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Fabrication of ozone sensors on porous glass substrates using gold and silver thin films nanoislands

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ABSTRACT

Porous glass has a vital role to enhance the optical properties in the sensors. In this paper, we reported a simple sensor developed on a porous glass substrate. Initially, we simulated the design in COMSOL Multiphysics and MATLAB environment. Using the simulation results as guidelines, we fabricated the porous formation on a glass plate by immersing in the HF (Hydrogen Fluoride) solution. Then, we fabricated the sensor on the porous glass plate with gold, silver nanoparticles and characterized the sensor using UV- Visible Spectroscopy and AFM. The outcome of this study revealed that gold and silver thin film nanoislands coated on the porous glass substrate exhibited high-performance enhancement in terms of optical, sensitivity, resistivity and surface morphology characteristics towards ozone sensing than the gold and silver thin film nanoislands coated on a non-porous glass plate. Further, of the two binding agents and two metallic nanoislands, the APTMS (Aminopropyl trimethoxysilane) based gold thin film nanoislands coated on the porous glass substrate exhibited better ozone sensing property than the other three sensors.

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1. Introduction

Porous silicon (PS) has its importance due to unique morphological features widely used in MEMS device applications. Many researchers extensively investigated and reported on the porous formation and its enhancement properties in various applications [1–6]. Huang et al. fabricated porous polyelectrolyte membrane coated thin-core fiber modal interferometer for ammonia sensing and confirmed that porous structure was found to be beneficial for diffusion of ammonia molecules in the detection range of 1–260 ppm [1]. Zhu et al. fabricated porous ZnO nanosheet film gas sensor for high sensitivity and fast response to acetone and ethanol at the operating temperature of 400 °C and H₂S at 200 °C [2]. Balde et al. demonstrated humidity sensors with anodic aluminium oxide (AAO) film using potentiostatic anodization method and characterized the morphological and electrical parameters [3]. Izumi et al. fabricated porous glass based NO₂ sensor with an oxidizer for measuring NO using a color agent [4]. Wang et al. developed chemical vapor sensor probe with alignment-free optical micro-resonator using porous glass microsphere (PGM) having features such as integrated structure, miniaturized size and reflection mode of operation [5]. Chen et al. investigated sensitivity enhancement, linearity and mechanism of AAO humidity sensor from low to high relative humidity (RH) using a NbFeB magnet [6]. Ensafi et al. proved that copper on porous silicon was found to be selective for electrochemical hydrogen peroxide (H₂O₂) and has many important characteristics such as low







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detection limit, good signal reproducibility, fast response and long-term stability with low fabrication cost [7]. Over et al. investigated on polystyrene particle (PS) diffusion or dispersion in a glassy porous matrix and analyzed the important steps to achieve pure homodyne conditions [8].

In recent years, sensing technologies have been improved with different parameters such as nature of the material, types of sensing techniques, transduction principles and cost of the sensor. Several researchers had reported on improving the performance and the functionality of ozone sensors [9–16]. Agarwal et al. investigated the influence of metal roughness on surface plasmon resonance performance and explained the degradation of the sensor performance with respect to increase in thickness [9,10]. Belaqziz et al. developed the SnO₂ thin films that could detect the ozone 3.5 times at room temperature, using triton surfactant as a dispersant [11]. Hattori et al. fabricated Sn doped indium oxide thin films by dip-coating method that could detect 1 ppm of ozone at 360 °C temperature [12]. Ebeling et al. developed the ozone sensor and studied its response with respect to flow velocity and atmospheric ozone concentration [13]. Korotcenkov et al. fabricated SnO₂ thin films sensors that exhibited a higher sensitivity of ozone with shorter recovery time [14]. Atashbar et al. developed thin films using sol-gel and RF sputtering techniques, which exhibited high sensitivity towards ozone than the coalescent and dense grains observed in sputtered thin films [15]. Carotta et al. analyzed the ZnO properties that could detect ozone at a low concentration of 10 ppb than the WS10 [16]. Wagner et al. developed indium oxide sensors that could detect ozone up to 20 ppb and the sensor response was found to increase with humidity and illumination of blue light, due to the formation of the hydroxyl group on the surface [17]. Hersch and Deuringer developed a new method for detecting ozone using a galvanic cell having platinum electrode, neutral halide electrode and carbon anode, without any influence of external electromotive force [18]. Hansford et al. fabricated a solid tungsten oxide sensing element for ozone detection operating at the temperature of 530 °C, which was found to be suitable for profile determination of atmospheric ozone [19]. Muller et al. developed sensor for the detection of ozone with a variety of coatings and confirmed that the poly-butadiene sensor could detect ozone as low as 55 ppb. By operating the crystal at the higher harmonic frequency with suitable flow rate, the sensitivity of the ozone detector can be improved [20]. Lee et al. fabricated ozone sensor using disposable film and observed variations in the phosphorescence emission intensity on exposure with ozone gas and ozonized water, which could detect ozone concentration of 0.1 ppm [21].

In this work, we presented the APTMS (Aminopropyl trimethoxysilane) and PVA (polyvinyl alcohol) based ozone sensors using gold and silver nanoislands thin films on a porous glass substrate and compared the results obtained from our previous work reported in [22]. Section 2 describes the simulation and analysis of the proposed ozone sensors on exposure to ozone on the surface of the gold and silver thin films nanoislands. Section 3 describes the porous formation on a glass plate using the Hydrogen Fluoride (HF) and analyzed the characteristics through SEM and AFM studies. Further, Section 3 describes the fabrication of gold and silver thin films nanoislands using APTMS and PVA as binding agents. In Section 3.6, we discuss the characterization of the fabricated sensors using UV–vis Spectroscopy and AFM before and after ozonation, and the obtained results were compared with our previously conducted results reported in [22].

2. Simulation and analysis

In the simulation studies, Mie theory of homogenous sphere was employed to calculate the surface plasmon resonance (SPR) shift in the proposed sensor before and ozone contacting as reported in [22,23]. In this work, we simulated the proposed sensor design using COMSOL Multiphysics 4.2 and MATLAB environment.

Fig. 1 shown below illustrates the dimensions taken for the proposed design as $1 \text{ cm} \times 1 \text{ cm} \times 0.1 \text{ cm}$ for glass plate and $1 \text{ cm} \times 1 \text{ cm} \times 0.1 \mu \text{m}$ for thin films. Initially, we created the porous formation on the glass substrate with uniform pore diameter along the surface of the glass plate and then formed the layers of the APTMS/PVA based gold and silver thin films nanoislands, with the assigned boundary conditions in order to analyze the ozone responses based on the conditions governed for the gold and silver nanoisland thin films deposited on the non-porous glass plate as reported in [22,23]. Analysis of ozone sensing was performed on passing the ozone gas through the structure and by studying the SPR shift based on the UV absorbance characteristics. For the calculation of the absorption efficiency and scattering efficiency, Mie theory was employed under the combined COMSOL-MATLAB environment.

The simulated images of APTMS/PVA based gold and silver thin films on porous substrates are shown in Figs. 1(A-D). Figs. 1(A) and 1(B) show the ozone response images of the APTMS based gold and silver thin films nanoislands, whereas Figs. 1(C) and 1(D) show the ozone response images of the PVA-based gold and silver thin film nanoislands. From these figures, we observed that the distribution of UV-light passing along the thin films after ozone contacting exhibited distinguishable variations in colours for the APTMS, whereas less distinguishable color variations were observed in the case of PVA based thin films.

The Ozone-UV absorbance characteristics of the simulated APTMS and PVA based gold and silver thin film nanoislands deposited on the porous glass substrate are shown in Figs. 2(A-D). From Fig. 2(A), a peak at 530 nm was observed for the APTMS gold thin films deposited on porous substrate, due to ozone absorption on the gold thin film nanoislands. Whereas the ozone absorption peak of PVA-based gold thin film nanoisland on porous glass substrate was found to be at 500 nm. The change in absorption wavelength from 530 nm (APTMS) to 500 nm (PVA) may be due to the high polymer matrix of PVA as reported in [22]. Further, the peak value was found to be shifted from 0.0010 to 0.0013 at 530 nm and from 0.00065 to 0.0008 at 500 nm after ozone contacting on the APTMS and PVA based thin film nanoislands, respectively.

Similarly, the Ozone-UV absorbance characteristics of the APTMS/PVA based silver thin film nanoislands deposited on the porous glass substrates exhibited same trends as shown in Figs. 2(B) and 2(C). Here, peak shifts from 0.10 to 0.12 at

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