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Abstract

ZIF-8 Films and Surface Plasmon Resonance for Chemical Vapor Detection †

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Abstract: In this paper, we present a sensor that employs Zeolitic Imidazolate Frameworks (ZIF-8) on a Surface Plasmon Resonance sensor based on diffraction gratings to detect ethanol vapors via refractive index change in the porous structure.

Keywords: nanomaterials; gas sensor; MOFs; ZIF-8; optical detection; surface plasmon resonance

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1. Introduction

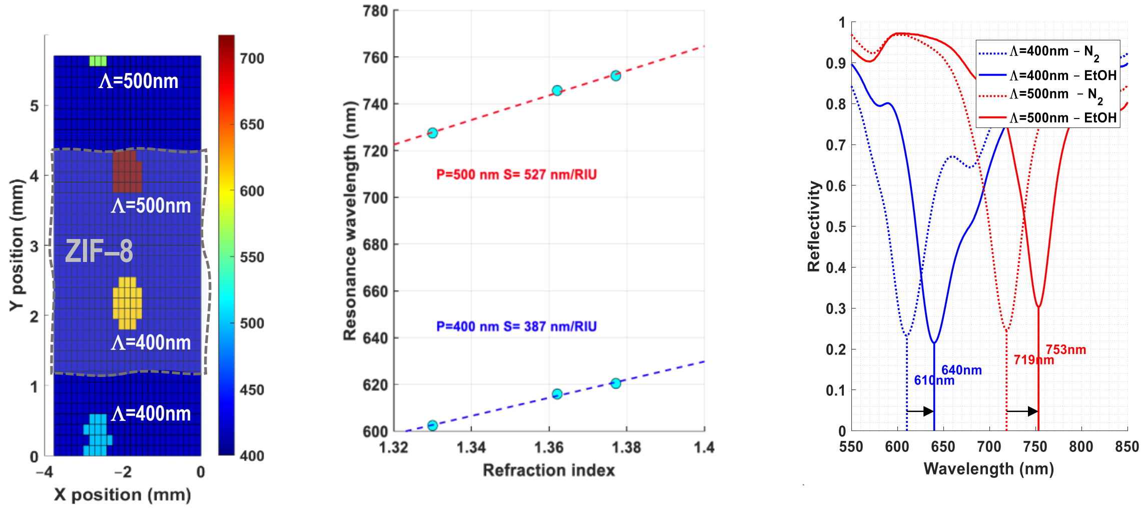
Since gaseous atmosphere changes induce refractive index variations in the order of $\Delta n = 10^{-4}$, some recent fashioned techniques used for gas detection, such as Fabry–Pérot interference measurements, SPR (Surface Plasmon Resonance) or LSPR (Localized SPR) [1], use sorption coatings to functionalize the samples and, thus, amplify the sensor response. In this regard, Metal–Organic Frameworks (MOFs) are porous materials that have attracted considerable attention due to the molecular adsorption of gases into their structure, inducing refractive index (RI) changes in the MOF film. In this work, a particular MOF, Zeolitic Imidazolate Frameworks (ZIF-8), has been used to design thin films on substrates with gratings to detect ethanol vapors via SPR at room temperature by monitoring the wavelength dip resonance in the different atmospheres.

2. Materials and Methods

The samples' fabrication process consisted of a LPCVD deposition of 100 nm of Si3N4 on an oxidized silicon wafer, followed by a 200 nm thick photoresist spun, on top of which a 20 nm thick Al layer was thermally evaporated, the purpose of which was the evacuation charge during e-beam lithography (Jeol JBX-9500FS). Afterwards, the Al was removed, and the photoresist was developed. The Si3N4 was then etched with a RIE system using CHF3 chemistry in a pattern consisting of two different grating periods, Λ = 400 nm and Λ = 500 nm, in a square area of 0.5 mm × 0.5 mm with a 30 nm depth. Lastly, the photoresist was stripped off, and a metal stack Cr (5 nm)/Au (40 nm) was deposited via e-beam evaporation. The Si3N4–metal interface worked as a SPR device.

To synthesize a ZIF-8 thin film on two of the gratings of the fabricated SPR samples (Figure 1a), these were immersed in a 1:1 volume mixture solution of 2-methylimidazole (50 mM) and Zn(NO3)2·6H2O (25 mM) for 40 min and then rinsed with pure methanol and dried with a nitrogen flow [2]. This process was repeated 3 times to obtain an estimated thickness of 500 nm.

Gas sensing measurements were tested on the fabricated samples under spectral interrogation inside a home-built aluminum chamber. The reflectivity spectra were acquired using an Ocean Optics SD 2000 spectrometer, which monitored the dependence of the wavelength dip resonance on the grating periods and the alcohol vapors, which were normalized to a ZIF-8-free reference spectrum.



(**a**) (**b**) (**c**)

Figure 1. (**a**) Dip wavelengths of the samples' gratings with and without ZIF-8. (**b**) Dip wavelengths with different liquids and bulk sensitivities of the Λ = 400 nm (blue) and Λ = 500 nm (red) grating periods. (**c**) Dip shift for Λ = 400 nm (blue) and Λ = 500 nm (red) from nitrogen to a saturated ethanol atmosphere.

3. Discussion

The bulk sensitivity of the sensor was measured with liquids (water, isopropanol and glycerol) and determined to be around 387 nm/RIU and 527 nm/RIU (refractive index units) for Λ = 400 nm and Λ = 500 nm, respectively (Figure 1b). Room-temperature gas sensing measurements on the ZIF-8-covered gratings were performed with nitrogen and saturated ethanol atmospheres (Figure 1c), to which the wavelength dip showed a response to an estimated RI value change of Δn = 35 nm/[400 nm/RIU] of 0.08 RIU, which is in accordance with the reported values [3].

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