Photonic bandgap amorphous chalcogenide thin films with multilayered structure grown by pulsed laser deposition method*

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Amorphous chalcogenide thin films were fabricated by the pulsed laser deposition technique. Thereafter, the stacks of multilayered thin films for reflectors and microcavity were designed for telecommunication wavelength. The prepared multilayered thin films for reflectors show good compatibility. The microcavity structure consists of $Ge_{25}Ga_5Sb_{10}S_{65}$ (doped with Er^{3+}) spacer layer surrounded by two 5-layer $As_{40}Se_{60}/Ge_{25}Sb_5S_{70}$ reflectors. Scanning/transmission electron microscopy results show good periodicity, great adherence and smooth interfaces between the alternating dielectric layers, which confirms a suitable compatibility between different materials. The results demonstrate that the chalcogenides can be used for preparing vertical Bragg reflectors and microcavity with high quality.

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Photonic bandgap (PBG) waveguides based on multilayered structure have promoted numerous applications, including optical communication[1], optical resonance[2], polarization discrimination[3], model filter[4], signal sensing[5], etc. The alternating layers that construct distributed Bragg reflectors (DBRs) are based on various semiconductor materials, such as nanocrystal Si, AlSi, GaAl and AlAs/AlGaAs. The two key prerequisites for facilitating distributed Bragg reflection are sufficiently high refractive index contrast (>0.7—0.8) between the material pairs forming multilayered thin films and high optical transmission of individual materials in wavelength range of interest. The amorphous chalcogenide multilayered thin films themselves or combined with low refractive index materials can satisfy mentioned criteria when designing reflectors for infrared (IR) region. W. Shen et al[6,7] reported narrow bandpass filters based on chalcogenides combined with cryolite. The so-called chalcogenide glasses were chosen and studied for their potential functionality, like transparent spectral range in the near and mid-IR (up to 10—20 μm), and they also show remarkable properties, like photosensitivity, high linear/non-linear refractive index and low phonon energy[8,9]. Especially in active optical applications, the low phonon energy of chalcogenide hosts warrants a low probability of multi-phonon relaxations between the energy levels of trivalent rare earth ions (RE^{3+}). Thus, the radiative efficiencies of the most rare earth emissions in near and mid-IR, for which the upper levels can be easily non-radiatively quenched by multi-phonon transitions, are improved.

This paper reports the preparation of amorphous chalcogenide thin film and their multilayered stacks by using pulse laser deposition (PLD). $Ge_{25}Ga_5Sb_{10}S_{65}$ chalcogenide glass was chosen as the matrix of Er^{3+} ions for its solubility of rare earth ions[10]. $As_{40}Se_{60}$ and $Ge_{25}Sb_5S_{70}$ chalcogenides were particularly selected to form the DBRs, which have large optical transmitting window covering the spectral range from the visible (VIS) to 11 μm, excellent resistance to devitrification, durability to water/solvent corrosion and suitable refractive index contrast (Δn=0.7 at 1.54 μm). Moreover, the manufacture feasibilities of glasses and thin films with these compositions are already reported.

There bulk targets with nominal composition of $As_{40}Se_{60}$, $Ge_{25}Sb_5S_{70}$ and $Ge_{25}Ga_5Sb_{10}S_{65}$ (doped with 5×10^{-3} of Er^{3+}) were prepared by conventional melt and quenching chalcogenide glass synthesis process[11]. The

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cylindrical samples with diameter of 25 mm and length of 20 mm were obtained by PLD from the same rod. Then the bulk samples with thickness of 1 mm were well polished for observing flat surfaces and parallel sides.

The single layer and multi-layer films were both grown by PLD. The thickness of each layer in multilayered structure was designed according to its deposition rate. Hence, the single layer films with thickness of around 1 μm were deposited to verify the deposition rate of each target. Targets were ablated using a pulse laser operating at 532 nm. To obtain the irradiation conditions as uniform as possible, the off-axis PLD technique with rotating targets and substrates was used. The ablated materials were collected on chemically cleaned microscope glass, SiO_2 glass and silicon substrate at room temperature. The substrates were positioned parallel to the target surface with the target-to-substrate distance of 5 cm. The optical refractive indices and thicknesses of single thin films were obtained from the spectroscopic ellipsometry data measured using an ellipsometer with automatic rotating analyzer (VASE, J. A. Woollam Co., Inc.). The ellipsometry data in the weak absorbing region were analyzed by Cauchy dispersion model. For understanding the changes of optical parameters for the single films compared with those for bulk targets, a scanning/transmission electron microscope (SEM/TEM) with an energy dispersive spectrometer (EDS, JSM 6400-OXFORD Link INCA) was used for determining the chemical compositions of bulk glasses and thin films. SEM/TEM techniques were also applied to observe the morphology of the thin films and multilayered PBG structure using a field-emission gun SEM (JSM 6301F). The thicknesses of each layer in multilayered stacks were measured schematically on the SEM image.

Thereafter, the PBG samples were grown successively by changing three targets as programmed in the vacuum chamber, and the thickness of each layer was determined on both the VASE deposition rate results as

$$T_{\mathrm{s}} = \frac{\lambda}{2n_{\mathrm{s}}}, \tag{1}$$

$$T_{\mathrm{DBR}} = \frac{\lambda}{4n_{\mathrm{DBR}}}, \tag{2}$$

where T_{s} and T_{DBR} are thicknesses of spacer layer and DBR layers, and n_{s} and n_{DBR} are refractive indices of spacer and DBR materials, respectively.

For simulating the reflectance in a multilayered system, the transfer matrix of the whole structure is introduced and given as

$$\boldsymbol{T} = \begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix} = \boldsymbol{I}_{\mathrm{air,1}} \left(\prod_{i=1}^{n-1} \boldsymbol{M}_i \boldsymbol{I}_{i,i+1} \right) \boldsymbol{M}_{i+1} \boldsymbol{I}_{i+1,\mathrm{Si}}, \tag{3}$$

where the notation i corresponds to the ith horizontal interface, $\boldsymbol{I}_{i,i+1}$ is the matrix corresponding to the wave propagation across the interface between i and i+1 media, and $\boldsymbol{M}_i$ is the propagation matrix.

The reflectance is then given as

$$R = \left| \frac{T_{21}}{T_{11}} \right|^2. \tag{4}$$

In this model, the dispersion of the refractive index of the individual chalcogenide layers in multilayered structures is taken into consideration. All the numerical simulation processes were taken under Matlab 7.12 R2011a.

The first DBR mirror was built by 5 pairs (N=5) of $As_{40}Se_{60}/Ge_{25}Sb_5S_{70}$ layers. The $Ge_{25}Ga_5Sb_{10}S_{65}$ spacer (doped with 5×10^{-3} of Er^{3+}) layer was sandwiched between two DBR mirrors to form a single wavelength cavity. A cavity structure with the central wavelength of 1.54 μm was designed. Optical reflectance spectra for multilayered PBG structure were recorded by VIS-NIR spectrophotometer (PerkinElmer) in the range of 1 100—2 100 nm using universal reflectance accessory (URA).

Tab.1 shows the chemical compositions of target materials and single films prepared by PLD measured by EDS. Generally, it has a good agreement between chemical compositions of target and corresponding single layer in case of $As_{40}Se_{60}$, and a selenium (Se) deficit (about 2%) is accompanied by an enrichment of arsenic (As). In cases of $Ge_{25}Sb_5S_{70}$ and $Ge_{25}Ga_5Sb_{10}S_{65}$, compared with targets, the signal films both show sulphur (S) deficits due to the volatility of S and the enrichments of germanium (Ge), gallium (Ga) and antimony (Sb) considering the measurement uncertainty. The sulphide PLD films show the modification of composition between targets and single films, which can lead to a change of optical properties, such as refractive index.

Tab.1 Nominal/real chemical EDS compositions (with weight percentage uncertainty of ±0.5%), refractive indices at 1.54 μm and the deposition rate of bulk targets and single films prepared by PLD

	Composition	As (%)	Ge (%)	Ga (%)	Sb (%)	S (%)	Se (%)	n (±0.01) at 1.54 μm	Deposition rate (nm/s)
Target	$As_{40}Se_{60}$	37.2	-	-	-	-	62.8	2.86	-
	$Ge_{25}Sb_5S_{70}$	-	23.3	-	5.0	71.7	-	2.16	-
	$Ge_{25}Ga_5Sb_{10}S_{65}$ +Er	-	18.7	4.6	9.5	67.2	-	2.25	-
Single film	$As_{40}Se_{60}$	39.0	-	-	-	-	61.0	2.57	0.94
	$Ge_{25}Sb_5S_{70}$	-	30.2	-	8.3	61.5	-	2.06	0.69
	$Ge_{25}Ga_5Sb_{10}S_{65}$ +Er	-	23.2	6.8	15.3	54.7	-	2.15	0.55

Fig.1 shows the refractive indices of single films prepared by PLD determined by VASE. Because the refractive index is very sensitive to the structure changes, the refractive indices of the PLD films can be significantly changed due to any changes of structure and chemical composition. We also compare the refractive indices of single films film with those of corresponding bulk target

as shown in the inset of Fig.1. It is found the refractive indices of sulphide films are slightly lower than those of corresponding bulk targets, but it is without clear correlation in respect with the chemical composition of samples, which is contrary with the result of our previous study[12]. This fact can be possibly explained by the instabilities of the wavelength of laser pulse, the output energy and the energy density of each laser pulse. It should be also noted that the deficit of S content in comparison with bulk target can contribute to the slight decrease of the refractive index. It is noted that $As_{40}Se_{60}$ film presents a larger decrease of refractive index corresponding to its target. Ignoring the changes of the refractive indices, the refractive index of each layer in multilayered PBG structure will be determined corresponding to refractive index of PLD single film for the following study.

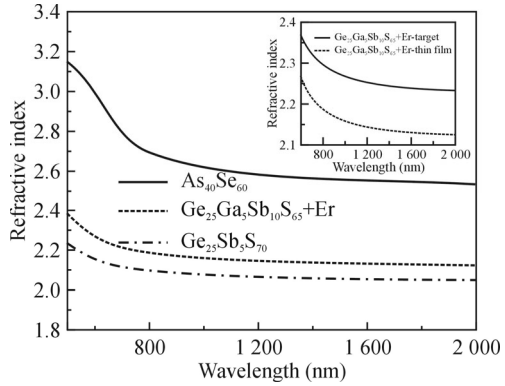
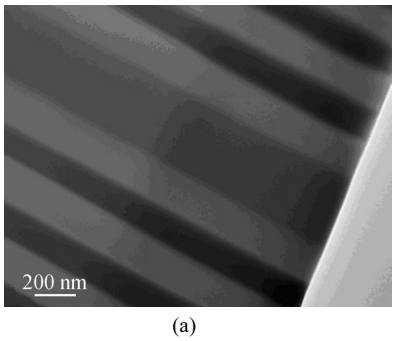
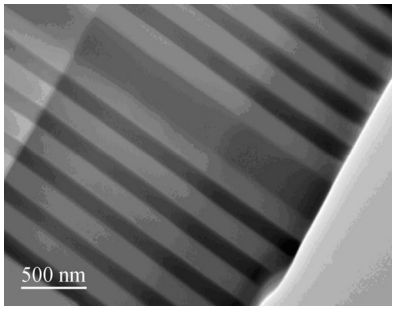


Fig.1 VASE refractive indices (with uncertainty of ±0.01) of PLD single films (Inset is refractive indices of $Ge_{25}Ga_5Sb_{10}S_{65}$+5×10^{-3} Er^{3+} target and single film.)

Fig.2 shows the SEM images of cross section of the multilayered PBG structure. These micrographs reveal strong contrast between the alternating layers because of the refractive index contrast. There is no obvious defect at the surface and the interface between adjacent layers. But the thicknesses of each layer are not in good agreement with the designed values. For example, the experimental thickness of spacer layer is much thinner (~250 nm) than the designed value (399 nm). This fact is resulted from the deviations of refractive indices and exact thicknesses of individual layers required for such structures.



(a)



(b)

Fig.2 SEM micrographs of cross section of multilayered PBG structure with different magnifications

Experimental and simulated reflectance spectra of the multilayered PBG structures with 5 pairs (N=5) of $As_{40}Se_{60}/Ge_{25}Sb_5S_{70}$ layers are illustrated in Fig.3, where the simulated results are based on the refractive indices of bulks and single films, respectively. The measured central wavelength is located at 1 484 nm, which is blue-shifted corresponding to the simulated value of 1 540 nm. The measured reflectance band with R>95% ranges from 1 345 nm to 1 590 nm, which is also blue-shifted. This fact is mostly due to the thickness nonuniformity of each layer in the multilayered PBG structure. The central wavelength shift $\Delta\lambda$ can be determined by optical thickness of the spacer layer as[13]

$$\frac{\Delta\lambda}{\lambda_0} = k\frac{\Delta(nd)}{(n_0 d_0)}, \tag{5}$$

where λ_0 is the central wavelength, n_0d_0 is the optical thickness of the spacer, and k is a positive coefficient typically between 0.3 to 1, whose exact value is connected to the structure of high reflection mirror. In our case, k is equal to 1.3. It indicates that the central wavelength shift $\Delta\lambda$ is linearly dependent on optical thickness change $\Delta(nd)$ of the spacer without consideration of spacer's photosensitivity. For a better characterization, Tab.2 shows the central wavelength of the bandpass and the full width at half maximum (*FWHM*) of the band for simulation and experimental results, respectively. The shift of central wavelength $\Delta\lambda$ for real sample is 56 nm.

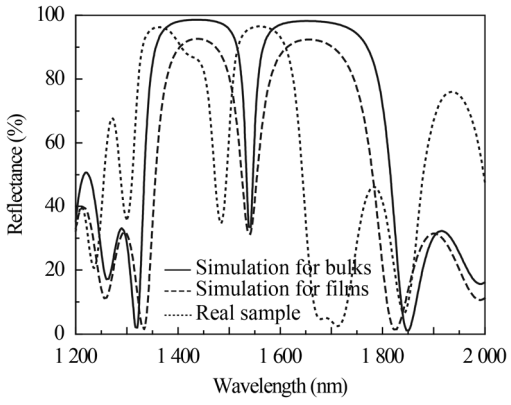


Fig.3 Experimental and simulated reflectance spectra of multilayered PBG structures with *N*=5

This work demonstrates the possibility of producing a Bragg reflector and a PBG structure using amorphous chalcogenide thin films prepared by PLD in the near IR and even mid-IR spectral range. Our further study is going to focus on controlling the optical thickness of each layer strictly in accordance with expected goals.

Tab.2 Central wavelength and *FWHM* for experimental and simulated results of multilayered PBG structures with *N*=5 based on refractive indices of targets and films

	Central wavelength (nm)	*FWHM* (nm)
Simulation for targets	1 540	20
Simulation for films	1 540	44
Real sample	1 484	35

We report a multilayered PBG structure merely based on chalcogenide thin films grown by PLD method. The spacer layer consists of $Ge_{25}Ga_5Sb_{10}S_{65}$ chalcogenide, and the DBR mirrors are made up of alternative $As_{40}Se_{60}$ and $Ge_{25}Sb_5S_{70}$ films. The quality of the films is controlled by SEM, EDS, TEM and VASE to determine their optical constants. Compared the single films with their corresponding bulks, the changes of refractive indices and chemical compositions are obvious. The shift of central wavelength in reflectance spectra of multilayered PBG structure is related to these changes and also connected to the optical thickness nonuniformity of each layers. Thus, amorphous chalcogenides show potentiality to form multilayered optical components in the near/mid IR region.

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References

[1] E. Yüce, G. Ctistis, J. Claudon, J.-M. Gérard and W. L. Vos, Optics Express **24**, 239 (2016).

[2] A. Naweed, D. Goldberg and V. M. Menon, Optics Express **22**, 18818 (2014).

[3] Chang S.-W., Optics Express **20**, 2516 (2012).

[4] Yang Liu and Lin Yi, Journal of Applied Physics **116**, 223102 (2014).

[5] BAI Yan, YAN Feng-ping, LIU Shuo, TAN Si-yu and WEN Xiao-dong, Optoelectronics Letters **11**, 421 (2015).

[6] W. Shen, M. Cathelinaud, M. Lequime, V. Nazabal and X. Liu, Optics Communications **281**, 3726 (2008).

[7] W. D. Shen, M. Cathelinaud, M. D. Lequime, F. Charpentier and V. Nazabal, Optics Express **16**, 373 (2008).

[8] Y. Shpotyuk, A. Ingram, O. Shpotyuk, A. Dziedzic, C. Boussard-Pledel and B. Bureau,. Nanoscale Research Letters **11**, 1237 (2016).

[9] LI Jun, CHEN Fen, SHEN Xiang, DAI Shi-xun, XU Tie-feng and NIE Qiu-hua, Optoelectronics Letters **11**, 203 (2015).

[10] V. Moizan, V. Nazabal, J. Troles, P. Houizot, J.-L. Adam, J.-L. Doualan, R. Moncorgé, F. Smektala, G. Gadret, S. Pitois and G. Canat, Optical Materials **31**, 39 (2008).

[11] S. Cui, C. Boussard-Plédel, J. Lucas and B. Bureau, Optics Express **22**, 21253 (2014).

[12] V. Nazabal, P. Nemec, A. M. Jurdyc, S. Zhang, F. Charpentier, H. Lhermite, J. Charrier, J. P. Guin, A. Moreac, M. Frumar and J. L. Adam, Thin Solid Films **518**, 4941 (2010).

[13] M. Lequime, R. Parmentier, F. Lemarchand and C. Amra, Applied Optics **41**, 3277 (2002).