



Enhanced resonant absorption in dye-doped polymer thin-film cavities for water vapour sensing



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ABSTRACT

We propose a novel and sensitive water vapour sensing scheme based on enhanced resonances in absorbing ultrathin-film cavity systems. In particular, we experimentally and numerically demonstrate the water vapour sensing ability of such cavity systems, which comprise ultrathin poly(vinyl alcohol) films doped with Rhodamine 6G dye molecules coated on silver substrates. Due to coupling between molecular absorption and Fabry–Perot resonances excited in the ultrathin-film cavity, the studied structure exhibits highly enhanced resonant absorption at certain wavelengths under certain illumination conditions. Upon exposure to water vapour (relative humidity from 10% to 73%) the resonant features show much larger spectral shifts (~ 60 nm) than those (~ 20 nm) reported in most previous studies and a three-fold enhancement of the absorption reduction ($>40\%$) as compared to that in an un-doped reference sample. In addition, the proposed ultrathin-film system demonstrates hysteresis-free sensing response to water vapour within a wide RH range (5–75%). Together with its flexibility of tuning sensing performance by adjusting dye-doping concentration, the absorbing ultrathin-film system provides an effective and versatile platform towards further development of practical water vapour sensing.

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1. Introduction

Relative humidity (RH) is a physical parameter which indicates the concentration of water vapour in ambient air. There is a growing need for monitoring and controlling RH levels in industrial processes, research laboratories and living spaces. In the past few decades a wide variety of mechanical, electrical, integrated and optical sensing methods have been investigated for developing low-cost, robust and sensitive RH sensors [1–4]. Among these techniques, RH sensors based on optical sensing scheme, e.g. distributed Bragg reflectors, tilted fibre Bragg gratings [5,6], photonic crystal fibres [7] and optical fibres with embedded with metal nanorods [8], show significant advantages in their high sensitivity, specificity and immunity to electric/magnetic noise. However, most of these photonic-based RH sensors are characterised by their expensive fabrication process and complicated characterisation techniques. In this context, thin-film based RH sensors using Fabry–Perot (FP) type resonances continues to be an active area of research due to their structural simplicity, ease of fabrication and robustness [9–12].

In this paper we present a novel sensing scheme and its proof of concept experimental results for highly improved RH sensitivity (an order of magnitude higher than conventional optical sensors) based on dye-doped ultrathin-film structures, namely subwavelength thick poly(vinyl alcohol) (PVA) thin-film coatings doped with Rhodamine 6G (Rh6G) coated onto a silver (Ag) surface (PVA_{Rh6G}-Ag). The presence of dye molecules allows the thin-film system to support strong FP resonances within subwavelength thickness, which significantly enhances the system's water vapour sensitivity by increasing the variation of resonance magnitude and inducing larger resonance spectral changes for certain ambient RH changes. To the best of our knowledge, our work is the first one to develop humidity sensing utilising ultrathin absorbing dielectric coatings on metal substrates enhanced by molecular absorption resonances, and the results show great promise for practical application.

2. Theory

2.1. Background

In dielectric thin-film structures FP type resonances can be excited upon light irradiation, as a result of interference between waves reflected from different interfaces of the structures, giving rise to resonant features such as maxima and minima in the optical

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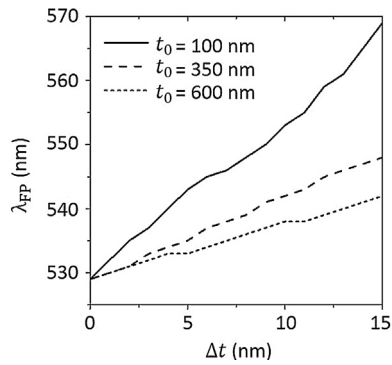


Fig. 1. Simulated Fabry–Perot resonance wavelength (λ_{FP}) as a function of change in thickness Δt for PVA film with $n_f = 1.51$ and thickness $t_0 = 100$ nm (solid), 350 nm (dashed line) and 600 nm (short-dashed line) on Silver substrate with $\theta = 81^\circ$.

spectra (transmission, reflection or absorption). Generally, these excitations are highly dependent on the angle of incidence (θ), the film thickness (t) and the refractive index of the film (n_f). If a thin film is made of a material that can absorb water molecules from its environment, the interaction with water molecules may cause changes in both t and n_f of the thin film (swelling/deswelling), leading to measurable modifications in the optical spectra, e.g. the magnitudes or spectral positions of resonant features may vary. Therefore by measuring the variation of resonance magnitudes or spectral shifts of resonances, we can detect the change of ambient humidity.

In conventional thin-film based RH sensors, in order to sustain strong FP resonances the constituent films generally have thicknesses on the order of the wavelength of the probing light. As a result, the large thickness ($t \geq \lambda$) of the films becomes one of the factors which limits the sensitivity of such sensors because for a film with a given refractive index n_f , the spectral shift $\Delta\lambda$ from its resonance wavelength λ_{FP} is proportional to the thickness change Δt from the film's initial thickness t_0 , i.e. $\Delta\lambda/\lambda_{FP} \propto \Delta t/t_0$. Therefore, reduction of the initial film thickness can lead to larger spectral shifts from a given resonance wavelength λ_{FP} .

In 2012, Kats et al. [13] demonstrated that strong interference effects can take place in a new type of ultrathin-film cavity, comprising nanoscale highly absorbing dielectric optical coatings on reflecting surfaces. The thickness of such coatings can be as small as a few nanometers because the nature of the reflection phase shifts for highly absorbing dielectric coatings on metal substrates preserves FP type resonances down to a very small film thicknesses. Here we propose that such absorbing thin-film cavity structures can be used for vapour sensing applications by taking FP-based sensors into the deep sub-wavelength regime combined with resonant absorption. The proposed sensing scheme offers higher sensitivity than the conventional thin-film FP-based sensors, because, (i) the small thickness of the sensing layer can induce larger spectral shifts; and (ii) the detection sensitivity can be significantly enhanced by incorporating suitable resonant absorbing species like dyes or metal nanoparticles, as the presence of absorbing species is known to enhance the resonances in thin-film based gas sensors [14–16].

2.2. Sensing mechanisms

2.2.1. Larger spectral shifts from thinner sensing layers

To demonstrate the influence of film thickness on resonance spectral shifts, we discuss a specific example of PVA films (refractive index $n_f = 1.51$) deposited on a Ag substrate (PVA-Ag) under s-polarised illumination (electric fields being perpendicular to the plane of incidence) at $\theta = 81^\circ$. Fig. 1 shows that the simulated

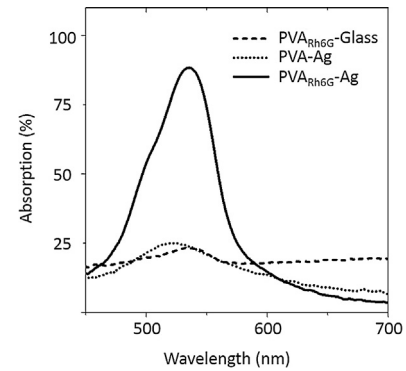


Fig. 2. Experimentally observed absorption spectra for 100 nm thick Rh6G-doped PVA film on glass (PVA_{Rh6G}-Glass, dashed line) and Ag (PVA_{Rh6G}-Ag, solid line) with $C = 0.002$ wt% of dye in PVA and an undoped PVA film on Ag (PVA-Ag, dotted line) when s-polarised light is incident at $\theta = 81^\circ$.

spectral positions λ_{FP} of FP resonances in PVA-Ag samples with initial thickness $t_0 = 100$ (solid line), 350 (dashed line) and 600 nm (short-dashed line) vary with the same thickness change Δt . It is clear to see that the least initial thickness ($t_0 = 100$ nm) acquires higher slope than others, indicating that ultrathin films ($t < \lambda/4n_f$) can induce larger spectral shifts of FP resonances than traditional thin-films ($t \geq \lambda/4n_f$) for the same thickness change.

2.2.2. Enhanced resonances

As we recently discovered [17], the resonances in an ultrathin-film structure can be significantly enhanced by doping absorbing species into the film. Fig. 2 shows comparisons of experimentally acquired absorption spectra of 100 nm thick Rh6G-doped PVA samples on silver (PVA_{Rh6G}-Ag), undoped PVA on silver (PVA-Ag) and dye-doped PVA on glass (PVA_{Rh6G}-Glass) under oblique ($\theta = 81^\circ$) s-polarised white-light illumination. The PVA coatings on all samples have the same thickness, and the doped samples (PVA_{Rh6G}-Ag and PVA_{Rh6G}-Glass) possess the same dye concentration ($C = 0.002$ wt%). The un-doped PVA-Ag sample (dotted line) shows a weak absorption maximum at $\lambda = 525$ nm associated with the FP resonance, while the PVA_{Rh6G}-Glass (dashed line) sample also shows a weak maximum at $\lambda = 536$ nm corresponding to the molecular absorption of Rh6G. Due to the weak excitation of FP resonances in PVA-Ag and the low concentration ($C = 0.002$ wt%) of dye doping in PVA_{Rh6G}-Glass, the magnitudes of these two features are all below 25% and would not be suitable for sensing. In contrast, as a result of coupling between FP resonances and molecular absorption, the sample PVA_{Rh6G}-Ag (solid line) shows much larger resonantly-enhanced absorption magnitude 88% at $\lambda = 536$ nm.

In this report, we will demonstrate how we can use this enhanced resonance in ultrathin films to improve the system's RH sensitivity. Specifically, any shift in FP resonances due to changes in the PVA film thickness can cause the decoupling of the two contributing resonances and lead to highly observable changes in absorption spectral peaks and/or absorption magnitude, thus making the system a good candidate for sensing applications.

2.3. PVA interaction with water molecules

PVA is the sensing material we use in our system with swelling/deswelling in the presence of water vapour being the physical change that is being transduced into optical spectral changes. Here we explain the polymer's interaction with water molecules that gives rise to this sensitivity. This type of polymer is made of carbon chain backbone with hydroxyl groups attached which assist in hydrogen bond formations as shown in Fig. 3(a). In presence of water vapour the polymer chains reorient to facilitate

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