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Sensitization of an optical fiber methane sensor with graphene

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ABSTRACT

We analyze the mechanism by which tin oxide can be utilized for the optical sensing of methane gas via surface adsorption and electromagnetic theory. Single-mode optical fibers with core diameters of 9 μm and cladding diameters of 12 μm were used. A 15 mm-long segment of each optical fiber was polished to the core via wheel side-polishing; the exposed fiber core areas were coated with graphene-doped tin oxide such that a novel graphene-based optical fiber methane sensor was fabricated. The experimental results show that the sensor exhibits excellent linear fitting and reproducibility, making it useful for the detection of low concentrations of methane.

1. Introduction

Methane is the main component of mine gas, and it can explode in air very easily; thus, it has been the focus of mining safety concerns. Currently, the main methods for detecting methane include catalytic combustible [1], semiconductor-based [2–4], electrochemical [4–5], and optical sensing [6] methods. Optical fiber-based methane sensors are suitable for use in harsh and dangerous environments due to their excellent electric insulation, strong anti-electromagnetic interference capabilities, and long-distance on-line monitoring. They also consist of elements with simple structures, and they are explosion-proof. Many researchers are investigating these types of sensors.

Tin (IV) oxide (SnO_2) is an n-type semiconductor, and it contains free charges. When light waves propagate inside SnO_2, absorption-induced loss can occur [7]. When methane molecules are in contact with the surface of a SnO_2 thin film, methane acts as a reducing gas because the work function of SnO_2 is larger than the dissociation energy of the adsorbed molecules. As a result, methane molecules eject electrons into SnO_2 and become positively charged [8]. Therefore, the number of charge carriers within the SnO_2 increases, resulting in enhanced conductivity and a higher refractive index, n.

Graphene is a single-layer, two-dimensional crystal in which carbon atoms are sp^2-hybridized to form hexagons that extend in a honeycomb structure. More broadly, carbon films with thicknesses of several atoms are also considered to be graphene. Graphene has many unique properties, such as a remarkable charge mobility [$\sim$10,000 $cm^2/(V{\cdot}s)$] [9], a large specific surface area [theoretical value $\sim$2630 $\frac{m^2}{g}$] [10], superior thermal conductivity [$\sim$5000 $W/(m{\cdot}K)$] [11], and low Johnson and 1/f noise values [12].

Scientists have discovered that pristine graphene can easily adsorb polar molecules; F. Schedin of the University of Manchester found that micrometer-sized sensors made from graphene can detect individual events when a gas molecule is adsorbed on or desorbed from the graphene surface. The adsorbed/desorbed molecules change the local carrier concentration in the graphene (as donors/acceptors), leading to changes in its physical parameters such as its conductivity. By detecting the change in output current as a function of the presence of foreign molecules under an applied external voltage, ultra-sensitive gas sensors could be prepared [13].

Researchers in South Korea, India, and Pakistan successfully grew graphene on the cross-section of a plastic, D-type optical waveguide with a large core diameter. The sensitivity of this sensing structure was found to be almost two orders of magnitude higher than that of traditional electronic thin-film sensors and traditional microphotonic sensors based on evanescent waves [14–17]. In 2012, a chemical gas sensor based on a graphene-micro/nanofiber composite structure was proposed. Through the attachment of micro/nanofibers to graphene, evanescent waves are coupled to the graphene waveguide plane. When gas molecules made contact with the graphene, the effective refractive index of

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each mode of the composite waveguide was altered, causing polarization attenuation [18–21]. Variations in chemical gas concentration could be detected by measuring the intensity changes in the output light signal. These results open up the possibility of utilizing graphene-based optical fiber waveguides as gas sensors and provide strong support for the effective combination of graphene and micro/nanofibers. Herein, thin graphene-doped tin oxide films were prepared and coated on side-polished optical fibers to fabricate methane sensors. The sensing characteristics and sensitivity of the as-synthesized methane sensors were investigated experimentally.

2. Sensing mechanism

Tin (IV) oxide is an n-type semiconductor, and electrons are its majority carriers. When light waves propagate inside SnO_2, absorption loss occurs. The electric vector satisfies the damped wave equation,

$$\nabla^2 E - \mu_0 \varepsilon_0 \varepsilon_r \frac{\partial^2 E}{\partial t^2} - \sigma \mu_0 \frac{\partial E}{\partial t} = 0 \quad (1)$$

where σ is the conductivity, ε_0 is the vacuum permittivity, ε_r is the relative permittivity, and μ_0 is the vacuum permeability.

After simplifying the light waves to plane electromagnetic waves, the optical admittance of the conducting medium can be derived from the wave Eq. (1),

$$N = n - jk \quad (2)$$

where n is the refractive index, k is the extinction coefficient, and

$$n^2 - k^2 = \varepsilon_r \quad (3)$$

$$2nk = \sigma / \varepsilon_0 \omega \quad (4)$$

From Eqs. (2) and (4), n follows from the following equation:

$$n^2 = \left(\frac{1}{2}\right)\varepsilon_r \left\{ \left[1 + \left(\frac{\sigma}{\omega \varepsilon_0 \varepsilon_r}\right)^2\right]^{1/2} + 1 \right\} \quad (5)$$

According to Eq. (5), the refractive index, n, increases with increasing conductivity, σ.

When methane molecules are in contact with the surface of SnO_2 thin films, the adsorbed molecules diffuse freely on the surface and lose their motion energy. These molecules eject electrons into SnO_2 and become positive ions. As a result, the number of charge carriers in the SnO_2 increases, leading to an increase in the conductivity and the refractive index, n. When the methane concentration increases, its transmittance increases. However, the resistivity of the pristine SnO_2 thin film is high; its carrier concentration is determined by the number of oxygen vacancies and is therefore difficult to control. Doping can improve the conductivity of SnO_2 thin films and help them maintain high transmittance in the visible light region. As a single-layer carbon system, graphene has a large specific area ($\geq$2600 m^2/g) and a high carrier mobility at room temperature. Graphene also displays a perfect quantum tunneling effect, a half-integer quantum hall effect, and permanent conductivity [22]. The doping of SnO_2 with graphene will result in a higher carrier concentration for SnO_2, thus giving rise to gas sensing thin films with enhanced performance.

3. Experimental

3.1. Preparation of the optical fibers

Single-mode optical fibers with core diameters of 9 μm and cladding diameters of 12 μm were used. A 15 mm-long segment of each optical fiber was polished to the core by wheel side-polishing. The polishing depth was monitored using a threadlet instrument. The optical fibers were immersed in an ethanol-containing tube and cleaned with an ultrasonicator to ensure that their surfaces were clean before they were coated with thin films.

3.2. Reagents and preparation of film coatings

Reagents: Tin (IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, AR), isopropanol (AR), and graphene (AR). Preparation process: Two aliquots of $SnCl_4 \cdot 5H_2O$ were weighed, and each samples was dissolved in 50 mL of isopropanol to prepare solutions with concentrations of 0.05 M; 0.05 g of graphene was added to one of the solutions. After the solutions were stirred at room temperature for 4 h with magnetic stirrers, the solutions were aged for 24 h. Then, the two solutions were drop-coated on the exposed areas of the abovementioned polished fibers. Each layer was allowed to air-dry before the next layer was applied; this procedure was repeated five times.

4. Results and discussion

The components of the optical fiber methane sensor setup are as follows: a graphene-doped, SnO_2-coated optical sensor, methane, nitrogen, a gas flow control device, a test gas chamber, and a bench top optical spectrum analyzer (MS9740A from Anritsu). In a typical experiment, gas samples with different concentrations (volume ratios) of methane were prepared by modulating the flow rates of methane and nitrogen. The built-in light source of the optical spectrum analyzer was set to a wavelength of 1550 nm, and the output intensities of the coated optical fibers (with SnO_2 or graphene-doped SnO_2) were measured at different methane concentrations.

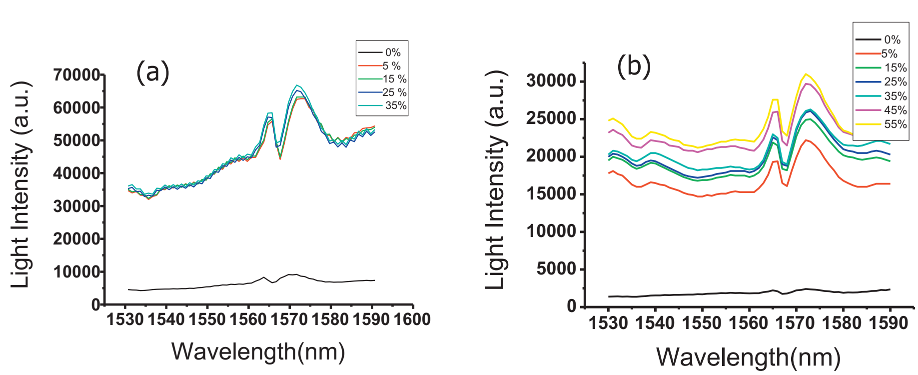

Fig. 1. a, Variations in the output light intensities of the SnO_2-coated fibers monitored using an optical spectrum analyzer at different methane concentrations. b, Variations in the output light intensities of the graphene-doped, SnO_2-coated fibers monitored using an optical spectrum analyzer at different methane concentrations.