A MINIATURIZED CMOS MICROELECTRODE ARRAY SYSTEM FOR SINGLE DROPLET ELECTROCHEMISTRY APPLICATIONS

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ABSTRACT

This paper presents an individually addressable 32x32 microelectrode array (MEA) system with built-in CMOS potentiostat for analyzing single droplets and ultra-small volume samples. The proposed system has advantages of smaller sample requirement, higher density, small form factor, low power and higher sensitivity and advanced functionality over the conventional electrode array. Each electrode is a square of side 7um with a center-to-center distance of 37um. The MEA integrated with potentiostat is robustly realized by employing electroless/electrochemical Au plating of native metal layers of CMOS process through a series of simple, maskless, clean-room free die-level post processing.

KEYWORDS: Microelectrode array, electrochemical, potentiostat, CMOS sensor

INTRODUCTION

An addressable microelectrode array with external switch to address each microelectrode has been reported [1] and many integrated potentiostat using CMOS technology have been developed [2,3]. In this work, we present implementation of a higher density of MEA with built-in potentiostat and interface circuitry on a single die, thus developing a miniaturized and individually addressable MEA system in a small size that can be used to perform electrochemistry on a pico-liter single droplet solution. As the number of microelectrodes increases, the highest ratio of faradic current to background current is achieved by averaging out the background noise. Moreover an integrated platform reduces the interconnect bottlenecks between the array and the potentiostat, thus reducing parasitics and noise, which could be detrimental for high sensitivity application. This system was fabricated using the AMI 0.5um CMOS technology. To demonstrate the characteristics of the MEA system on chip, cyclic sweep votammetric (CV) experiment is performed on a single droplet of ferricyanide($K_3Fe(CN)_6$) solution exhibiting desired behaviour.

In electrochemical analysis based on Cyclic Voltammetry(CV) experiments, the MEA provides great benefits compared to macro-electrodes, like time independence(scan rate) and high signal to noise ratio, which can only be achieved with radial diffusion of species to the electrodes (for reduction or oxidation). To avoid disturbance from adjacent electrode, distance(d) between electrodes is an important factor. For non-overlapping between adjacent diffusion layers, the distance should be more than twice the size of the diffusion[4],

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$$d > 2\sqrt{2D\frac{\Delta E}{\nu}} \quad (1)$$

Where ν is the voltage-scanning rate and ΔE is the potential difference between the onsets of electrolysis to the potential at which steady-state current is obtained. Traditional CMOS technology is not amenable for electrochemical applications since the aluminium electrodes oxidize readily to the atmosphere. As shown in Fig. 1, we use an electro-less 4-steps gold deposition technique at die level, popularly called as Electro-less Nickel Immersion Gold (ENIG) deposition ([5][6]): (1) Deoxidization (2) Zincation (3) Ni deposition and (4) Gold deposition to coat the aluminium with gold working electrodes.

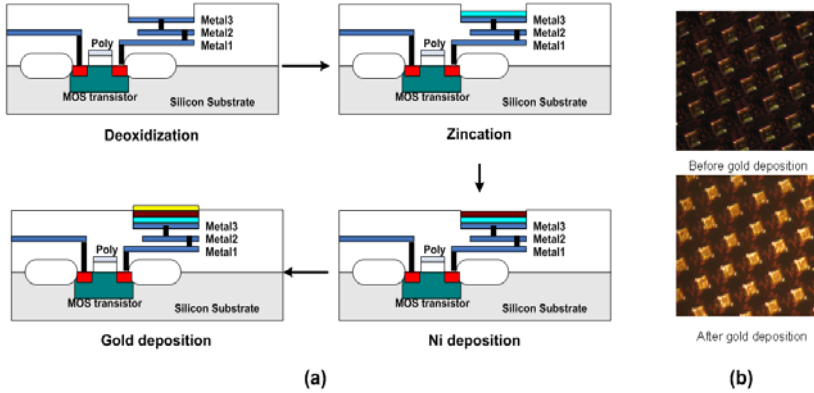

Figure 1. Sequence of steps for micro-fabrication of MEA on CMOS chip at die level(a) and photo of maskless coated gold MEA(size of 7um x 7um and distance of 37um) with integrated potentiostat on CMOS single chip(b).

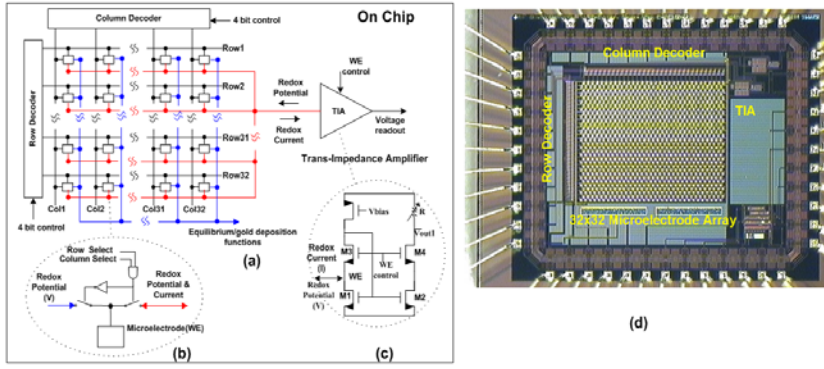

Figure 2. Block diagram of the CMOS chip(a), digital control circuit for individual addressability(b), built-in potentiostat(c), and Micrograph of the implemented 32x32 microelectrode array system based on CMOS.

Figure 2 shows the diagram of the proposed MEA system and the chip photograph of the fabricated MEA system. This system comprises of a 32x32 microelectrode array with an on-chip potentiostat and read-out control interface circuit implemented in standard CMOS process. An array is located on the surface of the chip with di-

mensions optimized to achieve steady-state current for microelectrode behavior. For experiments, the fabricated chip is placed inside a Faraday cage to shield the environmental noise coupling. A single droplet ferrycyanide $(K_3(CN)_6)$ solution is used as an electrolyte for the voltammetry. A standard Ag/AgCl electrode is used as the reference electrode. An epoxy is set to expose only the electrode array on the chip as shown in Figure 3(a). Figure 3(b) shows the result of CV experiment for the fabricated MEA on the chip. An external standard Ag/AgCl electrode was used as a reference electrode. The redox voltage was varied from 0V to 0.6V and the scan rate was swept from 0.1V/s to 0.005V/s. The performance of the entire system is verified by CV experiment. Single droplet of the ferricyanide($K_3Fe(CN)_6$) solution was placed on surface of the MEA using a syringe. The resulting CV shows steady-state current of 0.6 nA in figure 3(c). Such ultra-small MEA system is an ideal candidate for electrochemical sensors or biosensors due to their high sensitivity and ease of portability.

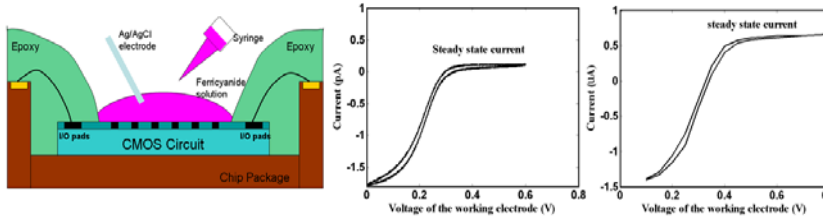

Figure 3. View of cross section in the system in faraday cage(a), CV at MEA in a ferricyanide solution(2mM) using external potentiostat(b), and CV of theMEA system in a ferricyanide solution(100mM) with built-in potentiostat on single chip

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