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A Flexible pH-Sensing Structure Using WO_3/IrO_2 Junction with Al_2O_3 Encapsulation Layer

Li-Min Kuo,[a,z] Kuan-Neng Chen,[b] Yi-Lin Chuang,[a] and Shuchi Chao[a]

[a]*Department of Electrophysics, National Chiao Tung University, Hsinchu 300, Taiwan*
[b]*Department of Electronics Engineering, National Chiao Tung University. Hsinchu 300, Taiwan*

A diode-like current-voltage characteristic in response to hydrogen-ions based on a WO_3/IrO_2 diode coated with a membrane–like Al_2O_3 is reported. Microsensors fabricated with the oxides (IrO_2 and WO_3) will suffer from interference errors in pH-measurements due to their strong responses to environmental redox species. With ionic-conductive and insulation properties, the membrane can mediate the transport of released protons and block the electrons from redox species in solutions. Invoking proton-electron double injection, H^+ and e^- produce redox reactions, which control the conductivity and preserve the continuity of currents across the interface with a good sensitivity (0.168μA/pH) between pH = 2 to 12.
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Significant attention has been paid to the use of solid-state materials as chemically sensitive devices.[1,2] Gate oxides were used by certain field-effect transistors known for detecting H^+ concentrations instantly.[3] InP/Pt Schottky diode was utilized to make a phenomenological model based on forming electric dipole layer by hydrogen ions in semiconductor applications.[4] A Ni/n-Si Schottky diode using the magnetization of a Ni layer modulates the diffusion rate of H^+ was reported.[5] However, electrical characteristics of solid-state, ion-conducting materials situated in liquids are barely addressed with regard to interfacial or material instability resulting from environmental variability.[6] Practical uses are less attractive due to the lack of a built-in "current turn-on" capacity, as is commonly found in microsensors.[7] Moreover, more sophisticated process flows should be investigated further.

In this letter, a solid-state and chemically sensitive device is proposed to operate as a basis for construction of durable microsensors that are operable in liquids. The sensor exhibits diode-like current-voltage characteristics in response to the presence of H^+. Microsensors built with the insertion oxides (IrO_2 and WO_3) will suffer from interference errors in media over pH-span values between 2 and 12. Based on the conception that Al_2O_3 film is an ionic conductor with electronic insulation property, the encapsulation layer was integrated on the diode surface in this work. Theoretically, the membrane can mediate the transport of released protons and block the transport of electrons from other redox species presented in solutions. According to proton-electron double injection, H^+ and e^- produce reversible redox reactions, which control the conductivity and preserve the continuity of current across the interface without incidences.

Experimental

As depicted in the inset (a) of Fig. 1, a pair of Pt-electrodes and sputtered WO_3 and IrO_2 films were fabricated by using procedures described earlier.[8] Initially, a n-type 4-inch silicon substrate was cleaned with piranha solution (H_2SO_4 :H_2O_2 = 3:1) at 80°C for 20 min, followed by a DI-water rinse for 5 min and a dry N_2-flow purge. A SiO_2 layer (2000 Å) was deposited on the Si-substrate, followed by a LPCVD deposition (Si_3N_4 4000 Å). Next, 50 Å of chromium, followed by 1200 Å of Pt, was deposited on the Si_3N_4 film by a dual electron-beam evaporator and then patterned using a lift-off technique. The Pt-electrodes, separated by distance of 400 μm, were 600 μm wide and 1400 μm long. An RF-sputtering of the WO_3 target (99.99%, 4.77 g/cm^3) was carried out (35% O_2 in Ar) at a pressure of 45 mTorr and temperature of 100°C. After acetone clean, DI-water rinse and a dry N_2 gas purge, annealing process was achieved in a high-temperature (350°C) chamber at a pressure of 15 mTorr for 3.5 hr. The IrO_2 film was fabricated using an Iridium target (99.95%, 21.8 g/cm^3) and carried out at a pressure of 60 mTorr (50% O_2 in Ar) by a sputtering approach. Next, the Al_2O_3 film was fabricated using sputtering of an Al_2O_3 target (99.99%, 3.26 g/cm^3) and carried out at a pressure of 70 mTorr (50% O_2 in Ar) for 1.5 hr using a magnetron sputtering. All sputtering films were patterned by a lift-off technique. The thickness of WO_3, IrO_2, and Al_2O_3 films were 3000 Å, 1200 Å, and 250 Å, respectively, as measured using an alpha-step stylus instrument. Electrical contacts to individual Pt-electrodes were made using Ag-epoxy (FA-705, Fujikura Kasei). An encapsulation process followed, using insulating epoxy (K-22 Conap) to prevent short circuits, which was cured to become solid in an oven at 150°C for 30 min. The reaction region was surrounded and encapsulated by the insulating epoxy resin.

Before measurements commenced, a two-point calibration was processed using three known pH-calibration buffers (pH = 4, 7 and 10) and then pH-meter (SA-250, Orion) indications were corrected accordingly. The sample solutions were prepared using Britton-Robinson buffer solution, which consisted of 0.04M H_3BO_3, 0.04M H_3PO_4 and 0.04M CH_3COOH; eleven samples were titrated to the desired pH-value (from pH = 2 to 12) with 0.2 M KOH pseudo-randomly dropping. The device packaged into an integral flow cell was tilted 30° to allow exposure to solutions and was implemented to be a smooth flow path of the solution supplied. The sample solutions were supplied by the flow rates from a microprocessor-controlled peristaltic pump (Rainin RP-1) with 3 rpm and Tygon tube (3.18 mm diameter) connected with a glass tube. The pH-sensor was connected to a Keithley 617 source-measure unit via Keithley Cable 6011 wires as simplified in the inset (b) and (c) of Fig. 1. All potentials measured were relative to Hg/Hg_2Cl_2 (z11311-5, Aldrich) electrode. A GPIB (General Purpose Interface Bus) and a LabView-based program were employed for recording the experimental results.

Results and Discussion

This study was inspired by the earlier work, as on a bicarbonate (HCO_3^-)-doped, PVA (polyvinyl alcohol), solid-polymer matrix interfaced with the contact of WO_3 and IrO_2, which can respond to CO_2 gas via detection of H^+.[8] Based on pH-sensitive properties of WO_3 and IrO_2, the device will interact with H^+ in redox reactions.[9] Both WO_3 and IrO_2-reductions to conducting $H_\chi WO_3$ ($0 < \chi < 0.5$) and insulating $Ir(OH)_3$, respectively (reactions 1 and 2). These redox transformations result from the insertion of ionic species into the oxides, which can produce large conductance changes.[10,11] $IrO_2 \cdot H_2O$ and $Ir(OH)_3$ are solid-state materials, and their concentrations will be easily affected as they are oxided or redox by other materials.

$$WO_3 \text{ (insulator)} + \chi H^+ + \chi e^- \leftrightarrow H_\chi WO_3 \text{ (conductor)} \quad [1]$$

$$IrO_2 \cdot H_2O \text{ (conductor)} + H^+ + e^- \leftrightarrow Ir(OH)_3 \text{ (insulator)} \quad [2]$$

In Fig. 1, the current-voltage characteristics of the sensor were measured by a Keithley 236 source-measure unit. The diode undergoes

[z]E-mail: lmkuo.ep97g@nctu.edu.tw

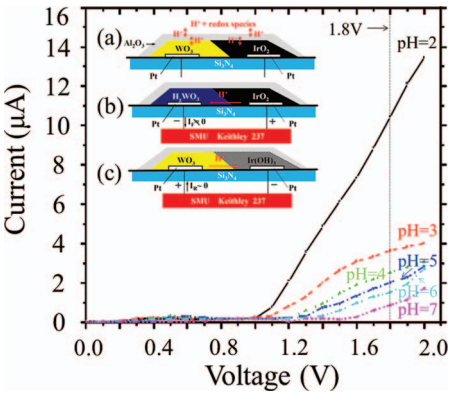

Figure 1. The I-V Characteristics of our pH sensor under the forward bias with different pH-levels (pH = 2 to 7). (The inset (a), (b) and (c) show no-biased, forward-biased and reverse-biased diode based on the contact WO_3 and IrO_2 on Si under H^+ modulation).

a current increase in the forward direction as the pH-level is decreased. This behavior is consistent with the WO_3 and IrO_2 redox processes (reactions 1 and 2) and electrochemical potentials in both reactions become more positive in more acidic environments. The inset (b) and (c) in Fig. 1 illustrates the forward and reverse-biased diodes under H^+ modulation schematically. Invoking proton-electron double injection, WO_3 film was reduced to $H_\chi WO_3$ by the combination of electrons from the Pt-electrode and H^+ through the Al_2O_3 layer. Under a fixed bias of 1.8 V applied to the sensor, the current response versus pH-level change with an interval step of pH = 1 and from pH = 2 to 12,

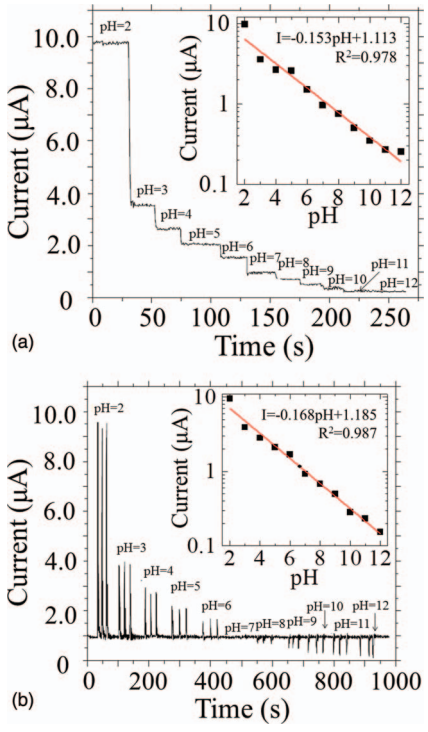

Figure 2. (a) Current response versus pH-level change with an interval step of pH = 1 and from pH = 2 to 12. (Inset shows a linear fitting slope of logarithmic current versus different pH-level) (b) Pulse current response of the pH sensor versus pH-level change with the interval step of pH = 1 from pH = 2 to 12. (Inset shows a linear fitting slope of logarithmic current and different pH-level according to the average of three peak-current values) The response and recovery time are defined as 20% to 80% of the rising and falling edge in the transient response.

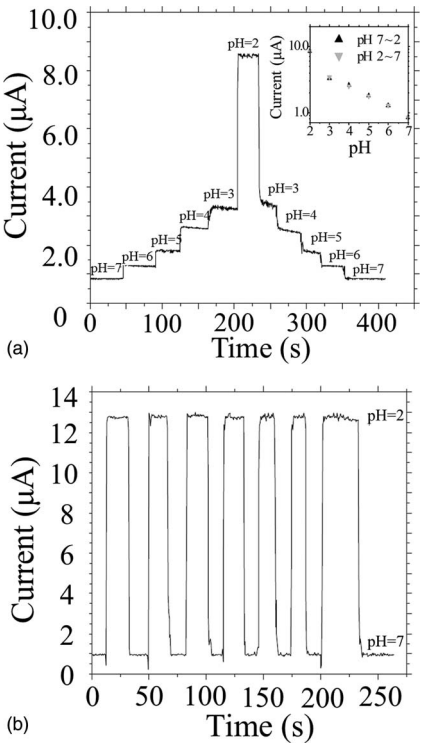

Figure 3. (a) Stepwise current response of our pH sensor to different pH-level from pH = 2 to 7 and pH = 7 to 2. (b) Stepwise Current response of our pH sensor from pH = 2 to 7 and pH = 7 to 2 after switching with seven times.

as shown in Fig. 2a. The repeatability experiments were measured by three sequential droplets (1mL per droplet) for each pH value. The next dropping followed up after the current value of the previous dropping was attenuated and settled down, as shown in Fig. 2b. Three peak-current values in each pH-level are almost identical. The maximum ramp-up time is 1.5 sec and the recovery time is within 7 sec. The rising and falling time in the transient response are longer than others due to more H^+ in the solution will produce a thicker Helmhotz layer generated at the interface of the encapsulation layer and the diode.[12] The larger parasitic capacitance and resistance will be produce at the interface and the response time will be increased.

In Fig. 3a, the reproducibility of the pH-sensor was shown by the measurement of a stepwise increase and decrease between pH = 2 and 7. The duration for each condition were applied about 40 sec. From Fig. 3a, it is apparent that the sensor provides excellent reversibility in the dynamic response transients. The discrepancy between the forward (pH = 7 to 2) and backward (pH = 2 to 7) sequential measurements is as slight as negligible as shown in the inset of Fig. 3a. Several switches between pH = 2 and pH = 7 performs the reliable repeatability according the identical current values as shown in Fig. 3b. The hysteresis is commonly existed in metal-oxide films for the pH-sensing, and substantially depends on the operation in each experiment, the material quality and fabrication batches.[13] The potential drift of the hysteresis may be due to dynamic processes of ion neutralization called the effect of liquid junction potential.[14]

N_2 and O_2 gas were supplied in buffer solutions to prepare N_2 and O_2-abundant solutions, which may produce voltage fluctuations caused by some factors such as the oxidation states from incomplete oxidation and surface ion exchanges in $IrO_{2-\chi}$ film.[13] These non-ideal effects will generate surface charge-variations with time and the new equilibrium after each reaction.[15] In Fig. 4, the current response shows slight and negligible deviations according the comparison of N_2 and O_2-abundant solutions of pH = 2, 6 and 12 at room temperature. The notches in Fig. 4 were due to the air bubble used for the separation during the solution rotations in the experiment.

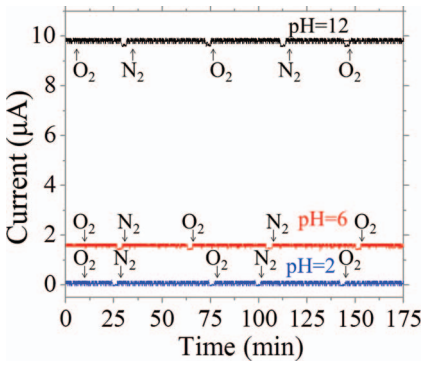

Figure 4. Current response of our pH-sensor measured in N_2 and O_2 saturated solution. (pH = 2, 6, and 12)

Conclusions

In conclusion, a new pH-sensor made of a sputtering WO_3/IrO_2 diode sealed thoroughly by an Al_2O_3 encapsulation layer in response to the presence of hydrogen-ions (H^+) has been investigated. With the inherently robust immunity to O_2 perturbation, the encapsulation layer of Al_2O_3 film fully covered the WO_3/IrO_2 diode and prevented $IrO_2/Ir[OH]_3$ from being increased as oxided by O_2. By proton-electron double injection, H^+ and e^- produce redox reactions, which control conductivity. The solid-state sensor exhibits good stability, repeatability, and reversibility in various pH environments ranging from 2 to 12 at room temperature. This chemically sensitive device will be useful as a basis for construction of durable microsensors for tracing the acidity in environmental and biological applications.

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