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Improved detecting sensitivity of long period fiber gratings by polyelectrolyte multilayers: The effect of film structures

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ABSTRACT

Novel polyelectrolyte multilayer (PEM) coated long period fiber gratings (LPFGs) are emerging as one of high-performance optical refractive index (RI) sensors. The influence of PEM film structures (i.e film thickness and chemical structures) on the transmission spectra and detecting sensitivity of LPFG sensors had been investigated theoretically and experimentally. The results demonstrated that the central wavelength of the attenuation bands of LPFGs will shift to the low value with increasing PEM film thickness. The optimized film thickness, where the highest variation of the resonant wavelength may take place, is strongly governed by the inner chemical structure of PEM film. For the dense and less-responsive film coated LPFG, its optimized film thickness will decrease when the RI of surrounding medium increases. This behavior is different with the responsive film coated one. In addition, the detecting sensitivity of PEM coated one is improved by two orders of magnitude as compared with the uncoated one. Therefore, these PEM coated LPFGs have great potentials in diverse fields of molecular diagnostic, environmental monitoring, food safety testing and homeland security.

1. Introduction

Owing to low cost, easy production, miniature size, immunity to electromagnetic interference, non-corrosiveness, remote operation and high reliability, long period fiber grating (LPFG) based optical sensors have been utilized in the diverse fields of molecular diagnostic, environmental monitoring, food safety testing and homeland security [1–7]. LPFG has a typical period in the range 100 μm–1 mm, as shown in Fig. 1. Due to the periodic refractive index (RI) modulation, a spectrally selective loss, so called attenuation bands, can be observed in the wavelength-dependence transmission spectra of LPFG. The central wavelength of the attenuation bands is described by

$$\lambda_{res} = \left(n_{co}^{eff} - n_{cl,m}^{eff}\right)\Lambda \quad (1)$$

where Λ is the period of the grating, λ_{res} is the central wavelength of the mth attenuation band, and n_{co}^{eff} and $n_{cl,m}^{eff}$ are the effective RI of the guided core mode and the mth cladding mode, respectively. As well known, $n_{cl,m}^{eff}$ is strong functions of the RI of the medium surrounding the cladding (n_{sm}) and the order of the particular cladding mode. When n_{sm} equals n_{cl}, the resonance bands (λ_{res}) disappear. For a given LPFG with fixed Λ of 500 μm and n_{co}^{eff} (i.e. $n \sim 1.468$ for silica), it can easily distinguish the RI changes of 10^{-6}–10^{-7} if the spectrometer resolution is 0.05 nm. To this reason, LPFG has been regarded as a novel RI sensor with high detecting sensitivity.

In theory, the higher detecting sensitivity can only be achieved when n_{sm} is close to n_{cl}. However, when LPFGs are used in RI measurement, n_{sm} is always smaller or higher than n_{cl}. Thus, the detecting sensitivity will become very poor. In order to overcome this problem, the deposition of thin-film overlays with higher RI (HRI, n_{ov}) on fiber surface is one of the most cost-effective methods [8–16]. By using HRI overlay, n_{ov}^{eff} can be facilely tuned to be close to n_{cl} [11–13,16], which will result in a higher detecting sensitivity. Until now, there are many approaches to deposit HRI overlays on fiber surface, for example Langmuir–Blodgett method, layer-by-layer self-assembly approach, dip-coating, and sol–gel techniques, etc. [8,15,17,18]. Among them, the layer-by-layer self-assembly approach had been paid more attention, mainly due to its ease of preparation, variety of potential layer constituents, possibility to tune the thickness in the nanometer range and flexibility on choices of substrates and overlay materials. Using

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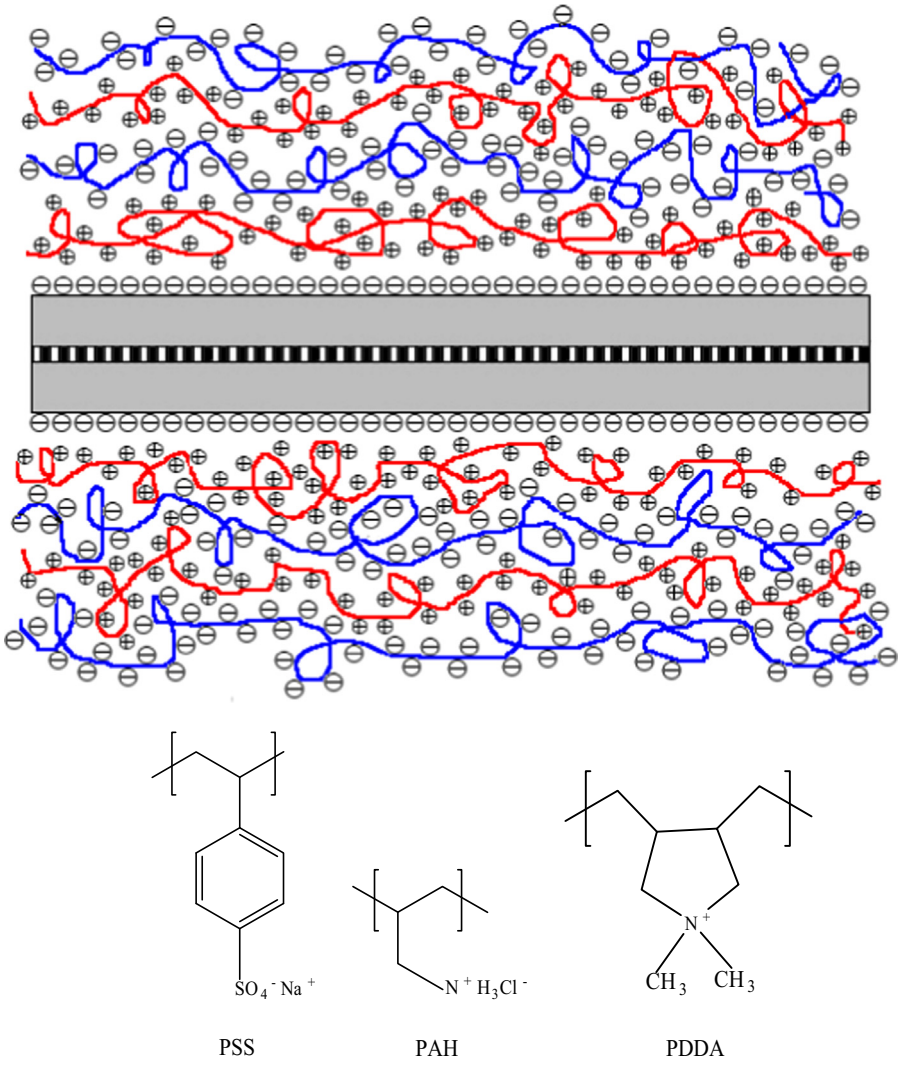

Fig. 1. The schematic of PEM coated LPFGs and the chemical structures of polyelectrolytes. The PEM films are fabricated by the electrostatic layer-by-layer self-assembly approach.

this technique, the polyelectrolyte multilayer (PEM) can be fabricated by alternatively immersing a charged substrate into aqueous solutions of opposite charged materials, followed by several rinsing and air-drying steps. Numerous PEM films [17,19–32], for example $(PAH/PCBS)_n$ (n: number of bilayers), $(PAH/PAA)_n$, $(PDDA/poly\text{-}R)_n$, $(PAH/PSS)_n$, $(PDDA/PSS)_n$, $(PDDA/metal\ oxide\ nanoparticles)_n$ etc., had been used to modify LPFG sensors for direct measurement of pH, ion, sugar and biomolecules. It had been demonstrated that the resonance of as-formed LPFGs can be tuned by a large magnitude after coated with several nm thickness. And its detecting sensitivity will be highly improved by careful optimization of the cladding mode order, film thickness and the film. Therefore, PEM coated LPFGs provide a robust platform for building high-performance RI sensors.

However, the effect of internal structure of these PEM films on transmission spectra and detecting sensitivity of LPFGs remains to be fully uncomprehended. Among the external stimulus, organic solvents can be used to regulate film thickness or porosity properties of PEMs because they can effectively screen the electrostatic interaction within the multilayer and strongly affect the interaction between hydrophobic fragments present in some polyelectrolytes [20,21,27,32]. Therefore, it is very interesting to understand how the subtle changes of the inner chemical structure of PEM film influence the optical property of LPFGs. To this end, two different PEM thin films of $(PAH/PSS)_n$ and $(PDDA/PSS)_n$ had been coated on LPFG sensor in order to measure the RI changes of organic solvent, i.e. methanol, ethanol, isopropanol, etc. Since $(PDDA/PSS)_n$ exhibits a significant response to organic solvent, as-formed LPFG shows different optical properties to the one coated with $(PAH/PSS)_n$. Experimental results demonstrate that the detecting sensitivity of PEM coated LPFG is dominated by both the film thickness and chemical structures.

2. Experiments

2.1. Reagents and chemicals

Hydrogen peroxide (H_2O_2, 30%), sulfuric acid (H_2SO_4, 98%), ammonia (NH_3, 28%), hydrofluoric acid (HF, 40%), sodium chloride, methanol, ethanol, isopropanol, n-butyl alcohol, n-amyl alcohol, 1-hexanol, ethylene glycol, polypropylene glycol, glycerol, diethanol amine, triethanolamine, ethyl benzoate, and benzaldehyde were obtained from Sigma-Aldrich and used without further purification. Polydimethyl diallyl ammonium chloride (PDDA 40%, wt% in water, M_W= 300,000), poly(sodium-p-styrenesulfonate) (PSS, M_W=100,000), and poly(allylamine hydrochloride) (PAH, M_W=56,000) were purchased from Sigma-Aldrich.