Vacuum deposited GeSbSe thin films for photonic applications

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Abstract. The potentialities are studied of Ge28Sb12Se60 thin films deposited by thermal evaporation in vacuum for preparing 1D photonic crystal arranged as a multilayered stack and operating in the NIR. Thin films of PMMA (poly (methyl methacrylate)) deposited by spin-coating are chosen as a second counterpart of the stacks. The morphological and optical characterization results show that both kinds of single layers have a smooth surface and exhibit a large difference in their refractive indices, which presupposes a high optical contrast of the system. Further, a 13-layer stack built by alternating deposition of the two materials is prepared. The formation of an omnidirectional reflectance band (ODR) centered at λ = 1.5 µm with a maximum value of R = 96.3% is demonstrated. The ODR’s width at half maximum is 320 nm. On the basis of the results obtained, the possible ways of optimizing further the system studied are outlined. Finally, the prospects of practical applications of the multilayered reflector developed are discussed.

1. Introduction

The 1D photonic crystals arranged as multilayered stacks of thin films of two materials with different dielectric constants have lately found ever widening applications in optical technologies. This has mainly been due to the recently achieved progress in designing the well-known Bragg’s stacks, which allow one to obtain a photonic band gap (PBG) in different spectral ranges, similarly to the 3D photonic structures [1]. As is known, in the frequency ranges of the PBG, the media are characterized by an “omnidirectional reflection” (ODR), i.e., reflectance of nearly unity for every angle of incidence and light polarization state [2]. The key prerequisite for this is the presence of a sufficiently high optical contrast of the system, which is determined by the difference in the refractive indices of the two materials building the structure of the 1D photonic crystal.

In searching for suitable combinations of materials for preparing multilayered reflectors operating in the NIR spectral range, it has been demonstrated that the chalcogenide glasses and organic polymers offer unique possibilities for creating and processing jointly structures with high optical contrast, which explains the continuously growing interest toward these media [3]. In the most successive devices so far, thin films of As2Se3 coupled with thermo-plastic polymers have been used [4]. This glass possesses numerous valuable properties, namely, high refractive index and transmittance in a wide spectral range in the IR; however, it has some disadvantages, such as low glass transition point.

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temperature $T_g$ and possibility for photodegradation at 1550 nm, as already shown for As$_2$S$_3$ [5]. To overcome these deficiencies, the efforts of scientists have been focused on synthesizing and using of high-temperature multicomponent glasses with high refractive indices and transparency in the IR. In this respect, the GeSbSe glassy system seems very promising, especially the composition Ge$_{28}$Sb$_{12}$Se$_{60}$, which has $T_g$ of about 285 °C, high transparency in the spectral range 1-16 µm and a refractive index of 2.61 at $\lambda = 5$ µm. This excellent optical glass has been widely studied recently and some potential applications have already been developed, for example as optochemical and biosensors operating in the near and mid-IR [6, 7], etc.

It is the aim of the present paper to study the potentialities of vacuum deposited Ge$_{28}$Sb$_{12}$Se$_{60}$ thin films coupled with organic polymer layers for preparing 1D photonic crystal with a photonic band gap in the NIR spectral region, centered at about $\lambda = 1550$ nm.

2. Experimental

The high-refractive-index component of the multilayered structures was obtained by thermal evaporation of preliminarily synthesized bulk material with composition Ge$_{28}$Sb$_{12}$Se$_{60}$. The synthesis of the glass from the pure constituent elements (99.999%) was performed in a quartz ampoule by a standard melt quenching method at 1000°C and continuous homogenization during 10 hours. The films were deposited at a rate of about 0.5 nm/s on BK-7 optical glass plates and Si wafers in a high-vacuum unit at a residual pressure of 5×10$^{-3}$ Pa. The thickness of the samples was calculated according to the criteria for fabrication of a quarter-wave stack, known to be the best structure for producing high-reflectivity optical coatings [8]. Thus, for the wavelength of interest $\lambda = 1550$ nm, a thickness value of 140 nm was obtained.

The low-refractive-index counterpart of the multilayered system studied was prepared by spin coating of PMMA dissolved in dichlorethane (Aldrich). In preliminary experiments, the concentration of the solution and the spin rate and duration were varied in order to obtain films with thickness of 260 nm, as calculated by using the above mentioned criteria [8]. This was achieved by a solution containing 3.5 wt. % PMMA coated at 3000 rpm for 30 s. To remove the extra solvent, the as-prepared films were annealed at 60°C for 30 min.

After optical and morphological characterization of the two kinds of single layers, a multilayered stack comprising 13 layers (7 of chalcogenide and 6 of polymer) was prepared by alternating vacuum evaporation of Ge$_{28}$Sb$_{12}$Se$_{60}$ and spin coating of PMMA with target thicknesses of 140 nm and 260 nm, respectively. During this step-by-step fabrication of the stack, transmittance and reflectance spectra at normal and oblique light incidence were taken periodically by a Cary 5E high-precision UV-VIS-NIR spectrophotometer ($\Delta T = 0.3\%$, $\Delta R = 0.5\%$). For the oblique measurements, a high-quality Glan-Taylor polarizer was used to obtain linear polarization and a self made Al-mirror [9] was used as a reference one (error in $R$ for oblique incidence of less than 1%).

The optical constants (refractive index, $n$, and extinction coefficient, $k$) and the thickness $d$ of the single layers were calculated based on the spectrophotometric measurements at normal incidence in the interval 800-2400 nm using an already-developed calculating procedure [10]. The optical constants were used for characterization of both kinds of single layers, as well as for modeling and optimizing the optical behavior of the stacks.

Morphological investigations were performed by a Philips 515 scanning electron microscope.

3. Results and discussion

Figure 1 shows the spectral dependences of the refractive indices of 140 nm Ge$_{28}$Sb$_{12}$Se$_{60}$ and 260 nm PMMA films deposited on BK-7 glass plates at the experimental conditions chosen. The large difference in the refractive index values in the whole spectral range studied is clearly seen. For example, at the wavelength of interest $\lambda = 1550$ nm, $n$ is 2.72 for GeSbSe and 1.49 for PMMA, which determines a high optical contrast of 1.23. This value gives one reasons to expect that a multilayered reflector could be built by a relatively small number of alternating single layers. Simultaneously, the SEM micrograph presented in figure 2 reveals the smooth surface morphology of a chalcogenide thin
film, which is an important prerequisite for the good quality of high-reflectivity optical coatings. A similar result was obtained for the polymer sample surface (the picture was not presented for simplicity). Therefore, the experimental conditions used allowed us to produce GeSbSe and PMMA films with properties appropriate for preparing a 1D photonic crystal in the form of a multilayered system operating in the NIR, in accordance with the aim of the study.

Figure 1. Dispersion curves of refractive indices of 140 nm GeSbSe and 260 nm PMMA films.

Figure 2. SEM micrograph of 140 nm GeSbSe film deposited on a BK-7 glass plate.

Figure 3 shows the transmittance (a) and reflectance (b) spectra measured at normal incidence during the step-by-step fabrication of a multilayered stack by alternating deposition of Ge28Sb12Se60 and PMMA films with thicknesses 140 nm and 260 nm, respectively. The gradual formation of a high-reflectance band centered at 1650 nm is clearly seen. As it was expected due to the high optical contrast, a broad band with a maximal value of \( R = 98.7\% \) is achieved by a relatively small number of layers (11 in this stack – 6 of GeSbSe and 5 of PMMA), in contrast with the data in the literature [11]. The transmittance value in the stop band is 0.35%. The small deviation from 100% is within the experimental error. A further increase in the number of layers with one more pair of constituents practically did not lead to any significant increase of reflectance (\( R \) changed by 0.5%).

Figure 3. Transmittance (a) and reflectance (b) at normal incidence of the stack measured during preparation; (c) ODR band in a stack comprising 13 alternating GeSbSe and PMMA layers.

In fact, the stop bands in Figure 3(a) and (b) observed are to be expected since the constructed stack is a typical Bragg’s reflector, in which photons are forbidden to proceed in certain spectral ranges for normal incidence of light [1]. To check the existence of an omnidirectional band, \( T \) and \( R \) were measured with s- and p-linearly polarized light varying the angle of incidence from 0 to 70°. It was established that by increasing the incident angle the band position is shifted to the shorter
wavelengths, while the band is wider for s-polarization and narrower for p-polarization, as compared to the band for normal incidence. This is demonstrated in Figure 3(c), which presents the reflectance spectra of a 13-layers stack as measured at 0° and 70° angles of incidence. As seen, there is a wavelength region positioned around 1500 nm where the bands overlap and, therefore, can be regarded as an ODR band. The ODR’s width at half maximum is about 320 nm and the \( R \) value in the maxima is 96.3%. Obviously, further optimization of the system studied is needed in view of obtaining a value of \( R \) in the stop band close to 100%. Since the optical contrast is very high, more attention must be paid to improving the thickness control of the single layers, their mutual adhesion, etc. We believe that, after a successful optimization, the 1D photonic crystals studied will be appropriate for practical applications, for example, as biosensors for various bacteria, which has already been demonstrated [7] in a multilayered waveguide based on the same GeSbSe and GeSe glassy systems.

Conclusions
The results of the present study demonstrate the possibility of preparing a 1D photonic crystal arranged as a multilayered stack built by alternating deposition of thin films of Ge\(_{28}\)Sb\(_{12}\)Se\(_{60}\) and PMMA. It is shown that both kinds of single layers are characterized by smooth surface morphology, which is an important prerequisite for the good quality of the optical coatings. Furthermore, the high optical contrast established of the system allows the formation of a band with omnidirectional reflectance (ODR) by a relatively small number of layers (7 of GeSbSe and 6 of PMMA). The photonic band gap obtained is centered at about \( \lambda = 1.5 \mu \text{m} \), the width at half maximum of the ODR is 320 nm and the \( R \) value in the maxima is 96.3%. The results obtained are very encouraging; nevertheless, further optimization is needed for bringing \( R \) in the band closer to 100%. This would open up opportunities for practical applications of the developed multilayered reflector in the NIR spectral region.

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