All-graphene strain sensor on soft substrate

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A B S T R A C T
We propose a transparent and stretchable all-graphene strain sensor that can detect various types of strain induced via stretching, bending, and torsion. The sensor is fabricated by introducing single-layer graphene as a force sensing material with a conductive film composed of graphene flake for the electrode. With the exclusive use of flexible materials, the completed strain sensor is fully flexible. Using a serpentine-shaped pattern for the single-layer graphene, the sensor is capable of stretching up to 20% with a high gauge factor (42.2). In addition, the sensor provides functional extension to bi-directional responses. This sensor can detect infinitesimal strain as low as 0.1% with a relative resistance change ($\Delta R/R_0$) of ~0.005. Finally, sensitive detection of strains induced via bending and torsion are successfully demonstrated.

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1. Introduction

Strain sensor as a component of soft electronics that is integrated in flexible substrate has recently attracted considerable attention with increasing demand in areas such as health-monitoring devices [1–5], artificial skin [6–9], and functionalized prosthetic limbs [10–12]. The sensor is required to exhibit a significantly large electrical change with applied strain, and to be highly stretchable and bendable in the general human perception range. Furthermore, materials employed in the sensor must be thin and light weight with high transparency for application in wearable electronic devices and their visual displays [13,14].

Until recently, attempts have been proposed to achieve flexible strain sensors satisfying the above requirements by introducing various nanomaterials [1–8,15–21]. Notably, graphene is a strong candidate due to its excellent optical, electrical, and mechanical properties [22]; although very few investigations have explored graphene-based strain sensors [13,19–21,23–28]. Zhao et al. demonstrated strain sensors based on piezoresistive nanographene films which displayed the ability to stretch up to 0.37% [23]. Bae et al. also reported CVD-grown graphene strain sensors with a gauge factor of 14 against tensile strain up to 7.1% [13]. Recently, scalable flexible strain sensors were fabricated using one-step laser scribing, showing a gauge factor of 9.49 with stretching up to 10% [27]. However, in this case the contact electrode for the sensor element suffers from inadequate flexibility and stretchability, since rigid metal electrodes have been introduced to incorporate a low resistivity. These electrodes represent a rapid increase in resistance, which is caused by the generation of irreversible defects in the metals following the application of strain in the range of a few percent [29], reducing the signal to noise ratio (SNR) for the output signals of the sensing channel. Thus, research is needed into optimize materials for fully flexible strain sensors, including conductive electrodes and greater sensitivity channels.

Here, we propose all-graphene strain sensor that introduces a single-layer graphene (SLG) channel for force sensing and graphene flake thin film (GFT) for the contact electrode, on stretchable substrate. Graphene is introduced for the channel and electrode because it is the only material that can satisfy all the requirements with its extraordinary optical, electrical, and mechanical properties [22]. The SLG channel is patterned with a serpentine shape for functional extension to bi-directional responses as well as enhancement of stretchability for the strain sensor. The GFTs are prepared for the highly-conductive electrode with a dense coating, the resulting strain sensor is fully stretchable on a PDMS substrate. Due to the excellent electromechanical properties of SLG, we achieve a high gauge factor (42.2) for stretching up to 20%. Our sensor can measure infinitesimal strain as low as 0.1% with distinguishable output signals. Finally, we demonstrate that the sensor can sensitively detect various types of strain induced via various mechanical deformations such as stretching, bending, and torsion.
2. Experimental details

2.1. Preparation and characteristics of SLG

Single-layer graphene (SLG) was obtained via a direct growing method using a thermal chemical vapor deposition (CVD) system built in our lab. As a catalyst, 25 μm copper foil (purity: 99.8%, Alfa Aesar Co.) was placed on a quartz holder and then heated to growth temperature (1000 °C) for 10 min in an argon atmosphere after pre-pumping down to 10⁻⁶ Torr. After an interval to allow stabilization of the substrate temperature, a mixture of methane (40 sccm) and hydrogen (10 sccm) gases was introduced into the quartz tube. Raman spectroscopy was used to confirm the typical resonance for the obtained SLG, which is a reasonably small intensity ratio (~0.23) of the G band (1587 cm⁻¹) to the 2D band (2682 cm⁻¹), and negligible D band (1340 cm⁻¹). The electrical resistance is estimated as 0.5–1.2 kΩ/sq from a standard bridge pattern for the transmission line measurement (TLM), with a width fixed at 20 μm and length varying from 5 to 250 μm.

2.2. Fabrication of the SLG channel

Conventional photolithography was utilized to pattern the SLG film grown on copper foil (Fig. 1a–c). AZ-5214E photo-resist (PR) was used. Using the PR as a hard mask, O₂ plasma etching (30 W, 20 s) was performed to achieve a serpentine shape in the SLG (Fig. 1d), which was introduced in order to enhance stretchability [30]. A layer of PMMA (Micro Chem. Co. 950 K, C4) 150 nm thick is coated on the patterned SLG to improve the adhesion energy between the SLG and the soft substrate (herein PDMS), since the adhesion energy of graphene on PMMA (66 mJ/m²) is larger than that of graphene on PDMS (41 mJ/m²) (Fig. 1e) [31]. After direct attachment of the PDMS on the PMMA-coated SLG (Fig. 1f), the copper foil below the graphene is removed via treatment with a FeCl₃ solution for 2 h (Fig. 1g). The graphene was cleaned using a diluted HCl solution and DI water several times, then followed by baking for 30 min at 85 °C (Fig. 1h).

2.3. Fabrication of GF electrodes

A film of graphene flakes (GFs) was introduced to function as contact electrodes on both sides of the SLG channel. Graphene nano-powder (Graphene Supermarket Co.), characterized by individual flake thicknesses of < ~3 monolayers, a lateral flake size of ~10 μm, and a surface area of 510 m²/g, was vigorously mixed in dimethylformamide (DMF). Sonication was then applied for 3 h in order to obtain a mixed graphene. The solution was then stirred with a magnetic bar for 1 h at 400 rpm. The GFs were coated using a spray coating method with a stencil mask (Fig. 1i). The distance between the nozzle and the substrate was ~15 cm. Spray deposition was performed on a heated substrate (85 °C) (Fig. 1j). After assembling the thin PDMS protecting layer, the sensor devices were finally completed by wiring them for two-channel electrical measurements (Fig. 1k) and casting the liquid PDMS layer which was then cured for 2 h at 85 °C under vacuum (Fig. 1l).

2.4. Characterization

Optical microscope (Nikon ME600L) and field-emission scanning electron microscopy (FE-SEM) (Hitachi S-4800) were used for the optical images for the sensor device. Raman spectrometer (NRS-3100) with 532 nm of excitation wavelength was used for characterizing the SLGs. The transmittance analysis was performed using a monochromator whose wavelength range is from 0 to 1600 nm and resolution is 0.2 nm. For the stretching tests, the samples were equipped on home-made stretching stage with micro-position controller whose resolution is ~7 μm. For the bending tests, the samples were fixed on a home-made bending stage equipped with a bending inductor. The NI precision system

Fig. 1. Fabrication processes of the all-graphene strain sensor. (a) SLG on Cu foil after growth. (b) SLG channel lithography with stencil mask. (c) SLG channel patterning with serpentine shape. (d) O₂ plasma etching of SLG. (e) PMMA coating the on etched SLG. (f) Attachment of PDMS on PMMA-coated SLG. (g) Cu etching with FeCl₃ solution. (h) Cleaning with HCl for the removal of Cu residue and DI water rinsing. (i) Attachment of stencil mask for spray-coating of GFs. (j) Spray coating of GFs on both sides of the SLG channel. (k) Wiring them for two-channel electrical measurements. (l) Assembling a thin PDMS protecting layer and casting of liquid PDMS. (A colour version of this figure can be viewed online.)
Fig. 2. Optical and SEM images of the SLG channel and GF electrodes in the sensor. Optical images of (a) the SLG channel and (b) the boundary between the SLG channel and the GF electrode. The red square in the insets describing the sensor schematic indicates each part of the optical images in the entire sensor device. SEM images showing (c) film morphology and (d) film thickness of the GF electrodes. Inset in (c) is high-resolution SEM image of GFs. Photographs of the completed sensor device displaying (e) stretchability, (f) foldability, (g) and torsional bendability. (A colour version of this figure can be viewed online.)

Fig. 3. Optical properties of the SLG. (a) Raman resonance of (bottom) the SLG and (top) the GFs on the PDMS substrate. The dotted lines indicate the D peak (1340 cm⁻¹), G peak (1587 cm⁻¹), and 2D peak (2682 cm⁻¹). (b) Comparison of the optical transmittance of the SLG on the PDMS/PMMA substrate with that of the substrate only. The PDMS-PMMA-SLG shows a transmittance of 86.9% at a wavelength of 550 nm, representing a loss of 2.5% at this wavelength relative to the substrate alone. (A colour version of this figure can be viewed online.)
SMU (PXIe-4139) and sourcemeter (Keithley 2400) were used for the collections of electrical data with two contact channels of the samples.

3. Results and discussion

The optical and SEM images for the completed sensor device, which is composed of an SLG channel and GFT electrodes on a PDMS substrate, are shown in Fig. 2. The SLG channel is patterned with a serpentine shape, which enhances the stretchability of the strain sensor. Fig. 2a displays a local portion of the SLG channel, which shows clear boundaries between the SLG and substrate. Fig. 2b displays an optical image of the boundary between the SLG channel and the GFT electrode. Each section of the optical image of the sensor device is corresponding to the area of the squares in the insets indicating the sensor schematic. As shown in Fig. 2c, the graphene flakes are densely connected to obtain high conductivity as a film with a thickness of ~120 μm (Fig. 2d). The natural softness and flexibility of the PDMS substrate allows the sensor device to be stretchable (Fig. 2e), bendable (Fig. 2f), and torsional bendable (Fig. 2g).

Note that the Raman resonance of the SLG and graphene flakes on the PDMS substrate retains the inherent original graphene resonant characteristics, as shown in Fig. 3a. The Raman shift for the SLG shows a typical single graphene layer with a reasonably low ratio of intensities (~0.32) for the G band (1586 cm\(^{-1}\)) to the 2D band (2683 cm\(^{-1}\)), without the feature of the D band. On the other hand, the result for the GFT exhibits a typical resonance pattern for multi-layered graphene (G/2D \(\geq 1\)), including many defects indicated by the noticeable D band intensity. Fig. 3b shows the transmittance of the SLG channel. It is measured as ~86.9% with a ~2.5% reduction by the SLG from the PDMS/PMMA substrate, whose transmittance is ~89.1%. This transmittance reduction is consistent with previously-reported values for SLG [32,33].

To measure the piezoresistive responses for applied tensile strain, the strain sensors were first put on the stretching stage. For size of the fabricated sensors (~7 cm), the sensors can be stretched by tensile strain of ~0.1% which is minimum resolution for stretching of the apparatus. Resistance changes due to gradual stretching were immediately checked using a sourcemeter. The resistance change were observed after the initial stretching of 1.4~3.2% which are corresponding to complete relaxation of inherent wrinkles in SLG formed during CVD growth [34,35] and transferring process to soft substrate [36,37]. The initial resistance (\(R_0\)) for the sensor was chosen as the resistance just before the resistance change begins. Fig. 4a shows a relative resistance change with application of a cyclic tensile strain of 5% along the electrode direction and consecutive measurements at 100 ms intervals with on and off durations of ~1 s. The initial resistance (\(R_0\)) of the sensor was measured at 23.4 kΩ. The resistance increases to 32.5 kΩ, which results in a relative resistance change (\(\Delta R/R_0\)) of ~0.39. This resistance change is caused by the change in total geometrical variation of the serpentine shaped SLG due to the applied tensile force. Fig. 4b displays resistance changes according to biaxial tensile strains from 0 to 20% where the stretching forces are independently applied to x- and y-directions in the sample plane (see insets for the measurement configuration). The strain resolution was 1%, which corresponds to a length increase of 0.7 mm in the sensor. Resistances were increased for both directed stretchings with the gauge factors (GF) of 42.2 and 71.4 for the x- and y-direction, respectively. The GFs were roughly estimated from GF = \((\Delta R/R_0)/\epsilon\) with assumption of linear tendency, where \(\Delta R\) is the resistance change and \(\epsilon\) is the applied strain denoting ratio of length change by stretching. It is noted that stretching of any film induces compression simultaneously along the vertical direction specified by the Poisson ratio as an elastic parameter. These geometrical variations reflected on resistance change with increase in length and decrease in width where the current path is along length direction. For the SLG case, resistance change is much dominant for the case where stretching is applied to the same direction of current path as shown in Supporting information S1. Introduction of a
serpentine shape for SLG provides a possible way to adjust GF for the bi-directional stretching. The serpentine shape in the sensor is composed of 40 segments of sheet resistor displayed in Supporting information S2. If we assume that stretching whose direction is parallel to current flow is mostly effected on the GF of the sensor, then it allows simple estimations of the GFs for bi-directional responses of the sensor. In the serpentine, 23 segments are actively working to increase resistance for x-direction of stretching. Here we neglect contributions for the rest 17 segments in which current flows vertically to the stretching direction. The GF with x-direction of stretching is estimated as 42.5 corresponding to 58% of intrinsic GF for SLG film. Similarly the GF for y-direction of stretching is also estimated as 57.3 with 31 segments whose stretched direction is parallel to the current flowing. GF for y-direction of stretching is under estimated comparing the observation value (71.4), but if we count on the assumption which doesn’t include geometrical variation details and strain localizations in the shape, deviation in the estimation from the observation could be acceptable to describe the role of the serpentine shape in sensor operation for bi-directional stretching. The sensor was worked up to 20% of strain without abrupt resistance change which is caused by structural breaking of SLG. Investigation of optical images also confirmed that the SLG keeps continuous surface for 0, 5, 10 and 15% of strain but is torn with 20% strain. (Supporting information S3). In addition, the sensor reliably detects the repeated loading and unloading of small strains as low as ~0.1%, resulting in a relative resistance change of ~0.005 (Fig. 4c).

When introducing the graphene flake thin film (GFT) for the contact electrode, the resistance variation of the electrode due to the applied strain should be considered, because the GFT also possesses piezo-conductive characteristics induced by variations in connectivity between individual GF particles. This characteristic makes the GFT an excellent candidate material for sensitive strain sensors [24,38]. However, the GFT is prepared in a dense form in order to obtain low resistance. The resulting resistivity is obtained as $-2.4 \times 10^{-2} \ \Omega \cdot m$ with repeating the spray coating method 200 times, significantly lower than that of the SLG ($-10 \ \Omega \cdot m$). Fig. 5a shows that the resistance of the GF electrode increases by only as little as 30% when a strain of 15% is applied, but this resistance increase is negligible in terms of contribution (less than 1%) to the total resistance change in the sensor. The optical images displayed in inset of Fig. 5a show a zero strain and stretching of 15%. In spite of being strained up to 15%, the film morphology of the graphene flakes remained close to its initial state; moreover, the GFT maintained constant resistance for repeated strains (10%) up to 1000 times (Fig. 5b). With the use of the GFT electrode, flexibility is extended to the entire device, as opposed to the practical device architecture for most soft electronics using the conventional metal, in which certain functional units are built on soft substrates. For comparison, a Pt film electrode can only withstand a strain of less than 3% before being torn (Supporting information S4). These defects are irreversible, and do not allow for consecutive operations (Supporting information S5).

Fig. 6a shows sensor response for compressive strain which induces curvature for the sensor. Bi-directional responses were evaluated with x- and y-direction strains where the applied current path was x-direction. The bending curvature ($k$) was defined as inverse of radius ($1/r$) with assumption for simplicity that the resulted bending makes a circular arc. The bending curvature driven by the compressive strain is displayed in Supporting information S6a with the apparatus for this measurement. For the compressive strain, resistance change for x-directed strain was 6 times larger than that for y-directed. Inset displays resistance changes with repeated compressive strains resulting bending curvature of $0–0.32 \ (cm^{-1})$ for both directions. Fig. 6b shows relative resistance change with the mechanical bending at a fixed point. The sensor provides a distinguishable linear response according to bending angle which increases the local strain focused on the bending center. The apparatus for this measurement is displayed in Supporting information S6b. The flexibility of the entire sensor makes it an easy fit for applications on human skin, as demonstrated in Fig. 6c. In this image, the sensor is attached to a finger joint to detect a bending motion of human finger. The measured value of $\Delta R/R_0 = 0.4$ indicates that the bending angle is $\sim20^\circ$, which corresponds to 5% of linear stretching of the finger skin. The sensor also enlarges its application area with the detection of torsion force (Fig. 6d), which can be generated with body motions such as twisting of the neck, wrist, waist, and foot.

4. Conclusion

In summary, we propose a strain sensor composed of graphene for both the sensing channel and contact electrode on a stretchable PDMS substrate. The sensor is fabricated using an SLG film as a force sensing material through direct patterning of the SLG on the copper catalyst. The contact electrode introduces a GF film that is densely prepared for high conductivity. With repeated spray coating (over 200 times), the resulting resistivity obtained is $-2.4 \times 10^{-2} \ \Omega \cdot m$, significantly lower than that of the SLG ($-10 \ \Omega \cdot m$), and thus is negligible in terms of contribution to the total resistance of the sensor. Using a serpentine-shaped pattern in the SLG to enhance stretchability, we not only achieved high gauge factors for bi-
directional stretching up to 20%, but also drove the controllable design parameters for bi-directional response of the sensor for the design of serpentine shape. The sensor can detect infinitesimal stretching strain as low as 0.1% with a relative resistance change ($\Delta R/R_0$) of ~0.005. To address the ability of our sensor to detect various types of strain, we presented sensor responses according to the bending and torsion forces. With the detection ability of various types of strain induced by stretching, bending, and torsion, which are required for sensors detecting human body motions, we suggest the use of stretchable all-graphene strain sensors for future applications in artificial skin.

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Appendix A. Supplementary data
Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2017.02.058.

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