



## Corrosion-resistant metal layers from a CMOS process for bioelectronic applications

M. Birkholz<sup>a,\*</sup>, K.-E. Ehwald<sup>a</sup>, D. Wolansky<sup>a</sup>, I. Costina<sup>a</sup>, C. Baristiran-Kaynak<sup>a</sup>, M. Fröhlich<sup>a</sup>, H. Beyer<sup>b</sup>, A. Kapp<sup>c</sup>, F. Lisdat<sup>c</sup>

<sup>a</sup> IHP, Im Technologiepark 25, 15236 Frankfurt (Oder), Germany

<sup>b</sup> Optical Technologies, Wildau University of Applied Sciences, Bahnhofstrasse, 15745 Wildau, Germany

<sup>c</sup> Biosystems Technology, Wildau University of Applied Sciences, Bahnhofstrasse, 15745 Wildau, Germany

### ARTICLE INFO

Available online 8 October 2009

**Keywords:**  
Bioelectronics  
CMOS  
Corrosion  
Electrodes  
Metal layers  
TiN

### ABSTRACT

The use of the dominant CMOS (complementary metal–oxide–semiconductor) process technology in perspective bioelectronic applications imposes severe restrictions on the materials used with respect to their stability in aqueous solutions with high concentrations of electrolytes. We report the results of a comparative study of Al:Cu, CoSi<sub>2</sub> and TiN metal layers that were prepared within a regular CMOS process and characterized by depth-profiling with X-ray photoelectron spectroscopy (XPS) in order to determine chemical composition and contaminants. The corrosion caused by isotonic NaCl solution was investigated and the most pronounced corrosion resistance was observed for TiN layers showing only negligible conductivity degradation when exposed to high concentration of electrolytes at elevated temperature for a time span of days. In addition, TiN layer electrodes turned out to be stable in an electrochemical cell over a large potential range and a wide pH range. No electrocatalytic activity for the conversion of hexacyanoferrate or catechol has been found. It is concluded that from the different metal layers available in CMOS processing, TiN layers are best suited for biomedical electrode applications.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

The continued scaling of semiconductor technology will soon cause the minimum feature dimensions of semiconductor processing to enter the scale of biological molecules. The dominant CMOS technology is scheduled by the International Technology Roadmap to enable less than 20 nm small structures beyond 2010 [1]. This will allow for the realisation of new hybrid nanosystems [2], for which the immobilisation of biomolecules on semiconductor surfaces can be locally controlled by nanotemplating the latter [3,4]. The major applications of bioelectronics will probably lie in the field of biomolecular sensing and bioanalytics, which dynamically develops due to the quest for more precise and inexpensive assays for medical applications [5,6].

Fundamental problems regarding the information transduction across the semiconductor–bio-interface still have to be resolved for the improvement of biomedical systems and for the development of new bioelectronic devices. In particular, for all kinds of solid electrodes, by which integrated microelectronic devices shall interact with the surrounding medium of aqueous solutions of biological molecules, there exists a high probability for corrosion and other

unintended electrochemical interactions to occur [7]. The most advantageous solution would be offered by electrodes to be prepared from standard CMOS materials that would render the introduction of new materials in the clean room and recipe developments for their contamination-free processing needless. From the materials used in front-end-of-line (FEOL) processes either highly doped silicon or CoSi<sub>2</sub> exhibiting conductivities up to mΩ cm would be qualified for electrode applications [8]. Of particular interest are the multilayer stacks of Al:Cu or TiN used in back-end-of-line (BEOL) processes for the preparation of planar conductors, with TiN serving as a diffusion barrier to avoid the diffusion of Al and Cu into the active areas. The sheet resistances of these metal-layer stacks typically amounts to some 10 mΩ/sq [8,9].

There are different fields of application for CMOS-produced structures in bioelectronics. They can be used as electrochemical transducers where often a current has to pass the layer/solution interface [10,11], but there are also several applications for which electrochemical reactions have to be avoided for example when these structures are used in SAW (surface acoustic wave) devices [12,13] or arrangements where only an electrical field has to be maintained and electrolysis is unwanted [14,15]. Complex load profiles occur in so-called BioMEMS applications, where microelectromechanical systems (MEMS) come in close contact with physiologically or electrochemically active liquids [16]. For instance, in case of a continuously monitoring glucose sensor currently under development and operating by the principle of affinity

\* Corresponding author.

E-mail address: [birkholz@ihp-microelectronics.com](mailto:birkholz@ihp-microelectronics.com) (M. Birkholz).

viscosimetry [17], a metallic cantilever is equally subjected to mechanical, electrical, thermal and electrochemical stresses [18] and highly resistant materials have to be applied to cope with such a complex load combination.

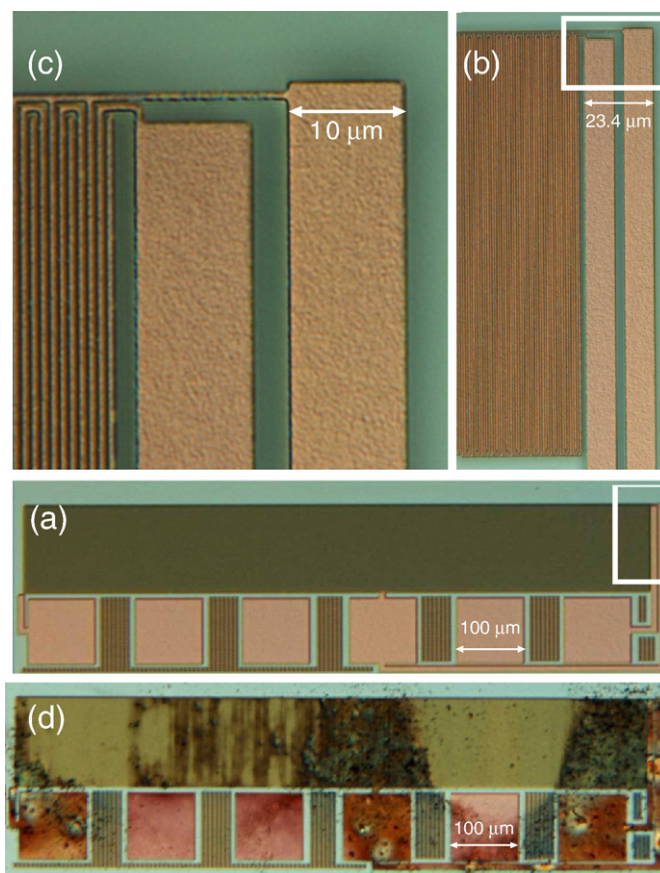
In this work, TiN/Al:Cu/TiN multilayers and single layers of CoSi<sub>2</sub> and TiN have been investigated with respect to their suitability to serve as electrodes for BioMEMS cantilevers and bioelectronic applications. Corrosion studies have already been performed mainly for TiN layers in different variants [19–22]. However, while previous studies focused on hard coating applications, this work addresses the question of corrosion resistance of CMOS-prepared metal layers for bioelectronic applications. It will be shown in the following that TiN layers appear particularly suited to operate as electrodes in aqueous solutions of electrolytes in a wide range of pH values.

## 2. Experimental

The preparation of metal layers was performed at the IHP pilot line on 200 mm CZ-Si wafers of (100) orientation. Metal layers were deposited by standard sputter processes, by which microelectronic circuits are prepared in different CMOS/BiCMOS technologies [23,24]. Firstly, single CoSi<sub>2</sub> layers were investigated that usually act as contact layers to active devices. The layers were prepared by DC magnetron sputtering (Applied Materials Endura) of 10 nm cobalt on Si and two annealing steps. The thin CoSi<sub>2</sub> films obtained typically exhibit a thickness of about 35 nm and a sheet resistance of about 6 Ω/sq. Secondly, multilayer metal stacks of TiN/Al:Cu/TiN were prepared, where – for reasons of brevity – TiN will stand for Ti/TiN in the following, since a few nm Ti layer is usually deposited first in order to improve adhesion to the substrate [25] and to assure a sufficient electrical contact. Such metal-layer stacks usually operate as planar interconnects at different heights in the back-end-of-line architecture and are denoted as metal 1 (M1) through metal 3 (M3) [8,26]. Their thicknesses usually range between 530 and 2000 nm, for which sheet resistances between 80 and 20 mΩ/sq are achieved. Also these layers were deposited by DC magnetron sputtering (Endura) from an Al:Cu and a Ti target, respectively, and which was carried out as a reactive process for TiN by introducing an argon–nitrogen mixture into the deposition chamber. Thirdly, single TiN layers of 50 nm thickness and a sheet resistance of 17 Ω/sq were prepared and investigated.

The prepared layers were characterized by subjecting them to different corrosion tests. For this purpose, 0.9 wt.% NaCl was dissolved in deionised water ( $\rho > 18 \text{ M}\Omega \text{ cm}$ ) and some cm<sup>2</sup> pieces from the cut and coated wafers were immersed in it. The solutions were buffered to a physiological pH value of 7.25 by adding 50 mM Tris-hydroxymethylaminomethane–hydrochloride (Tris–HCl) or Na<sub>2</sub>HPO<sub>4</sub>–KH<sub>2</sub>PO<sub>4</sub> (PBS), respectively. Samples were stored for days in closed vessels containing the buffered saline and inserted in a laboratory dryer at elevated temperatures in order to accelerate possible corrosion effects and to simulate a prolonged period of use. The samples were regularly taken out of the saline and checked for variations of morphology and sheet resistance by four-point probe measurements [9].

In addition to homogeneously coated silicon wafers, also photolithographically structured metal sheets were investigated, which were accomplished as elongated meanders. Fig. 1 shows such a structure including bond pads from a full M3 stack of TiN/Al:Cu/TiN and a total thickness of 630 nm. Also for these samples, possible corrosion effects were elucidated after immersion in aqueous saline via optical microscopy and determination of the sheet resistance. The layer composition was analyzed by depth-profiling a 3 × 3 mm surface area with X-ray photoelectron spectroscopy (XPS). Profiles were acquired with a Physical Electronics PHI 5600 system by monitoring the O1s, C1s, Si2p, N1s, Al2p, Cu2p and Ti2p photoemission signals after 60 s sputtering cycles (Ar<sup>+</sup> ions at 1 keV). Single element sensitivity factors from the spectrometer database (Multipak 8.2) were used to derive their concentrations with a precision on the order of ±5%.



**Fig. 1.** Optical micrographs of metallic meander structures of TiN/Al:Cu/TiN M3 multilayer stack. Shown are different magnifications with (c) and (b) giving the enclosed parts shown in (b) and (a), respectively. The bottom figure (d) displays the same structure as in (a) after five days in saline solution.

Electrochemical experiments were performed with a three electrode arrangement in a home-made cell of 1 ml volume at room temperature. TiN layer chips were used as working electrode, whereas the counter electrode was a Pt wire and the reference electrode was an Ag/AgCl electrode MI-401 (Microelectronics Inc., Bedford, USA). 0.5 M H<sub>2</sub>SO<sub>4</sub> or sodium phosphate buffer (100 mM) were used as electrolyte solutions. Concentrations of hexacyanoferrate(II/III) and catechol were varied between 10 and 50 mM. Cyclic voltammetry was performed with a CHI800 instrument (CH Instruments, Austin, USA) at scan rates of 100 mV/s, which is a standard scan rate for the characterization of redox systems at different electrode surfaces [27,28].

Impedance spectroscopy was carried out with the same electrode arrangement and a CHI660b (CH Instruments, Austin, USA). The ac amplitude was 5 mV and the fixed dc potential 0.2 V vs. Ag/AgCl. The frequency was varied between 0.1 Hz and 100 kHz. Data evaluation was performed according the common equivalent circuit for the electrode–electrolyte interface modeled by a parallel circuit of the double layer capacity and the charge transfer resistance [29].

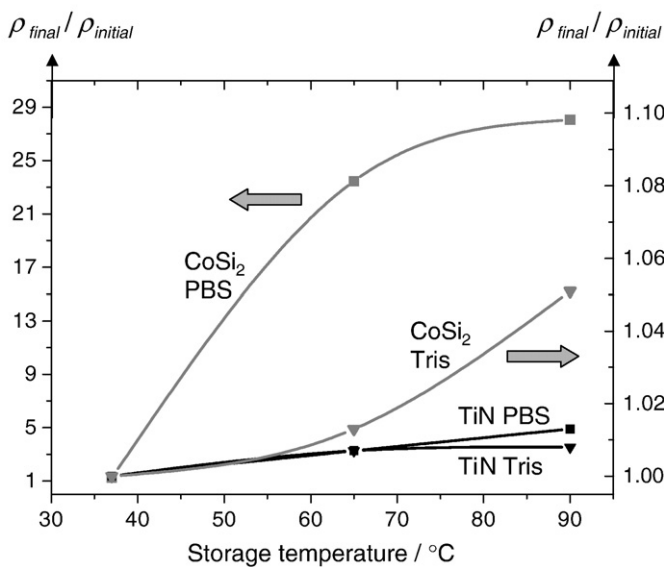
## 3. Results and discussion

Full metal 3 stacks from TiN/Al:Cu/TiN were found to exhibit severe corrosion damage already after a few days of immersion in normal saline solution at room temperature. The accompanying chemical oxidation is mainly related to the Cu-doped Al layer of the M3 stack. Fig. 1(d) displays an optical micrograph of the virginal structure given in Fig. 1(a) after five days in saline. Various μm-sized spots can be recognized on the metal surface, from where electrolytic pitting started and wide areas of the surrounding were contaminated with corrosion products. A fast corrosion of Al layers by oxidation in aqueous solutions

is well known; it appears a remarkable result, however, that the coating by TiN cannot prevent this process. According to the microscopic inspections, the effect may be understood from small holes and irregularities of the TiN layer, through which the isotonic saline solution could interact with the underlying Al:Cu layer. This interpretation is in accordance with previous results for TiN on stainless steels [21]. The occurrence of microscopically small irregularities and pores is generally unavoidable in conventional sputter deposited thin films. Only in sputter regimes working with a high ion bombardment that cause a high densification of the deposited material, sufficiently compact layers can be prepared [30]. Such high ion bombardment conditions are typically avoided in semiconductor processing and full CMOS metal multi-layer stacks can thus be concluded to do not apply for the high corrosion resistance that is required in biomedical electrode applications.

On the other hand, no corrosional damage could be observed by optical microscopy for CoSi<sub>2</sub> and TiN layers after prolonged storage at room temperature in pH = 7.25 buffered saline solutions. In order to simulate the complex BioMEMS load profile, the layers were subjected to an intensified corrosion regime. For this purpose, the samples were immersed in pH-buffered saline solution and stored in enclosed test tubes at 37, 65 and 90 °C for up to ten days. The layers were daily taken out from the solution and their sheet resistance was determined. Fig. 2 displays the ratio of final over initial resistivity  $\rho_{\text{final}}/\rho_{\text{initial}}$  as a function of storage temperature for both layer systems and both pH buffers. It can firstly be recognized from the figure that only negligible variations were to observe for a storage temperature of 37 °C. This result is compatible with microscopic inspection of samples immersed in saline at room temperature, for which no corrosional damage could be detected.

In addition, it can be recognized from Fig. 2 that the resistivity of CoSi<sub>2</sub> layers in PBS buffer suffered from the strongest variations for increasing test temperature (left scale). In fact, the PBS buffer compares more to the conditions in human blood and tissue than Tris buffer. Less variations of the sheet resistance were observed for the other test series of CoSi<sub>2</sub> in Tris and TiN in both buffers (right scale). Again, the silicide layers exhibit the strongest increase with increasing storage temperature. CoSi<sub>2</sub> layers can thus be concluded to appear less suited for electrode applications in physiological solutions or human tissues. On the other hand, thin TiN films were observed to exhibit only small resistivity changes on the order of 1%, when stored in 90 °C hot isotonic saline for days, which appears a remarkable result.

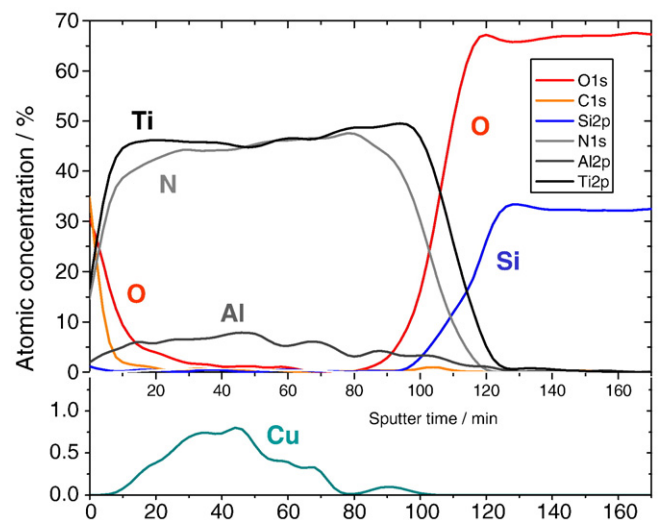


**Fig. 2.** Ratio of final over initial resistivity  $\rho_{\text{final}}/\rho_{\text{initial}}$  for CoSi<sub>2</sub> and TiN layers that were stored for days in isotonic saline solutions and buffered by either Tris or PBS at a pH value of 7.25. The storage was performed in closed test tubes and the  $\rho_{\text{final}}/\rho_{\text{initial}}$  ratios are displayed as function of storage temperature.

XPS depth profiles of the 50 nm TiN layer are displayed in Fig. 3. It can be observed that pronounced nitrogen deficiencies occur at the top and the bottom. This stoichiometry deviation is accompanied by an increased oxygen content in the vicinity of the surface and can thus be understood by a partial oxidation of the top-most parts of the layer. The latter effect may alternatively be understood from the usual surface contamination. Since the oxygen profile, however, extends deeper into the sample than the carbon profile, we assume a titanium-oxynitride phase to occur. Such phases with a thickness on the order of 10 nm are typically formed on TiN surfaces and are an important presupposition for the corrosion resistance of thin TiN films [22]. On the other hand, the N deficiency in the interface region is explained by the initial deposition of a titanium layer as it is usually prepared to ensure a sufficient adhesion of TiN on the SiO<sub>2</sub>/Si substrate [25]. Finally, a significant amount of Al and a small amount of Cu (separate plot at the bottom) could be detected within the TiN layer. These contaminants were introduced during the preparation process of the full metal 3 stack from which the TiN layer was derived by etching off the top TiN and the middle Al:Cu layer. This procedure has been applied to assure a compatibility with the standard metallization of our CMOS process. Obviously, the enhanced process temperature for the upper layer depositions led to a partial interdiffusion of Al and Cu into the bottom TiN.

In order to investigate the interface TiN/electrolyte solution in more detail, electrochemical experiments were performed by applying the TiN layer as working electrode in an electrochemical cell. Cyclic voltammetry in the potential range from −0.8 to +0.8 V vs. Ag/AgCl in phosphate buffer revealed no electrochemical process at the TiN surface as can be deduced from the missing of any significant signal in the upward and downward scan displayed in Fig. 4(a). Also in 0.5 M sulfuric acid voltammetry shows a high blocking activity for electrochemical reactions. It has to be emphasized that the absence of any electrocatalytic activity remained even after several days in electrolyte contact.

Furthermore the behaviour of electroactive species such as hexacyanoferrate II/III and catechol was evaluated. Fig. 4(b) shows as an example the cyclic voltammogram in a solution of the inorganic iron salt for the TiN layer electrode in comparison to a gold electrode. It is obvious that there is no voltammetric signal from the conversion of hexacyanoferrate in a rather wide potential window. The same is valid for the organic redox species catechol. Impedance spectroscopy was applied as a more sensitive method to study the solution/TiN interface. The impedance spectra reveal that the overall complex resistance of the cell is dominated by the impedance of this interface and can be described by a parallel circuit of the double layer capacity and the charge



**Fig. 3.** Depth-resolved XPS measurement of 55 nm thin Ti/TiN layer on SiO<sub>2</sub>. Results for Cu are given in the bottom plot with a different ordinate scale.



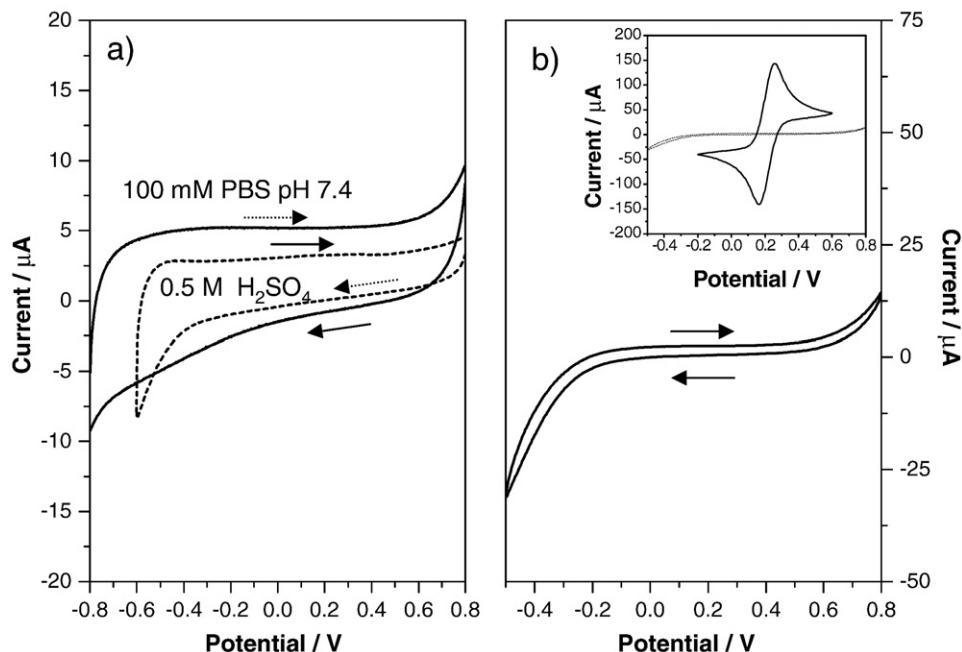


Fig. 4. Cyclic voltammograms of the TiN layer electrode in (a) 100 mM sodium phosphate buffer pH 7.4 and 0.5 M  $\text{H}_2\text{SO}_4$  as well as in (b) 5 mM  $\text{K}_4[\text{Fe}(\text{CN})_6]/5$  mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (phosphate buffer 100 mM pH 7.4). Inset shows for comparison the voltammogram of an Au electrode of the same area in the same solution.

transfer resistance. The measurements show that there is a rather high resistance for charge transfer at neutral pH; but it can also be seen that this resistance is decreasing in basic solution (obvious from the decreasing diameter of the semicircle in Fig. 5). However, even under these conditions the resistance is much higher than at other metal electrodes. For example at a gold electrode the charge transfer resistance is  $< 100 \Omega$  under the same measuring conditions. In conclusion it can be stated that TiN provides a very stable electrode material when polarised in electrolyte contact. It exhibited no electrocatalytic properties at acid and neutral pH; in alkaline solutions slow redox reactions can occur. These results are in accordance with previous investigations, where a wide stability range was identified to occur for TiN layers in the  $U/\text{pH}$  diagram (Pourbaix diagram) [20]. They thus appear from all CMOS metal layers investigated the best suited ones for bioelectronic applications.

#### 4. Conclusions

This investigation has shown that the usual TiN/Al:Cu/TiN metal-layer stacks cannot be applied as electrodes in aqueous solutions with high concentrations of electrolyte. These layers are comparatively fast subjected to corrosion, which may be understood from small pores and imperfections of the TiN layer via which the electrolyte may corrode the Al:Cu. Also thin  $\text{CoSi}_2$  films were found to suffer from changes of their sheet resistance when in contact with buffered saline solutions at elevated temperatures. From all metal layers prepared, only single layers of TiN appeared sufficiently corrosion-resistant and showed only negligible changes of their sheet resistance when in contact with a  $90^\circ$  hot saline solution for a time span of days. Even when polarised in an electrochemical cell between  $-0.8$  and  $+0.8$  V vs. Ag/AgCl, the TiN layer revealed high stability in buffered solution as well as in sulfuric acid. In the presence of redox active species such as hexacyanoferrate or catechol the layers showed no electrocatalytic activity. It can thus be concluded that TiN layers are well suited to serve as CMOS compatible electrodes in bioelectronic devices.

#### Acknowledgements

This study was performed within BMBF and BMWi funded projects for the development of a minimally invasive blood sugar sensor (contract numbers 0313862B and KF 0653901UL8). This work was also partially supported by the MWFK Brandenburg, Germany (project 3508-14/13). We thank the co-workers of IHP pilot line for the preparations as well as P. Schley and D. Schmidt for their support during the electrical characterization. Moreover, the IHP acknowledges the helpful cooperation with our project partners from BST Bio Sensor Technology GmbH, Sitec Sensortechnik GmbH and Humboldt Universität zu Berlin and last, but not least, the Aktionszentrum BioTOP Berlin-Brandenburg for continuously supporting the project.

#### References

- [1] International Technology Roadmap for Semiconductors, Update – Executive Summary, 2008 <http://www.itrs.net/Links/2008ITRS/Home2008.htm>.
- [2] R. Thewes, C. Paulus, M. Schienle, F. Hofmann, A. Frey, R. Brederlow, P. Schindler-Bauer, M. Augustyniak, M. Atzesberger, B. Holzpaff, M. Jenkner, B. Eversmann, G. Beer,

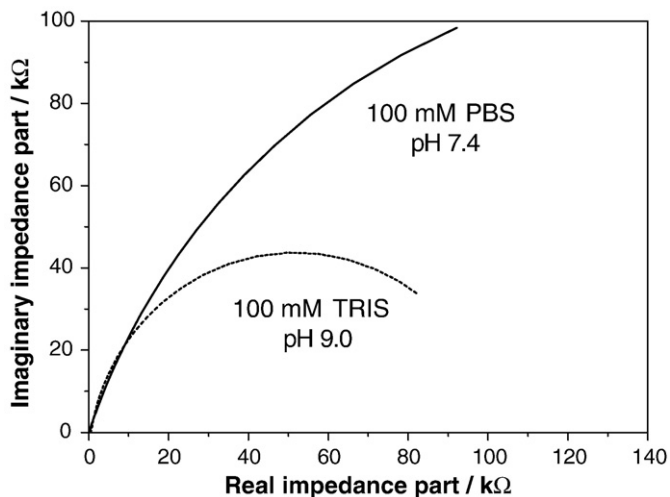


Fig. 5. Impedance behaviour of the TiN layer electrode in 5 mM  $\text{K}_4[\text{Fe}(\text{CN})_6]/5$  mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  measured at a) pH 7.4 (100 mM phosphate buffer) and b) pH 9.0 (100 mM TRIS buffer).

- T. Haneder, H.-C. Hanke, in: R.P. Mertens, C.L. Claeys (Eds.), 34th European Solid-State Device Research Conference (ESSDERC), Leuven, Belgium, 2004, p. 19.
- [3] M. Kittler, X. Yu, O.F. Vyvenko, M. Birkholz, W. Seifert, M. Reiche, T. Wilhelm, T. Arguirov, A. Wolff, W. Fritsche, M. Seibt, *Mater. Sci. Eng. C* 26 (2006) 902.
- [4] M. Birkholz, P. Zaumseil, M. Kittler, I. Wallat, M.P. Heyn, *Mater. Sci. Eng. B* 134 (2006) 125.
- [5] K. Dill, D.D. Montgomery, A.L. Ghindilis, K.R. Schwarzkopf, S.R. Ragsdale, A.V. Oleinikov, *Biosens. Bioelectr.* 20 (2004) 736.
- [6] A. Heller, B. Feldman, *Chem. Rev.* 108 (2008) 2482.
- [7] H. Hämmerle, K. Kobuch, K. Kohler, W. Nisch, H. Sachs, M. Stelzle, *Biomater.* 23 (2002) 797.
- [8] S.A. Campbell, *The Science and Engineering of Microelectronic Fabrication*, Oxford University Press, New York, 2001.
- [9] M. Ohring, *The Materials Science of Thin Films*, Academic Press, San Diego, 1991.
- [10] F. Lisdat, D. Schäfer, *Analyt. Bioanal. Chem.* 391 (2008) 1555.
- [11] F. Lisdat, R. Dronov, H. Möhwald, F.W. Scheller, D.G. Kurth, *Chem. Commun.* 3 (2009) 274.
- [12] T.M.A. Gronewold, S. Glass, E. Quandt, M. Famulok, *Biosens. Bioelectr.* 20 (2005) 2044.
- [13] K. Länge, B.E. Rapp, M. Rapp, *Analyt. Biochem.* 391 (2008) 1509.
- [14] K. Uhlig, M.S. Jaeger, F. Lisdat, C. Duschl, *J. Microelectr. Syst.* 17 (2008) 1322.
- [15] G.B. Salieb-Beugelaar, J. Teapal, J. van Nieuwkastele, D. Wijnperle, J.O. Tegenfeldt, F. Lisdat, A. van den Berg, J.C.T. Eijkel, *Nano Lett.* 8 (2008) 1785.
- [16] M. Grattarola, G. Massobrio, *Bioelectronics Handbook: MOSFETs, biosensors, and neurons*, McGraw-Hill, New York, 1998.
- [17] R. Ehwald, R. Ballerstadt, H. Dautzenberg, *Analyt. Biochem.* 234 (1996) 1.
- [18] M. Birkholz, K.-E. Ehwald, R. Ehwald, M. Kaynak, J. Borngänger, J. Drews, U. Haak, J. Klatt, E. Matthus, G. Schoof, K. Schulz, B. Tillack, W. Winkler, D. Wolansky, in: H. Seidel, H. Reichl, W. Lang (Eds.), *Proceedings Mikrosystemtechnik Kongress 2009*, Berlin, VDE-Verlag, Berlin, 2009, p. 124.
- [19] Y. Massiani, A. Medjahed, P. Gravier, L. Argème, L. Fedrizzi, *Thin Sol. Films* 191 (1990) 305.
- [20] N. Heide, J.W. Schultze, *Nucl. Instr. Meth. Phys. B* 80/81 (1993) 467.
- [21] J. Piippo, B. Elsener, H. Böhni, *Surf. Coat. Technol.* 61 (1993) 43.
- [22] I. Milosev, H.-H. Strehblow, B. Navinsek, *Thin Sol. Films* 303 (1997) 246.
- [23] D. Knoll, K.-E. Ehwald, B. Heinemann, A. Fox, K. Blum, H. Rücker, F. Fühnerhammer, B. Senapati, R. Barth, U. Haak, W. Höppner, J. Drews, R. Kurps, S. Marschmeyer, H.H. Richter, T. Grabolla, B. Kuck, O. Fursenko, P. Schley, R. Scholz, B. Tillack, Y. Yamamoto, K. Köpke, H.E. Wulf, D. Wolansky, W. Winkler, *IEDM Tech. Dig.*, IEEE, San Francisco, 2002, p. 783.
- [24] B. Heinemann, R. Barth, D. Knoll, H. Rücker, B. Tillack, W. Winkler, *Semicon. Sc. Technol.* 22 (2007) S153.
- [25] M. Birkholz, C. Genzel, T. Jung, *J. Appl. Phys.* 96 (2004) 7202.
- [26] J. Lee, A. Sauter Mack, *IEEE Trans. Semicon. Manuf.* 11 (1998) 458.
- [27] A.J. Bard, L.R. Faulkner, *Electrochemical Methods – Fundamentals and Applications*, Chapter 6: Potential Sweep Methods, Wiley, New York, 2001 p. 226.
- [28] F. Marken, A. Neudeck, A.M. Bond, *Cyclic voltammetry*, in: F. Scholz (Ed.), *Electroanalytical Methods: Guide to Experiments and Applications*, Springer, Berlin, 2005, p. 51.
- [29] C. Gabrielli, *Electrochemical impedance spectroscopy*, in: I. Rubinstein (Ed.), *Physical Electrochemistry*, Marcel Dekker, New York, 1995, p. 243.
- [30] M. Birkholz, U. Albers, T. Jung, *Surf. Coat. Technol.* 179 (2004) 279.