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Powerless and Reversible Color Humidity Sensor

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Abstract

One dimensional (1D) Photonic crystals (PC) are the simplest form of PC consisting of alternative layers of materials having different refractive indices. This periodic structure has very interesting optical properties allowing manipulation and control of light reflectance wavelength. Polymers have already been used as optical components in several devices and recently became candidate materials for the fabrication of PC. In the present work, a polymeric multilayer stack consisting of alternating hydrophobic and hydrophilic layers is fabricated and its response in controlled concentrations of humidity is evaluated towards the development of an optical humidity sensor.

Keywords: polymer photonic crystal,color humidity sensor

1. Introduction

Photonic crystals (PC) have already shown numerous interesting optical properties and their application has been suggested for a wide range of diverse applications. The simplest configuration of a PC is the 1-dimentional (1D) configuration that consists of a multilayer stack of two materials with different refractive indices. Upon illumination to broad-band light the 1D PC strongly reflects a particular spectral range, whereas all other wavelengths are transmitted through the multilayer stack giving, in this way, a narrow-band reflecting device, the optical properties of which depend on film thicknesses, refractive

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indices, number of alternating bilayers, thickness uniformity *etc*. The wavelength of the reflectance peak of the first-order reflection equation for such a structure is given by $\lambda_{refl}=2(n_1d_1+n_2d_2)$ where n_1, n_2 are the real parts of the refractive indices and d_1, d_2 the thicknesses. Furthermore, the photonic bandgap width is directly related to the index contrast.

Polymers are receiving considerable attention as components in novel 1-D PC because of the tailored functionality, easy manufacturing, and relatively low cost. The first polymeric PCs were fabricated by co-extrusion resulting in hundreds to thousands of alternating layers with thickness spanning the nanoscale to microscale in a single, one-step roll-to-roll process [1, 2]. Recently, several research groups are fabricating 1D PC with conventional film deposition techniques (spin-coating [3, 4], vapour deposition [5], e.t.c.) as well as more sophisticated methods like self-assembled block copolymer [6]. For example, in the case of 1D PC fabricated with spin coating, Bailey *et al.*[3] deposited 50 alternating layers of poly(vinylpyrrolidone) and polystyrene (refractive index contrast 0.08 at 600nm) on glass substrates. They developed three different multilayer stacks by altering the layer thickness of the polymers, resulting in reflectance light wavelength in the blue/violet, green and red range. The maximum reflectivity obtained by the authors was 55%. The use of such techniques increases the number of materials that can be employed in 1D PC and allows for the deposition of PC on planar substrates. However, in many cases one of the alternating layers is inorganic material in order to achieve easily a high refractive index that allows for increased reflectivity with a small number of layers.

A recently explored application of 1D polymeric PC is the measurement of the environmental humidity and detection of volatile organic compounds through the change of the color of the photonic crystal. For example, E. Tian et.al [7] have shown the colourful humidity detection of a 1D PC hydrogel that is fabricated by infiltrating acrylamide solution into a P(St–MMA–AA) PC template and subsequent photo-polymerization.

In the current work the design, development and first evaluation of a powerless color humidity sensor based on polymeric 1-D PC is introduced.

2. Experimental

In the present study the 1D PC polymeric multilayer stack was fabricated by spin-coating of two polymers, poly(2-hydroxyethyl methacrylate) (PHEMA) and a negative chemically amplified epoxy resist (EPR) [8]. The polymeric films are deposited with increasing refractive index order. First the PHEMA solution in ethyl lactate (3%wt) was spin-coated on a glass substrate followed by a post applied bake (PAB) at 110°C for 5 min on a hotplate. On top of the first PHEMA layer an EPR solution in propylene glycol methyl ether acetate, PGMEA, (5%wt) was spin-coated and the same PAB was performed. The EPR film was then flat exposed at 254nm and post exposure baked (PEB) at 110°C for 5 min in order to transform the EPR layer to a highly cross-linked film (Cross-EPR). This bilayer film procedure was repeated several times resulting in a multilayer stack fabrication (fig. 1).

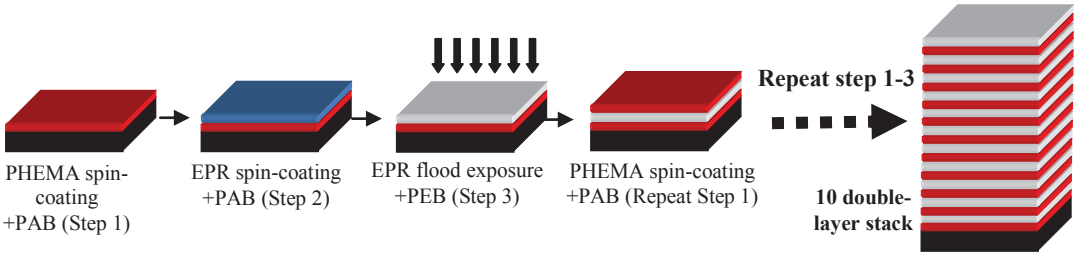

Fig. 1. 1D PC fabrication flow chart.

The thicknesses of each polymeric film have been selected to provide reflectance peak within the visible spectral range. In particular since the refractive index of PHEMA is 1.51 and of Cross-EPR is 1.59 the selected polymeric film thicknesses were 90nm and 85nm respectively resulting to a reflectance peak at 542nm (Green colour) in humidity free environment. The same stack can be easily fabricated either on Si or on flexible substrates. In fig. 2 the film thicknesses of all the spin coated layers for a typical 10-bilayer stack on Si wafer, as measured with White Light Reflectance Spectroscopy (ThetaMetrisis), are shown. The mean measured thicknesses are 87nm and 88nm for PHEMA and Cross-EPR respectively with a standard deviation of 6nm and 4nm respectively. The obtained thickness variation results in shifting the reflectance peak by just 1nm relative to the one of target thickness values, from 542nm to 543nm, which is negligible for the application studied here.

In order to reassure that no intermixing of the films occurs during spin coating of one film on top of the other, Dissolution Rate Monitoring (FR-Liquid, ThetaMetrisis) [9] of each film in the solvent of the solution of the other polymer was measured (fig. 3). From fig. 3 is clear that the solution of the polymers used do not affect the already deposited polymeric layers in the substrate, meaning that ethyl lactate does not affect Cross-EPR film and PGMEA does not affect PHEMA film.

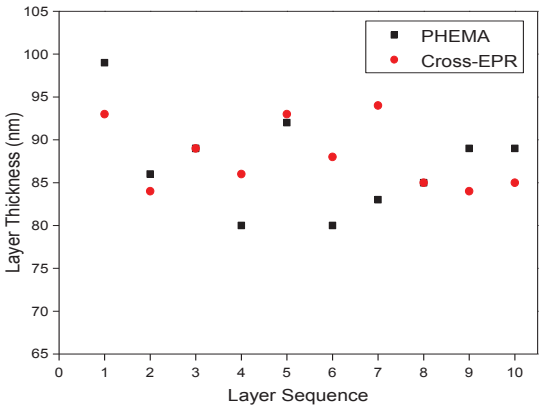

Fig. 2. Polymer film thickness distribution vs. layer location for the whole layer stack. Mean measured thickness for PHEMA is 87nm ±6nm and for Cross-EPR is 88nm ±4nm.

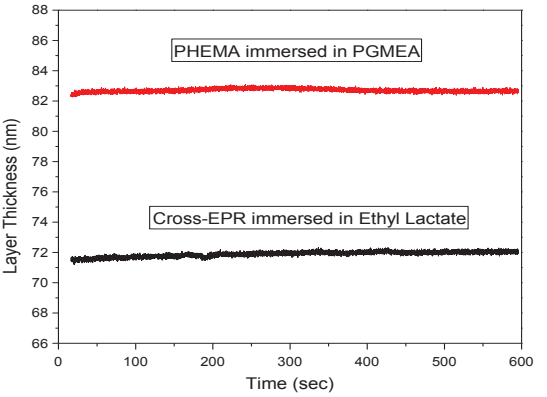

Fig. 3. PHEMA film thickness vs time when immersed in PGMEA solvent and Cross-EPR film thickness vs time when immersed in Ethyl Lactate solvent

PHEMA is a hydrophilic material that swells at a considerable level upon sorption of humidity from the environment while Cross-EPR is a strongly hydrophobic polymeric material that presents negligible humidity response even at very high humidity levels. Due to these properties, the fabricated photonic device does not need any power to operate since its color depends on the humidity level and can be used as a reversible low-cost color humidity indicator in any application. The sorption of water molecules by PHEMA layers causes a PHEMA layer thickness increase and, after a certain point at high humidity concentrations, a decrease of PHEMA refractive index.

In fig. 4 the reflectance spectrum changes for a wide humidity range are illustrated. The reflectance spectra were recorded by a FR-Basic VIS/NIR tool (ThetaMetrisis) equipped with a special Gas Chamber connected with a set-up able to provide nitrogen flows with controlled concentration of humidity. The reflectance peak clearly shifts to higher wavelengths due to the swelling of PHEMA layers and in particular by 6nm for 20% RH (Relative Humidity), 28nm for 40%RH and 98nm for 60%RH. By applying the equation for first-order reflection, $\lambda_{refl}=2(n_{PHEMA}d_{PHEMA}+n_{EPR}d_{EPR})$, and by considering that the refractive index of the swollen polymer remains the same, the film thickness, d_{PHEMA}, increases by 2.5nm for 20%RH, 9nm for 40%RH and 21nm for 60%RH (fig. 5). Consequently, the PC color

represents the humidity level of the environment without any need of power, neither for excitation nor for detection. Furthermore, since swelling is a physisorption process, the response is both reversible and reproducible.

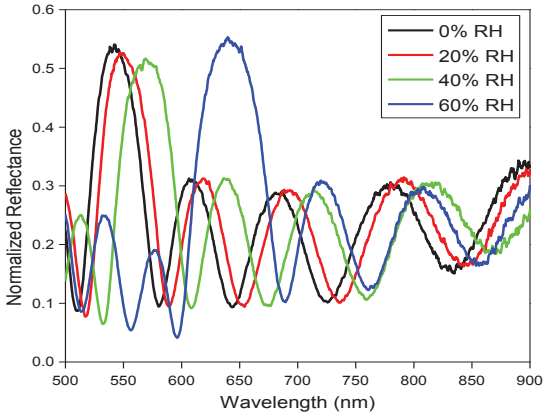

Fig. 4. Experimental Reflectance spectra for 0-60% Relative Humidity. Reflectance peak intensity can be further increased by increasing the number of alternating layers. Reflectance peak width can be further reduced by appropriate engineering of polymeric films refractive indices.

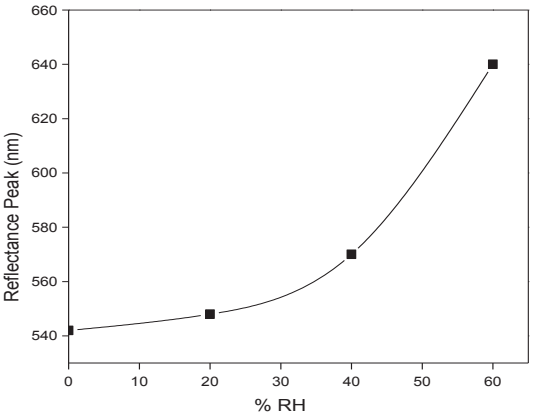

Fig. 5. Reflectance peak shift from green color to red color due to the sorption of water molecules

1. Summary and Conclusions

A one-dimensional polymeric photonic crystal (1-D PC) has been developed and evaluated for humidity sensing. The PC is fabricated by spin coating alternate hydrophilic and hydrophobic layers resulting in a reflectance peak at a wavelength defined by refractive indices and thicknesses of films. In the presence of humidity, the hydrophobic layers remain unchanged while the hydrophilic layers absorb water molecules and swell. This swelling causes film thickness increase and shift of the reflectance peak to higher wavelengths. That way the color of the PC represents the humidity level of the environment without any need of power. Since the swelling process is based on physisorption, the whole phenomenon is reversible and reproducible.

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