



## Spectroscopic studies of $(\text{AsSe})_{100-x}\text{Ag}_x$ thin films

V. Ilcheva<sup>a</sup>, T. Petkova<sup>a</sup>, P. Petkov<sup>b,\*</sup>, V. Boev<sup>a</sup>, G. Socol<sup>c</sup>, F. Sima<sup>c</sup>, C. Ristoscu<sup>c</sup>, C.N. Mihailescu<sup>c</sup>, I.N. Mihailescu<sup>c</sup>, C. Popov<sup>d</sup>, J.P. Reithmaier<sup>d</sup>

<sup>a</sup> Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 10, 1113 Sofia, Bulgaria

<sup>b</sup> Thin Films Technology Laboratory, Physics Department, University of Chemical Technology and Metallurgy, 8 Kl. Ohridsky Boulevard, 1756 Sofia, Bulgaria

<sup>c</sup> Laser-Surface-Plasma Interactions Laboratory, Lasers Department, National Institute for Lasers, Plasma and Radiations Physics, PO Box MG-54, Bucharest-Magurele, RO-77125, Romania

<sup>d</sup> Institute of Nanostructure Technologies and Analytics (INA), University of Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

### ARTICLE INFO

#### Article history:

Available online 21 April 2009

#### PACS:

78.20.-e

78.20.Ci

78.55.Qr

#### Keywords:

Chalcogenide glass thin films

Optical absorption

Optical band gap

### ABSTRACT

Thin  $(\text{AsSe})_{100-x}\text{Ag}_x$  films have been grown onto quartz substrates by vacuum thermal evaporation or pulsed laser deposition from the corresponding bulk materials. The amorphous character of the coatings was confirmed by X-ray diffraction investigations. Their transmission was measured within the wavelength range 400–2500 nm and the obtained spectra were analyzed by the Swanepoel method to derive the optical band gap  $E_g$  and the refractive index  $n$ . We found that both parameters are strongly influenced by the addition of silver to the glassy matrix:  $E_g$  decreases while  $n$  increases with Ag content. These variations are discussed in terms of the changes in the atomic and electronic structure of the materials as a result of silver incorporation.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Selenium is a promising material for a large number of applications in xerography, photocells, switching and memory devices. Nevertheless, in case of pure Se the carriers' life-time is short and sensitivity low. Se is often alloyed with Ge, Sb or As in order to achieve higher sensitivity and crystallization temperature as well as smaller aging effects [1–3].  $\text{As}_2\text{Se}_3$  and AsSe are predominantly covalent solids and they are among the most studied binary systems [4].

Silver-modified chalcogenide glasses exhibit a peculiar characteristic of mixed-ionic–electronic conductors, which provide dynamical ion movement by electron excitation. The preparation of thin films from these glasses with a good quality and desired composition can be a challenge in terms of their easy production and property reproducibility. The preparation techniques strongly influence the morphology and physico-chemical properties of prepared films. Mostly, authors report on the preparation of silver-containing thin films by photo doping [5], optically induced dissolution [6] or spin coating [7].

Availability of optical constants of chalcogenide materials (such as optical band gap, refractive index and extinction coefficient) is essential to evaluate their potential in optoelectronic applications [8]. Moreover, optical properties could also be closely related to material atomic structure, electronic band structure and electrical properties. An accurate measurement of optical constants can be easily performed on thin films. Optical properties of amorphous thin films can be determined by analysis of material transmission spectrum. This analysis pioneered by Manifcer et al. [9] and extended by Swanepoel [10] has been successfully applied to different chalcogenide glasses, including  $\text{As}_2\text{Se}_3$  [11]. Swanepoel's original work [10] was based on hypothesis of uniform film thickness. We note however that actual films usually exhibit a wedge-shaped profile, which may lead to errors in the analysis, if left unaccounted for. Later on, Swanepoel developed a method describing how to determine the optical properties of such non-ideal films [12], and since then the method was extended to most chalcogenide glasses [13]. The application of Swanepoel's methods is advantageous because they are non-destructive and yield the dispersion relation over a large range of wavelengths without any prior knowledge of the film thickness.

The aim of this work was the study of optical properties of thin As–Se–Ag amorphous films deposited by different methods and the evaluation of their dependence on composition, namely on silver amount added to the amorphous glassy matrix.

\* Corresponding author.

E-mail address: [plamen.petkov@abv.bg](mailto:plamen.petkov@abv.bg) (P. Petkov).

## 2. Materials and methods

The  $(\text{AsSe})_{100-x}\text{Ag}_x$  glasses used in our experiments have been obtained by two subsequent monotemperature syntheses. The first step consisted of the preparation of binary AsSe glass under the following conditions: the respective amounts of arsenic and selenium with 5N purity (Alfa Aesar) were placed in quartz ampoules evacuated down to  $\sim 10^{-3}$  Pa and heated in a rotary furnace. The temperature was maintained constant at the glass melting point while the melt was continuously stirred to ensure better homogenization. After preservation at 900 K for several hours the melt was quenched in a mixture of ice and water. For synthesis of  $(\text{AsSe})_{100-x}\text{Ag}_x$  glasses, the AsSe and commercial silver were mixed in required amounts followed by the same preparation procedure as described above.

Thin  $(\text{AsSe})_{100-x}\text{Ag}_x$  films were grown onto quartz substrates by vacuum thermal evaporation (VTE) and pulsed laser deposition (PLD) from the respective bulk glassy samples. The thermal evaporation process was conducted with a source-substrate distance of 0.12 m, a temperature of evaporation source of 700–800 K and a residual gas pressure of  $1.33 \times 10^{-4}$  Pa. In order to avoid thickness non-uniformities, the substrates were rotated during the evaporation process.

For PLD the synthesized bulk materials were prepared in form of targets of 13 mm diameter and 2 mm thickness by milling and pressing. The deposition process was carried out in a high vacuum chamber with a pulsed excimer KrF\* laser source ( $\lambda = 248$  nm,  $\tau = 25$  ns). The experiments were performed at RT in vacuum at  $10^{-4}$  Pa or in Ar at a dynamic pressure of 5 Pa. The quartz substrates were carefully cleaned with deionized water in a TRANSONIC T 310 ultrasonic bath. They were placed parallel with the target at a separation distance of 5 cm. For the deposition of each film we applied 3000 subsequent laser pulses at a repetition rate of 5 Hz. The laser beam was focused through an AR coated  $\text{MgF}_2$  lens placed outside the chamber to get an incident fluence of  $3.3 \text{ J/cm}^2$ . Some test depositions were performed with doubled fluence of  $6.6 \text{ J/cm}^2$ . The beam was incident at  $45^\circ$  on target surface.

X-ray diffraction (XRD) investigations of thin coatings were performed with a Philips Analyzer APD-15 with  $\text{CuK}\alpha$  radiation in the  $2\theta$  range from  $10^\circ$  to  $60^\circ$ . The thickness of the films was measured with a white light interferometer Zygo NewView 5000 with vertical resolution up to 0.1 nm,  $5\times$  Michelson and  $50\times$  Mirau objectives, X–Y motor desk for stitching and extended vertical scan length up to 20 mm.

The optical transmission spectra of the thin films were recorded in the wavelength range of 400–2500 nm at room temperature using a double-beam computer-controlled Cary 5E UV–vis–NIR spectrophotometer with an accuracy of  $\pm 0.5$  nm. The experimental data were processed by a computer program based upon the Swanepoel method.

## 3. Results and discussion

The  $(\text{AsSe})_{100-x}\text{Ag}_x$  films grown by both methods are amorphous as evidenced by XRD study. The absence of sharp peaks in diffractograms, verifying the amorphous structure, and the observed broad halo are characteristic for the films prepared by VTE as well as by PLD (Fig. 1).

The thickness of films varies depending on composition, namely on silver content, deposition technique and applied conditions (Fig. 2). The PLD films prepared in low pressure argon are thicker than those deposited in vacuum under identical conditions. This is due to confinement of plasma by the ambient gas [14,15], a well known phenomenon confirmed by us in case of AsSe–AgI thin films deposition [16]. The thickness decrease with the percentage of Ag,

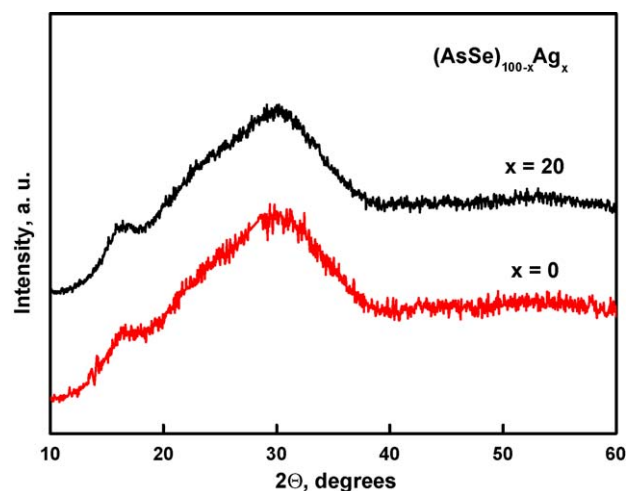


Fig. 1. Typical X-ray diffraction patterns of AsSe and AsSe–Ag films.

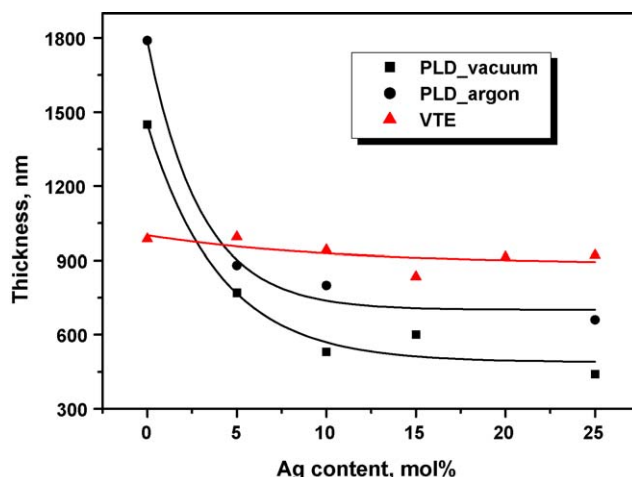


Fig. 2. The thickness of  $(\text{AsSe})_{100-x}\text{Ag}_x$  films prepared by PLD and VTE as a function of the Ag content.

clearly visible in case of PLD films, could be attributed to higher reflectivity of respective samples. Indeed, due to higher reflectivity, the laser beam energy transfer to target is worsening and the flux of ablated substance is decreasing. Conversely, in case of VTE deposited films the silver content has a marginal influence on thickness only.

The compositions of some of the films were measured by EDX [16]. The results exhibited some characteristic peculiarities, namely: (i) in some cases deviations from the unity ratio As/Se were found. This deviation increased significantly when changing the incident fluence from  $3.3$  to  $6.6 \text{ J/cm}^2$ . [17] This is why the most of the results reported in this paper referred to structures deposited at  $3.3 \text{ J/cm}^2$ . (ii) Some loss of Ag is observed and the higher the dopant concentration in the target materials, the bigger the differences in the film composition, including also the As/Se ratio, compared with the bulk samples. The deficiency of Ag in the film composition is most probably caused by the difference in the enthalpy of deposition of the evaporated fragments transported to the substrate. The enthalpy of deposition is different for various fragments and the quantity of each fragment deposited onto the substrate depends on it.

The transmission spectra recorded within the spectral range 400–2500 nm show interference maxima and minima at higher wavelengths approaching the transmission of substrate. A red shift

of the interference-free region is visible with increasing the Ag content. This red shift in film transmission proves that in the Urbach tail, i.e. below the optical absorption edge, the light can generate mobile carriers (holes) in AsSe–Ag films [18]. The absorption coefficient  $\alpha$  was determined for all investigated films from their transmission spectra using an equation based on the modified Swanepoel method.

Thus, above exponential tail, the absorption coefficient of amorphous semiconductors has been observed to comply with the

relation.

$$(\alpha h\nu) = B\{h\nu - E_g\}^m \quad (1)$$

Here  $h\nu$  is the effective photon energy,  $E_g$  the optical band gap,  $B$  a constant proportional to the square of the joint density of states, and  $m$  an index with values of 1/2, 3/2, 2 or 3, depending on the nature of electronic transitions and on relation between the localized state density and energy. The usual method applied to determine the  $E_g$  values involves plotting a graph of  $(\alpha h\nu)^{1/m}$  versus  $h\nu$ . We note that for the most of amorphous materials non-direct electron transitions are observed. Therefore  $m = 1/2$  is also well obeyed for the  $(\text{AsSe})_{100-x}\text{Ag}_x$  films used in our studies.

Fig. 3 illustrates the experimentally obtained relation of  $(\alpha h\nu)^{1/2}$  versus the photon energy  $h\nu$ . The films absorption gets stronger with the silver content as confirmed by the shift in the  $\alpha h\nu$  graphical dependence towards lower energies. This shift is commonplace for PLD films prepared either in vacuum or in argon, as well as for the VTE films in the region of lower absorbance – i.e. in the region of optical energy under investigation. The shift in the film transmission to higher energy values in VTE films compared to PLD films is most probably due to uneven surface of the latter films.

The optical band gap energy  $E_g$  was determined by two independent methods. Namely, we extrapolated the straight line part to the energy axis of zero absorption coefficient or consider the absorption coefficient  $\alpha$  equal to  $2 \times 10^{-4} \text{ cm}^{-1}$  (also known as  $E_g^{0.4}$  method). The obtained  $E_g$  values for the AsSe films were 1.67 eV (VTE) and 1.57 eV (PLD). The difference of 0.1 eV in optical band gap value is a consequence of the preparation method. VTE makes easier the deposition of films with higher concentration of defects. Difference between evaporation coefficients of particular elements in bulk glass and the more chaotic way of evaporated particles give rise to condensation of films with a structure defined by broken or bended bonds. This distortion delineates a band gap structure with more localized states where electrons could be located, resulting in higher values of the optical band gap for VTE films.

The doping with silver results in optical band gap decrease, as shown in Fig. 4. The decrease is consistent with the higher metallicity of the Ag atoms as compared with the As atoms. The almost linear variation of  $E_g$  with silver content is similar to that observed for other amorphous materials and can be accounted for in terms of differences in the structure of the films prepared by the two methods. The differences are both in medium and short range

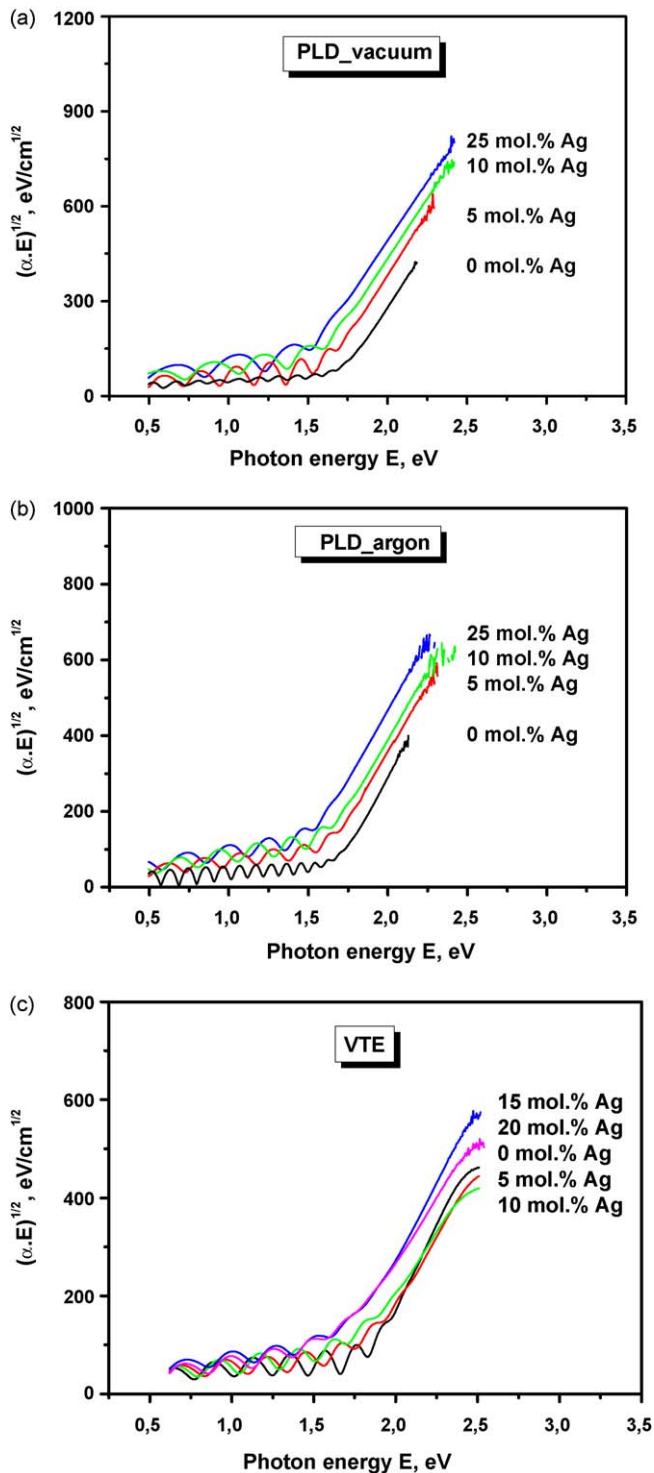


Fig. 3.  $(\alpha h\nu)^{1/2}$  versus photon energy  $h\nu$  plots, from which the optical band gap  $E_g$  of amorphous  $(\text{AsSe})_{100-x}\text{Ag}_x$  films with different Ag contents prepared by (a) PLD in vacuum, (b) PLD in Ar and (c) VTE was determined.

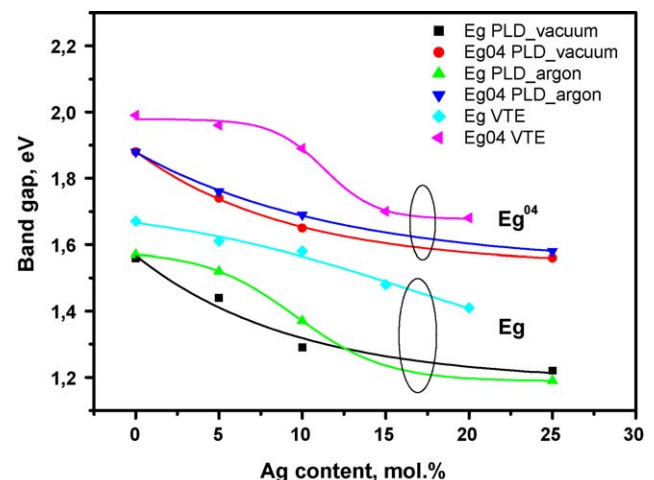


Fig. 4. Influence of the Ag content on the optical band gap of amorphous  $(\text{AsSe})_{100-x}\text{Ag}_x$  films prepared by PLD and VTE.

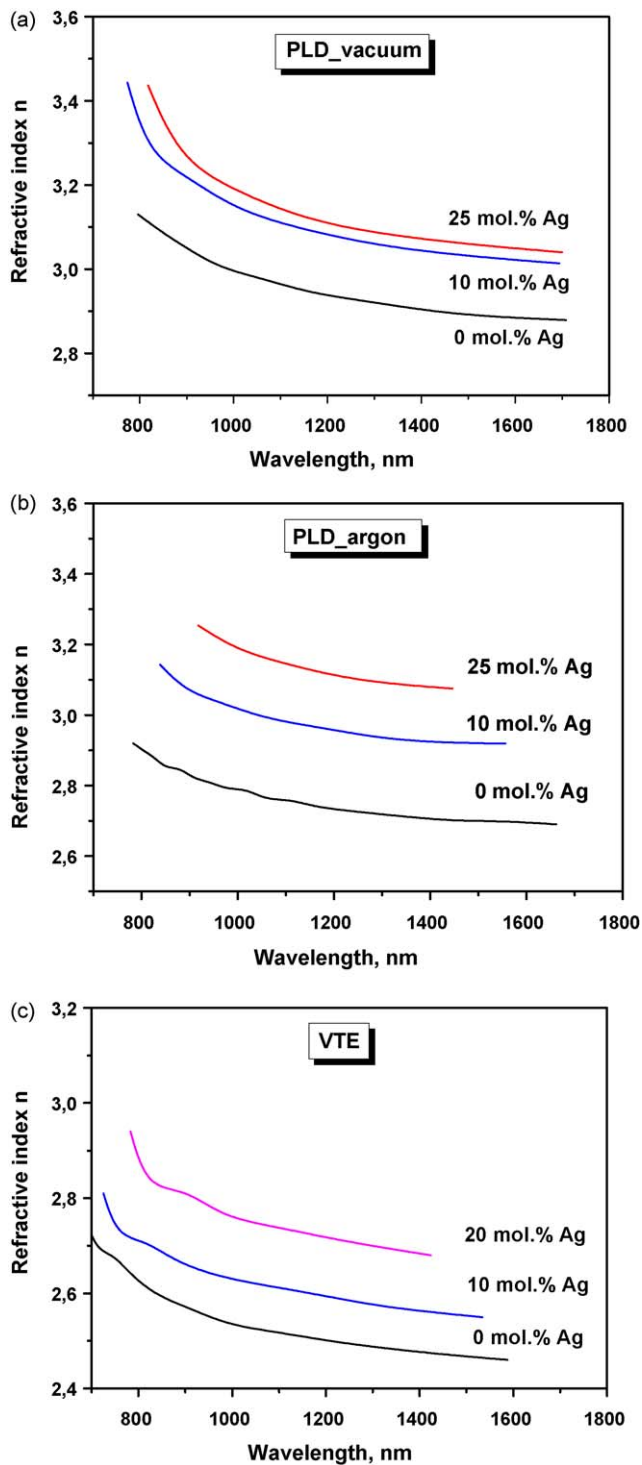


Fig. 5. Spectral dispersion of the refractive index  $n$  of amorphous  $(AsSe)_{100-x}Ag_x$  films with different Ag contents prepared by (a) PLD in vacuum, (b) PLD in Ar and (c) VTE.

order [7]. The atomic substitution of arsenic by silver slightly stiffens the network cohesion. The optical band gap is lowered down to 1.41 eV when Ag reaches 20 mol% in VTE films and to 1.22 eV in PLD films with 25 mol% Ag.

Fig. 5 shows the spectral dependence of the refractive index  $n$  of PLD and VTE films. The overall tendency is the increase of  $n$  with silver content over the entire studied spectral range. This increase is related to higher polarizability of larger Ag atoms (having an atomic radius of 134 pm) as compared to Se atoms (with an atomic radius of 116 pm). In case of VTE films the refractive index changes from 2.5 to 3.0, while for PLD films it varies from 2.7 to 3.4. The better ordered and denser PLD films exhibit a higher reflectivity as compared to VTE films, having a poorer and more defected structure.

#### 4. Conclusions

Thin amorphous  $(AsSe)_{100-x}Ag_x$  films were grown by vacuum thermal evaporation and pulsed laser deposition from the corresponding bulk glassy materials and characterized with respect to their optical properties. A red shift of the transmission of the films prepared by both methods was observed with the addition of Ag to the glassy matrix. The doping with silver causes both an optical band gap decrease, consistent with the higher metallic character of the Ag atoms versus As and Se matrix atoms, and a stiffness increase of the bond network due to atomic substitution. The refractive index  $n$  of PLD films is slightly higher as compared to VTE films, whose structure is poorer and more defected. A common trend for all films under investigation is the increase of  $n$  with the silver content due to the higher polarizability of Ag atoms and corresponding increase of optical density.

#### Acknowledgments

The authors gratefully acknowledge the financial support of NATO under the Collaborative Linkage Grant Program (CBP.EAP.CLG 982793). V.I. would like to thank to WSF for the scholarship providing a financial support during the implementation of this work. I.N.M. acknowledges with thanks the partial support of this work by GR 872/2006 CNCSIS.

#### References

- [1] K. Mietzsch, A.G. Fitzgerald, *Appl. Surf. Sci.* 162–163 (2000) 464.
- [2] J. Phillips, M. Thorpe, *Solid State Commun.* 52 (1985) 699.
- [3] T. Petkova, P. Petkov, S. Vassilev, Y. Nedeva, *Surf. Interface Anal.* 36 (2004) 880.
- [4] M. Thorpe, *J. Non-Cryst. Solids* 57 (1983) 355.
- [5] K. Ogusu, S. Maeda, M. Kitao, H. Li, M. Minakata, *J. Non-Cryst. Solids* 347 (2004) 159.
- [6] T. Wagner, J. Gutwirth, M. Krbal, Mir. Vlcek, Mil. Vlcek, M. Frumar, *J. Non-Cryst. Solids* 326–327 (2003) 238.
- [7] M. Krbal, T. Wagner, T. Kohoutek, P. Nemeč, J. Orava, M. Frumar, *J. Phys. Chem. Solids* 68 (2007) 953.
- [8] S. Elliott (Ed.), *Physics of Amorphous Materials*, Pitman Press Ltd., Bath, 2000.
- [9] C. Manificier, J. Gasiot, J. Fillard, *J. Phys. E: Sci. Instrum.* 9 (1976) 1002.
- [10] R. Swanepoel, *J. Phys. E: Sci. Instrum.* 16 (1983) 1214.
- [11] A. Giridhar, S. Mahadevan, *J. Non-Cryst. Solids* 134 (1991) 94.
- [12] R. Swanepoel, *J. Phys. E: Sci. Instrum.* 17 (1984) 896.
- [13] M. Hammam, M.A. Harith, W. Osman, *Solid State Commun.* 59 (1986) 271.
- [14] D.G. Chrisey, G.K. Hubler (Eds.), *Pulsed Laser Deposition of Thin Films*, Wiley, New York, 1994.
- [15] D. Bauerle, *Laser Processing and Chemistry*, 2nd ed., Springer, New York, 1996.
- [16] T. Petkova, C. Popov, T. Hineva, P. Petkov, G. Socol, E. Axente, C.N. Mihailescu, I.N. Mihailescu, J.P. Reithmaier, *Appl. Surf. Sci.* 255 (2009) 5318.
- [17] R. Eason, *Pulsed Laser Deposition of Thin Films: Applications-lead Growth of Functional Materials*, Wiley & Sons, 2006.
- [18] N. Mott, E. Davis, *Electron Processes in Non-crystalline Materials*, Clarendon Press, Oxford, 1979.