

A comparative study of chalcogenide thin films for micro sensor applications

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Cadmium chalcogenide thin films were deposited by different processes. Pulsed laser deposition, thermal evaporation, and sputtering were used to elaborate micro devices on glass substrate from CdS-AgI-Ag₂S-As₂S₃, CdS-Ag₂S-Sb₂S₃ and Cd-Ag-As₂S₃ starting materials respectively. The micro films were characterised using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and electrochemistry. Comparative structural characterisation leads us to understand sensors out-put signal. The best miniaturised sensor was selected. The very first electrochemical results are presented. The potentiometric response of Cd-Ag-As₂S₃ sensing matrix showed a quasi-Nernstian behaviour with a great detection limit. Moreover Cd-ISE is sensitive to silver (+I) in solution.

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1. Introduction

Rapid and accurate monitoring of heavy ions is of great importance for prevention of heavy metal pollution. However to date quality control of water results from reliable and expensive analytical measurements carried out in laboratory. As a promising alternative potentiometric micro sensors produced with silicon technology compatible methods [1] are aimed at the fabrication of primary systems for in-situ measurements. A rising interest in the possible use of electrochemical sensors based upon selective vitreous membranes for miniaturised devices has led to their extensive study in recent years [2,3]. The chalcogenide glasses have recently focused significant scientific interest for the investigation of their basic properties and the possibility for applications in optics and optoelectronics, electrochemistry, sensor technique [4,5]. Then, the use of metal chalcogenide layers for various applications has gained attention recently [5]. Chalcogenide glass sensors for determination of heavy-metal ions are well known. Moreover, microelectronics has allowed the miniaturization and integration of such micro sensors [6,7]. As major advantages of these amorphous inorganic materials we emphasize that they can be easily prepared in bulk or layered forms by various methods. Many deposition techniques have been used to deposit metal chalcogenides thin films, including PVD based deposition techniques (i.e. thermal evaporation, laser ablation, etc.) [8,9]. Alternatively, chalcogenide thin films can be deposited by solution based deposition techniques (i.e. spin-coating, dip-coating, spiral bar-coating, etc.) and electro deposition [10]. In recent years, extensive research has been carried out on the area of preparation and characterization of Cadmium chalcogenide thin films [11] because of its properties suitable for solar cell and sensor applications. [5]. Moreover chalcogenide glasses containing silver or silver salts are well known as ionic conducting glasses. In this paper, we report on comparative studies of pulsed laser deposited, thermal evaporated and sputtered thin films. In particular physical and electrochemical properties of sensing layers as ISEs for cadmium (+II) ions detection in solution are investigated.

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2. Experimental

Thin films were prepared by pulsed laser deposition (PLD) from chalcogenide targets (i. e. CdS-AgI-Ag₂S-As₂S₃). Bulk samples were first prepared by direct synthesis from pure elements in evacuated silica ampoules [12]. After this process, samples were sliced and polished to obtain PLD targets with parallel faces. Thin films were deposited on static substrates at room temperature. Si substrates were rinsed in acetone with ultrasonic vibration, and then rinsed in ethanol before they were put into the deposition chamber. The laser energy density was measured to be about 1.1-1.3 J/cm². Target was ablated by a Nd-YAG laser (Spectra-Physics Quanta-Ray Lab-150) operating at a 355 nm wavelength with a 5 ns pulse duration and a 10 Hz repetition rate. The deposition time of 30 min was maintained. The films were deposited in under vacuum. The laser beam angle of incidence was selected to get uniform target ablation.

Experimental chalcogenide glass (i. e. CdS-Ag₂S-Sb₂S₃) was prepared by standard melt-quenching method. The high purity elements were loaded in evacuated quartz ampoule. The synthesis was performed at 1000°C for 12 h. The quartz ampule with sensing matrix was then quenched in water. Samples were prepared by RF sputtering deposition of silver layer on substrate acting as a metallic connection, followed by evaporation of sensing chalcogenide membrane. 0.35 g of chalcogenide glass in a Mo crucible was evaporated for 40s. The deposition on the substrate was carried out while the current was increased from 80 A to 200 A.

3. Results

Preliminary information on the surface morphology was obtained using scanning electron microscopy (SEM). The chemical distribution of the constituent elements was monitored by energy-dispersive X-ray spectroscopy (EDX). The top-view SEM pictures of pulsed laser deposited film revealed the uniform and homogeneous character of surface (figure 1(a)).

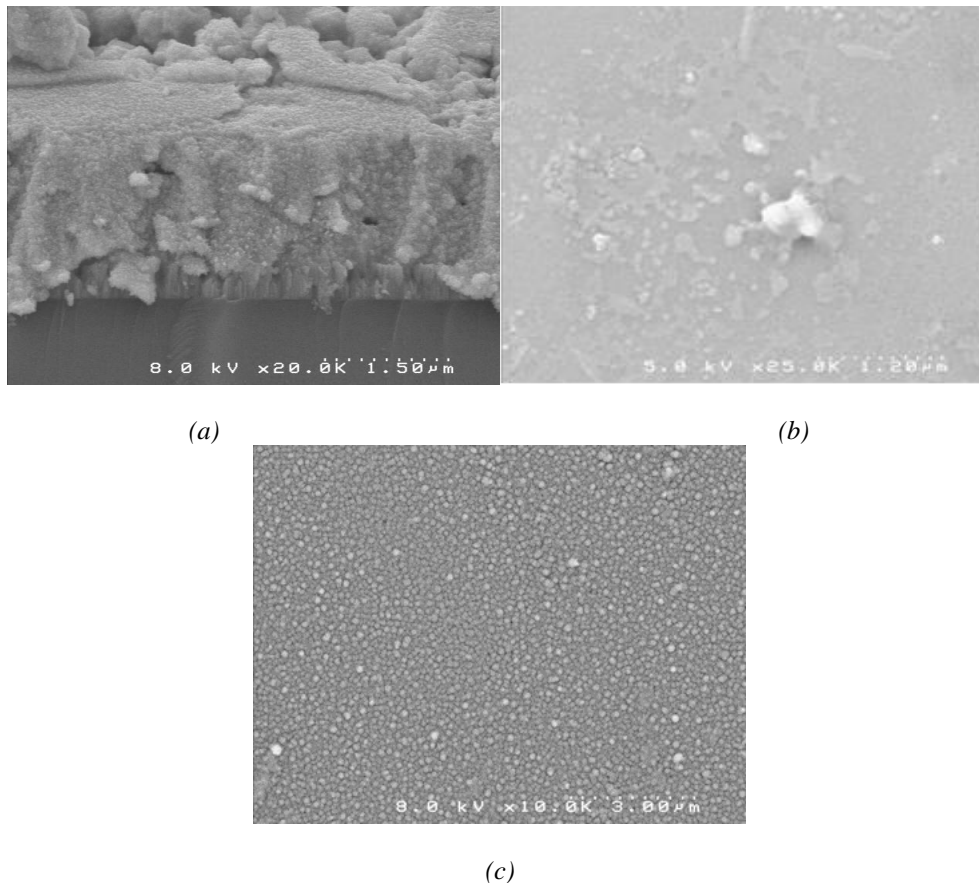


Fig. 1. Scanning electron microscopy images of pulsed laser deposited (a) thermal evaporated (b) and RF sputtered (c) thin films surface.

Table 1. EDX chemical composition of thermal evaporated sensitive layer.

	O	Si	Ca	Cd	S	Ag	Sb	Total
Experimental % at.	14,02	10,82	2,33	0	40,23	0	32,6	100
Theoretical % at.				2,5	44,5	20	33	100

Neither defects nor traces of initial nucleation were visible. Cross-sectional SEM view (figure 2(a)) revealed smooth and dense layer. Several large tower-like grains with parallel layer structure grown vertical to the substrate surface can be clearly seen (figure 2(a)). We note that the target substrate distance for pulsed laser deposition method doesn't seem to significantly affect the film surface morphology. The existence of particulates of various shapes and dimensions is a well-known phenomenon in PLD [4]. However, the ablation of droplets originating from the fast heating and cooling processes of the target, which is due to the pulsed laser illumination cannot completely be avoided [13]. During PLD, the kinetics of atomic arrangement is mainly determined by substrate temperature and the energy of deposition atoms [14]. In the literature it was reported that at a relatively high temperature, atoms on the surface have high mobility, otherwise, low substrate temperature results in low atoms mobility, which limits the formation of lower energy structure. PLD Thin film composition was investigated by EDS measurements the measured composition was fairly close to the nominal one in all measurements.

The chemical composition of the flash evaporated thin film was also checked by EDS. The results are reported in Table 1. A large loss in cadmium and silver is observed. It can be explained by the weak partial pressure of both elements during thermal evaporation. However a large excess in the relative amount of other elements (i. e. Sulfur and antimony) is observed.

The oxygen and foreign atoms presence can be explained by partial film oxidation during thermal process. Moreover, film contamination should be taken into account. Measured composition of as-prepared thermal evaporated thin film is slightly differs from planned composition. The difference between the planned glass composition and as-prepared evaporated thin film can be attributed to the non-ideality of evaporation process when partial fractionation can be expected [10]. Stoichiometry transfer between target and substrate is difficult to obtain with evaporation by using a single target, because in general the partial vapor pressures of the components are different from each other which gives rise to a different composition of the deposited film. The most commonly used technique to obtain Stoichiometric transfer is multiple source co-evaporation. In this case the composition of thermally evaporated films can be tuned by selecting the evaporation rates of each precursors [15]. The surface of the film fabricated by flash evaporation technique does not present any observable defects. The SEM micrograph shows a distribution of particles which covers the surface of the substrate completely. No pin holes or cracks could be observed for that sample. However, as can be seen in figure 1(b) atypic pellet is due to flash thermal evaporation technique. The thickness of the layer appears to be pinhole free (figure 2(b)). The quality of adhesion of the film onto the thin layer collector is satisfying. The amorphous character of the evaporated films was confirmed by X-ray diffraction while the electrical properties were investigated by the spectroscopy impedance technique. Experimental data shows that the conductivity in sensing matrix has a strong ionic character while a weak electronic conductivity cannot be excluded. This result is in agreement with the high relative amount of silver element in the sample.

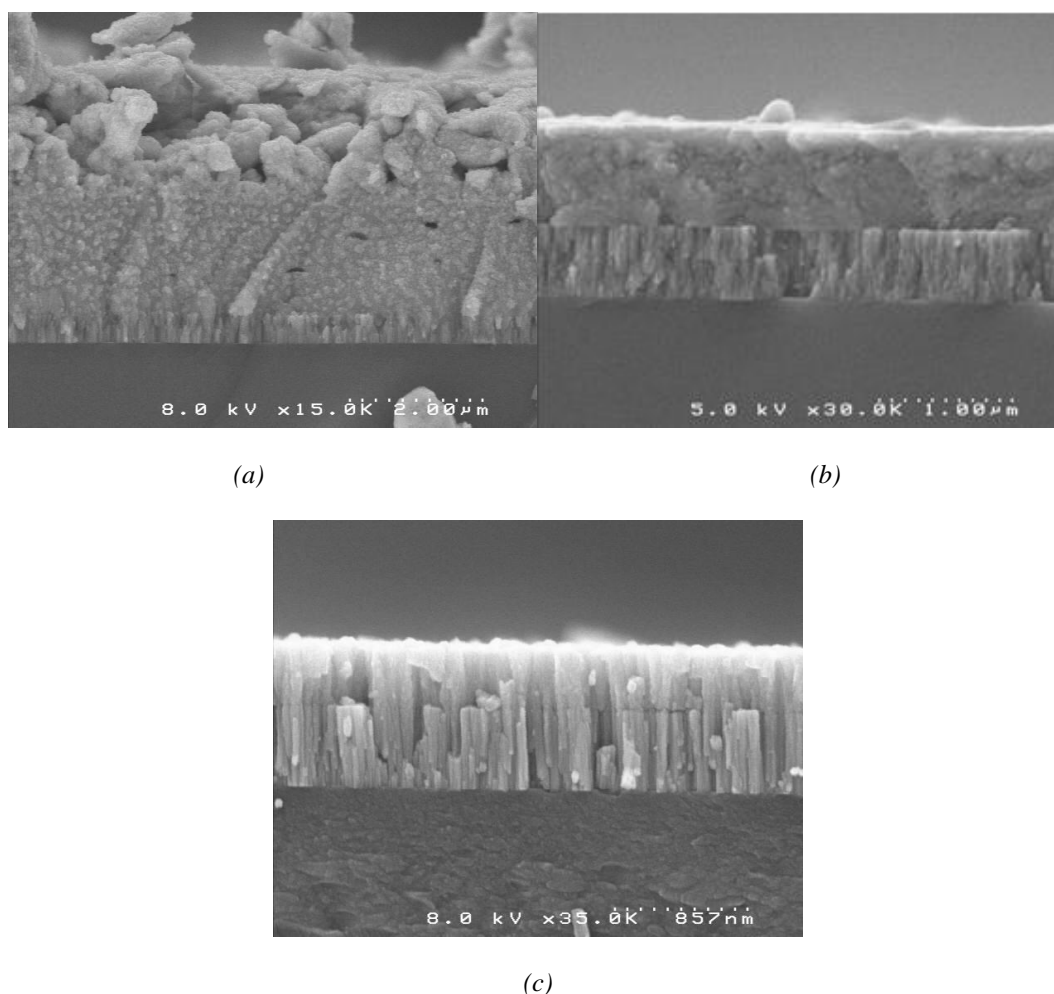


Fig. 2. SEM cross-sectional images of thin films deposited using pulsed laser deposition (a) thermal evaporation (b) and RF sputtering (c).

Experimental procedure for sputtering deposition is described elsewhere [3]. From the micrographs (figure 1(c)), it is observed that the RF sputtered film (i. e. Cd-Ag-As₂S₃) is without any pinholes or cracks and it cover the substrates very well. It is clearly evident that sputtering deposition process leads to a homogeneous and stoichiometric composition of sensitive layer. The resulting layer was homogeneous had a surface of good quality and was poorly contaminated. But the films grown from sputtering have shown a smooth surface with very small grains. As can be seen in figure 2(c) the grains expand through the thickness of the film deposited by RF sputtering with a columnar structure. Moreover, that grains are uniformly distributed and heavily densed throughout the entire film.

In agreement with literature we have demonstrated that PLD has two main specificities in comparison with other PVD methods, including thermal evaporation or sputtering. Firstly, synthesis is performed by a pulsed mode, meaning that a small amount of matter can be grown in a few microseconds. Secondly, because of the rapid intense heating of the target, stoichiometric growth can be readily achieved using PLD [16].

Based on our prior research into Cu-Ag-S hybrid thin films [5, 17, 18], Cd-Ag-S micro sensors were created on a glass substrates with the help of electrodeposition method. Anodic cadmium sulfide films were formed using sodium sulfide (Na₂S) in anodization process on Cd-Ag metal alloy [17, 19]. The electrodeposited Cd-Ag-S layer has showed uniform surface without pinholes. The electrodeposited film shows no cracks or holes. A columnar structure of the sputtered films is observed by SEM with a weak roughness estimated from AFM measurements. Electro deposition process leads to a homogeneous composition of the sputtered layer according to

target composition. However a weak amount of sulphur is observed at the ISE surface. Small size stone shape particles well covered the film surface. The nanostones are coalescent to form a continuous layer of multi-shape nano-stones.

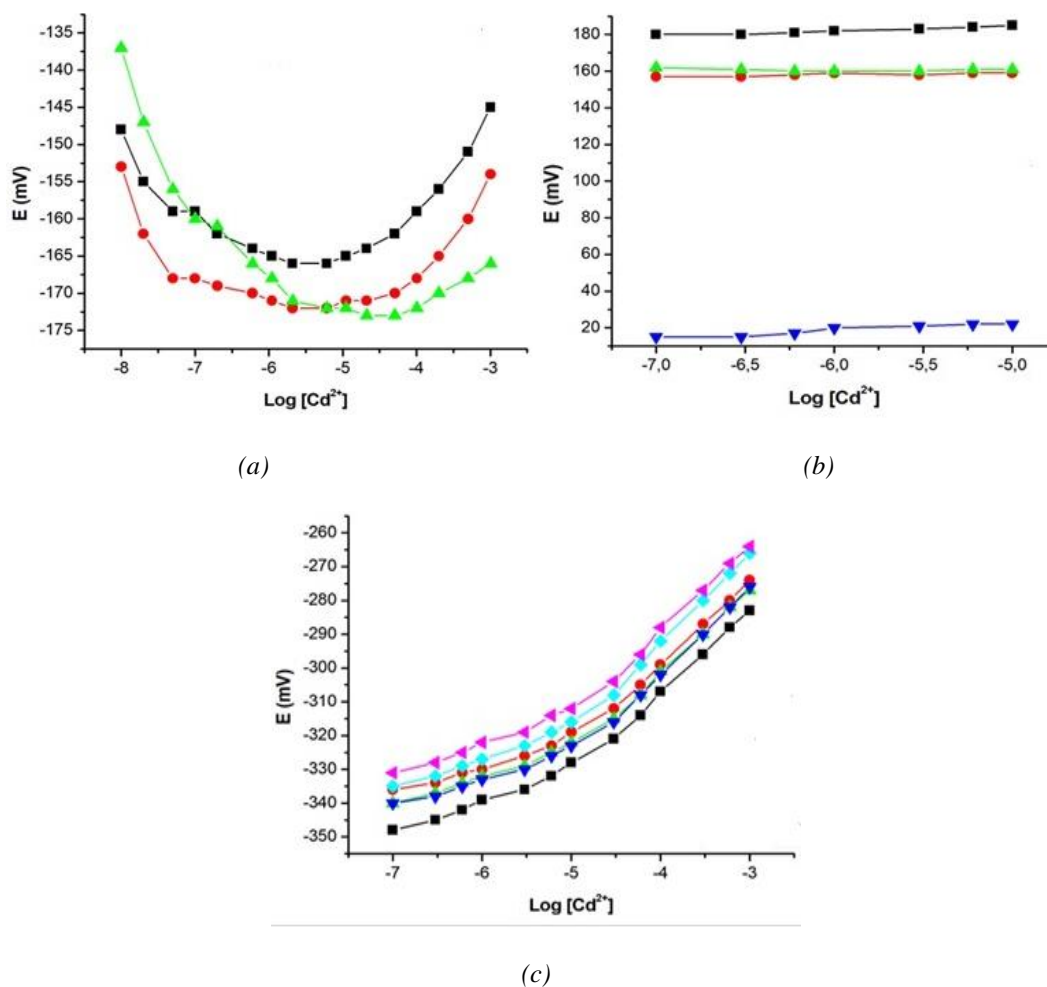


Fig. 3. Cd^{2+} ion response for pulsed laser deposited (a) thermal evaporated (a) and sputtered (c) sensing thin layers.

Figure 3 presents studied layers electrochemical out-put signal versus Cd^{2+} ions. Figure 3(a) shows improper shape of PLD membrane response. The thin film deposited by PLD is insensitive to cadmium ions in solution. On one hand the sensing layer is too thick one the other hand the layer morphology inhibits active sites access. Moreover, large tower-like grains do not allow specific exchanges between primary ion and active sites at the modified surface layer of the stoichiometric membrane. Thus, pulsed laser deposition conditions have to be fitted to decrease the thickness and the grain sizes of the films.

Figure 3(b) presents the response to Cd^{2+} ion of the thermal evaporated thin film. The flat out-put signal means that the electrode is also insensitive to the primary ion. We have demonstrated that thermal deposition induces a difference between the planned glass composition (i. e. starting powder) and as-prepared evaporated thin film. Resulting layer, with an unexpected composition gave a poor response. Moreover, as can be seen in SEM study the formation of atypical pellets inhibits specific exchanges.

Figure 3(C) presents the response to cadmium (+II) ions of the RF sputtered thin layer. In static measurements near Nernstian response is observed with a great limit of detection. Then, electrodes displayed stable and reproducible response. At laboratory scale the slope is close to 28 mV/pCd with a detection limit of 10^{-6} M. We have demonstrated that the first calibrations differ

from the further ones by the super Nernstian out-put signal. As can be seen in figure 3(c) the electrode parameters are reliable after few measurements. To reach a steady state potential the response time was less than 10 s in the high concentration range of Cd^{2+} species. Typical drift values stay in a range of 7 mV/day. The ISE has no significant sensitivity loss. We have confirmed the good selectivity in the presence of alkali, alkaline-earth species.

Table 2. Comparative performance of Cd-Ag-As₂S₃ sensor and Cu-As₂S₃ micro sensor.

	Cd-Ag-As ₂ S ₃	Cu-As ₂ S ₃
Sensitivity (mV/dec)	28	29
Response time (s)	10	3
Drift (mV/24H)	7	-
Detection Limit (mol/L)	10 ⁻⁶	10 ⁻⁶

Cd-Ag-S hybrid thin membrane response is not shown. However the worse electrode behaviour versus cadmium ions is due to the inhomogeneous composition of the sputtered layer with a poor amount of sulphur.

Table 2 presents sputtered membrane electrochemical parameters. A comparative study with our well known electrode Cu-As₂S₃ had confirmed that the studied sensor works properly with a satisfying out-put signal versus Cd^{2+} ions in solution.

The sputtered micro device sensing properties versus silver (+I) primary ions were tested. The very first results have indicated a promising response to Ag^+ species. In acidic media the Nernstian behaviour corresponds to the exchange of one electron. A great detection limit was then observed.

4. Conclusions

A comparative study of chalcogenide thin films was aimed to select reliable micro sensor for cadmium primary ions detection in solution. Pulsed laser deposited electrode is insensitive to cadmium ions in solution. To improve the out-put signal versus Cd^{2+} ions PLD experimental conditions have to be fitted. The thermal evaporated thin film was also insensitive to the primary ion. In this case the flat response to cadmium ions might be due to an unexpected thin film's chemical composition. The sputtered sample was able to give a reliable response to cadmium species in agreement with the Nernstian law. The slope is close to 28 mV/pCd with a detection limit of 10⁻⁶ M. The electrode displayed stable and reproducible electrochemical parameters. The RF sputtered thin layer is sensitive to silver (+I) species. Further experiments are in progress to understand sensor response to Ag^+ ions in solution

References

- [1] M. Essi, G. Cisse, V. Flaud, Chalcogen. Lett. 17, 495 (2020).
- [2] Thiago V. Moreno, Luis C. Malacarne, Mauro L. Baesso, Wei Qu, Eben Dy, Zhong Xie, Jason Fahlman, Jun Shen, Nelson G.C. Astrath, J. Non-Cryst. Sol. 495, 8 (2018); <https://doi.org/10.1016/j.jnoncrsol.2018.04.057>
- [3] M. Essi, G. Cisse, W. Atse, Chalcogen. Lett. 18, 303 (2021).
- [4] 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, 5318 (2009); <https://doi.org/10.1016/j.apsusc.2008.07.194>

- [5] R. Manivannan, S. Noyel Victoria, Sol. Energy 173, 1144 (2018); <https://doi.org/10.1016/j.solener.2018.08.057>
- [6] M. Essi, B. Kedi, Chalcogen. Lett. 16, 29 (2019).
- [7] R. Tomova, G. Spasov, R. Stoycheva-Topalova, A. Buroff, J. Non-Cryst. Solids 338-340, 582 (2004); <https://doi.org/10.1016/j.jnoncrsol.2004.03.047>
- [8] J. Schubert, M.J. Schöning, Yu.G. Mourzina, A.V. Legin, Yu.G. Vlasov, W. Zander, H. Lüth, Sens. Actuators B 76, 327 (2001); [https://doi.org/10.1016/S0925-4005\(01\)00616-5](https://doi.org/10.1016/S0925-4005(01)00616-5)
- [9] A. S. Baron , M. M. Abood , K. A. Mohammed, Chalcogen. Lett. 18, 759 (2021).
- [10] S.Slang, P. Janicek, K. Palka, L. Loghina, M. Vlcek. Materials Chemistry and Physics 203, 310 (2018); <https://doi.org/10.1016/j.matchemphys.2017.10.025>
- [11] M.A. Islam, F. Haque, K.S. Rahman, N. Dhar, M.S. Hossain, Y. Sulaiman, N. Amin, Optik 126, 3177 (2015); <https://doi.org/10.1016/j.ijleo.2015.07.078>
- [12] M. Essi, N. Kouame, G. Cisse. Chalcogen. Lett. 15, 379 (2018).
- [13] Krebs HU. et al. Advances in Solid State Physics. 43, 505 (2003); https://doi.org/10.1007/978-3-540-44838-9_36
- [14] X.M. Fan, J.S. Lian , Z.X. Guo, H.J. Lu. Appl. Surf. Sci. 239, 176 (2005); <https://doi.org/10.1016/j.apsusc.2004.05.144>
- [15] Y. Vaynzof. Adv. Energy Mater. 2020, 10, 2003073; <https://doi.org/10.1002/aenm.202003073>
- [16] Y. Bleu, F. Bourquard, T. Tite, A. S. Loir, C. Maddi, C. Donnet, F. Garrelie. Front. Chem. 6, 572 (2018); <https://doi.org/10.3389/fchem.2018.00572>
- [17] M. Essi, A. Pradel, Chalcogenide. Lett. 8, 15 (2011).
- [18] L. R. Singh, R. K. L. Singh, Chalcogen. Lett. 17, 375 (2020); <https://doi.org/10.1016/B978-0-12-821348-3.00031-8>
- [19] M. Essi, A. Pradel, Chalcogenide. Lett. 8, 301 (2011).