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ION-SELECTIVE MEMBRANES BASED ON CHALCOGENIDE GLASSES

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Ion-selective membranes on the basis of thin evaporated layers of pure and doped chalcogenide glasses have been developed. The membranes showed high sensitivity towards Ag^+ and Cu^{2+} ions –down to 10^{-6} mol/L, short response time and good selectivity to interfering ions. The electrochemical sensors for Pb^{2+} ions however are not at the same level. The reasons for this difference have been established by examining the physical properties, AES depth-profile and electrochemical behavior of the three types of membranes. In spite of the promising results and good electrochemical performance, the long-term stability of chalcogenide-based thin film sensors is still a problem. It was established that the plasma deposited polymer film of (PHMDSO) and vacuum deposited polyimide (PI) on the top of chalcogenide glass membrane improve the electrochemical characteristics - increases the sensitivity and long-term stability and keeps the response time. The results obtained are promising for the development of low-cost, highly reliable nanosensors on the basis of chalcogenide glasses.

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Keywords: Thin film sensors, Chalcogenide glasses, AES, Polyhexamethyldisiloxane, Polyimide

1. Introduction

Sensor technology is becoming one of the most important technologies of the future with a growing number and variety of applications especially in the fields of medicine and environment protection, as well as chemical process control, etc. Electrochemical sensors based upon selective vitreous membranes were extensively studied in the last years with an increasing interest for miniaturised devices [1]. Chalcogenide glasses with their flexible structure, enormous variations of properties and almost unlimited ability for doping and alloying were proven to be very promising materials for chemical sensors for analysis of industrial aqueous solutions and the environment monitoring of pollutant gases [2]. Chemical microsensors based on thin sensitive films produced by sputtering, spin-coating, ion-beam assisted pulsed laser deposition and related methods compatible with planar silicon technology are essential primary devices for integrated analytical microsystems capable of continuous in situ measurements [3].

We are developing ion-selective membranes on the basis of thin evaporated layers of pure and doped chalcogenide glasses [4-9]. We establish the excellent properties of these membranes with respect to Ag^+ and Cu^{2+} ions – sensitivity down to 10^{-6} mol/L, short response time and good selectivity to interfering ions. As far as Pb^{2+} ions are concerned, the membranes demonstrate lower detection limit, longer response time and poor reproducibility. We attempt to clarify the reasons for different properties of the membranes with respect to various heavy metals by examining the physical properties, AES depth-profile and electrochemical behavior of the three types of membranes. In spite of the promising results and good electrochemical performance, the long-term stability of chalcogenide-based thin film sensors is still a problem. Some attempts were done to

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increase the long term stability of the membranes with protective layers of plasma deposited polymer film of (PHMDSO) and vacuum deposited polyimide (PI).

2. Experimental

Samples were prepared by vacuum deposition of Cr layer on glass, Si or $Si/SiO_2/Si_3N_4$ substrates, followed by simultaneous or layer by layer evaporation of As_2S_3 or As_2Se_3 and suitable dopants – Ag, Cu, Pb. The content of the samples in atomic percent was determined by measuring the deposition rate with quartz microbalance technique. The thickness of the deposited ion-selective membranes varied from 100 to 250 nm. The evaporated layers were exposed with metal-halogen lamp or annealed at 150 ^oC in order to facilitate the uniform distribution of metals across the depth of the layers. The membranes were observed by scanning electron microscopy Philips 515 in order to control the film morphology, surface defects, etc.

Electrochemical investigations of evaporated membranes were made potentiostatically (with stirring) in the following electrochemical cell:

$$Ag, AgCl \mid KCl:KNO_3 : \text{solution} \mid \text{membrane}$$

The potential was measured by using a digital electrometer or pH-meter, recorder and a commercial Ag/AgCl electrode Metrom (E^0=0.2224 V) as reference. The test solutions were prepared with constant ionic strength and pH (Y=0.3, pH=2.1) through serial dilution of 0.1 M $AgNO_3$, $Cu(NO_3)_2$ or $Pb(NO_3)_2$ with a HNO_3 immediately before measurements.

Riber's microprobe ASC 2000 and ion gun CI 40 modules from the surface analyses combine LAS 3000 were used to study the depth distribution of the dopants in chalcogenide membranes. A 3 keV Ar ion beam bombarding the sample at 70^0 of normal was used for sputter depth profiling. The primary e-beam energy was 3 keV and current - about 7.10^{-2} μA. Auger electron peaks at energies 152 eV, 272 eV, 510 eV, 529 eV, 920 eV, 1228 eV, 94 eV and the doublet 351-356 eV [10] were chosen for the elements S, C, O, Cr, Cu, As, Pb and Ag respectively. The peaks were scanned in the differentiated mode at a modulation voltage 4V peak-to-peak. A semi-quantitative evaluation is made with the elemental sensitivity factors [11], determined according [12] to our own data (method based on reference profiles).

Thin layers of PHMDSO were obtained in glow discharge of low-temperature plasma from hexamethyldisiloxane monomer. The glow discharge ac voltage was about 400 V, 50 Hz frequency and current density 0.6 mA/cm^2, substrate temperature – 65 ^oC [13]. Polyimide layers (PI) were obtained by vacuum co-deposition of the precursor monomers pyromellitic dianhydride and 4,4'-oxydianiline following a thermal treatment – 6 hours at 170 ^oC [14].

3. Results and discussion

The optimal concentrations of chalcogenide membranes sensitive to Ag^+, Cu^{2+} and Pb^{2+} ions are established: $Ag_xAs_yS_z$ layers with Ag>30 at.% for ion-selective membrane for Ag^+ ions [5]; As_2S_3 and As_2Se_3, doped with 8-12 at.% Ag and 20-30 at.% Cu -for Cu^{2+} ions [4]; As_2S_3 doped with 15-50 at. % PbS and 10–20 at.% Ag - for Pb ions [7]. The calibration cures of the membranes for Ag^+, Cu^{2+} and Pb^{2+} ions with optimal concentrations were presented on Fig. 1. The sensitivity characteristics of thin-film sensors and the selectivity coefficients of interfering ions, determined by mixed interference method are presented in Table 1 and Table 2.

We attempt to clarify the reasons for different properties of the membranes with respect to various heavy metals studying the surface morphology and AES depth profile of as-deposited, light-exposed or annealed and electrochemically treated membranes sensitive to Ag^+, Cu^{2+} and Pb^{2+} ions [8,9].

3. 1. Ion-selective membranes sensitive to Ag^+ ions

SEM micrographs of deposited layer by layer As_2S_3/Ag membranes as-deposited, light-exposed and electrochemically treated are presented on Fig. 2 (a, b, c). The surface of the thin films is amorphous and homogeneous without defects and cracks even after electrochemical treatment, which is a prerequisite for good electrochemical response.

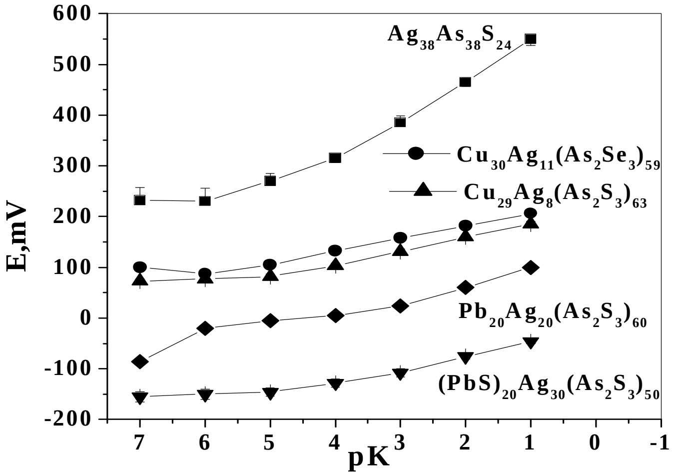

Fig. 1. Calibration cure of the membranes for Ag^+, Cu^{2+} and Pb^{2+} ions.

Table 1. Summary of the sensitivity characteristics of thin film sensors.

	Ag-As-S	Cu-Ag-As-S	Cu-Ag-As-Se	Pb-Ag-As-S	PbS-Ag-As-S
Ion	Ag^+	Cu^{2+}	Cu^{2+}	Pb^{2+}	Pb^{2+}
Sensitivity mV/pX	50-56	23-29	23-29	~ 30	~ 26
Response time (min)	<1	<1	<1	~ 5	~ 5
pH range		2-8	2-8		
Detection limit mol/L	1.10^{-6}	1.10^{-5}	1.10^{-6}	1.10^{-4}	1.10^{-5}

Table 2 . Selectivity coefficients $K^{pot}_{Ag,Me}$ for $Ag_{38}As_{38}S_{24}$ and $Cu_{29}Ag_8(As_2S_3)_{63}$ in the presence of interfering ions.

Interfering. ions	$-\text{Log } K^{pot}_{Ag,Me}$ (in 10^{-1})	$-\text{Log } K^{pot}_{Cu,Me}$ (in 10^{-1})	$-\text{Log } K^{pot}_{Cu,Me}$ (in 10^{-3})
Na^+	2.05	2.45	2.79
Pb^{2+}	2.6	1.6	1.96
Zn^{2+}	3.9	1.89	2.04
Fe^{3+}	2.67	1.67	2.05
Cr^{3+}	-	1.05	1.45
Cu^{2+}	1.67	-	-

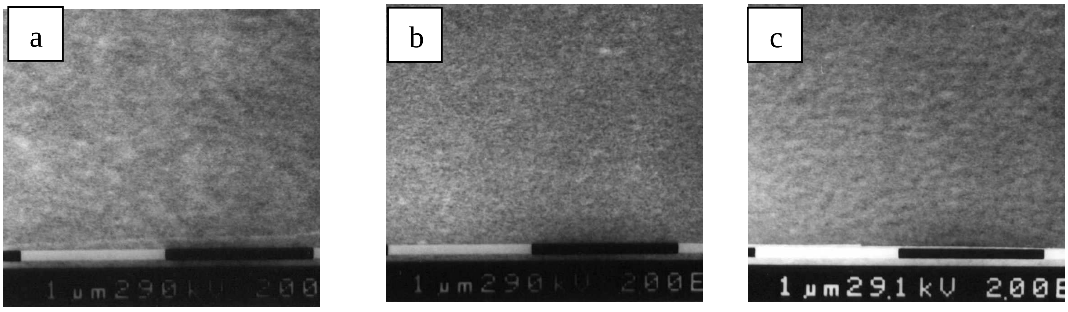

Fig. 2. SEM micrographs of As_2S_3/Ag membranes: (a) as-deposited, (b) -light exposed and (c) electrochemically treated.

AES depth-profiling reveals that Ag is homogeneously distributed in the chalcogenide matrix of light-exposed or annealed membranes (Fig. 3, solid symbols) and remains nearly undisturbed after electrochemical treatment (empty symbols) [8]. This is the reason for very good electrochemical behaviour of ion-selective membranes to Ag^+ ions.

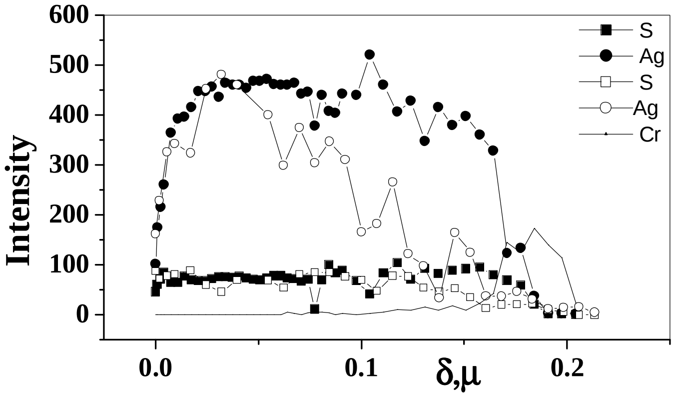

Fig. 3. AES depth-profile of As_2S_3/Ag membrane light exposed (solid symbols) and electrochemically treated (empty symbols).

3. 2. Ion-selective membranes sensitive to Cu^{2+} ions

SEM micrographs of the as-deposited, light exposed, and electrochemically treated As_2S_3/Ag/Cu membranes (Fig. 4 a, b, c) are very similar to that of As_2S_3/Ag membranes. The surface of the membranes is homogeneous without cracks even after electrochemical treatment that is the necessary conditions for good electrochemical behaviour of the membranes.

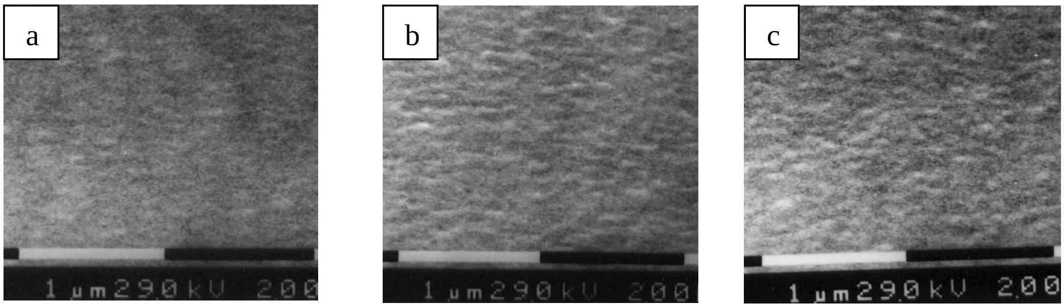

Fig. 4. SEM micrographs of As_2S_3/Ag/Cu (a) as-deposited, (b) light-exposed and (c) electrochemically treated.

According to the literature membranes with Cu and Ag up to 38-41 at% still have homogeneous structure [15]. AES depth profiles of membranes doped with 10-15 at.% Ag and 20-32 at.% Cu in dependence on the preparation method and electrochemical treatment are studied [9]. Some of the membranes are in the solubility range of the doping metals in chalcogenide matrix, others are out of this range.

It was established that in the membranes doped with metals up to the solubility range both metals Cu and Ag are distributed in the whole depth of the membranes independently on the order of thermal evaporation – $(As_2S_3)Ag/Cu$ and $Ag/Cu(As_2S_3)$. Cu depth profile of as-deposited and light exposed membranes is the same and does not depend on the sequence of evaporation and on exposure. As far as concerned to Ag depth profile, some dependence on the sequence of evaporation and on exposure is observed. AES profile of Cu in membranes out of the solubility range is similar to those of the membranes in the solubility range - does not depend on the sequence of evaporation and on exposure. Quite different is Ag depth profile in membranes with concentration of Cu+Ag higher than the solubility maximum (41 %). Cu diffuses predominantly, thus hindering the Ag diffusion. The excess Ag stays undissolved under or above As_2S_3 depending on the sequence of deposition. It was established that the interaction rate of As_2S_3 with Ag is about 4 orders of magnitude lower than that with Cu [16]. That's why one can expect most probably only the diffusion intermixing at As_2S_3/Ag system, while at As_2S_3/Cu fast exothermic exchange reaction should take place during the evaporation, producing Cu_2S and $Cu_{2-x}S$.

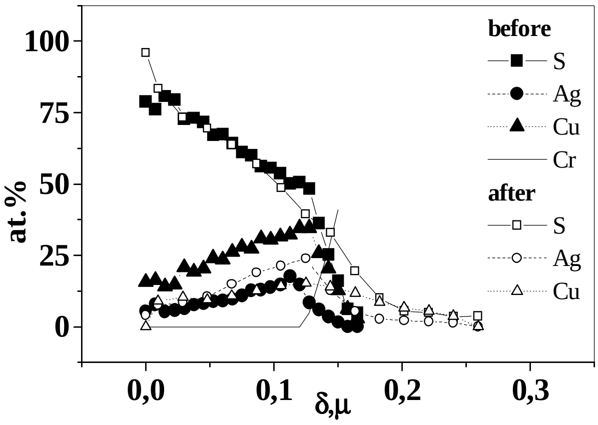

Fig. 5. AES depth profiles of membrane $Ag_{13}Cu_{26}(As_2S_3)_{61}$ with thermal deposited Cu before (solid symbols) and after (empty symbols) electrochemical treatment.

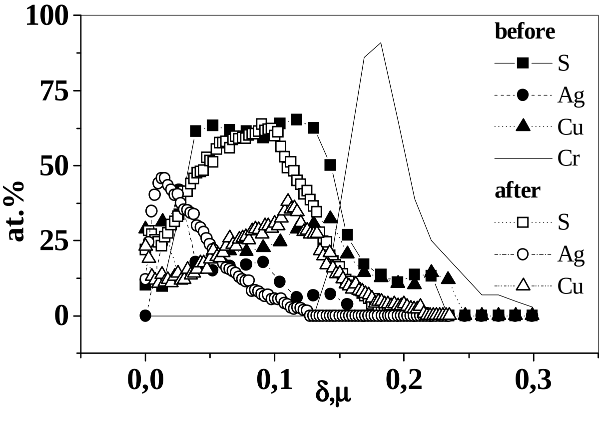

Fig. 6. AES depth profiles of membrane $Ag_{15}Cu_{30}(As_2S_3)_{55}$ with e-beam deposited Cu before (solid symbols) and after (empty symbols) electrochemical treatment.

Electrochemical investigations (40 calibration cycles in solutions at pH=1.4 during 2 weeks) of membranes obtained by thermal and e-beam deposition of Cu showed good reproducibility of electrode potential of both electrode. However, the "response time" of electrode with thermal deposited Cu increases 2x - up to 4 minutes in solutions with 1.10^{-6} Cu^{+2}, while the change of the response time of electrode with e-beam deposited Cu is insignificant.

Electrochemical treatment lowers the depth concentration of thermal deposited Cu in $Ag_{13}Cu_{26}(As_2S_3)_{61}$ membrane while Ag depth concentration is realtively higher (Fig. 5). The surface concentration of Cu decreases, while the surface concentration of Ag remains the same (Fig. 5). Obviously some part of Cu dissolves in the analyte during the exchange reaction, decreasing the density of subsurface layer. This change in the structure could be the reason for the faster deterioration of the properties of the membranes, increasing its "response time".

AES profiles of $Ag_{15}Cu_{30}(As_2S_3)_{55}$ electrode obtained with e-beam deposited Cu was presented on Fig. 6. The results show that excess Ag stays predominantly on the surface of the membranes (Fig. 6), while Cu is distributed in the whole depth. The changes in the depth distribution of both AES profiles for Cu and Ag after electrochemical treatment are smaller compared to electrode obtained with thermal deposition of Cu (Fig. 5) which could be the reason for more stable electrochemical behaviour of the membrane obtained with e-beam evaporation of Cu.

3. 2. Ion-selective membranes sensitive to Pb^{2+} ions

SEM micrographs of layer-by-layer As_2S_3/Ag/Pb membranes show that during the annealing fast recrystallization and oxidation takes place. The surface of the membranes becomes granular with nanocrystallites (Fig. 7a). During the electrochemical treatment some parts of the nanocrystallites dissolve in the analyte (Fig. 7b). SEM micrographs of the membranes prepared by simultaneous evaporation of As_2S_3 and Pb, followed by evaporation of Ag show that the crystallization and oxidation of Pb occur probably during the annealing (Fig. 7c) and some part of the forming Pb nanocrystallites dissolves in the analyte (Fig. 7d).

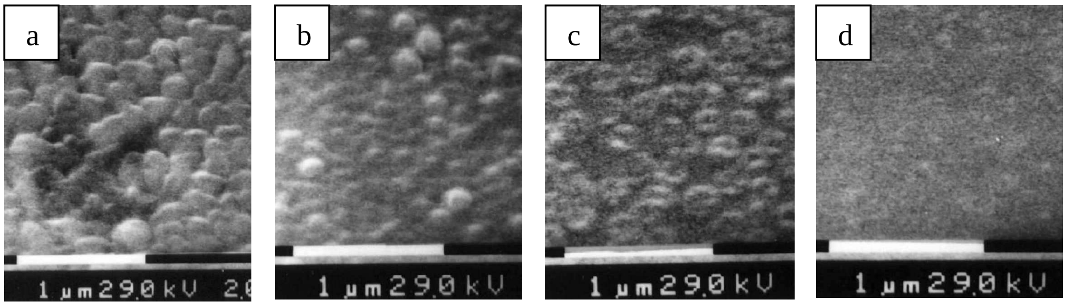

Fig. 7. SEM micrographs of As_2S_3/Ag/Pb (layer by layer) membranes: (a) annealed and (b) electrochemically treated and As_2S_3/Pb/Ag simultaneous deposited: (c) annealed and (d) electrochemically treated.

AES depth profiles of layer-by-layer As_2S_3/Ag/Pb membranes (Fig. 8 a) reveal that Ag and Pb stay on the surface of As_2S_3 even after exposure (or annealing) and only a small part diffuses in the chalcogenide matrix. The quantity of S in Fig. 8 is calculated as atomic percent of As_2S_3 in $(As_2S_3)_x/Ag_y/Pb_z$ membrane. Electrochemical treatment nearly completely dissolves Ag and Pb (Fig. 8a). This fact explains the low sensitivity and instability of the deposited layer-by-layer As_2S_3/Ag/Pb membranes towards Pb^{2+} ions.

AES profiles reveal the presence of Ag and Pb in the depth of simultaneously deposited and annealed membranes (Fig. 8b). Besides that, the electrochemical treatment strongly decreases the concentration of Pb in subsurface region (Fig. 8b). The electrochemical behaviour of these membranes is better than that obtained by layer-by-layer, but still the reproducibility is poor. Promising results are obtained with deposited layer-by-layer As_2S_3/Ag/PbS membranes [7].

The membranes As_2S_3/Ag, As_2S_3/Ag/Cu sensitive to Ag^+ and Cu^{2+} ions exhibit very good electrochemical characteristics. Our method of preparation – layer-by-layer or simultaneous vacuum deposition of components followed by further exposure to light or annealing relies on the well known phenomena – photodoping, photodiffuson, photodissolution, photo-reaction [15]. This is a simple, reproducible and very flexible method of obtaining sensors with various contents without requiring the complicated preparation of a target for sputtering or PLD.

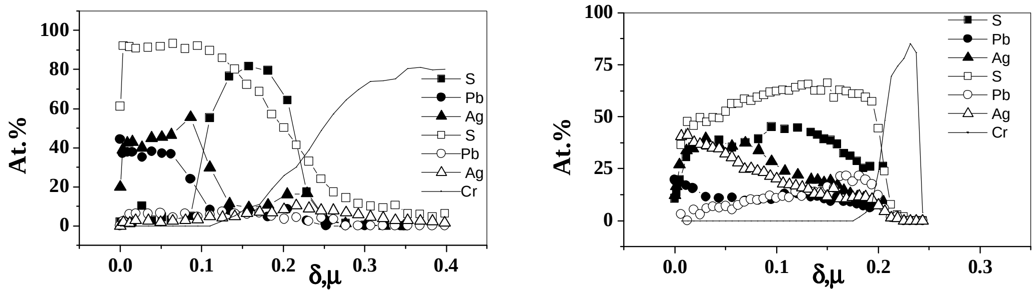

Fig. 8. AES depth-profile of (a) As_2S_3/Ag/Pb (layer by layer) membrane light exposed (solid symbols) and electrochemically treated (empty symbols) and (b) As_2S_3/Ag/Pb (simultaneously deposited) (a) annealed (solid symbols) and (b) electrochemically treated (empty symbols).

The results obtained showed that this method is very promising for systems with high rate of photodoping – for ex. As_2S_3/Ag, As_2S_3/Ag/Cu. As far as the As_2S_3/Ag/Pb system is concerned, we establish that photodoping of Pb in chalcogenide matrix does not occur and that's why these sensors have poor electrochemical performance.

Aiming to improve the electrochemical performance of chalcogenide membranes the influence of polyhexamethyldisiloxane (PHMDSO) [17] and polyimide (PI) was investigated. It could be stressed that both polymer layers were deposited by dry methods. PHMDSO was obtained in glow discharge of low-temperature plasma [13] and PI - by vacuum co-deposition of monomers [14]. Fig. 9 presents the calibration curves of chalcogenide membranes covered with 80 nm polymer layers. The electrochemical characteristics of both polymer coated membranes are better compared to the pure chalcogenide membranes. Nernstian dependence of the sensitivity to pCu^{+2} ions up to 1×10^{-6} for PHMDSO coated and 1×10^{-7} for PI coated membranes, 30% shorter response time, very good reproducibility and longer lifetime were established. It could be stressed that even after 6 months aging the membranes As_2S_3/Ag/Cu covered with polyimide still working very well.

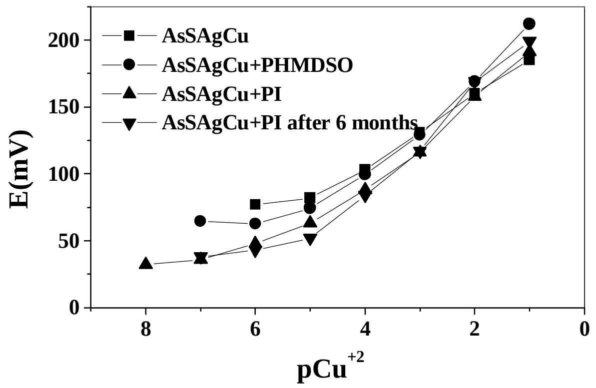

Fig. 9. Calibration curves of As_2S_3/Ag/Cu, As_2S_3/Ag/Cu+PHMDSO and As_2S_3/Ag/Cu+PI membranes.

4. Conclusion

The ion-selective membranes developed on the basis of thin evaporated layers of As_2S_3/Ag, and As_2S_3(As_2Se_3)/Ag/Cu showed high sensitivity towards Ag^+ and Cu^{2+} ions, respectively down to the concentration range of 10^{-6} mol/L, short response time and good selectivity to interfering ions.

It was established on the basis of AES investigations that the concentration of metals distributed in As_2S_3 matrix determines the electrochemical properties of the membranes. The metal distribution depends in some cases on the way of evaporation and the light exposure. Electrochemical treatment influences strongly the Cu concentration in the subsurface region of the membranes with thermally deposited Cu, which could be the reason for the rise in response time with the ageing of the membranes.

E-beam evaporation of Cu enhances the stability of ion-selective membranes due to the more stable metal distribution.

It was found that Pb does not photodoped in As_2S_3 matrix. Electrochemical treatment dissolves the Pb from surface, which explains the unstable electrochemical response of the membranes. Further study of the electrochemical characteristics of As_2S_3/PbS/Ag sensors by co-evaporation of As_2S_3 and PbS is in progress.

The obtaining of the membranes by simultaneous or layer by layer vacuum deposition of components is very promising especially for systems where photodoping occurs. Vacuum technology is compatible with silicon planar technology and represents a simple, reproducible and very flexible way for obtaining thin film sensors for different ions. Moreover, their incorporation into multi-sensor array is easier than in the case of bulk materials and will allow the simultaneous detection and determination of a multitude of substances in aqueous analytes.

We establish that the plasma deposited polymer film of polyhexamethyldisiloxane (PHMDSO) and vacuum deposited polyimide (PI) on top of chalcogenide glass membrane improve their electrochemical characteristics - increase the sensitivity, improve the detection limits and long-term stability while maintaining a stable response time and very good reproducibility. The results obtained are promising for the development of low-cost, highly reliable sensors.

References

[1] J. Kloock, Yu. Morzina, J. Schubert, M. Schoning, Sensors 356 (2002).
[2] Yu. Vlasov, Y. Ermolenko, A. Legin, Y. Murzina, J. Anal. Chem. **54,** 476 (1999).
[3] M. Schoning, Yu. Mourzina, J. Schubert, W. Zander, A. Legin, Yu. Vlasov, H. Luth, Sensors and Actuators **B 78**, 273 (2001).
[4] R.Tomova, R. Stoycheva-Topalova, A. Buroff, Thin Film Materials and Devices – Development in Science and Technology, ed. J. Marshal, N. Kirov, A. Vavrek, J. Maud, World Scientific, Singapore, ISCMP, Varna, Bulgaria, Sep.1-4, 1998, p. 501.
[5] R. Tomova, J. Assa, R. Stoycheva-Topalova, A. Buroff, J. Non-Cryst. Solids **260,** 195 (1999).
[6] R. Tomova, G. Spassov, R. Stoycheva-Topalova, A. Buroff, J. Non-Cryst. Solids **266-269,** 985 (2000).
[7] R. Tomova, R. Stoycheva-Topalova, A. Buroff, Journal of Materials Science: Materials in Electronics **14,** 843 (2003).
[8] R. Tomova, G. Spassov, R. Stoycheva-Topalova, A. Buroff, J. Non-Cryst. Solids **338-340,** 582 (2004).
[9] R. Tomova, G. Spassov, R. Stoycheva-Topalova, A. Buroff, Sensors and Actuators B, **103**, 277 (2004).
[10] Handbook of Auger Electron Spectroscopy, JEOL, ed: T. Sckine et al, Tokyo, 1982.
[11] L. Davis, N. MacDonal, P. Palmberg, G. Riach, R.Weber, Handbook of Auger Electron Spectroscopy, 2nd ed., Physical Electronics Industries Inc., Minesota, (1976).
[12] M. Seah, Practical Surface Analysis, **V.1.**, John Wiely & Sons, 202 (1990).
[13] E. Radeva, D. Tsankov, K. Boev, L. Spassov, J. of Applied Polymer Science **50**, 165 (1993).
[14] E. Spassova, Vacuum **70**, 551 (2003).
[15] A. Kolobov, S. Elliott, Advances in Physics **40**, 625 (1991).
[16] M. Sopinsky, M. Kostyshin, J. Optoelectron. Adv. Mater. **3**, 411 (2001).
[17] R. Tomova, R. Stoycheva-Topalova, A. Buroff, E. Radeva, T. Angelov, Nanoscience & Nanotech.'02, eds. E. Balabanova, Heron Press, Sofia 2002, p. 115.