Silicon-based Interdigitated Electrode Array for Highly Sensitive Heavy Metal Ion Sensing

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Highly sensitive sensors based on capacitance changes have been developed for the detection of heavy metal ions by utilization of self-assembled monolayer films on silicon oxide surfaces between interdigitated electrodes. The attractive ability of the sensor to efficiently preconcentrate trace amounts of Cu^{2+} allows a simple and ultrasensitive method for copper ion detection. The wide range linear calibration curve of 1.0×10^{-13} to 1.0×10^{-9} M Cu^{2+} is constructed at 53 Hz. This sensor is highly sensitive and can push the detection limit of copper ion down to 1.0×10^{-13} M.

With the development of everincreasing industrial sprawl, preventing the continued release of metal contaminants into natural resources becomes an important task. Heavy metals have potential impact on human health and the environment due to their high toxicity. Many methods for the detection of metal ion have been developed. Atomic absorption,[1] fluorescent sensors,[2] and inductively coupled plasma spectroscopy[3] have been used most frequently in the detection of copper ion. However, these methods are either expensive or time-consuming. To simplify the detection methods and improve sensitivity, electrochemical impedance spectroscopy[4] has been proposed because of high sensitivity, rapid response, and chemical specificity.[5] A copper ion nanosensor based on gold surface self-assembled monolayer (SAM) films has been reported and the detection limit is 5.0×10^{-10} M Cu^{2+}.[4d] Since interdigitated microelectrode arrays (IDAs) are more sensitive than conventional gold electrodes and compatible with IC manufacturing process, IDAs have been applied as biosensors and chemical sensors. An ultrahigh electrochemical IDA nano-biosensor with 100 times improvement in the detection ability has been studied for the detection of reversible redox species.[6] 38-mer target ssDNA with a complementary probe at the concentration of 1 nM can be detected in a microfluidic cell.[7] In addition, a heavy metal ion sensor using a conducting polymer nanojunction array allows real-time detection of Cu^{2+} and Ni^{2+} at ppt level.[8]

In this letter, we demonstrate a nanoscaled interdigitated electrode sensor for the detection of copper ion, which is fabricated using standard CMOS lift-off process technology. The gap between two electrodes is 500 nm. The capacitance of the nanogap indicated the permittivity of the medium filling the gap. Figure 1a displays the SEM image of IDA array. This structure is made of 170 interdigitated fingers that are 200 µm long. The pairs of electrode pads are connected to 40-pin DIP footprint using a wire bonding process. Figure 1b represents the whole device image after wire bonding.

Modification of the silicon oxide surface in gap areas is illustrated in Scheme 1. Chips are cleaned thoroughly with acetone and isopropyl alcohol to remove organic contaminants and then are washed with absolute ethanol and dried with nitrogen. Next, the clean chips are silanated with a solution of ethanol/H_2O/3-aminopropyltriethoxysilane (APTES) (95:3:2 v/v) by incubation for 4 h, then they are washed with absolute ethanol and allowed to dry under mild nitrogen flow. After that they are treated by aging at 110 °C for 10 min. Next the silane-modified nanogap areas are treated with ethanolic salicylaldehyde (SAL) solution (1:1, v/v) for 1 h at room temperature to form a Schiff base. Preconcentration of Cu^{2+} is performed by applying 20 µL solution of certain concentration in supporting electrolyte to form SiO_2–APTES–SAL–Cu^{2+}. Then the measurement is conducted immediately.

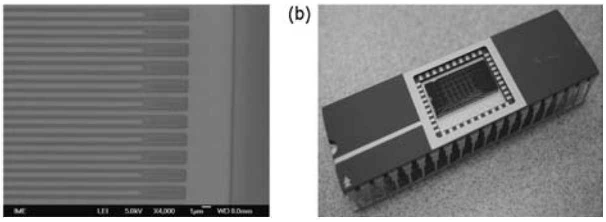
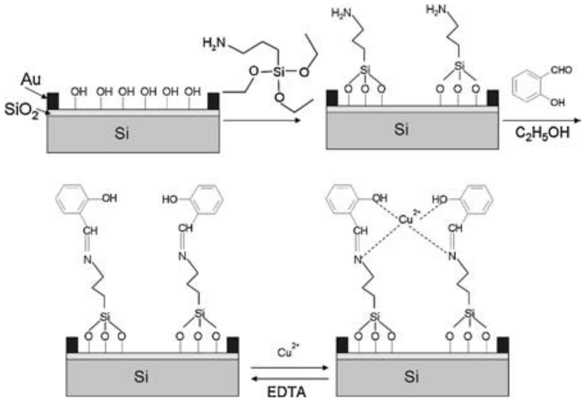


Figure 1. (a) SEM image of interdigitated electrodes array with 500-nm gap. (b) The entire device photograph after wire bonding to 40-pin DIP.



Scheme 1. Proposed mechanism for self-assembly process and copper interaction with the modified gap areas.

Copper metal ion sensing experiments are performed by monitoring the capacitance changes between nanogap under different frequency after the addition of buffer solutions containing desired concentration of copper metal ion. The capacitance between interdigitated microelectrodes is measured by a HP4294A LCR meter at 0 V DC, 50 mV AC and for a frequency band from 20 Hz to 1 MHz. Lab view program is used to control the LCR meter and record the capacitance data through a GPIB interface. Each sweep takes approximately 2 min. To investigate the effect of the solution matrix on determination steps of Cu^{2+} ions, several electrolytes such as NaOAc, KNO_3, $KLiClO_4$, and KCl electrolytes solution are analyzed. The capacitance change for different types of electrolyte solutions before and after the addition of 1×10^{-6} M Cu^{2+} ion at the same frequency of

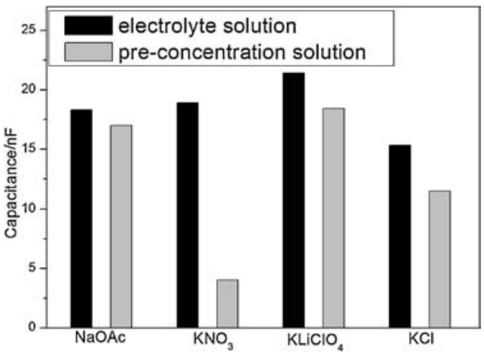


Figure 2. Capacitance response of SAM-modified gap areas for different types of electrolyte solutions. Preconcentration conditions: 1.0×10^{-6} M Cu^{2+}, 0.1 M electrolyte, frequency of 53 Hz.

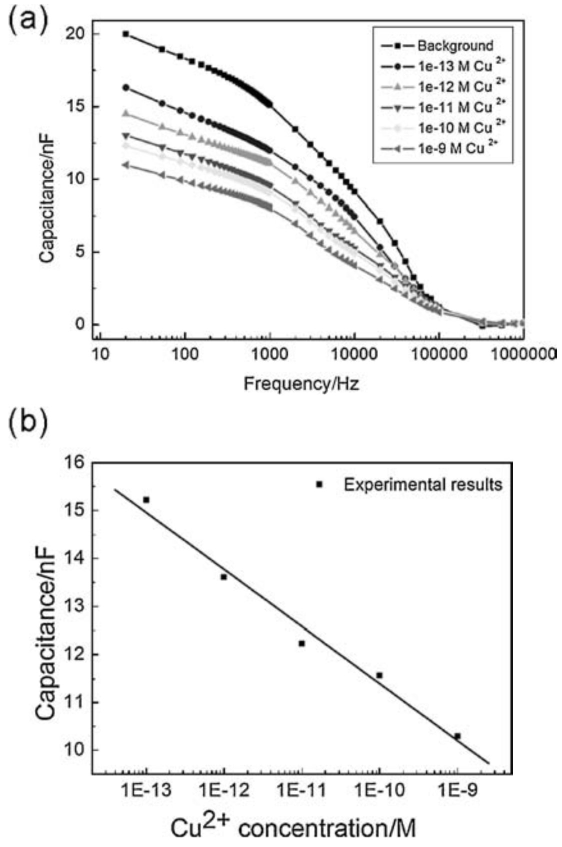


Figure 3. (a) Capacitance versus frequency after preconcentration in 0.1 M KNO_3 electrolyte containing 0, 1.0×10^{-13}, 1.0×10^{-12}, 1.0×10^{-11}, 1.0×10^{-10}, 1.0×10^{-9} M Cu^{2+} after SAM-modified nanogap areas. (b) Variation of the capacitance as a function of Cu^{2+} concentration at 53 Hz.

53 Hz is shown in Figure 2. We have observed that the maximum response happens when 0.1 M KNO_3 is used as electrolyte. So it can be deduced that if the KNO_3 is changed to other electrolyte, the sensitivity for Cu^{2+} ion detection would also be decreased.

Figure 3a plots the capacitance between the two multifingers electrodes as a function of frequency under the different concentration of Cu^{2+}. For each concentration, we have tested five sets of interdigitated electrode pairs in the same chip, and the variations of the measured capacitance are around 10%.

A simplified electrical model[9] can provide the best fit to our experiments. At low frequency range, the double layer capacitance dominates the signal.[10] It can be also seen from Figure 3a that the obvious change of capacitance profile for solution at the different ion concentrations can be observed in the frequency range of 20 Hz to 100 kHz, and the capacitance profile shifts down with the increase of copper ion concentration, which indicates that the conductivity of the solution is a dominant factor in defining the response of the sensor in the given frequency range. The double layer capacitance can be expressed as $C_{\mathrm{dl}} = \varepsilon_0 \varepsilon_{\mathrm{p}} A/d$, where ε_0 is the permittivity of free space, ε_{p} is the effective dielectric constant of the layer separating of the ionic charges and the electrode, A is the electrode area, and d is the thickness of the double layer. After the addition of copper ions, these ions binding interactions happen on SAM silicon oxide surfaces, which create a new charged layer as a capacitance that is in series with the double layer capacitance, hence decreasing the double layer capacitance.[10] The calibration curve (Cu^{2+} concentration from 1.0×10^{-13} to 1.0×10^{-9} M) is obtained from the capacitance versus ion concentration at 53 Hz, as shown in Figure 3b. From the diagram, we can see that the capacitance between interdigitated electrodes decreases linearly with the increase of copper ion concentration. The interference of other metal ions, i.e., Zn^{2+}, Ni^{2+} to this sensor is very small, which is consistent with reported results.[4b]

In summary, we have demonstrated a silicon-based interdigitated electrode array with SAM modification as an ultrasensitive copper ion sensor. The advantages of this capacitive sensor are high sensitively, fast response, small size, easily integration with other sensing elements, and a simple measuring method. Based on obtained results above, development of a CMOS sensor array for environmental monitoring can be expected.

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