STRUCTURE OF PULSED-LASER DEPOSITED As$_{50}$S$_{50}$ AMORPHOUS THIN FILMS

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As$_{50}$S$_{50}$ thin amorphous films were prepared by the pulsed laser deposition technique. The structure of the films is analyzed in detail on the basis of Raman scattering spectroscopy results. As-deposited layers contain pararealgar (γ-As$_4$S$_4$), χ-As$_4$S$_4$, β-As$_4$S$_4$ molecules, clusters of amorphous arsenic (probably As$_4$ structural units), S$_2$As-AsS$_2$, and As$_4$S$_5$ entities as well as α-As$_4$S$_4$, As$_4$S$_3$ molecules, and AsS$_3$ pyramids.

1. Introduction

Thin films (TF) of amorphous chalcogenides are due to interesting physico-chemical properties, their reversible and/or irreversible changes materials of great interest. The changes of properties induced by thermal-annealing or by exposure with electromagnetic radiation (irradiation with light of proper energy and intensity) are widely applicable in optics and optoelectronics [1]. Photoinduced changes of properties include such phenomena as photocrystallization (photoamorphization), photopolymerization, photodecomposition, photocontraction (photoexpansion), photovaporization, photodissolution of metals, photoinduced changes in local atomic configuration, photoinduced anisotropy etc. [2].

Generally speaking, many different deposition techniques can be used for fabrication of TF, for example vacuum thermal evaporation, DC/RF magnetron sputtering, chemical vapour deposition, spin-coating techniques, etc. One of the promising and prospective methods for TF preparation is pulsed laser deposition (PLD). The PLD has several advantages - relative simplicity of the process, often nearly stoichiometric transfer of target material to the films, easy control of the process by laser operating parameters and possibility to prepare films of unusual compositions [3].

In this work, we have focused our attention on PLD fabrication and detailed analysis of the structure of TF from As-S system.

2. Experimental details

Amorphous TF were prepared by PLD using rotating targets of chalcogenide glasses with nominal composition of As$_{40}$S$_{60}$ (As$_2$S$_3$). The target glasses were prepared by conventional melt-quenching method using high purity elements.

KrF excimer laser (LAMBDA PHYSIK COMPex 102) operating at 248 nm with constant output energy of 300 mJ per pulse ($\pm$1%), pulse duration of 30 ns and with repetition rate of 20 Hz was used for PLD of amorphous As-S TF. The energy fluency on the target varied from 1 to

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5 J cm^{-2}. The laser beam hits the target under an angle of about 45°. Amorphous TF were deposited in a vacuum chamber (background pressure ~6 × 10^{-4} Pa). The substrates used for PLD (chemically cleaned microscope glass slides) were positioned parallel to the target surface. The target to substrate distance was 5 cm. In order to obtain as homogeneous TF (in thickness) as possible, the off-axis PLD technique with rotating target and substrates was used.

      The composition of the films was controlled using electron microscope JEOL JSM-5500LV with energy dispersive X-ray micro analyzer (IXRF Systems).

      Raman scattering spectra were recorded at room temperature with the FT Raman spectrophotometer Bruker IFS 55/FRA106 using a backscattering method and excited by Nd:YAG laser (1064 nm).

3. Results

      As-S thin films prepared by PLD were homogeneous and amorphous according to optical and electron microscopy. The thickness of prepared films varied from ~930 to 1790 nm depending on the PLD parameters.

      The chemical composition of As-S PLD TF varied only slightly with the energy fluency of the laser beam used for PLD. In comparison with the chemical composition of glassy targets, overstoichiometry of ~ 7.6-10.7 at.% of As was found in prepared films. Minimum of arsenic overstoichiometry was observed in layers prepared using energy fluency of 3 J cm^{-2}.
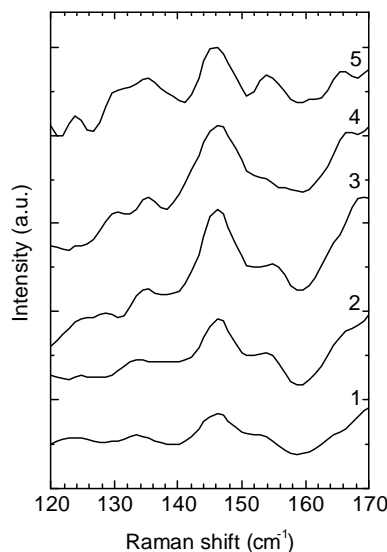

Fig. 1. Raman spectra of as-deposited As-S PLD TF - 120-170 cm^{-1} region; 1 - energy fluency 1 J cm^{-2}, 2 - 2 J cm^{-2}, 3 - 3 J cm^{-2}, 4 - 4 J cm^{-2}, 5 - 5 J cm^{-2}.

      Reduced Raman scattering spectra of PLD As-rich As-S TF are given in Figs. 1-3; Fig. 1-3 show 120-170 cm^{-1}, 170-290 cm^{-1}, and 290-450 cm^{-1} region, respectively. Dominant features of Raman spectra of as-deposited PLD TF are broad bands (i) in 200-270 cm^{-1} region with maxima at 224 and 235 cm^{-1} and (ii) in 290-410 cm^{-1} region with maximum at 349 cm^{-1} (Figs. 2, 3). Raman bands of lower intensity with maxima at 187 (with shoulder at 173), 201, and 274 cm^{-1} and weak bands at 146, 154, and 419 cm^{-1} (and probably shoulder at 260 cm^{-1}) were also observed (Fig. 1,2). The intensity of Raman 146 and 187 cm^{-1} bands increase with increasing energy fluency of laser beam used for PLD (2-3 J cm^{-2}) and evident shoulders are formed at 166, 211, 245, and 260 cm^{-1}. The intensities of above mentioned Raman bands decrease for highest energy fluencies (4-5 J cm^{-2}). It should be noted that Raman spectra of TF prepared using highest energy fluency (5 J cm^{-2}) are influenced by the luminescence of the films.

4. Discussion

As already reported, there are several stable compounds in As-S system: As_2S_3 (known as orpiment or auripigment mineral) [4], As_4S_5 (uzonite) [5], As_4S_4 (α-As_4S_4 – realgar, β- As_4S_4 – alacranite [6], γ-As_4S_4 – pararealgar [7-11], and χ-As_4S_4 [9-11]), As_4S_3 (α- and β-dimorphite) [12-14] and As_4S (duranusite) [15]. It is supposed that molecular units form crystal structure of As_2S_3, As_4S_5, As_4S_4, and As_4S_3.
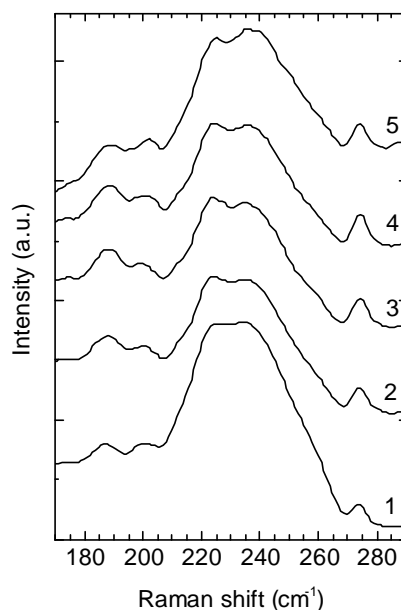

Fig. 2. Raman spectra of as-deposited As-S PLD TF - 170-290 cm^{-1} region; 1 - energy fluency 1 J cm^{-2}, 2 - 2 J cm^{-2}, 3 - 3 J cm^{-2}, 4 - 4 J cm^{-2}, 5 - 5 J cm^{-2}.

TF and bulk glasses of As-S system (including samples with As overstoichiometry) contain above mentioned molecular structural units – mainly AsS_3 pyramids, As_4S_4 molecules, and also other molecules, for example As_4S_3 – as results from previously published structural studies [16,17].

Dominant feature of Raman spectra of bulk As_2S_3 glass is broad band at 345 cm^{-1}, which is obviously connected with AsS_3 pyramids vibrations [18-20]. Frequency of this band corresponds to the frequency of main band in as-deposited PLD As-S layers (Fig. 3). Bearing in mind the chemical composition of our TF (As overstoichiometry up to ~ 11 at.%), we expected that the content of AsS_3 pyramids in as-deposited PLD TF would be significantly lower in comparison with stoichiometric samples. The presence of AsS_3 pyramids is confirmed by the weak Raman band with maximum at 134 cm^{-1} [19,21]. The intensity of this band increases with decreasing content of As. Band at 134 cm^{-1} can be thus connected with the structural units richer in sulphur as fulfilled by AsS_3 pyramids. It can be concluded from asymmetric shape of the whole Raman band in region 290-410 cm^{-1} (Fig. 3) that the band is composed by several overlapping bands, not only by the band related to vibrations of AsS_3 pyramids. Bands corresponding to vibrations of α-As_4S_4 (bands 341, 345, 355, and 370 cm^{-1}) [8,9,22-24], β-As_4S_4 (340-3, 352, and 362-3 cm^{-1}) [8,9,23], pararealgar (334, 340-6, and 363-4 cm^{-1}) [8,11], χ-As_4S_4 (315, 326, 345, 351, and 363 cm^{-1}) [9], α-As_4S_3 (335-6, 352-4, 367, and 374-5 cm^{-1}) [12,24,25], and β-As_4S_3 (335, 339-41, 348-51, 365-8, and 373 cm^{-1}) [12,24,25] can be found in Raman spectra of crystalline forms of As_4S_4 and As_4S_3. It is clear that the assignment of vibrational frequencies to individual structural units is quite complicated in dominant Raman band of as-deposited PLD As-S TF due to high number of possible Raman active vibrational modes and their strong overlapping.

For further analysis of structure of PLD As-rich As-S TF is therefore advantageous to use 100-280 cm^{-1} region of Raman spectra. Broad band in 200-270 cm^{-1} region is (similarly to main 290-

410 cm^{-1} band) evidently composed of several overlapping bands (Fig. 2). Vibrational frequencies assigned to α-As$_4$S$_4$ (band at 222 cm^{-1}) [8,9,22-24], β-As$_4$S$_4$ (211-2 and 216-7 cm^{-1}) [8,9,23], χ-As$_4$S$_4$ (222 cm^{-1}) [9], α-As$_4$S$_3$ (210, 214, and 217 cm^{-1}) [12,24,25], and β-As$_4$S$_3$ (209-14 and 221-4 cm^{-1}) [12,24,25], respectively, are known for ~220 cm^{-1} frequency region and were published in literature dealing with Raman spectra of crystalline As$_4$S$_4$ and As$_4$S$_3$.
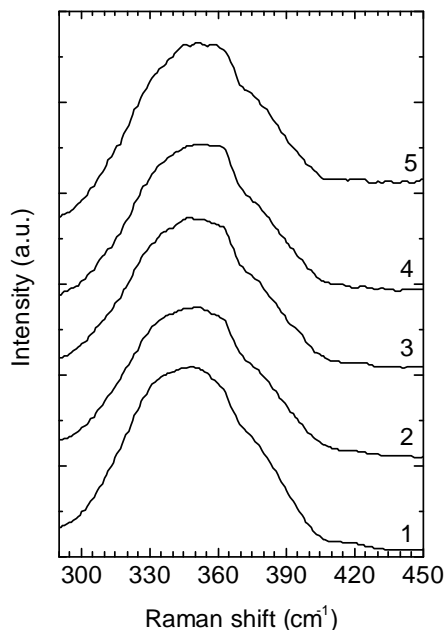

Fig. 3. Raman spectra of as-deposited As-S PLD TF - 290-450 cm^{-1} region; 1 - energy fluency 1 J cm^{-2}, 2 - 2 J cm^{-2}, 3 - 3 J cm^{-2}, 4 - 4 J cm^{-2}, 5 - 5 J cm^{-2}.

Lucovsky [18], assigned band at 225 cm^{-1} to the presence of S$_2$As-AsS$_2$ clusters in As-S glasses with As overstoichiometry; we believe that also in our TF such structural motifs are incorporated.

If we assume the presence of As$_4$S$_3$ (α- and β-modifications) structural units in as-deposited TF, then we should observe strong Raman band with maximum near 271-274 cm^{-1}, which is the most intensive band in Raman spectra of both modifications [12,24,25]. In Raman spectra of as-deposited PLD As-S TF one can observe only weak band in discussed frequency region (Fig. 2) and it can be thus concluded that as-deposited TF contain relatively small content of As$_4$S$_3$ entities. Weak band at 275 cm^{-1} was observed also in Raman spectra of pararealgar (γ-As$_4$S$_4$) and χ-As$_4$S$_4$ [8,9]. Main feature of Raman spectrum of pararealgar is doublet with maxima at 230 and 235 cm^{-1}, which is assigned to As-As vibrations in As$_4$S$_4$ molecules [8]. Strong bands at 222 and 235 cm^{-1} were observed in Raman spectra of χ-As$_4$S$_4$ [9]. Similar band should be present in as-deposited TF. The existence of pararealgar molecules in PLD TF is confirmed by the Raman bands with maxima at 153 and 173 cm^{-1} founded earlier in Raman spectra of crystalline pararealgar [8,9]. Intensity of the 275 cm^{-1} band is slightly increasing with rising of the energy fluency of laser beam used for PLD (Fig. 2). This trend can be explained in terms of increasing content of As$_4$S$_3$ units in as-deposited TF because the intensity of the 235 cm^{-1} band decreases simultaneously. One can also predict the presence of χ-As$_4$S$_4$ molecules; unfortunately, unambiguous assignment is not possible on the basis of Raman spectra due to the fact that all strong bands of Raman spectra of χ-As$_4$S$_4$ are overlapping with the bands of pararealgar and β-As$_4$S$_4$.

α- and β-As$_4$S$_4$ are other entities, which can be incorporated in as-deposited As-S PLD TF. As mentioned, bands at ~220 cm^{-1} were observed in Raman spectra of both modifications. It is known that β-As$_4$S$_4$ molecules were found in the structure of "virgin" thermally-evaporated As-S TF [26,27] and in bulk glasses of this system with As overstoichiometry [16,17] as well. Hence we expect the presence of β-As$_4$S$_4$ molecules in PLD TF, too. This assumption is confirmed by the

observation of Raman bands at 145 and 187 cm^{-1} (Figs. 1,2), respectively, typical for β-As_4S_4 [8,9]. Intensity of 145 cm^{-1} band is probably increased by the presence of α-As_4S_4 and pararealgar, respectively, because both these modifications have also their Raman active vibrations at this frequency [8,9,22-24]. An increase of the Raman bands intensity corresponding to β-As_4S_4 (145, 164, 187 cm^{-1}) and α-As_4S_4 (168, 173 cm^{-1}) [8,9] vibrations is observed with increasing energy fluency of the laser beam used for PLD. Raman bands typical for α-As_4S_4 [184 and 193 (196) cm^{-1}] [8,9] are probably overlapped by more intensive bands at 187 and 200 cm^{-1} as can be concluded from asymmetric shape of the band at 187 cm^{-1}. We therefore believe that the content of α-As_4S_4 in as-deposited TF is not high.

There is also shoulder at 260 cm^{-1} observable in broad 200-270 cm^{-1} Raman band of PLD TF as well as weak band at 419 cm^{-1} (Fig. 2). At this frequency no vibrational mode exists in Raman spectra of crystalline As_4S_5, As_4S_4, and As_4S_3, respectively, [5,8,9,12,18,22-24]. On the other hand, there was described broad band in 175-275 cm^{-1} frequency region with narrow maximum at 200 cm^{-1} and two shoulders at 245 and 260 cm^{-1} in Raman spectra of amorphous arsenic [28]. In satisfactory agreement, we have observed similar narrow maximum at 200 cm^{-1} together with another maximum at 225 cm^{-1} with shoulder near 260 cm^{-1} in Raman spectra of thin As film prepared by PLD using crystalline arsenic as target. Broad flat band at 235 cm^{-1} was identified in Raman spectra of sputtered amorphous arsenic TF [28]. Further, band at 260 cm^{-1} was observed in Raman spectra of mixture of As and S vapors and assigned to As_4 structural unit vibrations; weak band at 419 cm^{-1} as well as strong band at 350 cm^{-1} were also attributed to As_4 units [29]. It can be concluded that shoulders at 260 and 245 cm^{-1} (detected in TF prepared by 3 J cm^{-2} energy fluency) as well as bands at 200 and 419 cm^{-1} and partially bands at 225 and 235 cm^{-1} are connected with vibration modes of amorphous arsenic clusters in as-deposited layers. Arsenic clusters are probably formed by As_4 units; these were identified using mass spectrometry in vapour phase during thermal evaporation of As_2S_3 [30] and using Raman spectroscopy in mixture of As and S vapors as already mentioned [29]. Increasing energy fluency used for PLD results in overall decrease of 200-270 cm^{-1} band intensity and in disappearing of 419 cm^{-1} band (Figs. 2,3). This fact can be ascribed to decrease of content of As structural units in studied films.

Finally, As_4S_5 is possibly the last structural unit, which would be present in prepared As rich As-S PLD TF. The presence of As_4S_5 entities is assumed in thin As_2S_3 films by Treacy [31]. The assignment of Raman frequencies to individual vibrational modes of As_4S_5 unit can be done only speculatively, because there are known positions [5], but actually not the intensities of respective Raman bands. The positions of individual Raman bands of As_4S_5 units are (after [5]) overlapping with Raman bands of other above described entities. Relatively high intensity of the Raman spectra in 300-340 cm^{-1} region should lead to the presence of As_4S_5 units. In this region are situated also bands of AsS_3 pyramids ($\sim$ 312 cm^{-1}) [19,32-34], α-As_4S_4 (band at 345 cm^{-1}) [8,9,22-24], β-As_4S_4 (330-332, 340-343 cm^{-1}) [8,9,23], pararealgar (315, 322-326, 334, and 346 cm^{-1}) [8,9,11], weak bands of χ-As_4S_4 (315, 326, and 345 cm^{-1}) [9], weak bands of α-As_4S_3 (335-336 cm^{-1}) [12,24], and β-As_4S_3 (335, 339-341 cm^{-1}) [12,24]. As already mentioned, we suppose low concentration of AsS_3 pyramids in as-deposited TF. In [35] we discuss, that exposure causes increase of concentration of α-As_4S_4, β-As_4S_4, pararealgar, and As_4S_3 units, which should be followed by increase of the intensity of the bands in 300-340 cm^{-1} region. In fact, exposure results in decrease of the intensity of Raman bands in 300-340 cm^{-1} region [35], where vibrations of crystalline As_4S_5 (307, 312, 327 a 340 cm^{-1}) were found [5]. So we deduce that in as-deposited As-S TF are present also As_4S_5 molecules.

5. Conclusions

Thin amorphous As-S films with composition $As_{47.6}S_{52.4}$ - $As_{50.7}S_{49.3}$ were prepared by pulsed laser deposition technique using different energy fluency of laser beam (1-5 J cm^{-2}) on the target glass ($As_{40}S_{60}$).

The structure of as-deposited TF is formed by pararealgar (χ-As_4S_4), β-As_4S_4 molecules, clusters of amorphous arsenic (probably As_4 structural units), S_2As-AsS_2, and As_4S_5 entities. The presence of α-As_4S_4, As_4S_3 molecules, and AsS_3 pyramids was also confirmed by Raman spectra. With increasing energy fluency of laser beam used for PLD, content of β-As_4S_4, α-As_4S_4, and probably of As_4S_3 and AsS_3 units increases; the content of As clusters decreases simultaneously.

Acknowledgements

It is a pleasure for authors to acknowledge financial support of the Ministry of Education, Youth, and Sports of Czech Republic (project LC 523) and Grant Agency of the Czech Republic (project 203/04/P087).

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