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Electrochemical impedance spectroscopy study of Ta_2O_5 based EIOS pH sensors in acid environment

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ABSTRACT

To develop an on-line pH sensor for acidic environment application, a tantalum pentoxide (Ta_2O_5) based electrolyte-ion sensitive membrane-oxide-semiconductor (EIOS) pH sensor has been prepared and investigated by applying electrochemical impedance spectroscopy (EIS) and capacitance-voltage method (C-V). Nernstian behavior toward variable proton concentrations (∼56.19 mV/pH) in the pH range from 1 to 10 could be achieved. Atomic force microscopic (AFM) showed that the surface of the H^+ sensitive Ta_2O_5 film was uniform and smooth. Electrochemical impedance spectroscopy (EIS) revealed that the space charge capacitance easily distinguish pH changes. Possible interference from Cu^{2+}, Fe^{2+} and Fe^{3+} were studied in pH 2.2 solutions.

1. Introduction

pH is one of the most important parameters of an aqueous solution. To measure pH values accurately, a pH electrode based on a thin film of pH sensitive glass was commonly used, which was developed one hundred years ago by Haber and Klemensiewicz [1] and still remains the first choice in pH measurement. However, there are several drawbacks about the glass pH electrodes. Glass electrodes are unsuitable for some industrial process application, e.g. mineral leaching process under high pressure, corrosive environmental and high temperature. Moreover, the high resistivity of glass membrane leads to a slow response, especially when fouling happens on the glass surface. For applications where the volume of solution is restricted, glass membrane is again not suitable due to the difficulties in miniaturization, thus alternatives to glass pH electrode is desirable. Several types of non-glass pH sensitive electrodes have been developed, which can be categorized into three types: polymer membrane based, metal–metal oxide based and the silicon based sensors [2–4].

Among the variety of proposed concepts and different types of chemical sensors and biosensors, the integration of chemically or biologically active materials together with the semiconductor field-effect devices based on an electrolyte-insulator-semiconductor system is one of the most attractive approaches. In this context, ion-sensitive field-effect-transistors (ISFETs) and capacitive electrolyte insulator semiconductor sensors are two typical examples. The application of ISFETs as transducers in electrochemical sensors and their application in medical research was first described by Bergveld [5]. It has been broadly studied in theory and practice for potential measurements in recent years as an alternative to conventional pH glass electrode [6–8], and the capacitive electrolyte-ion sensitive membrane-oxide-semiconductor (EIOS) structure is also attractive [9–14].

These two kinds of sensors provide lots of potential advantages such as small size and weight, fast response, high reliability, on-chip integration of biosensor arrays and a signal processing scheme with the future prospect of low-cost mass production of portable microanalysis systems; Moreover, their possible field of application extends to medicine, biotechnology and environmental monitoring over food and drug industries. However, the ISFET based pH electrodes have a limited lifetime in the bioleaching process as the pH sensitive gate insulator can be irreversibly destroyed by caustic media and high temperature [15]. Therefore, these sensors should only be used in combination with an additional holder, which would increase the sensor price.

Due to the absence of a complicated encapsulation procedure, pH sensors based on EIOS structure can be a very attractive alternative for the in-line bioleaching process. The EIOS structure can

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be simply obtained from a Metal-Insulator-Semiconductor (MIS) structure by replacing the metal gate with an electrolyte and a reference electrode. For operation, a direct current (DC) polarization voltage is applied via the reference electrode to set the working point of the EIOS sensor, and a small alternating current (AC) voltage is applied to the system in order to measure the capacitance of the sensor, similar to the well-known measurements with a MIS capacitor. For both types of structures, the capacitance is the most important measurable parameter. The similarity between these structures is important because MIS properties have been intensively studied in silicon-device physics. Several membranes have been found to be having good hydrogen-ion sensitivity such as TiO_2, Er_2O_3, ZrO_2, Si_3N_4, Al_2O_3 and Ta_2O_5 [16–21]. M.J. Schöning et al. [15] reported that Ta_2O_5 combined both the high sensitivity and corrosion-resistant in pH 3–pH 10, and a lower drift compared to other pH sensing membranes. Only a few reports on the Ta_2O_5 sensor in high caustic media at very low pH values are known so far [15,22].

However, it is important to monitor pH in the mineral processing environment, where a low pH (pH 1–pH 4) [23–25] is favorable for both process and acidic bacteria growth. The focus of this study is the electrochemical impedance properties of Ta_2O_5 EIOS sensor and its pH response in acidic aqueous solutions (bioleaching environment). This EIOS sensor, based on capacitance measurement, could be an alternative to the conventional potentiometric pH sensors, where acid error likely happens due to a limitation of free proton carriers available on the surface [26]. The developed EIOS sensors have been studied by electrochemical impedance spectroscopy (EIS) and capacitance-voltage method (C-V) in acidic solutions.

2. Experimental

2.1. Chemicals and Ta_2O_5 EIOS sensor preparation

All solutions were prepared from analytical grade chemicals (Aldrich, USA) and were used without further purification. Millipore-Q water (resistance over 18 MΩ cm) was used in all aqueous solutions and rinsing process. The pH in each solution was measured using a commercial pH meter (SevenMulti^{TM}, Mettler Toledo, Switzerland).

The EIOS devices with Ta_2O_5 sensing membranes were fabricated on a 4-inch p-type (1 0 0) silicon wafer (resistivity 12 Ω cm) following the scheme shown in Fig. 1. The silicon wafer was cleaned using standard Radio Corporation of America (RCA) process and then dipped in 1% hydrofluoric acid to remove native oxide from the surface. Then 50 nm silicon dioxide (SiO_2) was thermally grown by dry oxidation at 1000 °C for 38 min. 60 nm Ta was radio-frequency (RF) sputtered onto the substrate in an argon atmosphere for 360 s, the RF power was set at 300 W and the working pressure was controlled at 3.3 mTorr. Then Ta_2O_5 film was obtained by the oxidation of the Ta layer in oxygen atmosphere for about 3 h at 525 °C, the thickness of the film was measured by ellipsometry, and was about 155 nm. Finally, a 200 nm thick Au film was electron beam assisted evaporated as the back side contact of the silicon wafer after the rear-side SiO_2 was removed with Buffered Oxide Etch (BOE) solution. The EIOS sensors were annealed in ambient condition at 400 °C for two hours. The 4-inch wafer was then cut into smaller chips (10 mm × 10 mm) as shown in Fig. 2b, which served as the EIOS sensor.

2.2. pH measurement

The Ta_2O_5 sensor chips were amounted into the measuring setup as shown in Fig. 2a and preconditioned in pH 7 buffer solution for at least 12 h before testing to achieve high potential stability [24,27]. The effective sensing area of the sensor was about 0.3 cm^2.

The electrochemistry measurements were carried out on an advanced electrochemical system (PARSTAT 2273, USA). A two-electrode configuration was adopted where a conventional Ag/AgCl (3 M KCl) electrode (CHI, USA) served as the reference electrode. A bias voltage with a superimposed 10 mV AC voltage at a frequency of 300 Hz was applied. Four independent assays of consecutive *C–V* curves were registered for each sample solution to evaluate measurement stability. The sensors have been characterized in solutions with different pH values from pH 1 to pH 10 by impedance spectroscopy (frequency range of 100 Hz–1 MHz) and capacitance–voltage method (frequency range of 60 Hz–1 MHz).

To investigate the hysteresis effect of the Ta_2O_5 based sensors, measurements in various pH buffer solutions were performed in the following sequence of steps: pH 7-4-1-4-7-10-7 [28]. The immersion time of each pH solution was 3 min, and the *C–V* measurements were performed at 0.5, 3.0, 5.5, and 8.0 min.

All the measurements have been carried out at room temperature (23 ± 2 °C) in a dark Faraday cage to minimize both photo and electrical interferences.

2.3. Atomic force microscopy imaging

The surface morphologies of the Ta_2O_5 sensing film was analyzed using an Agilent 5500 AFM (USA). The AFM was operated in tapping mode, which was a non-contact mode of operation. Images were taken using a silicon cantilever with a spring constant of 40 N/m and resonant frequency of 300 KHz at a scan rate of 1 Hz. All samples were dried with nitrogen before testing and tested in air.

3. Results and discussion

3.1. Ta_2O_5 surface characterization

Surface morphology of the Ta_2O_5 film has been studied by AFM, in a typical tapping mode, at standard ambient conditions (shown in Fig. 3). The results showed a very uniform and smooth surface, dominated by dispersed nano-particles of lateral size 20–25 nm, with a mean roughness less than 5 nm. For comparison, a SiO_2 surface prior to the deposition of Ta_2O_5 layer was also characterized with AFM, where the surface was dominated with 5–50 nm size particles sparsely covering the surface (data not shown). These AFM images showed that the Ta_2O_5 film had no obvious crack or crystal grains on its surface after annealing. A smooth and homogeneous sensor surface is crucial for the capacitance-based sensor.

3.2. Operation mechanism of the Ta_2O_5 based EIOS sensor

The basic concepts of solutions and interfacial electrochemistry are critical to understand the fundamentals of EIOS operation. As for electrolyte-oxide interaction, it is noted that when two phases of different electrochemical properties are brought into contact, a redistribution of charge and potential occurs at the interface until the electrochemical potentials of the charge carriers in both phases are equal, which is called equilibrium. This redistribution results in an electrified interface and determines the electrochemical properties of the electrolyte-solid system.

In the study of the electrified interface, different physical-chemical models have been proposed to explain the operation of pH sensitive field-effect-transistors. The most popular model is based on the site-binding theory, which was originally developed to describe the surface charging of oxides in electrolyte solutions [29]. This model accounts for the binding of potential determining ions (H^+ and OH^-) and furthermore, also considers the binding