Quality control of ultra-microelectrode arrays using cyclic voltammetry, electrochemical impedance spectroscopy and scanning electrochemical microscopy

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Abstract

Miniaturised amperometric transducers have been realised on silicon wafers integrating a disk ultra-microelectrode array (UMA) as working electrode, a large counter electrode and a Ag/AgCl pseudo-reference electrode in a three-electrode configuration. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electrochemical microscopy (SECM) have been evaluated as tools for rapid on-wafer determination of characteristic device parameters. Here, we report on the application of an automated wafer prober in combination with appropriate electroanalytical techniques to realise an automated quality control of UMA on wafer level. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

There is an increasing need for miniaturised sensors and systems in biochemical and biomedical analysis. This is mainly due to the specific properties of ultra-microelectrodes or ultra-microelectrode arrays (UMA) integrated in microanalysis systems such as high current density, inertness against stirring effects, and advanced signal-to-noise ratio [1–3]. Microelectronic fabrication techniques have been used to manufacture related transducers on silicon wafer making use of the well developed production lines and lithographic techniques used for the production of electronic circuits [4–6]. Here, the term 'ultra-microelectrode' is used for electrodes with diameters up to 20 μm, due to the fact that the term 'microelectrode' is frequently used for electrodes with significantly bigger dimensions [3].

A special type of transducer that has gained interest in recent years is the UMA for amperometric measurements, especially integrated within an on-chip three-electrode configuration [7]. However, although mass production techniques developed by the semiconductor industry are used for the fabrication of UMA prices are still high. This is at least partly due to the fact that up to now the quality of such UMA cannot be easily evaluated. Thus, the main costs turn up with the time consuming assembling and test of the devices and often much effort is put into a bad die. This had been very similar with microelectronic devices previously, and hence the semiconductor industry has developed sophisticated test equipment (e.g. wafer prober) for automated die tests on wafer level. It can thus be assured that each die is tested at maximum speed. Obviously, any attempt aiming on automated quality control systems has to be focused on wafer level in order to select those devices which meet the predefined quality at the earliest stage. Although the test equipment is commercially available, appropriate test methods for an automated test of each individual UMA on wafer level have to be developed.

2. Characterisation of ultra-microelectrode arrays

A variety of UMA-chips with different electrode geometry has been fabricated [8]. The investigated transducers integrate a working electrode, which consists of an array of parallel connected platinum disk ultra-microelectrodes, a platinum counter electrode and a chemically or electrochemically chloridised Ag/AgCl pseudo-reference electrode (Fig. 1). The passivation layer of the UMA-chips is made of a combination of silicon oxide, B–P-doped silicate glass and silicon nitride [18]. Its thickness is about 1.3 μm, decreasing to about 600 nm on the poly-Si plateau used

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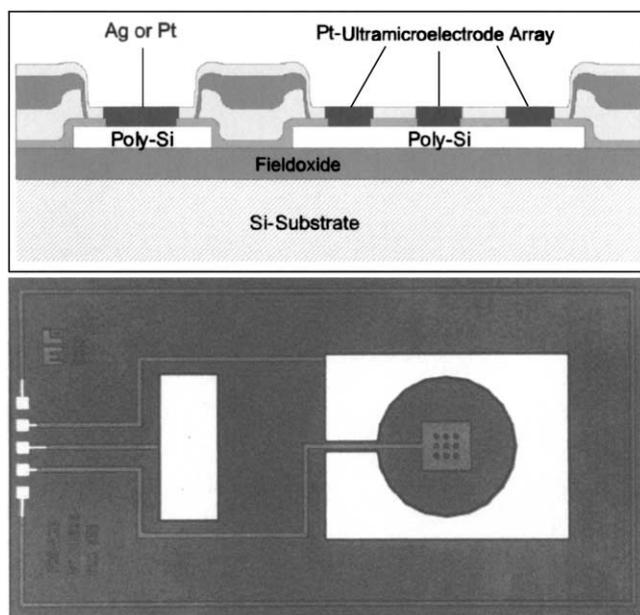*E-mail address*: koester@ims.fhg.de (O. Köster).

Fig. 1. Top: cross section of the fabricated transducers. Bottom: microphotograph of one of the fabricated transducers having ultra-microelectrodes made of platinum with diameters of 10 µm. The working electrode is a 3×3 UMA surrounded by a large silver layer. The third (platinum) electrode serves as auxiliary electrode.

for parallel electrical connection of the ultra-microelectrodes. The metal electrodes are recessed by about 300 nm leading to small aspect ratios down to 0.015–0.03. Table 1 shows the characteristic geometries of the transducers used in the present research.

For qualifying the UMA the following appropriate parameters have been selected: (i) the number of electroactive electrodes N; (ii) the position and stability of the equilibrium potential E_{eq} for a certain redox system and (iii) the uncompensated resistance R_u (at defined solution conductivity κ). The E_{eq} provides information concerning the quality of the pseudo-reference electrode (except when the working electrode is blocked or completely unstable; but then the die would be assigned 'bad' in any case, no matter of the exact reason), whereas N describes the function of the UMA and R_u has a significant impact in the integration of peripheral electronic components. As a further prerequisite only those test methods could be used which are potentially transferable to an automatic wafer prober, thus allowing only fairly

Table 1
UMA geometries of investigated transducers[a]

UMA type	1	2	3	4	5	6
a (µm)	5	5	5	5	10	10
d (µm)	100	200	200	100	100	200
L (µm)	370	250	370	250	900	250

[a] The a denotes radius of an individual microelectrode, d the interelectrode spacing and L the shortest distance of the pseudo-reference electrode to the working-electrode array.

simple electrochemical redox systems (in aqueous electrolyte solution) and implying a high test velocity. An automated test will make use of a probe card for external electrical connection of the UMA. Prior to testing a drop of an electrolyte solution containing the redox species could be dispensed on the die under test exclusively covering the three electrodes (e.g. by applying an ink-jet system). In order to prevent wetting by the electrolyte, the passivation layer of the UMA should be hydrophobic. This has already been demonstrated on wafer level for such devices by placing drops manually onto the electrode area and performing subsequent tests on a wafer prober [8]. Alternatively, a special capillary could be used, preventing dispersion by capillary forces, as described previously [19]. Therefore, we have selected cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electrochemical microscopy (SECM) as potentially suitable electroanalytical techniques for on-wafer testing of UMA.

3. Experimental

A single-chip potentiostat, which has been described previously [9,10] has been used in connection with a lock-in amplifier (SR830 from Stanford Research). The measurement systems were controlled using a personal computer. EIS measurements have been performed up to an ac-frequency of 5 kHz with typical amplitudes of 4–20 mV rms at the equilibrium dc potential. On setting up an automated test the used lock-in amplifier could be replaced by an electronic test system as frequently used for testing microelectronic devices in conjunction with a wafer prober. Thus, no special equipment or software would be needed at the final experimental set-up.

Details of the SECM set-up have been described elsewhere [11]. The spatial resolution was determined by the micro-tip electrode which was used as auxiliary electrode (Fig. 2). This way the micro-tip electrode acts as a current source and even a partially blocked electrode surface will just result in an increase of the electrode potential. Thus, the surface quality of the tip electrode is less important allowing even the use of conventional prober needles as tips for the localisation of the electrochemical reactions taking place at the investigated UMA.

All experiments were performed at room temperature in an air-saturated 0.1 M KCl-solution (pH 7.0) containing equimolar concentrations of ferro- and ferricyanide (2–12 mM). Prior to the measurement, the UMA has been pre-treated in 0.1 M KCl by sweeping the polarisation voltage versus on-chip reference between the hydrogen and oxygen evolution values, respectively, until the obtained cyclic voltammogram was showing no further changes. The diffusion coefficients of the redox species are shown in Table 2. They have been derived from CV using a glass-sealed microelectrode made of platinum with an electrode diameter of 10 µm [8].