

PROCESSING AND CHARACTERIZATION OF THIN FILM $\text{Cu}_x(\text{Ge}_{28}\text{Se}_{60}\text{Sb}_{12})_{1-x}$ ION-SELECTIVE ELECTRODE MEMBRANE

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This work relates to the elaboration and characterization of Ion-Selective Electrodes (ISEs) based upon chalcogenide membrane sensitive to Cu^{2+} ion in aqueous solution for continuous and in situ measurements. The membrane material is a thin film deposited by RF co-sputtering of $\text{Ge}_{28}\text{Se}_{60}\text{Sb}_{12}$ chalcogenide glass and metal copper. The composition of the film highly doped with copper was analysed using Energy Dispersive Spectroscopy (EDS) and Secondary Ion Mass Spectrometry (SIMS). The membrane / solution interface interactions were characterised using X-ray Photoelectronic Spectroscopy (XPS) and Electrochemical Impedance Spectroscopy (EIS). These miniaturised ISEs exhibit Nernstian responses (30 mV / pCu) in a large copper (II) concentration range and a detection limit close to 1×10^{-6} M.

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1. Introduction

The development of electrochemical sensors for the detection of various metal species, in environmental samples has been the subject of considerable research during the last three decades. A majority of this work has involved the use of solid-state ion-selective electrode (ISE) membranes. This work concerned the realisation of an ion-selective electrode for the detection of copper (II) in solutions. Since Jasinski et al. [1], which were the first to use a Cu-As-S system based sensor for the determination of Cu (II) ions, other systems, for example Cu-As-Se-(Te), Cu-Ag-As-Se-(Te) had been investigated [2-4]. Other way with the deposition by RF sputtering experiment of a chalcogenide As-Se and copper metal thin film had been developed [5-7]. Baker et al. [8] had shown in previous works the potentialities of the GeSeSb chalcogenide glasses doped with copper and iron for the ion-sensible electrode. Bychkov et al. [Bry05a] had worked in this way and had shown the good potentialities of the As-Se-Cu membrane with 40 and 50 at.% Cu. In our case, we had chosen to work with the chalcogenide glass $\text{Ge}_{28}\text{Se}_{60}\text{Sb}_{12}$ doped with copper [9], chalcogenide also use for the iron detection in the seawater [10].

The membrane will be deposits by RF-sputtering using and characterizes by EDS, SIMS and XPS. The electrochemical response will be study by EIS and an equivalent circuit explaining the electrical comportment will be place in a prominent position.

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2. Experimental methods

The deposition of the films was performed in a RF sputtering set-up type Alcatel DION 300. A base pressure of 2×10^{-6} mbar was first achieved in the deposition chamber using a turbomolecular pumping unit. Previous to deposited, the chamber was filled several times with Argon to eliminate any trace of residual oxygen which could pollute the deposited layer. The pressure was then brought back to 10^{-1} mbar which corresponds to the pressure of striking of the plasma, argon being the gas of discharge. After striking, the work pressure was fixed to 2×10^{-2} mbar. In order to prevent thermal damage of the targets, a RF sputtering power of 30 W was used. The distance target–substrate was equal to 5 cm.

The Cu-GeSeSb target was striking a thin copper fold (a composite target built by Alfa Aesar, Thickness 0.1 mm, Purity 99.9975%) onto a 2" diameter piece of $\text{Ge}_{28}\text{Se}_{60}\text{Sb}_{12}$ glass (Vitron, GmbH, Germany) and the thin layers were 500 nm thick. The speed deposition target ranged from 5 to 10 $\text{nm}\cdot\text{min}^{-1}$. The substrates were cleaned microscope slides onto which was deposited a Cr layer of 500 nm in thickness such a metallic layer was used to provide a good electrical contact with the sensitive layer and thus to produce an ion sensitive electrode (ISE).

The composition layer was controlled by Energy Dispersive Spectroscopy (EDS) and Secondary Ion Mass Spectrometry (SIMS). The microscope used for the EDS analysis was an ESEM XL 30, FEI Company, with a X-ray detector for the EDS spectra recording. Analyses were performed at 8 kV. SEM images were also collected using the same unit. The spectrometer used for the SIMS analysis was a VG SIMS Lab with a liquid metal gallium source. The coupling of a finely focused ion beam with a controlled scanning raster of the surface allowed $10 \times 10 \mu\text{m}^2$ to $2 \times 2 \text{mm}^2$ wide areas with lateral resolution down to 0.1 μm in image mode to be explored. The SIMS analyses were performed in dynamic conditions.

The electrode potential was measured with a Minisis high impedance millivoltmeter / Radiometer Tacussel. The external reference electrode was a saturated Ag/AgCl electrode used with a double junction. KNO_3 (0.5 M) was used as the supporting electrolyte. Tests solutions in the concentration $10^{-1} - 10^{-4}$ M were prepared by successive 10-fold dilutions of a 1 M $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ solution by the supporting electrolyte. Calibrations were performed in the concentration range $10^{-7} - 10^{-3}$ M by addition of a known volume of copper (II) nitrate test solutions to 100ml of supporting electrolyte (KNO_3 , pH=3).

Electrochemical Impedance Spectroscopy (EIS) studies were undertaken using Potentiostat/Galvanostat (PGSTAT100, Autolab) (100V, 10nA – 0.3A) coupled with a frequency response analyser (FRA). A three electrode configuration was used with the chalcogenide sensor as the working electrode, a calomel (saturate) electrode as the reference one and a platinum wire as the auxiliary electrode. The working electrode was a revolving one with a speed equal to 3000 rpm. Such a configuration could be chosen because of the predominant electronic conductivity of the membrane and the low resistance of the Cr/membrane interface. Impedance spectra were recorded in the frequency range 0.1 Hz – 1.10^5 Hz with an applied ac signal of 10 mV. The measurements were performed at open circuit potential in solutions of 0.5 M $\text{KNO}_3 + \text{Cu}(\text{NO}_3)_2$ at room temperature. All EIS spectra were fitted to equivalent circuits using the ZView software.

The X-ray Photoelectron Spectroscopy (XPS) analyses were performed with a Surface Science Instruments (S-Probe) spectrometer (model 301) using focused (diameter of the irradiated area equal to 300 or 600 μm) monochromatised Al K_{α} X-rays ($h\nu = 1486.6$ eV). The residual pressure inside the analysis chamber was c.a. $5 \cdot 10^{-8}$ Pa. The spectrometer was calibrated by using the photoemission lines of Au (Au 4f(7/2) = 83.9 eV, with reference to the Fermi level) and Cu (Cu 2p(3/2) = 932.5 eV); for the Au 4f(7/2) line the FWHM (full width at half maximum) was 0.86 eV under the recording conditions. The peaks were recorded with constant pass energy of 50 eV. Neutralisation of the surface charge was performed using a low energy flood gun. All the measurements were carried out on thin films. The binding energy scale was calibrated using the C 1s line (284.6 eV) from the carbon contamination.

3. Results and discussion

The produced Cu-GeSbSe layers have a smooth surface as shown on the SEM micrograph reported in Fig. 1. The chemical composition of the deposited thin films was checked by EDS. Both of the elements contained in the chalcogenide layer (Cu, Ge, Se and Sb) and in the substrate (Si and O) are detected and showed in Table 1, included C due to a contamination.

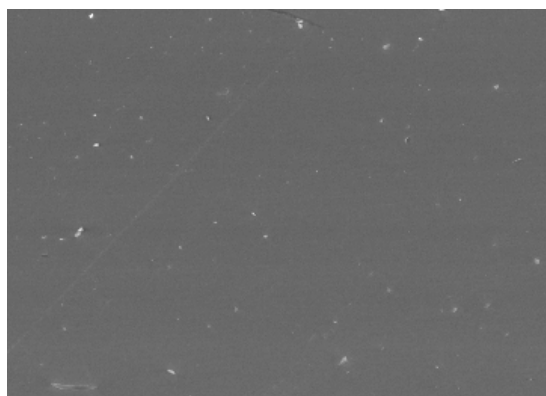


Fig. 1. Micrograph obtained by scanning electron microscopy showing the homogeneous surface of a typical Cu-GeSeSb thin film deposited by RF sputtering.

If are discords the foreign elements (Si, O and C) (line 1, Table 1), EDS data show the deposited films contained around 40 at.% in copper (line 2, Table 1), while the relative amount of the other elements Ge, Se and Sb (line 3, Table 1) was closed to the one existing in the bulk glass used as the target (line 4, Table 1).

Table 1. Chemical composition of the deposited films measured by EDS. The table shows the atomic percent data for the different element detected by EDS and the relative data for both for deposition layer (Cu-GeSeSb) and chalcogenide glass in comparison with the commercial target.

Line	Si	C	O	Cu	Sb	Ge	Se	Formulation
	at% of all the detected elements							
1	1.10	5.55	14.36	32.75	4.83	13.12	28.30	-
	at% of the elements in the chalcogenide layer							
2	-	-	-	41.46	6.11	16.61	35.83	Cu _{41.46} (GeSeSb) _{58.54}
	at% of the elements in the glassy matrix							
3	-	-	-	-	10.46	28.37	61.20	Ge _{28.37} Se _{61.20} Sb _{10.46}
	theoretical composition of the glassy part of the target							
4	-	-	-	-	12.00	28.00	60.00	Ge ₂₈ Se ₆₀ Sb ₁₂

Secondary, SIMS analysis was aimed as completing EDS analysis. It helps in determining matter the composition of the layer was constant in depth. Fig. 2 shows the SIMS depth profiles as the curve “log concentration vs. depth” obtained for both positive and negative ions.

A linear profile was obtained for all the elements of the membrane. It indicates that the composition was constant throughout the depth of the layer. C and O were detected in small quantities in the entire layer. It indicates a low contamination that occurred during the deposition process or pre-existing in the target and not a surface contamination due to contact with out for example (O). On the whole the data obtained by SEM, EDS and SIMS indicated that the layers were homogeneous, had surface of good quality and were poorly contaminated.

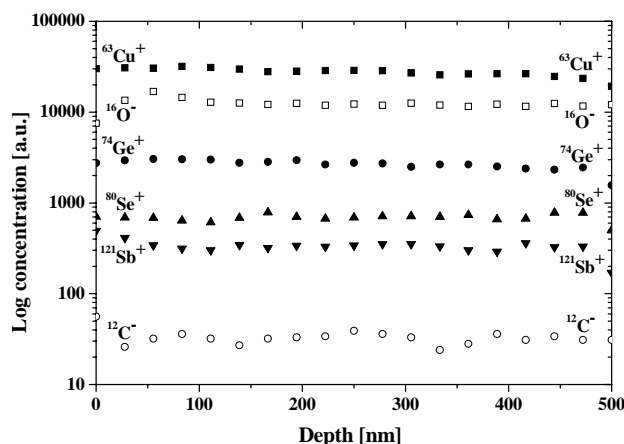


Fig. 2. SIMS depth profile of a Cu-GeSeSb chalcogenide glass membrane as the curve “log concentration vs. depth of analyses” obtained both for the positive and negative ions.

The electrode response in copper (II) nitrate solutions with constant ionic strength (KNO_3 ; 0.5 M) is shown in Fig. 3. Two calibrations are shown: one previous to any conditioning of the membrane and one fresh membrane after a conditioning in a 10^{-4} M copper (II) solution during 12 hours [11]. In both cases, the slope S of the calibration curve was about 30 mV / pCu corresponded to a theoretical $S_0 = RT / 2F$ in the Nernst equation (1).

$$E = E_0 + \frac{RT}{nF} \log[\text{Cu}^{2+}] \quad (1)$$

where,

E_0 is the formal electrode potential;

R is the universal gas constant, equal to $8.314510 \text{ J.K}^{-1}.\text{mol}^{-1}$;

T is the temperature in Kelvin;

n is the number of electrons transferred in the half-reaction;

F is the Faraday constant (charge per a mole of electrons), equal to $9.6485309 \times 10^4 \text{ C.mol}^{-1}$;

$[\text{Cu}^{2+}]$ is the concentration of the reducing agent (the oxidized species, Cu^{2+}).

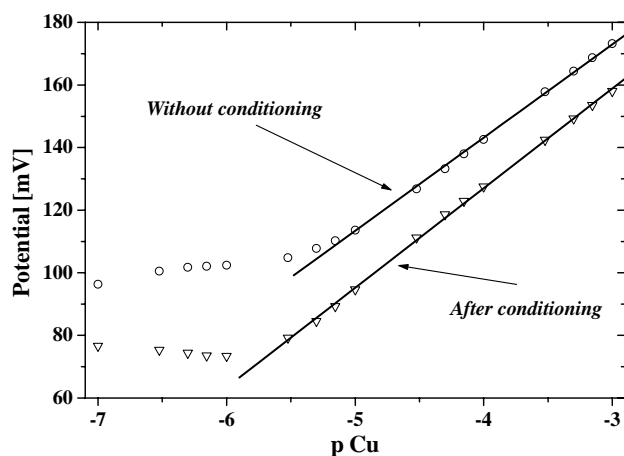


Fig. 3. Typical copper calibration curve of a thin film sensor of the chalcogenide glass system Cu-GeSeSb showing the detection limit and the slope both for a fresh membrane and after conditioning in a copper (II) nitrate solution.

The detection limit decreases such a value with the conditioning and reached an optimal value of $3 \cdot 10^{-6}$ M. The selectivity of the sensors against several interfering ions was tested and high selectivity in the presence of alkali and alkaline-earth metal ions was observed [9], whereas the only heavy-metal ion to interfere significantly with the sensors was Fe^{3+} . These results are comparable to those already reported for similar copper sensitive membranes based upon bulk or thin film chalcogenide glasses [9,12-14].

Fig. 4 shows the results obtained by electrochemical impedance spectroscopy (EIS) where a fresh membrane was placed in solutions of copper nitrate with different Cu(II) concentration ($10^{-3} - 10^{-7}$ M). On the whole, the impedance spectra can be described as a semicircle shifted from the origin. When the membrane was in contact with a concentrated copper (II) ions solution ($> 1 \times 10^{-3}$ M), an additional straight line was observed at lower frequency.

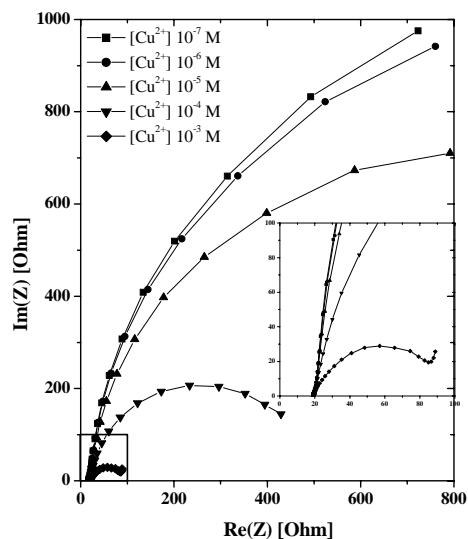


Fig. 4. Electrochemical impedance spectroscopy (EIS) plots of a Cu-GeSeSb fresh membrane placed in solutions of copper nitrate with different Cu(II) concentration ($10^{-3} - 10^{-7}$ M) and showing the real impedance ($\text{Re}(Z)$) in function the imaginary impedance ($\text{Im}(Z)$).

The part of the Zview software dedicated to equivalent circuits, written by Derek-Johnson, was used to simulate the impedance spectra with an electrical circuit. The impedance spectra were analyzed with the equivalent circuit shown in Fig. 5. Such a circuit was built on the basis of the following assumption. First, a resistance R_s (equal to 18 ohms) was introduced to take into account the electrical behaviour of the solution. The second resistance R_{ct} corresponded to the charge transfer resistance at the interface membrane-solution. R_{ct} is strongly dependant on the copper (II) concentration of the solution. Its decrease when $[\text{Cu}^{2+}]$ increases indicates that the kinetics of the charge transfer is favoured for an elevated copper (II) concentration.

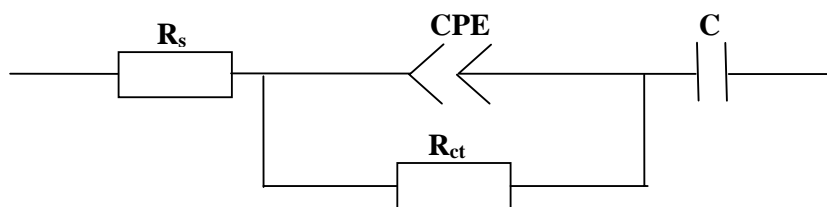


Fig. 5. Electrochemical equivalent circuit used to fit impedance spectra (shown Fig. 4) described using two resistances R_s and R_{ct} , a CPE (described by Q and n) and a capacity C , each parameters taking into account a specificity of the behaviour of the membrane and interface membrane-solution.

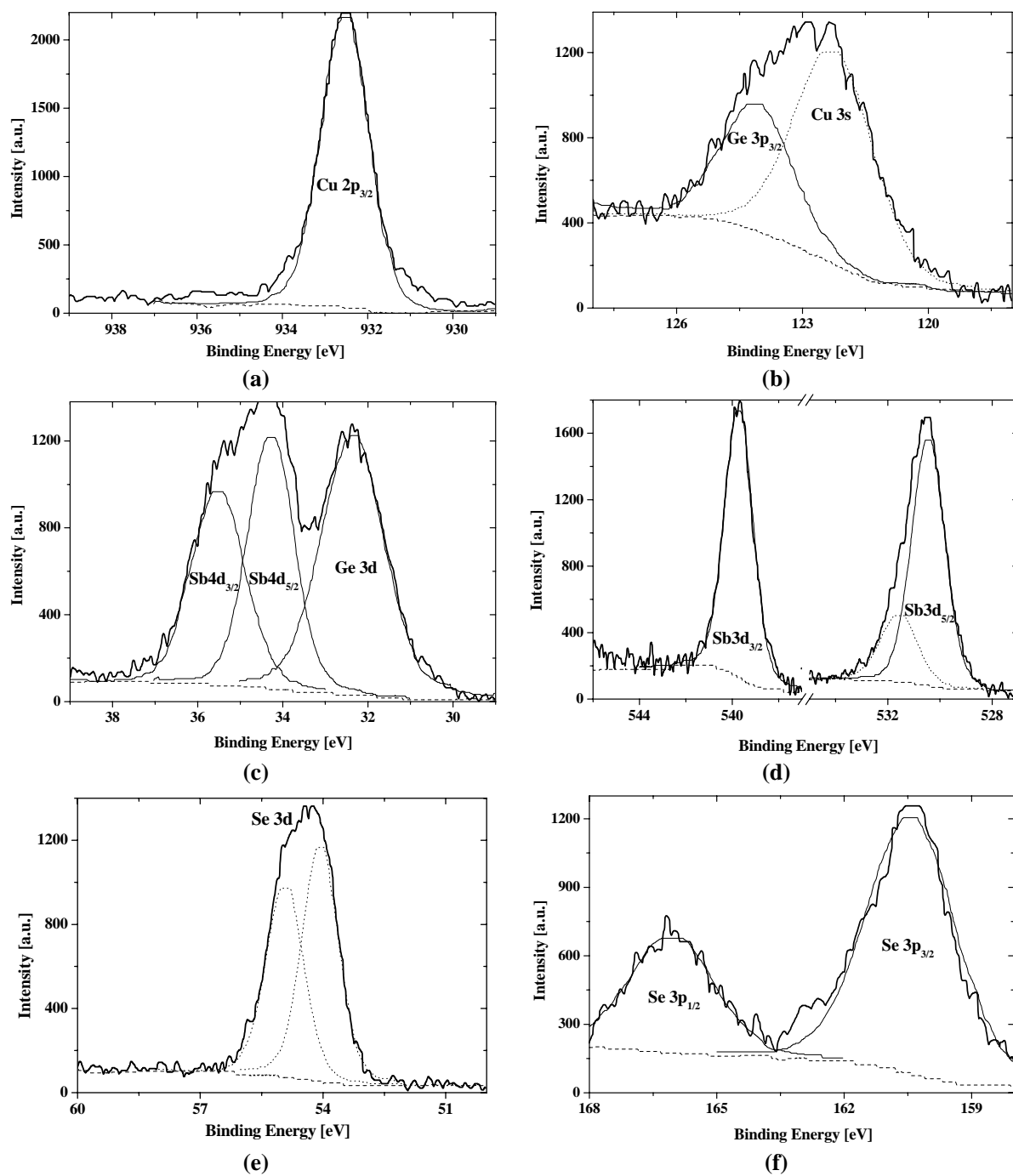


Fig. 6. X-ray photoelectron core-level spectra of the different element composed the fresh membrane Cu-GeSeSb thin film (a) Cu 2p_{3/2} (b) Ge 3p_{3/2} (c) Sb 4d_{3/2}, Sb 4d_{5/2} and Ge 3d (d) Sb 3d_{3/2} and Sb 3d_{5/2} (e) Se 3d_{5/2} in two different environment (f) Se 3p_{1/2} and Se 3p_{3/2}.

The CPE (Constant Phase Element) was used instead of double-layer capacitance to take into account the roughness of the thin film surface. It is described by two parameters Q and n (pure impedances, Warburg terms, capacitances and inductances corresponding to $n = 0, 0.5, 1$ and -1 respectively). The last element represented on the equivalent circuit is a capacity C, used at low frequencies for the 10^{-3} M copper concentration.

The model is used to fit the calculations to experimental data. The obtained fit is excellent (the values of the parameters are grouped in the Table 2). The following processes are taking into consideration in the model: solution resistance, interfacial charge transfer resistance and double layer.

Table 2. Values of the electrical parameter used in the equivalent circuit showing Fig. 5 and permitted to fit impedance spectra.

	pCu = 7	pCu = 6	pCu = 5	pCu = 4	pCu = 3
Q	0.00108	0.00105	0.00104	0.00118	0.00262
n	0.930	0.928	0.926	0.903	0.767
R _{ct}	2436	2275	1593	487	78

A XPS analysis of the surface was then undertaken in order to get information on the environment of the different elements of the membrane. The study reported here was carried out on a fresh membrane mentioned at an inert atmosphere after deposition. Fig. 6 shows XPS spectra obtained for all the customs of the membrane. The Cu 2p(3/2) peak reported in Fig. 7(a) at a binding energy of 932.5 eV characteristics of the Cu₂Se element [7,15]. Fig. 7(b) and 7(c) show respectively the Ge 3p(3/2) at a binding energy of 124.0 eV and the Ge 3d at 32.4 eV. These results show that the Ge is in an environment GeSe₂. Fig. 7(c) and 7(d) show respectively the Sb 4d(5/2) and 4d(3/2) peaks at a binding energy of 34.2 eV and 35.7 eV, the Sb 3d(5/2) peak at 530.4 eV and the Sb 3d(3/2) peak at 539.5 eV. These observations show the Sb is in an environment Sb₂Se₃. Finally, Fig. 7(e) and 7(f) show respectively Se 3d(5/2) peak at a binding energy of 54.5 eV and Se 3p(3/2) and 3p(1/2) peaks at 160.5 and 166.0 eV. The 3d(5/2) peak can be deconvolute in two peaks, one at a binding energy of 54.0 eV and put in a prominent position an copper (II) environment and a second one at a binding energy of 55.0 eV and characteristics of a germanium or antimony environment. In all case, the selenium is Se²⁻ (selenide) type.

4. Conclusions

The sensing response of the Cu_x(Sb₁₂Ge₂₈Se₆₀)_{1-x} material to copper (II) ions has been studied. The sensor displays a Nernstian response over a large range of concentration with a detection limit close to 1×10^{-6} M. XPS and EIS measurements were carried out in order to get some knowledge on the phenomena occurring at the membrane / solution interface and giving rise to the sensing properties of the Cu₄₀(Ge₂₈Se₆₀Sb₁₂)₆₀ membranes. This composition has been confirmed by EDS and SIMS analysis.

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References

- [1] R. Jasinski, I. Trachtenberg, Evaluation of the ferric ion sensitive chalcogenide glass electrode, J. Electrochem. Soc. **120**, 1169 (1973).
- [2] Yu G. Mourzina, J. Schubert, W. Zander, A.V. Legin, Yu.G. Vlasov, H. Lüth, M.J. Schöning, Electrochim. Acta **47**, 251 (2001).
- [3] M. J. Schöning, C. Schmitd, J. Schubert, W. Zander, S. Mesters, P. Kordos, H. Lüth, A. Legin, B. Seleznev, Yu.G. Vlasov, Sens. Actuators B **68**, 254 (2000).
- [4] R. Tomova, G. Spasov, R. Stoycheva-Topalova, A. Buroff, Sens. Actuators B **103**, 277 (2004).
- [5] E.A. Bychkov, M. Bruns, H. Klewe-Nebenius, G. Pfennig, W. Hoffmann, H.J. Ache, Sens. Actuators B **24-**

- 25**, 733 (1995).
- [6] E. Bychkov, M. Bruns, H. Klewe-Nebenius, G. Pfennig, K. Raptis, W. Hoffmann, H.J. Ache, *Sens. Actuators B* **26-27**, 384 (1995).
- [7] M. Bruns, H. Klewe-Nebenius, G. Pfennig, E. Bychkov, H.J. Ache, *Surf. Coat. Technol.* **97**, 707 (1997).
- [8] C.T. Baker, I. Trachtenberg, *J. Electrochem. Soc.* **118**, 571 (1971).
- [9] G. Taillades, O. Valls, A. Bratov, C. Dominguez, A. Pradel, M. Ribes, *Sens. Actuators B* **59**, 123 (1999).
- [10] R. De Marco, D. J. Mackey, *Mar. Chem.* **68**, 283 (2000).
- [11] F. Méar, M. Essi, P. Sifat, P. Huguet, A. Pradel, M. Ribes, *Proceeding in : 21st International Conference on Solid Waste Technology and Management, Philadelphia, USA, 2006*, p.582.
- [12] C. Cali, G. Taillades, A. Pradel, M. Ribes, *Sens. Actuators B* **76**, 560 (2001).
- [13] A. V. Legin, E. A. Bychkov, Yu.G. Vlasov, *Sens. Actuators B* **24-25**, 309 (1995).
- [14] Yu G. Vlasov, E. A. Bychkov, *Ion-sel. Electr. Rev.* **9**, 5 (1987).
- [15] C. Cali, D. Foix, G. Taillades, E. Siebert, D. Gonbeau, A. Pradel, M. Ribes, *Mat. Sci. Eng. C* **21**, 3 (2002).