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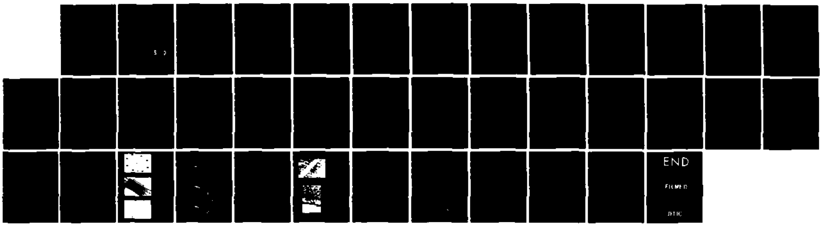

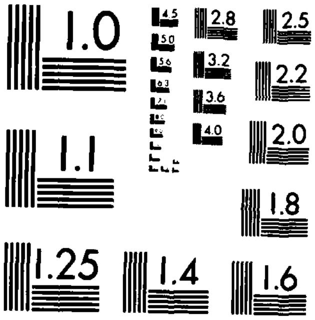

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"Resistance of Polyaniline Films as a Function of Electrochemical Potential and the Fabrication of Polyaniline-Based Microelectronic Devices"

by

Elizabeth W. Paul, Antonio J. Ricco and Mark S. Wrighton

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Abstract

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Anodic growth of polyaniline films on a Au microelectrode array has been carried out to add to the characterization of polyaniline and to fabricate polyaniline-based microelectronic devices, diodes and transistors, that function when the polyaniline-functionalized microelectrode array is immersed in an electrolyte solution. The microelectrode array is a set of eight Au electrodes, 0.1 µm thick, 4.4 µm wide, and 50 µm long, each individually addressable and separated from each other by 1.7 µm. Polyaniline can be deposited in controlled amounts by electrochemical oxidation of aniline. When the polyaniline is deposited in sufficient amounts, two or more of the eight Au microelectrodes can be connected in the electrical sense. Current can pass between two connected microelectrodes when there is an applied potential between them. The magnitude of the current at a given applied potential depends on the electrochemical potential of the polyaniline. In 0.5 M $NaHSO_4/H_2O$ the current (at a fixed applied potential) is maximum at an electrochemical potential of approx. ~+0.4 V vs. SCE and declines by a factor of $>10^6$ upon reduction to +0.1 or oxidation to +0.7 V vs. SCE. Owing to the large change in resistance upon change in electrochemical potential, the functionalized microelectrodes can function as diodes or transistors. The small spacing between the microelectrodes is crucial to device function, owing to the limited conductivity of the polyaniline. The switching time of a transistor-like device is faster than 0.1 s.

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Resistance of Polyaniline Films as a Function of Electrochemical Potential and the Fabrication of Polyaniline-Based Microelectronic Devices

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Abstract

Anodic growth of polyaniline films on a Au microelectrode array has been carried out to add to the characterization of polyaniline and to fabricate polyaniline-based microelectronic devices, diodes and transistors, that function when the polyaniline-functionalized microelectrode array is immersed in an electrolyte solution. The microelectrode array is a set of eight Au electrodes, 0.1 μm thick, 4.4 μm wide, and 50 μm long, each individually addressable and separated from each oth r by 1.7 μm. Polyaniline can be deposited in controlled amounts by electrochemical oxidation of aniline. When the polyaniline is deposited in sufficient amounts, two or more of the eight Au microelectrodes can be connected in the electrical sense. Current can pass between two connected microelectrodes when there is an applied potential between them. The magnitude of the current at a given applied potential depends on the electrochemical potential of the polyaniline. In 0.5 M $NaHSO_4/H_2O$ the current (at a fixed applied potential) is maximum at an electrochemical potential of ~+0.4 V vs. SCE and declines by a factor of $>10^6$ upon reduction to +0.1 or oxidation to +0.7 V vs. SCE. Owing to the large change in resistance upon change in electrochemical potential, the functionalized microelectrodes can function as diodes or transistors. The small spacing between the microelectrodes is crucial to device function, owing to the limited conductivity of the polyaniline. The switching time of a transistor-like device is faster than 0.1 s.

In this article we wish to present some new findings concerning the conductivity properties of polyaniline[1] immersed in an aqueous electrolyte solution and to demonstrate the fabrication of microelectronic devices based on the large change in resistance of polyaniline as a function of the electrochemical potential of the polyaniline. The study of the resistance of a film of polyaniline immersed in an aqueous electrolyte and the fabrication of devices having an electronic device function has involved the chemical derivatization of an array of Au microelectrodes, Figure 1. Fabrication of the microelectrode array itself was accomplished using techniques applied to the fabrication of Si-based microelectronic devices. The closely spaced, -1.7 μm, Au electrodes allow large currents to pass between two Au electrodes electrically connected with anodically deposited polyaniline.

Recent reports from this laboratory illustrate examples of molecule-based microelectronic devices, diodes and transistors,[2,3] based on derivatization of a microelectrode array with polypyrrole.[4] The polypyrrole-based devices were characterized in contact with non-aqueous electrolyte solutions. Polypyrrole is insulating at sufficiently negative (--0.4 V vs. SCE) potentials but becomes conducting at positive potentials and remains conducting at any positive potential where the polypyrrole is durable.[2,3] In contrast to the polypyrrole-based transistor, the polyaniline-based device described here can be turned "on" by either a positive or a negative shift of the electrochemical potential, because polyaniline films are essentially insulating at sufficiently negative (-0.0 V vs. SCE) or positive (-+0.7 V vs. SCE) electrochemical potentials. The response of the polyaniline-based transistors to a signal thus differs in a significant way from solid state transistors[5] where the current passing between source and drain, I_D, at a given source-drain voltage, V_D, does not decrease with increasing gate voltage, V_G.

The microelectrode-based devices described here and those reported previously based on polypyrrole[2,3] and poly-N-methylpyrrole[3] stem from work on chemically derivatized macroscopic electrodes.[6] In this regard, the work of Pickup and Murray[7] is especially relevant, showing diode-like behavior from a macroscopic electrode derivatized with a redox polymer and coated with a porous metal contact. Work on microsensors, especially so-called chemiresistors,[8] is related to the fabrication of coated microelectrode arrays that respond to chemical species.

Polyaniline is a material that has a long history in connection with electrochemistry. In their 1962 article on the kinetics and mechanism of aniline oxidation in aqueous H_2SO_4 Mohilner, Adams and Argersinger[9] recount the earlier work on oxidation of aniline at Pt in H_2SO_4 beginning with a paper by Letheby in 1862.[10] We use the basic methodology recently reported by Diaz and Logan[1] to deposit adherent thin films of polyaniline onto the Au microelectrode array illustrated in Figure 1. It is worth noting that conductivity of polyaniline has been measured to span fifteen orders of magnitude,[11] and specific mention has been made of the sensitivity of the conductivity to pH and other chemical parameters. Polyaniline has recently been used to coat semiconductor photoelectrodes,[12,13] as an electrochromic display material,[14] and to suppress corrosion of Fe.[15] The patent literature includes mention of polyaniline as a photoconductor, ion sensor material, and solar cell material. Our work represents the first *in situ* determination of the dependence of polyaniline resistance on electrochemical potential, an important fundamental parameter in certain devices and in understanding the mechanism of conductivity of the material.

ENTAL SECTION

tion of Microelectrode Arrays. The fabrication of microelectrode arrays ried out in the M.I.T. Microelectronics Laboratory, a class 100 clean The procedure begins with the design of the array and the preparation of to be used in the microfabrication procedure. A two mask process was ned. The first mask was made for a metal lift-off procedure to form the electrodes, leads, and contact pads. The second mask was made to pattern a resist overlayer leaving a 50 µm length of the microelectrodes and the act pads exposed. The microelectrode array was designed using the Computer d Design program HPEDIT at a Hewlett Packard Model 2648A graphics terminal on EC-20. The design file was translated into Caltech Intermediate Form (CIF). s CIF file was translated to Mann compatible code and written on magnetic e. Masks for photolithography were made from the file on magnetic tape using Gyrex Model 1005A Pattern Generator. E-K 5" x 5" x 0.090" Extra Flat high solution glass emulsion plates were used to make the photolithography masks. e emulsion plates were developed by a dark field process.

p-Si wafers of <100> orientation, 2" diameter, and 0.011" thickness were sed as substrates upon which to fabricate the microelectrode arrays. The Si afers were RCA cleaned in a laminar air flow hood. The wafers were immersed in ot aqueous H_2O_2 (6% by volume) aqueous NH_3 (14% by volume), briefly etched in F (diluted 10:1 with deionized water), immersed in hot aqueous H_2O_2 (6% by olume)/HCl (14% by volume), rinsed in deionized water (>14 MΩ·cm), and spun dry. The cleaned wafers were loaded immediately into an oxidation tube furnace at 1100°C under N_2. A dry oxidation cycle was used to grow a thermal oxide 11850 Å thick. Oxide thicknesses were measured using a Gaertner Model L117 ellipsometer. The oxidized wafers were taken immediately to the photolithography stage.

Each oxidized wafer was flood-coated with hexamethyldisilazane and spun at 000 rpm for 30 seconds. One milliliter of Shipley 1470 positive photoresist as syringed onto each wafer. The wafer coated with resist was spun for 30 econds at 6000 rpm and then prebaked 25 minutes at 90°C.

A GCA Mann 4800 DSW Wafer Stepper was used to expose the photoresist. The ann uses the 405 nm line of a 350 W Hg arc lamp as a light source. The mask mage is reduced 5:1 in the projection printing. An exposure time of 1.2 seconds as used. The photoresist was developed 60 seconds in Shipley 312 developer iluted 1:1 with deionized water. The wafers were then cleaned in a planar xygen etching chamber at 75-100 W forward power in 20 mtorr of oxygen for 15 econds.

A bilayer metallization was performed in a NRC 3117 electron beam vaporation system. A Cr adhesion layer of ~50 Å was first evaporated followed y ~1000 Å of Au. The combined Cr/Au thickness was measured to be 1052 Å on a ektak II surface profile measuring device.

At this point, Cr/Au was in contact with the SiO_2 substrate only in the areas hat were to form the microelectrodes, leads, and contact pads. The Cr/Au was eposited on the photoresist in all other areas. This resist/Cr/Au on the oxide as removed by a lift-off procedure. The metallized wafers were immersed in cetone at room temperature for 5 minutes. The soft-baked positive photoresist is oluble in acetone. The wafers were blasted with acetone from a Paasche air brush ith N_2 at 70 psi, sonicated for 30 minutes in acetone, then rinsed with acetone nd methanol before drying. The wafers were then cleaned in a mixture of hot queous H_2O_2 (6% by volume) and aqueous NH_3 (14% by volume), rinsed in deionized ater (>14 MΩ·cm) and spun dry. The wafers were then baked at 180°C for 40 inutes before repeating the photoresist spin coating process. Again the wafers ere prebaked at 90°C for 25 minutes. This photoresist was exposed in a Karl Suss nerica Inc. Model 505 aligner for 11 seconds, using a dark field mask. The hotoresist was developed in Shipley 312 developer diluted 1:1 with deionized ater to expose the bond pads and the array of 8 microelectrode wires. The xposed areas were cleaned of residual photoresist in the oxygen plasma etching hamber at 75-100 W for 1 minute. The remaining photoresist was hardbaked at 80°C for 15 hours.

Individual chips were scribed and separated. The chips were mounted on TO-5 eaders with Epoxi-Patch 0151 clear epoxy (Hysol). A Mech-El Ind. Model NV-827 Au all ultrasonic wire bonder was used to make wire bonds from the chip to the TO-5 eader. The bonding pads, wire bonds and header were encapsulated with poxi-Patch 0151. The header was connected through a TO-5 socket to external ires. The external wires were encased in a glass tube. The header was sealed t the distal end of the glass tube with heat shrink tubing and Epoxi-Patch 1C hite epoxy (Hysol).

lectrochemical Experimentation and Characterization of Polyaniline-Coated lectrodes. Prior to use as a microelectrode array, each microelectrode wire was ested with an ohmmeter to make sure it was not shorted to any other wire on the evice. Then each microelectrode was tested by running a cyclic voltammogram in .01 $\underline{M}$ $Ru(NH_3)_6^{3+}$/0.1 $\underline{M}$ $NaNO_3/H_2O$. The microelectrodes were derivatized by xidation of a stirred 0.44 $\underline{M}$ aniline solution in 0.5 $\underline{M}$ $NaHSO_4/H_2O$ at pH 1. The olyaniline was deposited at +0.9 V vs. SCE.[1] Electrodes were then examined by yclic voltammetry in 0.5 $\underline{M}$ $NaHSO_4$ at pH 1 to assess the coverage of polymer and o determine whether the polymer coated two or more electrodes resulting in a connection" between them. Macroscopic Au electrodes were derivatized with olyaniline by the same procedure to accurately relate the thickness of olyaniline to cyclic voltammetry response and the charge passed in the anodic eposition. Typically, a portion of the Au flag was covered with grease prior ısiting the polyaniline over the exposed Au surface. The grease was then ıved with CH_2Cl_2 to give a well defined step from Au to polyaniline.

Most of the electrochemical experimentation was carried out using a Pine el RDE4 bipotentiostat and potential programmer. In some cases where only a gle potentiostat was needed a PAR Model 173 potentiostat/galvanostat and a PAR el 175 universal programmer were used. Potential step experiments were carried using the RDE4 with a Tektronix type 564B storage oscilloscope as the order. All potentials were controlled relative to an aqueous saturated calomel erence electrode (SCE). Electrochemical measurements were carried out under Ar N_2 at 25°.

The microelectrode arrays were examined by electron microscopy using a ıbridge Mark 2A stereoscan with a resolution of 20 nm. The arrays were first ıted with ~200 A of Au to minimize problems from surface charging. Polyaniline lm thicknesses on the macroscopic Au electrodes were determined by using the ıtak II surface profile measuring device, as well as by electron microscopy.

lts and Discussion

racterization of Microelectrodes Derivatized with Polyaniline. Au micro-
ctrode arrays like that illustrated in Figure 1 can be derivatized with poly-
line by electrochemical oxidation of aniline under the conditions given in the
erimental. The derivatization can be controlled in the sense that the amount
polyaniline can be adjusted by variation in the charge passed in the electro-
mical polymerization; Table I gives some data for macroscopic Au electrodes.
one extreme the amount of polyaniline can be small enough to derivatize the
lividual microelectrodes but not electrically connect them. This fact can be
ablished by showing that a purposely derivatized microelectrode gives an
ctrochemical response in 0.5 M $NaHSO_4$ characteristic of electrode-bound
lyaniline.[12] At the other extreme, the polyaniline can be deposited in
ounts sufficient to electrically connect the microelectrodes. The cyclic
ltammetry appears as in Figures 2 and 3 for the coverages typically employed
re for derivatized devices.

At the extreme where microelectrodes are connected with polyaniline each of
e connected electrodes shows the same cyclic voltammogram at 50 mV/s in 0.5 M
HSO_4, consistent with one electrode being capable of oxidizing all of the
lyaniline present. Additionally, when all microelectrodes connected with
lyaniline are externally connected, the cyclic voltammogram is the same as when
ly one of the microelectrodes is driven as the electrode. This situation is
lustrated for two Au electrodes connected with polyaniline in Figure 2. When
jacent [illegible]atized microelectrodes are not connected the sum of the areas under
e cyclic voltammograms for the individual electrodes is the area found when the
croelectrodes are externally connected together and driven as a single
ectrode. Figure 4 shows an SEM of a polyaniline-coated microelectrode array
ere the microelectrodes are connected. The figure also shows a cross sectional

ble I. Correlation of Polyaniline Thickness and Area Under Cyclic Voltammogram.

asured ickness, μm[a]	Charge Passed In Synthesis, C/cm^2 [b]	Area Under CV Sweep, C/cm^2 [c]
0.25	0.024	3.62×10^{-3}
0.4	0.12	0.0566
9.0	0.72	0.338
10.5	0.72	0.366
26.5	2.4	0.562

Measured by Dektak or SEM in the reduced, dry state.

Charge passed in depositing polyaniline film.

Area under cyclic voltammogram from -0.3 to +0.9 V vs. SCE at 50 mV/s in 0.5 M $NaHSO_4$.

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Conclusions

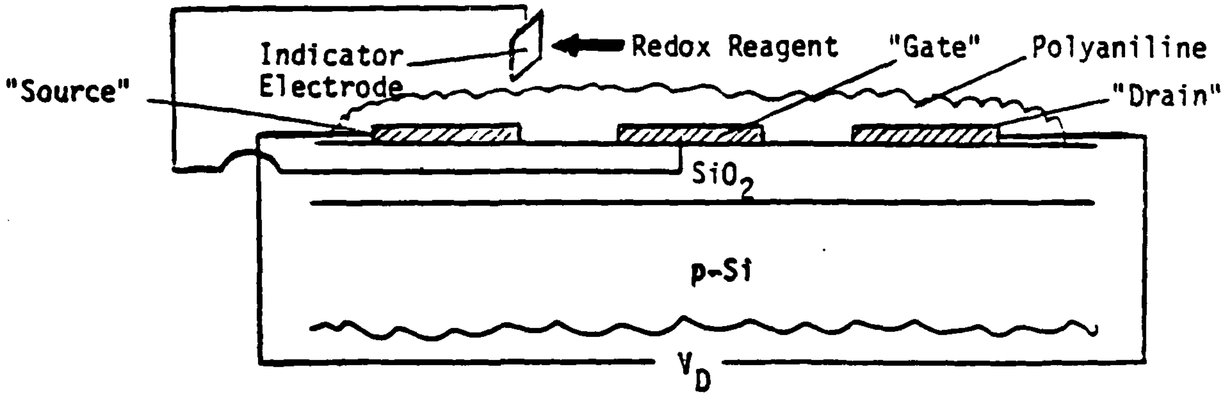
Polyaniline can be deposited onto a Au microelectrode array in a manner that allows the demonstration of diode-like and transistor-like electronic devices. The large change in electronic conductivity of polyaniline with change in electrochemical potential is the basis of the electronic device function. The polyaniline based transistor-like devices can be turned on and off by electrical or chemical signals that oxidize and reduce the polymer. Polyaniline-based devices for sensing redox reagents can be envisioned and response to $Fe(CN)_6^{3-}$ to turn on a polyaniline-based transistor and to $Ru(NH_3)_6^{2+}$ to turn it off establishes the viability of rapid response to simple, outer-sphere redox reagents. Approaches to achieve response to H_2 and O_2 include (1) use of an array of three polyaniline-coated microelectrodes, one of which is connected to a Pt indicator electrode or (2) deposition of Pd on the polyaniline connecting two microelectrodes to equilibrate the polyaniline with the H_2 and O_2 redox reagents. Preliminary results show that response of a transistor-like device, Scheme I, to pH changes can be achieved based on the pH dependence of the conductivity.

The fundamental finding of interest is that polyaniline in 0.5 M $NaHSO_4$ is much less conducting when reduced, -0.2 V vs. SCE, than when held at +0.4 V vs. SCE where it is oxidized. However, further oxidation reduces conductivity, Figure 5. These are the first definitive results relating the conductivity to electrochemical potential for polyaniline and give rise to an unusual I_D vs. V_G dependence, Figure 6, for the polyaniline-based transistor. Theoretical models for the conductivity of polyaniline must account for these new data. The experimental dependence of the polyaniline resistance vs. electrochemical potential is a demonstration of the utility of closely spaced microelectrodes in materials characterization.

source and drain are floating. The use of the three coated microelectrodes means slower response and larger signal to turn the device on, since more of the polymer must be oxidized and reduced to turn the device on and off.

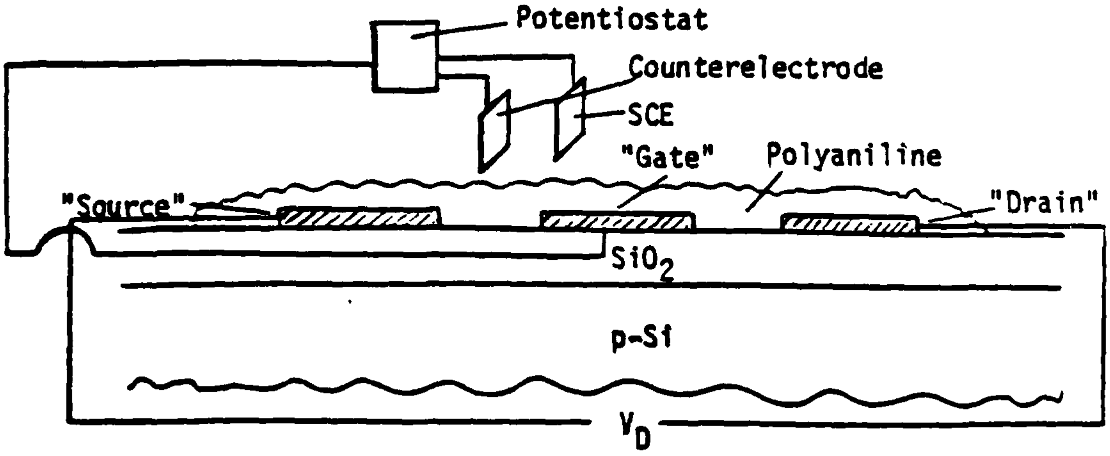
The more interesting chemical sensors will be those that can be made to be specific by further chemical functionalization of the polymer. One modest step in this direction has involved the deposition of Pd onto polyaniline that connects two microelectrodes. The deposited Pd provides a mechanism for equilibrating the polymer with H_2O/H_2 and O_2/H_2O. We do find that such a metallized polymer will give response to H_2 and O_2, but the time response is very slow compared to using an externally connected macroscopic Pt electrode as in Scheme III to equilibrate the polymer. Additional experiments to characterize the catalytic activity of the deposited metal are necessary. Several reports show that redox polymers can be equilibrated with H_2O/H_2 and O_2/H_2O using metals or metal oxides,[21] but it may be that the polymer diminishes the catalytic activity compared to oxide or other supports.[22]

that if the indicator electrode is Pt we are able to equilibrate the microelectrode array with H^+/H_2, as would be expected since Pt is known to equilibrate with H^+/H_2. It has been previously pointed out[2] that the arrangement



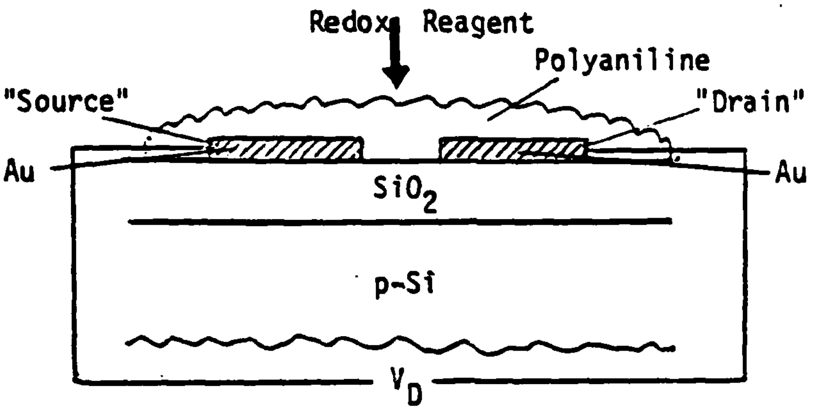
Scheme III. Polyaniline-based redox sensor where the indicator electrode equilibrates with the solution reagent to change the redox state of the polyaniline that also contacts the medium.

represented by Scheme IV is useful in characterizing the response of the chemically responsive system represented by Scheme III, since it is possible to quantitatively establish the amount of charge that must be passed to turn the device on. The difference between the device in Scheme IV and Scheme I, aside from employing three polymer-coated microelectrodes rather than two, is that the



Scheme IV. An electrically modulated analogue of the device represented by Sche III.

electrochemical potential of the polyaniline to a value that will allow current to



Scheme II. Redox responsive polyaniline-based device.

pass will be detected. This redox potential range is established by the data given in Figure 5. There may be additional inherent specificity depending on whether the polyaniline will equilibrate with a given redox reagent. To illustrate, the polyaniline does not equilibrate with the H^+/H_2 redox couple. However, there is rapid equilibration of the polyaniline with one-electron, outer-sphere redox reagents such as $Ru(NH_3)_6^{3+/2+}$, $E°' = -0.18$ V vs. SCE,[19] which has an E°' that is close to that of H^+/H_2 at pH = 1, $E°' = -0.3$ V vs. SCE. We also find that polyaniline equilibrates with $Fe(CN)_6^{3-/4-}$. In fact, we find that addition of the oxidant $K_3[Fe(CN)_6]$, $E°'(Fe(CN)_6^{3-/4-}) = +0.2$ V vs. SCE,[20] to a 0.5 M $NaHSO_4$ solution in which a polyaniline-based device is immersed will turn the device "on". Immersion of the device into a solution of 0.5 M $NaHSO_4$ containing $Ru(NH_3)_6^{2+}$ will then turn it "off". Exposure to $Fe(CN)_6^{3-}$ to turn on the device followed by exposure to H_2 will not turn it off at a measurable rate on the timescale on which the $Ru(NH_3)_6^{2+}$ will work. Quantitative aspects of the response to outer-sphere reagents is under investigation.

The change in resistance of the polyaniline with a change in electrochemical potential can be brought about by externally connecting the polyaniline-connected microelectrode array to a macroscopic indicator electrode, Scheme III, that will respond to reagents other than outer-sphere reagents. For example, we have shown should be stated that the maximum I_D values obtained in say 1 Hz cycles do not reach the I_D value that would be obtained in a steady state experiment like that illustrated in Figure 2 where I_D vs. time up to 16 h shows gradual increase in I_D. We find that I_D can become >80% of its ultimate value within 0.1 s of a V_G potential step from -0.2 to +0.3 V vs. SCE. The longer time changes may be due to subtle changes in the polyaniline structure or to slow redox reaction of polyaniline at the outer extremes of the device.

Response of Polyaniline-Based Devices to Chemical Signals. Various kinds of chemical sensors can be envisioned using polyaniline-based devices. For example, the device represented by Scheme I has characteristics that depend on the medium in which the device is immersed. To illustrate, the value of I_D at V_D = 20 mV and V_G = +0.2 V vs. SCE is reduced markedly upon raising the pH of the solution by adding NaOH. For an excursion from pH = 1 to pH = 6, for example, I_D declines by a factor of $\sim 10^2$. However, return to pH = 1 does not regenerate the original value of I_D. Loss of I_D of 50% can occur for excursions to pH = 6 for a period of time of the order of a few minutes. Apparently, chemically irreversible changes occur at high pH's that preclude the use of the polyaniline-based devices for pH sensing over a wide range of pH. However, modest excursions around pH = 1, pH = 0 to 2, are not grossly detrimental. Additional work is required to establish the quantitative aspects of the pH effects, but acid-base chemistry of the polyaniline is[11b,c,d] an example of the kind of chemistry that could give rise to chemical sensors.

Another kind of sensor that can be envisioned using the polyaniline-based devices would be one that responds to the presence of redox reagents that can equilibrate with the polyaniline. The simplest device would be that represented by Scheme II where the input signal is a redox agent that can equilibrate with the polyaniline to change the value of I_D at a given value of V_D. The specificity of the device stems from the fact that only those redox reagents that will bring the

the fact that the polymer actually undergoes chemical reaction at a particular potential that dramatically changes conductivity.

It is worth noting that it should be possible to achieve diode-like behavior by holding one of the microelectrodes at a sufficiently positive potential that the polyaniline is insulating, say +0.7 V vs. SCE, and moving the potential of the other microelectrode to a more negative potential. The difficulty is that the polyaniline cannot be held at +0.7 V vs. SCE without significant deterioration in properties. Thus, persistent diode behavior cannot be achieved when one of the microelectrodes is held at +0.7 V vs. SCE. The diode-like behavior when one microelectrode is held at a negative potential can be sustained for periods of time as long as several days. The limits to durability have not yet been defined.

A second important difference between the chemical-based devices and their solid state analogues is the switching time. The chemical-based devices depend on chemical redox reactions which occur relatively slowly compared to the speed of turn-on/turn-off for solid state diodes and transistors. Figure 8 shows several turn-on/turn-off cycles for a polyaniline-based transistor. The value of I_D is shown for a potential step of V_G from -0.2 to +0.3 V vs. SCE then back to -0.2 V vs. SCE at V_D = 0.18 V. The essential finding is that the device can be turned on and turned off in less than one second. Monitoring the rise and fall of I_D of the potential steps shows that the device switches from on to off in <50 ms and from off to on in a slightly longer time. These data support the conclusion that operation at >10 Hz is possible. This, however, is many orders of magnitude lower than the operational frequency of solid state devices.[5] The polyaniline-based devices can be cycled from "off" to "on" to "off" many times in a V_G step sequence such as V_G = -0.2 to +0.3 to -0.2 V vs. SCE. The sort of experiment represented by Figure 8 has been continued for periods of the order of 10 h with modest changes in characteristics (<20% change in I_D in the on state). However, it

$$\left.\frac{\partial I_D}{\partial V_G}\right|_{V_D} = g_m \qquad (1)$$

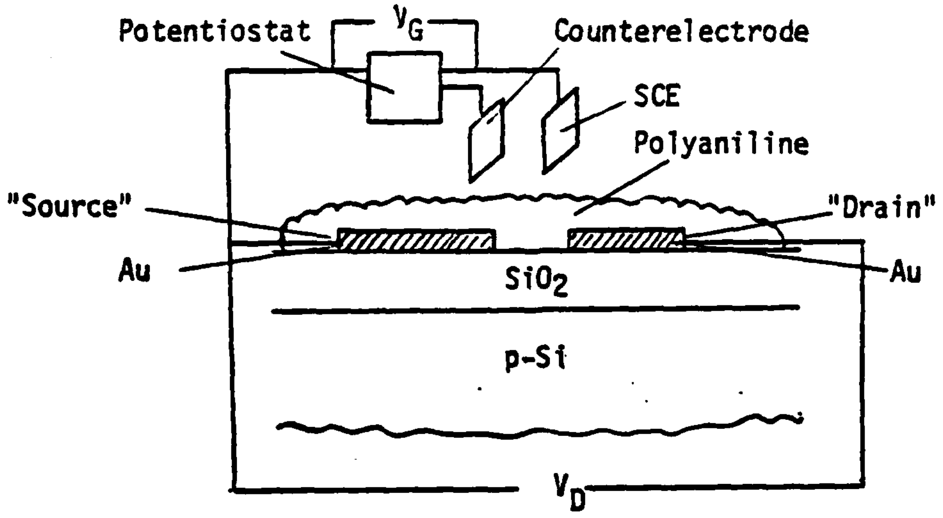
maximum value of g_m from the rising part of the I_D-V_G curve as V_G is moved positive is -0.1 mA/V. In units that can be compared to Si/SiO_2/metal field effect transistor (MOSFET) devices the maximum value of g_m is -20 millisiemens per millimeter of gate width. Note that gate length is by convention the separation of source and drain and the "width" is, therefore, the long dimension in our device. Good Si MOSFET devices have g_m values only about one order of magnitude higher than found for the polyaniline-based device represented by Scheme I. The importance of having a g_m value close to that of Si MOSFET's is that the signal from the polyaniline-based device, in the form of a voltage across a load resistance, can be fed to conventional MOSFET devices for further amplification.

While the device represented by Scheme I has some important features in common with a solid state transistor,[5] there are some important differences as well. For example, diode-like I_D-V_D curves can be obtained for V_G values where the polyaniline is reduced and insulating. Figure 7 shows such a curve. The point is that the current only passes between the two microelectrodes when one of the electrodes becomes oxidized. If the microelectrode labelled "drain" is moved negative of the "source", current does not flow because the polyaniline remains insulating. In a solid state device the I_D-V_D curve is not diode-like in the sense described here, though the I_D-V_D curve would not be symmetrical about V_D = 0. However, as pointed out for the polypyrrole-based devices,[2,3] the device represented by Scheme I is not an exact analogue of a solid state diode, because it is not a two-terminal device as is a p-n junction or a metal/semiconductor Schottky barrier.[5] The diode-like behavior of the device in Scheme I stems from considered to be as good a conductor as polypyrrole, under the proper conditions. Second, the polyaniline is less conducting negative and positive of -+0.4 V vs. SCE. This finding differs from the polypyrrole which was found to become conducting upon oxidation but did not become insulating again at accessible positive electrochemical potentials.[3] Third, the change in resistance is essentially reversible for potentials negative of -+0.6 V vs. SCE. Potentials significantly more positive give an increase in resistance when the polyaniline is returned to +0.4 V vs. SCE. Presumably, larger differences in resistance could be obtained but the negative limit for V_G is established by the onset of H_2 evolution and the limit at the positive extreme is limited by O_2 evolution and the fact that the polyaniline is not durable at more positive potentials. The properties established by the data in Figure 5 show that polyaniline-based transistor- and diode-like devices are possible.

The device represented by Scheme I can be regarded as a transistor-like (triode) device[3,7] where the charge passed in setting the gate to a potential where there is conductivity between source and drain can be regarded as an input signal. For the devices characterized here the charge necessary to turn the device completely on is -10^{-6} C. Figure 6 shows the output characteristics of a polyaniline-based triode, I_D vs. V_D at various values of V_G, and a plot of I_D vs. V_G at fixed V_D = 0.18 V. Unlike solid state transistors,[5] the polyaniline-based device shows an increase and then a decrease in I_D as V_G is varied from negative to positive potentials. A solid state device shows an increase in I_D as V_G is varied and I_D should either continue to increase or level off to a constant, V_G-independent value. The I_D-V_G curve for the polyaniline device, of course, stems directly from the raw data given in Figure 5 that show a minimum polyaniline resistance at -+0.4 V vs. SCE.

The data in Figure 6 allow determination of an important fundamental parameter, namely, the transconductance, g_m, which is given by equation (1).[5] The

the connected pair of electrodes is nearly constant for at least 16 h in that a rather constant steady state current passes between the two microelectrodes when wired as in Scheme I for V_D = 20 mV. In general, devices can be used for characterization for several days without significant deterioration.



Scheme I. Configuration of Polyaniline-Based Microelectrode Device.

Figure 5 shows data establishing that the conductivity of polyaniline immersed in 0.5 M $NaHSO_4$ depends on the electrochemical potential. The resistance between two polyaniline-connected electrodes can be measured by measuring I_D vs. V_D at a given V_G, Scheme I. The top half of Figure 5 shows a collection of raw I_D vs. V_D (for small V_D) data for a single device. The bottom half of Figure 5 gives the resistance vs. V_G of the polyaniline for the device. Note that variation in V_G is effectively variation in the electrochemical potential of the polymer. Thus, the data establish that the resistance of polyaniline depends on its electrochemical potential with a minimum in resistance in the vicinity of +0.4 V vs. SCE. Changes in resistance of $>10^6$ have been routinely found by this procedure.

Several points concerning the data in Figure 5 should be noted. First, the minimum resistance for the polyaniline is similar to that for polypyrrole connecting two microelectrodes spaced 1.4 μm apart.[3] Thus, polyaniline can be view of a macroscopic Au electrode coated with polyaniline to show thickness of the polyaniline in the dry state. The thickness of the polymer can also be measured in the dry state using a Dektak surface profile measuring device, and thickness values from the SEM accord well with the Dektak results. Table I lists measured thickness values of polyaniline on macroscopic Au electrodes vs. the area under cyclic voltammograms at a sweep rate (<50 mV/s) where peak anodic current is proportional to sweep rate. The thickness of polyaniline is not measured to be directly proportional to the integrated cyclic voltammetry wave as it is for surface-confined redox polymers derived from viologen studied in this laboratory.[16] The area of the cyclic voltammetric wave for polyaniline, however, includes capacitive charge that may not scale directly with coverage (thickness) as would faradaic charge. The lack of direct proportionality may be attributable to morphological changes in the polymer with increasing thickness. The relative importance of faradaic and capacitive currents has been dealt with for the cyclic voltammetry of polypyrrole,[17] and is presently under investigation in this laboratory for polyaniline.

Characteristics of Polyaniline-Based Microelectronic Devices. The ability to coat two or three adjacent Au microelectrodes and to connect them with polyaniline allows the demonstration of microelectronic devices, as has been shown for Au microelectrodes derivatized with polypyrrole.[2,3] All measurements to be described have been carried out for devices immersed in aqueous 0.5 M $NaHSO_4$ at 25° under an inert atmosphere of N_2 or Ar. Also, the polyaniline has been deposited by passing an amount of charge that should result in 5-10 μm thick polymer coatings.

Figures 2 and 3 show the cyclic voltammetry for a pair of microelectrodes that are connected with polyaniline. The electrochemical response in the cyclic voltammetry alone establishes that the two microelectrodes are connected using the procedure described above. The data in Figure 3 also show that the behavior of

Figure Captions

Figure 1. Scanning electron micrographs showing a completed chip containing one eight electrode array (top); a view of the area of the eight microelectrode array exposed for functionalization and electrochemical characterization (middle); and a close view of one of the 4.4 μm electrodes separated by 1.7 μm from two others.

Figure 2. Scan rate dependence of the cyclic voltammetry in 0.5 M $NaHSO_4$ for two adjacent Au wires coated with polyaniline (~5 μm thick). The fact that A alone, B alone, and A+B driven together give the same response shows that the electrodes are connected by the polyaniline. If electrodes were not connected A and B driven together would give the sum of A alone and B alone.

Figure 3. Typical cyclic voltammogram (100 mV/s) for a Au electrode coated with polyaniline (————). For this case two microelectrodes are connected and current, I_D, can be passed between the two electrodes when the value of V_G is at +0.3 V vs. SCE and V_D = 20 mV, cf. Scheme I. The inset shows I_D vs. time. The cyclic voltammogram after the 16 h experiment (·····) shows little change from the initial cyclic voltammogram.

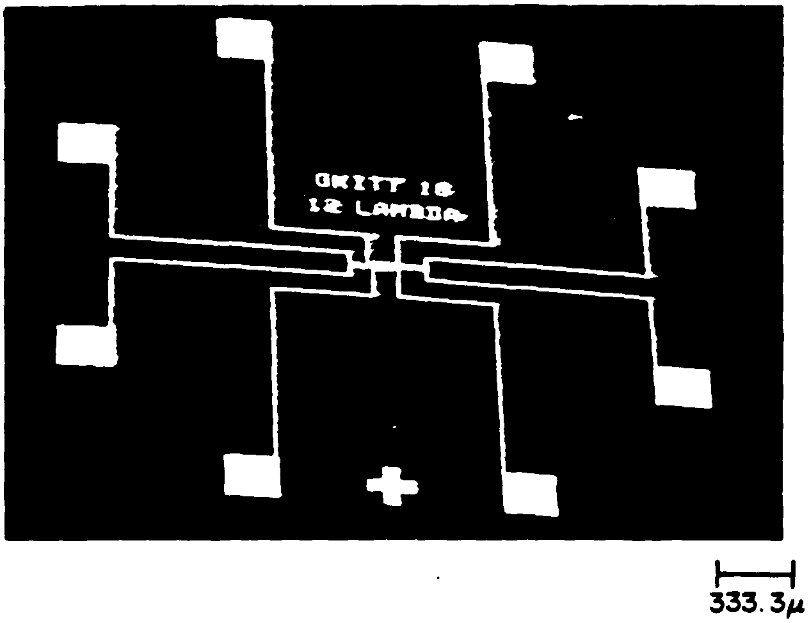
Figure 4. Scanning electron micrograph of the top surface of a microelectrode array derivatized with polyaniline (top) and a cross sectional view of polyaniline on a macroscopic Au electrode (bottom).

Figure 5. (Top) Current passing between source and drain upon a small potential excursion, V_D, around V_G as a function of V_G for a device like that in Scheme I. The data are for a device having a coating of polyaniline of ~5 μm. (Bottom) Plot of polyaniline resistance between two connected and adjacent microelectrodes as a function of V_G.

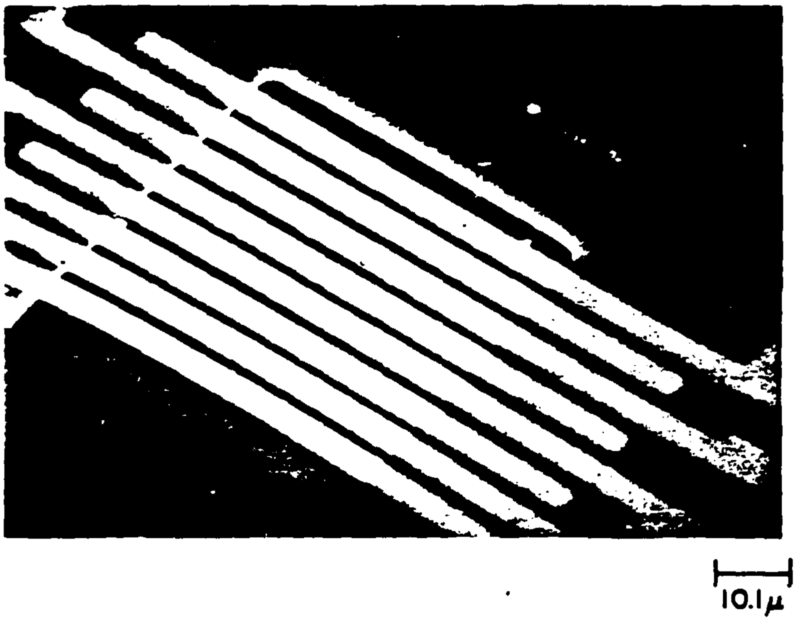
Figure 6. Characteristic of the device represented by Scheme I. The thickness of the polyaniline is ~5 μm. The I_D vs. V_D plots at fixed V_G were measured by varying V_D at 10 mV/s from 0 to +0.2 and back to 0.0. The plot of I_D vs V_G on the right curve is for V_D = 0.18 V.

Figure 7. Diode-like I_D vs. V_D curve when V_G is at a potential where polyaniline is reduced and insulating.

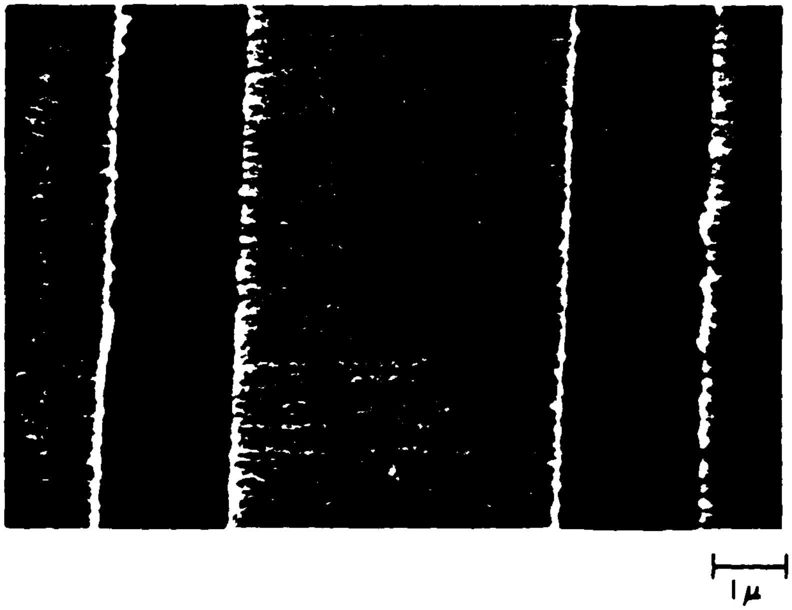
Figure 8. Turn-on, turn-off of I_D at V_D = 0.18 V upon changes in V_G as indicated.



Scanning Electron Micrographs of a Fabricated Microelectrode Array

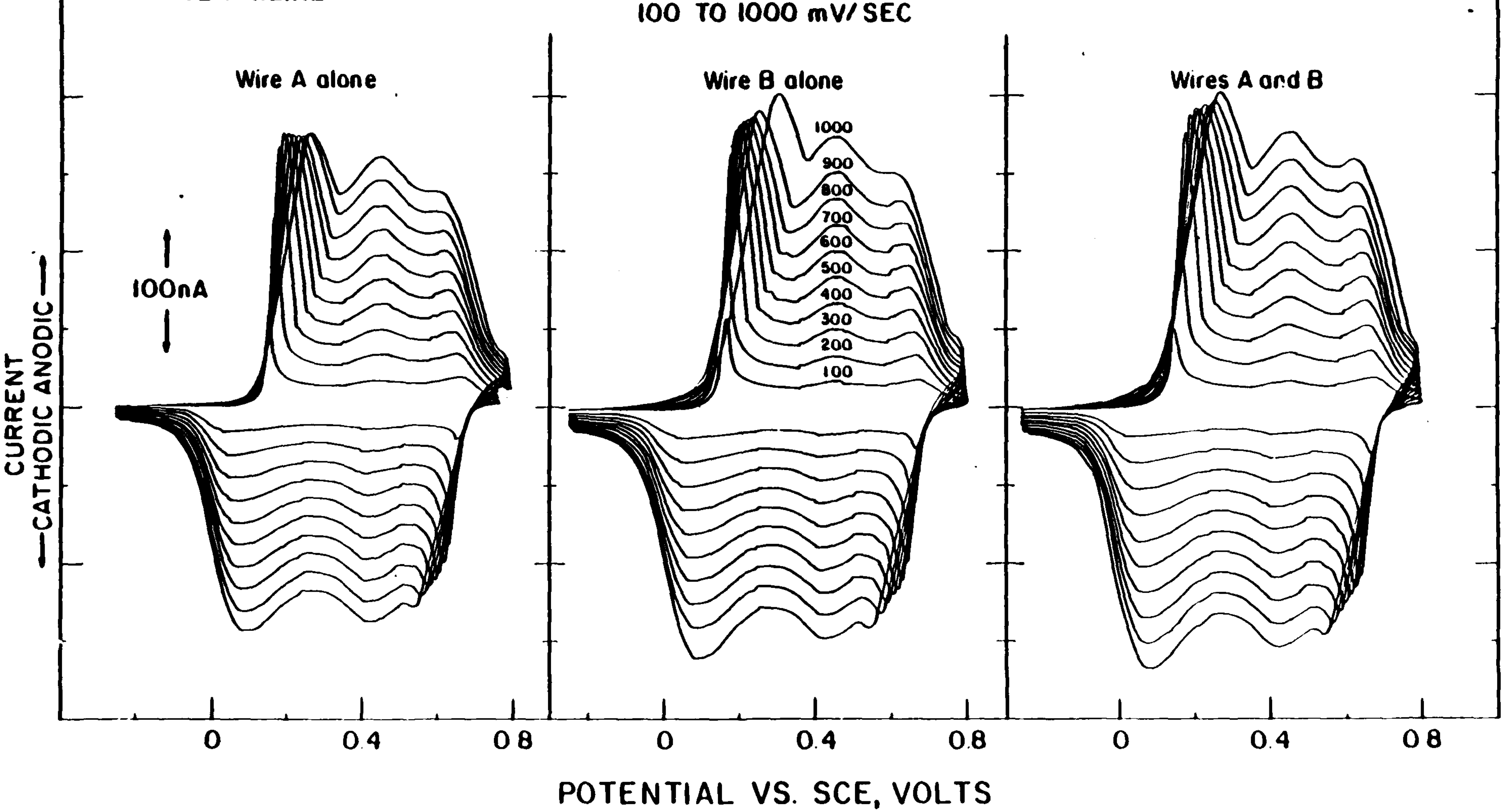


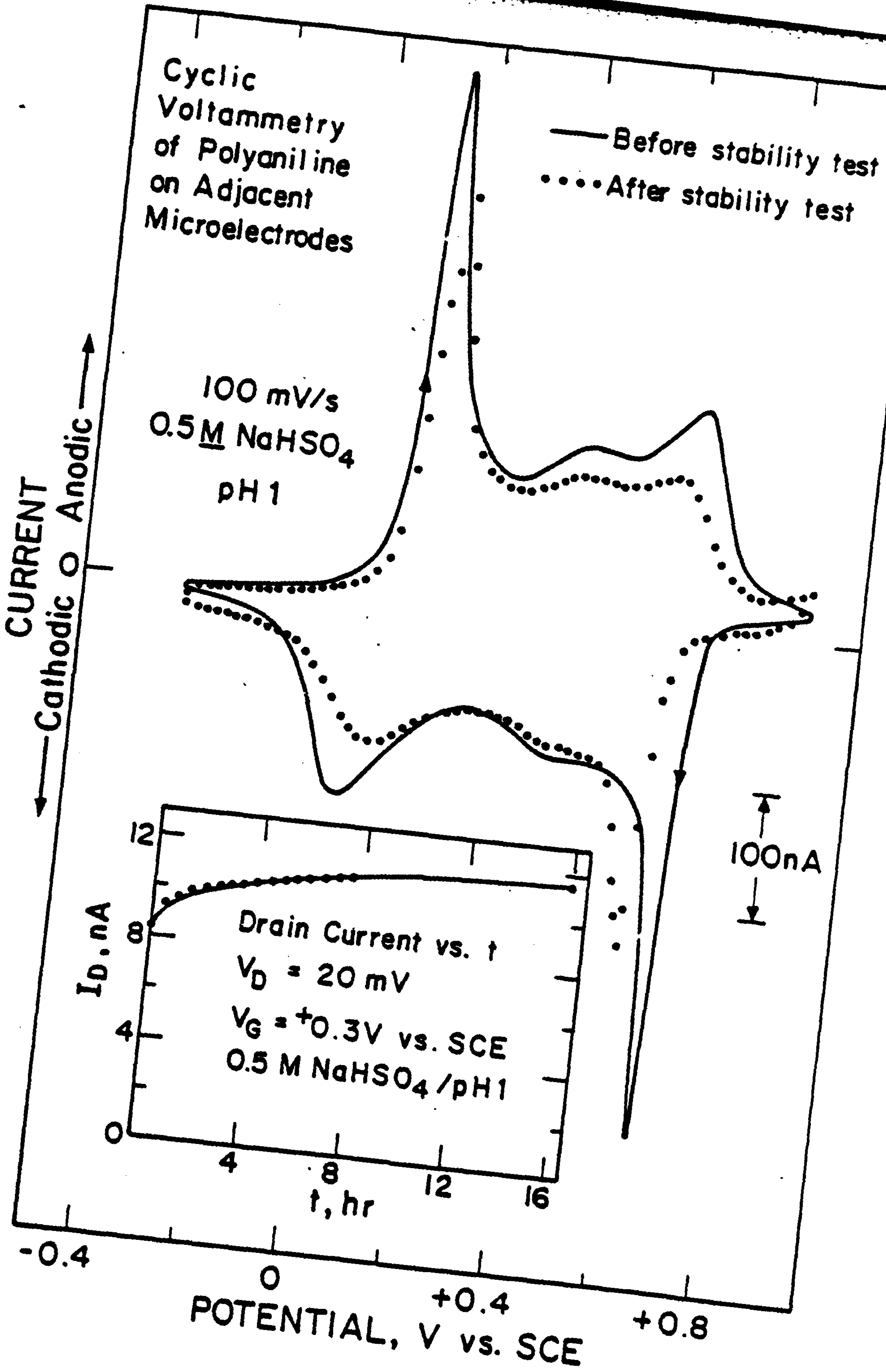
Wire Array Exposed to Solution

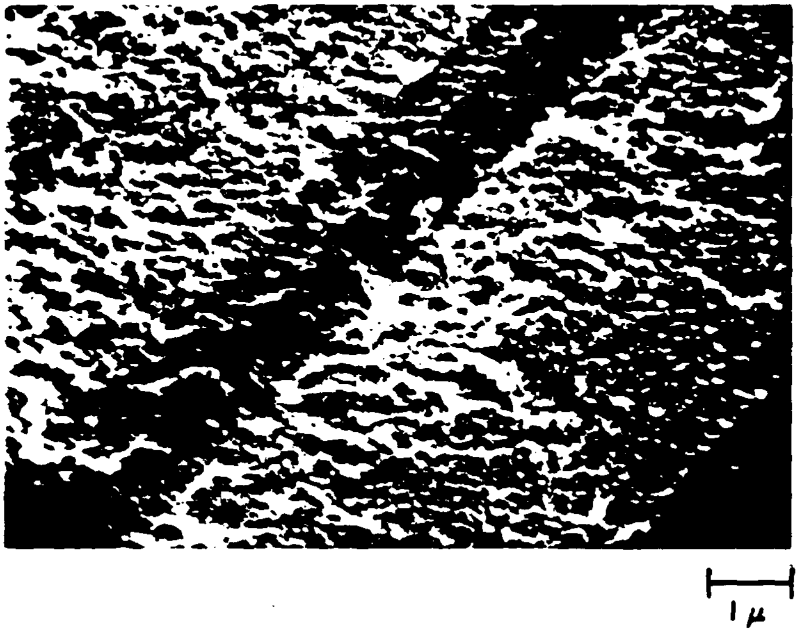


Gold Wires

SCAN RATE DEPENDENCE PLOTS FCR ADJACENT MICROELECTRODE WIRES A AND B CONNECTED WITH POLYANILINE

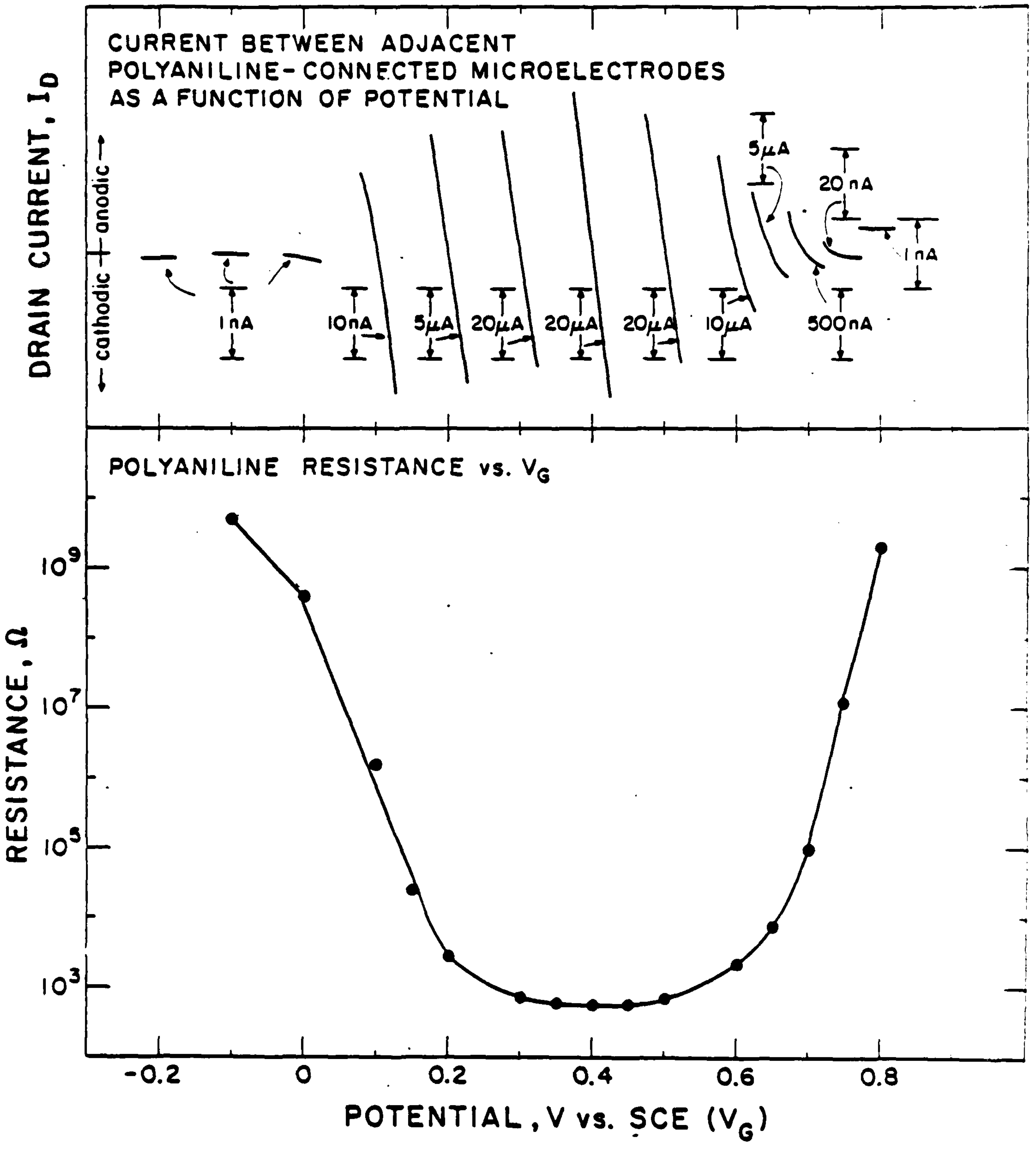


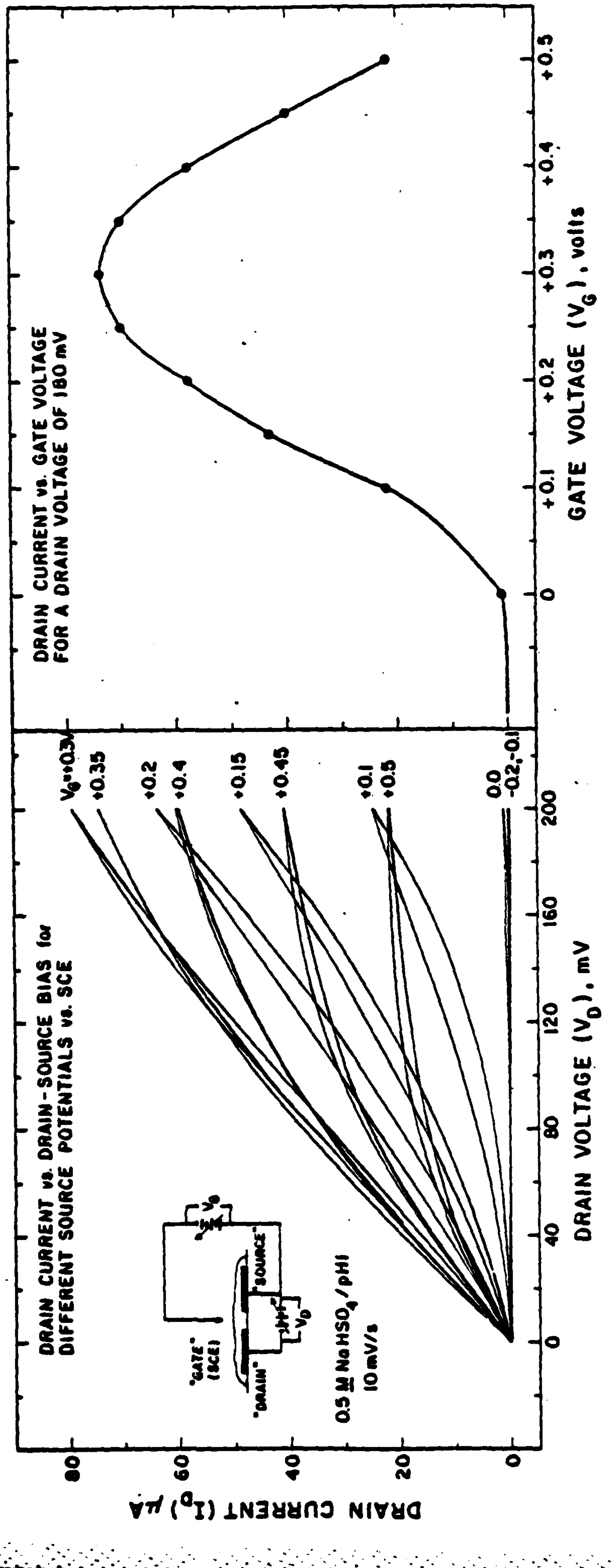

Cyclic Voltammetry of Polyaniline on Adjacent Microelectrodes
Before stability test
After stability test
100 mV/s
0.5 M NaHSO4
pH 1
CURRENT
Cathodic 0 Anodic
100nA
Drain Current vs. t
V_D = 20 mV
V_G = +0.3V vs. SCE
0.5 M NaHSO4 /pH1
I_D, nA
0
4
8
12
t, hr
4
8
12
16
-0.4
0
+0.4
+0.8
POTENTIAL, V vs. SCE

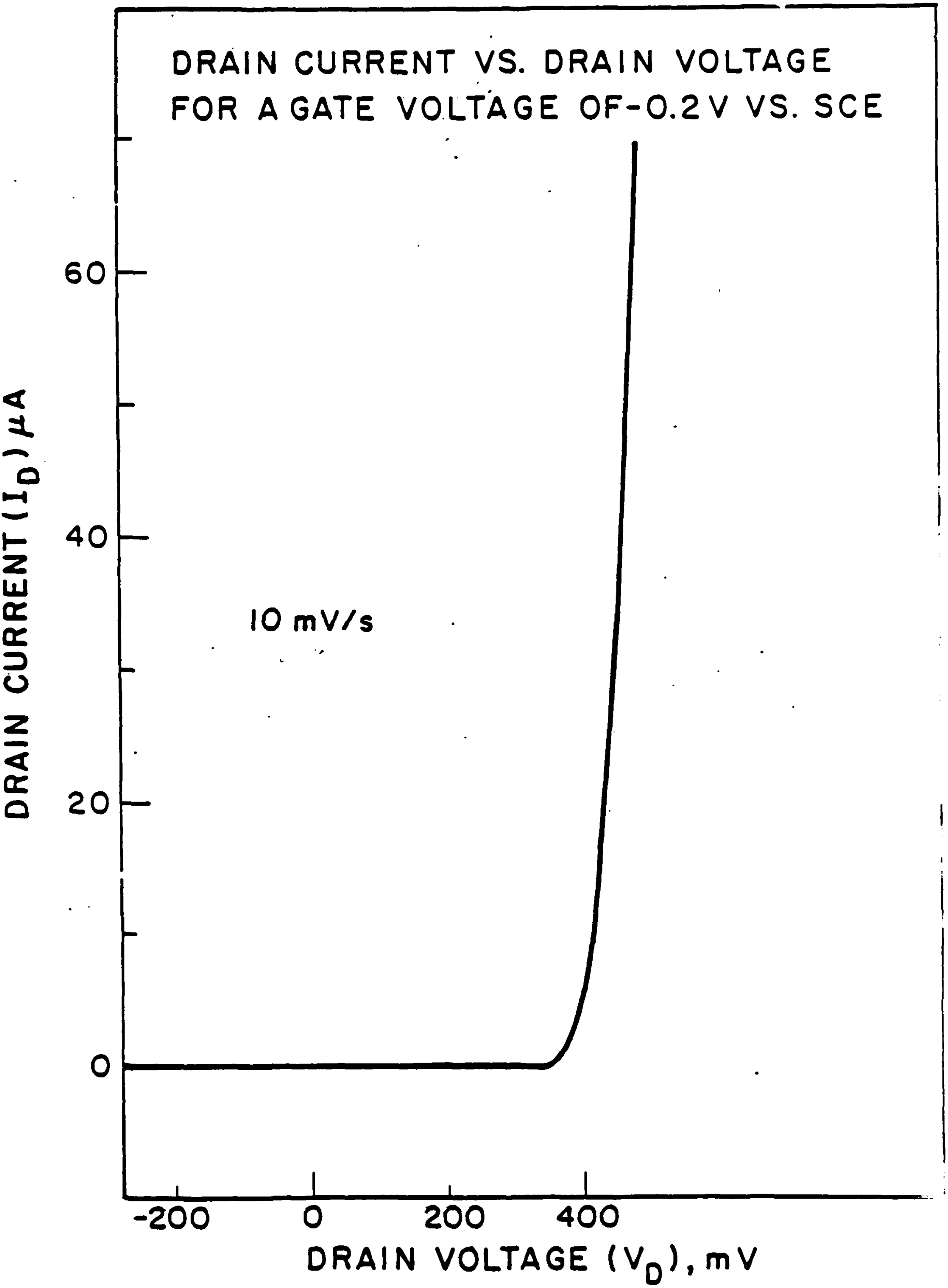


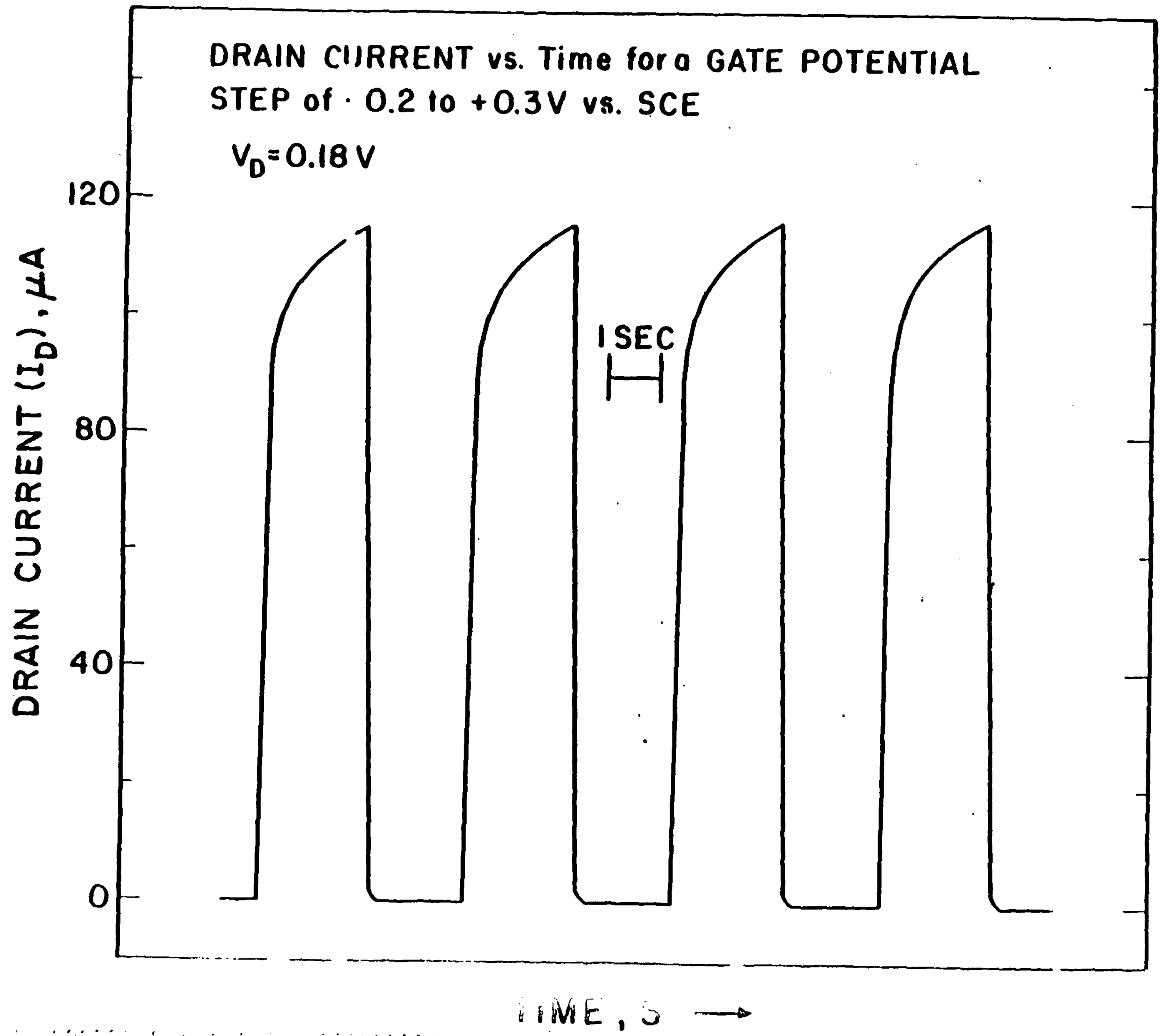
Scanning Electron Micrograph of Microelectrodes Coated with Polyaniline. Electrochemical measurements indicate that these wires are connected.

Cross Section of Polyaniline Coating


CURRENT BETWEEN ADJACENT POLYANILINE-CONNECTED MICROELECTRODES AS A FUNCTION OF POTENTIAL
DRAIN CURRENT, I_D
cathodic
anodic
1 nA
10 nA
5 μA
20 μA
20 μA
20 μA
10 μA
5 μA
20 nA
500 nA
1 nA
POLYANILINE RESISTANCE vs. V_G
RESISTANCE, Ω
10^9
10^7
10^5
10^3
-0.2
0
0.2
0.4
0.6
0.8
POTENTIAL, V vs. SCE (V_G)


DRAIN CURRENT vs. DRAIN-SOURCE BIAS for DIFFERENT SOURCE POTENTIALS vs. SCE
"GATE" (SCE)
"DRAIN"
"SOURCE"
V_G
V_D
0.5 M NaHSO$_4$/pH1
10 mV/s
V_G=+0.3
+0.35
+0.2
+0.4
+0.15
+0.45
+0.1
+0.5
0.0
-0.2,-0.1
DRAIN CURRENT (I_D) μA
80
60
40
20
0
0
40
80
120
160
200
DRAIN VOLTAGE (V_D), mV
DRAIN CURRENT vs. GATE VOLTAGE FOR A DRAIN VOLTAGE OF 180 mV
0
+0.1
+0.2
+0.3
+0.4
+0.5
GATE VOLTAGE (V_G), volts


DRAIN CURRENT VS. DRAIN VOLTAGE
FOR A GATE VOLTAGE OF-0.2V VS. SCE
10 mV/s
DRAIN CURRENT (I_D) μA
60
40
20
0
-200
0
200
400
DRAIN VOLTAGE (V_D), mV


DRAIN CURRENT vs. Time for a GATE POTENTIAL
STEP of · 0.2 to +0.3V vs. SCE
V_D=0.18 V
1 SEC
120
80
40
0
DRAIN CURRENT (I_D), μA
TIME, S →

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