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A piezo-resistive graphene strain sensor with a hollow cylindrical geometry

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ABSTRACT

We propose a resistance-type strain sensor consists of hollow tubing graphene fibers (TGFs) with dimethylpolysiloxane (PDMS) coating for millimeters-scale strain/bending detection applications. The TGFs were synthesized via graphene films grown on Ni wire by chemical vapor deposition (CVD). The TGFs are fundamentally folded continuous few-layered graphene films without edges maintained cylindrical tube supported by PDMS coating. Sensing properties were studied comparing with a multi-wall carbon nanotube (MWCNT)/PDMS composites (CNTCs) and the mechanism were discussed. In terms of the gauge factor, the sensor made of TGF is estimated to be in the range of 34.3–48.9 against 8% tensile strain.

For a feasibility study, we demonstrate the human finger monitoring by means of bending angle detection on a finger joint.

1. Introduction

Flexible, stretchable materials have attracted a tremendous attention because of their possibilities for applications in physiological activity monitoring [1], health care monitoring [2,3] and diagnosis systems [4], artificial e-skins [5,6], robotics [7,8], with a benefit of wearable characteristics [9]. The wearable e-skin is an artificial skin which mimics the ability of human skin as integrating sensors for the spatial distribution of temperature, a stress, a flexion and a strain, so called epidermal electronics [2,5,6]. Among these abilities, a strain sensor enables to convert direct electrical signals when an electrical conductor is stretched within the limits of its elasticity. Many researchers have been concentrated to find high elastic, highly sensitive conductive materials for stretching to meet a human body motion with so many kinds of curvature. Various conductive materials have been proposed, such as metal nano-wires (AgNW) [10,11], metal particles [12], carbon blacks [13], carbon nanotubes [8,14,15], and graphene [11,16–18] including graphene flakes [19], graphene forms [20,21] composed with a flexible/stretchable polymer substrates.

Graphene is a two-dimensional one-atom thick monolayer of carbon atoms, after the discovery of the graphene by Novoselov and Geim [22], it has been attracting interest due to its promising properties such as the molecular structure of one-atom thick two-dimensional structure, high Young's modules [23], a ballistic transport of carriers [24], a charge carrier behave mass less Dirac fermions [25], and capability of modifying band gap with applying strain [26,27]. Sakhaee-Pour et al. [28] first predicted that defect-free single-layered graphene sheets based strain sensors are possible highly sensitive to the applied stretch as well as the single-walled carbon nanotubes versions in the atomistic modeling. Lee et al. [29] have successfully grown wafer scale graphene films on Ni and Cu films by chemical vapor deposition (CVD) and transferred them onto poly(dimethylsiloxane) (PDMS) substrate. They showed the corresponding piezo-resistance gauge factor is 6.1 to the strain up to 1%. The strain response of graphene/epoxy composites showed the gauge factor of 11.4 within the range of 1000 micro-strain [30]. Huang et al. [31] performed in-situ nano-indentation to induce uniaxial tensile strain in suspended graphene devices and the electrical measurements indicates that the gauge factor of graphene is 1.9. Chen et al. [32] characterized mechanically exfoliated graphene sheets into strain gauge utilizing conventional photolithography and the corresponding gauge factor was high as ~150 at within 0.1% strain. Bae et al. [33] showed that graphene can be used for high strain up to 7.1% using a rosette geometry with a gauge factor of 2.4 in 1.8% strain and 4–14 over 1.8% strain. In this context, practical maximal strain range and sensitivity of graphene are still open for realizing a new category

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of human-interface device applications. Therefore, a detailed investigation including a sensor geometry and experimental demonstration of graphene based strain sensors are important. Furthermore, in recent attracting interest in wearable applications, the sensors should possess in stable for environmental fluctuations such as temperature, humidity, ambient gases, pressures, vibrations, and so on, including sensor's size and a fabrication cost.

In this article, we propose a graphene-based resistive strain sensor using a hollow tubing graphene fiber maintained cylindrical tubing to demonstrate a highly response against the strain. The strain sensor features that high quality (fewer defects) graphene layers in continuous films, free standing fibers with stabilized polymer coatings, and a high output signal/noise ratio. The cylindrical geometry of a strain gauge may have possible ability for detecting uniaxis strain (tensile and compressive), curvature (bending against to longitudinal), and the torsional strain, simultaneously as well as easy handling for installing. Sensing properties were studied comparing with a multi-wall carbon nanotube (MWCNT)/PDMS Composite (CNTCs) because the CNTCs are well known for the excellent sensing properties and there are valuable previous researches [34–37]. The detection mechanism responsible for the stability in a low electrical noise detection and the geometries of the TGFs was discussed. We also demonstrated bending sensors installed on a finger joint in writing characters' movement in order to detect the changes in human motions.

2. Experimental

2.1. Materials

The nickel wires (purity 99.99%) were purchased from the Nilaco Corporation. The diameter of the Ni is 500 μm. PDMS was used SYLGARD®184 silicone elastomer kit (Dow Corning Toray Co. Ltd., Japan). The PDMS rigidity can be controlled by the cross-linker agent concentration in the base PDMS solution, the baking temperature and the time. Multi-walled carbon nanotubes (MWCNTs) were purchased from EM Japan Co. Ltd. (G-24), typical length of 1–50 μm and diameters of 50–85 nm.

2.2. Sample preparation

The Ni wires were cut into 5 cm long and immersed in acetone and ethanol for 10 min, cleaned with deionized water, and dried in nitrogen gas. The Ni wires were loaded into a synthesized quartz tube reactor and heated to 850 °C by an electric furnace under the H_2:Ar = 40:60 sccm for min to remove the surface oxide layer on Ni wires. 20 sccm of ethanol vapor was introduced into the reactor for 30 min in the reactor pressure of 10 Torr. Afterward, the ethanol vapor was cut off and the reactor was cooled to room temperature (the cooling rate: 25 °C/min) while the H_2 and Ar flow rate and reactor pressure were maintained. After growth, PDMS was coated on the surface of the graphene films grown on Ni wires as a support to reinforce the graphene tubing structure, and they were baked for cross-linking at 145 °C for 10 min in an electronic oven. The sample was then immersed in an $FeCl_3$/HCl etching solution to dissolve the Ni wires. Then the graphene/PDMS micro-tubes can be readily taken out from the etchant and cleaned using deionized water. The graphene/PDMS micro-tubes were dried at room temperature for a night. Details about the fabrication process are shown in Fig. S1.

The reference CNT/PDMS composites were prepared by mixing 15 wt% multiwall carbon nanotubes in the other, both with 15:1 = base polymer:curing agent of PDMS, and baked at 145 °C for 10 min. The dimensions of the CNTCs strain sensor was 20 × 2 × 1 mm (length × width × thickness) shaped by a knife, while the contacts were made directly clamping with the commercial alligator clips.

2.3. Characterization of samples

Scanning electron microscope (SEM) was conducted using a JEOL JSM-7001F with an accelerating voltage of 15 kV. Raman spectroscopy (Jasco NRS-7000) with a laser excitation wavelength of 532 nm was used to evaluate the crystalline quality and uniformity of the graphene. X-ray diffraction (Rigaku RINT Ultima III) was used to analyze the crystalline orientation and whether the Ni residue was present or not. The electrical conductivity measurement was taken with a model 4200-SCS semiconductor characterization system (Keithley). The static characterization of the resistance variation on temperature were carried out that the temperature was monitored by the samples were placed on the hotplate (RSH-1DN, AS ONE Corp., Japan).

Electro-mechanical test was performed by measuring the resistance change ($\Delta R/R_0$) during the mechanical tensile strain applied to the samples by a hand-made tensile testing machine and a hand-made bending testing machine. Fig. 1 shows the pictures of testing equipment of the tensile testing machine (a) and the bending testing machine (b). Fig. 1(a) shows a photograph of the measuring system used to investigate the piezo-resistive properties of the TGF and CNTC strain sensor under tensile strain. For the measurement of piezo-resistive properties, the sensors were machined in a form of strip with a length of 2 cm and a diameter of 0.56 mm (including the PDMS thickness) for TGF, width of 2 mm and thickness of 1 mm for CNTC on assumption that the both strips are straightened in parallel. Then, both ends of the sensor were fixed on the sample stage with careful alignment between the tensile direction and the length direction. The sensors were stretched by the tensile machine, meanwhile, continuous voltage of 0.1 V was applied through the sensors to measure the change of electrical resistance during the tensile deformation of the sensor. Fig. 1(b) shows a photograph of the measuring system used to investigate the piezo-resistive properties of the TGF and CNTC strain sensor under bending strain. To appear in the detection of bending, we integrated the TGF and the CNTC onto a foldable plastic plate. Sensors folded the plastic plate holder and the bending angle were defined. The bending angle was determined by seeing a simplified protractor.

3. Results and discussion

The schematic procedure for PDMS coating graphene hollow tubing fibers using Ni wires as a catalyst is illustrated in Fig. S1. Graphene was grown on 3–5 cm long of Ni wires (0.1–0.5 mm diameter) by the CVD method using ethanol as a carbon source. Fig. 2(a, b) shows typical scanning electron microscope (SEM) images of a Ni wire (0.5 mm diameter) before and after the growth of graphene. A smooth surface of Ni wire was obtained by surrounding uniform graphene layers on the Ni wire surface. The graphene/Ni wires can be coated with PDMS (c), after Ni wires had been etched, the hollow tubing graphene fibers were obtained (d). When the graphene/Ni wires were etched without PDMS coating, the residue graphene fiber showed shrink and squashed appearance (e). Supplementary Fig. S2 shows the SEM images of the graphene/PDMS tubing fiber (a) and the GF without PDMS coating (b) grown on 0.1 mm diameter Ni wire. At the case of 0.1 mm Ni wire, the cross section of the graphene tube had a hexagonal star shaped, and the thickness of the PDMS coating layer about 0.15 mm which is larger than that of 0.5 mm Ni wire of about 0.05 mm. It is thought to be the graphene fiber cannot stand from the contraction of PDMS. Actually, the graphene/(0.1 mm) Ni