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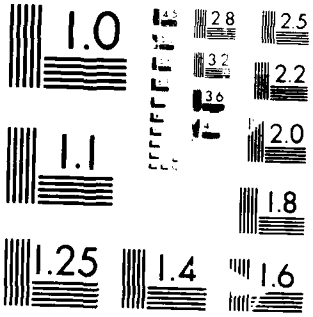

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Chemically Modified Microelectrode Arrays: New Kinds of Electronic Devices

by

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Massachusetts Institute of Technology
Department of Chemistry
Cambridge, MA 02139

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CHEMICALLY MODIFIED MICROELECTRODE ARRAYS: NEW KINDS OF ELECTRONIC DEVICES

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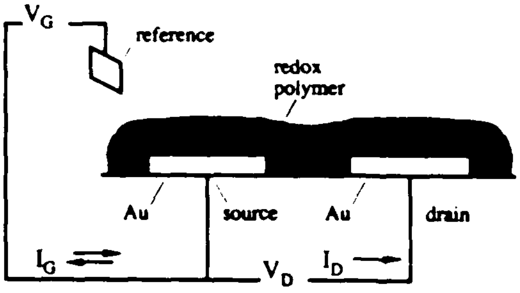
Abstract Modification of closely spaced (~1.5 μm) microelectrodes (~2.5 μm wide x 50 μm long x 0.1 μm high) with electroactive materials gives rise to a variety of new kinds of "electronic devices". Surface modification of microelectrode arrays with metal oxides, e.g. WO_3, conventional redox polymers, e.g. viologen-based polymers, and so-called conducting redox polymers, e.g. poly(3-methylthiophene), allows demonstration of a variety of microelectrochemical "transistors" having properties that depend on the electroactive material. While the response time of such devices is slow by solid state electronics standards, chemically sensitive transistors can be envisioned as sensitive, specific sensors. Solid state microelectrochemical devices can be made that involve the use of ionic conducting polymers as the "solvent"/electrolyte system. Solid state microelectrochemical transistors can be designed to be sensitive to certain gases.

INTRODUCTION

In this article we wish to summarize recent progress related to the surface modification of microfabricated structures with redox active materials. An objective of research in this area is to develop methodology that will lead to new systems "functions" based on one or more redox materials used as the active element in new kinds of microelectronic devices.[1] Since many redox materials are intrinsically chemically sensitive, there is the prospect that the new microelectronic devices will represent a novel class of chemical sensors. Indeed, specific, sensitive, small chemical sensors represent the most clearly defined area of practical opportunity. Surface modification of microfabricated structures may also find application in interfacing microelectronics with biological systems, owing to the need to make surfaces "biocompatible". Recent research has established that surface modification of microfabricated structures with one or more polymers does lead to new microelectronic devices with novel properties, including chemical sensitivity.[1-4]

CHEMICALLY SENSITIVE MICROELECTROCHEMICAL TRANSISTORS

Scheme I illustrates a cross-sectional view of a microelectrochemical transistor where the active material is a



Scheme I. Cross-sectional view of a redox polymer-based microelectrode transistor.

redox active material connecting the two microelectrodes comprising the source and drain of the transistor. The essential property of the redox material is that its "conductivity" is a function ot its state of charge, which can be controlled through the gate potential, V_G. Thus, upon variation in V_G, there will be a change in the drain current, I_D, for a fixed potential between source and drain, V_D. The function of the device is analogous to that of a solid state transistor.[5] All redox materials have the essential property required to make a microelectrochemical transistor. Further, many redox materials can be expected to have a chemically sensitive "conductivity" and a chemically sensitive potential for maximum conductivity. Thus, by connecting two electrodes with a single redox material a device results that will have electrical characteristics that depend on the medium to which it is exposed.

For a microelectrochemical transistor represented by Scheme I, a small spacing between the source and drain is desired because I_D will be larger for smaller spacings. In fact, so many redox polymers have such poor conductivity at any V_G that conveniently measureable values of I_D require spacings as small as possible. Further, the spacing between source and drain also defines the switching speed, or response time, of the device; smaller spacings give faster switching. Figure 1 shows a typical process for the fabrication of a microelectrode array consisting of eight, individually addressable Au (or Pt) microelectrodes each ~2.5 μm wide x ~50 μm long x ~0.1 μm high, separated from each other by ~1.5 μm.[6]

To illustrate the importance of small spacings consider the use of a conventional redox polymer such as a viologen-based polymer.[7] In such conventional redox materials the mechanism for charge transport in the polymer relies on self-exchange from one redox site to another.[8] That is, when there is a concentration gradient of oxidized and reduced centers there can be a steady state current that

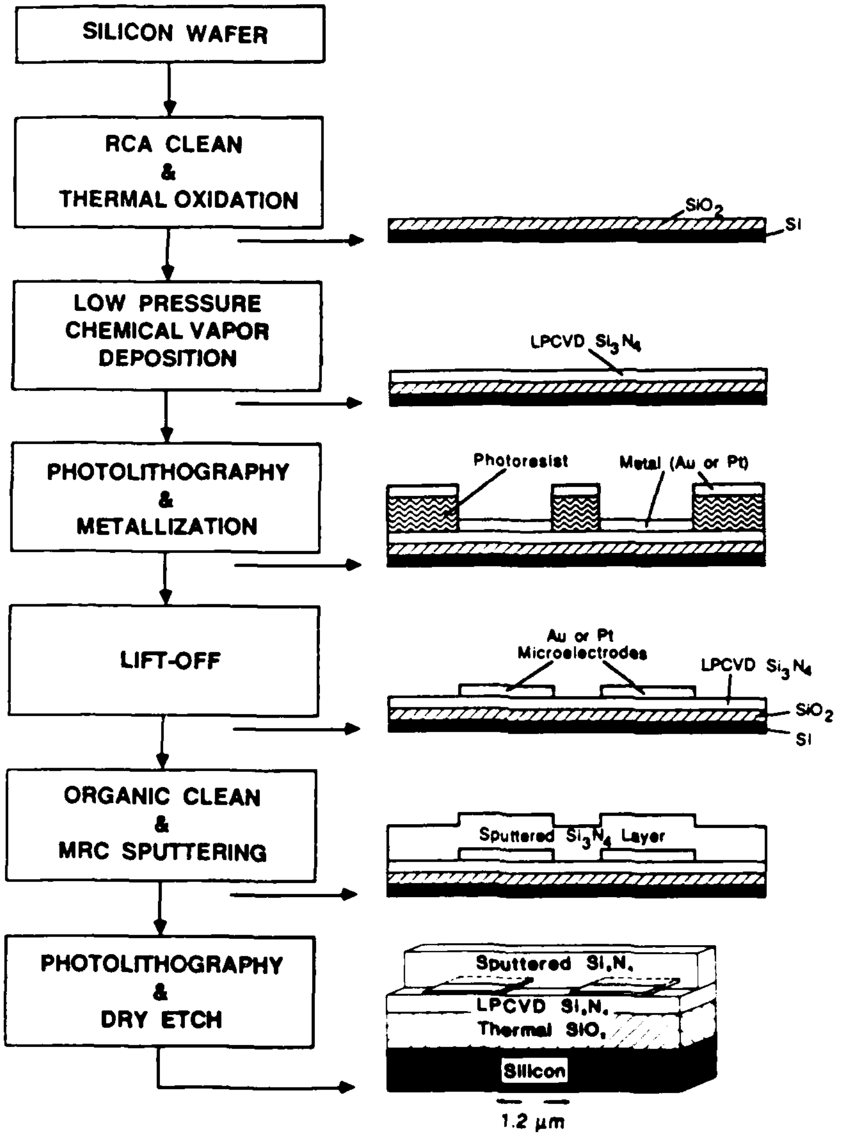
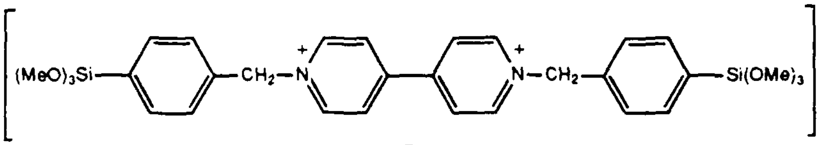


Figure 1. Flow chart for fabrication of microelectrode arrays.

depends on the diffusion coefficient for charge transport, D_{ct}, in the polymer; the distance across which the charge is transported, d; and the concentration of redox centers in the polymer, C:

$$I_{D(max)} = \frac{nFAD_{ct}C}{d} \qquad (1)$$

where n is the number of electrons transferred, F is the faraday, and A is the electrode area through which charge passes.[8c] $I_{D(max)}$ refers to the maximum current possible, which occurs at the maximum concentration gradient of oxidized and reduced sites. D_{ct} for the viologen-based redox polymer from hydrolysis of the Si-OMe bonds of I is



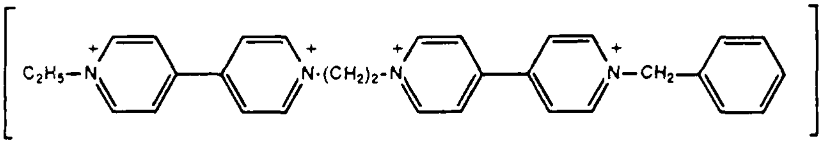
I

~10^{-9} cm^2/s and C is ~2.5 M.[7] For a value of d = 1.0 μm these values would give a maximum drain current density of ~2 mA/cm^2. This small value is to be contrasted with a drain current density in excess of 10^3 A/cm^2 in a solid state field-effect transistor with a 1.0 μm source-drain separation (gate length).[5] According to equation (1) $I_{D(max)}$ is inversely proportional to d, which underscores the importance of small spacings.

In terms of response time, equation (2)[9] gives the approximate switching time t, for a spacing of d and diffusion coefficient D_{ct}. For the values of d and D_{ct}

$$d^2 = 2tD_{ct} \qquad \text{or} \qquad t = \frac{d^2}{2D_{ct}} \qquad (2)$$

mentioned above a device based on the viologen polymer will involve a switching time of the order of seconds, obviously too slow to compete in applications where high frequency is required. Solid state transistors with a 1.0 μm gate length operate at frequencies exceeding 10^9 Hz.[5] Switching of the viologen-based device in 10^{-9} s would obviously require a gate length much smaller than 1.0 μm-- a value of d ≈ 1.5 x 10^{-9} cm, according to equation (2). This value of d is smaller than a single molecule, meaning that a 10^{-9} s switching time cannot correspond to physical reality for the viologen-based device (assuming that the model still holds). From the molecular perspective the slow switching at the molecular size regime can be deduced from studies of molecules such as II[10] where it is estimated that movement of an electron from one redox center linked to another may have a rate constant of less than 10^{-6} s^{-1}. For currently available microstructures having d ≈ 50 nm,[11] the switching time for a viologen-based device is predicted to be of the order of 10 ms. This switching speed is adequate for many applications in chemical sensing.



II

It is worth pointing out that all microelectrochemical devices will have a switching speed that is slower than that of a solid state device of the same dimensions. This follows from the fact that the microelectrochemical devices involve oxidation/reduction chemistry and accompanying movements of ions into or out of the active region between source and drain. In contrast, conventional solid state devices involve only movement of electrons which are less massive than any ion. The largest diffusion coefficients for ions are of the order of 10^{-5} cm^2/s at 298 K.[12] This suggests that for d ≈ 50 nm the fastest switching possible in the microelectrochemical devices will be about 10^{-6} s, equation (2). Microelectrochemical devices based on conducting polymers can have I_D values much larger than for conventional polymers. However, the switching time is governed by ion movement.

The sections below summarize results for microelectrochemical transistors employing three kinds of redox active materials: conducting polymers, conventional redox active polymers, and electroactive oxides. Use of solid state electrolytes allows these same redox materials to be used as the device material in "solid state" microelectrochemical transistors. The final section summarizes methodology for preparing 50 nm devices starting with microelectrode arrays produced as in Figure 1.

Conducting Polymer-Based Devices. Many redox active polymers are now known that undergo dramatic changes (greater than eight orders of magnitude) in conductivity depending on their state of charge.[13] Such materials have been used to demonstrate the first microelectrochemical devices, including polypyrrole,[14] poly(N-methylpyrrole),[14b] poly(3-methylthiophene),[15] and polyaniline.[15b,16] These materials can all be made by electrochemical oxidation of the monomer leading to electrode-confined, redox active polymer that is insulating when reduced and conducting when oxidized. The electrochemical polymerization method has been used to selectively deposit the redox polymer to connect two or more microelectrodes. Selective deposition of one polymer on a microelectrode and a second polymer on an adjacent microelectrode separated by only ~0.3 μm has been demonstrated.[17] The high absolute conductivity of conducting redox polymers, their good reversibility in terms of switching between their insulating and conducting states, and the ability to selectively deposit them by electrochemical methods make conducting polymers good candidates for the active material in microelectrochemical transistors.

Most work on conducting polymer-based devices has been done with poly(3-methylthiophene) and polyaniline. The poly(3-methylthiophene)-based transistor shows an I_D-V_G characteristic, Figure 2, resembling that of a solid state transistor: a region of V_G where the device is "off" ($I_D = 0$) and a region of V_G where the device is "on" ($I_D > 0$), corresponding to values of V_G where the polymer is reduced (insulating) and oxidized (conducting), respectively.[15a] A ΔV_G of ~0.5 V is required for switching, which can be effected in <50 ms for devices having a gate length of ~1.5 μm. The charge required for complete switching has been shown to be about 10^{-7} C for a device

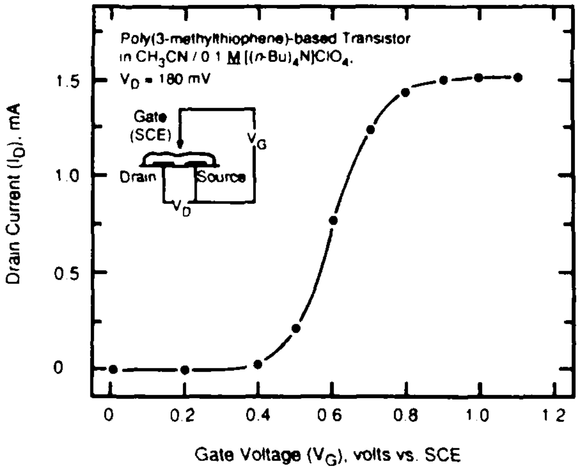


Figure 2. Transistor characteristic, I_D vs. V_G (steady state) for a poly(3-methylthiophene)-modified microelectrode array. Data points are taken from a family of I_D vs. V_D curves at fixed V_G's.

with a "footprint" of ~5 x 10^{-6} cm^2. In the "on" state the drain current density exceeds 10^3 A/cm^2 for a V_D of ~100 mV. Characteristics of the device are largely independent of solvent (H_2O, CH_3CN), electrolyte, and pH.[15,18] Thus, the poly(3-methylthiophene)-based transistor is not particularly chemically sensitive.

Impregnation of poly(3-methylthiophene) with a catalytic amount of Pt ($<10^{-7}$ mol/cm^2) allows demonstration[15c] of a two-terminal device that turns on upon exposure to aqueous O_2 and turns off upon exposure to aqueous H_2 at fixed pH, equation (3). At fixed O_2 concentration the poly(3-methylthiophene)/Pt device responds to pH changes, because the oxidizing power of O_2 is pH-dependent, equation (4). Results show that the

$$[\mathrm{PMT}]_{\mathrm{reduced}} \quad \underset{\substack{\text{"Pt"}/\mathrm{H_2} \\ \text{[fixed pH]}}}{\overset{\text{"Pt"}/\mathrm{O_2}}{\rightleftarrows}} \quad [\mathrm{PMT}]_{\mathrm{oxidized}} \qquad (3)$$

$$[\mathrm{PMT}]_{\mathrm{reduced}} \quad \underset{\substack{\text{"Pt"/base} \\ [\text{fixed } \mathrm{O_2}]}}{\overset{\text{"Pt/acid}}{\rightleftarrows}} \quad [\mathrm{PMT}]_{\mathrm{oxidized}} \qquad (4)$$

(Insulating, $I_D = 0$) (Conducting, $I_D > 0$)

incorporation of Pt can be carried out in a manner that brings about rapid response to O_2 and H_2 yet retains the property of state of charge dependent conductivity, Figure 3. The key is to use an amount of Pt that catalytically equilibrates the polymer with the H_2O/H_2 and O_2/H_2O redox couples, but not so much Pt that the metal impregnated polymer has a potential-independent conductivity dominated by a large volume fraction of metal in the polymer. Use of catalysts, including enzymes, is a route to specific sensor

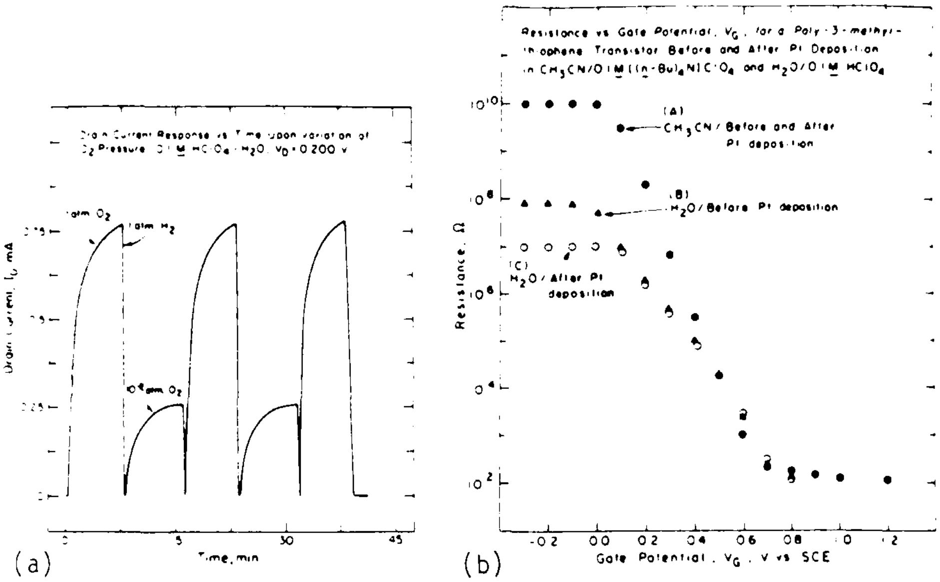


Figure 3. (a) I_D vs. time for a two terminal (poly(3-methylthiophene)/Pt-based device upon exposure to O_2 and H_2 in 0.1 M $HClO_4/H_2O$. The total pressure is 1 atm, with N_2 as a diluent for the 10^{-2} atm O_2 signal. (b) Resistance between two poly(3-methylthiophene) connected microelectrodes as a function of V_G in (A) CH_3CN/0.1 M $[(n\text{-}Bu)_4N]ClO_4$, before and after Pt deposition and (B) H_2O/0.1 M $HClO_4$ before Pt depostion and in (C) H_2O/0.1 M $HClO_4$ after Pt deposition. [Reprinted with permission from Reference 15c.]

functions for microelectrochemical devices.

Polyaniline-based devices differ from the poly(3-methylthiophene)-based devices in several important respects. First, the I_D-V_G characteristic shows a peak in I_D; a broad maximum in I_D occurs in the vicinity of V_G = +0.3 V vs. SCE when the device is operated in aqueous 0.5 M $NaHSO_4$, Figure 4.[16] This I_D-V_G characteristic thus gives a device that goes from off to on to off again as V_G is changed from reducing to oxidizing potentials. In this respect the polyaniline-based device characteristic resembles that expected for a conventional redox polymer (*vide infra*), which has a peak I_D at E°'. A second difference between

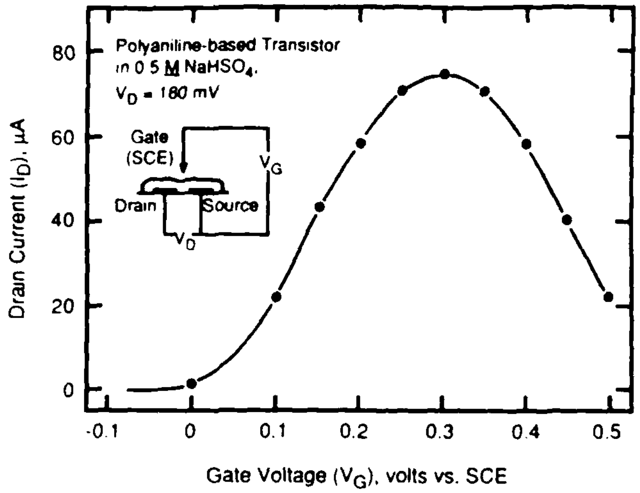


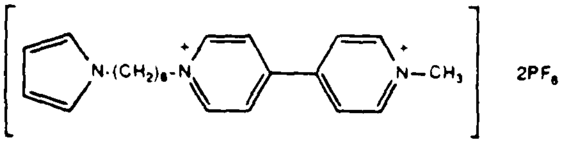
Figure 4. Transistor characteristic, I_D vs. V_G (steady state) at fixed V_D for a polyaniline modified microelectrode array.

polyaniline and poly(3-methylthiophene) is that the polyaniline is intrinsically chemically sensitive; the electrochemical behavior depends on pH in a manner that shifts the turn-on of the transistor to more positive potentials at lower pH's. Unfortunately, polyaniline is less robust at high pH's, and best results have been obtained at pH 1.5 or lower.[16] The third significant difference is that the maximum conductivity of the polyaniline is less than that of poly(3-methylthiophene), even though the polyaniline appears to show faster switching-- a fact that is not yet understood.[15b] A fundamental limitation in each case stems from the relatively slow movement of ions through the polymer that must accompany redox cycling. It is conceivable that polymer morphology and nature of the ion govern the switching speed. A more open structure and H_3O^+ as the moving ionic species would provide a rationale for faster switching of polyaniline compared to that of poly(3-methylthiophene). The energies associated with switching polyaniline and poly(3-methylthiophene) devices are about the same.

Transistor devices based on redox switching of conducting polymers do show that molecular materials can serve as the active materials in molecule based devices, albeit those demonstrated switch more slowly than do solid state devices of the same dimension. Both poly(3-methylthiophene)- and polyaniline-based devices have been shown to be capable of power gain.[15b] This means that the average power available in the drain circuit is larger than the average power in the gate circuit. However, for devices of ~1.5 μm gate length the poly(3-methylthiophene)-based device only shows power gain up to a frequency of $\sim 10^2$ Hz, while polyaniline-based devices give power gain up to $\sim 10^3$ Hz. Increasing the frequency where power gain can be realized depends on a combination of (1) making devices with smaller dimensions to reduce the distances over which ions must move and lessening the absolute energy required for switching, (2) developing redox active materials with higher maximum conductivity, and (3) developing redox active materials with a larger intrinsic change in conductivity per unit of charge added (or withdrawn) from a given volume. However, even for devices already made, the switching speeds are adequate for many sensor applications. The drawback in this regard is that specificity has not yet been well-demonstrated. Conventional redox polymers currently offer more opportunity to design for specificity, as developed below.

Conventional Redox Polymer-Based Devices. Modification of microelectrode arrays with conventional redox active materials such as polyvinylferrocene,[17] viologen-based polymers,[17] viologen/quinone polymers,[19] polycations charge compensated with electroactive anionic metal complexes,[20] and Prussian blue[21] has allowed demonstration of the characteristics of microelectrochemical transistors based on redox materials, for which the region of V_G where $I_D>0$ is very narrow (~200 mV) and is dependent on the chemical environment. Generally, any reversibly redox active molecule can be incorporated into a polymer of some sort, allowing preparation of a microelectrochemical transistor that shows a peak in I_D at $V_G = E°'$.[4,20,22] For V_G >100 mV away from E°' I_D approaches zero, because the self-exchange mechanism for charge transport requires a significant concentration of reduced and oxidized centers. Since $I_{D(max)}$ occurs at E°', the value of I_D at fixed V_G and V_D will depend on the chemical environment whenever the redox material has a chemically dependent E°'. Polyvinylferrocene- and viologen-based polymers have E°' values that are relatively insensitive to the chemical environment, but in general, E°' of a redox molecule is chemically sensitive.

Redox polymers derived from oxidation of III and IV have been used to illustrate the behavior of microelectrochemical transistors based on the viologen redox center, III, and a similar redox center, IV, which is pH-dependent.[23]



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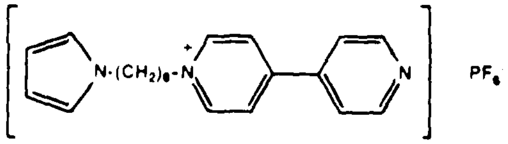


IV

The use of the N-alkylpyrrole unit allows the selective electrochemical deposition of polymer as for pyrrole itself.[14] Incidently, use of polymers from oxidation of III and IV permits demonstration of the behavior of a conducting polymer-based device (poly(N-alkylpyrrole)) and, simultaneously, of a device based on conventional redox material. The $E^{\circ\prime}$ values for the conventional redox centers are more negative than the potential where the poly(N-alkylpyrrole) is significantly conducting.[14] Thus, with respect to the study of conventional viologen-like redox centers in III and IV, the N-alkylpyrrole merely provides a convenient way to effect microelectrode modification.

Characteristics of the transistor devices based on polymers from oxidation of III and IV are as expected from the electrochemistry of III and IV in solution. For devices based on III there is a sharp (~100 mV width at half-height), pH-independent peak in the I_D-V_G plot at ~-0.5 V vs. SCE associated with the reversible, one-electron viologen redox couple. For IV a similar I_D-V_G characteristic is observed, but the peak position is pH dependent in a manner consistent with the reversible protonation of the terminal N in IV. It is worth emphasizing that the maximum absolute value of I_D for the conventional redox polymer-based systems is typically five or six orders of magnitude smaller than for poly(3-methylthiophene)-based devices.[15a,b] Moreover, these systems are slower in response time owing to the relatively poor absolute conductivity of the polymer in any conventional redox state.

The polymer from IV illustrates the prescription for designing chemical sensitivity: find a reversibly redox active molecule with the desired chemical effect on $E^{\circ\prime}$ and incorporate it into a polymer. Redox reagents are known that respond to gases (O_2, H_2, CO, etc.) and ions (H^+, Li^+, Na^+, etc.). A principal drawback with conventional redox polymers is the low conductivity compared to that of conducting polymers. The tradeoff is a remarkable range of intrinsic chemical specificity.

Metal Oxide-Based Devices. Many metal oxides undergo reversible electrochemical reactions that, like redox reactions of molecular polymers, are accompanied by changes in conductivity. Electroactive oxides include WO_3,[24] NiO,[25] and RuO_2,[26] which have been used as the active material in microelectrochemical processes. Not surprisingly, the electroactive oxides exhibit electrochemical behavior that depends on the environment to which the oxide is exposed. For example, WO_3, NiO, and RuO_2 all show pH-dependent properties that stem from the involvement of H^+ in the electrochemistry as represented in equation (5) for the reversible reduction of WO_3.[24] The point is that the

$$\underset{\text{(Insulating)}}{WO_3} + ne^- + nH^+ \rightleftharpoons \underset{\text{(Conducting)}}{H_nWO_3} \qquad (5)$$

potential at which the oxide becomes conducting depends on pH such that a microelectrochemical transistor will show a pH-dependent I_D-V_G characteristic. Thus, intrinsic chemical dependence of the electrochemical behavior of the oxides suggests their use as the active material in chemically sensitive transitor devices.

Metal oxides have an important advantage connected with the fabrication of devices. Many metal oxides can be deposited and patterned using more or less conventional microfabrication techniques. For example, Figure 5

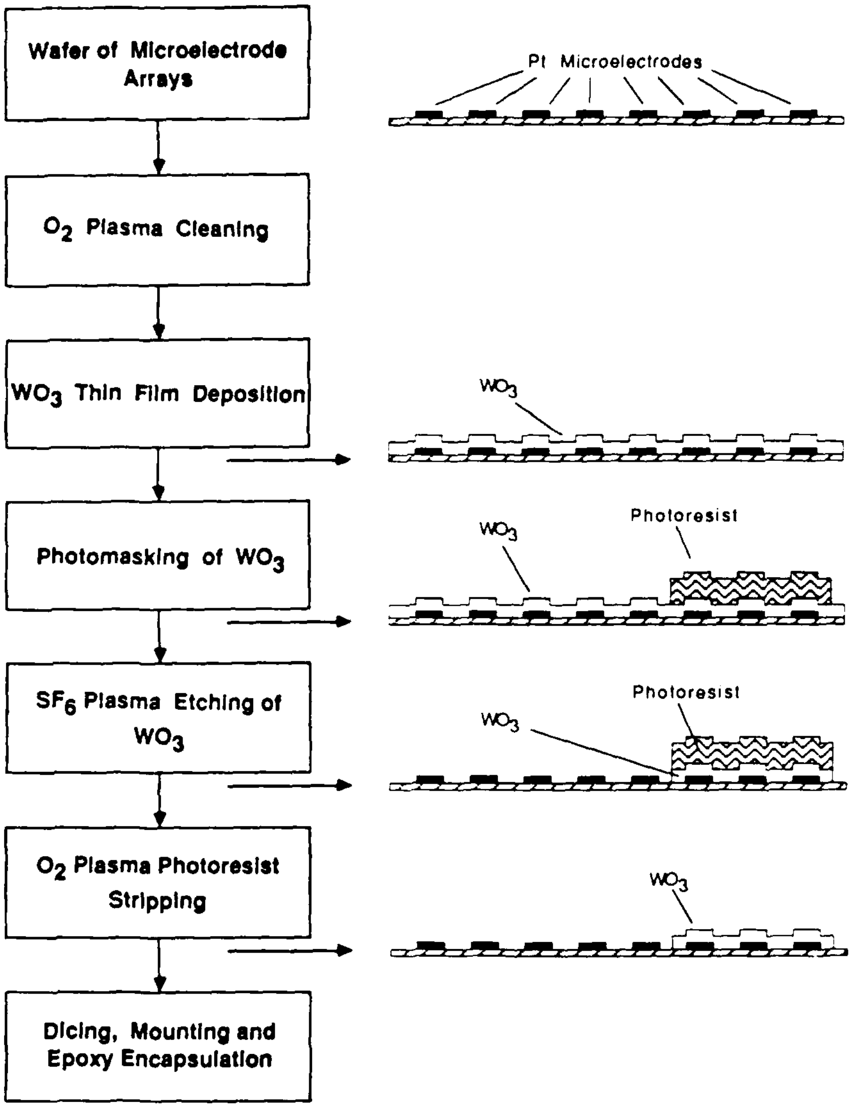


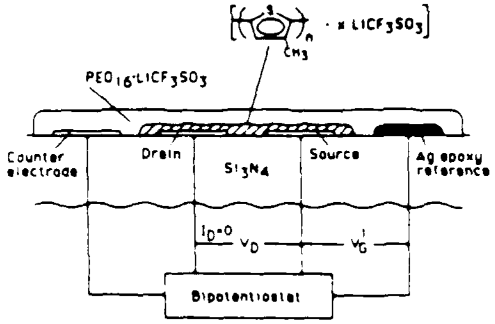
Figure 5. Flow chart for fabrication of WO_3-based devices.

illustrates a process for the fabrication of a WO_3-based device where WO_3 coats only three of eight microelectrodes of an array.[27] The WO_3 can be deposited by a plasma deposition and then selectively removed with an SF_6 plasma after first protecting the WO_3 to be retained with photoresist. The protecting photoresist is ultimately removed from the WO_3. Interestingly, in such cases the photoresist is like a protecting group in organic synthesis: material is added and removed to allow alteration in the structure in another region. Techniques such as optical and electron microscopy, surface profiling, and Auger electron spectroscopy establish that the microstructure desired can be made.[27] Importantly, Auger electron spectroscopy shows that the SF_6 plasma etching "cleans" the five microelectrodes leaving them available for further modification as described below.

Microelectrochemical devices based on the electroactive metal oxides show persistent, reproducible response to pH variation for fixed V_G and V_D for periods of time exceeding one hour. The response time of the oxide-based devices studied to date is, like that of conventional redox polymers, slow compared to the response time of conducting polymers such as polyaniline. However, response time (<1 s) to pH changes is adequate for many sensor applications. The minimum pH change detectable has not been established, but oxides having maximum sensitivity near pH 7 are available. Long term "testing" has not been carried out, but it should be noted that much effort has been directed towards evaluation of the reversibility of electrochemical processes of metal oxides in connection with electrochromic displays.[28] The literature suggests there may be problems in long term cycling between two redox extremes. It should be appreciated that there are large structural changes accompanying redox reactions of oxides, and these likely lead to a degree of irreversibility. In this regard, molecular polymers might be expected to be more reversible, since the backbone of the polymers can be flexible. Another important failure of the oxides is the lack of good adhesion to the metallic conductors and the insulating substrate.

SOLID STATE AND MULTICOMPONENT MICROELECTROCHEMICAL DEVICES

The microelectrochemical transistors based on conducting polymers, conventional redox polymers, and electroactive oxides can all be operated in fluid solutions containing electrolytes. The reference electrode and counter electrode in the typical experiment involving fluid solutions are conventional (macroscopic dimensions). By modifying a microelectrode array with a spot of Ag epoxy as a quasi-reference, redox active material for the transistor, and an ionic conducting polymer[29] as the electrolyte solution, Scheme II, all of the components for a microelectrochemical



Scheme II. A solid-state poly(3-methylthiophene)-based transistor in its "off" state.

transistor can be confined to the chip.[30] A "solid state" poly(3-methylthiophene)-based transistor employing poly(ethylene oxide)/$LiCF_3SO_3$ as an electrolyte solution, the first such device, shows an I_D-V_G characteristic like that found in CH_3CN or H_2O electrolyte solutions.[30] However, the switching speed of the solid state device was found to be much slower, even at 100 °C, owing to poor ionic conductivity.

A solid state polyaniline-based transistor with a poly(vinyl alcohol)/H_3PO_4 electrolyte solution[31] shows a characteristic like that in aqueous acid.[32] Again, however, the solid state device is slower, though 25 °C operation with power gain to $\sim 10^2$ Hz has been demonstrated. Most interesting is that the solid state polyaniline/poly(vinyl alcohol)/H_3PO_4 system shows variation in I_D upon variation in the atmosphere from 0% H_2O ($I_D = 0$) to H_2O-saturated (I_D = maximum) at fixed V_G and V_D. This system represents an example of a chemically sensitive, solid state, microelectrochemical device.

The WO_3-based transistor also operates as a solid state device with poly(vinyl alcohol)/H_3PO_4 as the electrolyte system and shows a characteristic similar to that in aqueous acid, Figure 6.[33] As mentioned above, the process for patterning WO_3 on an array of microelectrodes leaves clean microelectrodes that can be surface modified. Accordingly, polyaniline or poly(3-methylthiophene) has been electrochemically deposited onto two of the remaining five microelectrodes. The resulting two transistor chip is completed by depositing a spot of Ag epoxy as a quasi-reference, coating with poly(vinyl alcohol)/H_3PO_4, and using the remaining clean microelectrodes as the counterelectrode. The two transistors can be operated independently, and each shows the response expected of an isolated device. Aside from demonstrating the surface modification procedures to produce a chip having two transistors, the conducting polymer/WO_3 chip is interesting because the WO_3-based device turns on upon reduction while the conducting polymer device turns on upon oxidation. Thus, application of a potential (negative lead to WO_3, positive lead to conducting polymer)

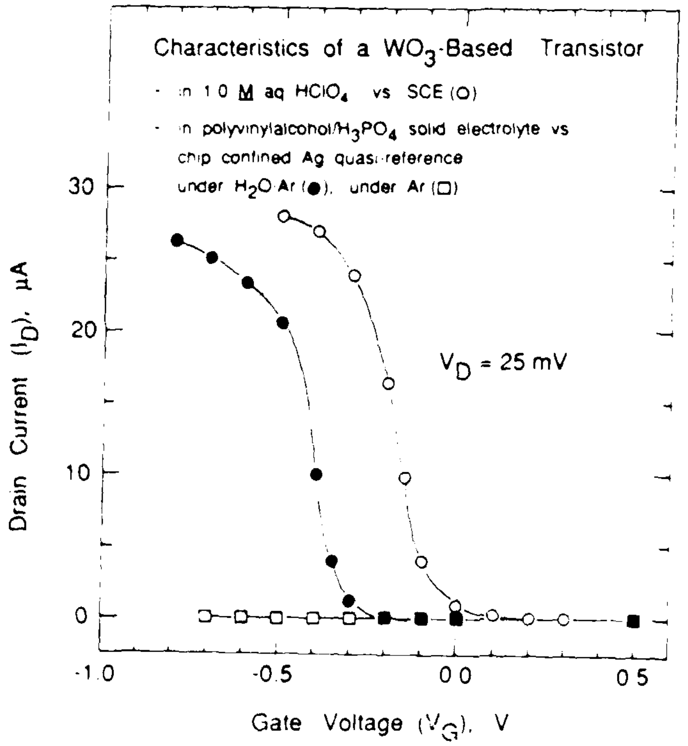


Figure 6. Steady-state transistor characteristics, I_D vs. V_G at fixed V_D, for a three-microelectrode-confined WO_3-based device. Comparison of device behavior in fluid acidic solution and in poly(vinyl alcohol)/H_3PO_4 solid electrolyte. The 0.25 V difference in the threshold voltage of the device in the two electrolytes is probably due to the different references employed.

across the sources of the two devices will turn them both on. Such a device is therefore a "self referencing" microelectrochemical transistor where the magnitude of V_G required for turn on of the two transistors depends on the properties of the redox active materials.

Solid state microelectrochemical devices are likely to be useful as gas sensors. Tailoring the characteristics of such a device follows the considerations for a device operated in fluid solution. However, the additional complication of the need for a solid state electrolyte poses new surface modification challenges including issues related to optimizing ion transport across interfaces.

HOW SMALL CAN WE GO?

The molecule-based devices described in this article do not have molecular dimensions. Indeed, as the introductory section suggests, molecular dimensions may not yield devices that are ultrafast. Nonetheless, there is the challenge of making molecule-based devices that are ultrasensitive. This requires the smallest dimensions possible. The process summarized in Figure 7, employing two shadow deposition steps, illustrates a route to dimensions substantially

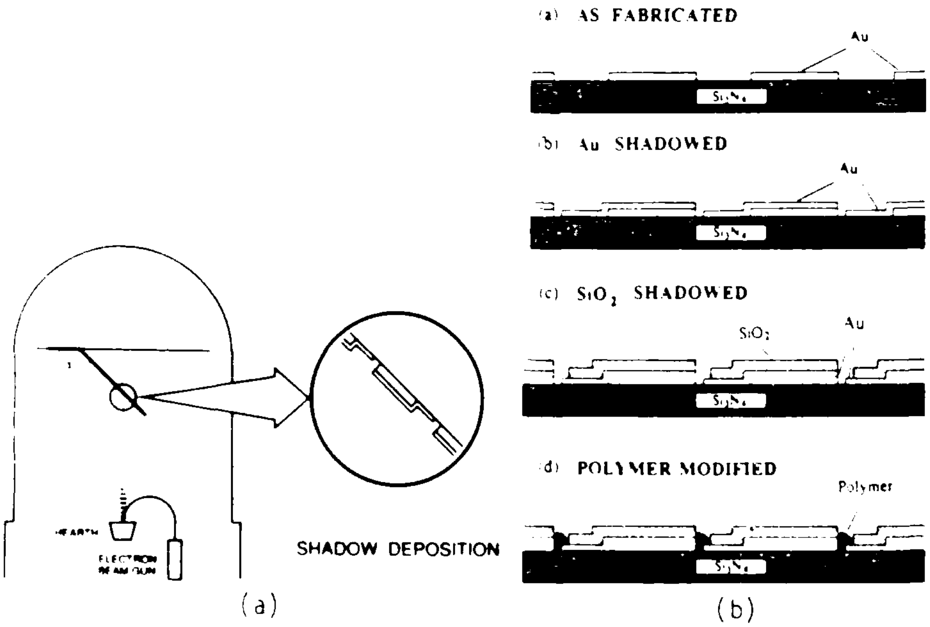


Figure 7. (a) Shadow deposition apparatus. (b) Fabrication sequence for a 50 nm device.

smaller than previously available. A separation of 50-100 nm between source and drain has been achieved[11] leading to faster, more sensitive molecule-based devices. Figure 8 shows data for a polyaniline-based device with a ~70 nm gate length. The data show that nearly complete turn on/turn off is achieved at frequencies in excess of 10^4 Hz with power gain. Power gain vs. frequency is shown for a device of 1.5 μm gate length for comparison, showing the 70 nm device to be nearly 10^2 times better in terms of gain at a given frequency.

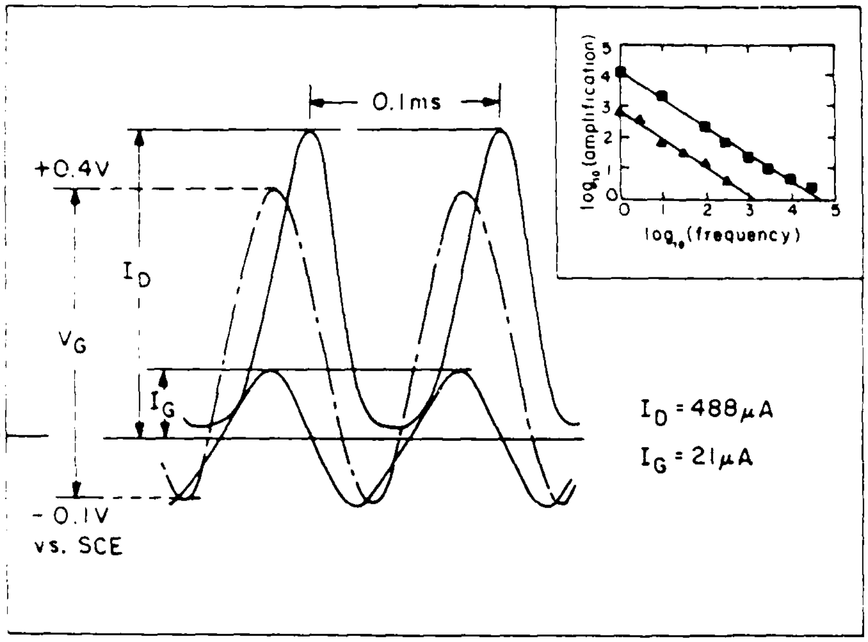


Figure 8. Gate potential (V_G), gate current (I_G), and drain current (I_D) at 10 kHz for an ultrasmall gap polyaniline-based transistor; drain voltage (V_D) is 100 mV. Inset shows $\log_{10}$ (amplification) vs. $\log_{10}$ (frequency) of a 1.5 μm gap (▲) transistor vs. a 70 nm gap (■) polyaniline-based transistor. [Reprinted with permission from Reference 11.]

The procedures used to prepare the 70 nm device may yield devices with a gate length as small as 10 nm. At this point it is conceivable that single molecules could be used to connect source and drain. Even so, such a device would not be a single molecule switch. Many single molecule connections would be involved. Challenges in surface modification in the 10 nm regime include making source-drain connections with oriented molecules, molecules that have chemically sensitive charge transport, and molecules that are photoconductors. Aside from preparing the microstructure and effecting surface modification with molecular materials, there is an important challenge in chemical synthesis to prepare relatively large molecules that have interesting, unique properties that will make molecule-based devices useful.

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