Fabrication of Blended Polyphenylenevinylene Nanowires By Scanned Electrospinning

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We report the fabrication of semiconductor polymeric nanowires and characterization of their electrical conductivity. The polymeric nanowires were extruded from a blended polymer solution of poly [(*m*-phenylenevinylene) - *co* - (2,5 - dioctoxy -*p*- phenylenevinylene)] copolymer (PmPV) and polyethylene oxide (PEO), and deposited on lithographically patterned gold electrodes by utilizing a scanned electrospinning technique that controls the orientation of nanowires. The current-voltage curves of polymeric nanowire were investigated and we have found that they have rectifying current-voltage characteristics due to the metal-semiconductor contact. Because of the ease of operation and high throughput of this scanned electrospinning process, it presents opportunities for the manufacture of nanowire electronic devices.

Keywords: Nanofiber, scanned electrospinning, nanodevice

1. Introduction

In the past decade, organic semiconductor and conducting materials have received considerable attention because of their unique electrical, mechanical and optical characteristics [1-5]. Sandwiched structures of thin polymer film, metal/polymer/metal, are commonly used for devices such as light emitting diodes, diodes (LED) and capacitors. Particularly, poly-phenylenevinylene (PPV) thin films have been studied as a LED material for producing large and flexible display panels [1, 6-10]. In addition to the sandwiched film format, one-dimensional organic nanostructures are being investigated because of improved electrospinning technology, which can control the deposition of polymeric nanowires as well as their integration with lithographically defined surfaces [11-12]. The oriented nanowires have been made from conducting or insulating polymers and used for nanodevice fabrication [11-13] or as a sacrificial structure [14-15].

In this letter, we report the fabrication of a semiconductor polymeric nanowire from a blended PmPV and PEO polymer and their integration with

gold electrodes for electrical characterization. To the best of our knowledge, this is the first fabrication of PmPV nanowires and characterization of their electrical conductivity as a one-dimensional building block.

2. Method

Nanowires were deposited from a blended PmPV and PEO polymer solution utilizing a scanned electrospinning system. The alkoxy side chains on the PmPV copolymer improved the solubility in common organic solvents relative to PPV. However, since extremely concentrated PmPV solutions were not viscous enough to create nanofibers, PEO polymer was blended with the PmPV solution to increase the viscosity. This method has been explored for the fabrication of other polymeric nanofibers such as polyaniline nanofibers [13, 16-17]. The blended polymer solution was prepared by dissolving PmPV polymer (MW 5700) at weight concentration of 10 % and PEO polymer (Mn 100000) at weight concentration of 0.5% - 5% in chlorobenzene. The scanned

Fig. 1 Oriented PmPV/PEO Nanofibers deposited on a silicon surface utilizing the scanned electrospinning (a) The optical micrograph of PmPV /PEO nanofiber. (b) The fluorescent micrograph of PmPV /PEO nanofiber. (c) The chemical structure of PmPV.

electrospinning system was composed of deposition source with a rotating counter electrode. The rotating motion of the counter electrode controls the orientation of the nanofiber by creating relative motion between the source and the counter electrode, with a linear velocity of more than 126 cm/s, during the deposition process. The details of this system were reported previously [13]. The blended PmPV and PEO polymer solution was dispensed on the electrospinning tip source to form a droplet. A polymer jet was extruded from the apex of the droplet to the counter electrode with electric field of 4000V/cm. The extruded polymer jet dried in transit to the surface and deposited on the surface of the rotating counter electrode. Fig. 1a shows the optical micrograph of PmPV /PEO oriented nanofibers (from the blended polymer solution of 10% PmPV and 5% PEO in weight concentration) deposited on silicon surface. The fluorescent micrograph of these nanofibers is shown in Fig.1b. PmPV molecules confined in nanofibers were excited by 488 nm light source. The average diameter of these fibers was 1.2 μm. The chemical structure of PmPV is shown in Fig. 1c. The average diameter of nanofibers can be controlled by changing the polymer concentration as demonstrated for other polymeric materials [11,

18]. In this experiment, the weight concentration of PmPV polymer was fixed to 10%, maximum solvable concentration, and the concentration of PEO was changed. A weight concentration of less than 1 % PEO resulted in the formation of polymer droplets because the viscosity of polymer solution was very low. The average diameter of nanofibers increases with PEO concentration. The smallest PmPV /PEO nanofiber had a diameter of 150 nm and was electrospun from the blended polymer solution with 10% weight concentration of PmPV and the 1% weight concentration of PEO in chlorobenzene.

3. Result

For the electrical measurements, a single polymeric nanowire must be organized and connected to electrodes. To address this requirement, a single PmPV / PEO nanofiber was deposited on lithographically defined gold electrodes patterned by a lift-off process. Two rectangular patterns with a 150 nm gap (1μm width and 2 mm long) were defined by electron beam lithography on a silicon oxide surface. The chip with two gold electrodes was attached to the rotating counter electrode and an oriented PmPV /PEO nanofiber with a 150 nm diameter was deposited on the chip. Fig. 2a and 2b

Fig. 2 Oriented nanofibers integrated with lithographically defined gold electrodes. (a) The optical micrograph of PmPV/PEO nanowire. (b) The fluorescent micrograph of PmPV/PEO nanowire. (c) The three dimensional schematic diagram of nanowire integrated with gold electrodes. (d) The scanning electron micrograph of PmPV/PEO nanowire on gold electrodes. The diameter of nanowire is 150 nm.

Fig. 3 The band diagram of PmPV / Au contact. The barrier height for electron is too high, thus, this is the hole-only device.

show the optical and the fluorescent micrograph of a nanowire deposited on the two gold electrodes. Fig. 2c shows the three-dimensional schematic diagram of a PmPV / PEO nanowire deposited on the gold electrodes. The scanning electromicrograph of the nanowire, integrated with gold electrodes, is shown in Fig. 2d. The nanowire is tightly connected with gold electrodes.

The schematic energy band diagram of Au/ PmPV-PEO/Au with the biased potential V is shown in Fig. 3. The metal/semiconductor contact prevents electron injections from the negatively biased electrode. Thus, this is a hole-only device. We have characterized two polymeric nanowires integrated with two gold electrodes. The current-voltage curves of nanowires were measured using a computer-controlled two terminal measurement system with a current amplifier.

Fig. 4 The current-voltage curves for PmPV/PEO and PEO nanowires. (a) current-voltage curve of 150 nm diameter of PmPV Nanowire, (b) current-voltage curve of 300 nm of PEO nanofiber. The graph on upper left corner is the current density-voltage curve of 150 nm diameter of PmPV.

The dimensions and materials of examined nanowires were as follows (1) 150 nm diameter of PmPV /PEO nanowire (2) 300 nm diameter of PEO nanofiber (electrospun from the weight concentration of 15% PEO in ethanol). Graph (a) in Fig. 4 shows the current (nA) –voltage (volts) curves (linear-linear plot) for 150 nm diameter of PmPV nanowire. The conductance of this nanowire is $3.1 \mu\text{S}/\text{cm}$ at 7 V bias potential. The current density (mA/cm^2) – voltage (V) curves (log-linear plot) is shown in left upper corner of Fig. 4. There is a threshold bias potential for tunneling the contact barrier, which is 3.8 volts. This barrier may be created by the blended PEO polymer. Graph (b) in Fig. 4 indicates the current-voltage characteristics of pure PEO nanofiber with 300 nm diameter. No current was detected because PEO is an insulating polymer.

4. Conclusion

This report has discussed the fabrication and characterization of semiconductor polymeric nanowires. It is achieved by utilizing a scanned electrospinning technique for a controlled deposition of polymeric nanowires and an integration of nanowires with microfabricated structures. The blended nanowire of PmPV and PEO was deposited on a chip with two gold

electrodes and metal-semiconductor nanocontacts were established with a barrier. The current-voltage curves for these devices were measured with the two terminal system and the rectification profile of current-voltage curve was measured. PPV family polymers were commonly used as light emitting diode (LED) material.

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