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A novel strain sensor based on graphene composite films with layered structure

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ABSTRACT

The use of graphene for strain sensors has attracted enormous attention due to its prominent mechanical and electrical properties. In this paper, we report on the preparation and characterization of a novel type of strain sensor based on graphene composite films with layered configuration. Highly reliable and sensitive composite films strain sensors based on graphene were produced from solution processed graphene flakes by spray coating method. The layered strain sensor which could sustain a large tensile deformation (25% strain) demonstrated high sensitivity to mechanical strain with gauge factors of 6–35. And the sensitivity of this type of strain sensors can be tuned over a relatively wide range of values by adjusting the deposition parameters. What's more, the layered composite films are more durable compared with the fragile pure graphene films. In addition the main mechanisms are investigated, resulting in theoretical models which predict very well the observed behavior.

1. Introduction

Strain sensors are ubiquitous smart devices which have a wide range of application where the mechanical deformation or structural change has to be detected, such as damage detection, characterization of structures, fatigue studies of materials and the internal activities in human body.

A common figure of merit to show the sensitivity of electrical shift to mechanical deformation is the gauge factor (GF) that relates the change in electrical resistance to the applied strain, through

$$GF = (\Delta R/R)/\varepsilon \qquad (1)$$

where $\Delta R/R$ is the normalized electrical resistance variation, and ε is the mechanical strain.

Traditional strain sensors are fabricated by employing various metals and semiconductors. The metal based strain sensors, relying on the geometrical change of conduction path, have GF in the range of 2–5 [1,2], and represent a reliable and well-established technology [3]. Other strain sensor types (semiconductor), such as silicon strain gauges, exploit the piezoresistive effect of the material and offer gauge factors larger than 100 [3]. This type of sensor, however, is more fragile and only designed for little straining. Along with the relentless pursuit of novel type of strain sensors with higher sensitivity, lower cost, and easier use, different candidate materials have been developed including low-dimension carbons [3–16]. Carbon nanotubes (CNTs) and graphene are two examples applicable for strain sensors which have attracted enormous attention in recent years due to their remarkable mechanical, electrical, piezoresistive and other physical properties. CNTs have been shown to have extremely high gauge factors up to 2900, which is 1 order of magnitude higher than silicon based strain sensors [17,18]. In comparison, graphene based strain sensors have lower sensitivity [19–21]. However, compared to CNTs with the quasi one-dimensional structure, graphene is an ideal two-dimensional structure thus has advantages in scalable devices fabrication via top-down approaches, which is compatible with existing fabrication technology [18,22]. In addition, the high price as well as the availability of large scale industrial production hinders the usage of CNTs compared to low priced graphene.

Graphene is a single layer of carbon atoms densely packed in a hexagonal lattice that was thought not to exist in its freestanding form until obtained by the group of Geim in 2004 [23]. Structural and electrical characteristics of graphene include a large surface area, electrical and mechanical properties that make it a promising smart strain sensor material. In addition, graphene known as the truly two-dimensional gapless semiconductor and the strongest material ever measured, can sustain up to 25% in-plane tensile elastic strain [22]. For perfect graphene, its electrical conductivity could change under strain induced structural deformation thus this piezoresistive effect can be used for strain sensing applications.

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Attributed to its piezoresistive effect, graphene strain sensors with gauge factors of 0.55 and 6.1 have been demonstrated [20,21]. The piezoresistive sensitivity of perfect graphene is low due to its weak electrical conductivity response upon structural deformation. New types of strain sensor devices based on graphene with higher sensitivity, fortunately, can be achieved due to other different piezoresistive sensing mechanisms besides structural deformation. Fu et al. fabricated the strain sensor devices using CVD-grown graphene with higher sensitivity (GF $\sim$ 151) [24]. Zhao et al. achieved nanographene strain sensors with gauge factor over 300 [19]. They put forward a charge tunneling model to explain the piezoresistive characteristics of nanographene films. Marek Hempel et al. used a sprayed solution to make high performance strain sensors based on layered percolative films of graphene with gauge factor over 150 [3]. The model of percolation networks was used to explain the properties of the film. Further, Li et al. made graphene woven fabrics with the gauge factor of 10^3 under 2–6% strains and 10^6 under higher strains [25]. The exceptional property was explained through the fracture model of graphene woven fabrics. However, one possible route to harnessing the fascinating properties of graphene for applications would be incorporate graphene sheets in a composite material. Recently there is an increased interest in the area of strain sensing in structural health monitoring using novel polymer nanocomposites due to the distinct advantages of the polymer and graphene. Alternatively, graphene/epoxy composite has been developed in order to increase the sensitivity of graphene-based strain sensors. The electromechanical response from graphene composites showed the gauge factor as $\sim$11.4, with the range of 1000 microstrain [26].

The shortage of graphene growth and patterning techniques, however, has become a challenging issue hindering the application of graphene based strain sensors. To the best of our knowledge, most of the reported fabrication processes for graphene devices are mainly based on CVD method [9,14,19,20,24,25], in which hours of graphene growth, transfer and patterning are needed. The gauge factor obtained by these approaches compares favorably with metal based strain gauges, but this improvement comes at the cost of higher complexity of manufacturing those graphene based strain gauges. The CVD process is highly energy-consuming and the use of high temperatures makes the integration of graphene into practical devices complicated, especially on flexible substrates [27]. It is necessary to seek other methods to make large-scale high-sensitivity graphene strain sensors. In addition most of the graphene based strain sensors are only designed for litter strain (<10%) [3,9,14,16,19,20,24–26], which would seriously hinder the application of the devices. What's more, to some extent, the overall performance for the traditional graphene/polymer composite material can be dominated by matrix properties rather than the intrinsic properties of graphene [2]. Therefore, it is necessary to develop novel sensors to reduce the possible impact from polymer matrix and take the advantage of the intrinsic characteristics of graphene. And the graphene films are extremely fragile and difficult to be used for practical applications. To the best of our knowledge, no reports exist for strain sensors that combine low stiffness, high durability, high gauge factor (tunable sensitivity), high deformation behavior with the potential for simple and cheap fabrication. Moreover, the mechanism for graphene strain sensors is still not understood clearly. A detailed investigation and experimental demonstration of graphene based strain sensors are quite important of the exploration of the future applications.

In present work, we have developed a novel type of strain sensor that combines cheap, facile and scalable production with high sensitivity. The strain sensor is based on graphene composite films (a graphene film covered on a polymer film) with layered structure. And it was prepared by sandwiching a polymer layer between a graphene layer and the substrate. The strain sensor was fabricated on the solid substrates, using spray coating method with a good dispersion of graphene solution. Here, in order to characterize the performance of the strain sensor more clearly and obviously, the thin and stretchable rubber was chose as substrate material. In practical application, it can be a wide variety of substrates (i.e. concrete, cement, toughened glass, iron and steel). And Styrene-Acrylate emulsion was used to form a polymer film between graphene and substrates by spray coating. Selection of Styrene-Acrylate emulsion was based on its unique properties such as good optical transparency, flexibility and green environmental protection. In addition, graphene can be closed integrated with the substrate material as the emulsion acted as an effective binder. The spray coating is a painting technique where a spraying device based on forced air is used to apply the coating material through air onto the substrate surface [28]. Compared with other deposition methods, spray coating can be carried out in preparation of films on large and even complex-shaped surface. It is fast and low-cost with simple process which is ideally suitable for mass production. In addition, compared with existing strain sensors, the sensitivity of this type of sensors can be tuned over a wide range of values by adjusting the deposition parameters. The electrical models of the graphene based strain sensor were derived and verified based on the strain testing. The models are useful for designing graphene strain sensor systems. The described novel strain sensor has several advantages over existing strain sensors, such as compatibility with a wide range of materials, ease of deposition, low stiffness, high durability, tunable sensitivity, high strain endurance (up to 25%). Based on the above, this work has the potential for improving existing strain sensor technology and open up new fields of application.

2. Experimental

The graphene aqueous dispersion (Fig. 1a) was prepared by sonicating a mixture of graphene raw materials (50 mg, C750, XG Science Inc., USA) and a surfactant Polyvinylpyrrolidone (PVP, 1 mg, Sinopharm Chemical Reagent, China) in deionized water (100 mL). In addition, anhydrous ethanol was used to improve the wettability between the graphene dispersion and the rubber substrate (store-bought, natural rubber with the thickness of 0.3 mm). Styrene-Acrylate Emulsion (Acronal PS 608 ap, BASF SE, Germany) supplied by BASF was used as an effective binder to protect the graphene layer. Styrene-acrylic emulsion is a copolymer of styrene and acrylate, which styrene replacing methylmethacrylate partly in polymerization process. Leveling agent (Zonyl FSN-100, DuPont, USA) was used to improve the emulsion layer flatness.

Spray coating was carried out with a commercial airbrush (Ustar CD-601, Taiwan) (Fig. 1b). In the spray process, the rubber substrate was heated by a hot plate set at 100 °C to accelerate the solvent evaporation and facilitate thin film formation. A fixed amount of Styrene-Acrylate emulsion (1 mL) was first deposited onto a 15 mm $*$ 90 mm rubber substrate. Then, graphene solution (0.5 mg/mL) was spray deposited on the emulsion layer to prepared graphene thin film. The graphene film with different distribution density of graphene (DD, g/m^2) was obtained by varying the volume of graphene dispersion from 2.5 mL to 8 mL. And DD was calculated based on the following formula

$$\mathrm{DD} = \frac{m}{A} = \frac{c \cdot V}{A} \qquad (2)$$

where m is the graphene content, A is the area of the substrate (15 mm $*$ 90 mm), c is the concentration of graphene dispersion, V is the volume of graphene dispersion. A big advantage of this parameter is that it can easily estimate the cost of production. In addition the values of the DD of the samples are listed in Table 1.