Fabrication of nanometer-sized structures by C-NEMS technology

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ABSTRACT

Herein, we report a C-NEMS (Carbon Nano Electrical Mechanical Systems) technique for the synthesis carbon structures by pyrolysis of thin film SU-8 photoresist patterned by electron beam lithography (EBL). We have demonstrated the technique to fabricate carbon nano wires of controllable dimension and location using a top-down methodology. The width and thickness of the wires are in the tens of nanometer range. Additionally, the technique is able to produce conducting aligned carbon nano wires with addressable positioning, controllable length, and high aspect ratio (length vs width). These carbon nano wires can be exploited in large-scale assembly to make highly integrated nano wire sensor arrays or electronic devices.

Keywords: nano wires, carbon NEMS, electron beam lithography (EBL), SU-8

1 INTRODUCTION

Carbon as material is broadly used in different applications. There are a wide variety of carbons available, ranging from bulk commodity carbons i.e. coke, graphite, etc. to the specialty formats such as carbon fibers or carbon nanotubes. With the increasing interest in various aspects of nano devices, carbon nanotubes or carbon nanofibers become highly attractive carbon formats in modern science and engineering. They have great potential to be used as nanoscale devices such as field effect transistors [1-3], field emitters [4,5] and chemical or biological sensors [6]. Within those different applications, it is becoming apparent that synthesis method is the key to motivate underlying research. In spite of the success of the laser ablation [7] or chemical vapor deposition (CVD) [8] methods in developing those carbon nano structures, those nanoscale building blocks still can not be synthesized with precisely controlled and tunable structure, morphology, and size. The ability to control the size, shape, and/or orientation of structural materials on the nanometer scale is very important since it determines nano device properties and applications. To meet this goal, it is necessary to develop methods that enable rational design and predictable synthesis of those building blocks. Besides, it is essential to explore the limits of functional devices built on those elements. In the future, manufacturing nano-systems will require the development of efficient and scalable strategies for assembly of building blocks into the complex architectures that enable high-density integration with desired functions.

Over the past several years, well-defined carbon structures have been obtained by pyrolyzing positive photoresists that are commonly used in optical lithography [9]. This "diamond-like" carbon has many advantages in different applications. First, it is atomically smooth (i.e. surface roughness of about 30Å) [10] as protective and/or tribological coatings. Second, it has wider stability window as electrodes in aqueous solution [9]. Higher potentials can be applied to electrodes of carbon without electrolysis of water. Third, the process of making these carbon structures is totally compatible with MEMS processes. There exists a wealth of knowledge on making "microstructures" by photolithography can be the starting point to make the carbon structures. Thin layer of photoresist was spin coated on silicon wafers and subsequent photolithographic patterning using well-developed technologies in MEMS or in semiconductor industry. The micro structures that are routinely produced can directly transfer to fabricate microscopic structures or devices in carbon that may be useful in many different applications. This method provides the controllability of dimension and location of the carbon devices. Besides, the capability to pattern the structures can be exploited in large-scale assembly to make highly integrated arrays or electronic devices.

Although the efforts in fabricating and investigating carbon structures that are obtained by pyrolysis of photoresists have been made, the pyrolyzing photoresist precursors of carbon, so far, are positive tone such as AZ 4330. The dearth of using negative photoresist will restrict many applications using pyrolysis carbon as devices material. For example, high aspect ratio structures made by negative photoresist SU-8 can not be formed by positive photoresist and then pyrolyzed to carbon. Recently, Madou

et al. have reported successfully made high aspect ratio (aspect ratio > 10) carbon posts by pyrolyzing negative photoresist SU-8 for micro-batteries applications [11]. More material characterizations have been done on the carbon made by pyrolyzing commercially available negative photoresist SU-8. Besides, investigation of different process techniques on SU-8 making various carbon structures have been carried out.

The chemically amplified resist epoxy novolak SU-8 was first introduced by researchers at IBM [12]. It is a negative acting, solvent developed epoxy based resist with excellent UV sensitivity and high aspect ratios characteristics for MEMS processes. It has been used in many applications to fabricate thick or ultra thick structures by optical UV lithography [13-15]. However, there is much less effort aimed at developing this resist in thin film (thickness in sub micron range) process by using electron beam lithography (EBL). Pun and Wong [16] recently published the fabrication optical waveguides by electron beam lithography of a formulation of thinner layer SU-8. The minimum feature size of lines as narrow as 100 nm using the same patterning technique has also been published [17]. SU-8 has several advantages compared to the widely used e-beam resist, polymethyl methacrylate (PMMA). First, it has much higher electron sensitivity than PMMA. This reduced the necessary time to expose a given pattern which made it ideal for patterning over large writing fields. Second, it has a much lower contrast than pattering on PMMA. This leads to smooth surface roughness making multilevel exposures possible.

In this work we report the fabrication of 30-nm-wide lines with diluted SU-8 2 by e-beam lithography. Thin film SU-8 with thickness less than 20 nm has been achieved. The patterned SU-8 structures have been carbonized by thermal pyrolysis and different dimensions of carbon nano wires are reported. Our results demonstrated that, although SU-8 is design for thick film processes by optical lithography, it may be used for thin film e-beam lithography to make surface architectures with sub micron feature size. The technique is capable of producing conducting carbon nano wires with addressable positioning, controllable length, high aspect ratio (length vs width).

2 EXPERIMENT

2.1 Materials

For all experiments we used the commercially available NANO^{TM} SU-8 from MicroChem Corp. (Newton, MA). Gamma-btytolactone (GBL) and SU-8 developer were purchased from MicroChem.

2.2 Electron beam lithography

All the pattern exposures were carried out with a FEI SIRION nanowriter system at 30 KeV. Beam current is 25 pA. Patterns are generated by JC Nobity Lithography system.

2.3 Procedures

The fabrication process sequence is schematically showed in Figure 1. Single-crystal Si (001) wafers were used as the substrate material throughout this work. Before the resist was dispensed, the substrates were cleaned using a RCA clean (5 parts deionized water, 1 part NH_4OH, 1 part H_2O_2) and dehydrated in a 100 °C oven for overnight. For all the experiments we used the commercially available NANO^{TM} SU-8 formulation 2 from MicroChem Corp. (Newton, MA) as the original coating resist. It is composed of three components. The first component is an EPON epoxy resin. The chemical formula of EPON resin SU-8 is a multifunctional glycidyl ether derivative of bisphenol A Novolac epoxy oligomer. The second component is the photoinitiator triarylium-sulfonium salts. Epoxy resins are cationically polymerized by utilizing a photoinitiator which generates strong acid upon irradiation to the power source such as ultraviolet light or electron beam and the acid facilitates polymeric cross-linking during post-exposure bake. The third component is the gamma-butyrolactone (GBL), an organic solvent. The viscosity of resist is determined by the quantity of the solvent. The viscosity can also determine final thickness of the spin-coated film. The resists were spun onto the wafer by a 1275 rpm/s ramped to final 6000 rpm for 40 seconds. Before exposure, samples were pre-baked at 65 ºC for 2 min, then at 95 ºC for 2 min in the ovens. Post exposure bake (PEB) was carried out using ovens of 65 ºC for 1 min and 95 ºC for 1 min. Samples were developed for 30 second in MicroChem SU-8 developer and then blew dry under nitrogen flow. Before the pyrolysis process, samples were hard baked at 120 ºC for 30 min.

In process, if pyrolysis occurs too fast, the carbon structures will peel off from substrate. Here, we used a two step heating profile to pyrolyze the photoresist. First, samples were placed in a Lindberg furnace, purged with forming gas (N_2:H_2 = 9:1), heated to the 200 ºC and kept at the same temperature for 30 min. The purpose for this step is to release thermal stress of substrate and photoresist owning to the thermal expansion coefficient difference between two materials. Next, the temperature was increased to 900 ºC and held for 1 h to pyrolyze the photoresist. Samples were removed from the furnace at room temperature.

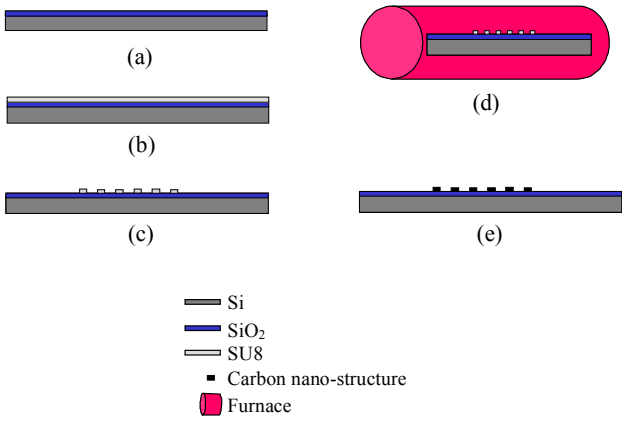


Figure 1: Schematic illustration of the process for fabrication of carbon nano-structures. (a) SU-8 photoresist spin coating. (b) SU-8 nanostructure patterning by Electron beam lithography (EBL). (c) Photoresist development. (d) Carbon nano-structures pyrolysis process. (e) Carbon nano-sturctures on substrate.

3 RESULTS AND DISCUSSIONS

In order to test the feasibility of the technique we proposed, first, the commercial available resist SU-8 2 has been coated and exposed by e-beam. Then, samples were pyrolyzed by the process mentioned above. Fig 2 (a) and (b) are SEM images of the resulting structures. (a). Three different carbon lines with width 300 nm, 400 nm, 500 nm (from left to right) and each width having three lines. (b). Arrays of aligned carbon nano wires. Each array has the same pattern as in (a).

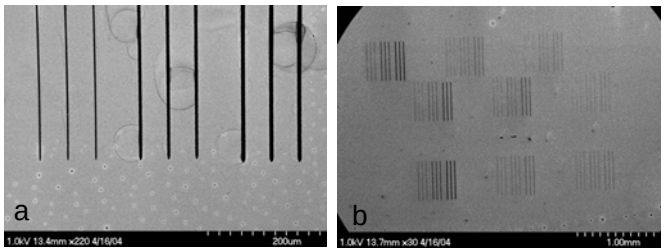
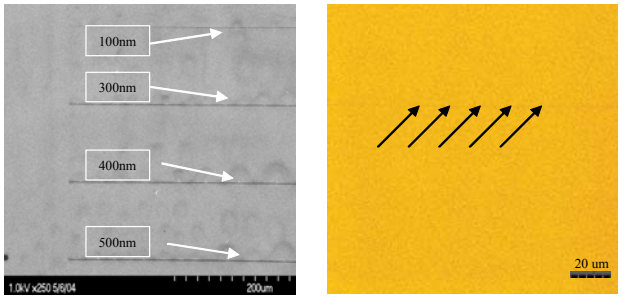


Fig 2

Upon inspection of the dimensions of the wires, we found that the thickness of the photoresist decreases dramatically during pyrolysis process, i.e., a decrease from 2 μm to about 500 nm. Assuming the width does not change, this corresponds to a weight loss of about 75% occurring in pyrolysis process. A weight loss of about 87% by pyrolyzing positive photoresist had been reported [18]. The patterned SU-8 lines have profiles more rectangular prior to heat-treatment. After pyrolysis, however, the lines have profiles wider at the base in contact with substrate and narrower at the top. The top regions of photoresist have more freedom to shrink than the photoresist at the structure/substrate interface. The volume change is easier on the top when the sample is slowly heated in the furnace.

E-beam lithography can be used with thin resists to generate very high resolution patterning. Although SU-8 is designed for thick film processes, its viscosity determined the thickness of coating films. In order to get thinner resist coating, we diluted the less viscose commercially available SU8 2 resist with GBL to a volume ratio (GBL: SU-8 2 (v/v)) 100. The thickness of carbon structures made by this photoresist formula have been investigated. AFM data (data not shown here) show the thickness to be around 10 nm. We believe this is the thinnest carbon film made by thermal pyrolysis and a top down approach. More work needs to be done to systematically predict and control the photoresist coating in order to get the desired thickness of carbon structures.

To assess the resolution limit of this resist, single pixel lines were used to expose the resist with varied doses. Fig 3 (a) and (b) display SEM images of the testing results. (a). paralleled carbon wires with different line widths. Clearly, the size of SU-8 patterns made by EBL depended on the dose modulation. The main purpose of this part of work was to determine the smallest possible feature size using our technique. (b) shows the smallest wire (30nm wide) made to date. Similar high resolution EBL results on SU-8 2000 were recently reported in the literature [17], which outline further interest in large arrays of nanoscale patterning.



(a) **(b)**

Fig 3

4 CONCLUSIONS

In summary, we have reported a technique for fabrication of carbon nanowires of controlled dimensions and location using a top-down methodology. The width and thickness of the wires are down to tens of nanometers range. Additionally, the technique is able to produce conducting carbon nanowires with addressable positioning, controllable length, and alignment. In addition, we have demonstrated the electron beam lithography patterning of thin film SU-8 with high aspect ratio lines and line width down to the tens of nanometers range. It should be possible

to extend this technique to fabricate the nanometer structures in NEMS. Generally, the addressable and patternable carbon nanowires we developed can be exploited in large-scale assembly to make highly integrated nanowire sensor arrays or electronic devices.

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