

## CHALCOGENIDE GLASSES AS SENSITIVE MEMBRANES FOR THE DETECTION OF IONS IN SOLUTION

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The sensing properties of two chalcogenide materials, i. e. a glass ceramic of composition  $\text{Cu}_{10}(\text{As}_{0.4}\text{S}_{0.6})_{90}$  and an amorphous thin film obtained by RF sputtering of a composite target  $\text{Cu} / \text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$  glass, were investigated. The glass ceramic was shown to be sensitive to both sulphide and copper in solution while the thin film only shows a response to  $\text{Cu}^{2+}$  ions. The  $\text{Cu}_{10}(\text{As}_{0.4}\text{S}_{0.6})_{90}$  membrane was included in a module which allowed continuous monitoring of sulphide in thermal waters. A miniaturised device for the detection of  $\text{Cu}^{2+}$  ions was developed by depositing the film  $\text{Cu} - \text{Ge} - \text{Sb} - \text{Se}$  onto the gate of a pH ISFET.

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### 1. Introduction

In the last years the need for analytical devices to be used for environmental, industrial or medical controls has been growing very quickly. Depending upon the concerned field two main requests can be noticed : 1) one for systems which could be used continuously on line and 2) one for miniaturised systems. Laboratory techniques involving conditioning of the sample to be analysed are not well adapted to these requirements. Even though they usually do not give as precise data as the above cited techniques chemical sensors could bring some interesting solutions. In particular chemical sensors based upon chalcogenide materials are well adapted to the detection of chemical species in solution. They can reach the present needs for in situ use and miniaturisation since they are very durable in particular in neutral and acidic media and they can be easily shaped in thin films by the usual techniques of microelectronics. Moreover their very versatile composition allows the fabrication of specific membranes for many different types of ions (heavy metals such as  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ , anions such as  $\text{S}^{2-}$ , halide ions..) [1-5].

The present work is related to the use of two different chalcogenide membranes for the detection of ions in solution, i. e. a glass ceramic of composition  $\text{Cu}_{10}(\text{As}_{0.4}\text{S}_{0.6})_{90}$  and an amorphous thin films obtained by RF sputtering of a composite target  $\text{Cu} / \text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$  glass. An autonomous monitoring system for sulphide in solution including an ion selective electrode based upon the first material has been developed in the framework of the work. The  $\text{Cu} / \text{Ge-Sb-Se}$  thin film has been used to modify the gate of a pH ISFET and thus to produce miniaturised devices for the detection of copper in solution.

### 2. Experimental

#### 2. 1. Preparation and characterisation of ion sensitive materials

The compound  $\text{Cu}_{10}(\text{As}_{0.4}\text{S}_{0.6})_{90}$  was synthesised by melting appropriate amount of  $\text{As}_2\text{S}_3$  and copper metal (99.99%, Aldrich) in silica tubes evacuated to  $10^{-5}$  Pa at  $950^\circ\text{C}$  for 24 h and further water quenching.  $\text{Cu-Ge-Sb-Se}$  glassy thin films were obtained by RF sputtering of a composite target comprising a 50mm copper metal disk with 10mm  $\text{Ge}_{28}\text{Se}_{60}\text{Sb}_{12}$  glassy disks stuck on the top of it.

The films were deposited either directly on a Si / Si<sub>3</sub>N<sub>4</sub> substrate (ISFET gate) or after deposition of a thin Cr layer on the Si / Si<sub>3</sub>N<sub>4</sub> substrate (ISE structure). The obtained materials, either bulk or thin films, were characterised by X ray diffraction (Seifert) and scanning electron microscopy (Cambridge 360). Chemical analysis was performed using an EDS probe. Conductivity measurements were performed with a HP4192A impedance meter in the temperature range 25-130°C.

## 2.2. Preparation and characterisation of ion selective electrodes (ISE)

In the case of bulk Cu<sub>10</sub>(As<sub>0.4</sub>S<sub>0.6</sub>)<sub>90</sub> the ion selective electrodes were prepared from discs (1 mm in thickness and 10 mm in diameter) cut from the melts and polished. A platinum layer was then deposited on a face of the disk by sputtering. The microelectrode comprised two parts: the Cu-Ge-Sb-Se glassy thin film as the sensitive membrane and a Cr layer as a collector. In both cases a wire was attached to the metallised face with silver micro-adhesive. This inner part of the electrodes was isolated from the external medium with an epoxy resin.

The potentiometric measurements were made with the following electrochemical cells:

Hg, Hg<sub>2</sub>SO<sub>4</sub> (or Hg<sub>2</sub>Cl<sub>2</sub>) || K<sub>2</sub>SO<sub>4</sub> (or KCl (sat)) || 0.1 M KNO<sub>3</sub> | test solution | test electrode  
Test solutions in the concentration range 10<sup>-2</sup> – 10<sup>-6</sup> M were prepared by successive tenfold dilutions of 1 M Cu(NO<sub>3</sub>)<sub>2</sub> or 1 M Na<sub>2</sub>S·9H<sub>2</sub>O solutions by the supporting electrolyte (0.1 M potassium nitrate) for copper and sulphide calibrations respectively. The selectivity of the sensors was tested using the mixed solution method with a constant concentration in interfering ion.

The determination of sulphide in solution was also carried out by employing a potentiometric titration with mercuric chloride and end point determination with a selective silver electrode type ISE25S-9 (Radiometer, Denmark).

## 2.3. Preparation and characterisation of microsensors based upon an ion sensitive field effect transistor (ISFET)

The ISFET based sensors sensitive to Cu<sup>2+</sup> ions were obtained by first depositing the Cu-Ge-Sb-Se sensitive membrane onto the whole surface of Si wafers containing ISFET structures initially designed for the fabrication of pH ISFET at the Centro Nacional de Microelectronica in Barcelona [6]. The film was then selectively removed so that it covered only the surface of the gate (Si<sub>3</sub>N<sub>4</sub>). Removal of the chalcogenide film was achieved either by chemical etching and by lift off. In both cases the optimisation of the process was carried out on test samples. Masks used for chemical etching allowed the design of four plots of 1mm in diameter on Si<sub>3</sub>N<sub>4</sub> substrates. Several acid and/or oxidising etching solutions were tested. The test samples for lift off were silicon nitride substrates covered with a photoresist layer into which hexagonal motives were opened.

The electrical characterisation of the Cu<sup>2+</sup> sensitive ISFET sensors was carried out using a HP 4145B semiconductor parameter analyser allowing the measurement of current as low as 1000 pA with a 1 pA resolution. The electrochemical characterisation of the ISFETs were performed using an home-made ISFET meter developed at CNM. It consisted in measuring the variations of the gate voltage while dipping the sensors in solutions containing different concentrations of copper nitrate. Identical test solutions as those used for the electrochemical characterisation of the Cu<sup>2+</sup> ISE were used for the calibration of ISFET.

## 2.4. Fabrication of a prototype for continuous on line detection of sulphide

The Cu<sub>10</sub>(As<sub>0.4</sub>S<sub>0.6</sub>)<sub>90</sub> electrode, a commercial pH electrode (Heito) and a temperature sensor (Pt100) were included in a measurement module developed by the company TMI-Orion in order to monitor the variation in sulphide concentration in two thermal springs. The programmable module could be immersed at a depth of 1 meter and allowed measurement and data storage over periods of several months.

## 3. Results and discussion

### 3.1. Characterisation of ion sensitive materials

The two selected chalcogenide membranes have very different characteristics. Indeed while the X ray diffraction pattern of the Cu-Ge-Sb-Se films deposited by RF sputtering is that of an

amorphous material, the X-ray diffraction pattern of bulk  $\text{Cu}_{10}(\text{As}_{0.4}\text{S}_{0.6})_{90}$  indicated partial crystallisation with the presence of sinnerite  $\text{Cu}_{6.3}\text{As}_4\text{S}_9$  in its triclinic form. In agreement SEM observations of  $\text{Cu}_{10}(\text{As}_{0.4}\text{S}_{0.6})_{90}$  material indicated the presence of an heterogeneous multiphase system with a crystalline material distributed throughout an amorphous matrix while the surface of the Cu-Ge-Sb-Se thin films observed by SEM was very smooth. In that case EDS measurements helped in knowing the film composition i. e.  $(\text{Sb}_{11}\text{Ge}_{29}\text{Se}_{60})_{50}\text{-Cu}_{50}$  with variation of about 5% in copper from one film to the other. We can note that the relative amount of Ge, Sb, Se is close to that existing in the bulk glass used for the target. It is noteworthy that the material the richer in copper is amorphous while the poorer shows partial crystallisation. It is attributed to the very different procedures of preparation, RF sputtering inducing easily disorder.

It is known that materials with very low conductivity cannot be used successfully as sensitive membranes for the detection of ion in solution since it induces very long response times and unstable electrochemical characteristics [1]. In our case the room temperature conductivity for both samples, i.e.  $2 \times 10^{-2} (\Omega \text{ cm})^{-1}$  for  $\text{Cu}_{10}(\text{As}_{0.4}\text{S}_{0.6})_{90}$  and  $3 \times 10^{-2} (\Omega \text{ cm})^{-1}$  for  $(\text{Sb}_{11}\text{Ge}_{29}\text{Se}_{60})_{50}\text{-Cu}_{50}$  film, should be large enough to overcome such drawbacks. We also noted in the course of the experiment the absence of polarisation phenomena (a single circle in the Cole-Cole plots) which is indicative of a large part of electronic conduction in both samples.

### 3.2. Ion selective electrodes (ISE)

#### (i) ISE for the detection of $\text{Cu}^{2+}$ ions in solution

Both chalcogenide membranes, i. e.  $\text{Cu}_{10}(\text{As}_{0.4}\text{S}_{0.6})_{90}$  material and  $(\text{Sb}_{11}\text{Ge}_{29}\text{Se}_{60})_{50}\text{-Cu}_{50}$  film, were tested as sensitive membrane for the detection of  $\text{Cu}^{2+}$  ion in solution.

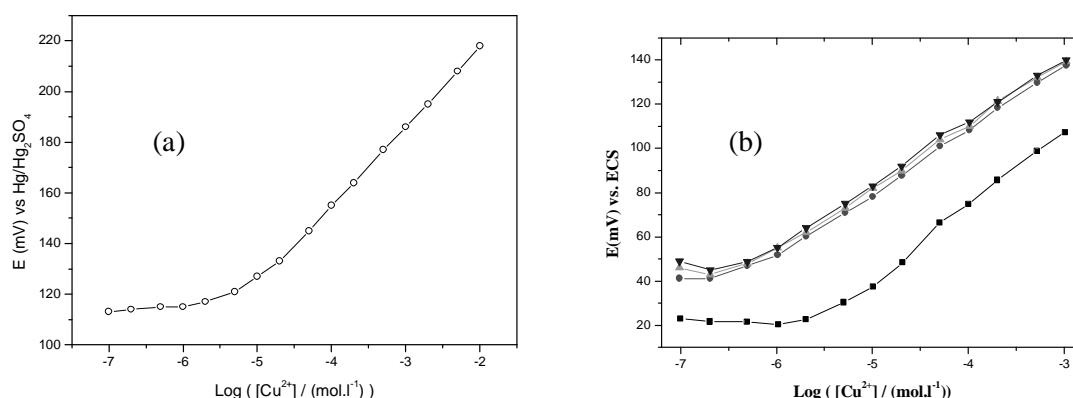


Fig. 1. Potentiometric response of (a) the  $\text{Cu}_{10}(\text{As}_{0.4}\text{S}_{0.6})_{90}$  membrane sensor and (b) the  $(\text{Sb}_{11}\text{Ge}_{29}\text{Se}_{60})_{50}\text{-Cu}_{50}$  microsensor.

Typical calibration curves are shown in figure 1. Both sensors exhibited a fast  $\text{Cu}^{2+}$  ion response. As shown in Fig. 1 for the  $(\text{Sb}_{11}\text{Ge}_{29}\text{Se}_{60})_{50}\text{-Cu}_{50}$  microsensor the result of the first calibration previous to conditioning differed from the subsequent ones by lower values of both standard potential and slopes. After few measurements the sensor characteristics became more stable. For both materials the potentiometric response obeyed the Nernst law with a slope of about 30 mV / pCu above pCu = 5. The limit of detection was close to  $10^{-6} \text{ M Cu}^{2+}$ .

The microsensor based upon the  $(\text{Sb}_{11}\text{Ge}_{29}\text{Se}_{60})_{50}\text{-Cu}_{50}$  film alone was investigated more thoroughly since we were looking more specifically for a miniaturised device for the  $\text{Cu}^{2+}$  detection to be used in a multisensor array in the future.

The  $(\text{Sb}_{11}\text{Ge}_{29}\text{Se}_{60})_{50}\text{-Cu}_{50}$  sensors showed good long term stability over periods of several weeks as shown in Fig. 2. However a slight drift in absolute potential with time, i. e. a change of about 1.5 mV per day, was observed.

Selectivity coefficients of the sensors against several interfering ions were measured and are given in Table 1. A high selectivity in the presence of alkali and alkaline-earth ions was observed whereas the only heavy-metal ion to interfere significantly with the sensors is  $\text{Fe}^{3+}$ . These results are

comparable to those already reported for similar sensitive membranes based upon bulk or thin film chalcogenide glasses [7,8].

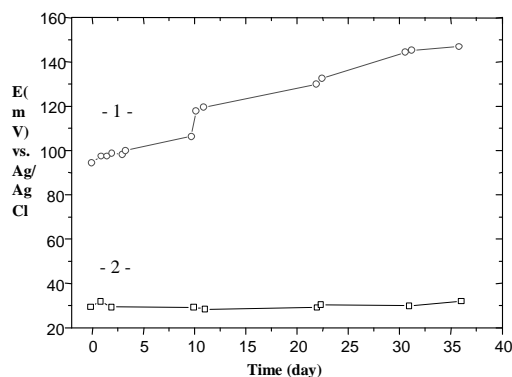


Fig. 2. Changes in time in the potential (1) and the slope (2) of the  $(\text{Sb}_{11}\text{Ge}_{29}\text{Se}_{60})_{50}\text{-Cu}_{50}$  membrane electrode in  $\text{Cu}(\text{NO}_3)_2$   $10^{-4}$  M solution.

Table 1. Selectivity coefficients against several interfering ion species for the Cu-Ge-Sb-Se membrane.

Interfering ion	Log $K_{\text{Cu}^{2+}/\text{Mz}^{+}}$
$\text{K}^{+}$	-5.1
$\text{Na}^{+}$	-5.3
$\text{Ca}^{2+}$	-5.1
$\text{Ni}^{2+}$	-4.1
$\text{Cd}^{2+}$	-4.1
$\text{Pb}^{2+}$	-2.5
$\text{Mn}^{2+}$	-3.4
$\text{Fe}^{3+}$	-1.3

(ii) ISE for the detection of sulphide ions in solution

$\text{H}_2\text{S}$  is a diprotic acid ( $\text{pK}'_1 = 7$  and  $\text{pK}'_2 = 14$ ), so the concentration of the three sulphide species depend strongly of pH.

A first series of calibrations was based on the  $S_T = [\text{S}^{2-}] + [\text{HS}^-] + [\text{H}_2\text{S}]$  variation using pH 7 buffered solutions. While the electrodes based upon  $(\text{Sb}_{11}\text{Ge}_{29}\text{Se}_{60})_{50}\text{-Cu}_{50}$  films always gave unstable response whatever the conditioning the electrodes based upon  $\text{Cu}_{10}(\text{As}_{0.4}\text{S}_{0.6})_{90}$  material revealed to be interesting sensors for the detection of sulphide ions in solution. Indeed after conditioning in a solution of 0.01 M  $\text{Na}_2\text{S}$ ,  $9\text{H}_2\text{O}$  the electrodes gave stable electrochemical characteristics. A typical calibration curve is shown in Fig. 3. The potentiometric response displayed a near-Nernstian slope of about  $55 - 65 \text{ mV} / \text{pS}_T$ . The limit of detection was close to  $2 \times 10^{-6} \text{ M } S_T$ . It corresponds to a high sensitivity to total sulphide concentration since the limitation of the standard method (as described in the experimental section) is reached for  $S_T = 10^{-4} \text{ M}$ . Note that similar results for the standard method and the  $\text{Cu}_{10}(\text{As}_{0.4}\text{S}_{0.6})_{90}$  electrode were obtained for solutions where the total sulphide concentration lies in the range  $10^{-4} - 10^{-2} \text{ M}$ .

A second set of electrochemical measurements for the  $\text{Cu}_{10}(\text{As}_{0.4}\text{S}_{0.6})_{90}$  electrode was based on the  $\text{S}^{2-}/\text{HS}^-$  ratio variation using pH modification with constant  $S_T$ .

Calibrations were performed in solutions containing concentrations in total sulphide equal to  $10^{-4}$ ,  $10^{-3}$ ,  $10^{-2} \text{ M}$ . The pH of the solutions was monitored in the range 3 – 12 by adding adequate amount of HCl (1M) or NaOH (1M). A constant voltage drop close to 60 mV between the different curves as shown in figure 4.a demonstrates that the sensor is sensitive in the entire pH range investigated. Moreover, the variation of potential is nearly constant for  $\text{pH} > 7$  while a Nernstian behaviour was observed in the 3-7 pH range. These variations are closely correlated with the variation of  $\text{HS}^-$  concentration with pH. Indeed according to the equilibrium between the different sulphide

species (Fig. 4.b) for a given  $S_T$ , the  $HS^-$  concentration increases linearly versus pH in the range 3 – 7 then reaches a nearly constant value above pH 7. Such a correlation might indicate that the electrode is sensitive to  $HS^-$  species.

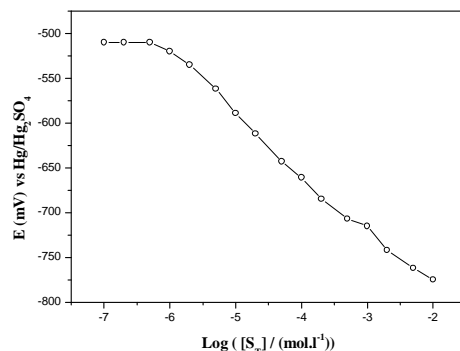


Fig. 3. Potentiometric response of a  $Cu_{10}(As_{0.4}S_{0.6})_{90}$  membrane electrode vs total sulphide concentration.

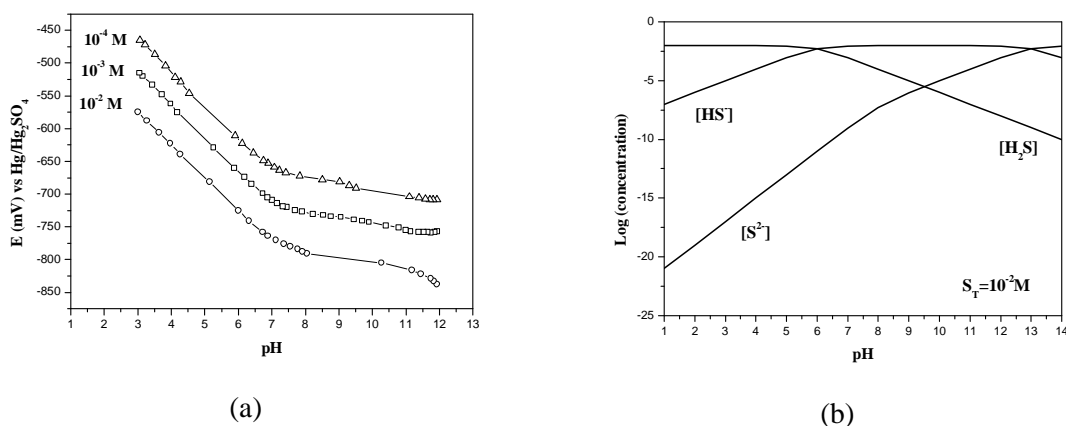


Fig. 4. (a) pH influence on potentials in different total sulphide concentration and (b) pH influence on the concentration of the different sulphide species.

Table 2. Selectivity coefficients against several interfering ion species for the Cu – As – S membrane electrode.

Interfering ion	Log $K_{Cu^{2+}/Mz+}$
$Cl^-$	-5.1
$I^-$	-5.3
$NO_3^-$	-5.1
$SO_4^{2-}$	-4.1
$CH_3COO^-$	-4.1

The selectivity of the  $Cu_{10}(As_{0.4}S_{0.6})_{90}$  electrode against several interfering anions was tested. The results are summarised in table 2.  $10^3$ - $10^6$ -fold amounts of sulphate, chloride, iodide, nitrate and acetate do not influence the electrode potential. These results are comparable to those already reported for glassy-crystalline sensors sensitive to bromide [4]. The sensor was also shown to be insensitive to alkali and alkaline-earth ions. Obviously as shown in the previous section the sensor is sensitive to copper ions.

### 3.3. ISFET sensors for the detection of $Cu^{2+}$ in solution

#### (i) Preparation of modified ISFET

Owing to the interesting electrochemical characteristics of the  $(Sb_{11}Ge_{29}Se_{60})_{50}-Cu_{50}$  film, we considered them as potential candidates for the fabrication of ISFET sensors sensitive to  $Cu^{2+}$  ions in solution. The gate of ISFET structures had to be modified by deposition of the chalcogenide film. The

procedure that was developed to achieve this goal was to deposit the film on the whole surface of wafers containing the ISFETs then to remove the film selectively so that only the gate remained covered. Two photolithography processes were developed. First chemical etching of the film was considered since it usually leads to high resolution of the desired pattern. Because of the high copper content in the film strong oxidising acid etching solutions were tested at once. In fact the first solution used is that developed for chemical polishing of InSb. It contains  $\text{CH}_3\text{COOH}$ ,  $\text{HNO}_3$ ,  $\text{HF}$ ,  $\text{H}_2\text{O}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ . Many trial and error tests showed that  $\text{HF}$  and  $\text{CH}_3\text{COOH}$  could be discarded. Adjustment of the volume ratios of the remaining components in order to obtain reasonable etching time and high resolution of the patterns led to the following optimised solution :  $\text{HNO}_3$  /  $\text{K}_2\text{Cr}_2\text{O}_7$  /  $\text{H}_2\text{O}$  in volume ratio 1 / 4/ 45.

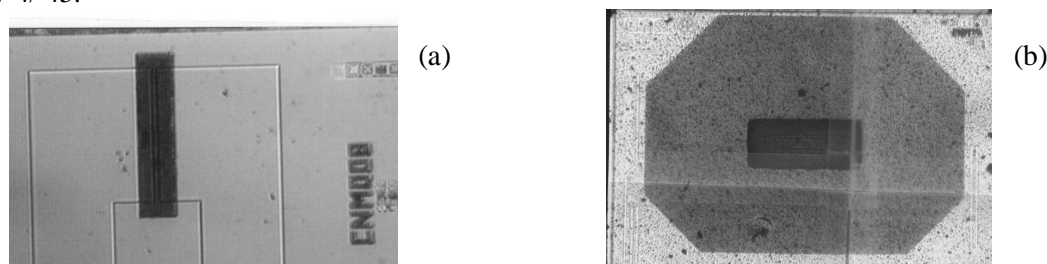


Fig. 5. Preparation of modified ISFET by (a) chemical etching and (b) lift off process.

While the chemical etching gave excellent resolution of the pattern on the gate as shown in Fig. 5 (a) it appeared impossible to remove the chalcogenide film from the Al current collector of the ISFET. Obviously the Cu-Ge-Sb-Se films had reacted with the Al current collectors and the resulting Al/Cu alloy could not be removed by etching. An additional step had then to be added to the original design of the ISFET structure. It consisted in protecting the Al current collector by an epoxy layer previous to the deposition of the Cu chalcogenide film.

The lift off process was then considered since in that case the Si wafer and thus the Al current collectors were already protected by the photoresist previous to the deposition of chalcogenide film. The hexagonal patterns observed on Fig. 5 (b) correspond to the chalcogenide glass over the gate of the ISFET (dark rectangular). The resolution of the pattern is very good. After deposition of the chalcogenide films the best resolution of the patterns was obtained by immersing the sample in an ultrasonic bath containing acetone for 30 seconds.

Even though chemical etching can be used it appeared that the lift off process was preferable since 1) it helps in reducing the number of steps in the photolithography procedure and 2) it can be used as such for the development of other modified ISFET using other types of chalcogenide films.

#### (ii)Electrical characterisation of the modified ISFET

The electrical characteristics of the modified ISFETs prepared by lift off were checked before to perform the electrochemical characterisation. As a matter of fact it was not possible to discard at once eventual damage which could occur during the deposition of the chalcogenide films due to some polarisation effect for example.

A typical  $I_{\text{gs}}\text{-}V_{\text{gs}}$  curve for a  $(\text{Sb}_{11}\text{Ge}_{29}\text{Se}_{60})_{50}\text{-Cu}_{50}$  modified ISFET prepared by lift off when  $V_{\text{ds}} = 500$  mV is shown in figure 6. The maximum remaining current  $I_{\text{gs}}$  is 0.65 nA which is negligible and will not affect the ISFET behaviour. The characteristics  $I_{\text{ds}}\text{-}V_{\text{gs}}$  for several modified ISFETs measured with  $V_{\text{gs}} = 500$  mV are given in Fig. 7. Threshold voltages (obtained by extrapolation of the linear part of the curves) are largely smaller than the upper acceptable limit of  $\pm 3$  V. All ISFETs are sensitive to changes in gate voltage and therefore should be sensitive to any change in the  $\text{Cu}^{2+}$  ion concentration of the solution in contact with the gate.

#### (iii) Electrochemical characterisation of the modified ISFET

The electrochemical characterisation of several ISFET prepared by lift off was carried out. A typical calibration curve obtained after conditioning the sensor in a  $10^{-3}$  M  $\text{Cu}(\text{NO}_3)_2$  is reported in figure 8. A near-Nernstian response with a slope of 28 mV per pCu was obtained. The limit of detection was close to  $10^{-6}$  M. The response time was about 5 seconds. These characteristics are very

similar to those obtained with the ISE prepared with the same membrane and somewhat comparable to the two other modified ISFETs for the detection of copper ion in solution described to date and based upon a Cu-As<sub>2</sub>Se<sub>3</sub> layer on one hand [9] and a calix[11]arene grafted gate on the other [10]. The main drawback of the present ISFETs is a very short lifetime, 20 to 40 hours in the average. The ISFETs fail by detachment of the membrane from the gate. It seemed to be due to constraints induced in the film during the drying and hardening of the encapsulation layer. Such a technological problem is currently being considered and should be settled down soon.

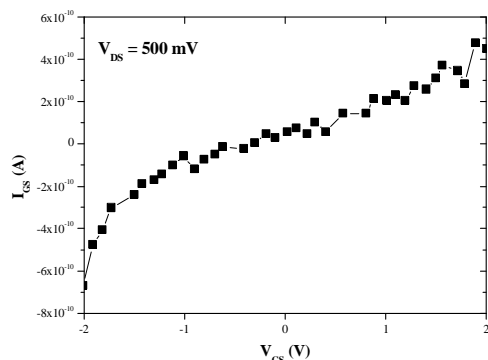


Fig. 6.  $I_{gs}$  –  $V_{gs}$  curve for a  $(Sb_{11}Ge_{29}Se_{60})_{50}-Cu_{50}$  modified ISFET.

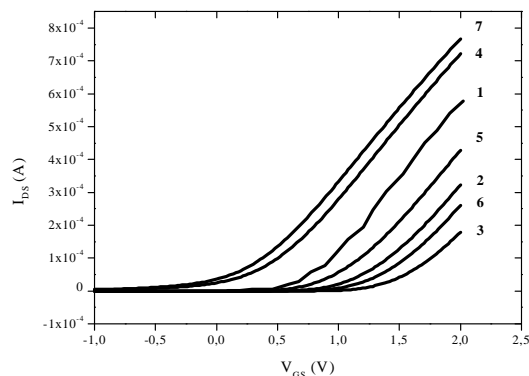


Fig. 7. characteristics  $I_{ds}$  –  $V_{gs}$  for several modified ISFET from the same wafer.

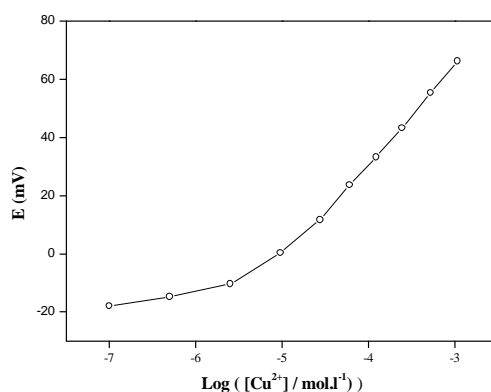


Fig. 8. Typical calibration curve of the ISFET in  $Cu(NO_3)_2$  solution.

### 3.4. Fabrication of a prototype for continuous on line detection of sulphide

The main interest for developing new ISE lies in original properties and experimental advantages that existing systems would not have. To date commercial electrodes for the detection of sulphide in solution work only at basic pH. The sensors based upon the  $Cu_{10}(As_{0.4}S_{0.6})_{90}$  can work at neutral and slightly acidic media which is the case of most natural media. Therefore these sensors could be considered for continuous in situ control of sulphide in natural solution e. g. in thermal water. To test the validity of the concept a programmable module was developed in collaboration with the company TMI-Orion and tested for several months in two thermal waters, i. e. where the sulphide concentration lies in the range 90 – 100  $mg.l^{-1}$  for a temperature of about 17°C and where the sulphide concentration lies in the range 1 – 3  $mg.l^{-1}$  for a temperature of about 40°C.

Fig. 9 depicts the profiles of electrode potential and temperature recorded for a period of 5 days in thermal water containing significant amounts of sulphate ( $1g.l^{-1}$ ), chloride ( $9.4 mg.l^{-1}$ ) and fluoride ions ( $1.3 mg.l^{-1}$ ). The fluctuations in potential, i. e. in sulphide concentration, are closely related to the pumping cycles. As a matter of fact the sensor potential increases (i.e. the sulphide concentration decreases) when the pumping system is turned off which corresponds to out gassing of  $H_2S$ . Note that it corresponds also to nights which is in agreement with the lower temperature. This results indicated the good sensitivity of the sensor to sulphide. The sensor was tested continuously during more than 3 months. It remained sensitive for such a long period of time in this medium and showed high long term stability.

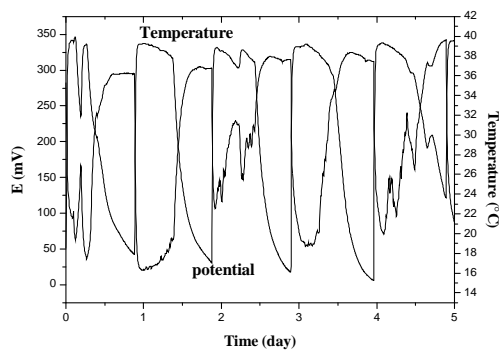


Fig. 9. Profiles of electrode potential and Temperature in thermal water.

## 5. Conclusion

Two chalcogenide materials were studied for their ion sensing properties. One is a glass ceramic of composition  $\text{Cu}_{10}(\text{As}_{0.4}\text{S}_{0.6})_{90}$ , the second is an amorphous thin film obtained by RF sputtering of a composite target  $\text{Cu}/\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$  glass.

Even though they are very different materials both proved to be sensitive to  $\text{Cu}^{2+}$  ion in solution.

The  $\text{Cu}_{10}(\text{As}_{0.4}\text{S}_{0.6})_{90}$  glass ceramic was also shown to be sensitive to sulphide in solution. The ability of such a sensor to work in neutral and slightly acidic medium led us to develop an in situ on line monitoring system for sulphide in thermal water.

On the other hand the sensitivity of the amorphous  $(\text{Sb}_{11}\text{Ge}_{29}\text{Se}_{60})_{50}\text{-Cu}_{50}$  thin film to copper ion in solution led us to use them as the sensitive membrane of modified ISFET. The good electrical and electrochemical characteristics of the ISFET obtained in this work show the potentiality of these films even though technological problems need still to be solved before having devices with satisfying lifetime.

In conclusion we have shown in this work the ability of chemical sensors based upon chalcogenide membranes to bring interesting solutions for the current needs for 1) devices which could be used continuously on line and 2) which could be miniaturised.

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