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Electrical Characteristics of CO₂-Sensitive Diode Based on WO₃ and IrO₂ for Microsensor Applications

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We present a new diode as a basis of construction for fabricating durable microsensors that are operable in gases and liquids at 1 atm and room temperature. The device is based on pH-sensitive WO₃ and IrO₂, which interact with H⁺ in the reversible redox reactions, \[ \text{WO}_3(\text{bleached}) + x\text{H}^+ + xe^- \leftrightarrow \text{H}_x\text{WO}_3(\text{colored}), \quad \text{and} \]
\[ \text{IrO}_2 \cdot (\text{H}_2\text{O})(\text{colored}) + \text{H}^+ + e^- \leftrightarrow \text{Ir(OH)}_3(\text{bleached}). \]

Both WO₃ and IrO₂ reductions to the conducting HₓWO₃ and insulating Ir(OH)₃ occur at more positive electrochemical potentials in acidic media over a range of pH values between ~2-12. \(^1\) \(^2\) These redox transformations arise due to the insertion of ionic species into the oxides, which can produce large conductance changes. \(^3\) \(^4\) \(^5\) The present work is inspired by the earlier discoveries in this laboratory that a bicarbonate (HCO₃⁻)-containing polymer exhibit reversible and reproducible CO₂-dependent, diodelike current rectification at 1 atm and room temperature. The gain or loss of current in the forward direction as a function of CO₂ concentration is found to be tunable by controlling the thickness ratio of the WO₃ and IrO₂ films. The rectification mechanism is uniquely governed by the thermodynamic free energies; this is the key to the durability previously not attainable using conventional diodes in microsensor applications. These diodes are useful as a basis of construction for durable microsensors operating in gases or liquids.

KEYWORDS: diode, microsensor, CO₂, rectification, sputtered WO₃, IrO₂

The Pt-pad electrodes in Fig. 1 are fabricated using similar procedures as described earlier. \(^6\) The electrodes are typically 290 μm wide and 580 μm long (excluding the lead portion) and are separated by a distance of 480 μm. To avoid annealing the IrO₂ due to heating by subsequent WO₃ deposition, sputtering of the WO₃ target (99.99%, Pure Tech) at radiofrequency is carried out first under 20% O₂ in Ar at a total pressure of 90 mTorr, in the same apparatus as used before. \(^7\) A Si wafer with micromachined V-grooves is used as...
the deposition mask. The mask and devices on the wafer are pressed onto a heated substrate platen at 676 K. The WO₃ films exhibit broad cyclic voltammograms in aqueous 1.0 M HClO₄ over the potential range of 0.3 to −0.3 V vs a saturated calomel electrode, as reported previously. Characterization of the films on indium-tin oxide glass shows electrochromism in the visible region and a wide range of absorption change under potential cycling in aqueous 1.0 M H₂SO₄. The change is ≈15–85% in transmittance at 650 nm, near the wavelength of maximum difference in the absorption band. The process for derivatizing the Pt electrode with the amorphous IrO₂ film, next to the WO₃ film (Fig. 1), by the reactive sputtering method and the characterizations have been described earlier. The prepared WO₃ and IrO₂ 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 deposition of the oxide films, electrical contact of individual Pt electrodes is made using Ag epoxy, which is later encapsulated using insulating epoxy. Next, the whole device active area is covered with the polymer blend, polyvinyl alcohol (PVA, average molecular weight=1.33 × 10⁵ g/mol) with potassium bicarbonate (Fig. 1). The polymer blend, PVA-KHCO₃, used for creating a CO₂-modulated pH environment for the diodes, is ready for use as an aqueous solution with 0.06 mM of PVA and 2 mM of KHCO₃. No other supporting electrolyte has been added since the polymer blend functions only as a source or sink for H⁺, and not as an electrolyte to carry ionic current. After evaporation of H₂O at 35°C for 24 h, the cured polymer blends form transparent films that are highly adhesive to WO₃ and IrO₂. No peeling or fogging of the films has been encountered throughout the electrical and light transmission experiments. The current-voltage sweeps are generated using a Keithley 236 source-measure unit (Fig. 1). The relative transmittance through the optical-quality oxide films is measured by reflection off the Pt surfaces on which the films are deposited, Fig. 1. Since colored IrO₂ films show featureless transmission in the visible region and colored H₂WO₃ films show the optimal absorption difference near 650 nm, a stabilized He–Ne laser (632.8 nm) is used as the light source. Optical microscopy reveals that uniform bleaching and coloring can occur in each of the oxide films on Pt. As shown in Fig. 1, each film has only one underlying Pt electrode. This forces the potential drop to be confined to the WO₃/IrO₂ interface, leaving the individual films on Pt approximately at equipotential and of the same color. Light is chopped and split for simultaneous focusing onto one Pt surface within the diode sample (Fig. 1) and a second Pt surface that is oxidic within a specially made “diode” reference blank. The reflected beams are each collected by a detector (UDT 10DP) whose photocurrents are ratioed by lock-in amplifiers (Stanford 830) to obtain the relative transmittance as a function of the bias voltage. When the CO₂ atmospheres are needed, the diodes packaged into integral flow cells are used, as earlier. The %CO₂ concentration in N₂ and the %H₂O saturation conditions are generated as described earlier.

The current-voltage characteristic of diodes based on WO₃ and IrO₂ are shown in Figs. 2 and 3. The CO₂ gas creates a pH-regulated environment for the diodes (Fig. 1), through its pH-lowering effect, as previously reported. It equilibrates in the bicarbonate-blended polymer PVA-KHCO₃ according to the dissociative reaction

\[
(CO₂ + H₂O \leftrightarrow H₂CO₃ ↔ H⁺ + HCO₃⁻ ↔ 2H⁺ + CO₃^{2⁻}).
\] (3)

It has been established in this laboratory that the pH in PVA-KHCO₃ can be reversibly modulated using CO₂ gas. It has also been determined that this pH is proportional to the negative logarithm of the concentration of CO₂, -log[CO₂], to which PVA-KHCO₃ is exposed. Accordingly, changing -log[CO₂] in the atmosphere in Fig. 1 is, in effect, equivalent to linearly shifting the pH in the PVA-KHCO₃ coating of the diode. As the results of the CO₂-dependent experiment in Fig. 3 show, diodes based on WO₃ and IrO₂ undergo a cur-
rent decrease in the forward direction when the CO₂ concentration is increased within the range of 1–100% in N₂. In the inset of Fig. 3, the voltage at which an arbitrary small current (1.4 µA) in the forward direction is derived, V_SC, is plotted vs -log[CO₂] for each of the CO₂-dependent I/V curves. The observed proportionality reveals that V_SC of the diode is also proportional to the pH in the diode environment. These results are consistent with the WO₃ and IrO₂ 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. On the potential scale, the shifting of redox potentials towards the positive region renders reductions more favorable than oxidations under fixed driving force. When the bias voltage is unchanged, the current passing through a less fully oxidized IrO₂ in series with a more fully reduced H₂WO₃ in the forward direction still shows a loss due to the current-limiting effect exerted by the higher resistance (Fig. 3). The fact that the experimentally determined pH sensitivity for our IrO₂ (~58 mV/pH) in aqueous solutions is higher than that for our WO₃ (~52 to 54 mV/pH), is relevant and should be noted. This means that up to ~5 mV/pH positive displacement of IrO₂ potential in excess of that of WO₃ can be expected in the more acidic diode environments created by CO₂, that should further contribute to the current loss in the forward direction.

In Fig. 2, the light transmission through the oxides is measured as direct evidence of the CO₂ sensitivity observed in Fig. 3. As shown by the relative transmittance changes in Fig. 2, Ir(OH)₃ only begins to conduct and turn colored last at a more positive bias than WO₃, which is approximately the threshold voltage for initiating current in the forward direction. The threshold voltages, or currents, are therefore “pinned” by the potential for oxidizing Ir(OH)₃ as the pH is varied in the PVA-KHCO₃ by CO₂ gas. The current loss in Fig. 3 in the forward direction is also confirmed by the observed progressive coloration in H₂WO₃ and discoloration in IrO₂ as the pH is lowered in PVA-KHCO₃ by CO₂ gas under a fixed positive bias.

Our new diodes are markedly durable and reproducible. Repeated voltage sweeps under each CO₂ concentration in Fig. 3 give almost identical current-voltage signals. Neither the threshold voltages nor the currents show signs of degradation. Under a fixed 1.2 V bias, switching the atmosphere between 1% and 100% CO₂ in N₂ turns the diodes to the “on” and “off” states with 4 µA and only 1 µA in the forward direction, respectively. The current sweepings are reversible and reproducible without significant deterioration for >5 h. Since the rectification in Fig. 2 is thermodynamic in nature, direct physical contacts between the WO₃ and IrO₂ are not essential, as long as a hard-wire link between the films can be established. Separate experiments show that the WO₃ and IrO₂ films, when contacted via a third Pt electrode in between, can still be used to generate the same rectification as in Fig. 2. Our results also show that geometrical areas involved in the direct overlap of WO₃ and IrO₂ affect the current magnitude shown in Fig. 2 but the overall rectification is not changed.

During the course of our experiments, efforts directed at achieving maximum conductance in each material reveal that thicker H₂WO₃ films are necessary to properly offset the conductivity of metallic IrO₂ in the diodes. For this reason, 360-nm-thick WO₃ and only 90-nm-thick IrO₂ are normally deposited on Pt (Fig. 1) to obtain almost equal conductance in the reduced H₂WO₃ and oxidized IrO₂. However, when we tested WO₃:IrO₂ thickness ratios that are further unbalanced, reaching about the 720-nm-thick WO₃ to 60-nm-thick IrO₂ mark, instead of the previous current decrease shown in Fig. 3, a current gain in the forward direction under high CO₂ concentrations is observed. The light transmission experiments also indicate a change in the previous order of coloring in Fig. 2. Finally, WO₃ begins to conduct and becomes colored at a more positive bias than Ir(OH)₃, which, as before, is approximately the threshold voltage for initiating current in the forward direction. Apparently, the thin Ir(OH)₃ with much less redox material is now easily completely oxidized and is conducting, while the thick WO₃ is still fractionally reduced and is not conducting. As H⁺ becomes more abundant under CO₂, the current change in the forward direction changes to a gain since more of the WO₃ is reduced. This can work to our benefit since it means that choices in the derived device sensitivity and in switching the device on or off in the forward direction using CO₂ gas, can be made by tuning the thickness of the oxide films. The relation between conductivity and film thickness for both WO₃ and IrO₂ are, therefore, critical to the rational design and electrical modulation of diode systems.

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 this diode in microsensors. Preliminary results show that the blended layer of PVA in Fig. 1 and similar polymer blends can sense gas molecules such as CO₂, SO₂ and NH₃. The diode can also function with an insoluble enzyme layer to sense glucose in biological fluids.

Acknowledgments

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