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Increase in graphitization and electrical conductivity of glassy carbon nanowires by rapid thermal annealing

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ABSTRACT

Glassy carbon (GC) exhibits numerous desirable properties such as high thermal and chemical stabilities, good hardness, and good thermal and electrical conductivities. Moreover, GC can be manufactured into micro-/nanostructures through the versatile microfabrication technology, or carbon-micro electromechanical systems, which includes polymer patterning and pyrolysis. However, despite these advantages, there are growing demands for enhancing the electrical conductivity of GC, so that it can compensate or be substituted for other carbon allotropes such as graphite, carbon nanotubes, and graphene. In this study, we demonstrated that simple rapid thermal annealing (RTA) can dramatically enhance the electrical conductivity of pyrolyzed GC nanostructures by ~ 300%. In this research, two different architectures of 1D carbon nanostructures such as a suspended nanowire that was separated from the substrate with a fixed distance and a substrate-bound nanowire were fabricated using conventional UV-lithography and pyrolysis processes, and their conductivity enhancement behaviors via RTA were studied. After the RTA process, the carbon/oxygen content and G-/D-band intensity ratios, which are correlated to the electrical conductivity, were enhanced, depending on the pyrolysis temperature. GC structures pyrolyzed at relatively low temperatures became more electrically conductive after the RTA process owing to their relatively higher oxygen content. This is because carbon atoms interconnected to oxygen atoms tend to align more readily than those corresponding to other carbon compositions because of the graphene healing mechanism. In addition, the architecture of the carbon nanostructures (*i.e.*, whether they were suspended or substrate-bound nanowires) influenced the RTA-induced increase in electrical conductivity; the former showed a greater increase in electrical conductivity owing to its larger portion of well-aligned carbon atoms at the surface compared to the latter carbon structure. This is because graphitization is initiated on the surface and then proceeds to the carbon core in the heat treatment. In addition, tensile stress generated only at the suspended carbon nanowires during the pyrolysis process is assumed to enhance further the electrical conductivity via RTA. For instance, the electrical conductivity of the suspended carbon nanowires formed by pyrolysis at 600 °C was enhanced to ~59,000 S/m after the RTA process.

1. Introduction

Carbon exhibits various allotropes such as graphene, carbon nanotubes (CNTs), diamond-like carbon, pyrolytic carbon, and glassy carbon (GC), which have been studied widely owing to their distinctive properties [1–5]. Their electrical characteristics are determined by their crystal structure, including that of the sp^2 and sp^3 orbitals. Micro-/nanosized carbon structures exhibit enhanced electrical and chemical properties and their mass production has attracted significant research interest [6–8]. Of all the nanoscale carbon materials available, graphene exhibits the highest electrical conductivity owing to its perfect sp^2 structure. However, the defects

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induced during the synthesis of graphene affect its electrical conductivity, limiting its suitability for making electrodes of various shapes [9–11].

To overcome this limitation, pyrolytic-carbon- and GC-based electrodes have been considered as substitutes for those based on graphene or other conductive materials, because it is possible to fabricate micro-/nanodevices at the wafer level in the former case [12–17]. Pyrolytic carbon has been used in various applications, including for trench capacitors for volatile memory, phase-change cells for flash memory, gate electrodes, and fuses [18–20]. Pyrolytic carbon processed using chemical vapor deposition (CVD) exhibits several advantages, including good electrical and chemical properties. Further, it can be patterned into micro-/nanodevices using microelectromechanical systems (MEMS) processes such as electron-beam (e-beam) lithography, photolithography, and reactive ion etching [21]. However, complex, time-consuming, and expensive nanofabrication technologies such as e-beam lithography are required to fabricate nano-sized pyrolytic-carbon-based structures [22]. Moreover, the fabrication of micro-/nanosized three-dimensional (3D) structures is limited owing to the low thickness of the films deposited by CVD and the difficulty of aligning structures and patterns during e-beam lithography.

Compared to pyrolytic carbon, which shows a highly oriented graphitic phase, GC exhibits a fullerene-related microstructure. Thus, it shows numerous unique material properties, including different electrical characteristics [5]. For instance, the electrical conductivity of GC ranges from that of pyrolytic carbon to that of graphite, depending on the process temperature. Furthermore, glassy carbon can be patterned into 3D micro-/nanoarchitectures in a user-defined manner using the carbon-MEMS process. Using this process, complex 3D carbon structures can be converted from pre-patterned 3D polymer structures via pyrolysis. Various polymer patterning processes such as e-beam lithography, nanoimprinting, photolithography, and electrospinning can be used for this purpose [14–17,23–25]. Surprisingly, sub-micrometer-/nanometer-scale GC structures with complex geometries, such as suspended meshes and single wires, can be fabricated readily using only a wafer-level batch process (e.g., photolithography) [14–17]. Generally, while the pyrolysis temperature is lower than that used for graphite synthesis, the electrical conductivities of GC and graphite are comparable [14,26]. However, as the size of GC devices reduces, the iR drop effect becomes more pronounced with the increase in the electrical resistance, which is attributable to the size reduction, and the resulting high iR drop becomes an issue in the case of sensors [25].

To overcome these drawbacks resulting from the relatively low electrical conductivity of GC, researchers have developed various pre-/postprocesses for enhancing the electrical conductivity, such as doping and annealing. The polymeric photoresist SU-8 was mixed with CNTs and patterned into nanowires using electrospinning, and the resulting wires were pyrolyzed [27]. The doping with the CNTs enhanced the graphitic phase, with the electrical conductivity of the thus-formed wires being ~3.1×10^6 S/m and higher than that of graphite. However, this doping process requires that the CNTs be conformally mixed with the photoresist such that the mixture remains in this state for the duration of the post-polymer-patterning processes. In contrast to the doping process, annealing treatments have been used widely with various materials, including metal oxide semiconductors, because of their simplicity [22]. It has been reported that the electrical conductivity of pyrolytic carbon processed using CVD is enhanced by three times and that its crystallization and thermal stability are also enhanced after annealing [22]. Thus, in addition to the electrical conductivity, other material properties such as the degree of crystallization and thermal stability can also be enhanced through doping and annealing.

In this study, we report that the electrical conductivity and electrochemical reactivity of one-dimensional (1D) GC nanostructures fabricated by carbon-MEMS are enhanced after rapid thermal annealing (RTA). The effect of RTA on the electrical conductivity varies with the architecture of the carbon nanostructures. The effect was investigated for suspended and substrate-bound nanowires; the suspended wires exhibited an increase in conductivity that was twice as high as that in the case of the substrate-bound wires. The cause of the observed increase in the electrical conductivity owing to the RTA process was investigated by analyzing the changes in the chemical compositions of the samples after the RTA process using Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). After the RTA process, the G-/D-band intensity ratio as well as the carbon/oxygen (C/O) content ratio increased, depending on the pyrolysis temperature. The effect of the architecture of the carbon nanostructures on their electrical conductivity was also further characterized using transmission electron microscopy (TEM). The TEM results revealed that a higher exposed area/total volume ratio made the effect of the RTA process on the electrical conductivity more pronounced in the case of the suspended carbon nanowires because the degree of crystallization at the surface was greater than that in the bulk carbon (See Fig. 1). The effect of the RTA process on the electrochemical reactivities of the GC structures was further characterized by measuring the separation between the peak potentials using cyclic voltammetry.

2. Experimental

Suspended and substrate-bound 1D carbon nanostructures were fabricated using the carbon-MEMS process, as shown in Figs. S1 and S2, respectively. First, a 1-μm-thick SiO_2 layer was grown on a 6-inch Si wafer (p-type, boron doped, 5–20 Ω cm, thickness of 660 μm, LG Siltron Co. Ltd, Korea) using a wet oxidation process (KHD-306, KSM, Korea). The SiO_2/Si substrate was then cleaned using a piranha solution (H_2SO_4:H_2O_2 = 4:1), dried using a N_2 gun, and dehydrated on a hotplate at 200 °C for 5 min. To fabricate the suspended carbon nanowires, a 20-μm-thick layer of a negative photoresist (SU-8 2025, Microchem. Corp., USA) was spin-coated on the SiO_2/Si substrate and soft-baked at 95 °C for 7 min. To define the post-like polymer structures used for supporting the suspended carbon nanowires, the photoresist layer was exposed to ultraviolet (UV) light (180 mJ cm^{-2}) using a mask aligner (MA-6, SUSS MicroTec, Germany). Then, a second UV exposure was performed through a photomask, which had wire-shaped windows, at a low dose (18 mJ cm^{-2}); this polymerized only a top shallow region of the photoresist layer. The fabrication of the suspended microsized polymer wires (width ≈ 1.0 μm, thickness ≈ 1.7 μm, length ≈ 60 μm) and their supporting polymer posts was completed with a post-exposure bake (95 °C for 8 min) and a development process. The 3D polymer structures, including the suspended microwires, were converted into GC structures via pyrolysis under vacuum conditions (1.0×10^{-5} Torr) at various temperatures, as shown in Fig. S3 (a). During the pyrolysis process, the microscale photoresist wires shrank dramatically, by ~90%, and transformed into GC nano-sized wires [14]. These GC structures were annealed at 1000 °C for 5 min, using an RTA process (KVR-6000, Korea Vacuum Tech. Ltd., Korea) under vacuum (3.0×10^{-3} Torr) [28]. In the RTA system; the substrate temperature was measured using a k-type thermocouple that was directly connected to the substrate susceptor during the RTA process; accuracy was ±5 °C. The details of the heating profile are presented in Fig. S3 (b).

The substrate-bound carbon nanowires were fabricated following the same steps as those for the suspended carbon nanowires; the only differences were in the photoresist coating and