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Sensor properties of asymmetric Bragg stack from chalcogenide glass and PMMA

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Asymmetric Bragg stack with one defect layer was designed and prepared through layer-by-layer deposition of spin coated Poly (methyl methacrylate) (PMMA) and vacuum deposited chalcogenide film. In this work, first the thickness changes, Δd of the thin films from poly (methyl methacrylate) following exposure to chloroform vapors in the concentration range 1000 - 9000 ppm were determined. Two layered structure from PMMA and vacuum deposited chalcogenide film was consecutively prepared. The ability of the thin chalcogenide films to let the chloroform vapors passing through was investigated. The asymmetric photonic structure consists of 11 alternating layers from $As_{30}Ge_{10}S_{60}$ chalcogenide glass and PMMA. The defect layer from PMMA is situated before the last high refractive index film from chalcogenide glass. The thickness of the defect layer from poly (methyl methacrylate) was determined so that the pass band to be centered at wavelength of 520 nm. It was observed an offset of the position of the pass band to larger wavelengths after exposure to chloroform vapors. The proposed multilayered structure exhibits potential for applications as optical sensor.

Keywords: Bragg stack, chalcogenide glass, PMMA, thin films, sensor properties

INTRODUCTION

Photonic crystals can be defined as structures in which the dielectric constant (refractive index) shows a periodic variation in one, two or in all three orthogonal directions [1]. 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. The thickness of the layers in the Bragg stack is determined by the following equation:

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

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. It is known that gases possess a refractive index close to that of air, differing of 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, the manufacture of 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 Δd = 13.6-19.7% [3]. In previous works [4, 5] the possibility was shown for preparation of a Bragg stack from $As_{30}Ge_{10}S_{60}$/PMMA for the infrared spectral range and the potential for gas sensing application. In the present paper we demonstrate modeling and deposition of multilayered coating from chalcogenide glass and polymer working as Bragg stack in the visible spectral range. The potential for gas sensor application is demonstrated. The chalcogenide glass composition was chosen such that the material would be transparent in the larger part of the visible region and at the same time would possess sufficiently high refractive index. Our previous studies [6] have shown that thin films of this composition have a band gap of 2.45eV (506 nm).

EXPERIMENTAL DETAILS

Thin films from $As_{30}Ge_{10}S_{60}$ were deposited in high vacuum of 10^{-3} Pa by thermal evaporation of previously weighted quantities of the bulk material. Bulk glasses from $As_{30}Ge_{10}S_{60}$ were synthesized in a quartz ampoule from elements of purity 99,999 % by the method of melt quenching [7, 8]. The deposition rate was 0.4 nm/s, and it was monitored

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by the change of the intrinsic frequency of oscillation of a quartz crystal. The composition of the bulk samples and thin films deposited on graphite substrates was determined by scanning electron microscopy with an X-ray microanalyser (Joel Superprobe 733, Japan). The conditions of EDX analyses are given in [9].

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

The filter was modelled from quarter-wave multilayered stacks comprising 9 layers and was prepared by alternating thermal evaporation of $As_{30}Ge_{10}S_{60}$ as high refractive material and spin coating of PMMA as low refractive index material. The nine layers that build the stack are with thicknesses ~ 56 nm and ~ 92 nm for $As_{30}Ge_{10}S_{60}$ and PMMA, respectively. The defect layer from PMMA with thickness $d_L = \lambda/(2n_L) = 176$ nm was deposited on top of them. The preparation of the stack finished with a thin chalcogenide film with thickness again equal to a quarter of the wavelength. To infiltrate chloroform through the chalcogenide layer and reach the defect layer from PMMA, one has to produce $As_{30}Ge_{10}S_{60}$ film with a high degree of porosity. To accomplish this task we used the well-known oblique deposition technique at 75°. The conditions of fabrication are detailed in [6].

The optical constants (refractive index, n and extinction coefficient, k) and thickness, d, of the thin $As_{30}Ge_{10}S_{60}$ films were calculated using transmittance and reflectance measurements and applying the double methods developed by Theye and Abeles [10], and a procedure developed in [11,12]

RESULTS AND DISCUSSION

In the present paper we demonstrate modeling and fabrication of multilayered coating from chalcogenide glass and polymer working as Bragg stack with one defect layer. As high and low refractive index materials were used chalcogenide glass with composition $As_{30}Ge_{10}S_{60}$ and PMMA, respectively. Dispersions of the refractive indices of the thin films from $As_{30}Ge_{10}S_{60}$ evaporated on rotated substrates (0^o) and oblique deposition (75^o) are shown in Fig. 1a. It is seen that in the visible spectral region (in the range of 500 to 800 nm) $As_{30}Ge_{10}S_{60}$ thin layers have a relatively high refractive index 2.40 -2.55 (Fig. 1a). The refractive index of the obliquely deposited film at angle of incidence of vapors 75° is shown in Fig. 1a. According to [2] to provide sufficient penetration of the gases to the inner layers of the photonic crystal layers their porosity is required to be in the range of 50-70%. Applying the Bruggeman formula for calculation of the porosity, ϕ [6] and the data for the refractive index for the bulk glass with the same composition [13], we found that the value for ϕ of the obliquely deposited film is 58.8 %.

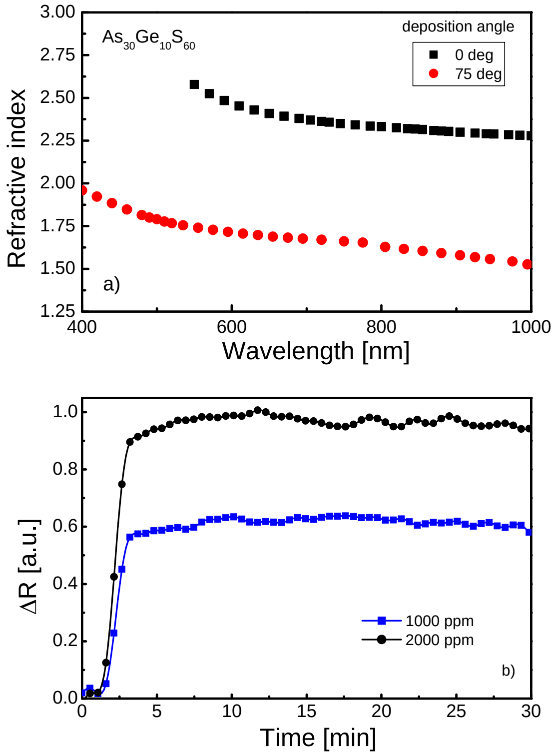

Fig. 1. Dispersion of the refractive index of thin $As_{30}Ge_{10}S_{60}$ films evaporated on rotated substrates (0^o) and oblique deposition (75^o) (a) and the changes in the reflection of a single PMMA film exposed to chloroform in gas phase with concentration 1000 ppm and 2000 ppm in argon atmosphere (b).

In the next step we have probed the sensitivity of single layered coatings from PMMA and $As_{30}Ge_{10}S_{60}$ film under exposure to chloroform vapours. Fig.1b is a plot of the changes in the reflectance at $\lambda = 450$ nm of a single PMMA film with thickness 92 nm during its exposure to chloroform with concentrations 1000 and 2000 ppm. The desired quantity of gaseous chloroform was pushed in the camera. It is seen that the notable changes in the reflectance due to of thickness changes of PMMA are started after ~ 30 s exposure to chloroform and achieved saturation after 2.5-3 minutes.

In our previous work [6] we showed that chloroform vapors induced negligible changes in thin $As_{30}Ge_{10}S_{60}$ films. To determine the time for penetration of chloroform through the chalcogenide layer and its interaction with PMMA film we used three-layer coating consisting of one polymer film sandwiched between two chalcogenide films. The changes in the transmittance spectra due to the changes in film's thickness during exposure to chloroform are shown in Fig.2.

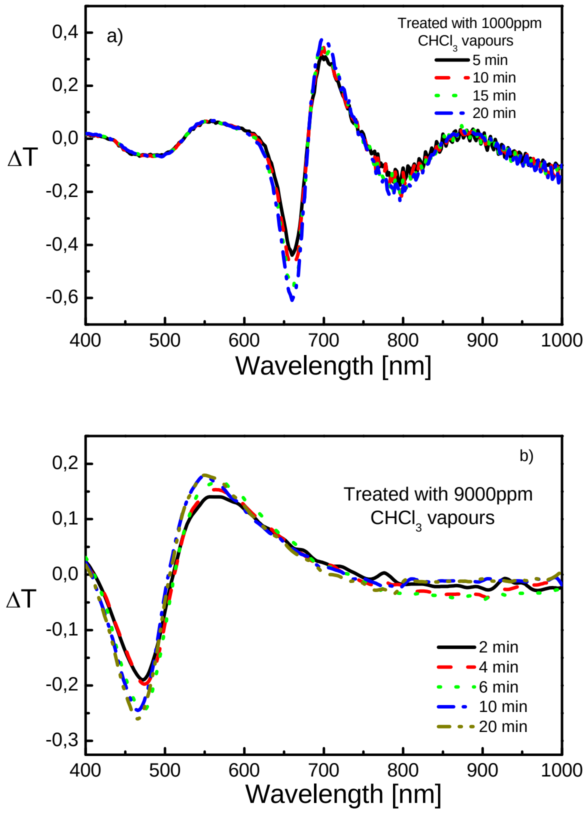

Fig. 2. Changes in the transmittance, ΔT of three-layered structure exposed of chloroform in gas form at concentrations 1000 ppm (a) and 9000 ppm (b).

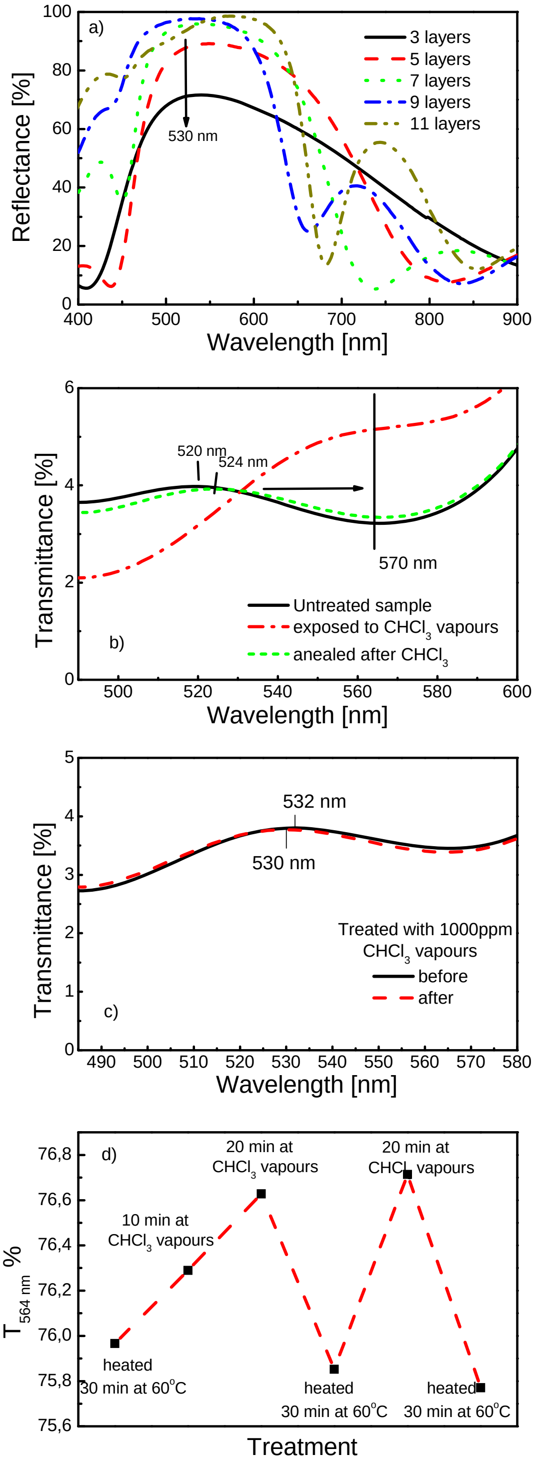

Fig. 3. Evolution of the reflectance band with the number of the layers in the filter structure (a); changes of the pass band in the spectral range 500-570 nm under exposure to vapors of chloroform (b) in gas form at concentration 1000 ppm (c); and cyclic changes of the value of T at wavelength λ = 564 nm for 11 layered filter consecutively exposed to chloroform and thermal treatment (d).

The quarter-wavelength stack, i.e., $n_H d_H = n_L d_L = 1/4\lambda_0$ with a target wavelength of $\lambda_0 = 550$nm was prepared from PMMA and chalcogenide thin films with composition $As_{30}Ge_{10}S_{60}$. In Fig. 3a the reflectance spectra of a multilayer coating is shown. The changes of the position of the pass band centered at ~ 520 nm are shown in Figs.3b-c. Due to the increase of the thickness of the defect layer a shift was observed to the longer wavelengths. It is seen that even concentration of the gaseous chloroform of 1000 pm induces 2 nm shift of the pass band. The obtained changes probably are due to the volume changes of defect PMMA film. It is known that chloroform in gas phase possess refractive index (*n* = 1.001) close to those of air [2]. In the case of vapors significant shift from 520 nm to 570 nm was observed (fig. 3 b). The significant changes of vapor probably are due not only of the increase of the thickness of the defect layer but higher refractive index of vapors (*n* = 1.36) [2]. After annealing at 60°C the band nearly restores its original position. The cyclic changes of transmittance of pass band are shown in fig. 3d.

CONCLUSION

The subject of the present work is modeling and preparation of an asymmetric Bragg stack with one defect layer from chalcogenide glass and organic polymer – PMMA. Taking advantage of the low absorption of the glass with composition $As_{30}Ge_{10}S_{60}$, a Bragg stack with a stop band in the range 400-700 nm was prepared. The deposition of a defect layer was used to realize of pass band in fundamental reflection band. In the next step the sensitivity of single layers and multilayered coatings was probed. It was established that the pass band is sensitive to concentration of chloroform 1000 ppm.

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СЕНЗОРНИ СВОЙСТВА НА АСИМЕТРИЧЕН БРАГОВ СТЕК ОТ ХАЛКОГЕНИДНО СТЪКЛО И PMMA

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(Резюме)

Асиметричен Брягов отражател с един дефектен слой е моделиран и получен чрез послойно нанасяне на центрофужно нанесени покрития от поли (метил метакрилат) (ПММА) и вакуумно изпарени халкогенидни филми със състав $As_{30}Ge_{10}S_{60}$. Изследвана е промяната на дебелината на тънки слоеве от ПММА при излагането им на пари на хлороформ в аргонова атмосфера с концентрация 1000-9000 ppm. Двуслойни покрития от тънки слоеве от ПММА и халкогенидно стъкло са използвани за определяне способността на халкогенидния филм да пропуска пари на хлороформ. Асиметричият фотонен кристал е изграден от 11 редуващи се слоеве от халкогенидно стъкло със състав $As_{30}Ge_{10}S_{60}$ и ПММА. Дефектният слой от ПММА е разположен преди последния филм от халкогенидно стъкло. Неговата дебелината беше определена така, че ивицата на пропускане да бъде разположена при дължина на вълната 520 нм. В резултат на излагането на пари на хлороформ беше наблюдавано отместване на ивицата на пропускане към по-големи дължини на вълната. Предложената многослойна структура показва потенциални възможности за приложения като оптичен сензор.