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Pyrolysis Temperature and Time Dependence of Electrical Conductivity Evolution for Electrostatically Generated Carbon Nanofibers

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Abstract

Carbon nanofibers were produced from polyacrylonitrile/N, N-Dimethyl Formamide (PAN/DMF) precursor solution using electrospinning and vacuum pyrolysis at temperatures from 773-1273 K for 0.5, 2, and 5 h, respectively. Their conductance was determined from $I-V$ curves. The length and cross-section area of the nanofibers were evaluated using optical microscope and scanning probe microscopes, respectively, and were used for their electrical conductivity calculation. It was found that the conductivity increases sharply with the pyrolysis temperature, and increases considerably with pyrolysis time at the lower pyrolysis temperatures of 873, 973, and 1073 K, but varies, less obviously, with pyrolysis time at the higher pyrolysis temperatures of 1173 and 1273 K. This dependence was attributed to the thermally activated transformation of disordered to graphitic carbons.

Keywords

Carbon, conductivity measurement, electrostatic processes, nanotechnology

Comments

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Yu Wang, Jorge J. Santiago-Aviles, Rogerio Furlan, and Idalia Ramos

***Abstract*—Carbon nanofibers were produced from polyacrylonitrile/N, N-Dimethyl Formamide (PAN/DMF) precursor solution using electrospinning and vacuum pyrolysis at temperatures from 773–1273 K for 0.5, 2, and 5 h, respectively. Their conductance was determined from I–V curves. The length and cross-section area of the nanofibers were evaluated using optical microscope and scanning probe microscopes, respectively, and were used for their electrical conductivity calculation. It was found that the conductivity increases sharply with the pyrolysis temperature, and increases considerably with pyrolysis time at the lower pyrolysis temperatures of 873, 973, and 1073 K, but varies, less obviously, with pyrolysis time at the higher pyrolysis temperatures of 1173 and 1273 K. This dependence was attributed to the thermally activated transformation of disordered to graphitic carbons.**

***Index Terms*—Carbon, conductivity measurement, electrostatic processes, nanotechnology.**

I. INTRODUCTION

ELECTROSTATIC generation, or electrospinning, uses electrostatic forces to spin fibers from a precursor solution. So far, the technique has been mostly used to produce ultrafine polymer fibers [1]–[3]. Chun *et al.* [4] and Wang *et al.* [5] pyrolyzed electrospun polyacrylonitrile (PAN) fibers in the vacuum into carbon nanofibers, whose diameter is in the range of 100 nm, much less than that of carbon fibers produced by other methods of spinning [6]–[8]. Wang *et al.* [9] also synthesized ultrafine piezoelectric (PZT) fibers by sintering electrospun metal alkoxide fibers. Because of their high specific surface area, electrospun ultrafine fibers can be used as high performance filters, scaffolds in tissue engineering, and sensors. These applications become possible only after enough knowledge of the electrostatically generated fibers is gained. However, many properties remain to be investigated. Take electrical conductivity as an example. Although these fibers can be very important in sensor applications, so far only a few investigators have looked into it. Norris *et al.* [10], using the indirect four-point probe method, measured the conductivity of their electrospun nonwoven ultrafiber mats of polyaniline doped with camphorsulfonic acid blended with polyethylene oxide (PEO). MacDiarmid *et al.* [11] obtained I–V curves of single 50 wt%PAn.HCSA/PEO fibers. The lack of conductivity data of electrospun carbon nanofibers can, to a large degree, be attributed to the difficulties in evaluating the cross-section area of the fibers. The authors evaluated the cross-section area using scanning probe microscope (SPM), and measured the room temperature electrical conductivity of PAN-based carbon nanofibers pyrolyzed at 1073 K [5]. This paper reports pyrolysis temperature and time dependence of the electrical conductivity evolution of carbon nanofibers.

II. EXPERIMENT

Commercial PAN powder and N, N-Dimethyl Formamide (DMF) (Aldrich), in a ratio of 800 mg PAN to 10 cm^3 DMF, were used to prepare the precursor solution. Thermal gravimetric analysis (TGA) and thermal differential analysis (DTA) were conducted in Argon atmosphere, using a Simultaneous Differential technique module (SDT 29600, TA Instrument), from room temperature to 1573 K at a heating rate of 10 K/min.

Single crystal silicon wafers (p-type, 0.1 Ωcm), with an silicon oxide layer $\sim$150 nm thick, were used as substrates. Before the deposition, arrays of 1 mm $\times$ 1 mm or 50 μm $\times$ 50 μm gold contacts were fabricated onto the oxidized surface using lithography and vacuum evaporation. The large sheet resistance of silicon oxide makes contacts almost electrically insulated to each other. In fact, there is no detectable conductance between two neighboring contacts without any fiber. Electrospinning was conducted in a homemade setup reported in details previously [5]. The deposition was conducted for a very short time so that only single fibers ran between two neighboring gold contacts.

The as-deposited samples were pyrolyzed in a Brew Model 466-S vacuum furnace at 773, 873, 973, 1073, 1173, and 1273 K for 0.5, 2, and 5 h, respectively. The vacuum was maintained at pressures lower than 1.33×10^{-4} Pa. The substrates, with 50 μm $\times$ 50 μm gold contact pad arrays, were used only for fibers pyrolyzed at 773 and 873 K. All other samples, pyrolyzed at higher temperatures, used 1 mm $\times$ 1 mm gold contact pad arrays.

An HP Model 4145B semiconductor parameter analyzer was used to measure the I–V characteristics of the carbon

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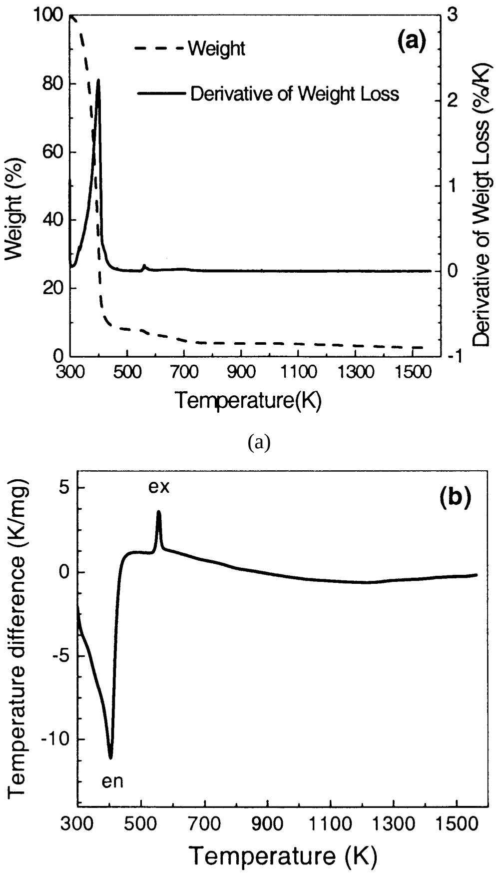


(a)

(b)

Fig. 1. (a) TGA and (b) DTA curves of the precursor PAN/DMF solution.

nanofibers at room temperature. The testing voltage ranged from −20 to 20 V, with a step of 0.1 V. Measurements were conducted on the same segment of fiber for 10–20 times under the same conditions.

An optical microscope was used to observe the fiber after pyrolysis and to measure their length l. A Digital Instruments Dimension 3000NS-III SPM, operated in tapping mode, was used to record the height and amplitude images of the fibers as data files. Offline image processing software was used to obtain the average cross-section profile, from which cross-section area was evaluated. To ensure reliable results, a scanning electron microscope (SEM) was used to record the image of fibers, from which the horizontal diameter of the imaged fibers was also evaluated. The gold contact pads served as excellent internal length references. The conductivity was finally determined using $\sigma = Gl/S$, where G, S, and l are conductance, average cross-section area and length of the fibers, respectively.

III. RESULTS

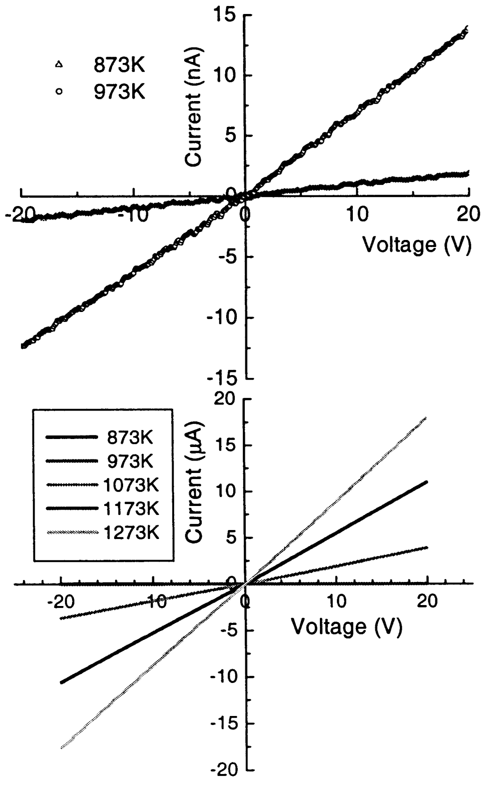


Fig. 2. I–V curves of carbon nanofibers pyrolyzed at different temperatures.

The TGA-DTA curves (Fig. 1) show a dramatic weight loss and an endothermic DTA peak between room temperature and 473 K, indicating the solvent (DMF) evaporation. Beyond 473 K, weight decreases at a much slower rate, from 8.34 wt% at 473 K to 3.88 wt% at 873 K, and to 3.35 wt% and 2.62 wt% at 1273 and 1573 K, respectively. The exothermic DTA peak centered around 570 K [Fig. 1(b)] is produced by PAN decomposition [12].

Fig. 2 shows the I–V curves of carbon fibers pyrolyzed at different temperatures for 0.5 h. Their linearity implies an ohmic contact between the contact pad and the fibers. The linear slope, or the conductance of the fibers G increases sharply with the pyrolysis temperature.

Fig. 3 shows SPM height and amplitude images of a typical single fiber. The apparent semicircular profile of the cross-section [Fig. 3(c)] may be misleading because the cone-shaped tip could not track the lower half of the cross-section [Fig. 3(d)]. However, the height of the fiber, or the vertical diameter, is real. The full width at half maximum (FWHM) was taken as the horizontal diameter of the fibers, since the measured values of vertical and horizontal diameters on the same cross-section are different, and the cross-section is elliptical rather than circular, as previously supposed.

The SEM image of the fiber revealed by SPM in Fig. 3 clearly shows its irregularity (Fig. 4). The average horizontal diameter of the fiber was measured to be 120 nm, approximately the same as the FWHM value obtained from SPM cross-section profile, justifying the use of FWHM as the horizontal diameter. This paper uses the diameter values measured from SPM height images since they give both horizontal and vertical diameters.

Pyrolysis at 773 K did not generate a conductance high enough as to be detected. Since the detection limit of the measurement system is estimated to be 0.2 S/m, the conductance of the fibers pyrolyzed at 773 K must be lower than this value. At temperatures higher than 873 K, the conductivity

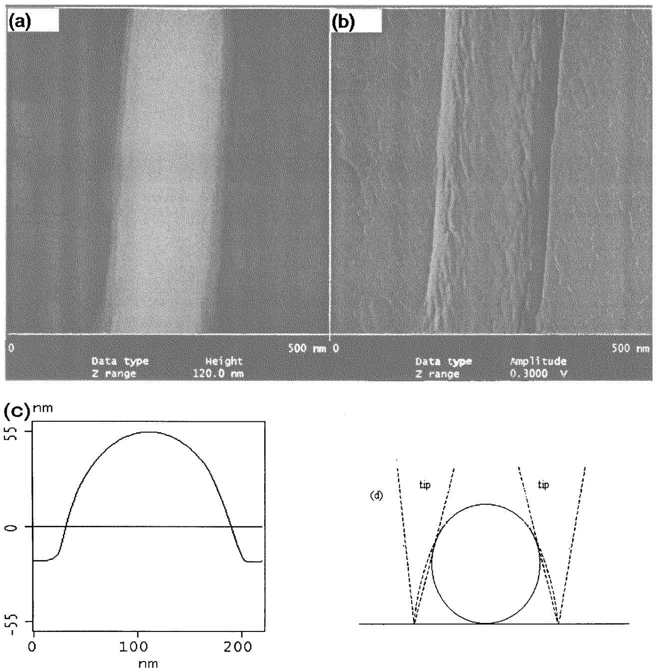


Fig. 3. SPM micrograph of carbon nanofiber and its cross-section profile.

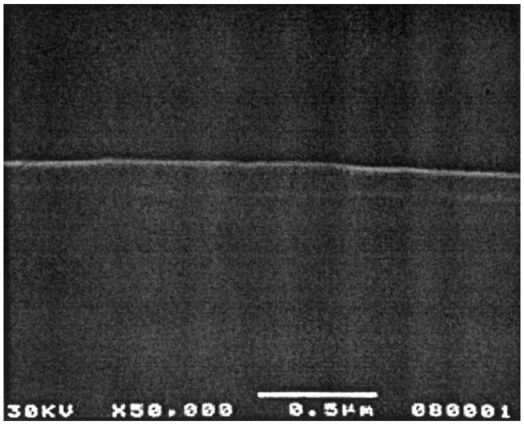


Fig. 4. SEM image of the same fiber revealed by SPM in Fig. 3.

increases sharply with pyrolysis temperature. It also increases with the pyrolysis time at lower pyrolysis temperatures (873, 973, and 1073 K) [Fig. 5(a)], but levels off at higher pyrolysis temperatures (1173–1273 K) [Fig. 5(b)]. In fact, at the pyrolysis temperature of 1173 K, the conductivity decreases slightly with the pyrolysis time. Such abnormal independence may be attributed to the increased porosity, and needs further investigation.

IV. DISCUSSIONS

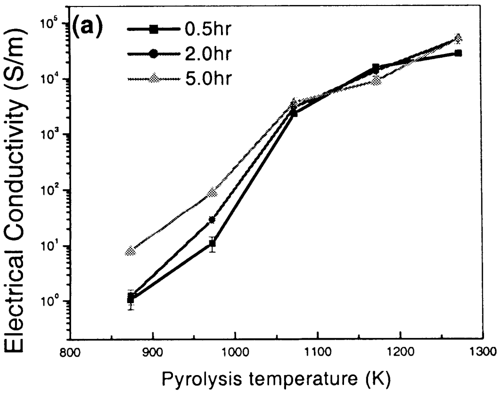
A. Error Analysis

The error in conductivity measurement arose mainly from two sources: 1) the contact resistance between the fibers and the contact pads, and 2) the irregularities of the fibers, and consequently, the difficulties in the evaluation of the cross-section area. To reduce the effect of the contact resistance, gold contact pads were used. They were heat-treated together with the fibers during the vacuum pyrolysis. The diffusion of carbon and gold atoms between the contacts and the fibers not only enabled an ohmic contact (Fig. 2), but also reduced the contact resistance. Furthermore, the distance between the neighboring contacts was intentionally kept not too small: 50 μm for fibers pyrolyzed at 773 and 873 K and 1 mm for fibers pyrolyzed at higher temperatures, so that the resistance of the fibers itself is much larger than the contact resistance. Fiber samples too irregular were discarded for reliable measurement, and the average cross-section profiles were used to evaluate the cross-section area.

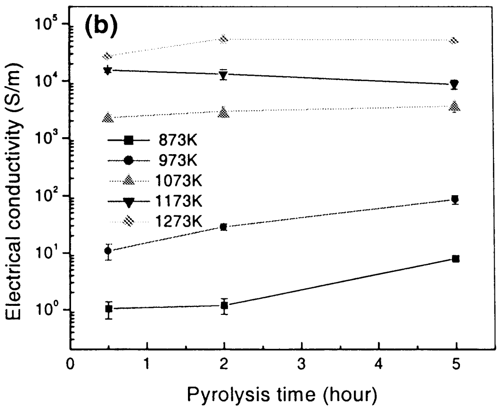
B. Change During the Pyrolysis of the Precursor Fiber

The pyrolysis process in this paper differs from the general case in two respects: the precursor solution contains 92% (weight) DMF and the precursor fibers contain some residual DMF even if the solvent mostly evaporated during the electrospinning; the precursor fibers were pyrolyzed in the vacuum, where the residual oxygen content is minimized. The dramatic weight loss and endothermic process between room temperature and 473 K, shown by TGA and DTA curves (Fig. 1), indicates the evaporation of DMF. Above 473 K, the weight remains about 8.34 wt%, very close to the PAN concentration of the precursor solution. Considering the fact that the volatile DMF kept evaporating as soon as it is loaded into the pan, and before starting the analysis, it is reasonable to think that DMF has totally evaporated by 473 K. Although the DMF content of our precursor solution and precursor fibers are quite different, the TGA-DTA curves of the precursor solution, shown in Fig. 1, may truly represent the pyrolysis change of precursor fibers at temperatures higher than 473 K.

During the complicated pyrolysis process, PAN generally goes through stabilization between 473 and 673 K, and carbonization at higher temperatures. Stabilization involves dehydrogenation, cyclization and, if in the air, oxidation. The exothermic process is due to the uncontrolled thermal polymerization of the nitrile group with the release of the heat of polymerization. During carbonization the fibers lose noncarbon elements, as well as partial carbon, in the form of volatile byproduct gases, such as HCN, NH_3, and H_2, and a graphite-like structure is formed. The basic structural unit (BSU) of carbon fibers consists of a stack of conductive turbostratic layers. The BSU can split, twist, fold, and join other BSUs to form microdomains, which can also split, twist, fold, and join, etc., to form carbon fibers. Thus, the fine structure of carbon fibers is not a homogeneous, monolithic carbon but rather a somewhat chaotic collection of BSUs formed into microdomains interspersed with uncarbonized intermediate products and pores [6]–[8]. At low temperatures, or immediately after stabilization, the oriented BSUs are isolated, and the fibers are not conductive. After the disappearance of the heteroatoms, which is believed to take place between 600 and 873 K, isolated columns of materials are formed, followed by microdomains as the columns form more coherent structures. Once the microdomains become continuous, and the layers of turbostratic carbon appear across the fibers, constituting a



(a)



(b)

Fig. 5. Pyrolysis (a) temperature and (b) time dependence of the conductivity.

conducting channel, the fibers start to be conducting. This takes place around 873 K.

The formation of graphite carbon at near 873 K was confirmed by an earlier Raman scattering investigation. Raman spectra showed coexistence of graphitic and disordered carbons [5]. It is interesting that although weight decreases only slightly from 3.88% at 873 K to 3.35% at 1273 K, the conductivity increases by almost five orders of magnitude. It is strongly suggested that the change in this temperature range is not mainly the extraction of heteroatoms but rather the transformation of disordered carbons and isolated BSUs to continuous graphite domains, or the early stage of graphitization. This process is a kinetically thermally activated process. The higher pyrolysis temperature and/or the longer pyrolysis time, the higher graphite molar fraction in the pyrolyzed carbon fibers. So, the increase of pyrolysis temperature results in a sharp increase in the conductivity [Fig. 5(a)]. The effect of time is more pronounced at lower temperatures than at higher temperatures, because it takes a longer time for the system to reach its quasiequilibrium state at lower pyrolyzing temperatures than at higher temperatures.

V. CONCLUSION

The conductivity of PAN-based carbon nanofibers produced by electrospinning was measured. It increases sharply with the pyrolysis temperature, and also increases considerably with pyrolysis time at lower pyrolysis temperatures (873, 973, and 1073 K), but varies less obviously with pyrolysis time at higher pyrolysis temperatures (1173 and 1273 K).

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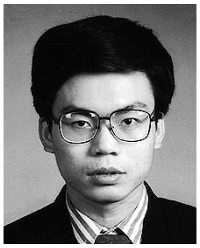

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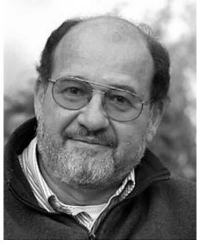

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