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Fabrication and Characterization of DBR Porous Silicon Chip for the Detection of Chemical Nerve Agents

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Abstract

Recently, number of studies for porous silicon have been investigated by many researchers. Multistructured porous silicon (PSi), distributed Bragg reflector (DBR) PSi, has been a topic of interest, because of its unique optical properties. DBR PSi were prepared by an electrochemical etch of P^{++}-type silicon wafer of resistivity between 0.1 mΩcm with square wave current density, resulting two different refractive indices. In this work, We have fabricated a simple and portable organic vapor-sensing device based on DBR porous silicon and investigated the optical characteristics of DBR porous silicon. DBR porous silicon have been characterized by FT-IR, Ocean optics 2000 spectrometer. The device used DBR PSi chip has been demonstrated as an excellent gas sensor, showing a great senstivity to a toxic vapor (TEP, DMMP, DEEP) at room temperature.

Key words : Bragg, Sensor, TEP, DMMP, DEEP

1. Introduction

Photonic crystals of porous silicon (PSi) have been a topic of interest because of their unique properties which led to their use in chemical and biological sensors [1-4], biomaterials[5], and optical devices[6]. PSi has a large surface area and exhibits convenient surface chemistry, as well as their optical signal transduction capability. Rugate PSi having rugate structure such as rugate PSi have been recently investigated in terms of their possible applications[7-12]. Distributed Bragg reflectors (DBR) PSi exhibits unique optical properties providing the reflection of a specific wavelength in the optical reflectivity spectrum. DBR structured porous silicon having the photonic structure of a Bragg filter has been generated by applying a computer generated square current density waveform.

Recently, organophosphorus nerve agents have been a matter of international concern. 'Nerve agent' or 'nerve gas' represents a generic name for a class of highly toxic compounds. Some organophosphorus compounds (e.g., sarin, soman, tabun, diisopropylfluorophosphonate (DFP) and organophophorus surrogates such as dimethyl methylphosphonate (DMMP), triethylphosphate (TEP), and diethyl ethylphosphonate (DEEP), simulants for G-type nerve agent, displaying extremely toxic activity are widely used as chemical nerve agent weapons and pesticide toxins[13]. Many studies have been done for determination and safe destruction of several nerve agents. Nevertheless, the best way is under process. Here, we discovered the easy way to find nerve agents using the DBR porous silicon chip[14] and fabricated nerve agents vapor sensing device[15-16].

2. Experimental Section

2.1. Materials

Degenerately boron doped P^{++}-type Si wafers with resistivities in the range 0.8~1.2 mΩcm, with<100>orientation, and of a 500~550m thickness were purchased from Siltronix, Corp. Aqueous HF (48%), ethanol (99.9%) cupric sulfate, TMEDA (N,N,N',N'-Tetramethylethylenediamine), TEP (Triethylphosphate), DMMP (Dimethyl methylphosphonate) and DEEP (Diethyl ethylphosphonate) were obtained from Sigma-Aldrich, Inc. All gases were high purity grade.

2.2. Preparation of DBR PSi.

DBR Porous Si sample were prepared by anodization

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of the degenerately doped P^{++}-type Si wafers in ethanolic HF solution (3:1 v/v 48% aqueous HF : ethanol) in a two-electrode configuration using a platinum mesh counter-electrode. Silicon wafer with an exposed area of 1.2 cm^2 were contacted on the backside with a strip of aluminum foil and mounted in a teflon etching cell. Galvanostatic anodization was performed in the dark. Low current layers were etched by applying 5 mA/cm^2 for 90 s and high current layers were etched by applying 50 mA/cm^2 for 3 s. After etching, the samples were rinsed with ethanol and then dried under N_2 gas.

2.3. Instrumentation and Data Acquisition

The anodization current was supplied by Keithley 2420 high-precision constant current source which is controlled by a computer to allow the formation of PSi multilayers. Optical reflectivity spectra were measured using a tungsten-halogen lamp and an Ocean Optics S2000 CCD spectrometer fitted with a fiber optic input. A tungsten-halogen lamp was focused onto the center of DBR PSi surface with a spot size of approximately 2 mm^2. Reflectivity data were recorded with a CCD detector in the wavelength range of 400~1000 nm, with a spectral acquisition time of 60 s. The reflected light collection end of the fiber optic was positioned at the focal plane of the optical microscope. Scanning electron microscope (SEM) images were obtained by a cold field emission scanning electron microscope (FE-SEM, S-4700, Hitachi).

2.4. Synthesis of Copper (II) Catalyst.

Copper (II) catalyst was obtained from the reaction of cupric sulfate with TMEDA. TMEDA (1.16 g, 10 mmol) was added to 2.5 g (10 mmol) of cupric sulfate dissolved in 30 mL of methanol. the reaction was allowed to proceed overnight (10 h). the blue color product was dried under vacuum.

2.5. Surface Derivatization of DBR PSi.

Suface derivatization of DBR PSi were prepared by dropwise of copper (II) catalyst solution, which was dissolved in water, onto the surface of fresh DBR PSi sample. Then, the reaction was allowed to dry solvent thoroughly.

3. Result and Discussion

Figure 1 showed some organophosphorus nerve agents and organophophorus surrogates.

The schematic diagram for the preparation of nerve agents sensor chip containing copper(II) catalyst in DBR PSi was illustrated in Fig. 2. Copper(II) catalyst solution was spin-casted onto the surface of DBR PSi. When the surface of DBR PSi were derivatized with copper(II) catalyst, the vapor of organophosphorus surrogates (DMMP, DEEP, TEP) were ready to adsorb through coordination bond between the oxygen of phosphorous and copper(II) catalyst of the surface of PSi.

Reflection spectrum was obtained by using Ocean Optics S2000 CCD spectrometer and exhibited a reflection resonance at 583 nm.

When DBR PSi chips were exposed to the vapor of organophosphorus, the reflectivity in reflection spectrum exhibited a red shift, indicating that the pore layer of DBR PSi chips filled with organophosphorus vapors and resulted in the change of refractive indices.

Figure 4 displayed the reflectance spectra under the exposure of the vapor of TEP, DMMP, and DEEP,

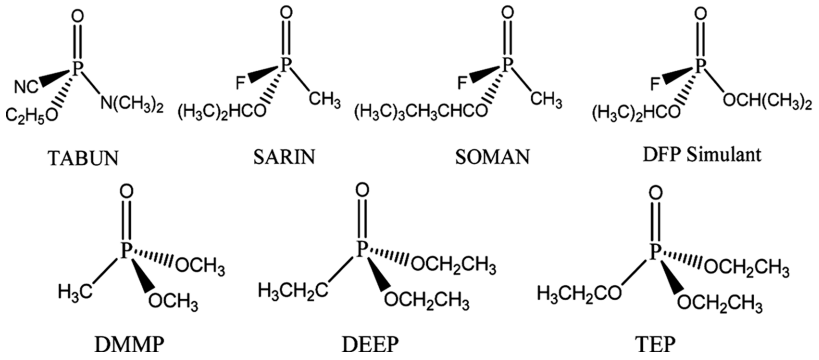

Fig. 1. Structures of highly toxic nerve agents and organophophorus surrogates.

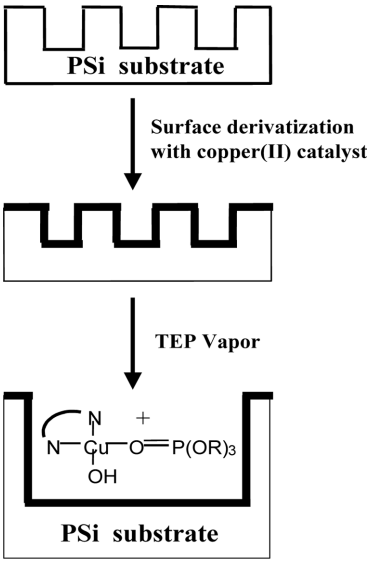

Fig. 2. Schematic diagram for the fabrication of DBR PSi sensor chip indicating the interaction between the copper(II) catalyst and organophosphorus surrogate (TEP) inside of pore of DBR PSi.

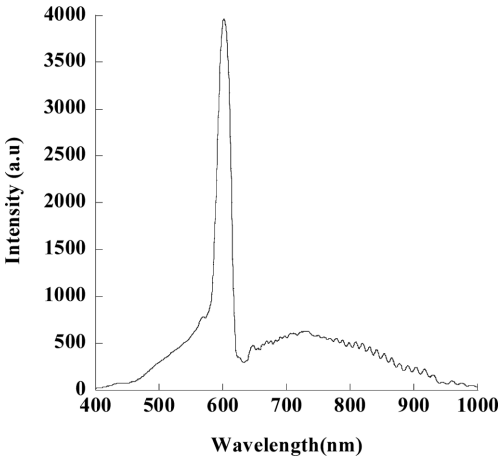

Fig. 3. Reflection spectrum of DBR PSi sensor chip including copper(II) catalyst.

respectively. DBR PSi sample is exposed to a flux of nerve agent in air with a flow rate of 5 L/min. When the PSi sample is exposed to analytes in the gas phase, capillary condensation causes an increase of its effective refractive index by the replacement of air to liquid of analyte. The positions of reflection peak were monitored as a function of time after an analyte vapor was introduced. Diffusion and capillary condensation effects

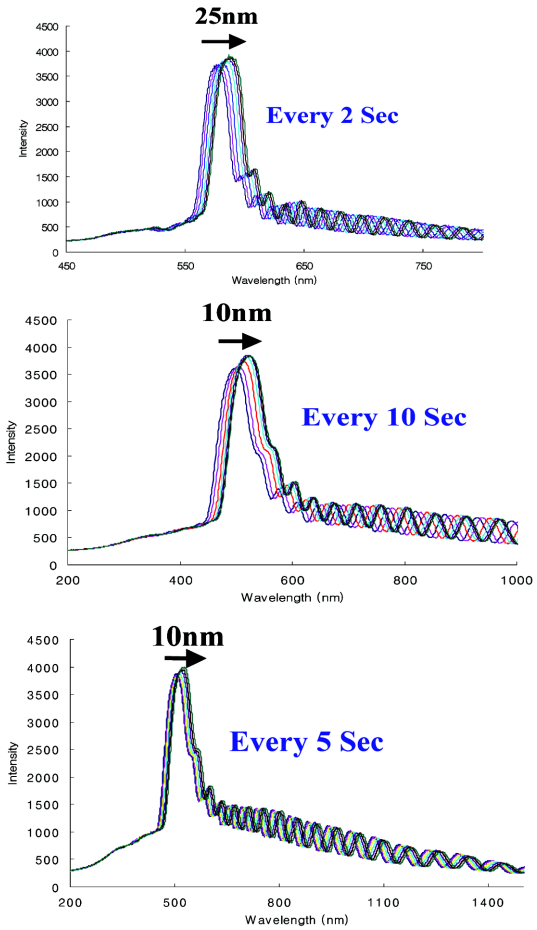

Fig. 4. Change of reflectance spectra under the exposure of the vapor of organophosphorus surrogates (from top TEP, DMMP, and DEEP).

determined the response, because the pressure of analyte is constant.

The amplitude of the red shift of the reflection peaks depends on both refractive index and vapor pressure of the analyte condensed in the sample as well as the surface characteristics including hydrophilicity and varied pore diameter. It should be noticed that TEP shows larger red-shift even its vapor pressure (135 ppm) is lower than DMMP (290 ppm).

4. Conclusion

In this work, we have presented a detailed research on DBR PSi which can detect nerve agent (sarin, soman, tabun, DFP, organophophorus surrogates. etc).

The DBR PSi with TEP vapors has shown good sensitivity, high stability and reversibility.

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