

1-D Polymeric Photonic Crystal Humido-Chromic Sensor

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Abstract— The fabrication of a power-free, reversible, color-indicator sensor of the relative humidity in the environment has numerous applications and is considered a challenging task. The device to be developed should be able of color changing according to the degree of humidity change and have a number of characteristics, i.e., reversibility, fast response, low cost, and, ideally, should be flexible. The proposed solution, based on a 1-D polymeric Photonic Crystal (PC) configuration on a microscope glass, can successfully fulfill all the above requirements.

I. INTRODUCTION

Humidity sensors are widely used in many applications from general industry (semiconductor, automobile) to medicine (pharmaceutical processing, biological products) and agriculture (green house air-conditioning, soil moisture monitoring). Several humidity sensing principles have been developed so far and are based on ceramic, semiconductor and polymer materials. The most common ceramic sensing materials are aluminum oxide (Al_2O_3), in particular γ - Al_2O_3 (amorphous) and α - Al_2O_3 (corundum) phase, anatase-titanium dioxide (TiO_2) made by sol gel, silicon dioxide (SiO_2) grown by wet or dry oxidation and lithium chloride-doped manganous tungstate (LiCl -doped MnWO_4) prepared by bulk-sintering. Usually as semiconductors are used stannic oxide (SnO_2) which is an n-type wide band gap, indium oxide (In_2O_3) and Zing oxide-Yttrium oxide ($\text{ZnO-Y}_2\text{O}_3$). Particular

polymers are broadly used in available humidity sensors being either of resistive type or of capacitive type. Polymers containing phosphonium, copolymers, reactive copolymers, polyelectrolytes, conjugated polymers and hydroscopic polymers are mainly used for those types of sensors. In all these sensing principles energy is needed for the operation of the sensor and for the visualization of the humidity level [1-3].

On the other hand the use of photonic crystals (PC) in sensing devices, such as biosensors, chemical sensors, vapour sensors, oil sensors, humidity sensors e.t.c. has recently gain the attention of the researchers [4,5]. PC can be either 1-D, or 2-D or 3-D. One dimensional photonic crystals (1-D PC) are the simplest type of PC and consist of alternated layers (periodic structure in one direction) of two transparent materials having different refractive indices. Due to their periodic structure, 1-D PC have the ability of reflecting selectively a narrow band from a broad band incident light, acting as a Bragg deflector. The wavelength of the reflectance peak of the first-order reflection equation for such a structure is given by:

$$\lambda_{\text{refl}}=2(n_1d_1+n_2d_2) \quad (1)$$

where n_1 , n_2 are the real parts of the refractive indices and d_1 , d_2 the thicknesses of the two alternating films [6]. In addition

to this equation, it is found that the photonic bandgap width is narrowed as the index contrast of the materials increases. An important aspect of PC is that the reflectance peak wavelength can be manipulated through the thickness and the index difference of the films used, choosing in this way the desired wavelength for each application. PCs are mostly fabricated using inorganic materials in order to fulfill the index contrast required. Recently, polymeric PCs have been introduced having an index contrast of around 0.1 [7]. For that reason in order to achieve a very high reflectance value a large number of bilayers is needed.

In the present work a power-free, color changing upon humidity 1-D polymeric PC sensor is demonstrated. It is fabricated using alternated layers of a hydrophilic and a hydrophobic polymeric materials using spin-coating. The hydrophilic layer of the PC swells upon humidity and thus the reflectance peak of the PC shift to higher wavelengths (red shift). In addition to address the small refractive index contrast between the polymeric layers, one of them is doped with a high dielectric constant inorganic material allowing that high reflectance values with moderate number of bilayers. A first evaluation and a comparison between the doped and non-doped humido-chromic sensors are presented.

II. EXPERIMENTAL

Two polymeric materials were selected for the realization of the 1-D PC humidity sensor, a hydrophilic poly(2-hydroxyethyl methacrylate) (PHEMA) (Mw 300K purchased from Aldrich) and a hydrophobic negative chemically amplified epoxy novolac resist (EPR) [8]. First, an evaluation of the swelling (film thickness increase) due to humidity of a 90nm thick PHEMA film and of a similar PHEMA film covered by 80nm EPR, all spin coated on standard Si wafer was performed (fig. 1) by applying the White Light Reflectance Spectroscopy (WLRS) methodology (FR-Basic with a gas chamber by ThetaMetrisis). In WLRS the film thickness is measured with high accuracy allowing for measurement of spin coated polymeric films in real-time.

Fig. 1 shows that PHEMA film swells highly upon exposure to humidity, gaining 15nm in thickness on 40% relative environmental humidity (RH) and 45nm on 70% RH. When the PHEMA film is covered on top with hydrophobic EPR film the thickness swelling is reduced to 5nm on 40% RH and 15nm on 70% RH. Clearly, swelling of PHEMA depends on the relative humidity (RH) and is lower in the PHEMA/EPR case, due to the limited sorption of water molecules within the EPR film. The film thickness change of at least one of the two films is required in order to achieve a reflectance peak shift of the PC sensor according to the equation given above.

Therefore the shift peak when is realized in the visible spectra range can be an indication of the environmental relative humidity change. Therefore in this implementation, no external power is needed in order to have indication of the environmental humidity.

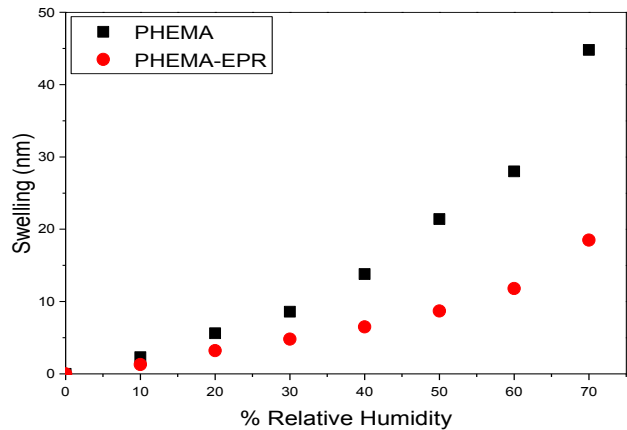


Fig. 1: Swelling of single PHEMA film (black) and PHEMA film covered with EPR (red). EPR swelling is negligible (measurements are not shown here). Swelling is smaller in the latter case due to the existence of the hydrophobic crosslinked EPR film.

The 1-D PC is fabricated by sequential spin coating/post apply bake (PAB) of the two polymeric films with additional deep UV exposure and post exposure bake (PEB) steps for the EPR layer. A PHEMA solution in ethyl lactate (3%wt) was used and spin-coated at 2100 rpm for 45s on a glass substrate followed by a PAB at 110°C for 5 min on a hotplate giving a film thickness of 90nm. On top of the first PHEMA layer an EPR solution in propylene glycol methyl ether acetate (PGMEA) (3%wt) with a sulfonium salt as photoacid generator (PAG) (5% wt with respect to the polymer concentration) was spin-coated at 1500rpm for 45s and the same PAB was performed. The EPR film was then flat exposed at 254nm (DUV) and PEB was made at 110°C for 5 min on a hot plate in order to transform the EPR layer to a highly cross-linked film (cross-EPR).

In order to increase the real part of the refractive index of EPR (the high refractive index of the stack) dielectric particles (titanium oxide) have been added. The EPR doped titania solution was spin-coated at 4800rpm for 45s, the rest of the process was the same as the EPR film. This bilayer film procedure (PHEMA/cross-EPR or PHEMA/titania doped cross-EPR) was repeated several times resulting in a multilayer stack formation. This way, samples of 10 bilayers were successfully fabricated on microscope glasses, showing reflectance peaks at wavelengths that depend on the refractive indices and film thicknesses (fig.2). In fig.2 a schematic representation of the fabricated multilayer stack is presented as well as the theoretical reflectance spectra of this PC. The refractive index values are 1.51 (PHEMA), 1.59 (cross-EPR) and 1.64 (titania doped cross-EPR) for 632nm wavelength. The increased refractive index of titania doped cross-EPR film allows for higher refractive index contrast with PHEMA and thus more intense reflectance peaks. For the given refractive index values and film thicknesses the reflectance peaks in dry environment, were at 520nm (green light) for cross-EPR PC and 625nm for titania doped cross-EPR PC (red light).

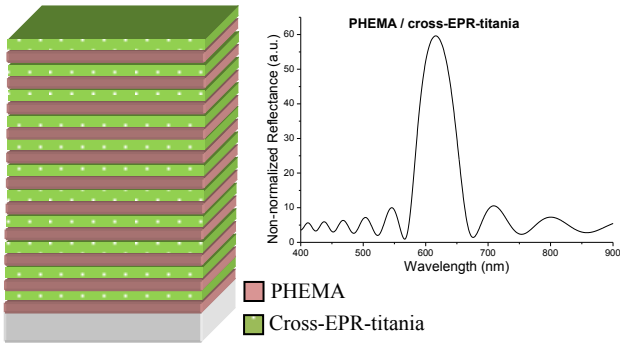


Fig. 2: Schematic representation of 10 PHEMA/titania doped cross-EPR layers and the theoretical reflectance spectra

The reflectance peaks shift upon exposure to humidity in a 0-70% humidity range was studied for both bilayer stacks and was found that they exhibit practically the same red-shift of the main peak (figs. 3 and 4). From fig. 3 is clear that the inclusion of titania increases the reflectance signal for the same number of bilayers thus giving brighter color. In fig. 4 it is shown that both multilayer stacks have a shift peak of 10nm at 20% RH whereas at 60% RH the shift is 31nm for cross-EPR stack and 28nm for titania doped cross-EPR, when RH reaches 70% there is a rather exponentially increase of the shift peak in both cases but is more pronounced at the cross-EPR stack. Although not shown here, in both cases swelling of PHEMA is reversible.

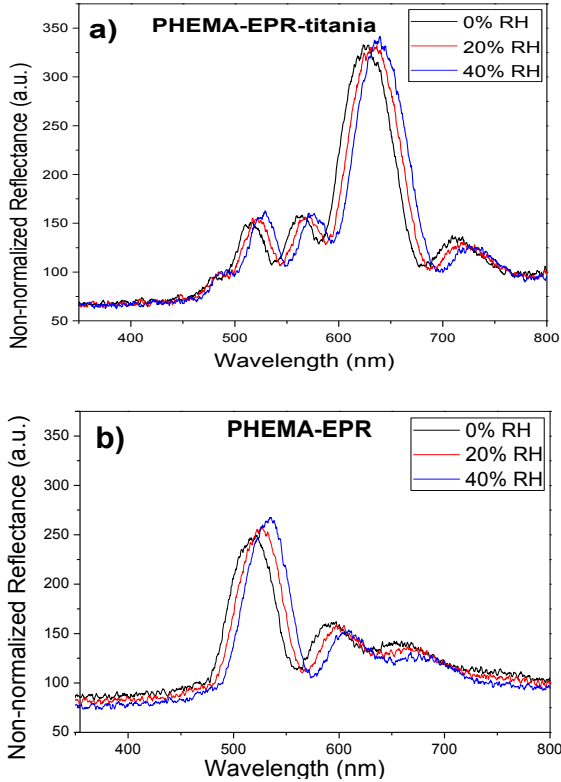


Fig. 3: Reflectance peak shift due to 20% and 40% humidity for a) PHEMA/EPR and b) PHEMA/EPR-titania 10 double layer stacks.

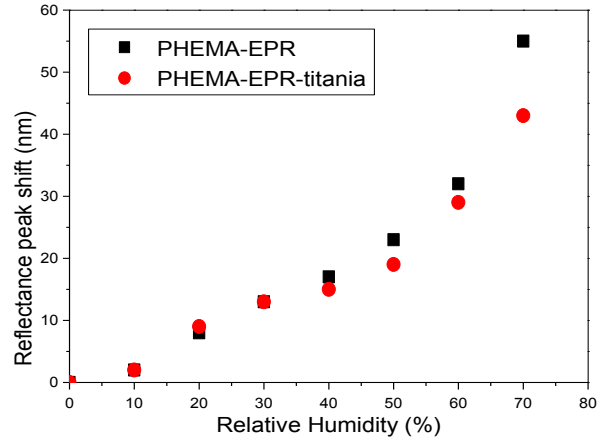


Fig. 4: 1-D PC Reflectance peak shift vs. humidity level for devices fabricated by using plain EPR and EPR doped with titania. Shift is similar for both devices; however, refractive index contrast is higher in the later case.

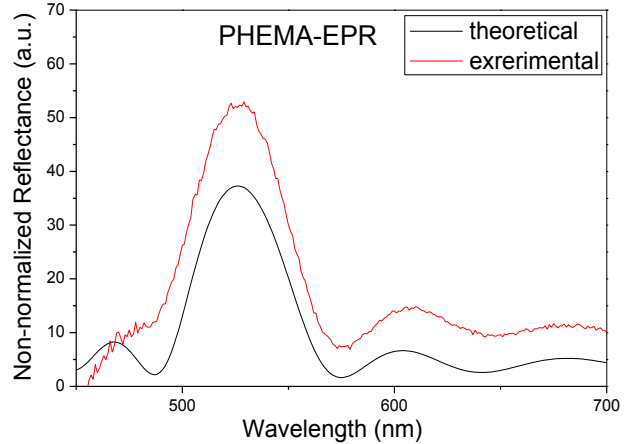


Fig. 5: Theoretical and experimental reflectance spectra of a 10 double layer PHEMA-EPR stack. Layer thicknesses for theoretical spectrum are: 90nm for PHEMA and 70nm for EPR.

In fig.5 the theoretical and experimental reflectance spectra of 10 bilayer PHEMA / cross-EPR stacks in dry environment is given and is shown that their essential spectral features are almost identical. In addition, the similarity of the theoretical and experimental reflectance peaks and band width of the peaks that the multilayer stack exhibits upon exposure to white light, gives a clear indication that there is no intermixing of the experimental polymeric film layers during spin coating and post apply bake.

III. SUMMARY AND CONCLUSIONS

A hydrophilic and a hydrophobic polymeric material, PHEMA and cross-EPR, were evaluated as a one-dimensional photonic crystal (1-D PC) humido-chromic sensor. A second sensor having as hydrophobic material cross-EPR doped with titania giving a higher refractive index contrast between the polymeric layers was also evaluated and compared to the first one. Both PCs were fabricated by spin coating of alternate layers of the polymers, giving a reflectance peak wavelength

at the visible range, green color in the case of cross-EPR and red for titania doped cross-EPR at humidity free environment. In the presence of humidity, the hydrophobic layers remained almost unchanged while the hydrophilic layers absorbed 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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