MONITORING OF THE pH USING ISFET SENSORS IN ELECTROPLATING PROCESSES

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ABSTRACT

It is well known that electroplating with metals has achieved quite a significant importance and has become a lucrative area. The present paper looks at the electroplating processes as a part of the metallurgical industry that are carried out with diverse aims. The quality and characteristics of the metal deposit depend on the electrochemical conditions imposed, such as pH. During an industrial electroplating process, when an undesirable change is detected first in the metal coating attained, is a common occurrence that a complete change of the plating bath is carried out. Due to this, the application of analytical systems to enable in situ precise monitoring of any compositional changes of the bath during the electroplating process, is an unquestionable need to be carefully satisfied. The design of such systems should allow close control of the concentrations of specific components during the process, constituting thus a desirable aim entailing both, financial and time savings. In the present work, the construction of an analytical system based on the coupling of a continuous sampling system with pH ISFET sensors is described. Comparative studies between a glass electrode and the proposed analytical system in copper, silver and nickel electroplating baths are carried out.

RESUMEN

Es bien conocido que el electrodepósito de metales ha adquirido una importancia significante como actividad industrial y que representa un área especialmente lucrativa. La calidad y características del depósito metálico dependen de las condiciones electroquímicas impuestas especialmente del pH. Durante electrodepósitos industriales, cuando se detectan los primeros cambios indeseables en el depóstido metálico, es muy común detener el proceso para la completa sustitución del baño de electrodepósito. Lo anterior hace incuestionable la importancia de la aplicación de sistemas de análisis en el monitoreo in situ de cambios en los componentes del baño durante el proceso de electrodepósito. Estos sistemas permitirían el control y ajuste de las concentraciones de los componentes específicos durante el proceso lo que se traduce en ahorros tanto económico como de tiempo. En el presente trabajo se describe la construcción de un sistema de análisis basado en el acoplamiento de un sistema de muestreo continuo con sensores al pH tipo ISFET. Se realizan estudios comparativos entre un electrodo de vidrio y el sistema de análisis propuesto en el monitoreo de baños de depósito de cobre, plata y niquel.

KEYWORDS: ISFET, Electroplating, Sensor.

1. INTRODUCTION

Within the numerous operations and processes of the metallurgical industry, one which has become widely known for its varied applications is metal electroplating. This process is used with very diverse aims, for example: protection against the many forms of corrosion, including its synergistic associations with mechanical phenomena, metal processing (electrowinning and electrorefining), alloy synthesis, thin layer-tayloring for the electronic industry, decoration, etc [1]. It is well known that during these processes the quality of the resulting deposits depends on specific concentration values of the chemical components in the electrolytic bath, where proton ion (H+) is the most important one since its variation can change the properties of the rest of the components [2]. Due to the lack of reliable, technologically enabling analytical systems (given that many sensing systems may become destroyed, at variable, but mostly high rates in such aggressive solutions), there is a need to replace frequently the electrolytic bath when the metal deposits loose quality. A suitable and robust system for in situ monitoring of the bath components should allow close control of the composition during the process without needing to replace the bath periodically. As it can be expected, this certainly leads to considerable time and chemicals savings. In this respect, it is of great interest to develop suitable analytical systems to quantify different species in the bath, simultaneously fulfilling an important set of requirements: sensitivity, reproducibility, versatility and low price, as these are all very frequently sought in the metallurgical industry. An alternative to the conventional glass sensors for pH are the Ion Selective Field Effect Transistors (ISFET) with a silicon nitride membrane as recognition material developed by Bergveld [3&4]. An ISFET is an all-solid state sensor, hybrid of transistor technology and chemical selective membranes technology, so it has characteristics that in other classic sensors are almost impossible to achieve like micrometric miniaturization without stabilization loose [5&6]. Due to this, a lot of research has been developed to construct different kinds of ISFET to determine other ions in water solutions (commonly known as ChemFET) [7-10]. If a chemical sensor and a continuous sampling system are coupled, a complete analysis system can be constructed for in situ monitoring of chemical species [11-14]. In this work, a novel analytical system based on a selective ISFET and a continuous sampling system was designed for in situ monitoring of pH changes in copper, silver and nickel electroplating baths commonly used in electroplating techniques.

2. MATERIALS

Chemicals and electroplating baths

All reagents used were analytical graded. When pH measurements are concerned, these are referred to using –log10 of the proton ions activity as recorded by the sensors.

- *Silver bath* [15]. A 1M chloride solution, with 1.5 M ammonia and 0,01M silver nitrate was prepared with distilled water; the initial pH is adjusted in the range 10-11 with concentrated sodium hydroxide.
- *Copper bath* [2]. A solution containing 31g copper sulphate in sulfuric acid with 0.0125g thiourea and 0.0013g of dextrin were dissolved in 500 milliliters distilled water.
- *Nickel bath* [2]. It was prepared with 9g hexahidrated nickel sulphate, 1.125g boric acid and 1.125g ammonium chloride, all components dissolved in 150 milliliters distilled water. Initial pH was adjusted between 5 and 6 with sodium hydroxide.

Instrumentation

In order to carry out the electroplating, stainless steel was used as working electrode and a titanium/ruthenium oxide mesh as auxiliary-electrode. To impose the polarization during the plating process, a Phillips PE1516 DC source was used. ISFET devices were constructed in the Centro Nacional de Microelectrónica (CNM-CSIC), Barcelona. The response mechanism of the ISFET is based on the Metal-Oxide Semiconductor Field Effect Transistor (MOSFET) technology, Figure 1 shows a scheme of its design.

When the metal gate is positively charged with respect to the source, due to the application of a potential known as gate potential (Vg), the positive sites in the p-type semiconducting lattice are repelled, and by the same token, the electrons are attracted toward the surface of the substrate, underneath the silicon dioxide layer which acts as an

insulator. When Vg is increased, a conducting channel consequently arises at the surface of the substrate; the electron density within this channel is directly proportional to Vg applied. If a potential Vd is applied between both n silicon blocks, an electric current will pass through the conducting channel formed; the block which originated this current is called source, while the block where the current exits is called drain. The current thus receives the name of drain current (Id). As Vg is directly proportional to the electron density in the channel, so it happens that Vg also controls the magnitude of the drain current.. This way the transistor not only controls the flow of current in one direction, but can also interrupt its flow (switching). An ISFET has the same working principle and the same configuration as a MOSFET transistor (see Figure 1), with the only difference that the metal gate has been replaced by an H+ ions selective membrane, which is in contact with the electrolytic solution and with a reference electrode. As mentioned before, an ISFET having a Si3N4 membrane selective to H+ ions was used for the present work. When the activity of the H+ ions in solution changes, then the surface charge distribution at the interface between the Si3N4 and the solution also changes: consequently, the Vg will necessarily change along with the Id in the sensor. The value of Id may be kept constant in order to compensate for the changes in Vg; this compensation potential is directly proportional to the concentration of H+ ions, with the sensor displaying nernstian behaviour and a sensitivity of 59.14 mV/ pH decade at 25 °C.

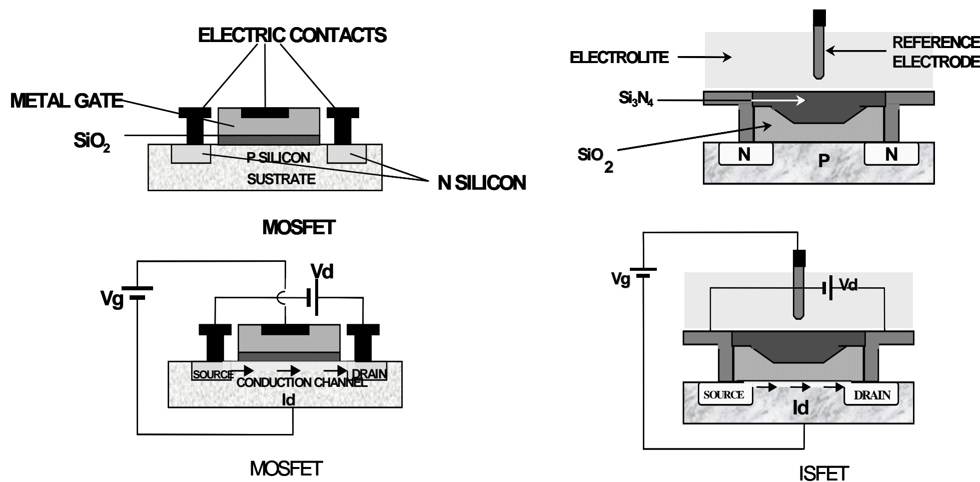

Figure 1. Design and electric operation of a MOSFET transistor and of an ISFET sensor

The ISFET response was obtained using a customized amplifier designed for the purpose in the same center. To polarise the ISFET, a Tacussel Electronique calomel saturated electrode was used. In order to construct the sampling system, an Ismatec peristaltic pump and PTFE Omnifit tubes 0,7 mm diameter were used. The system used for monitoring the pH is shown in Figure 2.

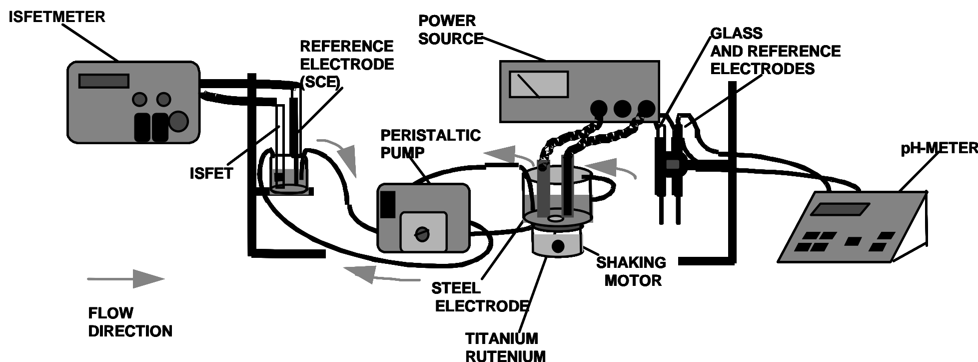

Figure 2. Monitoring system used in the experiments.(The arrows show the flow direction of the sample)

3. METHOD

The pH changes in the nickel, silver and copper electroplating baths (described below) were monitored. The glass electrode and the ISFET were calibrated using standard buffer solutions. Once the electroplating process starts, the sample acquisition is carried out using the peristaltic pump. Data is periodically collected, however, the electroplating process is suspended during the data acquisition to avoid polarization of the chemical sensors, though the sample circulated approximately 10 seconds more to ensure that the sample and bath characteristics remained invariant. Once the pH data was collected, the electroplating process was restarted.

4. RESULTS AND DISCUSSION.

Silver electroplating bath.

Silver plating was carried out passing a 3 mA current between the working and the auxiliary electrode. Before plating starts, an ISFET drift of 3mV constant was recorded every 5 minutes. The comparative results between the glass electrode and the ISFET (considering the drift) are shown in figure 3.

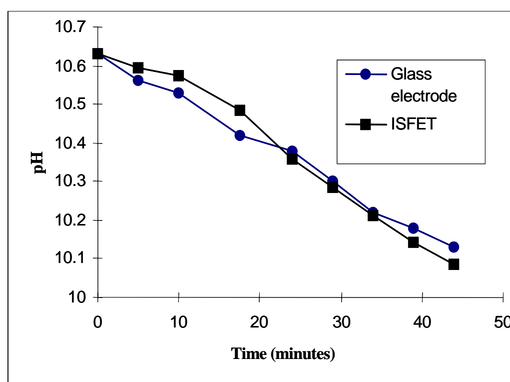

Figure 3. Silver plating with an applied current of 3 mA

It can be observed that the pH slowly decreases during the process. However, it is relevant to underline that even minimum variations of the pH (or the concentration of other chemicals) can produce changes in the predominant species in the baths, this consequently alters the quality of the metal deposits. Taking the glass electrode response as reference, the ISFET response is considered acceptable. The maximum difference between the recorded values for both sensors is less than 0.1, and the maximum calculated error of about 5.3%. These results show that it is possible to use the proposed monitoring system in electroplating baths with the conditions already mentioned.

Copper electroplating bath.

Copper electroplating was carried out applying a current of 240 mA. The resultant drift for the ISFET in bath was about 1 mV every 10 minutes. Considering this drift in the data analysys, the results are shown in figure 4.

It is remarkable the good response of the ISFET in such a strong acid bath, where only some kinds of glass electrodes (as the one used) give a reliable response. Similarly to the case for silver deposition, the pH variation during the copper electroplating process was small, using the response of the glass electrode as the reference for the evaluation of the ISFET response. From the plot in figure 5.3, it can be observed a very good response with a maximum error of 4.6%. These results also demonstrate that the monitoring system has an acceptable performance for this class of electroplating baths.

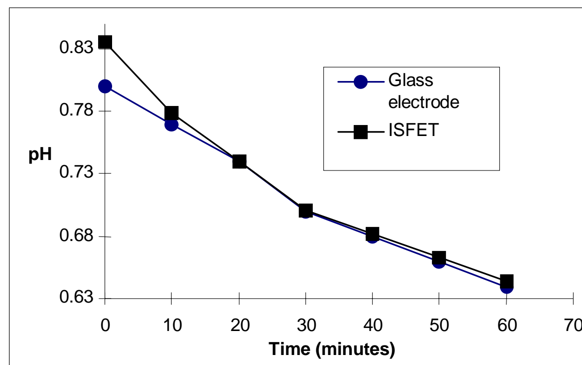

Figure 4. Copper plating with applied currents of 240 mA

Nickel electroplating bath

For the first experiment with this nickel bath, the deposition was carried out applying a current of 120 mA. However, before the experiment could be successfully performed, the measured drift reached 1 mV per hour, therefore we decided not to consider it for the analysis of the data. The results for the experiment are shown in figure 5.

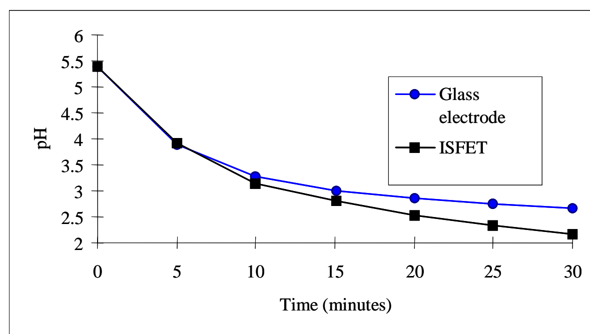

Figure 5. Nickel plating with an applied current of 120 mA

The observed ISFET behavior is considered unusual. During the experiment it began to develop a negative drift potential that increased with time. Usually, a negative drift indicates flights in the sensor device, which makes replacement necessary. After, the sensor was evaluated by means of acid-base tritations, showing a good performance during the evaluation. Possible interferences of some of the components of the nickel bath are likely to be responsible for the modification to the silicon nitride membrane of the ISFET. It has been reported that the ISFET response and drift depends not only of the determinant ion, but also of other ions in solution [16-18]; in this work it becomes evident that the drift of the ISFET sensor is not the same for each electroplating bath. Although more investigation has to be done, it seems that the drift variation depends on the progressive loose of the Ni2+ ion in solution, indicating a strong interaction of this ion with the silicon nitride membrane of the ISFET.

5. CONCLUSIONS

Monitoring the pH in situ was carried out in various electroplating baths using a continuous analytical system with pH-sensitive ISFET sensors. The response was compared with that for a glass membrane electrode, and the results were indeed similar as demonstrated by the behavior for copper and silver baths. We may conclude that the ISFET sensor represents a good alternative as detection system for the species involved. In the case of the nickel baths studied, an unusual behavior with a negative drift was observed, which suggests interference of some of the components of the bath affecting the measurement with the ISFET sensor. By the results obtained and considering that Ni2+ is been lost during plating, it can be assumed that this ion interacts strongly with the silicon nitride membrane of the sensor.

6. ACKNOWLEDGMENTS

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