

Asymmetric one-dimensional photonic crystal for optical sensing in the visible spectral range

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Abstract. A gas sensor based on an asymmetric one-dimensional (1D) photonic band gap structure with one defect layer was designed and fabricated through layer-by-layer deposition of spin-coated poly methyl methacrylate (PMMA) and vacuum-deposited As₂S₃. Initially, the thickness variations, Δd , were determined of the thin films resulting from the poly methyl methacrylate exposure to chloroform vapor in the concentration range 100 – 9000 ppm. It was found that the value of Δd depends on the gas concentration and the exposure time. A two-layer structure was prepared consisting of PMMA and vacuum-deposited As₂S₃. Further, the permeability of thin As₂S₃ films to chloroform vapors was investigated. The asymmetric photonic structure consisted of 11 alternating layers of As₂S₃ and PMMA. The defect PMMA layer was located before the last high-refractive-index film of chalcogenide glass. The thickness of the defect layer of PMMA was pre-calculated so that the pass band be centered at the wavelength of 550 nm. An offset was observed of the position of the pass band to the larger wavelengths after exposure to chloroform vapor. The multilayered structure proposed is promising for optical sensor applications.

1. Introduction

Photonic crystals can be defined as structures in which the dielectric constant (refractive index) has a periodic variation in one, two or in all three orthogonal directions. 1D photonic crystals, or the so-called multilayer structures, consist of alternating layers of two materials with different refractive indices resulting in a periodically varying refractive index in one direction but homogeneous in the other two directions. Optical elements based on quarter-wave stacks are widely used in different optical devices, such as reflectors, filters, and waveguides [1]. Planar omnidirectional reflectors have been reported with fundamental stop bands centered at the wavelength $\lambda = 1.55 \mu\text{m}$ made of chalcogenide glass/polymer [2] or chalcogenide glass/chalcogenide glass [3-4].

The thickness of the layers in the Bragg stack is determined by the following equation:

$$nd = \lambda_0 / 4 \quad (1)$$

Where n is the refractive index of the layer, d is the thickness and λ_0 is the wavelength of the center of the fundamental reflection band of the Bragg stack. Making one of the layers with a different thickness, the so-called defect layer, results in the appearance of a pass band in the stop band of the

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Bragg stack. The defect layer behaves, in principle, as a cavity resonator when the resonant condition is satisfied. To this end, the thickness of this defect layer is usually chosen to be $nd = \lambda_0/2$. The position of the pass band is very sensitive to small changes of the thickness of the defect layer. This phenomenon makes the Bragg stacks with defect films very attractive as sensors for various external stimulus.

The sensitivity of the photonic band gap to small changes of the refractive index of the materials defining a photonic crystal is well known. The photonic crystal systems are responsive to external stimuli, such as solvents, vapors, temperature, pH [5], biomolecules [6], and mechanical force [7]. It is also known that gases possess a refractive index close to that of air, differing in the order of 10^{-4} [2]. It is easily estimated then from formula (1) that different gases permeating into the structure cannot cause a significant change in the position, λ_0 , of the fundamental reflection band. Therefore, fabricating a gas sensor based on the changes of the refractive index is not possible and materials must be sought that change their volume under the influence of the gas that would be the object of detection. From the literature it is known that upon contact with chloroform thin PMMA (poly methyl methacrylate) films increase their thickness by $\Delta d = 13.6 - 19.7\%$ [8]. In a previous work [9], the possibility was demonstrated of preparing a Bragg stack from As_2S_3 /PMMA for gas-sensing application in the infrared spectral range.

The aim of the present work is modelling an asymmetric photonic structure that switches from transparent to Bragg reflector states (characterized by a photonic stop band in the visible range), as well as its subsequent testing as a gas sensor. The chalcogenide glass composition was chosen such that the material would be transparent in the larger part of the visible region while at the same time possessing a sufficiently high refractive index. Our previous studies [10] have shown that thin films of this composition have a band gap of 2.4 eV (516 nm).

2. Experimental details

A multilayered filter was fabricated comprising eleven alternating thermally-evaporated As_2S_3 and spin-coated PMMA layers. The thickness of all films was calculated using equation (1) for $\lambda_0 = 550$ nm with the exception of the last PMMA film before the chalcogenide film which completes the Bragg filter. The thickness of this PMMA film satisfies the relation $nd = \lambda_0/2$. The polymer layers are obtained by pouring a drop of 0.3 ml of a 2.5 wt % polymer solution. The speed and duration of spinning were 2000 rpm and 30 s, respectively. To remove the extra solvent, the samples were annealed for 30 min at a temperature of 60 °C. The chalcogenide films were deposited by conventional thermal evaporation at a base pressure of 2×10^{-3} Pa and a deposition rate of 0.1 nm/s.

Optical transmittance and reflectance measurements at normal incidence of the light beam were carried out in the spectral range from 350 nm to 2000 nm using a Cary 05E UV-VIS-NIR spectrophotometer. The spectrophotometer is equipped with a gas cell which allows *in situ* measurements of spectrophotometric quantities in the presence of a gas with a given concentration.

The optical constants (refractive index, n , and extinction coefficient, k) and thickness, d , of the thin films were calculated using transmittance and reflectance measurements and applying the double methods developed by Abeles and Theye [11] and a procedure developed in [12, 13].

3. Results and discussion

We modelled and prepared a multilayered coating from chalcogenide glass and a polymer operating as a Bragg stack with one defect layer and a stop band in the visible spectral range. As_2S_3 chalcogenide glass and PMMA were used as high- and low-refractive-index materials, respectively. The dispersion of the refractive indices of both materials are given in figures 1a and 1b respectively.

Further, in a separate experiment, the gas sensitivity of a PMMA layer to chloroform was determined. Figure 2a represents a plot of the variation in the reflectance at $\lambda = 450$ nm of a thin PMMA film with a thickness of 92 nm during exposure to chloroform at concentrations ranging from 100 to 2000 ppm. It is seen that notable variations in the reflectance as a result of

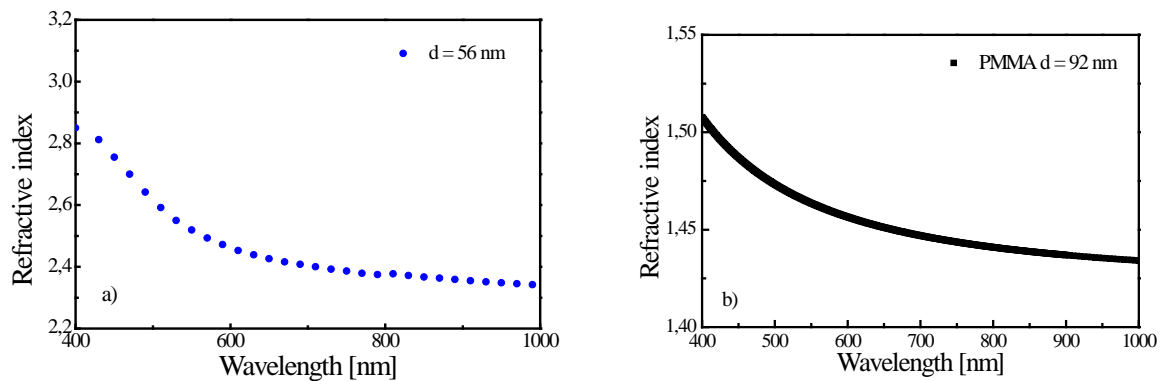


Figure 1. Dispersion of the refractive indices of thin films of As₂S₃ (a) and PMMA (b).

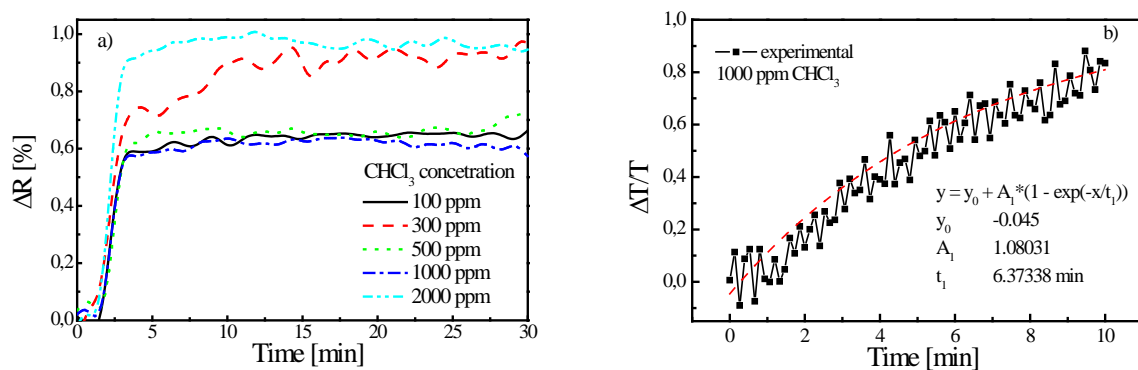


Figure 2. Variations in the reflectance of a single PMMA film exposed to chloroform gas in the concentration range 100 – 2000 ppm (a), and transmittance, ΔT , of a three-layer structure exposed to gaseous chloroform at a concentration of 1000 ppm (b).

the changes in the PMMA thickness start after ~ 30 s of exposure to chloroform and reach saturation after 2.5 – 3 minutes.

In a prior work [9, 10], we demonstrated that chloroform vapor induces negligible variation in the thickness and refractive index of the thin chalcogenide films. This is why our next step was to determine the permeability to chloroform of the thin As₂S₃ film. To this end, three-layer coatings consisting of As₂S₃/PMMA/As₂S₃/substrate were prepared. The relative changes of the transmittance at a CHCl₃ concentration of 1000 ppm are shown in figure 2b. It is seen that the time necessary to reach a 1 % variation is approximately 10 min. It is thus concluded that the chalcogenide film delays the reaction of the PMMA film by approximately a factor of 20. It is seen in figure 2b that the time dependence of $\Delta T/T$ follows an exponential law of the type $y = y_0 + A_1(1 - \exp(-t/t_1))$, where y_0 is the initial value of the transmittance, and $A_1 = 1.08$ and $t_1 = 6.37$ min are parameters. A similar functional dependence was observed in [14] for the penetration of oxygen in silver films.

Further, the investigations continued with testing the sensitivity of the Bragg stack. The thickness of the layers in the stack is calculated to be a quarter-wavelength at the target wavelength, λ_0 , i.e., $n_H d_H = n_L d_L = \lambda_0/4$. The center wavelength in the present work is $\lambda_0 = 550$ nm. The target thickness of the As₂S₃ films was calculated to be 56 nm. The spin coated poly-methyl methacrylate films were with a thickness of ~ 92 nm for the layers in the Bragg stack and $d_D = \lambda_0/2n_L = 183$ nm for the defect film. An evaluation of the reflectance as a function of the number of layers in the stack is shown in figure 3. An increase of the reflectance in the spectral range 450 – 700 nm and the formation of a stop band are clearly seen. The maximum reflectance value is $R = 98.2$ %, which was achieved for a nine-layer coating. The presence of a defect layer creates defect modes located within the photonic band gap, which

are analogous to the defect states generated in the forbidden band of a doped semiconductor [15]. The choice of the optical thickness of $\lambda_0/2$ for this layer is the reason for the appearance of a pass band centered at the wavelength $\lambda = 550$ nm in the 11-layer coating. The photonic band is split into two stop bands, the first one having a maximum in the blue spectral range at $\lambda = 490$ nm, with the second one being centered at $\lambda = 602$ nm.

Figure 4 presents the variations in the transmittance spectra in the area of the photonic band gap when the multilayered structure is exposed at different durations to saturated chloroform vapor and to a 1000 ppm concentration of CHCl_3 in an argon atmosphere.

It is seen that the changes in the transmission increase with the time. Maximum values for ΔT of $\sim 3.5\%$ and $\sim 1.5\%$ are observed in the spectral range 500 – 650 nm for saturated chloroform vapor of and 1000 ppm gas, respectively.

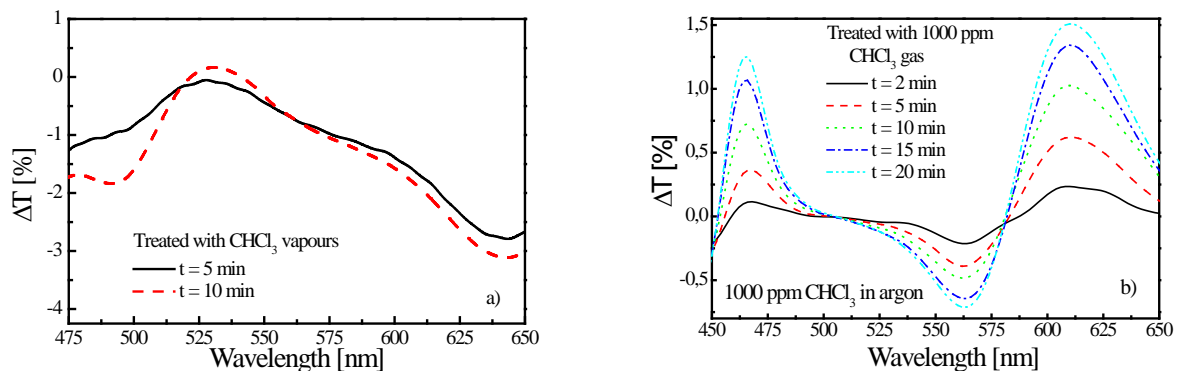


Figure 4. Variations of the transmittance in the area of fundamental reflection of the Bragg stack under exposure to saturated chloroform vapor (a), and to a gas mixture of chloroform at 1000 ppm concentration in an argon atmosphere (b).

4. Conclusions

A Bragg stack was designed with a stop band in the visible spectral range consisting of alternating layers of chalcogenide glass and PMMA with one defect polymer layer. The asymmetric one-dimensional photonic structure was tested as a gas sensor operating on the principle of optical detection. To this end, the penetration of chloroform through a single- and a three-layer coating was initially investigated. An offset of the pass band was observed after exposure to chloroform vapor. The structure fabricated demonstrates variation of the transmission in the blue, green and red spectral ranges after exposure to chloroform. The multilayered structure proposed represents a promising platform for optical sensing applications.

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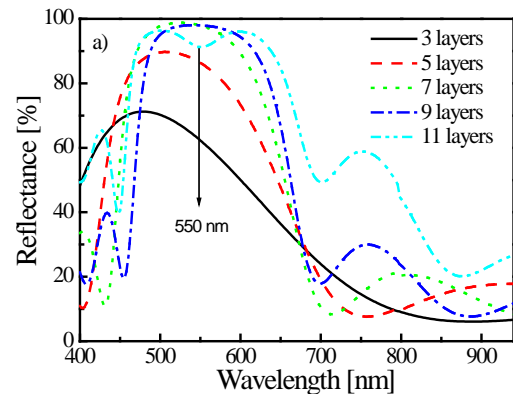


Figure 3. The formation of a stop band in the Bragg reflector depends on the number of layers in the stack.

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