Journal of Industrial and Engineering Chemistry 39 (2016) 188–193

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Facile construction of electrically-conductive carbon patterns from a cheap coal-type pitch and their application to electric heating devices

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ARTICLE INFO

Article history:
Received 11 April 2016
Received in revised form 11 May 2016
Accepted 23 May 2016
Available online 31 May 2016

Keywords:
Conductive carbon patterns
Pitch
Proton beam lithography
Pyrolysis
Electric heating

ABSTRACT

Electrically-conductive carbon patterns (ECPs) from cheap pitch thin films were fabricated using a simple proton beam lithography and pyrolysis. Well-defined negative-type pitch patterns were formed at the optimized fluence of 3×10^{15} ions cm^{-2}, and then pyrolyzed at various temperatures to create ECPs. The precursory pitch patterns formed at the optimized conditions were successfully temperature-dependently converted to the ECPs by pyrolysis. The formed ECPs through pyrolysis at a higher temperature exhibited good electrical conductivity. Moreover, the ECPs exhibited good electric heating characteristics, demonstrating the possibility of using the ECPs as a cheap electric heating element.

Introduction

Electrically conductive carbon patterns (ECPs) have attracted enormous attention in various applications, including biosensors, field-effect transistors, supercapacitors and fuel cells [1–4], because they offer significant advantages over the metal-based electrodes: a reduction in cost, eco-friendliness, chemical resistance and compatibility with integrated devices [1,5–7].

ECPs have been mainly prepared by three methods [1,8]: (1) the patterning of carbon nanomaterials such as carbon nanotubes and graphene; (2) the pyrolysis of photoresist patterns prepared by various lithographic methods; (3) and plasma etching of carbon thin films prepared by pyrolysis of organic thin films, such as polyacrylonitrile, poly(vinyl alcohol), pitch and polyaromatic compounds (3).

Although the ECPs prepared by the first method exhibited high electrical and optical properties, their drawbacks, such as high surface roughness, a complicated multi-step fabrication process and high cost, are great bottlenecks for their practical applications [9–12]. The second one can prepare ECPs with high resolution and good electrical properties, but it needs an expensive photoresist for semiconductor manufacturing. The last one has been preferred over the other methods because it can produce ECPs with a higher mechanical robustness, lower surface roughness and higher thermal and chemical stability and is a simpler process. However, this method requires pre-treatment, time- and energy-consuming thermal oxidative stabilization for the formation of oxidized cyclic network structures and additional plasma etching steps [8]. Therefore, a simpler and more efficient method for the preparation of the ECPs with higher resolution and conductivity is still a demand for their practical applications.

Proton beam lithography is a promising strategy to create well-organized patterns of organic materials due to its high linear energy transfer and straight penetration trajectory of the proton beam [13,14]. This method offers several merits such as direct formation of crosslinked network structures and carbon clusters without any chemical additives, independence of temperature, controllability and reliability [15,16]. Owing to these benefits, the patterning of various polymers using this method has been widely studied [17–19]. In spite of its advantages, the creation of ECPs from the thin films of pitch by a combination of proton beam lithography with pyrolysis has not been studied yet.

Pitch, a polyaromatic compound produced as a by-product of coal- or petroleum-based industries, has been regarded as one of the promising precursors for the fabrication of carbon fibers and

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http://dx.doi.org/10.1016/j.jiec.2016.05.023
1226-086X/

carbon nanosheets due to its thin film formability, cheap cost, and high carbon yield [20]. Due to its benefits, the pitch-derived ECPs were prepared by pyrolysis followed by plasma etching [21]. However, this method also needs an additional process such as thermal oxidative stabilization and plasma etching-based pattern generation steps.

In this study, we investigated simple construction of pitch-derived ECPs by proton beam lithography followed by pyrolysis, which offers several benefits, including simplicity, low processing cost, no thermal oxidative stabilization process or etching process and the capability of forming well-defined ECPs with moderate electrical conductivity. We optimized the proton beam lithography by plotting the contrast curve to generate well-defined pitch patterns. We confirmed the successful creation of ECPs by pyrolysis of the formed pitch patterns in terms of morphology, chemical structure/composition, crystalline structure and electrical resistance. We proposed a plausible mechanism for the formation of ECPs without any thermal oxidative stabilization and additional etching process. Furthermore, the electric thermal behavior of the formed ECPs was investigated to demonstrate the potential of using the ECPs as an electric heating element.

Materials and methods

Materials

Coal-tar pitch with a softening temperature of 108 °C (OCI Co. Ltd., Korea) and toluene (purity: 99.5%, Showa Company) were used as a negative-type resist material and a solvent for proton beam lithography, respectively. All the chemicals were used as received. Laser-trimmed 50-μm-thick stainless-steel pattern masks with 100-μm-wide line openings were supplied from Youngjin Astech Co., Ltd.

Proton beam lithography of pitch thin films

To prepare a homogenous pitch solution, 6.4 g of pitch was dissolved in 10 g of toluene and was filtered to eliminate the insoluble part. The homogeneous solution underwent evaporation to obtain the soluble pitch solid. The obtained pitch was re-dissolved in toluene to produce an 8 wt% homogeneous solution. Then, the resulting pitch solution was spin-coated on a well-cleaned 300 nm-thick SiO_2-deposited Si (SiO_2/Si) wafer (2 cm × 2 cm) at 5000 rpm for 40 s, and subsequently dried in a vacuum oven at 50 °C for 24 h. A 300-keV ion implanter in the Advanced Radiation Technology Institute (ARTI) of the Korea Atomic Energy Research Institute (KAERI) was used in the proton beam lithography of pitch thin films. To obtain the contrast curve for the optimal lithographic conditions, 100 nm thick films were irradiated by 150 keV H^+ in the presence of a pattern mask with an incremental fluence. The current density was fixed at 1.0 $\mu A\,cm^{-2}$ and the fluence ranged from 5×10^{14} to 9×10^{15} ions cm^{-2}. Then, the resulting samples were immediately developed with toluene, blown with a nitrogen gas, and finally dried in a vacuum oven at 50 °C for 24 h to completely remove the remaining solvent.

Formation of ECPs by pyrolysis

To create ECPs, the pyrolysis of the formed pitch patterns on the SiO_2/Si wafer was carried out in a horizontal tube furnace (Lindberg/Blue M, USA). The furnace was heated up to the temperatures of 800, 900, and 1000 °C at a rate of 5 °C min^{-1} under a nitrogen atmosphere, whereupon it was held at these temperatures for 1 h. Then, the furnace was naturally cooled to room temperature.

Characterization

The thickness of the pitch patterns was measured using an Alpha Step IQ surface profiler (KLA Tencor, USA) and the normalized thickness for the contrast curve was taken as the ratios of the remaining thickness to the initial thickness. Surface morphologies and profiles before and after pyrolysis of the pitch patterns were observed using a field emission scanning electron microscope (FE-SEM, JSM-7500F, JEOL, Japan) and a 3D surface profiler (NanoSystem, Korea), respectively. The chemical structures and compositions of pitch patterns and ECPs were investigated by an attenuated total reflectance Fourier transform infrared spectrometer (ATR-FTIR, 640-IR, Varian Inc., USA) and X-ray photoelectron spectrometer (XPS, MultiLab 2000, ThermoElectron Corporation, England) employing MgKα radiation. The X-ray diffraction (XRD) analysis was carried out on an X-ray diffractometer (X'Pert Pro Multi-Purpose, PANalytical, Netherlands) with CuKα radiation in a range of 2θ from 10 to 50°. Raman spectra was collected on a LABRAM-HR Raman spectrometer (Jobin Yvon LabRAM system) with an Ar-ion laser at an excitation wavelength of 514.5 nm. To investigate the current–voltage (*I*–*V*) behavior of the ECPs, silver electrodes were thermally deposited at both length direction ends of the formed ECPs, and the average distance between the electrodes was about 9000 μm. The *I*–*V* was measured using a probe station (MST-4000A, MS Tech, Korea) equipped with a Keithley 2400 source meter and the measurement of sheet resistance was performed with a 4-point probe system (Advanced Instrument Technology, SR-1000N system). The electric heating performance of the ECPs was measured by using an infrared camera (SE/A325, FLIR Systems) and a Keithley 2400 source meter at voltages ranging from 1 to 100 V.

Results and discussion

Formation of ECPs by proton beam lithography and pyrolysis

The formation of ECPs by proton beam lithography and pyrolysis is illustrated in Fig. 1. Pitch thin films spin-coated on a substrate

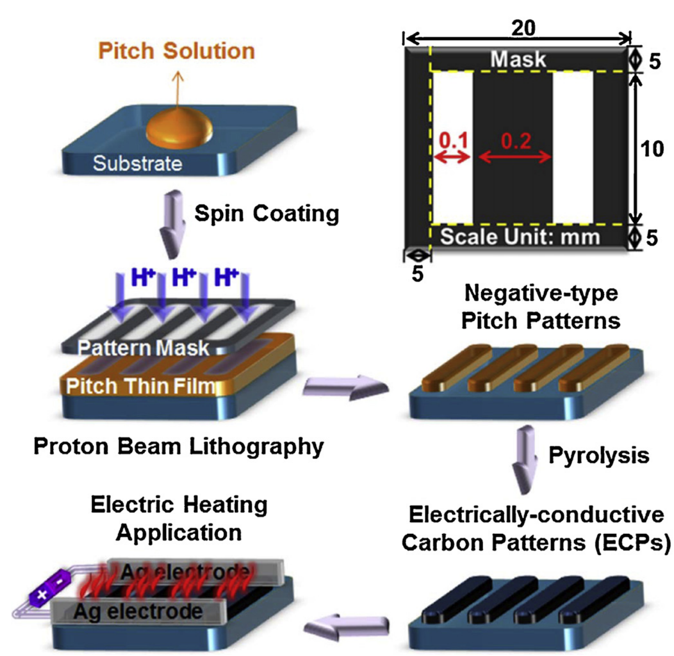

Fig. 1. Schematic illustration for the formation and electrical heating application of ECPs by proton beam lithography and pyrolysis.