



An optimized process for fabrication of high-aspect-ratio photoresist-derived carbon microelectrode array on silicon substrate

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ARTICLE INFO

Article history:

Received 15 December 2008

Received in revised form 1 September 2009

Accepted 11 September 2009

Available online 20 September 2009

Keywords:

Glassy carbon

High-aspect-ratio

Microelectrode array

Pyrolysis

Micromechanical interlocking

ABSTRACT

An optimized process was developed for fabrication of high-aspect-ratio photoresist-derived carbon microelectrode array on silicon substrate. This process consisted of conventional photolithography, three-step linear pyrolyzing process and micromechanical interlocking. Comparing with previous two-step pyrolysis, three-step linear pyrolysis process can better preserve the geometry of microstructure during pyrolysis, and micromechanical interlocking was introduced to improve bonding strength between carbon microstructure and substrate. As a result, it can be achieved that high-aspect-ratio carbon microelectrode array remained upright and robustly with substrate. The experimental results confirmed that the optimized process is very effective, and the technology will be helpful for integration of 3-dimensional carbon-based devices in the fields of bioMEMS and electrochemical analysis.

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1. Introduction

Elemental carbon exists in a variety of families such as diamond, graphite, C₆₀, carbon nanotubes, carbon nanofibers, and glassy carbon (GC). Among them, GC shows a very wide electrochemical stability window, excellent biocompatibility, chemical inertness, good thermal conductivity, and mechanical stability [1]. Thermal treatment of organic materials has become a valuable method for obtaining various kinds of carbons. For example, when organic materials were exposed to high temperatures from 600–1000 °C in an inert atmosphere, the materials can be converted into GC [2,3]. Structural and functional GC will have a large number of highly specialized applications in biological, chemical and electronic devices. Recently, it was found that electrochemical reactions on pyrolyzed photoresist exhibit reaction kinetics comparable to those on glassy carbon, and different temperature treatments will also result in different electrical resistivities and mechanical properties of glass-like carbon [4–6]. The use of photoresists as the starting material for microfabrication of various glass-like carbon structures has many advantages. Firstly, photoresists can be finely patterned by lithography techniques and hence a wide variety of repeatable shapes are possible; Secondly, photoresists constitute perhaps some of the most controlled chemicals available today. Moreover, photoresists have a very wide processing window. However, most pyrolyzed photoresist structures

described in the literature were derived from positive photoresist and have very low aspect-ratio [4,5,7,8].

The fabrication of high-aspect-ratio is very challenging because it is very difficult to design a kind of thick positive tone photoresist chemistry with the necessary transparency and at the same time maintain reasonable exposure doses and good control of sidewall angles during photolithography process. Until recently, a proposed method called “C-MEMS technology” was explored by Madou et al. to fabricate high-aspect-ratio carbon micro/nanostructures, which combines mature photolithography technology with pyrolyzing process of photoresist micro-patterning [9]. It was based on deep UV resist technology with high transparency SU-8 series negative tone photoresist and it was reported that high-aspect-ratio carbon structures could be easily fabricated such as carbon electrodes, suspended carbon wires, bridges, plates and networks. The fabricated microstructures have particular importance in bioMEMS applications including manipulation of biological particles, glucose sensors and microbatteries [10–12].

However, at present, not much work has been done in the area of fabrication of high-aspect-ratio carbon microstructures, issues such as stress-induced peeling off and delamination of carbon microstructure from substrates, high-aspect-ratio induced microelectrode deformation and self-organization of electrodes will prohibit the wide applications of the technology [13,14]. Therefore, it is of great importance to further study and optimize the fabrication process of high-aspect-ratio carbon microstructures.

Our following research emphasized on the fabrication of high-aspect-ratio microelectrode array on silicon substrate through

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improved method. Previously, micromechanical interlocking was studied for silicon-polymer [15] and glass-polymer [16] to improve heterogeneous bonding strength, and great bonding improvement was demonstrated. In this work, micromechanical interlocking approach was also applied in the fabrication of GC microelectrode array to improve bonding strength between carbon microstructure and silicon substrate. Furthermore, the pyrolysis process was also studied with SU-8 photoresist for excellent chemical and electrical material performance and integrity of high-aspect-ratio microelectrode array. The research started with our extreme effects for further fabrication of sensing application-oriented micro/nanostructures and will explore a possible route for scalable integration of carbon microstructures with silicon based technology.

2. Experimental details

UV photolithography process requires UV transparent photoresist and thick-film coating requires the photoresist with high UV transparency and viscosity. SU-8 photoresist from MicroChem (Newton, MA, USA) shows very high UV transparency, which makes it ideally suited for imaging near vertical sidewalls in very thick films. In this study, SU-8 2100 was selected as polymer precursor to glass-like carbon and silicon wafer with a layer of oxidized thickness of 300 nm was selected as supporting substrate. The overall process for fabrication of carbon microelectrode array mainly comprises substrate pretreatment, photolithography and pyrolyzing process as illustrated in Fig. 1. The following will present the overall experimental process in detail.

2.1. Substrate pretreatment for fabrication of micromechanical interlocking structure

In the fabricating process shown in Fig. 1 (a), the substrate was first treated with a procedure to generate micromechanical interlocking for photoresist-derived microstructure. The mechanism of a typical interlocking structure is illustrated by the three steps shown Fig. 2 (a), (b) and (c). Fig. 2 (a) shows the process for defining the opening of silicon dioxide aimed to form overhang profile for micromechanical interlocking. After cleaned for 15 min in a solution of H_2SO_4 and H_2O_2 mixed with

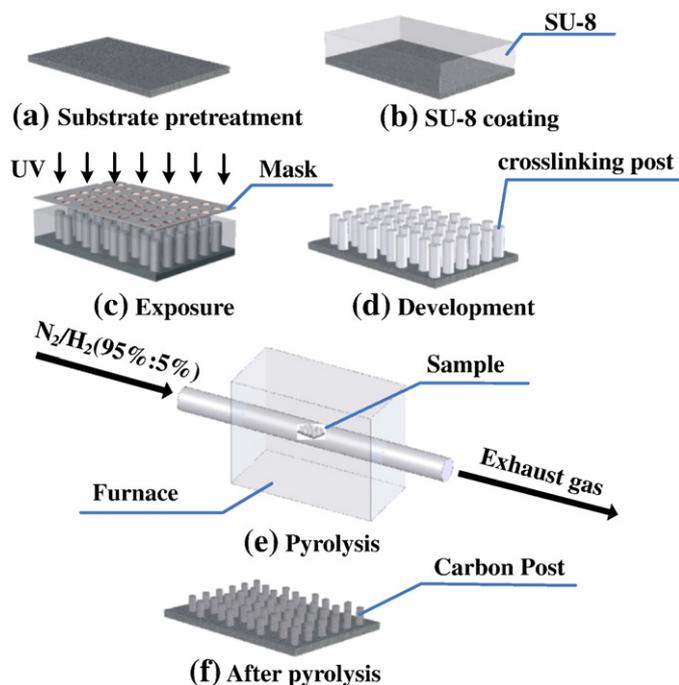


Fig. 1. Schematic of overall fabrication process.

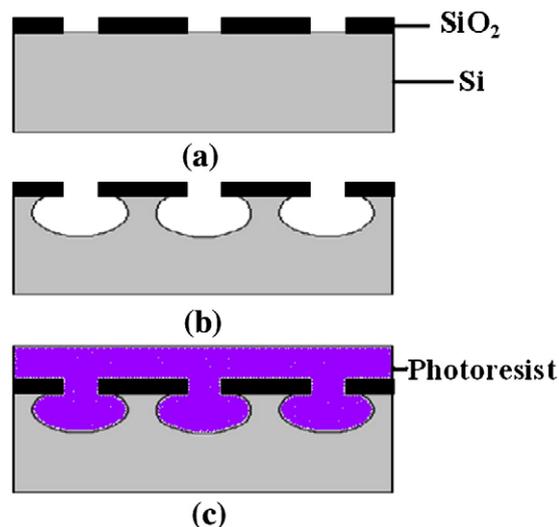


Fig. 2. Schematic of micromechanical interlocking process, (a) defining the opening, (b) forming pits, (c) filling SU-8 photoresist.

volume ratio of 2:1 at 150 °C, the substrate was baked for 15 min in a 200 °C convection oven. Then, positive photoresist BP218 was spin-coated and baked onto the substrate for pattern transfer with a mask. The mask was designed with opening diameter of 25 μm and center-to-center distance of 130 μm . Exposure to define the openings on the underlying silicon dioxide was carried out in a Karl Suss MA6 contact aligner. The mask pattern transferring to underlying silicon dioxide was achieved by reactive ion etching (RIE). After the mask pattern was transferred onto the substrate surface, RIE was then applied to achieve isotropic pits underlying the silicon dioxide film. Fig. 2 (b) schematically shows the formation of isotropic pits in silicon substrate with RIE, where RIE etching was carried out for around 6 min with SF_6 flow rate of 20 ml/min, radio frequency power of 20 W and air pressure of 8.00 Pa. Fig. 2 (c) shows the process for filling SU-8 photoresist into the pits in silicon substrate. A two-stage spin process was employed, where the first stage was to ensure uniform spreading and pit filling and the second to achieve the desired film thickness at higher speed. Comparing with the smooth substrate surfaces, adhesion will be improved due to the new source of adhesion by mechanical keying of the structural materials into the irregularities of the substrate surfaces [15]. The irregularities of the substrate surface could be further optimized through the design of interlocking structure.

2.2. UV photolithography process for SU-8 photoresist

The photolithography process used for SU-8 photoresist micro-patterning includes spin coating as illustrated in Fig. 1 (b), soft bake, near UV exposure as illustrated in Fig. 1 (c), post bake, and development as shown in Fig. 1 (d).

For a typical process of coating a 250 μm thick SU-8 film, it involves spinning using a Laurell photoresist spinner at approximately 500 rpm for about 15 s then at approximately 1250 rpm for about 30 s, followed by baking for about 7 min at 65 °C and another baking for about 55 min in a 90 °C oven. Then SU-8 film was ready for exposure with a mask designed with the open diameter of 50 μm and center-to-center distance of 130 μm . For the photolithographic process, near UV exposure of the photoresist was performed in a Karl Suss MA6 contact aligner. Exposure using broadband mercury lamp (calibrated with 6 mW/cm² illumination at 365 nm and 10 mW/cm² illumination at 405 nm) was carried out at a power setting of 4.1 mW for about 40 s. The post bake was then carried out for about 5 min at 65 °C and followed by another 20 min at 95 °C. And after every baking step, the sample should be left to

cool down for about 10 min. Development was then carried out in a SU-8 developer, where the SU-8 developer was from MicroChem (NANO™ SU-8 Developer). At last, deionized water was used to rinse the sample and then it was dried, and the microelectrode array would be obtained as shown in Fig. 1 (f). The summary of critical parameters for the process was also presented in Table 1.

2.3. Three-step linear pyrolysis process

The following pyrolysis process was implemented in a high temperature quartz-tube furnace under inert atmosphere as shown in Fig. 1 (e). The inert gas can be nitrogen or forming gas (95% N₂, 5% H₂) atmosphere with flow rate of 2000 sccm. After pyrolysis, the final carbon microelectrode array was obtained as shown in Fig. 1 (f).

The electrical properties and chemical composition of carbon that depend on the pyrolysis process, different temperature treatments and temperature ramp rate will affect the final properties of carbon microelectrodes, in the meanwhile, affecting the repeatability and the stability of the process. For example, too high temperature ramping rate may generate very high thermal stress between the carbon electrode and the substrate.

Due to the fact that glass transition temperature (T_g) of the photoresist rises as it is heated, the temperature ramp rate should be controlled such that the temperature in the oven should always be lower than T_g of the photoresist/carbon to preserve the geometry during pyrolysis. This was done by slowly heating the sample at a ramp rate of 10 °C/min, and a three-step pyrolyzing process was developed based on pyrolyzing mechanism for typical adhesive resin such as SU-8 2100. The three-step comes from the fact that three critical controlling temperatures (300 °C, 600 °C and 1000 °C) during temperature ramping as shown in Fig. 3 indicated as B to C, D to E, and F to G were set up as controlling periods for each temperature.

3. Results and discussions

The carbon microstructures were fabricated through above mentioned process and following are the results of fabricated microstructures and their characterizations for composition, electrical and mechanical properties. In this study, the microstructures were characterized by scanning electromicroscopy (SEM) in the Testing Center of Huazhong University of Science and Technology, the model of SEM is Quanta 200 made in Holland and the applied voltage was 20 kV for all SEM images. Electrical measurements of samples were carried out with a 4-probe testing instrument (RTS-8, made in China), and chemical characterizations were carried out with energy spectrometer (Genesis, made by EDAX Inc. in USA).

3.1. The formation of carbon microstructures

For comparing purpose, some carbon microstructures were also fabricated without interlocking structure. The fabrication of low aspect-ratio microstructure was easier as shown in Fig. 4, where photoresist thickness was 50 μm with diameter of 200 μm, and the obtained carbon microstructure thickness is around 20 μm with diameter of around

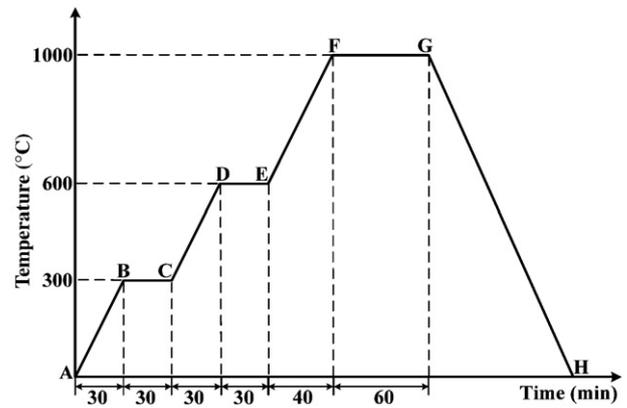


Fig. 3. Three-step linear pyrolyzing process.

130 μm. Since the process relies on mature photolithographic process of thin photoresist films, the bonding between the carbon microstructure and the substrate remains stable. While during the fabrication of high-aspect-ratio carbon microstructures, delaminating, deformation, collapse or self-organization may happen, as shown in Fig. 5 (a) and (b), where photoresist thickness is 250 μm with diameter of 50 μm. The mechanisms that might account for these results include the duration and intensity of UV light that caused inefficient exposure during thick-film based lithographic process, out-gassing during heat-treatment that caused the formation of micro-cracks in electrodes, and SU-8 adhesion to the substrate that resulted in tensile stress in the carbon electrodes near the interface.

In general, these issues can be solved when micromechanical interlocking is applied and 3-step linear pyrolysis procedure is followed. The micromechanical interlocking pits fabricated with the process conditions mentioned earlier showed that the pit opening was from 25–28 μm, the vertical depth varied from 4–8 μm, while the sidewall overhanging was not very obvious, which might be due to the process conditions. For comparison purpose, the process conditions to fabricate the interlocking microstructure remained consistent throughout the study.

As shown in Fig. 6 (a) and (b) with microstructures before and after pyrolysis respectively, the microstructures remain upright before and after the pyrolysis step except shrinkage. The SU-8 post has the height of 250 μm with diameter of 50 μm, while after pyrolysis, carbon post has the height of 100 μm with diameter of 33 μm. It is shown that the height-to-diameter aspect ratios before and after pyrolysis are around 5:1 and 3:1 respectively. The vertical shrinkage rate is much larger than that of lateral direction. Furthermore, suspended ribbon carbon microstructure can also be fabricated following the same photolithographic process

Table 1
Summary of critical process parameters.

Substrate type	Silicon substrate 2 × 2 cm
Photoresist	SU-8 2100, viscosity 45 × 10 ³ cSt
Spin process	2-step, 500 rpm (15 s) → 1250 rpm (30 s)
UV source	6 mW/cm ² at 365 nm, 10 mW/cm ² at 405 nm
Soft bake	65 °C (7 min) → 90 °C (55 min)
Exposure process	40 s (4.1 mW)
Post exposure bake	65 °C (5 min) → 95 °C (20 min)
Photoresist thickness	250 μm

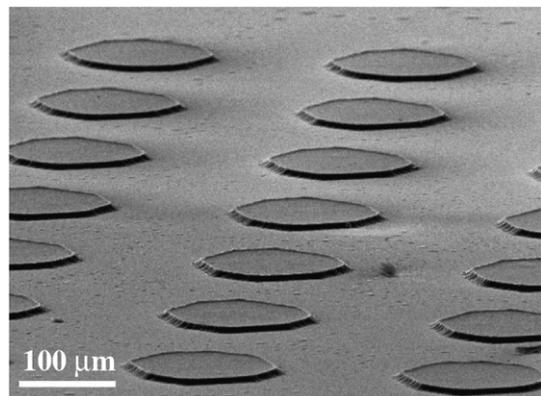


Fig. 4. SEM photo of thin microelectrode array fabricated from negative photoresist.

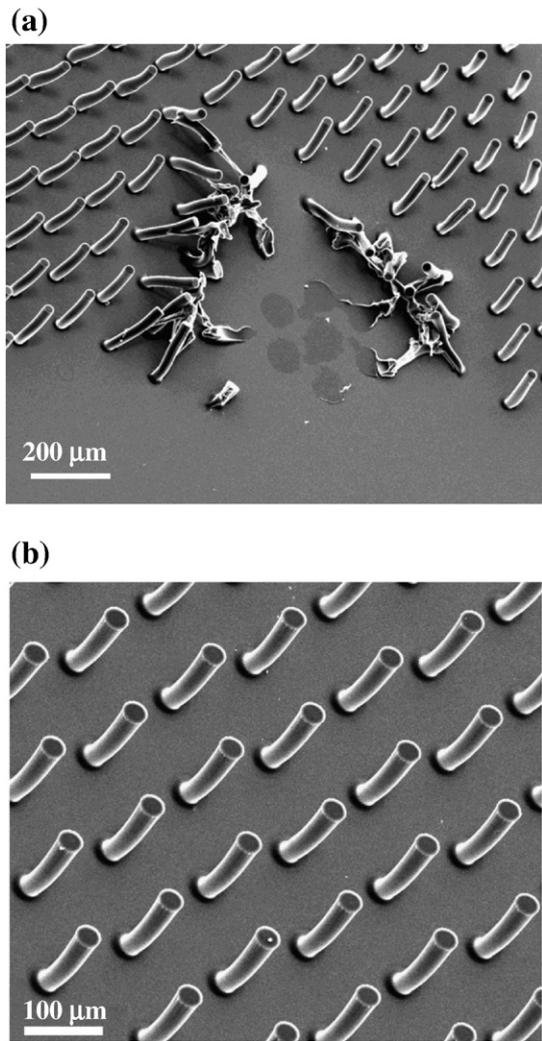


Fig. 5. SEM photo of issues during conventional fabrication of high-aspect-ratio carbon microelectrode array, (a) collapse, delamination and self-organization of microelectrodes, and (b) deformation of microelectrodes.

with overexposure. As shown in Fig. 7 (a) and (b) with suspended ribbon microelectrode arrays before and after pyrolysis respectively, the microstructures also remain upright before and after pyrolysis. The overexposure was done with prolonged exposure duration of 80 s which resulted in suspended ribbon structure with minimal carbon ribbon width of around 1 μm.

3.2. Electrical performance of microelectrode array

Following the fabricating process proposed above, the final pyrolyzing temperature is very critical for the formation of carbon microstructure. Therefore, the characterization of the electrical performance versus the final pyrolyzing temperature was conducted. In this study, the sheet resistance of carbon film sample was characterized for each process with the final pyrolyzing temperature set to 800 °C, 850 °C, 900 °C, 950 °C, and 1000 °C, respectively. For each sample, the testing of the sheet resistances was conducted with 4-point resistive probe through standard procedure, and each sample was tested 10 times on different positions of the sample surface. As plotted in Fig. 8, the sheet resistance decreases with the increase of pyrolyzing temperature for both resist thickness of 10 μm and 20 μm with diameter of 150 μm. The resistivity of carbon film is around $1.56 \times 10^{-5} \Omega\text{m}$ at the pyrolyzing

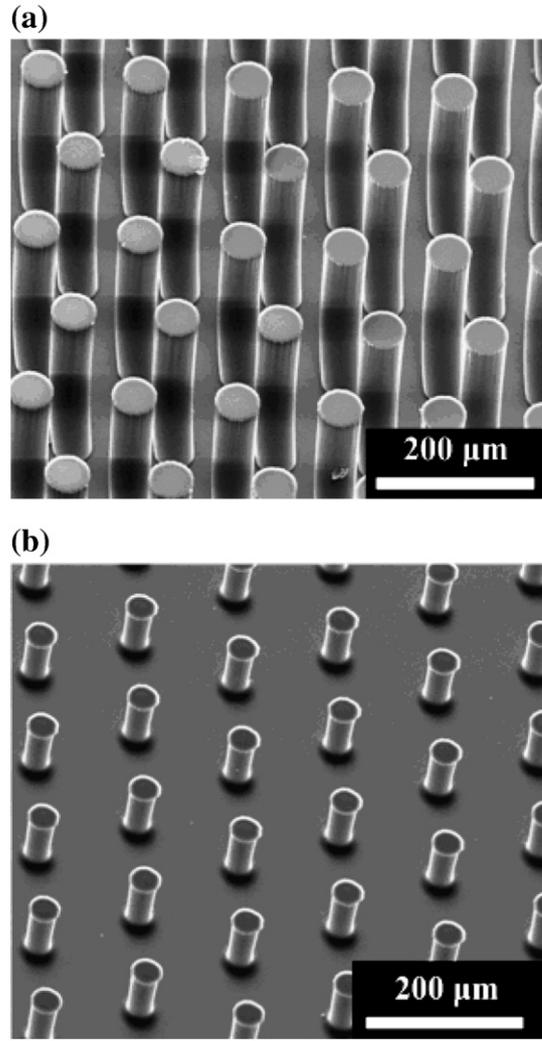


Fig. 6. SEM photo of high-aspect-ratio microelectrode array before and after pyrolysis.

temperature of 1000 °C, and the sheet resistance of formed carbon film is typically 2.8 Ω/square at the pyrolyzing temperature of 1000 °C.

3.3. Chemical composition of microelectrode array

The composition characterization of photoresist-derived carbon microstructure was carried out by microanalysis instruments from EDAX Inc. USA, where the composition of carbon and oxygen element could be obtained simultaneously. In this study, 10 samples for each process condition were prepared and characterized, where the final pyrolyzing temperature was set to 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C, respectively. The size of each sample was tailored from one carbon post to fit in the sample room for testing, and the output results of carbon and oxygen element were in both weight percent (wt.%) and atom percent (at.%) for each test under applied voltage of 20 kV. As shown in Fig. 9, the composition ratio of oxygen versus carbon element (O/C) was plotted with different final pyrolyzing temperatures. With the increase of final pyrolyzing temperature, the ratio decreases and tends to stabilize at 1000 °C. At 1000 °C, the atom and weight composition of carbon element in the sample are around 93.6% and 91.67%, respectively.

3.4. Mechanical integrity of microelectrode array with silicon substrate

Soaking tests were conducted for the final carbon microelectrode array to check its mechanical integrity with silicon substrate. 40%

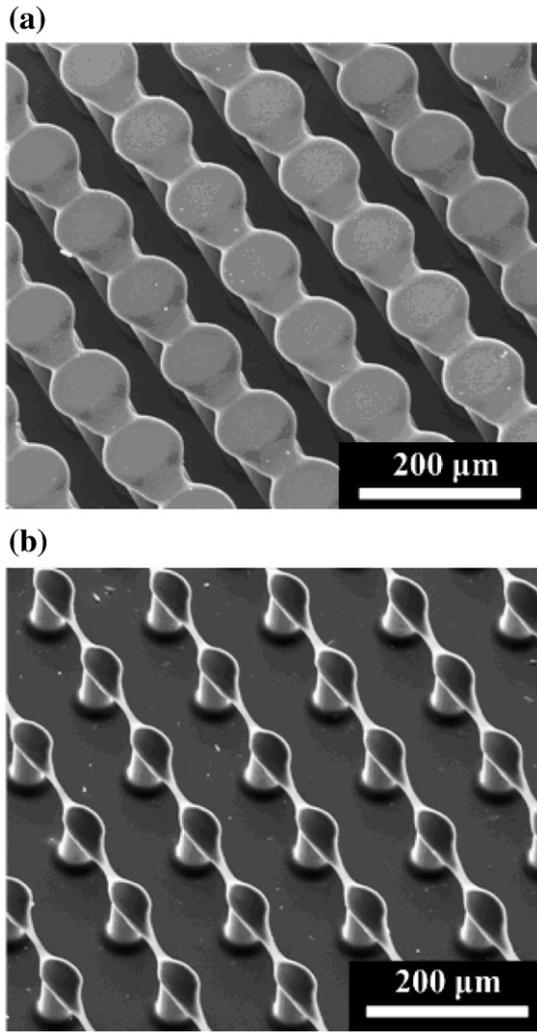


Fig. 7. SEM images of suspended ribbon microstructures, (a) SU-8 photoresist microstructure; (b) carbon microstructure after pyrolysis.

potassium hydroxide (KOH) solution was used for soaking of samples at 80 °C, the etching of which over silicon at the interface of carbon microstructure would produce H₂. With the increase of soaking time, the failure will be observed at the interface. Fig. 10 presents the time-to-failure (soaking duration) of samples fabricated with and without

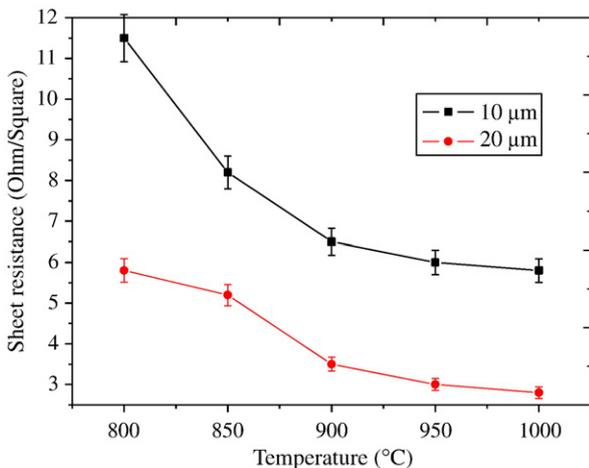


Fig. 8. Sheet resistance of photoresist-derived carbon film changes with pyrolyzing temperature.

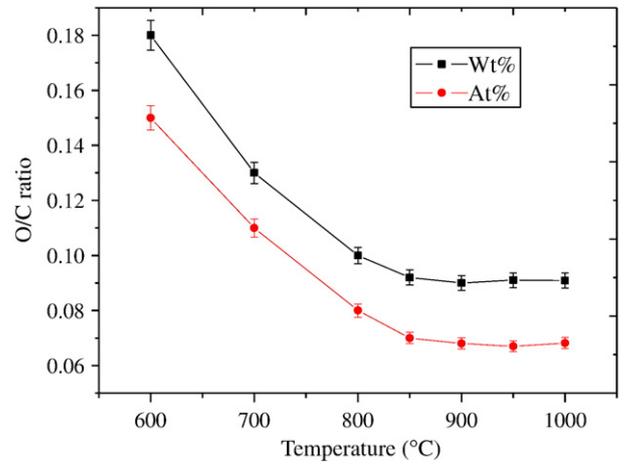


Fig. 9. The composition ratio of oxygen versus carbon element (O/C ratio) in the carbon film changes with final pyrolyzing temperature.

interlocking for different final pyrolyzing temperatures (set to 800 °C, 850 °C, 900 °C, 950 °C, and 1000 °C, respectively) under soaking in the KOH solution, where interlocking microstructures were fabricated following the procedure presented earlier in the step of substrate pretreatment, with the silicon surface oxide thickness of 300 nm, opening diameter of 25 μm and center-to-center distance of 130 μm. It showed that the resistance to etching of the KOH solution has been increased from less than 5 h to over 20h.

In general, the issues encountered previously with conventional process such as delaminating, deformation and collapse were well solved through the optimized process. Micromechanical interlocking improves bonding strength between the carbon microstructure and silicon substrate, and the process of implementing micromechanical interlocking approach can be further optimized to achieve better bonding by optimal design of interlocking microstructure and its fabrication process since pit depths and vertical profile varied as a function of the mask opening dimensions and etch process conditions, while three-step linear pyrolyzing process improves the formation of high-aspect-ratio microstructures in terms of repeatability of electrical performance and chemical composition.

4. Conclusions

The results in this work obtained with massive arrays on substrate were as large as 2 × 2 cm, and we have demonstrated that the process

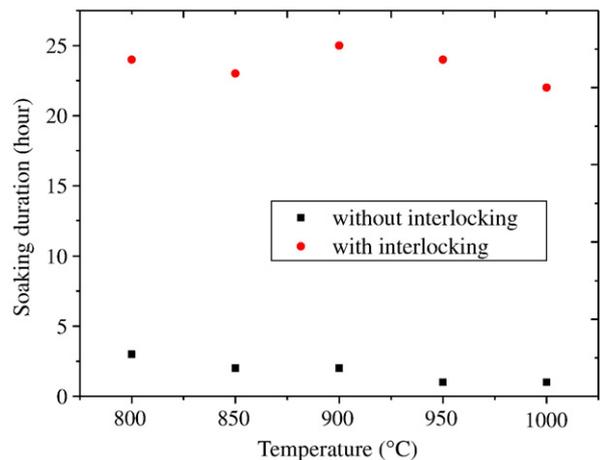


Fig. 10. Time-to-failure (soaking duration) of fabricated microstructures with and without interlocking for different final pyrolyzing temperatures under soaking in 40% KOH solution.

was simple with reproducibility for carbon microstructures. Further research is going on in order to fabricate more complicated structures and integrate with silicon based technology. In conclusion, we have established the optimized fabrication process for high-aspect-ratio carbon microelectrode array on silicon substrate with SU-8 photoresist as starting material. Repeatability of microstructures and their improved properties was verified by experiments. Enhanced bonding between carbon microelectrode array and silicon was also achieved through micromechanical interlocking and three-step linear pyrolysis process. The developed process will speed up the applications of carbon microelectrode array in bioMEMS and electrochemical sensors.

Acknowledgements

This project was partially funded by the National Major Fundamental Research Program of China (Grant no. 2009CB724204) and National Natural Science Foundation of China (Grant nos. 50875103, 50805061 and 50775090).

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