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Creation of functional layers for pH Sensors by galvanic deposition of antimony and bismuth

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Abstract: Current requirements for measuring applications in biotechnology and biomedical applications require the use of planar sensors or sensor arrays. Previously used techniques for preparing pH-sensitive surfaces have various disadvantages. An interesting alternative is the electroplating of such surfaces. In this work, opportunities for the galvanic deposition of pH-sensitive antimony- and bismuth-layers are presented. The properties of the deposited films in terms of suitability as a pH-sensitive surface are compared. The results indicate that both antimony and bismuth with pH-sensitive layers can be electrodeposited. The separation results can be achieved by varying the parameters and the electrolyte composition influence far reaching. The issue of long-term stability of the deposited layers requires further investigation.

Keywords: Galvanic Deposition, Antimony, Bismuth, Sensor, Miniaturization, pH-Value

1. Introduction

An ever increasing miniaturization in the field of sensor technology requires new methods for the production of sensors. Especially in biotechnology and biomedical sector, therefore, an increased interest for planar sensors is available [1]. Further studies showed that it was in principle possible to use planar sensors for this kind of applications [2]. The measurement of the pH value is carried out with electrodes which are always performed in a cylindrical shape. Due to their limits in the miniaturization they are not suitable for planar sensor systems. Therefore metal/metal oxide electrodes like antimony/antimonyoxide and bismuth/bismuthoxide are used for planar sensors. Both metals have been examined in previous studies [3] [4] for use as a pH electrode but only for some special applications.

The preparation of planar pH sensors can be done with different techniques. From the viewpoint of resource conservation and the elimination of adverse aspects of thick-film process more alternatives are being sought. Thus, for example pH-sensitive materials can be realized by sputtering applications on base substrates. This has been successfully carried out with antimony [5]. Another way to produce pH-sensitive layers is the galvanic deposition of antimony or bismuth. These layers should be uniform, pH-sensitive and it should be possible to realize pure antimony- and bismuth-layers. With this application it is possible to eliminate mistakes by production-related impurities, such as the screen printing process. Long time ago some studies have been performed the galvanic deposition of antimony and bismuth [6] [7]. Due to lack of practical applications, these studies were not continued. They showed in principle that antimony and bismuth can be electrodeposited. Some newer investigations are concerned with alloy layers of bismuth [8]. Currently no other investigations with pure layers of antimony or bismuth are performed.

The aim was the galvanic deposition of antimony and bismuth-layers, which can be used as a functional layer of a pH sensor with a good resistant to aggressive media. These layers should be work stable for the duration of use of biotechnology and biomedical research. In this field common investigations have been outlined within a running period from up to 100 days. Previously produced planar sensors do not reach this value and this should also be improved by the galvanic deposition of the functional layers. The evaluation of antimony- and bismuth-layers was performed according to the following criteria: structure, layer composition and layer thickness. Finally, the sensor properties were determined and compared with each other.

2. Experimental

In preliminary experiments, the deposition of various approaches electrolyte was initially on brass substrates. These studies were only a preliminary assessment of whether it is generally possible to deposit adherent layers of antimony- or bismuth-electrolytes. For the following studies basic sensor-like structures (Figure 1a and 1b) were used. These consisted of a ceramic base body, which was applied to the screen printing method a structure made of gold or graphite. Subsequently, follows a cover with a polymer paste. This structure corresponds to that of a practical sensor system (Figure 1b). The surface to be coated varied between 0.1 cm² and 1.0 cm².

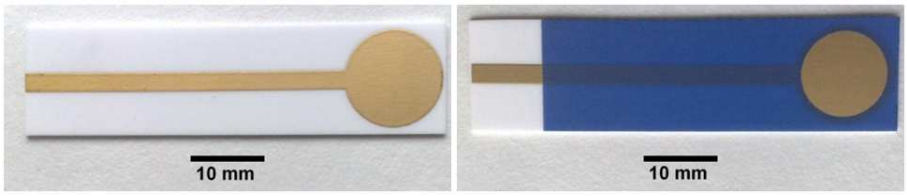

***Figure** 1a) without cover Figure 1b) with cover*

The experiments were carried out in beakers with volumes 200 and 400 ml. The range of the current density varied from 0.05 to 2.5 A/dm². The potentiostat PS 2000 and PS 6 from the company Sensortechnik Meinsberg was used for power supply. A magnetic stirrer was used for the agitation and temperature control.

***Table 1.** Used Metal compounds*

Antimony (Sb)	Bismuth (Bi)
Antimony(III)-chloride	Bismuth(III)-oxide
Antimony(III)-oxide	Bismuth(III)-nitrate,
Kaliumantimonyltartrate	Bismuthmethanesulfonate

In table one metal salts of antimony or bismuth compounds are shown which were considered in previews for the tests to be suitable. All electroplating experiments were carried out in aqueous solutions. With the results of preliminary tests several basic electrolytes of antimony and bismuth could be defined. With the in table one mentioned antimony compounds tow basic electrolytes were evaluated. The first consisted of a solution with potassium antimonytartrate and the second included antimony (III) chloride, hydrochloric acid and tartaric acid. Antimony (III) oxide electrolytes were unsuitable for the electroplating of antimony-layers.

Two basic bismuth electrolytes based on an aqueous solution of bismuth (III) oxide. The first electrolyte according to Harbaugh [7] with bismuth (III) oxide composed with perchloric acid. The second electrolyte based on various inorganic and organic acids with bismuth (III) oxide or bismuth (III) nitrate. Electrolytes which contained bismuth methanesulfonate were unstable and unsuitable because they did not provide useful layers.

To determined pH sensitivity of the galvanic platted antimony- and bismuth-layers the resulting potential of the measurements in pH buffer solutions in the pH range between 4 and 9 was measured. Using these measured values the value and continuity of the Nernst slope was determined. The resulting potential of the system of coated substrate and silver/silver chloride reference electrode in a buffer solution of pH = 6.86 in according to DIN 19266 was determined in a long time till failure of the sensor measurement. Statements could be made about the stability of the measurement signal and the lifetime of the deposited layer. Furthermore, the structure of the deposited layer and the composition was investigated. For this purpose, the investigated layers were analyzed with scanning electron microscopy (SEM) images and analysis of the layer composition by energy dispersive X-ray spectroscopy (EDX). The layer thickness was primarily determined by determining current yield. The deposited mass in relation to theoretical mass deposition showed the current yield.

3. Results and discussion Antimony

With an electrolyte based on potassium antimony tartrate without any additives were deposited non adherent antimony layers. The addition of various acids, complexing agents and additives (Sb-A-electrolyte) adherent, dull and gray antimony layers were obtained. By SEM investigations distinct layer errors were identified (Figure 2). Layer thicknesses greater than 2 microns were non adherent. These layers are resolved from the substrate during the electroplating process. Only minor impurities were found in the antimony layers by analyzing of the layers by EDX. The current efficiency of these electrolytes was 85 - 90%. The stability of the electrolytes was inadequate because after a few days precipitations were observed.

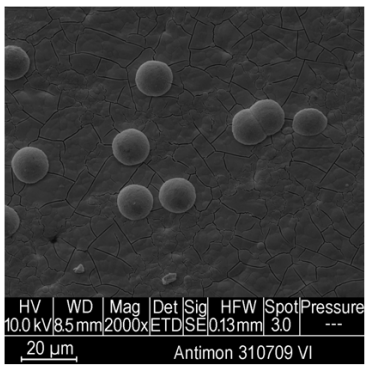

***Figure 2.** Deposited layer of Sb-A-electrolytes*

The evaluation was carried out according to the description above if the deposited layer is a functional layer of a pH sensor. A good Nernst behavior of the deposited layer was detected. But the long-term stability with a working life of 20 to 30 hours was nonsatisfying. After this time a potential jump was observed and the entire antimony layer was replaced.

A further galvanic deposition of antimony was carried out with an electrolyte which is based on an aqueous solution of antimony (III) chloride, hydrochloric acid and tartaric acid (Sb-B-electrolyte). The addition of various complexing agents is necessary to reach adherent and gray layers of antimiony. The achievable layer thickness with more than 30 µm exceeded significantly from the Sb-A electrolytes. By SEM investigations closed layers were found and the structure looked like undirected rod-like structures (Figure 3). This structure is also reflected in findings of naturally occurring Stibinit in Hungary and Bolivia. The EDX analysis of the deposited layer showed some contaminants on the layer which were ingredients of electrolyte.

Figure 3. *Deposited layer of Sb-B-electrolytes*

The current yield of the Sb-A-electrolyte was nearly 100%. Furthermore, the electrolyte had a good long time stability. The formation of degradation products could not be observed at any time. The Nernst behavior of the coated antimony-layer showed also good results. Gradients in the range of -50 to -60 mV / pH could be determined (Figure 4) and the long time behavior with more than 100 h was much better than the deposited antimony layer of the Sb-A-electrolyte. Generally, the gold substrates were more suitable for the electro platted antimony layer.

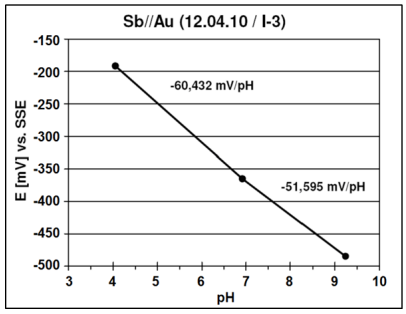

Figure 4. *pH sensitivity of an electrodeposited Sb-layer (Sb-B-electrolyte)*

Table 2 shows an overview of the depositions parameters and a complete comparison of the antimony electrolytes A and B.

Table 2. *Summary of the depositions parameters and the electrolyte Sb-A and Sb-B*

	Sb-A-electrolyt	**Sb-B-electrolyt**
Sb-compound	Potassium Antimonytartrate	Antimony(III)-chloride, Hydrochloric acid,Tartaric acid
Concentration	2 - 4 g/l Sb	10 - 15 g/l Sb
Temperature	23 - 28°C	65 - 70°C
Current density	0,05 - 1 A/dm²	0,1 - 0,8 A/dm²
Current yield	85 - 90 %	~ 100 %
Thickness	max. 2 µm	30 µm (even thicker)
Structure	compact	Rod-like, like Stibinit
Surface errors	Cracks, bud	non
Impurities in the layer	non	Chloride
long-term stability	stable signal till 20-30 h	stable signal up to 100 h
Nernst behavior (pH-range)	Slope: 54 - 58 mV/pH pH-range: 1,68 - 9,18	Slope: 54 - 58 mV/pH pH-range: 1,68 - 9,18

4. Results Bismuth

For the electrodeposition of bismuth an electrolyte was used first, as by Harbaugh [7] has been described (Bi-A-electrolyte). This is the mixture of an aqueous solution of bismuth (III) oxide with perchloric acid. The deposited layers were gray, dull with a good adhesion. The current density, shown in Table 3, varies in a large area without changing significantly the coating properties. In the experiments layer thickness up to 30 microns could be deposited. Thicker layers are possible but not necessary for the pH-sensitive functional coating. One result of investigations by SEM is shown in Figure 5. It is clearly a coarse crystalline, closed layer. By EDX studies small scale impurities (chloride from the electrolyte) were analyzed in the layer. The stability of the electrolyte was also very good.

Degradation products were not formed during the period of use. The current efficiency of this electrolyte could be determined with close to 100%.

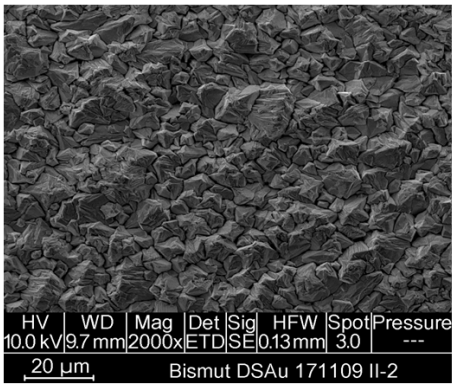

Figure 5. *Deposited layer of Bi-A-electrolyte*

A further possibility for the galvanic deposition of bismuth is an electrolyte which is based on bismuth (III) oxide with inorganic and organic acids is (Bi-B-electrolyte). In combination with complexing agents and additives gloss, dull gray with ~~a~~ good adherent bismuth layers were deposited. Even in these studies thicknesses up to 30 microns were easily produced. The layer structure (Figure 6) was studied by SEM investigation and showed fine crystalline coating in comparison to the layers which were deposited from the electrolyte with perchloric acid. By EDX studies small scale impurities were analyzed in the layer. The stability of the electrolyte was also very good. Degradation products were not formed during the period of use. The current efficiency of this electrolyte could be determined between 85 to 90 %.

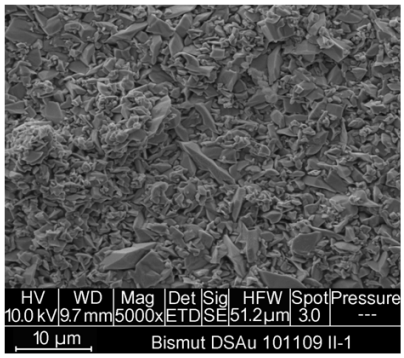

Figure 6. *Deposited layer of Bi-B-electrolyte*

Between the deposited bismuth layers from different electrolytes no differences were found for the Nernst behavior. The slopes were examined in the pH range (4-9) -48 to -58 mV / pH (Figure 7). In studies the long-term stability of the electrodeposited Bi-layer was 100 days. After that time no layer failure may be determined from the Bi-A-electrolyte deposited layers. The layers which have been obtained by electrode position from the Bi-B-electrolyte resulted in a slightly shorter life span.

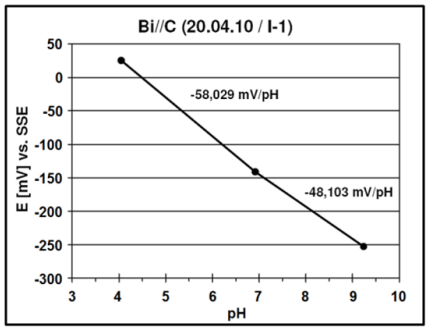

Figure 7. *pH sensitivity of an electrodeposited Bi-layer*

In contrast to the prepared antimony layers graphite substrates were better suitable for the galvanic deposition of bismuth. By appropriate preparation of the graphite substrates the coatings with bismuth were very even. A summary of the used electrolytes is shown in Table 3.

Table 3. *Summary of separation results with bismuth*

	Bi-A-electrolyt	**Bi-B-electrolyt**
Bi-compound	Bismuth(III)-oxide, Perchloric acid	Bismuth(III)-oxide with inorg. and org. acids
Concentration	40 g/l Bismuth(III)-oxide	10 - 14 g/l Bi
Temperature	23 - 28°C	23 - 28°C
Current density	0,5 - 2,5 A/dm²	0,2 - 0,7 A/dm²
Current yield	~ 100 %	85 - 90 %
Thickness	30 µm (even thicker)	30 µm (even thicker)
Structure	coarsely crystalline	finely crystalline
Surface errors	non	non
Impurities in the layer	Chloride	Chloride
long-term stability	stable signal up to 100 h	stable signal up to 100 h
Nernst behavior (pH-range)	Slope: 54 - 58 mV/pH pH-range: 4,0 - 9,18	Slope: 54 - 58 mV/pH pH-range: 4,0 - 9,18

5. Conclusion

This study showed that pH senitive functional layers of antimony and bismuth can be electrodeposited. The prepared layer structures of antimony and bismuth are sometimes very different. The pH-sensitivity of these layers is good and showed no influence by electrolyte-related impurities in the deposited layers. The achievement of a lifetime of 100 days for the measurement in the biomedical and biotechnological applications was an imported goal achieved. Also, it was found that the long-term stability with electrodeposited Sb layers could not be realized. Further studies with alloys of Sb and Bi are performed. Finally, the findings for the electrodeposition of pH-sensitive functional antimony- and bismuth-layers will be incorporated for planar sensor array.

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References

[1] Vonau, W.; Herrmann, S.; Berthold, F.; Enseleit, U.; Bieger, E. P.; Mayer, W.: Multiparameter-Messsystem. Patent Germany 10 2007 022 323.6, 13.11.2008

[2] Vonau, W. et al.: Elektrochemische Dickschichtsensoren in der Umwelttechnik. GIT Labor-Fachzeitschrift 44 (2000) S. 127-131

[3] Uhl, A.; Kestranek, W.: Die elektrometrische Titration von Säuren und Basen mit der Antimon-Indikatorelektrode. Monatshefte für Chemie 44 / 1-2 (1923) S. 29-34

[4] Schwabe, K.: Die pH-Indikation an Wismutelektroden. Zeitschrift für Elektrochemie und angewandte physikalische Chemie 53 (1949) S. 125-132

[5] Hanzalova, Jitka (Beroun, CZ): A sensing electrode for pH measurement chiefly in bodily fluids. United States 20100116646; 13.05.2010

[6] Mathers, F. C.; Means, K. S.; Richard, B. F.: Electrodeposition of antimony from fluoride baths containing addition agents. Trans. Am. Electrochem. 31 (1917) S. 293-301

[7] Harbaugh, M.; Mathers, F. C.: The electrodeposition of bismuth from perchloride acid solutions. Trans. Electrochem. Soc. 64 (1933) S. 293-298

[8] Krastev, I.; Valkova, T.; Zielonka, A.: Elektrolytische Abscheidung und Eigenschaften von zyklisch modulierten Silber-Wismut-Legierungsüberzügen. Galvanotechnik 96 (2005) S. 1790-1795