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Fabrication and characterization of optical sensors using metallic core-shell thin film nanoislands for ozone detection

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ABSTRACT

Core-Shell nanostructures play a vital role in the sensor field owing to their performance improvements in sensing characteristics and well-established synthesis procedures. These nanostructures can be ingeniously tuned to achieve tailored properties for a particular application of interest. In this work, an Ag-Au core-shell thin film nanoislands with APTMS (3-Aminopropyl trimethoxysilane) and PVA (Polyvinyl alcohol) binding agents was modeled, synthesized and characterized. The simulation results were used to fabricate the sensor through chemical route. The results of this study confirmed that the APTMS based Ag-Au core-shell thin film nanoislands offered a better performance over the PVA based Ag-Au core-shell thin film nanoislands. Also, the APTMS based Ag-Au core-shell thin film nanoislands exhibited better sensitivity towards ozone sensing over the other types, viz., APTMS/PVA based Au-Ag core-shell and standalone Au/Ag thin film nanoislands.

1. Introduction

Core-Shell nanostructures established a new trend in the sensor field, owing to their performance improvements in sensing characteristics and well-established synthesis procedures. These core-shell nanostructures can be ingeniously tuned to achieve tailored properties for a particular application of interest. Several researchers attempted sensor applications using noble metals like Au and Ag and their SPR characteristics, in particular, ozone sensors. Borisov et al., studied ozone sensor using WO_3 thin and thick films, which exhibited a high ozone sensitivity of 70 ppb and has the characteristic stability that depends on temperature, impulse magnitude and time [1]. Ermel et al., reported new methods to optimize the performance of sensors used in ozone analyzers that saved the solid chemicals up to 80% and exhibited strong adsorption matrix on O_3 sensitivity [2]. Doroodmand et al., fabricated FeOOH/SWCNT (Single-Walled Carbon Nano Tubes)-modified FET (Field Effect Transistor) based ozone gas sensor, which showed a linear output of 20–450 ppb within the response time of ~1.5 min [3]. Chung et al., fabricated the NO_2 gas sensor for enhancing the response time, detection limit and percentage of response of ozone treated graphene (OTG) sensor with estimated signal to noise ratio of 1.3 ppb [4]. Bejaoui et al., demonstrated CuO based ozone gas sensor property as a function of working temperature, grain size and ozone concentration [5]. Carotta et al., reported the ozone sensing properties of ZnO (Zinc oxide) and WS10 ($(W_{0.9}Sn_{0.1})\ O_{3-x}$) oxide thin films, in which the WS10 could detect ozone concentration as low as 10 ppb that is found to be less than the ZnO thin film [6]. Hansford et al., developed ozone detection instrument for measuring the atmospheric ozone at 530 °C [7]. Le and Tao developed a liquid core waveguide (LCW) that could detect ozone in water at 254 nm without any chemical reagents [8]. Wongwiriyapan et al., developed an ozone sensor using single-walled carbon nanotube, which exhibited sensing of ozone at 6 ppb level with fast response rate [9]. Muller et al., fabricated an acoustic wave sensor for the detection of atmospheric ozone that could sense ozone up to 55 ppb, owing to its higher harmonic frequency operation [10]. Guérin et al., modeled and tested the adsorption-desorption mechanism of ozone sensing in WO_3 thin films [11]. Thirumalairajan et al., investigated the ozone sensing properties of $CuAlO_2$ nanoparticles, which exhibited good response and recovery time of 25 s and 39 s, respectively and could sense ozone up to 200 ppb at 250 °C owing to the improved features such as size, shape and grain boundaries [12].

Wang et al., developed GaInN/GaN (Gallium Nitride) based ergonomic sensor having light emitting diodes integrated with In_2O_3 nanoparticles for ozone detection, which detected ozone up to 40 ppb [13]. Hawe et al. studied the detection of ozone with an integrated spherical cavity optical absorption cell at the wavelength of 603 nm [14]. Labidi et al., deposited and analyzed ozone sensing properties of

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WO_3 thin films that could sense ozone in the temperature range of 250–300 °C [15]. David et al., developed an ozone sensing instrument based on the conductivity changes in solar-heated tungstic oxide [16]. Kuzma et al., analyzed the properties of Au-Ag nanoparticles for ozone sensing through plasmonic excitation spectra of different metal arrangements such as bimetallic, mixture of pure metal and core-shell models using numerical simulations [17]. Singh et al., analyzed the chemical nature of various types of nanoparticles such as Au, Ag and Ag coated with Au using surface enhanced Raman scattering spectroscopy, which exhibited enhanced Raman activity [18]. Pal et al., investigated Au, Ag and Au-Ag nanoparticles in the aqueous polymer solution having particle size of 5–50 nm, which showed surface plasmon absorption maxima at 410 and 548 nm for the Ag and Au, respectively [19]. Samal et al., found that Au-Ag core-shell nanoparticles have maximum SERS efficiency at specific size and excitation wavelengths for SERS-based biomedical applications [20]. Sun et al., synthesized Au-Ag alloy nanoparticles having smallest average size of 4.0 nm through size controllable approach [21].

This paper presents the simulation, modeling and fabrication of Ag-Au core-shell thin film nanoislands and the performance estimation of the proposed sensor configuration with respect to other three configurations as reported in [22,23]. This study comprised of the following steps:

- Design, modeling and simulation of the Ag-Au core-shell.
- Synthesis of Ag-Au core-shell nanoparticles.
- Fabrication of Ag-Au core-shell nanoparticles on the glass substrate, employing APTMS or PVA as binding agent.
- Analyzing Ag-Au thin film responses with respect to ozone gas absorption.
- Characterization of the synthesized sensors and performance comparison with their simulation counterparts [22,23].

2. Simulation and analysis of Ag-Au core-shell thin film nanoislands

The absorption of ozone on thin films before and after ozonation is determined using surface plasmon resonance (SPR) shift. The SPR shift due to UV absorbance of ozone was calculated using Mie theory of homogeneous spheres as reported in [22,23]. The model dimension, parameters, simulation and characterization procedures are similar to the Au@Ag core-shell model reported in our previous work [22,23], with the exception that instead of the Au@Ag core-shell nanoparticles, Ag-Au core-shell nanoparticles were simulated and analyzed for ozone sensing through absorption mechanism. The dimensions of the model were taken as 1 cm×1 cm×0.1 cm and 1 cm×1 cm×0.1 μm for the glass substrate and the thin film nanoislands coating, respectively as shown in Fig. 1. The extinction coefficient of the proposed model was calculated using the analytical Eq. (1).

$$Q_{ext} = \frac{8\pi^2 R_s^3}{\lambda\sqrt{\varepsilon_{ozone}}} \mathrm{Im}\left(\varepsilon_{ozone}\frac{(R_s/R_C)^3(2\varepsilon_s+\varepsilon_c)(\varepsilon_s-\varepsilon_{ozone})-(\varepsilon_s-\varepsilon_c)(2\varepsilon_s+\varepsilon_{ozone})}{(R_s/R_C)^3(2\varepsilon_s+\varepsilon_c)(\varepsilon_s+2\varepsilon_{ozone})-(\varepsilon_s-\varepsilon_c)(\varepsilon_s-\varepsilon_{ozone})}\right)\ldots \quad (1)$$

where R_s/R_c is the ratio of the shell to core radius, *Im* stands for the imaginary part of the expression and ε_c, ε_s, ε_{ozone} are the dielectric constants of the core (Au), shell (Ag) and ozone, respectively, [17]. In this simulation, the boundary conditions are implemented using the meshing technique similar to the methodology adopted for a single core-shell nanoparticle. The simulated images of the proposed model are shown in Fig. 1(A) and (B). Fig. 1(A) shows the APTMS based Ag-Au core-shell thin film nanoislands with color variations indicating the ozone absorption mechanism, whereas Fig. 1(B) shows the PVA-based Ag-Au core-shell thin film nanoislands. The scattering efficiency and absorption efficiency of the model were calculated through the Mie theory in the combined COMSOL-MATLAB environment.

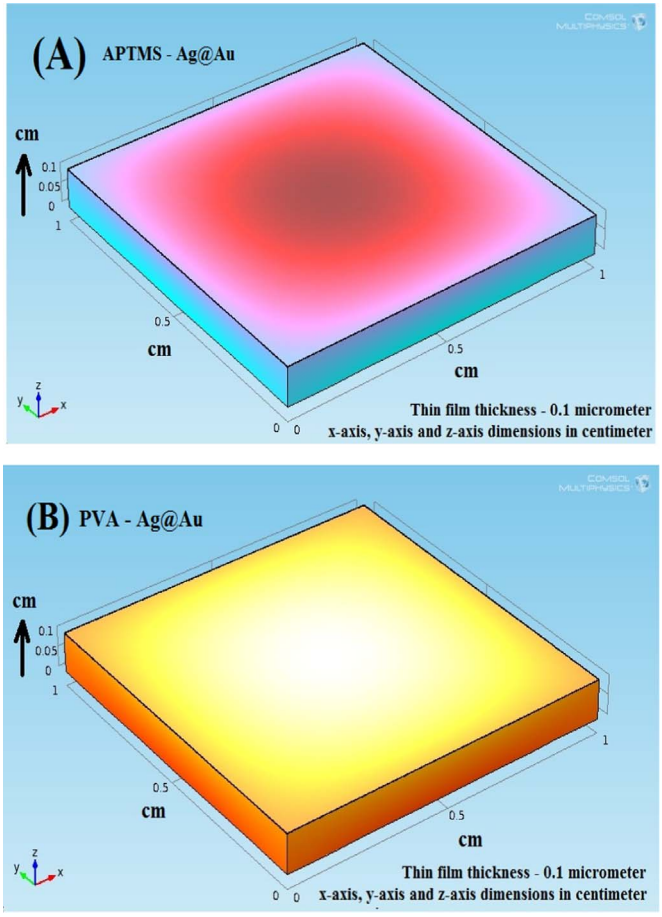

Fig. 1. Simulated images of (A) APTMS based Ag-Au core-shell thin films and (B) PVA based Ag-Au core-shell thin films.

2.1. Simulation analysis

The UV–Visible spectra for the APTMS and PVA-based Ag-Au core-shell thin film nanoislands are shown in Fig. 2(A) and (B), respectively.

In Fig. 2(A) and (B), the orange line indicates before ozonation and the blue line indicates the ozone absorption on thin films after ozonation. From Fig. 2(A), it is observed that the APTMS based Ag-Au core-shell thin film nanoislands exhibited UV absorbance peaks of Ag and Au at 420 nm and 540 nm, respectively and the amplitude of the respective absorbance peaks was found to increase from 1.52 to 1.70 for Ag and 0.92–1.06 for Au on exposure to ozone gas. Similarly, Fig. 2(B) shows the PVA-based Ag-Au core-shell thin film nanoislands, the absorbance peaks observed at 420 nm and 530 nm were found to shift their amplitudes from 0.75 to 0.89 and 0.42–0.50 for the Ag and Au, respectively. Further, the amplitude of the PVA-based Ag-Au core-shell thin film absorbance peaks was found to be smaller when compared to the APTMS peaks. These simulation results showed that the APTMS based Ag-Au core-shell thin film nanoislands were found to exhibit high sensitivity towards ozone sensing than the PVA-based core-shell thin film nanoislands. From these observations, we inferred that the APTMS based Ag-Au core-shell thin films exhibited highly sensitive ozone characteristics in line with standalone Au, Ag, and Au@Ag core-shell thin film nanoislands, which is evident from the results presented in our previous work [22,23].