

## Analysis of Heavy-Metal Ions Using Mercury Microelectrodes and a Solid-State Reference Electrode on a Si Wafer

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(Received July 10, 2000; accepted for publication September 19, 2000)

Micro working electrodes and a solid-state reference electrode have been fabricated using semiconductor processes for electrochemical detection of heavy-metal ions in aqueous media. The working electrodes are mercury-coated platinum microelectrodes 5  $\mu\text{m}$ , 10  $\mu\text{m}$  and 25  $\mu\text{m}$  in diameter. The smaller electrode shows the higher sensitivity and the detection limits of the 5- $\mu\text{m}$ -diameter electrodes are about 0.2 ppb and 0.4 ppb for cadmium and lead ions, respectively. The reference electrode is a Ag/AgCl electrode coated by polyvinyl chloride (PVC)/Nafion layer containing  $\text{Cl}^-$  ions. The potential variation of the fabricated solid-state reference electrodes is about 55 mV under a 0.1 M  $\text{Cl}^-$  concentration.

KEYWORDS: microelectrode, solid-state reference electrode, heavy-metal-ion, stripping voltammetry, SWASV, mercury electrode, microfabrication

### 1. Introduction

The necessity of a rapid method of detection of water pollution has gradually increased. In particular, even infinitesimal amounts of heavy-metal ions can threaten an ecosystem or human life, so *in situ* monitoring system of heavy-metal ion concentration is desired.

Electrochemical analysis offers good sensitivity and can be realized in an *in situ* analysis system using semiconductor processes.<sup>1,2)</sup> With microelectrodes, we can detect trace metals with superior sensitivity compared to macroelectrodes.<sup>3-5)</sup> However, the resultant small currents are a drawback for their practical realization into a portable or handheld field analysis system. In the case of heavy-metal ions like cadmium and lead, anodic stripping voltammetry (ASV) shows remarkable sensitivity with a larger electrode current.<sup>6,7)</sup> This analysis uses mercury electrodes. If the applied potential to the mercury electrode is more negative than the standard redox potentials of heavy-metal ions, then the ions present in the liquid are amalgamated into the mercury electrode. After this pre-concentration step for a few minutes, the potential is increased linearly in the opposite direction and the amalgamated metals are stripped out into the solution. By measuring the current peaks while sweeping the voltage, we can detect heavy-metal ions and their concentrations dissolved in the liquid.

One important problem which needs to be addressed in the field analysis system is the integration of a reference electrode with the working electrodes and auxiliary electrode and other components such as a micro control unit and signal process unit. The conventional reference electrode is a saturated Ag/AgCl electrode or calomel electrode which is a metal wire immersed in a glass tube filled with electrolyte solution. Some reports have described solid-state reference electrodes fabricated using semiconductor processes and electrochemical reactions.<sup>8-10)</sup>

We report the fabrication of mercury working electrodes and a solid-state reference electrode, and present experimental results that describe the size effect of working electrodes and the performance of the reference electrode.

### 2. Electrode Design

An electrochemical measurement system can be fabricated using two or three electrodes. In the two-electrode configuration, the bulk resistance,  $R_s$ , induces an error that depends on the bulk solution concentration, electrode geometry, electrode position and electrode surface quality. The three-electrode configuration offers more accurate measurements of working electrode potential at the expense of complex control electronics.<sup>11)</sup> In this work, we used a three-electrode configuration composed of a platinum/mercury working electrode, a platinum auxiliary electrode and a solid-state Ag/AgCl reference electrode.

#### 2.1 Working electrode

Electrode currents consist of two components, that is, Faradaic current ( $i_F$ ) which is the signal current of interest and capacitive current ( $i_C$ ) which is the non-Faradaic component caused by the double-layer capacitance of the electrode-liquid interface. The Faradaic current for hemispherical microelectrodes is expressed as

$$i_F(t) = nFAC_o^* \sqrt{\frac{D_o}{\pi t}} + nFAC_o^* \left( \frac{D_o}{r_0} \right), \quad (1)$$

where  $n$  is the number of electrons transferred,  $F$  is the Faraday constant ( $9.6485 \times 10^4 \text{ C mol}^{-1}$ ),  $A$  is the electrode area ( $\text{m}^2$ ),  $D_o$  is the diffusion coefficient of the species of interest ( $\text{m}^2 \text{ s}^{-1}$ ),  $C_o^*$  is the bulk concentration of the species ( $\text{mol m}^{-3}$ ) and  $r_0$  is the radius of the hemisphere ( $\text{m}$ ).<sup>12)</sup> In the above equation, the dynamic first term gradually decreases with increasing time and is directly proportional to the electrode area, that is, the square of the electrode radius. However, the steady-state second term is proportional to the electrode radius. The current behavior at a disk microelectrode is similar to that at a hemispherical electrode.<sup>13)</sup> Figure 1 shows the diffusion profile of a disk microelectrode. In general, for a microelectrode, the smaller the size, the more dominant the steady-state component. The capacitive current ( $i_C$ ) is

$$i_C = C \frac{dv}{dt}, \quad (2)$$

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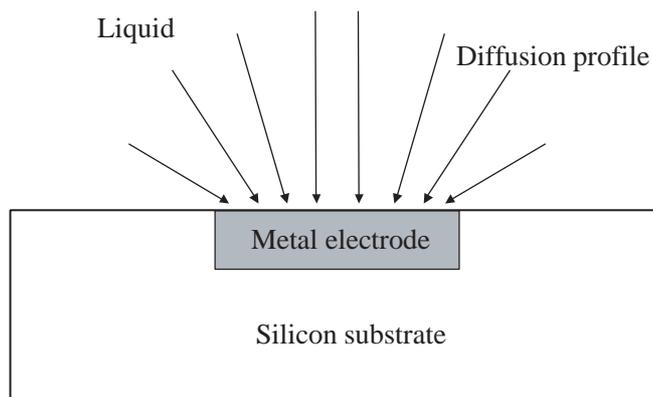


Fig. 1. Diffusion profile of electrolyzed species on a disk microelectrode.

where  $C$  is the electrode capacitance and  $v$  is the voltage applied to the electrode. The current is proportional to the electrode capacitance, namely, the square of the electrode radius. Hence, for the smaller electrode, the capacitive current is negligible compared to the Faradaic current and we can obtain a higher signal-to-noise ( $S/N$ ) ratio. In this paper we have carried out experiments for various electrode sizes (diameters of  $5\ \mu\text{m}$ ,  $10\ \mu\text{m}$  and  $25\ \mu\text{m}$ ) and examined the minimum detection level.

To obtain a measurable current level, we used ten array electrodes for the  $5\text{-}\mu\text{m}$ -diameter electrodes. In the case of array electrodes, the electrodes must be arranged so as not to overlap the diffusion layer at each electrode. In this experiment, the geometry of the mercury working electrode is a hemisphere, and the concentration profile for spherical electrodes is<sup>12)</sup>

$$C_O(r, t) = C_O^* \left[ 1 - \frac{r_0}{r} \operatorname{erfc} \left( \frac{r - r_0}{2(D_O t)^{1/2}} \right) \right]. \quad (3)$$

From this equation, for the electrode  $2.5\ \mu\text{m}$  in radius, we can know that the ion concentration is about 95% of the bulk concentration at distance of  $25\ \mu\text{m}$  from the electrode after the preconcentration time of 30 s. Using this information, we designed the center-to-center spacing of  $50\ \mu\text{m}$ .

## 2.2 Reference electrode

The reference electrode in an electrochemical system must provide stable potential under various solution compositions. The Ag/AgCl electrode maintains its equilibrium potential as a function of the aqueous  $\text{Cl}^-$  activity according to the Nernst equation

$$E = 0.22 + \frac{RT}{nF} \ln(a_{\text{Cl}^-}), \quad (4)$$

where  $E$  is the potential between the electrode and the electrolyte,  $R$  is the gas constant ( $\text{JK}^{-1}\text{mol}^{-1}$ ),  $T$  is the temperature in degrees Kelvin and  $a_{\text{Cl}^-}$  is the  $\text{Cl}^-$  activity. The electrode potential changes logarithmically with the  $\text{Cl}^-$  activity with a theoretical slope of  $58.5\ \text{mV/dec}$  at  $22^\circ\text{C}$ . In conventional reference electrodes, the Ag/AgCl electrode is immersed in a saturated KCl solution for a constant and invariant potential. For a solid-state reference electrode, we coated the Ag/AgCl electrode with a thin polymer layer containing chlorine ions.

## 3. Fabrication

The fabrication processes of the working electrode are shown in Fig. 2. Thermal oxide is grown on a silicon substrate to the thickness of  $5000\ \text{\AA}$ , and a  $2000\ \text{\AA}$  Pt layer is patterned by the lift-off method (a). The gold signal lines and contact pads for wire bonding to printed circuit board (PCB) are patterned by lift-off as well (b). Next, a plasma enhanced chemical vapor deposition (PECVD) silicon nitride layer is deposited and the areas used to form electrodes and contact pads are etched by reactive ion etching (RIE) (c). Figure 3(a) shows a scanning electron microscope (SEM) micrograph of the Pt electrode with the diameter of  $3\ \mu\text{m}$ . By applying  $150\ \text{mV}$  to the Ag/AgCl reference electrode in the solution containing  $10\ \text{mM}\ \text{Hg}^{2+}$  ions, the mercury ions are electrodeposited onto the Pt surface. A micrograph of the electrode covered by hemispherical mercury and a cross-sectional view are shown in Fig. 3(b).

To fabricate the reference electrodes, the Cr  $200\ \text{\AA}$ /Au  $200\ \text{\AA}$ /Ag  $4000\ \text{\AA}$  layers are patterned by lift-off on the oxidized silicon wafer. Next, Ag electrodes are converted to Ag/AgCl electrodes (chloridation) by dipping in  $\text{FeCl}_3$  solution for 2 min. To obtain a stable potential, the Ag/AgCl electrodes are dipped in 12 mL tetrahydrofuran (THF) solution containing 0.4 g polyvinyl chloride (PVC) and saturated NaCl and dried for 48 h. Finally, by dipping in 5% Nafion solution, the protective polymer layer is coated and the solid-state reference electrodes are complete.<sup>10)</sup>

## 4. Experimental Results and Discussion

Figure 4 is the result of square-wave anodic stripping voltammetry (SWASV)<sup>14)</sup> for successive additions of Zn, Cd, Pb and Cu ions to deionized water containing 1 mM acetate

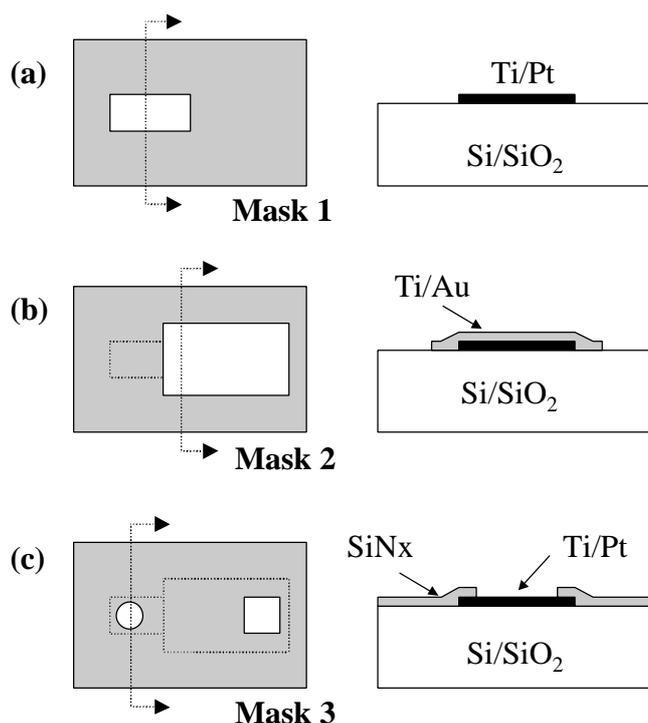
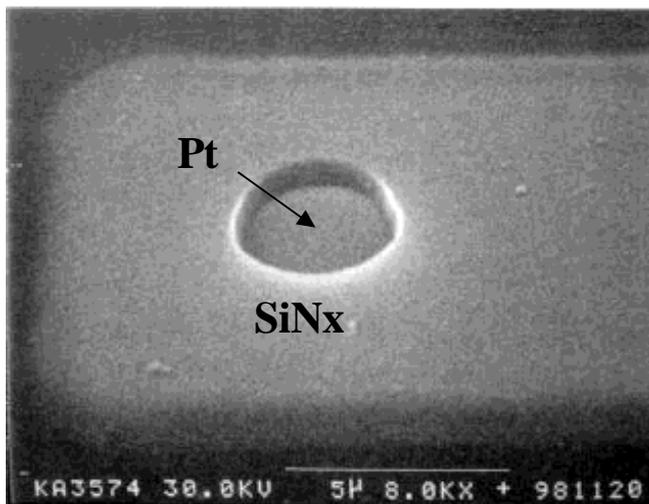
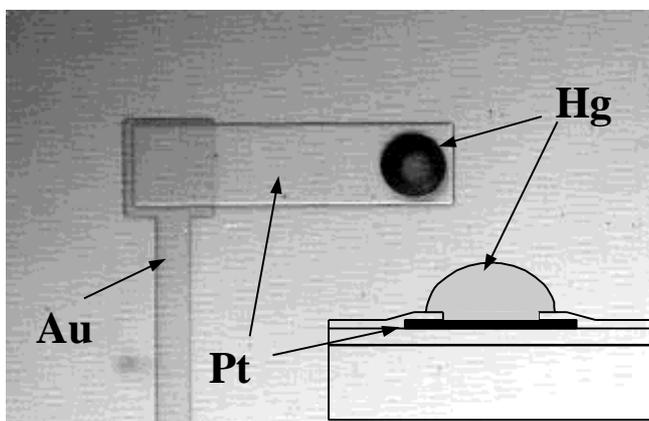


Fig. 2. Fabrication process of the microelectrode: (a) patterning of electrode metal (b) patterning of pad and signal line (c) opening the areas for electrodes and pads.



(a)



(b)

Fig. 3. (a) SEM micrograph of a Pt electrode with a diameter of 3 μm. (b) An electrode covered by hemispherical Hg and a cross-sectional view.

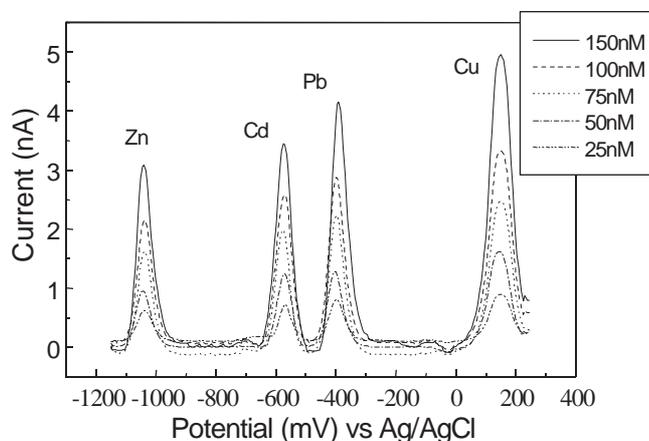


Fig. 4. SWASV for successive additions of four kinds of ions to deionized water containing 1 mM acetate buffer.

buffer. All data are averaged values of three measurements and the standard deviation is less than ±10%. In this experiment, a single working electrode with a diameter of 25 μm

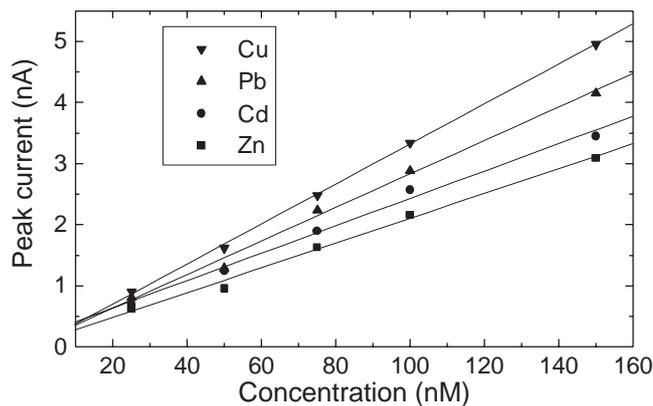


Fig. 5. Linear relationship (curves in Fig. 4) between peak currents and ion concentrations.

and a commercial reference electrode are used. The SWASV was carried out with  $E_{sw} = 25$  mV,  $\Delta E_s = 5$  mV,  $f = 30$  Hz and preconcentration at  $-1.1$  V for 240 s. The peak potentials are  $E_p = -1.04$  V for zinc,  $E_p = -0.57$  V for cadmium, and  $E_p = -0.4$  V and  $E_p = 0.15$  V for lead and copper, respectively. The linear relationship between peak currents and ion concentrations is shown in Fig. 5. The direct detection limit for this size of electrode is 25 nM, that is, 2.8 ppb for cadmium and 5 ppb for lead.

The theoretical peak current of the hemispherical micro-electrode can be approximated by the following equation<sup>15)</sup>

$$i_p = \frac{n^2 F^2 |v| l A C_M^* \psi_p}{2.7 RT}, \quad (5)$$

where  $v$  is the potential scan rate,  $l$  is the average mercury film thickness,  $C_M^*$  is the concentration of metal in the amalgam,  $\psi_p$  is a numerically calculated dimensionless current function for a square-wave voltammetry, and the other symbols have their conventional meanings. As an example, the peak current of the 100 nM lead ion is calculated to be 2.87 nA ( $d = 25$  μm) and this value corresponds well to the measured value of 2.83 nA (Figs. 4 and 5).

The SWASV for electrodes of various sizes without any additional supporting electrolyte is shown in Fig. 6. The preconcentration was carried out for 240 s, 60 s and 30 s at  $-0.8$  V and the frequencies of the square wave were 30 Hz, 120 Hz and 200 Hz each for the 25 μm, 10 μm and 5 μm electrodes, respectively, and for all electrodes,  $E_{sw}$  and  $\Delta E_s$  are 25 mV and 5 mV, respectively. These experiments show that the smaller electrode has superior sensitivity or  $S/N$  ratio to larger ones, but the detection range is restricted due to the early saturation of the Hg electrode. Figures 6(a) and 6(b) are the results of a single electrode with a diameter of 25 μm and 10 μm, respectively, and Fig. 6(c) is the result of 10 array electrodes with the diameter of 5 μm. Using 5 μm electrodes, we can sense the heavy-metal ions to the extent of 2 nM and this value is in the sub-ppb range for each metal.

The experimental result of the fabricated solid-state reference electrode is shown in Fig. 7. This figure shows the potential variation versus a commercial Ag/AgCl reference electrode with respect to the  $Cl^-$  concentration. The pure Ag/AgCl electrode has the slope of about  $-53$  mV/dec, and this value corresponds well to the theoretical value of  $-58.5$  mV/dec. The PVC/Nafion-coated electrodes have

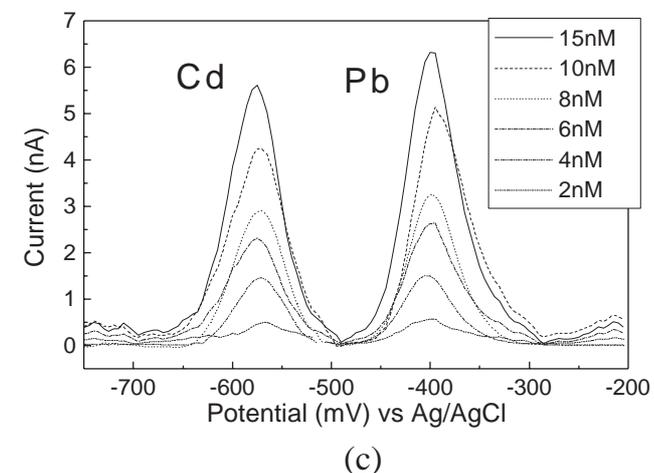
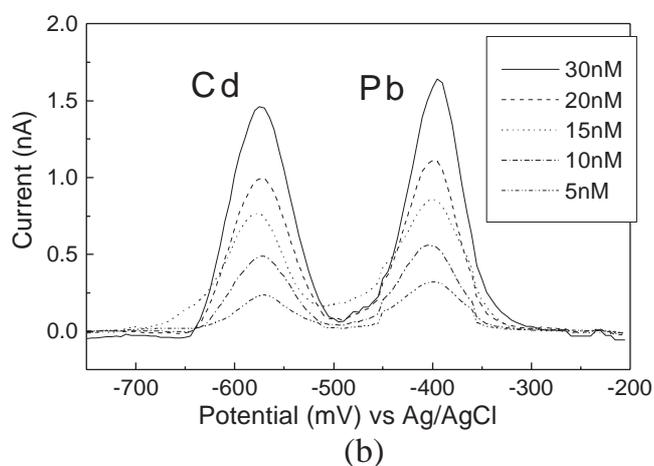
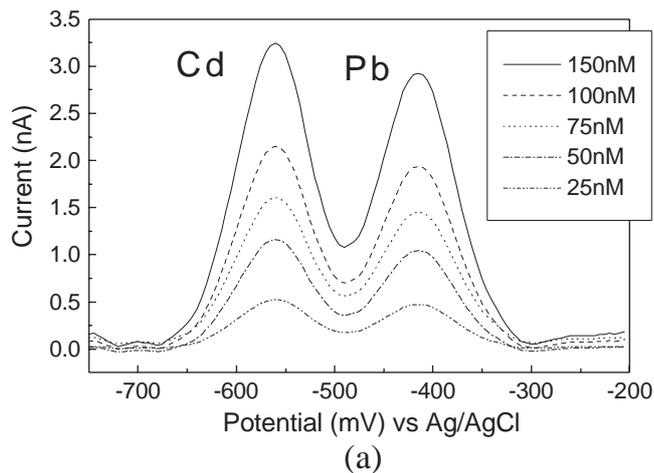


Fig. 6. SWASV for electrodes of various sizes. (a) single electrode of  $d = 25 \mu\text{m}$  (b) single electrode of  $d = 10 \mu\text{m}$  (c) ten array electrodes of  $d = 5 \mu\text{m}$ .

small variation with respect to  $\text{Cl}^-$  concentration. The potential variations,  $\Delta E$ , are 40 mV and 55 mV for two samples under the 0.1 M  $\text{Cl}^-$  concentration and these are sufficient to define the metal ions. The PVC-coated electrode has quite stable reference potential, but is physically unstable, so the polymer layer was stripped in successive experiments.

Figure 8 is the result of the experiments using the fabricated solid-state reference electrode. The working electrode is a single  $10 \mu\text{m}$  electrode and the other conditions are the same as those of Fig. 6(b) which used a commercial refer-

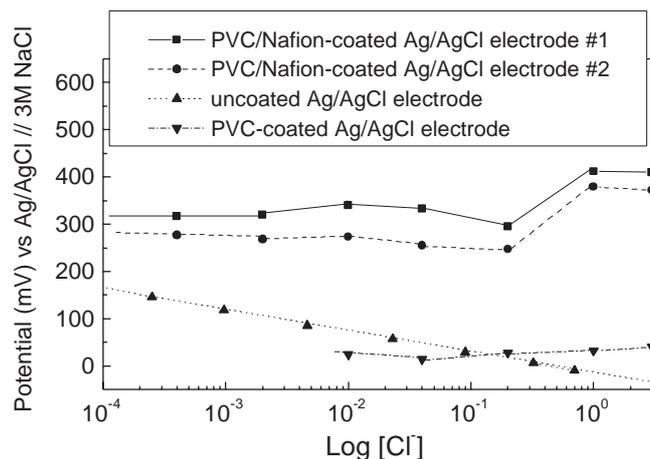


Fig. 7. Potential variation of the fabricated solid-state electrodes versus the commercial Ag/AgCl reference electrode with respect to  $\text{Cl}^-$  concentration.

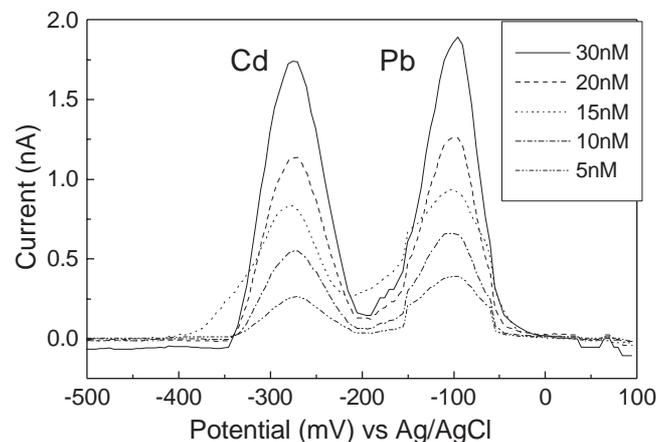


Fig. 8. SWASV using a single  $10 \mu\text{m}$  electrode for a working electrode and the PVC/Nafion-coated Ag/AgCl electrode for a reference electrode. No supporting electrolyte has been added.

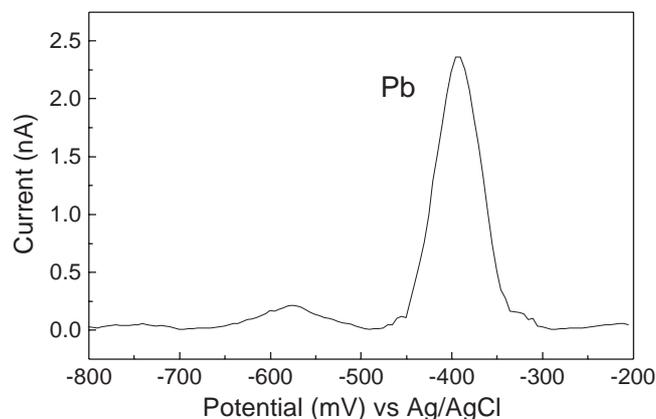


Fig. 9. SWASV for tap water without any additional supporting electrolyte or stirring.

ence electrode. Using pure Ag/AgCl electrodes, we were unable to obtain stable and reproducible data without additional supporting electrolytes. However, when using a PVC/Nafion-coated Ag/AgCl electrode, the results are very similar to the

case of using the commercial reference electrode except for the voltage shift of about 300 mV as was expected in Fig. 7.

To demonstrate the possibility of using the sensor in an *in situ* field analysis system, SWASV testing was performed on unbuffered tap water without stirring (Fig. 9). In this case, ten array electrodes with the diameter of 5  $\mu\text{m}$  were used and the SWASV conditions were the same as in the experiment in Fig. 6(c). By the standard addition method, the experiments have shown that tap water contains about 10 nM (2 ppb)  $\pm$  1 nM ( $n = 3$ ) Pb ions.

## 5. Conclusions

We have fabricated mercury-coated microelectrodes of various sizes and demonstrated the size effect, that is, superior sensitivity and  $S/N$  ratios can be obtained by reducing the electrode size. Using working electrodes and solid-state reference electrodes fabricated through semiconductor processes, we successfully detected the heavy-metal ions in deionized water and tap water without any additional electrolyte with the sensitivities down to the ppb range in aqueous media. The detection limit of the 5- $\mu\text{m}$ -diameter electrode is about 0.4 ppb and the potential variation of the fabricated solid-state reference electrodes is about 55 mV for the 0.1 M  $\text{Cl}^-$  concentration.

The repeatability and long-term stability of the working electrodes and reference electrodes are under evaluation, as well as one chip integration of three electrodes, i.e., the work-

ing electrode, reference electrode and auxiliary electrode.

## Acknowledgements

This work was supported in part by the Korea Science and Engineering Foundation through the MICROS center at KAIST and the BK21 project, Korea.

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