

SPR-grating: spectral vs intensity interrogation for ethanol detection

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Summary:

In this work we present a comparison of the response of SPR-grating sensors covered with ZIF8 for vapors ethanol detection, using spectral interrogation and intensity interrogation. We show that using the spectral interrogation method we can detect a value of 200 ppm of ethanol.

Keywords: Gas sensor, optical detection surface plasmon resonance, metal-organic frameworks (MOFs), volatile organic compounds, ethanol.

Introduction.

Chemical sensors are attractive because they are sensitive, fast, compact, and consume limited power, although they often lack selectivity. Commercial gas sensors are mainly based on three technologies: electrochemical, chemoresistance or NDIR. NDIR sensors operate by measuring gas absorption in the infrared spectrum. They are highly selective, but detecting low gas concentrations requires a long optical path length and, consequently, they are bulky.

Alternative optical sensing methods include Fabry-Pérot interferometry, fiber-optic gratings, and surface plasmon resonance (SPR). Since gases induce only very small refractive index changes when compared to air, sensitive coatings are often used to enhance detection. Metal-organic frameworks (MOFs) are porous materials with high surface area that are suitable for gas adsorption and sensing applications. Among them, ZIF-8 (zeolitic Imidazolate Framework) is especially promising due to its large pore size and hydrophobic nature, which minimizes humidity interference [1-3].

Sensing method and results.

In this work, a nanostructured gold diffraction grating coated with ZIF-8 is used as the sensing platform. The sensor is fabricated on oxidized silicon wafers with a gold-coated diffraction grating structure. The diffraction grating (period of 500nm) is created using electron beam lithography, followed by reactive ion etching and gold deposition (50nm). A thin ZIF-8 film is then

synthesized on selected gratings through immersion in a solution containing zinc nitrate and 2-methylimidazole. The resulting ZIF-8 layer has a thickness of approximately 280 nm.

Two optical interrogation methods were tested. 1) In Spectral interrogation measurements, a white light source is focused on the sample inside a gas chamber. The reflected light was collected and analyzed with a spectrometer to obtain the reflectivity spectrum. 2) In intensity interrogation, the white light source was replaced with a 780 nm laser diode, and the spectrometer was replaced with a silicon photodiode used to measure reflectivity at a fixed wavelength.

In the spectral interrogation experiments, exposure to ethanol vapor caused a redshift in the SPR resonance, indicating an increase in the refractive index of the ZIF-8 film as ethanol molecules were adsorbed. Fig. 1 shows the resonance spectra during exposure to the reference gas, synthetic air, with a resonance at about 755 nm, while under saturated ethanol vapor, using a bubbling system, the resonance shifted to 781 nm ($\Delta\lambda=26$ nm). Using a reference gas cylinder and mass flow controllers, we have been able to detect 200 ppm (Fig. 2).

In the intensity interrogation setup, which is much simpler, the reflected light intensity decreases with increasing ethanol concentration. In Fig. 3, the variation of reflectivity between pure synthetic air and different pulses of ethanol dissolved in SA.

The minimum ethanol concentration that produces a measurable variation within a 1-minute

measurement cycle is ≈ 2000 ppm, which is a tenfold increase compared to spectral interrogation previously described.

In Figure 1, the vertical line represents the laser diode wavelength (780 nm). The variation in reflectivity between the two extreme cases, synthetic air and ethanol (EtOH), is shown by the red and magenta lines. These correspond to the green and black dotted lines in Figure 3, which represent the response to a pulsed concentration.

In this work the results of both methodologies will be presented and critically discussed.

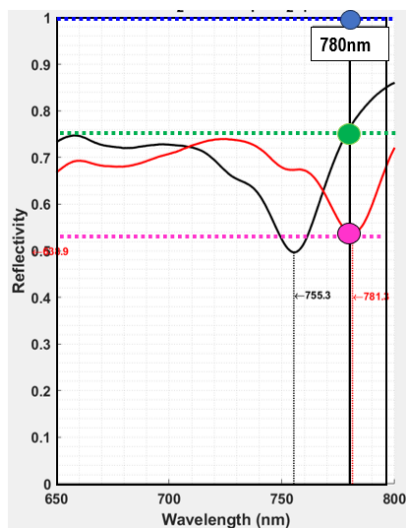


Fig. 1. The black spectrum corresponds to the cleaning state, synthetic air, while the red spectrum shows the redshifted response for fully saturated ethanol vapor. The total redshift observed is $\Delta\lambda = 26$ nm.

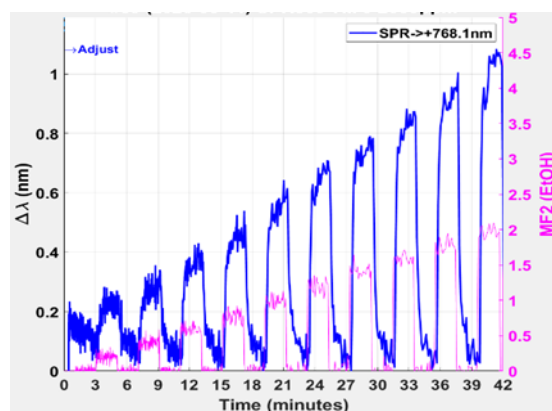


Fig. 2. Redshift of a 500 nm diffraction grating under different ethanol vapor concentrations. The minimum concentration tested is 200ppm

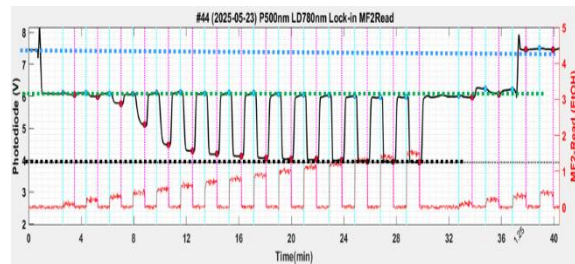


Fig. 3. Decrease of reflectivity using a 780nm laser diode. Blue line is the 100% of reflectivity in flat-gold. Green line is the maximum reflectivity on diffraction grating in cleaning cycles. Black line is the reflectivity under different concentrations. Red line is the Mass-flow voltage. Reflectivity decrease from 80% to 53% at maximum concentration of EtOH.

References

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