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Polymer top covered Bragg reflectors as optical humidity sensors †

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Abstract: Thin films from double hydrophilic copolymer of complex branched structure containing poly(N,N-dimethyl acrylamide) and poly(ethylene oxide) blocks are used as humidity sensitive media andtwo types of Bragg reflectors having different optical contrast and operating wavelengths are implemented as transducers of humidity changes. The required film thickness is pre-optimized through theoretical modelling in order to achieve the highest sensitivity. Single films and Bragg reflectors are characterized by transmittance measurements at different humidity levels in the range from 5 % to 95 % relative humidity. The influence of number of the layers in the stack, the operating wavelength and optical contrast on the sensitivity is studied. The potential and advantages of using top covered Bragg reflector as humidity sensor with simple optical read-out are demonstrated and discussed.

Keywords: optical sensing; humidity; Bragg reflectors; branched polymers.

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1. Introduction

Bragg reflectors are multilayered systems comprising layers with alternating low and high refractive index and quarter-wavelength optical thickness, i.e. film thickness multiplied by the film's refractive index equals a quarter of the operating wavelength of the Bragg reflectors (λ_{BR}). Due to the quarter-wavelength thickness of all layers in the reflectors, all multiple reflected waves are in phase, interfere constructively and a band of high reflectance centered at λ_{BR} appears in the spectra. Simultaneously a stop band of low transmittance is generated that is also centered at λ_{BR}. If Bragg reflector is design in a way the operating wavelength to be in the visible part of the spectra, then a distinctive color called structural color is observed, although transparent and colorless layers are used for building the reflector [1,2]. The position of λ_{BR} and reflector's color depend strongly on refractive index and thickness of the layers and change when one of these parameters or both change [3,4]. Thus the optical behavior of Bragg reflectors could be controlled by external stimuli, for example vapors of volatile organic components or humidity [5-8]. The concept of optical sensing has already been demonstrated for multilayered structures comprising diverse materials such as oxide nanoparticles [1,8], mesoporous films [4,5], zeolite nanoparticles [9,10], metal organic frameworks [11,12], polymers [13-15], 2D-materials [16,17], etc. However, the reflectance band depends also on the direction of the incident light and shifts toward smaller wavelengths when the incident angle increases [7]. It is obvious that this will be a problem when visual inspection of color is used as a detection approach because the observer will not be able to distinguish properly the real reason of color change. We have already demonstrated [10,15] that a possible solution is to prepare structures with omnidirectional reflection that have high reflectance for all directions and polarizations of light. In this case one and the same color will be observed at all viewing angles.

In this paper we consider a different approach. Instead of measuring or observing reflectance we use transmittance. Undoubtedly, measuring transmittance is simpler, more accurate and less expensive compared to reflectance measurement. Moreover, observing sample color in transmittance configuration, i.e. using the light transmitted through the sample, could overcome to a great extent the problem related to the angle dependence of the color because it is easy the sample color to be observed at normal light incidence when transmittance is considered. In order to simplify further the sensing approach we deposit the sensitive film on top of specially designed Bragg reflectors, instead to incorporating it in the reflector, thus overcoming possible issues of incompatibility that may arise when organic and inorganic materials are used for Bragg reflector.

In this study we prove the concept of implementing top covered Bragg reflectors as optical sensors for humidity. As humidity sensitive media we use thin films of previously developed poly(N,N-dimethyl acrylamide)-poly(ethylene oxide) block copolymer with branched macromolecular architecture that are deposited on top of two types of Bragg reflectors, having different optical contrast and operating wavelengths. The humidity sensing ability are demonstrated through i) transmittance measurements at relative humidity of 5 % and 95 % and ii) color change of the sensor in transmitted light at different humidity levels . The influence of number of the layers in the stack, the operating wavelength and optical contrast on the sensitivity is studied.

2. Materials and Methods

PDMA/PEO copolymer of branched macromolecular architecture was synthesized by means of redox polymerization of N,N-dimethyacrylamide DMA in deionized water using ammonium cerium(IV) nitrate as initiator, poly(ethylene oxide (Mn 2000 g mol-1; Fluka) as hydroxyl functionalized initiating moiety and poly(ethylene glycol) diacrylate (av. Mn 575 g mol-1; Sigma-Aldrich) as cross-linker according to the previously described synthetic procedure [18]. The polymerization was carried out in nitrogen atmosphere for 3 hours at 35 °C under vigorous stirring and terminated by diluting the reaction mixture with methanol (1:1 volume ratio). The diluted reaction mixture was used for thin polymer film deposition without further polymer isolation or purification.

Thin polymer films with thickness in the range 140 – 550 nm were deposited by spin-coating method (4000 s^{-1}, 60 s) both on silicon substrate and Bragg reflectors using polymer solutions with different concentrations. All films are annealed at 180 ^{o}C for 30 min in air. Five- and seven-layers Bragg reflectors are prepared on glass substrates by alternating deposition of sol-gel Nb_2O_5 [19] and SiO_2 [20] films or dense and porous Nb_2O_5 films [21]. The optical thickness of the films in the reflectors was calculated so that their stop bands to be at 550 and 450 nm, respectively.

Optical constants (refractive index and extinction coefficient) and thickness of the films were calculated using previously developed two-stages nonlinear curve fitting of reflectance spectra measured with UV-VIS-NIR spectrophotometer (Cary 5E, Varian) [19]. The sensing behavior was tested by measuring transmittance spectra at low and high levels of relative humidity, realized using homemade bubbler system that generates vapors from liquids [10].

3. Results and Discussion

The sensor under investigation consists of polymer film as sensitive element that is spin-coated on top of multi-layered stack (Bragg reflector) regarded as a transducing element. The detection is performed by measuring transmittance (T) of the stack or by visual inspection of its color. When the relative humidity in the environment changes the thickness and refractive index of the polymer film also change. This leads to alteration of T and subsequent change of reflector's color. The implementation of Bragg reflector enables monitoring transmittance instead of reflectance when detecting humidity because Bragg reflector is transparent, opposite to the previously used silicon wafer that is opaque [18,22]. Measuring transmittance is simple, accurate and inexpensive and therefore it is always preferable comparing to measuring reflectance. Further, Bragg reflector gives additional opportunity of visual inspection of sensor's color as a method for detecting humidity that is not possible in the case of bare glass substrate because the system polymer film / glass is colorless.

In order to achieve the highest sensitivity toward humidity we optimize the thickness of polymer film through theoretical modelling. We calculate humidity induced change in transmittance (ΔT) of Bragg reflector covered with polymer films with different thicknesses in the range 100 – 400 nm. In the first modelling step, we calculate transmittance T_1 using particular thickness of the polymer film and refractive index that equals to 1.5. Then in the second step we increase polymer film thickness with 30% and decrease its refractive index with 7 % [22] thus simulating high humidity and calculate transmittance again - T_2. The absolute value of the difference T_1-T_2, that could be regarded as a change in transmittance due to change of humidity from 5 % RH to 95 % RH, is plotted in Figure 1 as a function of the thickness of polymer film deposited on top of 5-layers Bragg reflector.

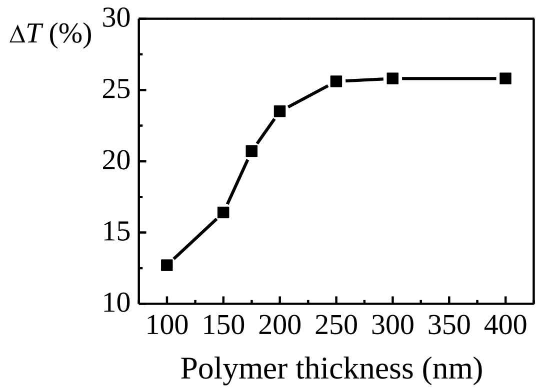

Figure 1. Calculated humidity induced change of transmittance ΔT (=$T_{95\%RH}$-$T_{5\%RH}$) of 5-layers Bragg reflector covered with polymer film with different thicknesses.

It is seen that ΔT increases with thickness of the polymer film reaching steady state for thickness higher than 250 nm. Therefore in the next step of our investigation we decided to use polymer film with thickness of 290 nm and deposit it on four different Bragg stacks. Thicker films are not suitable because the time response of the sensor will increase due to the longer diffusion path length in thicker polymer films. Moreover, there is no enhancement of the sensitivity when films thicker than 250 nm are used (Figure 1).

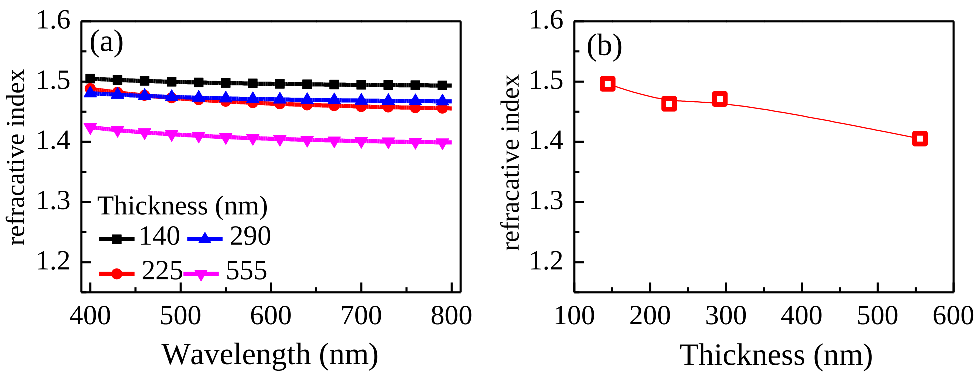

Figure 2. (a) Dispersion curves of refractive index of polymer films with denoted thicknesses; (b) thickness dependence of refractive index (the values are taken at wavelength of 600 nm).

It is interesting to check how the thickness of branched polymer film influences its refractive index. Polymer films with different thicknesses in the range 140 – 550 nm are deposited on silicon substrate using polymer solutions with different concentrations. Refractive index (n), extinction coefficient (k) and thickness (d) of the films are determined simultaneously using previously developed two-step algorithm [19]. Briefly, nonlinear minimization of discrepancies between measured and calculated reflectance spectra is used for determination of *n*, *k* and *d* [19]. The calculated dispersion curves of refractive index of polymer films with thicknesses in the range 140 – 550 nm are presented in Figure 2a. The thickness dependence of *n* at 600 nm is plotted in Figure 2b. All studied samples obey normal dispersion, i.e refractive index decreases slightly with wavelength that could be expected because polymer films are transparent in the studied spectral range. Calculated values of extinction coefficient are smaller than 0.003 thus confirming the good quality and transparency of the studied polymer films. Refractive index is almost the same for films with thickness values up to 300 nm and decreases for thicker films. Most probably when *d* increases the influence of substrate adhesion weaken and as a result less dense films are deposited.

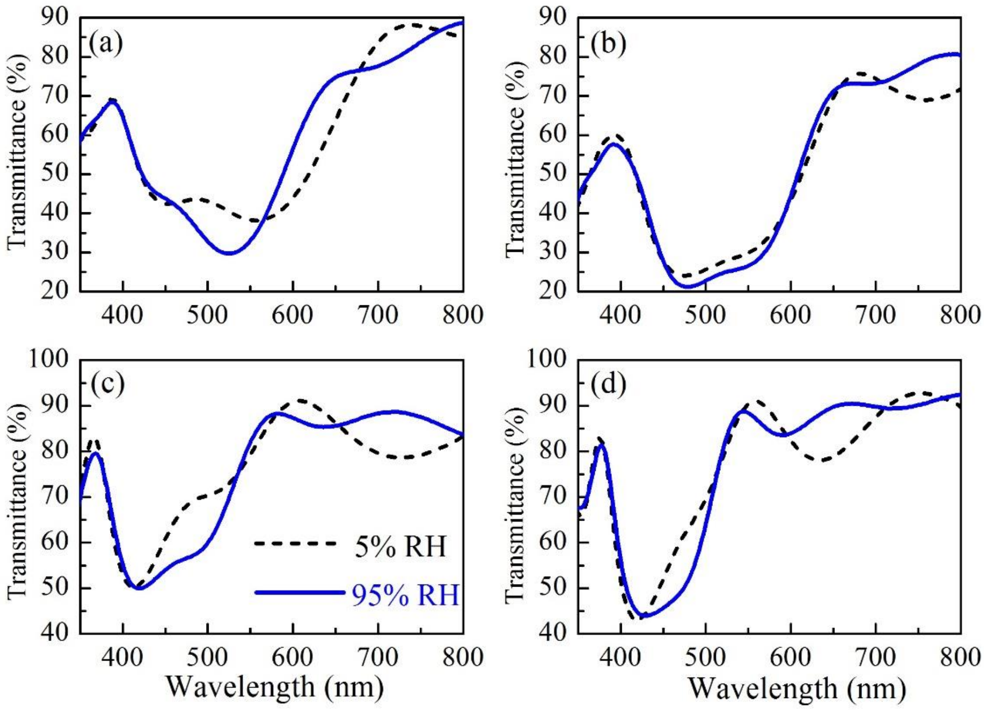

Figure 3. Transmittance spectra at low (5%) and high (95%) relative humidity of branched polymer film with thickness of 290 nm deposited on top of Bragg reflectors consisting of 5 (a, c) and 7 (b, d) alternating layers of Nb_2O_5 and SiO_2 (a, b) and dense and mesoporous Nb_2O_5 (c, d)

To study the sensing behavior toward humidity, branched polymer film with thickness of 290 nm is deposited on four Bragg reflectors consisting of 5 and 7 alternating layers of Nb_2O_5 / SiO_2 and dense / mesoporous Nb_2O_5. The top-covered reflectors are put in the measuring cell and their transmittance spectra are taken at low (5 %) and high (95 %) relative humidity. The transmittance spectra of all Bragg reflectors are shown in Figure 3. The stop band, i.e. the band with low transmittance, is well seen even after polymer film deposition. The optical contrast of constituent layers in the stacks (the difference between the refractive index of Nb_2O_5 and SiO_2 from one hand and dense and mesoporous Nb_2O_5 films for other) is different which explains the different widths of the stop bands (Figure 3). The dissimilarity of wavelength positions of the bands is also seen. It originates from different optical thicknesses of the layers of the studied Bragg reflectors.

The thickness and refractive index of polymer films are strongly affected by the humidity such as the film thickness increases and refractive index decreases at high humidity levels. These alterations in *n* and *d* of the polymer film modify also the optical behavior of the entire Bragg reflector and its transmittance spectra are changing with humidity (Figure 3).

Figure 4a presents the humidity induced changes in transmittance for single polymer film with thickness of 290 nm deposited on bare glass substrate (GS) and on Bragg reflectors (BR). The advantage of using Bragg reflectors over bare glass is obvious: a fourfold increase in ΔT is obtained when Bragg reflectors are used. Besides, from Figure 4a it is also seen that the characteristics of reflector such as operating wavelength, number of layers, optical contrast etc. do not influence substantially the measured signal. The average sensitivity (S_{av}) and the accuracy / resolution (ΔRH) of detection are calculated from eq. 1 and eq. 2, respectively and are presented in Table 1:

$$S_{av} = \frac{\Delta T\ (\%)}{95\%RH - 5\%RH}\ , \tag{1}$$

$$\Delta RH = \frac{errT\ (\%)}{S\ (\%)}\ . \tag{2}$$

ΔT is the humidity-induced change of film's transmittance and $errT$ is the measuring error in transmittance that in this study is assumed to be 0.2%.

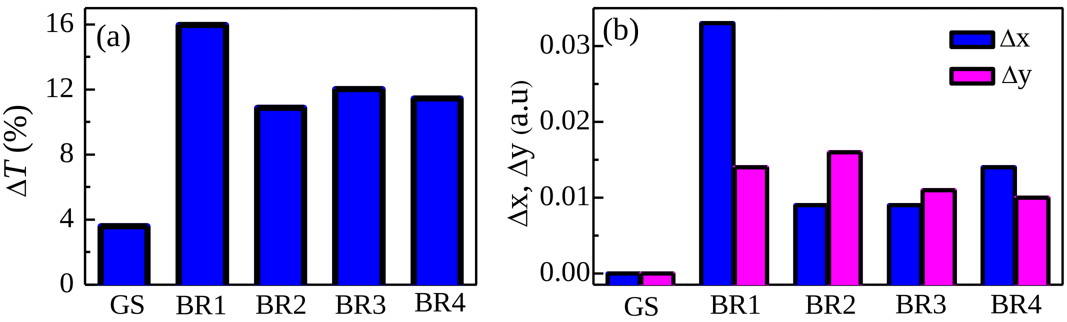

Figure 4. Humidity induced changes in transmittance (a) and CIE color coordinates x and y (b) for single polymer film with thickness of 290 nm deposited on bare glass substrate (GS) and on Bragg reflectors (BR) (BR1-5 layers, BR2-7 layers - Nb_2O_5 and SiO_2; BR3-5 layers, BR4-7 layers – dense and mesoporous Nb_2O_5).

Table. 1. Average sensitivity in [% / % RH] and accuracy ΔRH in [% RH] for single layer deposited on bare glass substrate (GS) and on Bragg reflectors (BR)

	GS	**BR1**	**BR2**	**BR3**	**BR4**
Sensitivity	0.04	0.18	0.12	0.13	0.13
ΔRH	5	1.1	1.7	1.5	1.5

It is seen from Table 1 that the implementation of Bragg stack as a sensor's transducer enhances more than 4 time the sensitivity compared to this of glass substrate. The sensitivity of 0.18 % / % RH is comparable with those of single film on silicon substrate (0.16 % / %RH) [ ] but due to the smaller experimental error of transmittance measurement the accuracy of humidity detection (1.1 % RH for T- measurements) is smaller than in the case of reflectance measurement.

In our previous investigations [22] we have demonstrated the possibility of color sensing of humidity using single film on opaque (silicon) substrate. For example the color of film with thickness of 215 nm changes substantially from yellow to dark magenta. The main problem that exists in color sensing in reflection mode is the dependence of color on the viewing angle. This means that the sample color changes not only with humidity but also with the angle of the observation and it is difficult the real reason for color change to be distinguished unambiguously. This problem could be overcome to a great extent if color sensing in transmittance mode is used that means monitoring of color of the sensor using the transmitted light instead of reflected.

To check this we calculated x, y and z CIE color coordinates using transmittance spectra measured at low and high humidity by previously developed computer code [22]. Humidity induced changes in CIE color coordinates x and y for single polymer film with thickness of 290 nm deposited on bare glass substrate and on Bragg reflectors are shown in Figure 4b. As it can be expected there is no color change for film on glass substrate, while for all Bragg reflector the color changes mostly pronounced for 5-layers Bragg stack comprising SiO_2 and Nb_2O_5 films (BR1).

Figure 5 presents the calculated CIE color coordinates for BR1 for low and high humidity levels. It is seen that the color of the sample observed using transmitted light changes from blueish to magenta. The separation of colors in the color scheme is substantial for visual color detecting of humidity to take place.

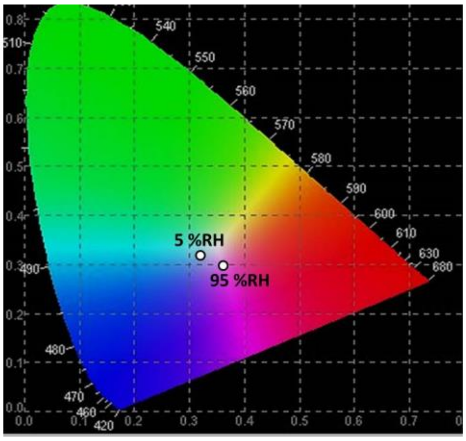

Figure 5. CIE color coordinates for polymer films with thickness of 290 nm deposited on 5-layers Bragg stack comprising SiO_2 and Nb_2O_5 films at denoted values of relative humidity.

4. Conclusions

The concept of using Bragg reflectors top covered with polymer film for optical sensing of humidity is verified and confirmed. Thin films of branched poly(N,N-dimethylacrylamide)-based copolymer with optimized thickness are used as humidity sensitive media while 5- and 7-layers Bragg reflectors comprising SiO_2, dense and porous Nb_2O_5 films are used for transducing elements. The detection of humidity is performed both by measuring transmittance spectra and monitoring the change of sensor's color in transmission mode. It is demonstrated that the implementation of Bragg reflector as a sensor's transducer element enhances more than 4 time the sensitivity compared to this when glass substrate is in operation. The obtained sensitivity of 0.18 % / % RH is comparable with those of single film on silicon substrate (0.16 % / % RH) while the accuracy of humidity detection (1.1 % RH) is higher as compared to the case of reflectance measurement due to the smaller experimental error of transmittance measurement. Although the change of color is comparable with this of film deposited on Si-substrate, the transmittance measuring approach has the advantage of experimental convenience and overcomes the ambiguity related to dependence of the color on the viewing angle. Top covered Bragg reflectors are promising sensing platforms and after proper optimization could be used for sensitive optical detection of humidity and vapors.

Supplementary Materials: none

Author Contributions: Conceptualization, Darinka Christova and Tsvetanka Babeva; Investigation, Katerina Lazarova and Rosen Georgiev; Theoretical modelling, Tsvetanka Babeva; Writing – original draft, Tsvetanka Babeva and Darinka Christova.

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Conflicts of Interest: The authors declare no conflict of interest

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