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A disposable ozone sensor based on a grating-coupled glass waveguide coated with a tapered film of copper tetra-*t*-butylphthalocyanine

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Abstract

An integrated optical sensor specifically sensitive to ozone has been developed by vacuum evaporating a tapered thin film of copper tetra-*t*-butylphthalocyanine (CuPc^t) through a mask onto a slab waveguide made by K$^+$–Na$^+$ ion-exchange in glass. A pair of photoresist gratings fabricated on the waveguide offer the sensor a good long-term stability in optical coupling. The evaporated dye film composed of CuPc^t H-aggregates has a large absorption at 633 nm and a high-index of refraction relative to that of glass substrates. Therefore, the waveguiding mode excited with a 633 nm laser beam in the CuPc^t film-coved waveguide is highly attenuated. The CuPc^t film is very stable in air but ozone exposure at room temperature can result in a rapid and irreversible decoloration of the film. In the presence of a given concentration of ozone in the ambient air about the senor, the output light intensity was detected to linearly increase with time. It has been demonstrated that the sensor containing a 15 mm long and tens-of-nanometers thick dye film can detect 33 ppb ozone in air at room temperature.

Keywords: PIE waveguide; Tapered film of CuPc^t; Ozone sensor; Decoloration; High selectivity; Low detection limit

1. Introduction

Ozone is a very strong oxidizer and has a broad range of practical applications, including sterilization, deodorization and decoloration [1]. The ozone layer in the upper atmosphere absorbs ultraviolet (UV) light from the sun and therefore plays an important role in protecting human being from UV irradiation. However, ozone present in the indoor environment is an air pollutant and harmful to the respiratory system. In addition to the accidental leakage of ozone in the workshops where ozone is used, emission of ozone in air can easily occur in some places. The processes of UV irradiation and electric arc welding and cutting are generally accompanied with ozone generation. Therefore, the detection of ozone in air is of considerable interest. The ozone standard is given in America that the 8 h average concentration does not exceed 0.08 ppm [2]. Because low concentration ozone in air is colorless and odorless, the environmental monitoring of ppb-level ozone requires use of high-performance ozone sensors. To our knowledge, two types of ozone sensors are commercially available nowadays. One type of ozone sensors is based on metal oxide semiconductor conductance measurement [3,4]. The low-cost metal oxide semiconductor gas sensors, when being used for specific gas detection, are not adequately reliable because of their considerable cross-sensitivity. Another type of ozone sensor is based on the inherent ability of ozone to absorb light at 254 nm. The UV-absorption ozone sensor is highly selective yet expensive. The use of such sensors for ppb-level ozone detection is challenging because their sensitivity is proportional to the light-ozone interaction pathlength and a long path would be limited by the device size. These limitations would make such existing ozone sensors unsuitable for use in some cases.

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In the present study, integrated optical ozone sensors with a low detection limit, a high selectivity and a good stability have been developed using potassium ion-exchanged (PIE) glass slab waveguides locally covered with tapered thin films of copper tetra-*t*-butylphthalocyanine (CuPc^t). The PIE waveguide employs a pair of photoresist gratings for long-term stable input and output coupling. The CuPc^t film as the sensing layer is highly absorbing at 633 nm and highly refractive relative to slide glass substrates. With the use of a He–Ne laser as the light source the waveguiding mode in the dye film-covered PIE waveguide is therefore highly attenuated. The CuPc^t film is resistant to nitrogen oxide exposure but can easily react with ozone in air at room temperature. This reaction causes decoloration of the CuPc^t film and consequently decreases the guided-wave absorption of the dye film. Therefore, the output light intensity of the sensor would increase in the presence of ozone in the ambient air. For a given sensor, increases per unit time of the output light intensity are determined by ozone concentration in the ambient air. Owing to the irreversible reaction between the CuPc^t film and ozone, the present sensor is single-use, but this limitation is not serious because of dirt-cheap PIE waveguides.

CuPc^t as an important metallophthalocyanine derivative has been extensively studied in the form of the Langmuir–Blodgett (LB) film because it is highly soluble in nonpolar solvents such as chloroform and toluene [5,6]. Like its analogue of copper phthalocyanine (CuPc), CuPc^t also permits to form uniform thin films by vacuum evaporation. CuPc is well known as an organic p-type semiconductor, and it has also been used to fabricate ozone sensors based on the conductance measurement at an elevated temperature [7,8]. Such electric ozone sensor is sensitive to NO_2 to a considerable extent compared with the present IO ozone sensor containing a sensing layer of CuPc^t. Although ozone exposure can make a large variety of dyes decoloration, the selection of CuPc^t as the ozone-sensitive agent is based on that CuPc^t not only allows for easily fabricating stable and smooth thin film but can also specifically react with ozone in air at room temperature. In this paper, we describe in detail the fabricating process of the sensor, the characterization of the evaporated CuPc^t film and the investigation of the sensor response to ppb-level ozone.

2. Fabrication of the integrated optical ozone sensor

2.1. Preparation of PIE slab waveguides with a pair of photoresist grating couplers

Colorless soda-lime slide glass substrates with refractive index of 1.515 were obtained from Matsunami Glass Ind., Ltd., Japan. K^+-Na^+ ion-exchange was accomplished by immersing the substrates in molten KNO_3 at 400 °C for 30 min. After natural cooling to room temperature, the substrates were sufficiently washed with water. By using a pair of glass prism couplers and a linearly polarized He–Ne laser beam, the ion-exchanged glass substrates were investigated to be single-mode waveguides with a low loss ($\alpha < 0.5$ dB/cm). The effective refractive index of the transverse electric (TE) mode in these waveguides was determined to be $N_{TE} \sim 1.519$. That of the transverse magnetic (TM) mode is typically 2×10^{-4} larger than N_{TE} based on the modal birefringence measurement [9]. Prism couplers as discrete elements are unsuitable for integrated optical sensor application. We fabricated a pair of photoresist grating couplers on the PIE waveguides by standard photolithography. Prior to spin-coating photoresist, the hydrophilic waveguides were treated in hexamethyldisilazane ($((CH_3)_3SiNHSi(CH_3)_3$, Wako) vapor at 90 °C for 1 h. The treatment resulted in a CH_3-terminated monolayer on the glass surface that can enhance the adhesion between the photoresist layer and the substrate. The UV exposure of the photoresist layer was performed through a transparent glass photomask that contains two metal-film gratings with a periodicity of $d = 1$ μm. After development to dissolve the excessive photoresist layer into the developing agent, a pair of gratings, being 3.5 cm apart from each other, was replicated on the substrate. The gratings have a trough depth of 300–400 nm, as indicated by atomic force microscopy (AFM image not shown). With the use of the grating-coupling method a 633 nm laser beam was launched into the PIE waveguide at an angle of $\theta \sim 62.5°$ between the laser beam and the grating normal. From the equation $N = \sin\theta + \lambda/d$ the effective refractive index is determined to be $N \sim 1.520$, which is very close to that measured with the prism coupling method.

2.2. Vacuum evaporation of the tapered thin CuPc^t films on the PIE waveguides

CuPc^t powder was obtained from Wako Pure Chemical Ind., Ltd., Japan. CuPc^t thin film was deposited by vacuum evaporation on the waveguide region between two gratings. To taper the dye film and to protect the gratings from being covered with the dye, a glass mask with a rectangular window was used during evaporation. Tapering the dye film is for suppressing the scattering loss induced by an abrupt change of N at the stepped edges of a uniform film. The effective-refractive-index calculations indicate that a tapered film can result in a gradual increase (or decrease) of N when the guided mode propagates into (or out of) the waveguide region covered with the tapered film [10]. Therefore, with a tapered film the scattering loss induced by non continuous changes of N in the mode-propagating path is avoided. Note that such scattering loss may not be a serious problem for low-index films but could be significant for high-index ones. Since refractive index of CuPc^t films is higher than that of glass waveguides, tapering CuPc^t films is therefore vital to successful fabrication of the sensor. Prior to the dye evaporation, the mask was mounted 4 mm below the substrate and its position was adjusted to make the window face the waveguide region between two gratings. To control the film thickness by controlling the dye amount to be evaporated, CuPc^t powder was dissolved in alcohol and a given amount of the solution