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Novel Fabrication of Flexible Graphene-Based Chemical Sensors with Heaters using Soft Lithographic Patterning Method

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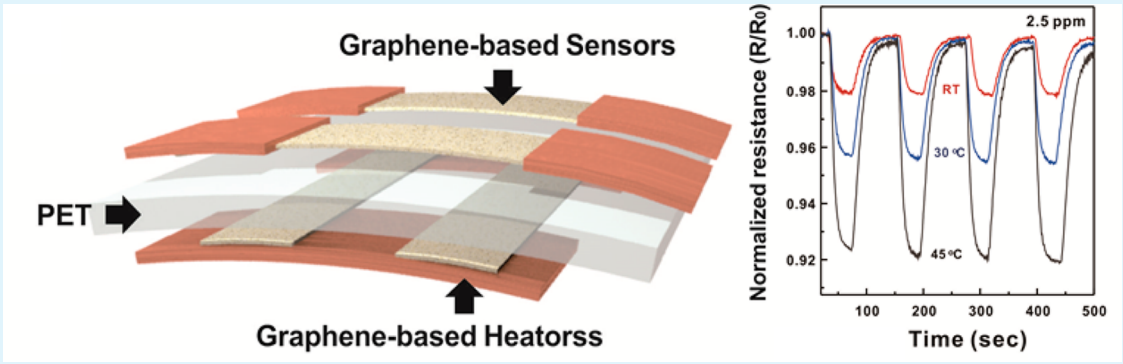

ABSTRACT: We have fabricated graphene-based chemical sensors with flexible heaters for the highly sensitive detection of specific gases. We believe that increasing the temperature of the graphene surface significantly enhanced the electrical signal change of the graphene-based channel, and reduced the recovery time needed to obtain a normal state of equilibrium. In addition, a simple and efficient soft lithographic patterning process was developed via surface energy modification for advanced, graphene-based flexible devices, such as gas sensors. As a proof of concept, we demonstrated the high sensitivity of NO_2 gas sensors based on graphene nanosheets. These devices were fabricated using a simple soft-lithographic patterning method, where flexible graphene heaters adjacent to the channel of sensing graphene were utilized to control graphene temperature.

KEYWORDS: *graphene sensor, graphene heater, soft lithographic patterning*

INTRODUCTION

Carbon-based materials such as zero-dimensional (0D) fullerenes,[1] 1D carbon nanotubes (CNTs),[2] and 2D graphene[3] have received significant attention for use in flexible electrical devices because of their excellent electronic, optical, and physical properties.[4−7] In particular, the low-cost fabrication processes for nanoelectronic graphene devices are featured in many recent studies. For example, Kang et al. reported flexible, transparent heaters composed of a graphene film using a roll-to-roll method.[8] Kim et al. developed a soft-lithographic patterning method for TCVD-grown graphene created via the modification of surface energy using hydrophilic molecules, and reported a simple capacitor based on graphene patterns using this patterning technique.[9] Many groups have studied the potential of carbon-based materials for chemical or biosensing applications using graphene nanosheets or their composites.[10] In spite of its high carrier mobility and low noise level, due to a lack of band gap, the on−off ratio of a graphene device is significantly low which limits its use in applications such as bio or chemical sensors. Herein, we discuss our graphene-based gas sensor, which was built with a graphene heater and utilizes a soft-lithographic patterning method. Single-layer graphene sensor patterns as well as multilayer patterns were transferred to a polyethylene terephthalate (PET) substrate. Graphene sensors with graphene-based heaters exhibit high sensitivity to chemical gases and a short response/recovery time when compared to sensors without heaters. Our fabrication method is comprised of simple and efficient soft lithographic processes without the complicated and time-consuming methods used in processes such as photolithography or wet-etching. This method can be effectively used to build future flexible transparent devices based on graphene nanosheets, and integrate carbon nanostructures for advanced hybrid devices such as logic circuits or chemical/bio sensors.

EXPERIMENTAL METHODS

Synthesis and Transfer of Graphene Sheets. 100 μm Cu foil was mechanically polished with metal polish paste for the graphene synthesis. The Cu foil was heated from room temperature to 1050 °C inside a thermal chemical deposition

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(TCVD) reactor. H_2 (6 sccm) and Ar (150 sccm) gases were introduced at a pressure of 1.9 Torr for 45 min. When TCVD growth was performed in a quartz tube reactor at the target temperature, methane (CH_4, 10 sccm) was introduced as a carbon feedstock with the H_2 gas for 20 min in order to synthesize graphene. The graphene layer on the Cu foil was then cooled to room temperature. After the graphene synthesis, a single layer graphene was spin-coated on the Cu foil by PMMA, and the Cu foil was removed by the copper etchant (dilute $FeCl_3$ solution in deionized water). The graphene layer was transferred onto SiO_2 (300 nm)/Si(001) via a transfer method similar to those mentioned in previous works.[11] The qualities of the TCVD-grown graphene were monitored by Raman spectroscopy and optical microscopy.

RESULTS AND DISCUSSION

Figure 1 shows a schematic diagram of the fabrication of graphene-based chemical sensors with graphene-based heaters

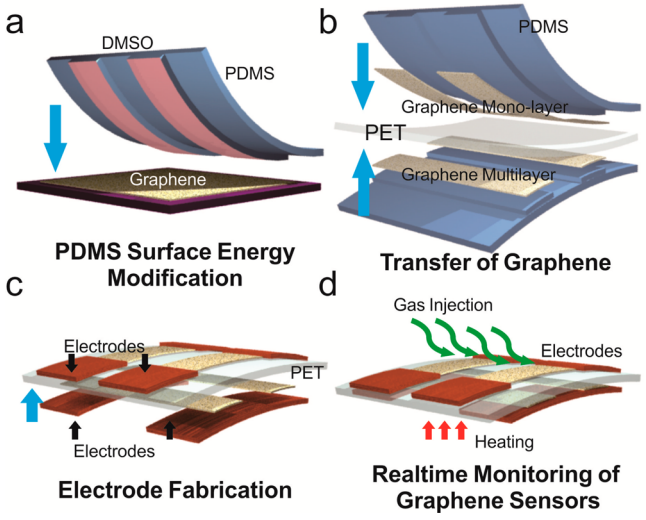

Figure 1. Schematic diagram of (a) the facile wet transfer and soft lithography patterning of graphene films. (b) Patterned graphene was transferred to the top and bottom of the PET film to produce the graphene sensor and heater. (c) Au/Ti electrode deposited on the end of the graphene line via sputtering, and (d) sensor properties measured via gas injection and heating.

(GSGH) using the soft lithographic patterning method.[9] Initially, as-synthesized graphene was transferred onto SiO_2 (300 nm)/Si(001) via PMMA-assisted wet transfer method. Dimethyl sulfoxide (DMSO) diluted in deionized water was vaporized at 200 °C and subsequently coated on prepatterned polydimethyl-siloxane (PDMS) mold for 1 min. DMSO molecules on the PDMS surface increased the surface energy of the PDMS stamp, which resulted in a greater adhesive force between the graphene and the PDMS stamp than the graphene and the SiO_2/Si substrate. After the DMSO-coated PDMS stamp was pressed on contact with the graphene/SiO_2/Si for 1 min, the graphene patterns was attached to the stamp (Figure 1a). When the stamp was recontacted to the PET film at 70 °C for 3 min, the interfacial force between the graphene and the PDMS stamp decreased, resulting in the detachment of the graphene patterns from the PDMS stamp and eventually transferred onto the PET film. Using this technique, monolayer and multilayer graphene patterns were formed onto both sides of the PET film for the fabrication of the GSGH (Figure 1b). Finally, the GSGH were completed by depositing Au/Ti (50 nm/10 nm) electrodes using thermal evaporation through a shadow mask (Figure 1c, d).

An ultraviolet−visible spectrometer (UV-2501PC) was used (Figure 2a) for the optical transmittance measurements of 1 × 1 cm^2 graphene patterns for chemical sensors and heaters. We transferred the graphene film to a PET substrate and prepared graphene patterns on the PET film using the soft lithographic technique (inset in Figure 2a). The transmittance of a graphene sheet on a PET substrate is ∼97.40% in the visible range, similar to results found for previously studied graphene films.[12] Because the opacity of an individual graphene layer is ∼2.3%, this transmittance value indicates that the graphene for the sensor channel is almost single layer. The graphene line pattern (500 μm in width), which was transferred to a PET film was found to have a higher transmittance value than the single graphene sheet. Although multiple graphene layers have high opacity, they are suitable for graphene heaters, which require high current through the heater channels. We controlled the number of graphene layers by repeating the wet-transfer process of a graphene sheet to a SiO_2 substrate, and transferred the graphene line-shaped patterns from SiO_2 to the backside of the PET film. Three graphene sheets grown via TCVD synthesis were used for heater channels. Compared to the 90.54% transmittance of GSGH based on graphene sheets without a patterning process, pattern-based GSGH show a higher transmittance value of 92.85%. Raman spectroscopy was utilized to examine the optical, structural and mechanical properties of graphene sheets for GSGH. The Raman spectra of a single graphene layer which is for sensors and multilayer which is used for heaters, both on SiO_2, are shown in Figure 2b. Typical D, G, and 2D band Raman signatures of a single graphene sheet were observed at approximately 1351, 1582, and 2687 cm^{-1}, respectively, and the intensity ratio (I_{2D}/I_G) was found to be 5.5. On the basis of the I_{2D}/I_G value, the 2D band position, the 2D band full-width at half-maximum (∼40 cm^{-1}), and a single Lorentzian fit of the 2D band, our TCVD-grown graphene is predominantly monolayer with a low defect level. Raman spectra from the multiple graphene layers could also be obtained by repeating this process (Figure 2b). The spectra of single and multiple graphene layers were normalized to compare the intensity ratio of G and 2D bands. As expected, the intensity ratio (I_{2D}/I_G) of multilayer graphene has a low value of 0.6, and the 2D band blue-shifted by approximately 12 cm^{-1}, corresponding to the differences between single and multiple graphene layers. These results stem from the change in electron bands caused by the interaction of graphene layers,[13] and are consistent with the presence of misoriented multilayer graphene.

Figure 3a−c shows an optical image and infrared pictures of the GSGH taken using an infrared camera while the graphene heaters were on. These images show that when a heating voltage of 20 V was applied for 10 s to a graphene-based heater that was initially at room temperature, only the graphene heaters reached a steady-state temperature of 58.3 °C. Line-shaped graphene patterns 100 μm in width were used for flexible heater channels; their narrow pattern size allowed us to apply localized heating to enhance the sensing performance. The time-dependent temperature of the GSGH was depicted in Figure 3d at three heating voltages. Graphene patterns for heaters were placed over a 2 × 2 cm^2 area. The temperature responses of the GSGH were measured via an infrared camera (Figure 3b, c). We applied 10, 15, and 20 V to graphene heaters

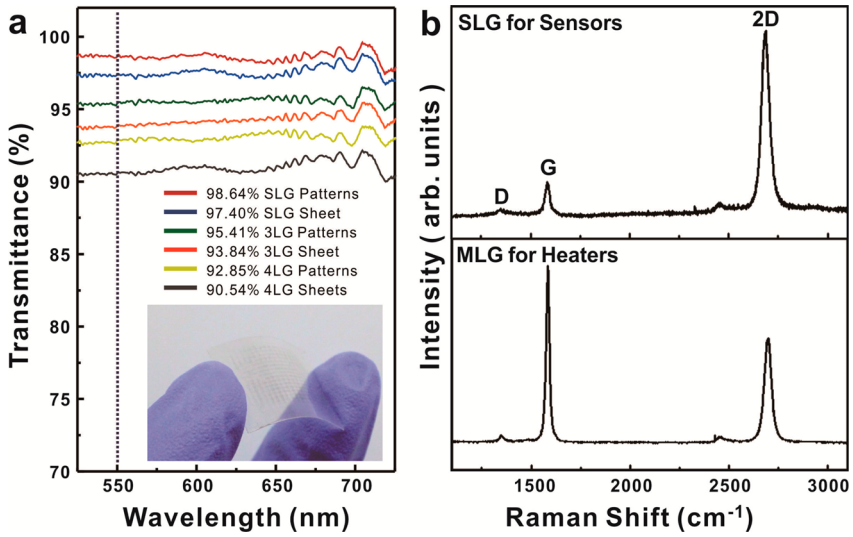

Figure 2. Optical properties and Raman spectroscopy with an excitation wavelength of 514 nm of graphene sheets for GSGH. (a) Transmittance measuring of patterned and nonpatterned graphene, and the optical image of flexible graphene-based chemical sensors with heaters on a PET film. (b) Raman spectroscopy of the single graphene layer for the sensors (top), and the multiple graphene layers used as heaters.

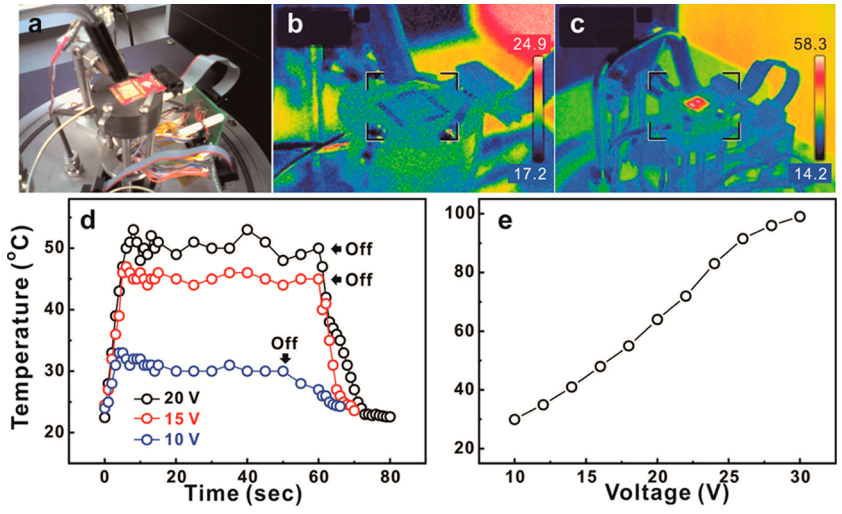

Figure 3. (a) Optical image of GSGH in the vacuum chamber. Representative thermal profiles of the GSGH graphene heater taken from a thermal infrared imaging camera (b) without heating current, and (c) while applying an input voltage. (d) Temperature profiles of GSGH with three heating voltages. (e) Temperature change as a function of the heating voltage.

of the GSGH using a DC power supply (4200-SCS parameter analyzer), and the current flowing through the graphene sensor was monitored. The time to reach a steady-state temperature increased, and the rate of temperature increase at the three heating voltages was found to be ~3.6 °C/s. The temperature change as a function of the heating voltage is also shown in Figure 3e; the range of temperatures is approximately from room temperature to 100 °C at 30 V. These results show that graphene-based heating patterns could be applied as transparent heaters capable of enhancing sensitivity to chemical gases, and reducing the response/recovery time of sensors.

As mentioned previously, a soft lithographic patterning method via the modification of surface energy was used to fabricate the graphene patterns on a flexible PET substrate. First, single graphene line patterns with 100 μm in width were transferred onto a 50 μm thick PET substrate and metallic electrodes were fabricated on the graphene patterns. Secondarily, multiple-layer graphene patterns for graphene heaters were also transferred to the back side of the PET film (Figure 4a). In this study, we demonstrated NO_2 gas sensors comprised of single graphene patterned for use as sensor channels, multiple layer patterned as heaters and a PET substrate. The resistance change of the graphene sensor was measured by various NO_2 concentrations from 2.5 to 100 ppm in dry nitrogen at room temperature, indicating that the sensitivity increased with increasing the NO_2 concentration, as shown in Figure 4 b. Figure 4c exhibits the time response of graphene-based NO_2 sensors at various temperatures, obtained by controlling the input voltage from 0 to 15 V between the electrodes of the graphene heaters. When the graphene sensors were exposed to the 2.5 ppm of NO_2 gas in dry nitrogen, the resistance decreased significantly with increasing the temperature. At 45 °C (applied voltage: 15 V), resistance change (R/R_0) of 8% of an initial resistance level, the response time of 24 s, and the recovery time of 50 s were observed. The resistance change and the recovery time of the GSGH are compatible with previous

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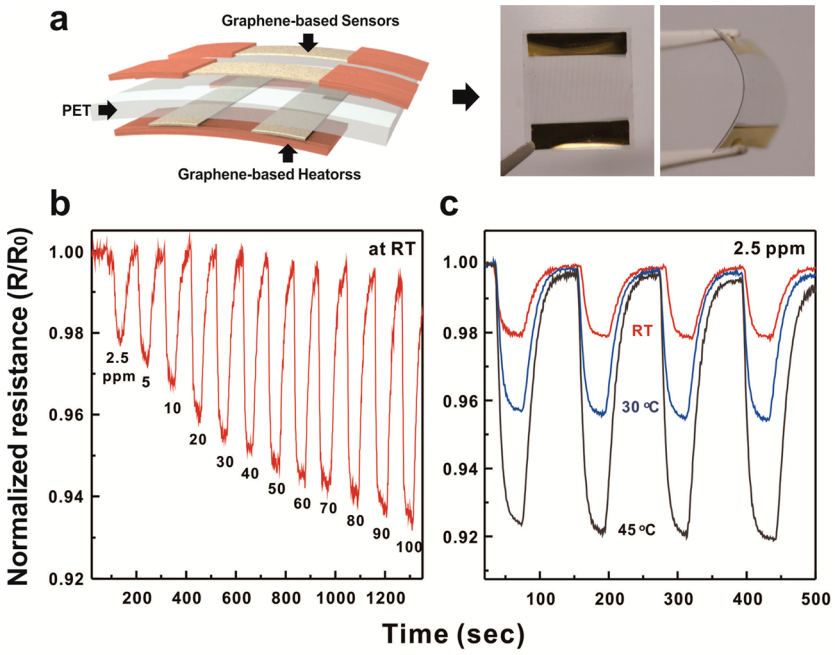

Figure 4. Real-time detection of NO_2 gas using GSGH. (a) Schematic diagram and photographs of GSGH. Resistance change rate of graphene-based NO_2 sensors at (b) various NO_2 concentrations (2.5−100 ppm) and (c) various temperatures (RT to 45 °C).

results on graphene-based gas sensors reported in the literature.[14−21] In general, the physical adsorption of NO_2 gas on the graphene channel is the dominant sensing mechanism; the resistance change of the GSGH is induced by a charge transfer between NO_2 gas molecules and graphene. At high temperature or high gas concentration, many NO_2 molecules are easily adsorbed or desorbed, resulting in a large resistance change for the GSGH.

CONCLUSIONS

In this article, we have developed a soft lithographic patterning and transfer process for graphene-based gas sensors with flexible heaters for the highly sensitive detection of specific gases. Graphene patterns for gas sensors and heaters were transferred and patterned to a flexible PET substrate via the simple and efficient soft lithographic technique with surface energy modification. Graphene patterns for sensors were locally heated using flexible graphene-based heaters adjacent to graphene sensors; detection sensitivity was enhanced at high temperatures because of the weak interaction between gas molecules and graphene. The response and recovery in the sensing process were rapid and reproducible. The ease of fabrication in addition to the excellent electrical and mechanical properties of graphene makes our graphene gas sensors combined with flexible heaters ideal candidates for advanced chemical- or biosensing applications.

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Notes

The authors declare no competing financial interest.

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