

METAL-SULPHIDE ISE FOR COPPER (II) DETECTION

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The present work relates elaboration and characterization of a metal sulphide Ion-Selective Electrode. Sensors were built using chemical and electrochemical techniques to convert sputtered metallic thin films into metal sulphide membranes. The resulting films were characterised using X-ray diffraction, Scanning Electron Microscopy and Energy Dispersive Spectroscopy. Comparative investigations have been carried out in order to check the sensing properties as a function of elaboration process. The electrochemical characterization of the optimised ISE is presented.

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1. Introduction

Heavy metal ions are ones of the most toxic species. During the last three decades, a majority of research has involved the use of electrochemical sensors for the detection of metal species in environmental sample [1, 2]. It is clearly demonstrated that various types of ion-selective electrodes are used to check the water quality in laboratory, but only few of them can really be applied for in-situ monitoring in waste effluents [3].

Because of their specific properties [4, 5], chalcogenide materials have been mainly used for the development of potentiometric sensors for the determination of heavy metal ion in solution. The present trend in modern electrochemical analysis tends to miniaturise continually the measuring techniques. Moreover, the miniaturisation and integration of micro-sensors by the techniques of microelectronics allows the development of multisensory system for the simultaneous detection of several chemical species [6].

In this paper we describe an original procedure to synthesise a conventional ion-selective electrode according to the potentiometric principle. Referring to the model of macro-ISE with CuS/Ag₂S-pellet [7], we tried to develop an all-solid-state micro-ISE based on metal-sulphide material. Several techniques are used to build metal-sulphide films. For instance, spray-pyrolysis [8], S.I.L.A.R. [9] and sintering process [10] are well-known deposition techniques. In our study we used chemical bath deposition [11] and electro deposition techniques, which were already tested and proved to be successful for such preparation, to develop a miniaturised ion-selective electrode for Cu²⁺ ions. Preparation and characterisation of the resulting chemical micro sensors are presented.

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2. Experimental methods

The metallic layers were converted into metal-sulphide sensing membrane by treatment in a sulphidic electrolyte. By means of cathodic sputtering [12] using a Alcatel Dion 300 set up equipped with a PFG hutting, 13.56 MHz, 300 W generator thin copper or copper-silver layers were produced on the top of glass substrate covered on one side by a chromium film of 300 nm in thickness such as sensor internal reference. First of all, a base pressure of 2.10^{-6} mbar was achieved in the deposition unit. The deposition chamber was filled with argon to avoid ambient contamination. To strike the Ar-plasma the pressure was brought back to 10^{-1} mbar. Microscope slides were used as substrates. Before being introduced in the vacuum chamber, they were cleaned with a commercial detergent in an ultrasonic bath, rinsed in alcohol and dried with dry air. An appropriate target-substrate distance was observed in order to obtain the optimum thickness of the deposited metallic thin film (500 nm). The pressure was fixed to 2.10^{-2} mbar and a power of 60 W was used. The thickness was estimated by profilometry using a DEKTAK 3 Veeco. Optimised layers resisted to the “toothbrush test” very well. The substrate holder was cooled down by water circulation. The targets were polished systematically previous to deposition in order to ensure reproducibility. Thin film of copper-silver were prepared by RF co-sputtering of copper metal and silver small pieces assembled with silver micro-adhesive as a composite sputtering target. After deposition, a wire was attached with silver micro-adhesive on chromium layer and then the inner side was coated with an epoxy resin. The film surface aspect and roughness were inspected using a digital instrument D3100 Atomic Force Microscopy.

The sensors were built using two techniques in order to make comparative investigations. To elaborate the first ion-selective electrode (S_1) we used chemical bath deposition technique. Then, the copper thin film was immersed in the sulphide precursor electrolyte. The immersion time ranged from 1 to 2 min. The sensitive membrane is finally rinsed in deionised water. This procedure takes few minutes and no maintenance or exsiccator apparatus are required. The necessary sulphide precursor is developed from Na_2S , $9\text{H}_2\text{O}$ under addition of deionised water (Na_2S 4.10^{-2} M). If the colour of the black- brownish layer does not change any more, the end of the reaction is reached. The second micro sensor (S_2) was elaborated by electro deposition process. The Cu^{2+} selective electrode was built by electrolysis in a two electrode system, using copper thin film as working electrode (anode) and Pt wire as auxiliary electrode (cathode). The deposition cell was a standard 250 cm^3 glass laboratory beaker that contains aqueous Na_2S solution of 4.10^{-2} M concentration and both electrodes. Using a Velleman PS 907 generator, a direct current of 5 mA is applied during 1 min to the electrolysis cell. Anodic oxidation is observed since copper released electrons. Therefore, brownish coloration indicates metal – sulphide deposition by reaction of anions with metallic ions at working electrode surface. Reduction of water was observed at the cathode. At last sensitive layer is rinsed in deionised water. The third sensor (S_3) was prepared by electrolysis process using copper – silver thin film as working electrode. Figure 1 shows the electrolysis cell.

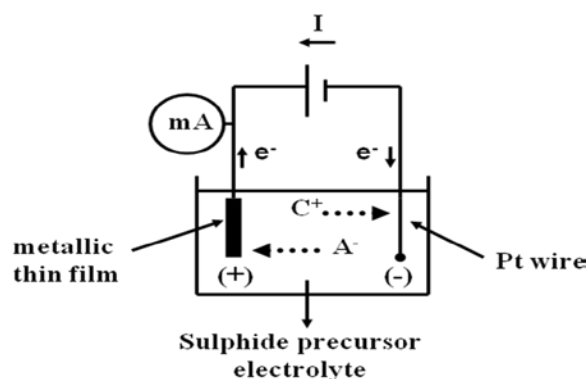


Fig. 1. Principle of electrolysis cell used to convert metallic thin film into sensitive membrane.

The sensitive materials were observed by scanning electron microscopy (SEM) using a Cambridge 360 instrument in order to control the films morphology, surface defects and to check the thickness. The conversion of the metallic thin layers to metal-sulphide was examined by Energy Dispersive Spectroscopy (EDS) probe. Structural characteristics of the materials were checked by X-ray diffraction. The XRD measurements were performed using a SEIFERT diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). An operating voltage of 40 kv and a beam current of 25 mA were selected.

The electrode potential was measured with a high impedance millivoltmeter under stationary conditions (i.e. analyte change by hand and electrolyte movement by means of magnet agitators during the potential measurement). The external reference electrode was a saturated Ag/AgCl electrode used with a double junction. KNO₃ (0.1 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 Cu(NO₃)₂, 5H₂O 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. The pH of the solution was maintained at the same value (pH=3) for all measurements to avoid Cu(OH)₂ formation. After calibration sensors were kept in deionised water to limit membranes ageing [13, 14]. The electrochemical measuring cell can be schematically present as following:

Ag,AgCl||KCl,AgCl (sat.) ||0.1 M KNO₃||Analysed solution||ISE||Inner reference electrode

3. Results and discussions

Thickness measured at different points of the sputtered films was shown to be maximum at the centre and to decrease as the point moves away from it, following the Knudsen's law (1).

$$d/d_0 = 1/(1+(L/H)^2)^2 \quad (1)$$

Where d_0 is the thickness at the film centre, L the distance between the target and the substrate (i.e. 5cm) and H the distance between the centre of the layer and its extremity (i.e. 3.5 cm). These results are comparable to those already reported for sputtered thin films when the substrates are not rotated. Layers deposited under the same conditions were characterised by the same thickness at the centre. The compositions were proved to be reproducible and independent of the film thickness. It can be noted that the roughness is different from one point of the film to another. It is maximum at the centre of the layer and decreases as the point moves away from the centre. Such a variation was expected taking into account the change in the thickness at different points of the thin films. We can observe in figure 2 the X-ray pattern of copper – silver sputtered thin film. A poor crystallization of the film is observed while diffraction patterns of copper and silver from the composite target indicated the presence of both elements in the film.

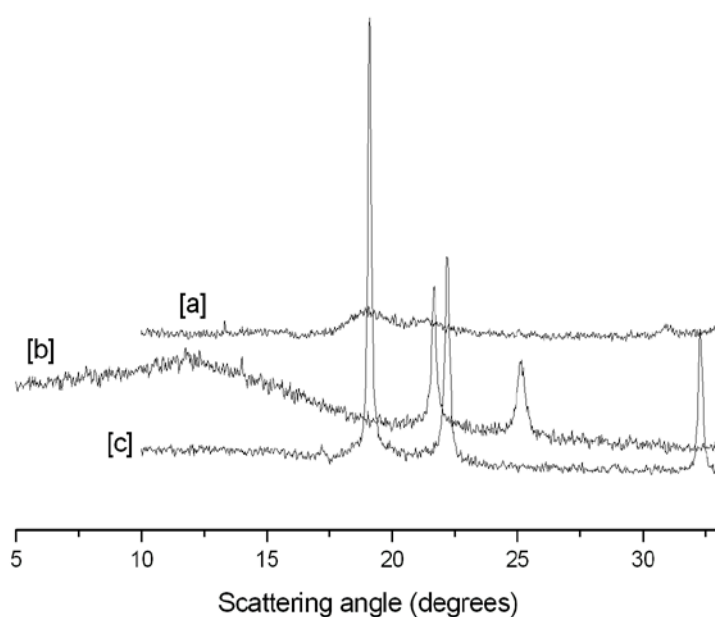


Fig. 2. X-ray diffraction patterns of copper-silver thin film [a] and of both elements contained in the target (i.e. copper [b] and silver [c]).

The surface morphology and the chemical composition of studied sensors have been checked in order to compare elaboration processes. Such as reference sample, sample (A) is an untreated copper – silver thin film. Sample (B) is elaborate by electrolysis of similar thin film using aqueous solution of $4 \cdot 10^{-2}$ M Na_2S as electrolyte. At last to build sample (D) alloys thin film is immersed in the same sulphide precursor solution. Table 1 presents the chemical composition of membranes. Performed EDS analysis showed that oxygen contained in the substrate is detected, due to the low thickness of the films while a great amount of sulphur is observed by using electrolysis process.

Table 1. Chemical composition of the samples measured by EDS. The table shows the atomic percent data for the different element detected by EDS.

	Sample	Electrolysis Process			Immersed thin film
		A	B	C	D
	Electrolyte	-	Na_2S deionised water	Na_2S ethylene glycol	Na_2S deionised water
Chemical Composition (% at)	Cu	73	64	Inhomogeneous chemical composition	72
	Ag	10	8		8
	S	-	25		6
	O	17	3		14

It is clearly evident that electro deposition process leads to a homogeneous composition of sensitive layer. The resulting layer was homogeneous had a surface of good quality and was poorly contaminated. As shown on the SEM micrograph reported in figure 3(a) the smooth surface of

sample B does not present any observable defects. A columnar structure of the sputtered films is observed by SEM. The roughness estimated from AFM images measured over an area of $1\mu\text{m} \times 1\mu\text{m}$ was about 5.5 nanometers. Effect of ethylene glycol [10], such as sulphide precursor solvent has been studied. Then, sample (C) is elaborate by electrolysis of copper – silver thin film. $4 \cdot 10^{-2}$ M electrolyte solution is prepared by adding appropriate amount of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ salt to ethylene glycol. Table 1 indicated that glycol electrochemical treatment leads to an inhomogeneous composition of the membrane. The surface alteration of the membrane occurred as soon as the membrane is soaked in a glycol electrolyte. Moreover, a clear tendency of partial lifting off of the metal-sulphide layer is observed. A typical SEM picture of the corresponding membrane is presented in figure 3(b). The film surface presents defects and cracks.

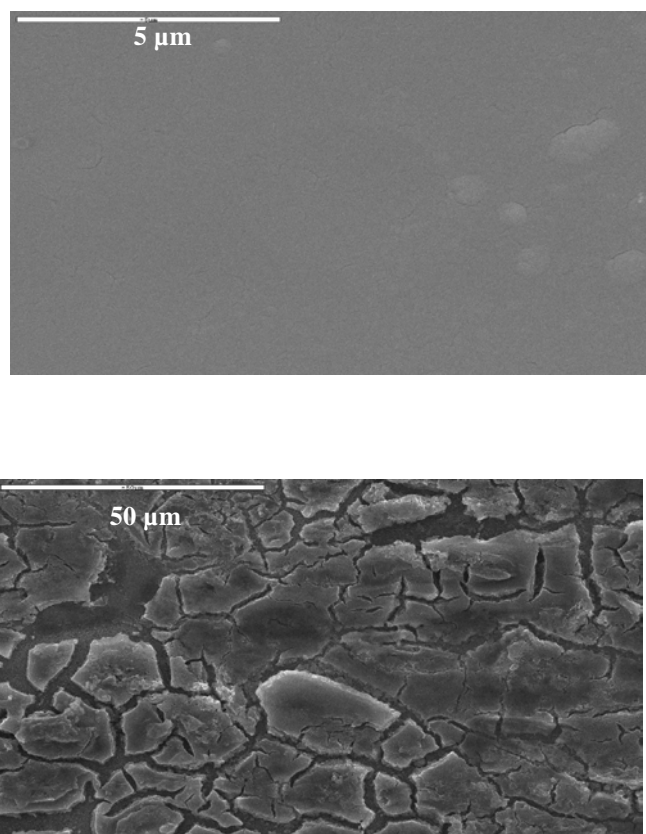


Fig. 3. Micrographs obtained by scanning electron microscopy showing the homogeneous surface of a typical sample B (a) and sample C surface with defects and cracks (b)

Comparative potentiometric measurements have been carried out in order to check the sensitivity behaviour as a function of elaboration procedure.

Electrodes responses in copper (II) nitrate solutions with constant ionic strength (10^{-1} M KNO_3) are shown in figure 4. The linear range of S_2 and S_3 sensors response is $10^{-3} - 2 \cdot 10^{-6}$ M and the detection limit is about 10^{-6} M. S_2 electrode calibration measurement exhibits sub-Nernstian response with a slope of 22 mV/pCu. It should be noted that this membrane showed a worse potential reproducibility. On the other hand, S_3 ISE calibration displayed near-Nernstian slope of 26 mV per decade. The electrode displayed stable and reproducible response during several weeks. This quasi-Nernstian out-put signal is comparable to those already reported for similar sensitive membranes based on chalcogenide glasses. For instance, $\text{CdS-AgI-Sb}_2\text{S}_3$ membrane exhibits sensitivity close to 28 mV/pCd while the detection limit is close to 10^{-6} M [15]. The slope of the calibration curve is close to the theoretical $S_0 = RT/2F$ from the Nernst equation (2).

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

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 $9.6485309 \times 10^4 \text{ C.mol}^{-1}$;

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

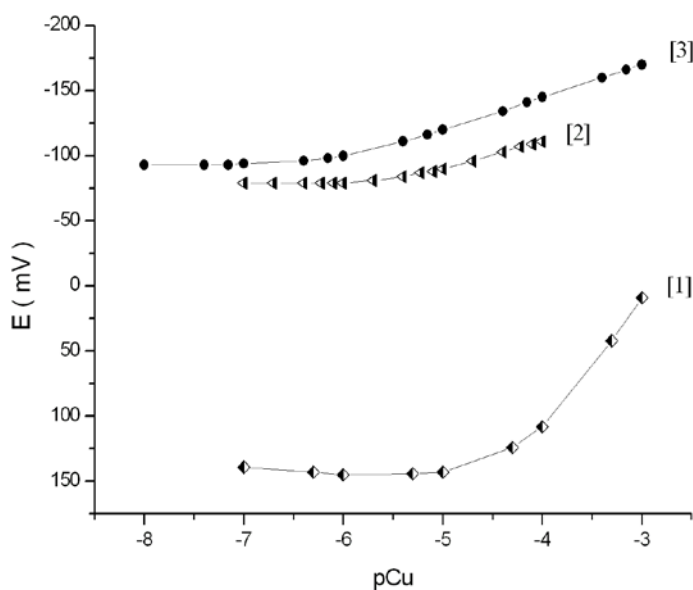


Fig. 4. Typical copper calibration curves of S_1 [1], S_2 [2] and S_3 [3] sensors

Since S_2 sensor and S_3 sensitive layers gave different potentiometric responses to Cu^{2+} ions, one can consider that both sensing mechanisms are different. Concerning S_3 micro sensor, the potential-generating process can take into account “modified surface layer” formation. It is shown that the surface of chalcogenide membrane is modified after exposure to the test solution. The exposure involves chemical composition modification of the membrane surface. Previous works on chalcogenide membrane Ag-Cu-S [16] indicate a decrease in the copper content of the membrane surface soaked in copper (II) solution. It suggests different interfacial phenomena compared to S_2 sensor. Such a difference might be due to the presence of silver in the S_3 electrode. Due to the very poor sulphur amount in the membrane as shown by EDS experimental data, S_1 sensor has a worse potentiometric response to copper (II) ions.

Since S_3 micro sensor displays near-Nernstian behaviour versus Cu^{2+} in solution, further investigations have been carried out in order to characterize the chemical micro-sensor. The electrochemical characterization of the Cu-ISE was done by means of potentiometry.

Dry storage of the electrode over one week caused only some millivolts change in the initial value of the electrode potential, but no degradation of the sensing behaviour. The life time of the ISE is essentially limited by the adhesion of the sensing thin layer on the substrate after several calibration cycles. Sensitivity measurements were performed stationary. Stable potential values were measured immediately after immersing the electrode into the measuring solution. Fast response time within few seconds was observed, also with solution change from more concentrated to more diluted one. This result had shown the reversibility of the out-put signal. To calculate the response time the membrane response was recorded depending on the time and the varying copper (II) concentration. As shown in figure 5 the time require to obtain response equilibrium (t_{95}) was close to 18 s when Cu^{2+} concentration increase from 10^{-4} M to 10^{-3} M .

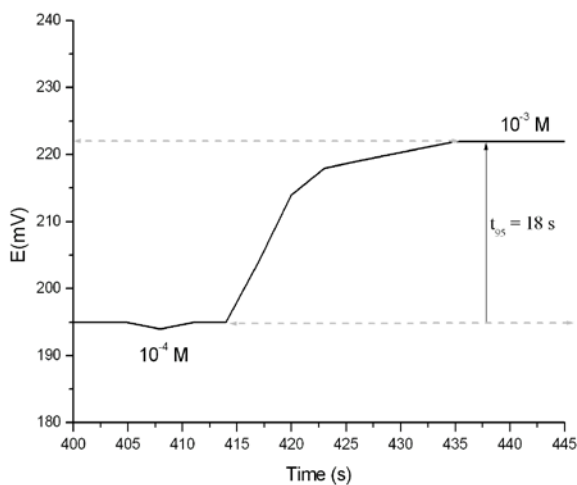


Fig. 5. Response time (t_{95}) of S_3 ISE. The Cu^{2+} concentration was changed from 10^{-4} to 10^{-3} M

Concerning long-term drift it is to be noticed that the electrodes have no significant sensitivity loss after repeated measuring cycles. Typical drift values stay in a range of 6 mV/day. The electrode potential was found to be independent of change in pH in the range of 3-5. High selectivity in the presence of alkali and alkaline-earth metal ions was observed, whereas the only heavy-metal ion to interfere significantly with the ISE is Cr^{3+} . The response of S_3 sensor to Ag^+ ion was tested in silver (I) nitrate solution with constant ionic strength. KNO_3 10^{-1} M was used as electrolyte. Test solutions were prepared by dilution of silver (I) nitrate solution by the electrolyte. Calibrations were performed by addition of test solution to the electrolyte. The electrode potential was measured using high impedance millivoltmeter and Ag/AgCl double junction electrode. The sensor response was studied in the pH range of 3-6. Figure 6 indicated that the membrane worked well over a wide concentration range of Ag^+ with a Nernstian slope of $58 \pm 2 \text{ mV}$ per decade of Ag^+ activity which corresponds to the exchange of one electron. The detection limit was closed to 10^{-6} M . It is shown that the micro electrode exhibit a Nernstian behaviour at acidic pH (3 and 4) and at neutral pH (6). The response time of the micro sensor is fast (less than 10 s) and the membrane can be used several times with good reproducibility.

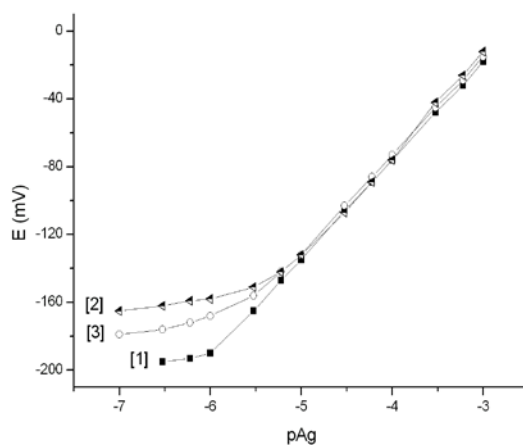


Fig. 6. Typical silver calibration curves of S_3 sensors. pH=6 [1], pH=4 [2] and pH=3 [3].

4. Conclusions

Cu – Ag – S sensitive device for copper (II) ion detection in solution has been studied. Electrolysis of sputtered copper – silver thin film leads to a homogeneous membrane composition with a great sulphur amount. The corresponding sensor displayed a reliable and reproducible response to Cu²⁺ ion. The sensitive membrane is suitable for the detection of silver.

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