PHOTONICS-2018: International Conference on Fiber Optics and Photonics
December 12-15, 2018, IIT Delhi, New Delhi - 110016 India

Nanoporous alumina as an optofluidic alcohol sensor

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Abstract: We developed a sensor based on gold-coated nanoporous anodic alumina membrane which can distinguish alcohols like methanol, ethanol, and isopropanol. The alcohol infiltrates into the nanoporous volume and causes a spectral shift in the Fabry-Perot modes of the membrane which is monitored to distinguish them.
OCIS codes: (160.4236) Nanomaterials; (260.2065) Effective medium; (280.4788) Optical sensing and sensors.

1. Introduction

Sensors are common devices which react to specific stimuli and generate typically, a detectable electrical signal. Nanosensors are attractive due to their small size, a large surface area to volume ratio, and excellent chemical compatibility and are are used to detect gases, chemicals, volatile elements, and various biomolecules, etc. [1]. In recent years, nanoporous structures like zeolites, mesoporous silica, and porous carbon have gained particular since their surface can have versatile surface functionalization [2]. Nanoporous anodic alumina (NAA) membranes have also been explored for various sensing applications such as proteins, bacteria, viruses, cholesterol, DNA, and blood serum. The added advantages of NAA are high mechanical strength, chemical compatibility, and thermal stability [3].

In this work, we used gold coated NAA for the detection of various alcohols by the change in the effective refractive index of the NAA when alcohol is incorporated into the nanopores. The thin gold film has been deposited on the top surface of NAA to increase the finesse of the membrane, which allows us to monitor the wavelength shift of the Fabry-Perot (F.P.) modes due to the variation in the refractive index of different alcohols. Various alcohols are infiltrated in the nanochannels of the gold-coated NAA by dipping one edge of the sample in the container containing alcohol, and the spectrum of the membrane is recorded [4].

2. Results and discussion

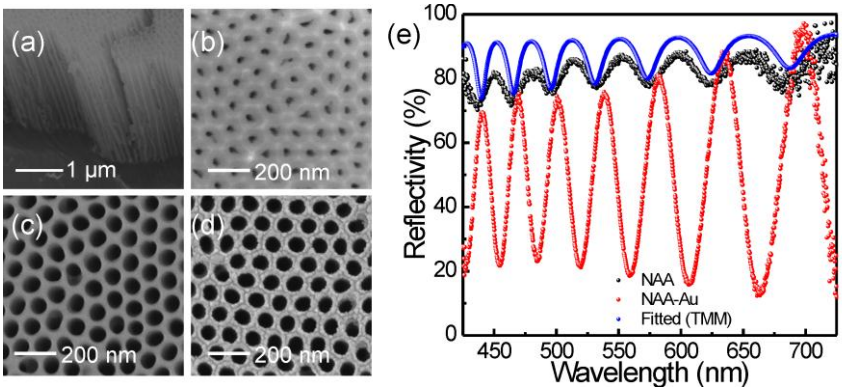

Fig. 1 FESEM images of NAA. (a) Cross-sectional view. (b) Top view of NAA. (c) After etching. (d) Gold coated NAA. (e) Reflectivity spectra of NAA membrane without (black curve) and with (red curve) gold coating, the blue curve is the spectrum calculated using TMM.

NAA membrane is fabricated by anodizing the aluminum substrate with 40 V DC supply twice in 0.3 M oxalic acid at 0° C [5]. The First anodization is carried out for 3 hours. We then etched the sample in the mixture of 0.2 M chromic acid and 0.4 M phosphoric acid at 60° C. Next we performed the second anodization for 25 minutes resulting in an optically transparent nanoporous membrane. Figure 1 (a) and 1 (b) shows the FESEM image of the cross-section view and top view of the NAA membrane. The length of the nanopores is about 2.8 um and arrange in a hexagonal fashion. Figure 1 (c) shows the NAA membrane after chemical etching. The nanopore diameter increases to about 80 nm. Figure 1(d) shows the image of the membrane after depositing a thin layer of gold (~ 20 nm) on its top surface. The thin gold layer does not form a uniform homogeneous coating on the surface, and the nanopores remain open which allows us to load the alcohol into its nanopores. Figure 1 (e) shows the reflection spectrum of the bare NAA (black curve) and gold coated NAA (red curve) membrane. The gold coating increases

the finesse of the membrane which results in a more substantial modulation in the reflection spectrum. The blue curve shows the calculated reflection spectrum of the gold deposited membrane using the Transfer Matrix method (TMM). We find the refractive index (n_{eff}) of alcohol infiltrated membrane using Maxwell-Garnett theory wherein the effective dielectric constant is given by:

$$\varepsilon_{eff} = \varepsilon_h \frac{(1+\eta\Gamma)}{(1-\Gamma)}, \text{ where } \Gamma = f_g \frac{(\varepsilon_g - \varepsilon_h)}{(\varepsilon_g + \eta\varepsilon_h)}$$

ε_h, and ε_g are the dielectric constants of the host and guest, η is the screening factor, $f_g = (2\pi/\sqrt{3})(r/D_{in})^2$ is the filling fraction of guest, r is the radius of the pore, and D_{in} is the inter pore separation [6]. The effective refractive index of the NAA membrane changes, when we load the membrane with different alcohols. For example, methanol loaded NAA membrane has ε_g = 1.77, for ethanol ε_g=1.85, and for isopropanol ε_g=1.91. The change in n_{eff} of the NAA changes its reflectivity curve.

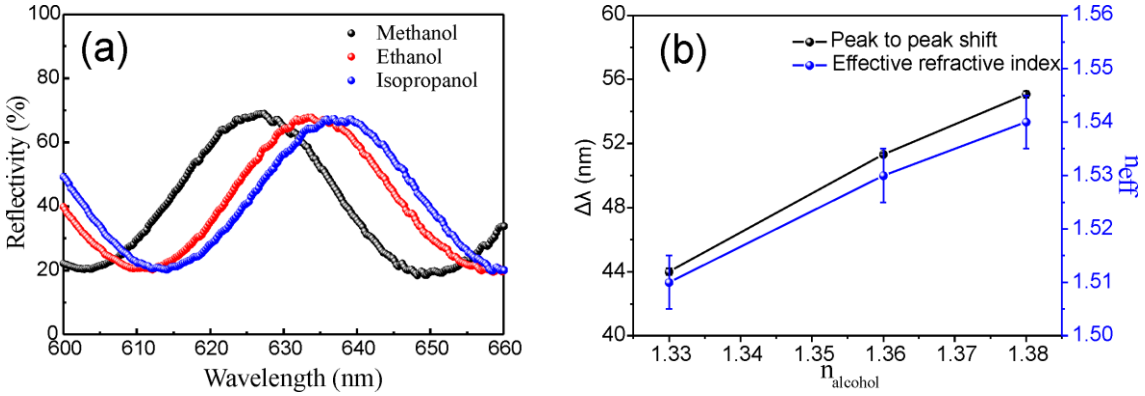

Fig. 2 (a) Reflectivity spectra of alcohol infiltrated NAA membrane. (b) Plot of the peak shift and n_{eff} for different alcohols.

We first infiltrate the alcohol by dipping one end of the NAA sample in the alcohol. Due to the wetting effect, the alcohol quickly fills the nanopores volume of the membrane. Figure 2 (a) shows the plot of the reflection curve for methanol (black symbol), ethanol (red symbol) and isopropanol (blue symbol). The corresponding neff each alcohol (methanol (n = 1.33), ethanol (n = 1.36), and isopropanol (n = 1.38)) is shown by the blue symbol. The black curve shows the shift in the Fabry-Perot peak wavelength ($\Delta\lambda$) from the reference point (582.5 nm, resonance without infiltrating any alcohol). The shift increases with the increase in neff. We measured $\Delta\lambda$ of about 7.3 nm in between methanol and ethanol (Δn_{eff} = 0.03), $\Delta\lambda$ of about 11 nm in between methanol and isopropanol (Δn_{eff} = 0.05). We also mixed a small amount of methanol in ethanol to determine the amount of methanol in the mixture. Using this device, we were successful to detect up to 10% of methanol in ethanol.

3. Acknowledgement

We acknowledge financial support through project No. DST/PHY/20130147. Anjani Kumar Tiwari also thanks DST for the INSPIRE faculty award DST/INSPIRE/04/2016/002068.

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