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Detection of Acetone Vapor Using Graphene on Polymer Optical Fiber

Hang Zhang¹, Atul Kulkarni², Hyeongkeun Kim^{1, 2}, Daekwang Woo², Young-Jin Kim^{1, 2}, Byung Hee Hong^{1, 3}, Jae-Boong Choi^{1, 2}, and Taesung Kim^{1, 2, *}

¹SKKU Advanced Institute of Nano Technology (SAINT) and Center for Human Interface Nanotechnology (HINT). Sungkvunkwan University. Suwon 440-746. Korea ² School of Mechanical Engineering, Sungkyunkwan University, Suwon 440-746, Korea

³ Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea

Recently, many studies have been focused on the development of fiber optic sensor systems for various gases and vapors. In the present study, an intrinsic polymer optical fiber (POF) sensor using graphene is described for the purpose of acetone vapor sensing for the first time. Observations on the continuous measurement of acetone vapor in dehydrated air are presented. The principle of operation of sensor transduction relies on the dependence of the reflectance on the optical and geometric properties of the sensitive over layered when the vapor molecules are adsorbed on the graphene film. For the same purpose the CVD synthesized graphene film was transferred on the POF end. The synthesized graphene film thickness was evaluated using atomic force microscopy (AFM), Raman spectroscopy and transmission electron microscopy (TEM). For the preliminary evaluation using volatile organic compounds, we evaluated the sensor performance for acetone. Upon the interaction of the sensor with acetone vapor, the variation in the reflected light was monitored as a function of the acetone concentration. The sensor response shows a significant change in sensitivity as compared with the POF probe without a graphene coating. The present sensor shows a satisfactory response upon exposure to various concentrations of acetone vapor from 44 ppm to 352 ppm. To the best of our knowledge, the use of graphene film along with POF for the sensing of volatile organic compounds has not previously been reported.

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non-reversible way. In all cases, the transduction produces

concentration of the gas or gases to be detected.

changes in the optical properties of this layer that modu-

lates the light guided through the fiber, depending on the

Earlier carbon nanotubes showed feasibility towards var-

ious chemical and bio sensing applications.⁵⁻⁸ However,

recently graphene has emerged as an attractive material

for sensing applications because of its unique properties.

Graphene is a zero band-gap semimetal with extraordinary

electronic^{9, 10} and mechanical properties.¹¹ Comprised of

a single layer of carbon with every atom on its surface,

graphene is a purely two-dimensional material and an ideal

candidate for use as a chemical vapor sensor.¹² It has been

reported that the adsorption of individual gas molecules

of our knowledge; the changes in the optical properties of

graphene upon its interaction with VOCs have not previ-

Keywords: Graphene, Polymer Optical Fiber, Vapor Sensor.

1. INTRODUCTION

In recent years, many studies have been focused on the development of optical sensor systems;^{1,2} these types of devices offer interesting advantages compared to electronic ones, for example their low weight, remote measuring capability, and electromagnetic immunity. Furthermore, they do not need to be biased for operation, so no electric signal is necessary, which eliminates any risk of explosion in the detection of specific volatile organic compounds (VOCs).

Several optical fiber VOCs sensors are based on gas spectroscopy; a light beam at a wavelength matching an absorption line of the gas of interest is guided through the fiber reaching the target. This interaction can take place in an intrinsic³ or extrinsic way.⁴ Another approach consists of the deposition onto the fiber of a sensitive layer which reacts with the gas or vapor in a reversible or

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ously been reported.

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^{*}Author to whom correspondence should be addressed.



Fig. 1. Schematic view of the graphene film coated polymer optical fiber sensor for acetone vapor sensing applications.

In this study, an intrinsic optical-fiber sensor is described. Continuous measurements of a volatile organic compound, acetone, in dehydrated air are presented. The transduction principle of the sensor is discussed, with an example of detection achieved with a sensitive cladding. The characteristics of the graphene monolayer films¹⁴ synthesized by chemical vapor deposition (CVD) were

evaluated using transmission electron microscopy (TEM) and atomic force microscopy (AFM). The sensitivity and response of the graphene film coated sensor were systematically evaluated.

2. EXPERIMENTAL DETAILS

A polymer optical fiber (POF) with 1×2 fiber coupler (50:50, Industrial Fiber Optics Inc., IF-562) is used for the detection of the reflected signal by providing the necessary connections between the light sources and sensing interface. The synthesized graphene film was then deposited on the distal end of the optical fiber as depicted in the Figure 1. The fiber end was cleaved with a precision cleaver and polished to obtain a uniform and plane cross section before deposition of the graphene films.

The large-area graphene layers were synthesized by the CVD of methane gas on Cu foils at 1000 °C.¹⁵ After the graphene film was spin-coated at 3,000 rpm with 5 wt% polymethylmethacrylate (PMMA) in chlorobenzene, the



Fig. 2. CVD synthesised graphene film (a) TEM image (inset SEM image), (b) Raman spectra of graphene film and (c) AFM image along with thickness profile.

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underlying Cu foil was etched by a 0.1 M aqueous $(NH_4)_2S_2O_8$ solution. Subsequently, the PMMA-supported graphene layer was transferred onto the polymer optical fiber distal end two times and dried in an oven at 60 °C. Finally, dilute acetone was used to remove the PMMA layer. The Raman spectra, after each monolayer graphene film transfer is depicted in the Figure 2(b). The thickness of the synthesized graphene film before transferring onto the polymer optical fiber end was measured using AFM and it shows that the thickness of the synthesized graphene film is around 0.8 nm which means transferred single layer of graphene film consists of >95% monolayers¹⁵ as shown in Figure 2(c).

A schematic view of the basic sensor design and experimental setup is shown in Figure 1. Reflectance measurements were performed by illuminating a standard polymer optical fiber (POF) with a white light source operating in the wavelength range of 400 to 800 nm and emitting an optical power of 2 mW. The diameters of the cladding and core were 1000 μ m and 980 μ m, respectively. The sensor output was retrieved using a Si photodiode detector (Thorlab, PDA36A), which has a spectral range of 350 nm to 1100 nm, and a digital multimeter (Keithley, 2700). The data recorded on a PC was used to analyze the sensor performance.

The experimental set-up used to evaluate the sensor performance towards acetone vapor is shown in Figure 1. The POF sensor appropriately coated with graphene is located in a flow cell (10×70 mm, I. D. × Length, respectively) for the VOC exposure measurements. Compressed dry air was used as the reference gas and carrier gas to transport the VOC, acetone, with different vapor concentrations into the flow cell containing the POF sensor. The total flow rate was kept constant at 1000 ml min⁻¹. The gas flow rate was controlled by a mass flow controller. The VOC vapors were generated by the bubbling method with a thermostatic flask containing the liquid analyte. The experiments were conducted at room temperature.

3. RESULTS AND DISCUSSION

The TEM image in Figure 2(a) shows that the graphene film is a high-quality monolayer. As the graphene monolayer was transferred two times one after another¹⁶ onto the distal end of the POF, the Raman spectrum of the similar bilayer graphene transferred on the Si/SiO₂(300 nm) wafer was recorded. The intensities of G and 2D band peaks increased together, but their ratios did not change significantly as seen in Figure 2(b).¹⁵ It indicates that even though the monolayer is stacked into few-layers, the original properties of the monolayer are still unchanged because the hexagonal lattices of upper and lower layers are oriented randomly, unlike graphite.¹⁵ The Raman spectra of the graphene layers did not show D peaks near 1350 cm⁻¹, indicating their high quality.^{15–19}

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Fig. 3. Schematic representation of the sensor transduction principle showing multiple reflections from the graphene film.

The principle of operation of sensor transduction relies on the dependence of the reflectance on the optical and geometric properties of the sensitive over layer when the vapor molecules are adsorbed on the graphene film, as depicted in Figure 3. This means that any change occurring in the features of the graphene layer, due to the chemical adsorption of a target analyte, would induce a consequent change in the film's reflectance. The relative reflected power in the interface between two media depends on the refractive index of the media, the incidence angle and on the polarization of the incident wave. When the light impinges perpendicular to the interface, the reflected power between two media with refractive indices n_1 and n_2 is

$$I = \left(\frac{n_2 - n_1}{n_2 + n_1}\right)^2 I_0 \tag{1}$$

where I and I_0 are the optical powers received from the sample and reference signal, respectively.

In the case of the graphene overlayer directly deposited on the fiber end, the reflectance (R_{graphene}) can be expressed according to the following expressions:²⁰

$$R_{\text{graphene}} = \left| \frac{r_{12} + r_{23} e^{-i\beta \text{graphene}}}{1 + r_{12} r_{23} e^{-i\beta \text{graphene}}} \right|^2$$
(2)

with

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$$r_{12} = \frac{n_{\text{eff}} - n_{\text{graphene}}}{n_{\text{eff}} + n_{\text{graphene}}}; \qquad r_{23} = \frac{n_{\text{graphene}} - n_{\text{ext}}}{n_{\text{graphene}} + n_{\text{ext}}};$$

$$\beta = \left(\frac{4 \cdot \pi}{\lambda}\right) \cdot n_{\text{graphene}} \cdot d \qquad (3)$$

where the coefficients r_{12} and r_{23} are the reflectivity at the fiber-graphene and graphene-vapor interfaces, respectively; $n_{\rm eff}$ is the effective refractive index of the fundamental mode of the optical fiber, $n_{\rm graphene}$ is the refractive index of the graphene film, $n_{\rm ext}$ is the refractive index of the external medium, λ is the optical wavelength and *d* is the thickness of the graphene film.

According to Eqs. (2) and (3), the variation in the refractive index of the graphene film and external medium, here acetone, will lead to changes in the reflectance at the fiber



Fig. 4. Response of the sensor for a fixed concentration of acetone vapor (352 ppm) using polymer optical fiber sensor tip with and without graphene.

film interface and, therefore, to changes in the sensor out-b put signal.

The typical transient optical response to acetone (352 ppm) for the POF sensor with the graphene film coating is depicted in Figure 4, along with that of the POF without the graphene coating. As observed, the presence of the graphene film leads to a significant improvement in the sensitivity by an average factor of 1.5 to 2, in spite of the extremely small thickness of the sensing graphene film of 2 to 4 nm. Unlike mass sensitive measurements, which always exhibit a decreasing response due to VOC adsorption, the fiber optic sensor measurements indirectly monitor the changes of the complex refractive index of the sensitive layers, taking into account not only the density effect, that should induce essentially an increase of the refractive index, but also the specific interactions between the sensing material and the analyte, leading to a substantial change of the polarizability. The graphene film coated sensor exhibits a negative variation of the reflectance for a given VOC, as



Fig. 5. Response of the graphene coated polymer optical fiber to varying concentrations of acetone vapor from 44 ppm to 352 ppm.

in the case of acetone. The measured vapor response is in agreement with the transduction principle discussed earlier, where the analyte molecules are located very close to the surface of the graphene film, which then provides a high sensitivity in terms of the reflected optical signal.

Figure 5 shows the recording of the change in the reflected optical power during successive injections of a mixture with different acetone concentrations ranging from 44 ppm to 352 ppm. It is clear that the greater the dilution of the acetone vapor, the smaller the variation in the reflected optical power. Furthermore, we hope that the lower detection limit may be further extended to a few ppm of acetone vapor with a more sensitive photo detector than that used in the present research.

4. CONCLUSIONS

Until now, many studies have been performed on the development of gas/vapor sensors with superior performance. However, it is difficult to make a comparison between them. One of the obstacles to such a comparison is that the investigations were carried out using diverse measurement apparatuses upon exposure to different compounds with various concentrations. The sensor performances, such as the detection sensitivity and time, are dependent on the measurement system, so that they can vary even for the same sensor. This paper presents a polymer fiber optic sensor for the measurement of acetone vapor with a graphene film synthesized by CVD as the sensing element. The sensor response was evaluated systematically using a simple lab developed bubbler based measurement system appropriate for evaluating the vapor sensing characteristics. The acetone concentration variation response the sensor had repeatable response. The sensor response is reversible, highly sensitive, and capable of sensing acetone vapor concentrations as low as 44 ppm with the existing setup.

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