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


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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$_2$ 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.

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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$_2$ exhibiting conductivities up to m$\Omega$ 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 m$\Omega$/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...
deposited by standard sputter processes, by which microelectronic line on 200 mm CZ-Si wafers of (100) orientation. Metal layers were

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 CoSi2 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 CoSi2 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 (ρ > 18 MΩ cm) and some cm² 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-hydroxymethylammonomethane–hydrochloride (Tris–HCl) or Na2HPO4–KH2PO4 (PBS), respectively. Samples were stored for days in closed vessels containing the buffered saline and inserted in a laboratory dryer at elevated 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 (Microelectrodes Inc., Bedford, USA). 0.5 M H2SO4 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 multilayer 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 CoSi2 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 CoSi2 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 CoSi2 in Tris and TiN in both buffers (right scale). Again, the silicide layers exhibit the strongest increase with increasing storage temperature. CoSi2 layers can thus be concluded to appear less efficient 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 SiO2/Si substrate [22]. 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. 2. Ratio of final over initial resistivity $\rho_{\text{final}}/\rho_{\text{initial}}$ for CoSi2 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.](image)

![Fig. 3. Depth-resolved XPS measurement of 55 nm thin Ti/TiN layer on SiO2. Results for Cu are given in the bottom plot with a different ordinate scale.](image)
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/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 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° 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.

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