Electrical Characteristics of Glucose-Sensitive Diode Arrays Based on WO_3 and IrO_2 for Microsensor Applications

2003 Jpn. J. Appl. Phys. 42 L1337

(http://iopscience.iop.org/1347-4065/42/11A/L1337)

Jpn. J. Appl. Phys. Vol. 42 (2003) pp. L 1337–L 1339
Part 2, No. 11A, 1 November 2003

Electrical Characteristics of Glucose-Sensitive Diode Arrays Based on WO_3 and IrO_2 for Microsensor Applications

Shuchi CHAO

Department of Electrophysics, National Chiao-Tung University, Hsin-Chu, Taiwan, R.O.C.

(Received August 29, 2003; accepted September 9, 2003; published October 22, 2003)

Arrays based on the contacts of sputtered WO_3 and IrO_2 that are covered by a glucose-oxidase-containing polymer exhibit reversible and reproducible glucose-dependent, diodelike current rectification. The glucose concentration as a function of current in the forward direction can be spatially resolved. These chemical-sensitive diode arrays are useful as a basis of construction of durable microsensors for tracing the concentration gradient of biological molecules, as in food freshness sensing. [DOI: 10.1143/JJAP.42.L1337]

KEYWORDS: chemical-sensitive diode array, microsensor, glucose, WO_3, IrO_2

This article presents a new diode array as a basis of construction of durable microsensors that are operable in liquids at room temperature. The device is based on pH-sensitive WO_3 and IrO_2, which interact with H^+ in reversible redox reactions,[1,2)]

$$WO_3\ \text{(bleached)} + xH^+ + xe^- \leftrightarrow H_xWO_3\ \text{(colored), and} \quad (1)$$

$$IrO_2{\cdot}(H_2O)\ \text{(colored)} + H^+ + e^- \leftrightarrow Ir(OH)_3\ \text{(bleached).} \quad (2)$$

Both WO_3 and IrO_2 reductions to the conducting H_xWO_3 and insulating $Ir(OH)_3$ occur at more positive electrochemical potentials in acidic media over a pH range between $\sim$2 and 12[3,4)] (reactions (1) and (2)). These redox transformations arise due to the insertion of ionic species into the oxides, which can produce large conductance changes.[4,5)] The present work is inspired by earlier discoveries in this laboratory such as that of a bicarbonate (HCO_3^-)-doped, polyvinyl alcohol (PVA) solid polymer matrix interfaced with the contact of WO_3 and IrO_2 that can respond to CO_2 in terms of rectification current across closely spaced microelectrodes at 1 atm and room temperature.[6)] As shown in Fig. 1, both oxides become conducting under positive bias in the forward direction and insulating under negative bias in the reverse direction. However, the device function cannot be fully explained by treating the oxides simply as variable series resistors. Since H_xWO_3/WO_3 is cathodically electroactive whereas $Ir(OH)_3/IrO_2$ is anodically electroactive, the transport of charge across the WO_3/IrO_2 interface is allowed only in the forward direction and disallowed in the opposite direction. The current growth in the forward direction can occur readily via the thermodynamically favored reduction of IrO_2 by the reduced H_xWO_3. In fact, the attenuation of current in the reverse direction is more an indication that the oxidation of $Ir(OH)_3$ by the oxidized WO_3 is thermodynamically not feasible. In our view, this type of rectification governed by thermodynamic free energies is the major advantage for constructing such diodes based on the contacts of WO_3 and IrO_2. The devices will be durable since they are made of robust materials. Unlike previous microsensors based on conventional or organic diodes,[7,8)] their electrical functions in gases and liquids are not susceptible to environmental variabilities arising from interfacial or material instability. Exploratory experiments in this area have led to our results that the electrical contact of solid WO_3 and IrO_2 films, sputtered on adjacent Pt electrodes and covered by an insoluble glucose oxidase enzyme layer, can be used to generate diodelike current-voltage outputs that respond to glucose concentration. By simply connecting the contacts of WO_3 and IrO_2 in series, a glucose-sensitive diode array can be constructed, as shown in Fig. 1.

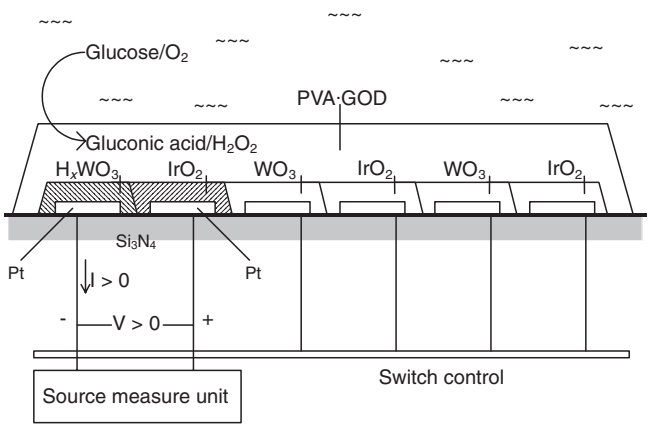

Fig. 1. Schematic of the 5-diode linear array and one forward-biased diode based on the contact of WO_3 and IrO_2 on Si under glucose modulation in H_2O.

The Pt pad electrodes, and sputtered WO_3 and IrO_2 films in Fig. 1 are fabricated and characterized using similar procedures as described earlier.[6,9,10)] The Pt electrodes are typically 600 μm wide and 1,400 μm long (excluding the lead portion) and are separated by a distance of 400 μm. The prepared WO_3 (360 nm thick) and IrO_2 (90 nm thick) films are robust and adhere strongly to the Pt surface. No difficulty such as peeling has been encountered throughout the course of our experiment. After the deposition of the oxide films, the electrical contact of individual Pt electrodes is made using Ag epoxy, which is later encapsulated using insulating epoxy. As shown in Fig. 1, the next process is covering the entire device active area by the insolubilized polyvinyl alcohol (PVA, average molecular weight $= 1.33 \times 10^5$ g/mole, Polysciences) containing the immobilized glucose oxidase (GOD, Type VII from *Aspergillus niger*, Sigma). This newly developed enzyme layer, PVA·GOD, is used for creating a glucose-modulated pH environment for the diodes. The layer is generated in two sequential steps, as shown in Fig. 2. The first step involves the photoinitiated crosslinking of PVA to make the polymer insoluble. The

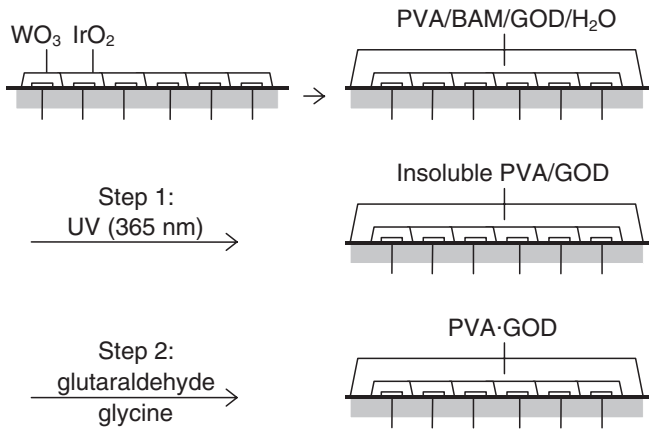

Fig. 2. Preparation of enzyme layer on glucose-sensitive diode array by PVA insolubilization and GOD immobilization.

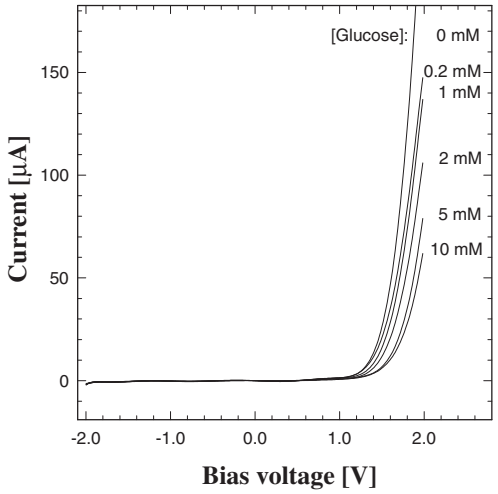

Fig. 3. Typical diode current-voltage characteristics under glucose modulation in 10 mM phosphate solution at pH 7.0.

enzyme GOD (1,200 units) and bovine serum albumin (BSA, RIA grade, Fraction V, Sigma, 10 mg) are dissolved in a solution containing the photoinitiator 2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone (BAM, Aldrich, 15 mg), PVA (20 mg) and H_2O (0.2 ml). The photopolymer solution (100 μl) is syringed onto the diode array and exposed to UV irradiation (365 nm, 100 W, 90 s). The second step is the immobilization of GOD to prevent the enzyme from detaching from the polymer matrix. This involves the preparation of enzyme derivatives through the use of the bifunctional reagent glutaraldehyde in the presence of protein albumin.[11] The diode array is immersed in aqueous glutaraldehyde solution (25%, room temperature) for 5 min. After washing with deionized H_2O, the array is immersed in 0.1 M glycine for 15 min to terminate the immobilization reaction by glutaraldehyde. The prepared PVA·GOD forms light-yellow films that are highly adhesive to WO_3 and IrO_2. No peeling of the films has been encountered throughout the electrical experiments. Enzyme layers insolubilized separately with the same procedure on glass slides have been immersed in H_2O at 90°C without any visible sign of disintegration. No other supporting electrolyte has been added since the enzyme layer functions only as a source or sink for H^+, and not as an electrolyte to carry ionic current. The current-voltage measurement sweeps are generated using a Keithley 236 source-measure unit (Fig. 1). The diode arrays packaged into integral flow cells are used, as reported earlier,[12] to allow exposure to glucose solutions. The concentration conditions of glucose in weakly buffered carrier solution (10 mM potassium phosphate, pH 7.0) are generated by proportioning the flow rates of two microprocessor-controlled peristaltic pumps (Rainin RP-1).

The glucose-dependent, current-voltage characteristics of diodes on the array based on WO_3 and IrO_2 are shown in Fig. 3. The glucose creates a pH-regulated environment for the diodes (Fig. 1), through its pH-lowering effect.[13] It equilibrates in the enzyme-containing polymer PVA·GOD according to the catalytic reaction[14]

$$\text{Glucose} + O_2 \xrightarrow{\text{GOD}} \text{Gluconic acid} + H_2O_2. \quad (3)$$

The pH-lowering effect of glucose in PVA·GOD is due to the gluconic acid and possibly the H^+-releasing H_2O_2 oxidation at Pt electrode[14] via microchannels[15] that exist in the IrO_2 material (Fig. 1). From the results of the glucose-dependent experiment in Fig. 3, diodes based on WO_3 and IrO_2 undergo a current decrease in the forward direction when the glucose concentration is increased between 0.2 and 10 mM in phosphate solution. This behavior is consistent with the WO_3 and IrO_2 redox processes (reactions (1) and (2)). The electrochemical potentials in both reactions become more positive in more acidic environments. This shift can be considered to result from the pH-dependent changes in the potential drop across the Helmholtz layer at the surface of both oxides, as stated earlier.[9,10] On the potential scale, the shifting of redox potentials towards the positive region renders reductions more favorable than oxidations under a fixed driving force. When the bias voltage is unchanged, the current passing through a less fully oxidized IrO_2 in series with a more fully reduced H_xWO_3 in the forward direction still shows a loss due to the current-limiting effect exerted by the higher resistance (Fig. 3). The current loss in the forward direction is also confirmed by the observed progressive coloration in H_xWO_3 and discoloration in IrO_2 as the pH is lowered in PVA·GOD by glucose solution under a fixed positive bias. The likely H_2O_2 oxidation[14] at the Pt electrode (Fig. 1) may have also contributed partially to the current response in Fig. 3 by lessening the current decrease.

The diodes on our new array are markedly durable and reproducible. Repeated voltage sweeps under each glucose concentration in Fig. 3 give almost identical current-voltage signals. Neither the rectification behavior nor the current amplitudes show signs of degradation. Under a fixed 1.6 V bias (Fig. 3), switching the solution between 0.2 and 10 mM glucose in the phosphate solution turns the diodes on the array to the "on" and "off" states with ~25 μA and only ~10 μA in the forward direction, respectively. The current switchings are reversible and reproducible and can be carried out for all diodes on the array without significant deterioration for >5 h. As shown in Fig. 3, the diodes on the array have a range valid for glucose concentrations between 0.2 and 10 mM. Separate experiments show that the diodes can actually respond to glucose from 30 mM down to the 0.02 mM concentration range with an acceptable signal-to-

noise ratio. The range valid for glucose concentration is found to be a function of the pH of the carrier solution used. Glucose is capable of inducing an even larger pH drop in PVA·GOD when the phosphate solution used is buffered to be more basic at pH 7.5. Through proper storage[13] and intermittent use, the GOD on the diode array (Fig. 1) has shown activity after a period of >4 weeks.

The five-diode linear array (Fig. 1) has been characterized by allowing sufficient time for equilibration with glucose concentrations for each diode individually. The diodes are sequentially sampled using a simple switch control and the forward current changes vs time are recorded in Fig. 4. All five diodes have shown consistent forward current changes that can equilibrate with glucose concentrations. The time required for reaching equilibrium is ~3 min, as shown in Fig. 4. It has also been determined that the glucose-induced current change in the forward direction is proportional to the logarithm of the glucose concentration to which PVA·GOD is exposed (Fig. 5). Since the diodes are positioned 1,000 μm apart, as shown in Fig. 1, the linear array can offer a one-dimensional spatial resolution of 1,000 μm for glucose. It is designed for tracing the concentration gradient of biological molecules, as in sensing the freshness of food materials.[16] Spoilage of food products by microorganisms in the air normally progresses from the surface to the inside, consuming or producing biological molecules on their way. Knowledge on the bulk-to-surface concentration gradient of such biological molecules can provide information on food freshness.[16] This work reveals that oxide-based microsensors are durable and that, in principle, many oxides with widely varying properties can be used to fabricate sensing devices with special electrical characteristics. Work is already under way in this laboratory to incorporate the diode array in other chemical-sensitive microsensor systems.

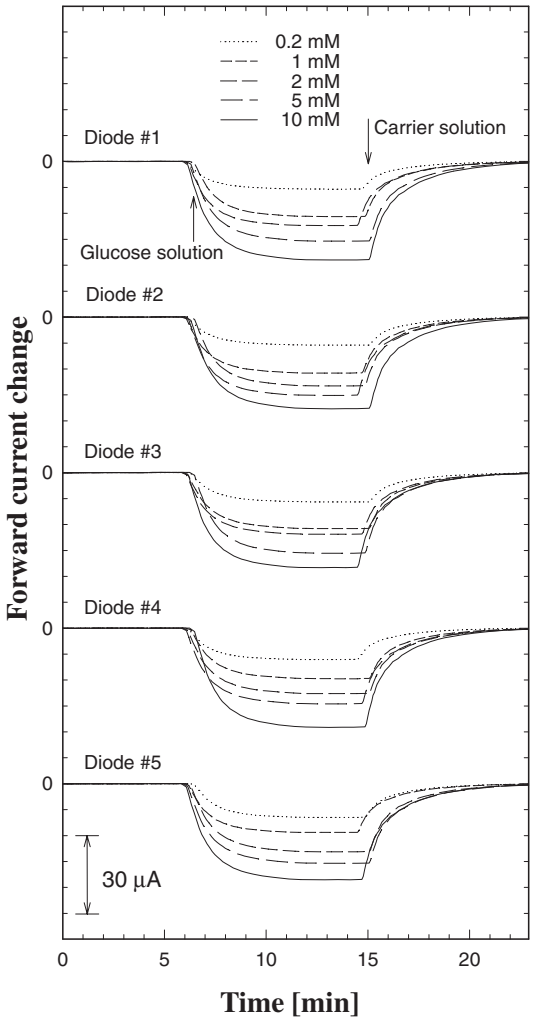

Fig. 4. Typical current changes in the forward direction (1.6 V bias) induced by glucose concentrations in 10 mM phosphate solution at pH 7.0.

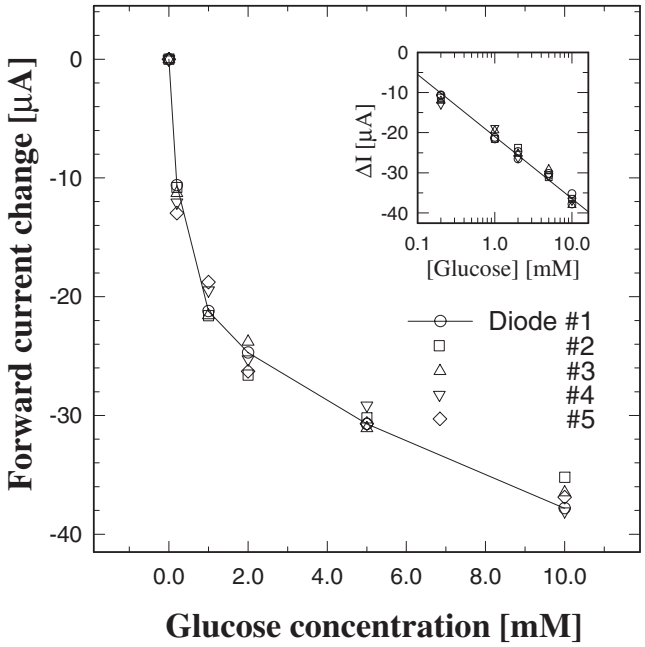

Fig. 5. Current change in Fig. 4 as a function of glucose concentration.

We thank the Nano Device Laboratory at National Chiao-Tung University for assistance in the Si fabrication process. The National Science Council of the Republic of China under contract NSC91-2215-E009-061 sponsored this work.

1) M. O. Schloh, N. Leventis and M. S. Wrighton: J. Appl. Phys. **66** (1989) 965.
2) B. Scrosati: *Applications of Electroactive Polymers*, ed. B. Scrosati (Chapman & Hall, London, 1993) p. 256.
3) M. J. Natan, T. E. Mallouk and M. S. Wrighton: J. Phys. Chem. **91** (1987) 648.
4) K. Pásztor, A. Sekiguchi, N. Shimo, N. Kitamura and H. Masuhara: Sens. & Actuat. B **12** (1993) 231.
5) M. J. Natan and M. S. Wrighton: Prog. Inorg. Chem. **37** (1989) 391.
6) S. Chao: Jpn. J. Appl. Phys. **37** (1998) L245.
7) J. W. Gardner: *Microsensors, Principles and Applications* (John Wiley, Chichester, 1994) p. 235.
8) N. Leventis, M. O. Schloh, M. J. Natan, J. J. Hickman and M. S. Wrighton: Chem. Mater. **2** (1990) 568.
9) S. Chao: Jpn. J. Appl. Phys. **32** (1993) L1346.
10) J. C. Lue and S. Chao: Jpn. J. Appl. Phys. **36** (1997) 2292.
11) P. W. Carr and L. D. Bowers: *Immobilized Enzymes in Analytical and Clinical Chemistry* (J. Wiley & Sons, New York, 1980) p. 163.
12) S. Chao: Meas. Sci. Technol. **7** (1996) 737.
13) Y. Hanazato, M. Nakako and S. Shiono: IEEE Trans. Electron Devices **33** (1986) 47.
14) B. R. Eggins: *Biosensors: an Introduction* (Wiley & Teubner, Chichester, 1996) p. 160.
15) S. Hackwood, A. H. Dayem and G. Beni: Phys. Rev. B **26** (1982) 471.
16) Leatherhead Food Research Association: Sensor Rev. **9** (1989) 15.