To confirm the experimental result, we simulated diffusion-limited currents of the suspended nanowire and an on-plane nanowire of which surface area is equal to that of the suspended nanowire. The simulated current of the suspended nanostructure was 40.1 nA. This result confirms that the suspended carbon nanowire is reactive enough to collect electrons from redox species as good as other conductive materials. The on-plane type nanostructure shows less efficient mass transfer than the suspended nanowire resulting in low current of 28.3 nA.

CONCLUSION

We successfully fabricated monolithic suspended carbon nanostructure only using conventional batch microfabrication technologies. Especially, this simple fabrication process enables to pattern complex suspended morphologies in a designed manner with high reproducibility. Owing to their good electrochemical behavior and enhanced mass transfer in addition to the advantages of the suspended morphology, the suspended carbon nanostructures are expected to find applications in variety of sensors inclusive of gas sensor and biosensors.

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