

## Electrical Characteristics of CO<sub>2</sub>-Sensitive Diode Based on WO<sub>3</sub> and IrO<sub>2</sub> for Microsensor Applications

This content has been downloaded from IOPscience. Please scroll down to see the full text.

1998 Jpn. J. Appl. Phys. 37 L245

(<http://iopscience.iop.org/1347-4065/37/2B/L245>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 140.113.38.11

This content was downloaded on 28/04/2014 at 12:07

Please note that [terms and conditions apply](#).

## Electrical Characteristics of CO<sub>2</sub>-Sensitive Diode Based on WO<sub>3</sub> and IrO<sub>2</sub> for Microsensor Applications

Shuchi CHAO

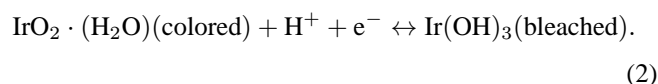
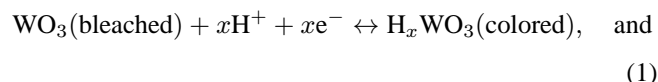
Department of Electrophysics, National Chiao-Tung University, Hsin-Chu, Taiwan, ROC

(Received October 22, 1997; accepted for publication December 26, 1997)

Devices based on the contact of sputtered WO<sub>3</sub> and IrO<sub>2</sub> that are covered by an HCO<sub>3</sub><sup>-</sup>-containing polymer exhibit reversible and reproducible CO<sub>2</sub>-dependent, diodelike current rectification at 1 atm and room temperature. The gain or loss of current in the forward direction as a function of CO<sub>2</sub> concentration is found to be tunable by controlling the thickness ratio of the WO<sub>3</sub> and IrO<sub>2</sub> 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, CO<sub>2</sub>, rectification, sputtered WO<sub>3</sub>, IrO<sub>2</sub>

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 WO<sub>3</sub> and IrO<sub>2</sub>, which interact with H<sup>+</sup> in the reversible redox reactions,<sup>1,2)</sup>



Both WO<sub>3</sub> and IrO<sub>2</sub> reductions to the conducting H<sub>x</sub>WO<sub>3</sub> and insulating Ir(OH)<sub>3</sub> occur at more positive electrochemical potentials in acidic media over a range of pH values between ~2–12<sup>3,4)</sup> (reactions (1) and (2)). These redox transformations arise due to the insertion of ionic species into the oxides, which can produce large conductance changes.<sup>4,5)</sup> The present work is inspired by the earlier discoveries in this laboratory that a bicarbonate (HCO<sub>3</sub><sup>-</sup>)-doped, polyvinyl alcohol (PVA) solid polymer matrix interfaced with WO<sub>3</sub> or IrO<sub>2</sub>, can respond to CO<sub>2</sub> in terms of resistance or potential across closely spaced microelectrodes at 1 atm and room temperature.<sup>6,7)</sup> Despite the advantages of such relatively simple chemical-sensitive resistors and potentiometers, practical use is less attractive due to the lack of a built-in current “turn-on” capacity commonly found in diode and transistor-based microsensors.<sup>8)</sup> However, WO<sub>3</sub> and IrO<sub>2</sub> are known to be complementary cathodic and anodic electrochromic materials,<sup>9)</sup> and have been used to demonstrate optical attenuation. By connecting WO<sub>3</sub> and IrO<sub>2</sub> in series, 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<sub>x</sub>WO<sub>3</sub>/WO<sub>3</sub> is cathodically electroactive whereas Ir(OH)<sub>3</sub>/IrO<sub>2</sub> is anodically electroactive, the transport of charge across the WO<sub>3</sub>/IrO<sub>2</sub> interface is allowed only in the forward direction and forbidden in the opposite direction. The current growth in the forward direction can occur readily via the thermodynamically favored reduction of IrO<sub>2</sub> by the reduced H<sub>x</sub>WO<sub>3</sub>. In fact, the attenuation of current in the reverse direction is more an indication that the oxidation of Ir(OH)<sub>3</sub> by the oxidized WO<sub>3</sub> 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 contact of WO<sub>3</sub> and IrO<sub>2</sub>. The devices will be durable since they are made of robust materials. Unlike previous microsensors based on conventional or organic diodes,<sup>8,10)</sup> their electrical functions in gases and liquids are not susceptible to the environmental variabilities arising from interfacial or material instability. Exploratory experiments in this area have led to our results that the electrical contacts of solid WO<sub>3</sub> and IrO<sub>2</sub> films, sputtered on adjacent Pt electrodes and covered by the polymer blend PVA·KHCO<sub>3</sub> (Fig. 1), can be used to generate diode-like current-voltage outputs that respond to CO<sub>2</sub> changes in the atmosphere.

The Pt-pad electrodes in Fig. 1 are fabricated using similar procedures as described earlier.<sup>6)</sup> 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 IrO<sub>2</sub> due to heating by subsequent WO<sub>3</sub> deposition, sputtering of the WO<sub>3</sub> target (99.99%, Pure Tech) at radiofrequency is carried out first under 20% O<sub>2</sub> in Ar at a total pressure of 90 mTorr, in the same apparatus as used before.<sup>7)</sup> A Si wafer with micromachined V-grooves is used as

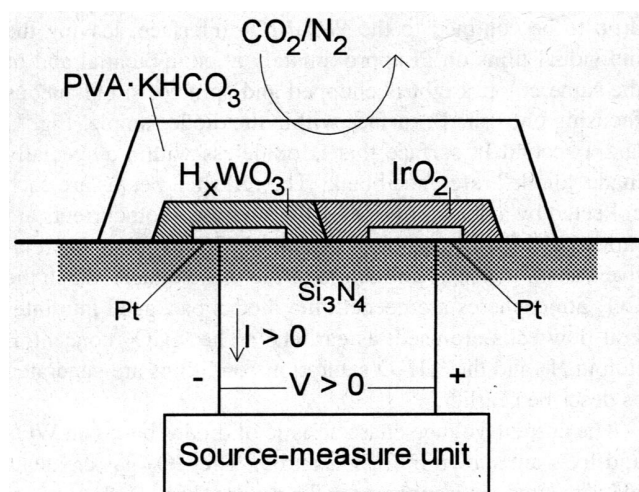


Fig. 1. Scheme showing the forward-biased diode based on the contact of WO<sub>3</sub> and IrO<sub>2</sub> on Si under CO<sub>2</sub> modulation.

the deposition mask. The mask and devices on the wafer are pressed onto a heated substrate platen at 676 K.<sup>3)</sup> The WO<sub>3</sub> films exhibit broad cyclic voltammograms in aqueous 1.0 M HClO<sub>4</sub> over the potential range of 0.3 to -0.3 V vs a saturated calomel electrode, as reported previously.<sup>3)</sup> 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 H<sub>2</sub>SO<sub>4</sub>. 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 IrO<sub>2</sub> film, next to the WO<sub>3</sub> film (Fig. 1), by the reactive sputtering method and the characterizations have been described earlier.<sup>7)</sup> The prepared WO<sub>3</sub> and IrO<sub>2</sub> 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 × 10<sup>5</sup> g/mol) with potassium bicarbonate (Fig. 1). The polymer blend, PVA·KHCO<sub>3</sub>,<sup>7)</sup> used for creating a CO<sub>2</sub>-modulated pH environment for the diodes, is ready for use as an aqueous solution with 0.06 mM of PVA and 2 mM of KHCO<sub>3</sub>. No other supporting electrolyte has been added since the polymer blend functions only as a source or sink for H<sup>+</sup>, and not as an electrolyte to carry ionic current. After evaporation of H<sub>2</sub>O at 35°C for 24 h, the cured polymer blends form transparent films that are highly adhesive to WO<sub>3</sub> and IrO<sub>2</sub>. 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 IrO<sub>2</sub> films show featureless transmission in the visible region<sup>7)</sup> and colored H<sub>x</sub>WO<sub>3</sub> 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 WO<sub>3</sub>/IrO<sub>2</sub> 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 oxideless 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 CO<sub>2</sub> atmospheres are needed, the diodes packaged into integral flow cells are used, as earlier.<sup>11)</sup> The %CO<sub>2</sub> concentration in N<sub>2</sub> and the %H<sub>2</sub>O saturation conditions are generated as described earlier.<sup>11)</sup>

The current-voltage characteristic of diodes based on WO<sub>3</sub> and IrO<sub>2</sub> are shown in Figs. 2 and 3. The CO<sub>2</sub> gas creates a pH-regulated environment for the diodes (Fig. 1), through its pH-lowering effect, as previously reported.<sup>7)</sup> It equilibrates in the bicarbonate-blended polymer PVA·KHCO<sub>3</sub> according to

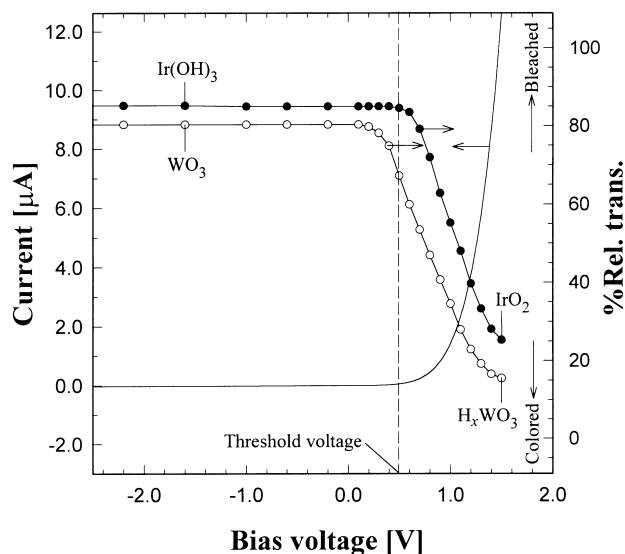


Fig. 2. Typical diode current-voltage characteristics and the relative transmittance changes in the oxides under 1% CO<sub>2</sub> in N<sub>2</sub> at 1 atm, 298 K and 100% H<sub>2</sub>O saturation.

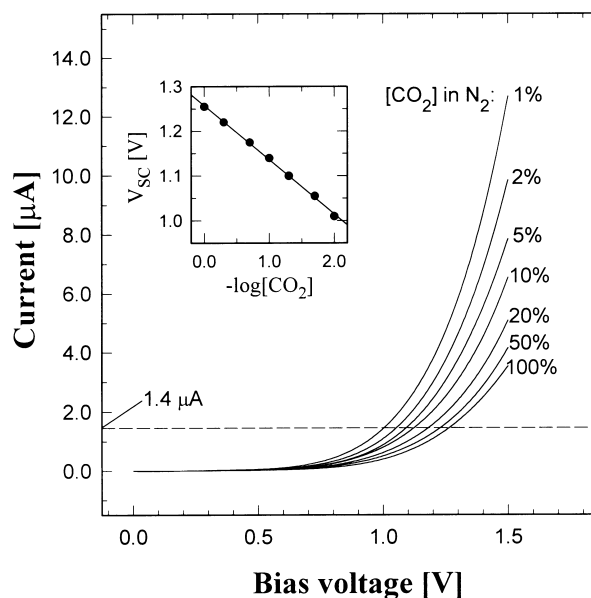
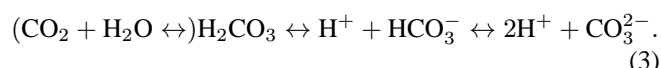


Fig. 3. The current in the forward direction under CO<sub>2</sub> modulation at 1 atm, 298 K and 100% H<sub>2</sub>O saturation.

the dissociative reaction



It has been established in this laboratory<sup>7)</sup> that the pH in PVA·KHCO<sub>3</sub> can be reversibly modulated using CO<sub>2</sub> gas. It has also been determined that this pH is proportional to the negative logarithm of the concentration of CO<sub>2</sub>, -log[CO<sub>2</sub>], to which PVA·KHCO<sub>3</sub> is exposed. Accordingly, changing -log[CO<sub>2</sub>] in the atmosphere in Fig. 1 is, in effect, equivalent to linearly shifting the pH in the PVA·KHCO<sub>3</sub> coating of the diode. As the results of the CO<sub>2</sub>-dependent experiment in Fig. 3 show, diodes based on WO<sub>3</sub> and IrO<sub>2</sub> undergo a cur-

rent decrease in the forward direction when the  $\text{CO}_2$  concentration is increased within the range of 1–100% in  $\text{N}_2$ . In the inset in Fig. 3, the voltage at which an arbitrary small current ( $1.4 \mu\text{A}$ ) in the forward direction is derived,  $V_{\text{SC}}$ , is plotted vs  $-\log[\text{CO}_2]$  for each of the  $\text{CO}_2$ -dependent  $I/V$  curves. The observed proportionality reveals that  $V_{\text{SC}}$  of the diode is also proportional to the pH in the diode environment. These results are consistent with the  $\text{WO}_3$  and  $\text{IrO}_2$  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.<sup>6,7</sup> 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  $\text{IrO}_2$  in series with a more fully reduced  $\text{H}_x\text{WO}_3$  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  $\text{IrO}_2$  ( $\sim 58 \text{ mV}/\Delta\text{pH}$ ) in aqueous solutions,<sup>7</sup> is higher than that for our  $\text{WO}_3$  ( $\sim 52$  to  $54 \text{ mV}/\Delta\text{pH}$ ), is relevant and should be noted. This means that up to  $\sim 5 \text{ mV}/\Delta\text{pH}$  positive displacement of  $\text{IrO}_2$  potential in excess of that of  $\text{WO}_3$  can be expected in the more acidic diode environments created by  $\text{CO}_2$ , 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  $\text{CO}_2$  sensitivity observed in Fig. 3. As shown by the relative transmittance changes in Fig. 2,  $\text{Ir}(\text{OH})_3$  only begins to conduct and turn colored last at a more positive bias than  $\text{WO}_3$ , 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  $\text{Ir}(\text{OH})_3$  as the pH is varied in the  $\text{PVA}\cdot\text{KHCO}_3$  by  $\text{CO}_2$  gas. The current loss in Fig. 3 in the forward direction is also confirmed by the observed progressive coloration in  $\text{H}_x\text{WO}_3$  and discoloration in  $\text{IrO}_2$  as the pH is lowered in  $\text{PVA}\cdot\text{KHCO}_3$  by  $\text{CO}_2$  gas under a fixed positive bias.

Our new diodes are markedly durable and reproducible. Repeated voltage sweeps under each  $\text{CO}_2$  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%  $\text{CO}_2$  in  $\text{N}_2$  turns the diodes to the “on” and “off” states with  $4 \mu\text{A}$  and only  $1 \mu\text{A}$  in the forward direction, respectively. The current switchings 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  $\text{WO}_3$  and  $\text{IrO}_2$  are not essential, as long as a hard-wire link between the films can be established. Separate experiments show that the  $\text{WO}_3$  and  $\text{IrO}_2$  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  $\text{WO}_3$  and  $\text{IrO}_2$  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  $\text{H}_x\text{WO}_3$  films are necessary to properly offset the conductivity of metallic  $\text{IrO}_2$  in the diodes. For this reason, 360-nm-thick  $\text{WO}_3$  and only 90-nm-thick  $\text{IrO}_2$  are normally deposited on Pt (Fig. 1) to obtain almost equal conductance in the reduced  $\text{H}_x\text{WO}_3$  and oxidized  $\text{IrO}_2$ . However, when we tested  $\text{WO}_3:\text{IrO}_2$  thickness ratios that are further unbalanced, reaching about the 720-nm-thick  $\text{WO}_3$  to 60-nm-thick  $\text{IrO}_2$  mark, instead of the previous current decrease shown in Fig. 3, a current gain in the forward direction under high  $\text{CO}_2$  concentrations is observed. The light transmission experiments also indicate a change in the previous order of coloring in Fig. 2. Finally,  $\text{WO}_3$  begins to conduct and becomes colored at a more positive bias than  $\text{Ir}(\text{OH})_3$ , which, as before, is approximately the threshold voltage for initiating current in the forward direction. Apparently, the thin  $\text{Ir}(\text{OH})_3$  with much less redox material is now easily completely oxidized and is conducting, while the thick  $\text{WO}_3$  is still fractionally reduced and is not conducting. As  $\text{H}^+$  becomes more abundant under  $\text{CO}_2$ , the current change in the forward direction changes to a gain since more of the  $\text{WO}_3$  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  $\text{CO}_2$  gas, can be made by tuning the thickness of the oxide films. The relation between conductivity and film thickness for both  $\text{WO}_3$  and  $\text{IrO}_2$  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  $\text{CO}_2$ ,  $\text{SO}_2$  and  $\text{NH}_3$ . The diode can also function with an insoluble enzyme layer<sup>12</sup> to sense glucose in biological fluids.

## Acknowledgments

This work was sponsored by the National Science Council of the Republic of China under contract NSC86-2215-E009-049.

- 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.* **32** (1993) L1346.
- 7) J. C. Lue and S. Chao: *Jpn. J. Appl. Phys.* **36** (1997) 2292.
- 8) J. W. Gardner: *Microsensors, Principles and Applications* (John Wiley, Chichester, 1994) p. 235.
- 9) R. D. Rauh and S. F. Cogan: *J. Electrochem. Soc.* **140** (1993) 378.
- 10) N. Leventis, M. O. Schloh, M. J. Natan, J. J. Hickman and M. S. Wrighton: *Chem. Mater.* **2** (1990) 568.
- 11) S. Chao: *Meas. Sci. Technol.* **7** (1996) 737.
- 12) Y. Hanazato, M. Nakako and S. Shiono: *IEEE Trans. Electron Devices* **33** (1986) 47.