One dimensional photonic crystals from As$_2$S$_3$ and PMMA films for photonic and sensor applications

T Babeva$^1$, G Marinov$^1$, J Tasseva$^1$, A Lalova$^1$ and R Todorov$^1$

$^1$Institute of Optical Materials and Technologies "Academician Jordan Malinowski", Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 109, 1113 Sofia, Bulgaria

E-mail: babeva@iomt.bas.bg

Abstract. One dimensional photonic crystal (1D-PhC) in form of 19 layered stack was prepared through layer-by-layer deposition of spin coated Poly (methyl methacrylate) ($n = 1.49$ at 1.55 $\mu$m) and vacuum deposited As$_2$S$_3$ ($n = 2.27$ at 1.55 $\mu$m) as low and high refractive index materials, respectively. The optical properties of the single layers and the multilayered stack are studied at normal and oblique incidence of linearly polarized light. The possibility of using the 1D-PhC as an omnidirectional reflector was exploited theoretically and confirmed experimentally. Besides, the prospect of using the studied structure for chemical sensing with optical read-out is demonstrated.

1. Introduction

One dimensional (1D) photonic crystals (PhC) are structures comprising two media with different refractive indices arranged in a 1D periodic manner. Among the numerous areas for their application the most attractive ones are in organic light emitting devices to enhance their white light emission [1], as omnidirectional reflectors in hollow optical fibers [2], dielectric reflectors and filters [3].

The widely accepted concept of 1D - PhC is a quarter-wave stack of alternating low- and high-refractive index layers ($n_L$ and $n_H$) ($nd = \lambda/4$, $n$ - refractive index, $d$ - physical thickness, $\lambda$ - operating wavelength) [4]. For a wave propagating normally to the stack (zero angle of incidence) 1D photonic band gap (i.e high reflectance band) exists that is shifted towards shorter wavelengths with increasing of the angle of the light incidence (oblique incidence). For application of 1D PhC as reflector in optical fibres an omnidirectional reflectance (ODR) is required that means reflectance of the stack to be close to 100 % for all incident angles and polarizations of light. It has been shown that if the optical contrast $\Delta n (=n_H - n_L)$ and number of the layers are sufficiently high, an omnidirectional reflectance band would be open [5]. Additional requirements towards $n_L$ and $n_H$ values are placed for ODR band to be open: $n_H > 2.264$ [6], $\Delta n > 0.75$ [6] and a large value of the ratio $n_L / n_0$, ($n_0$ being the refractive index of the incident medium) [7]. Apart from the mentioned optical requirements for ODR band, it is very important the chemical and mechanical compatibility of the layers in the stack to be guaranteed in order to prevent multilayers from cracking and delaminating.

One good alternative to high temperature processed systems is the combination of chalcogenide glasses ($n_H > 2.2$ at 1550 nm) and polymer layer ($n_L \sim 1.5-1.7$) [8-10]. Quarter-wave stacks from
As$_{33}$Se$_{67}$ ($n_H = 2.64$), Ge$_{20}$Se$_{80}$ ($n_H = 2.58$) and Ge$_{25}$Se$_{75}$ ($n_H = 2.35$) as high refractive index materials and polyamide–imide films (PAI) ($n_L = 1.67$), polystyrene (PS) ($n_L = 1.53$) and polyvinyl-butyral (PVB) ($n_L = 1.47$) as low refractive index materials were prepared by alternating vacuum deposition of chalcogenide thin films and spin coating of polymer films [8-10]. The stacks comprised between 15 and 17 layers and exhibited high reflection band in NIR (near infrared) region both for normally and obliquely incident s-polarized light.

It was demonstrated that broadening of ODR band could be achieved in Ge$_{33}$As$_{12}$Se$_{55}$/polyamide-imide polymer stacks by photo- or thermo- doping of chalcogenide glass with silver resulting in increasing of the optical contrast due to higher refractive index of the doped chalcogenide glass [7].

It was shown that the deposition of a thin 50 nm Au film on the substrate under Ge$_{33}$As$_{12}$Se$_{55}$ ($n_H = 2.55$)/PAI ($n_L = 1.65$) stack provided higher angle-averaged reflectance for a low number of layers as compared to all-dielectric case [11]. Furthermore significantly increased omnidirectional bandwidth was observed compared to nonmetallized mirrors comprising the same materials [12].

Another possibility for achieving ODR band is combining two suitably chosen chalcogenide glasses, i.e fabrication of all-chalcogenide reflectors. Stacks from 15 alternating layers of Ge-S and Sb-Se [13] with optical contrast higher than 1 were fabricated by thermal evaporation. Further 17 layered stack from exposed As$_2$Se$_3$/GeS$_2$ with optical contrast higher than 0.8 have been already realized [14].

Planar chalcogenide NIR filters (Fabry-Perot filters) were prepared as quarter wave stacks made of Ge–S / Sb–Se pairs surrounding low refractive index Ge-S spacer [15] and alternating As$_2$S$_3$ and Ge$_{15}$As$_2$Se$_{15}$Te$_{45}$ layers with As$_2$S$_3$ spacer layer [16, 17].

In this study we designed, fabricated and investigated one-dimensional photonic crystals from As$_2$S$_3$ and Poly (methyl methacrylate) (PMMA) film as high and low refractive index films deposited layer-by-layer using thermal evaporation and spin coating methods, respectively. The good optical contrast (~0.8), mutual compatibility and low optical losses are the main factors that have determined the particular choice of the materials. The possibility of using the 1D PhC as omnidirectional reflector was explored theoretically and confirmed experimentally. Besides, the prospect of using the studied structure for chemical sensing with optical read-out is discussed.

2. Experimental details

The stock solution of the polymer was prepared by dissolution at ambient temperature of one gram of PMMA (Poly (methyl methacrylate)) in 10 ml of Dichloroethane (Aldrich) using magnetic stirrer for accelerating the process. The polymer films with different thicknesses were obtained by the method of spin coating using the stock solution further diluted by adding dichloroethane. Polymer layers with thicknesses of 260 nm were obtained by pouring a drop of 0.5 ml of 2.45 w/v % polymer solution on the preliminarily cleaned substrate. The speed and duration of spinning were 2000 rpm and 30 s. To remove the extra solvent the samples were annealed for 30 minutes at temperature of 60 °C.

The bulk As$_2$S$_3$ glass was synthesized in a quartz ampoule by the method of melt quenching from elements of purity 99.999 % [18]. The layers were deposited by thermal evaporation at deposition rate of 0.5 – 0.7 nm/s in vacuum of $10^{-3}$ Pa. The X-ray microanalysis showed that the film composition is close to that of the bulk samples. The thickness was controlled in situ by quartz oscillator monitoring and ex situ by optical and profilier measurements.

Multilayered stacks comprising 19 layers were prepared by alternating vacuum evaporation of As$_2$S$_3$ with target thickness of 170 nm and spin coating of PMMA with target thickness of 260 nm. The target thicknesses of both layers were calculated aiming at their optical thicknesses ($n_d$) to be a quarter of the operating wavelength (1.55 µm in our case).

Transmittance, $T$ and reflectance, $R$ spectra of single layers and multilayered stacks were measured at normal and oblique incidence of light with high precision UV-VIS-NIR spectrophotometer Cary 5E (errors in $T$ and $R$ at normal incidence are 0.3% and 0.5 %, respectively). For oblique measurements a
high quality Glan-Taylor polarizer for obtaining linear polarization and an in-house made Al-mirror [19] as a reference mirror were used (error in $R$ for oblique incidence is less than 1%).

3. Results and discussion

3.1. Characterization of a single layer

The knowledge of the optical parameters of the stack’s building blocks is very important for a correct design of the stack. Figure 1 presents refractive index, $n$ and extinction coefficient, $k$ of As$_2$S$_3$ with thickness, $d$ of 170 nm and PMMA layers with thickness of 260 nm. For determination of $n$, $k$ and $d$ the As$_2$S$_3$ layers were deposited simultaneously on two types of substrates - optical glass BK7 and Si-wafer. Optical constants and thickness were calculated from transmittance and reflectance measurements at normal light incidence using already developed calculating procedure [20]. PMMA polymer layers were deposited onto high refractive index substrate - flint glass with refractive index in the range 1.67 - 1.71 in order to guarantee high optical contrast between the substrate and the investigated layers. $n$, $k$ and $d$ of PMMA were determined through minimization of a function consisting of the discrepancies between measured and calculated $T$ and $R$ spectra using nonlinear curve fitting [21].

![Figure 1](image1.png)

**Figure 1.** Dispersion curves of refractive index $n$ and extinction coefficient $k$ for As$_2$S$_3$ (170 nm) and PMMA (260 nm) films, calculated by the procedures described in the text.

![Figure 2](image2.png)

**Figure 2.** Maximum Reflectance ($R$) in the photonic band for normal light incidence as a function of the number of the layers in the quarter-wave stack ($n_H=2.27, n_L=1.49$). Triangles present the experimental points.

The refractive indices (figure 1) at the wavelength of 1550 nm are 2.27 and 1.49 for As$_2$S$_3$ and PMMA films, respectively ($\Delta n = 0.78$) that means that the two conditions for existing of ODR band are fulfilled. Both layers are transparent at 1550 nm - the calculated values for extinction coefficients of layers are insignificant and almost zero within the framework of the experimental errors.

3.2. Theoretical modelling of the optical performance of the stack

For design and optimization of the optical behavior of the stack we used the transfer matrix method. A very comprehensive description of the calculations can be found in [6, 22]. Figure 2 presents the simulated and measured values of maximum reflectance at normal light incidence in the stop band of the quarter wave stack with $n_H=2.27$ and $n_L=1.49$ as a function of the number of the layers in the stack. It is important to note that each stack in our calculations consists of odd number of layers: the first and last layers of the stack are from the high refractive index material. In this case the reflectance is higher as compared to the case when the stack is terminated with low refractive index material.
It is seen from figure 2 that the increase of $R$ is mostly pronounced until the deposition of the 15th layer. The deposition of next layers leads to a slight rise. Very good agreement between the calculated and measured values was obtained.

3.3. Characterization of multilayered stack

Figure 3 (a) presents the positions (in nm) of the reflectance edges of the photonic bands measured at a level $R = 80\%$ as a function of the incident angle for p- and s-polarization. The ODR band is defined between the short reflectance edge at 0° and long reflection edge at 90° for p-polarization (see for example [6]). It is seen that for angles smaller than or equal to 70° a quasi ODR band centered at wavelength of 1396 nm with width of 48 nm exists in our case. It is located between the short $R$ edge of 0° and long $R_p$ edge for 70°. This means that the quarter-wave stack of alternating As$_2$S$_3$ and PMMA layers exhibits $R > 80\%$ for incident angle range 0° - 70° and all polarizations in the spectral range 1372-1420 nm. Theoretical calculations have shown that ODR band with width of 2 nm is opened at wavelength of 1369 nm.

Figure 3 (b), (c) and (d) present the measured spectra at 0°, 50° and 70° for both polarizations. The widening of s- and narrowing of p-reflection band as well as their shifts toward smaller wavelengths with the increasing of the incidence angle are clearly seen.

It is worth noting that the position of ODR band can be tuned simply by changing the thicknesses of the layers building the stack. Widening of the band can be achieved by increasing the optical contrast between the layers through selecting chalcogenide glass with a higher refractive index (GeSbSe for example [23]) or using the well known photo- and thermo-induced phenomena in chalcogenide glassy materials [14, 15, 24]. For example the photodarkening after illumination by light or the photodoping with silver increases the refractive index of As$_2$S$_3$ layer with 0.12 [24] and 0.25 [25], respectively.

3.4. Sensing experiments

Considering that PMMA swells when exposed to organic vapors [26, 27] we expected that this would lead to a shift of the photonic band gap of the stack. For the sensing experiments we prepared stacks with a 'defect' layer in the middle illuminated for 1 h (luminescence lamp, 200 W) in order to guarantee stable layers insensitive to further illumination. The defect layer is a PMMA film with doubled thickness (520 nm) which results in a transmission peak in the stop band (figure 4). We performed initial sensing experiments by exposing the fabricated stack to the vapors of water,
ammonia and chloroform. The sensing experiments are conducted by putting the sample above the analyte vapor originated from evaporation of the liquid of chloroform or ammonia analyte at ambient temperature and pressure or water at 100°C. The transmittance spectra are measured prior to and after the exposure to the analyte. Special attention is paid on conducting the measurements at one and the same spot.

Figure 4. a) Transmittance spectra of As$_2$S$_3$ / PMMA stack before and after exposure to chloroform vapors; b) and c) selected magnified regions of the spectra denoted on the figure

Figure 4 presents the $T$ spectra before and after chloroform exposure. It is seen that the chloroform vapors bring forth a shift of the band toward longer wavelength (about 10 nm) and consequent decrease of transmittance with value of 10 % at a wavelength of 1906 nm that is an easily detectable difference. Exposure to water and ammonia vapors provokes no changes in $T$ spectra. These sensing experiments aimed at showing a possible application of the fabricated stack as a chemical sensor with optical read-out. We are aware of the fact that although the initial results are promising, a lot of work is still to be done. The scientific efforts will be focused on enhancing the porosity of the layers enabling the analyte to penetrate easily into the multilayered structure. Besides the photonic band gap shift at different temperature and vapor pressure will be study.

4. Conclusions

The design, fabrication and characterization of one-dimensional photonic crystal (1D-PhC) are presented. The 1D-PhC consists of 19 quarter-wavelength layers of alternating As$_2$S$_3$ ($n_H = 2.27$ at 1.55 μm) and Poly (methyl methacrylate) ($n_L = 1.49$ at 1.55 μm) films as high and low refractive index layers deposited by thermal evaporation and spin-coating, respectively. The optical parameters derived from single layers characterization were used for theoretical modeling of the stacks performance. It was experimentally demonstrated that a 'quasi' ODR band was open for incident angles up to 70° with the central wavelength of 1396 nm and width of 48 nm.

A 19-layer quarter-wave stack from As$_2$S$_3$ and PMMA with a defect layer of PMMA with thickness of 520 nm in the middle was fabricated. The initial sensing experiments, conducted by exposure of the stack to the vapors of water, ammonia and chloroform showed that As$_2$S$_3$ / PMMA stack could be used for selective detection of chloroform. A shift of the transmittance band of about 10 nm toward longer
wavelengths and consequent decrease of $T$ with 10% at wavelength of 1906 nm are observed due to exposure to chloroform. No changes are detected for water and ammonia vapors. Further experiments focused on enhancing the porosity of stack's building blocks are needed.

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