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Microfabrication of WO_3-Based Microelectrochemical Devices

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Abstract

A new photolithographic process for the patterning of WO_3 is reported. A layer of RF sputtered polycrystalline WO_3 can be patterned by a combination of photolithographic and dry etching processes to selectively cover a fraction of eight Pt microelectrodes each ~50 µm long, 2 µm wide, and 0.3 µm thick and spaced 1.2 µm apart. The modified microelectrode arrays were characterized by electrochemistry, by surface profilometry, and by scanning electron microscopy. A pair of microelectrodes connected by WO_3 comprises a microelectrochemical transistor with pH-dependent electrical characteristics based on the pH and potential dependent conductivity of WO_3 associated with the reversible electrochemical reaction

$WO_3 + nH^+ + ne^- \rightleftarrows H_nWO_3$.

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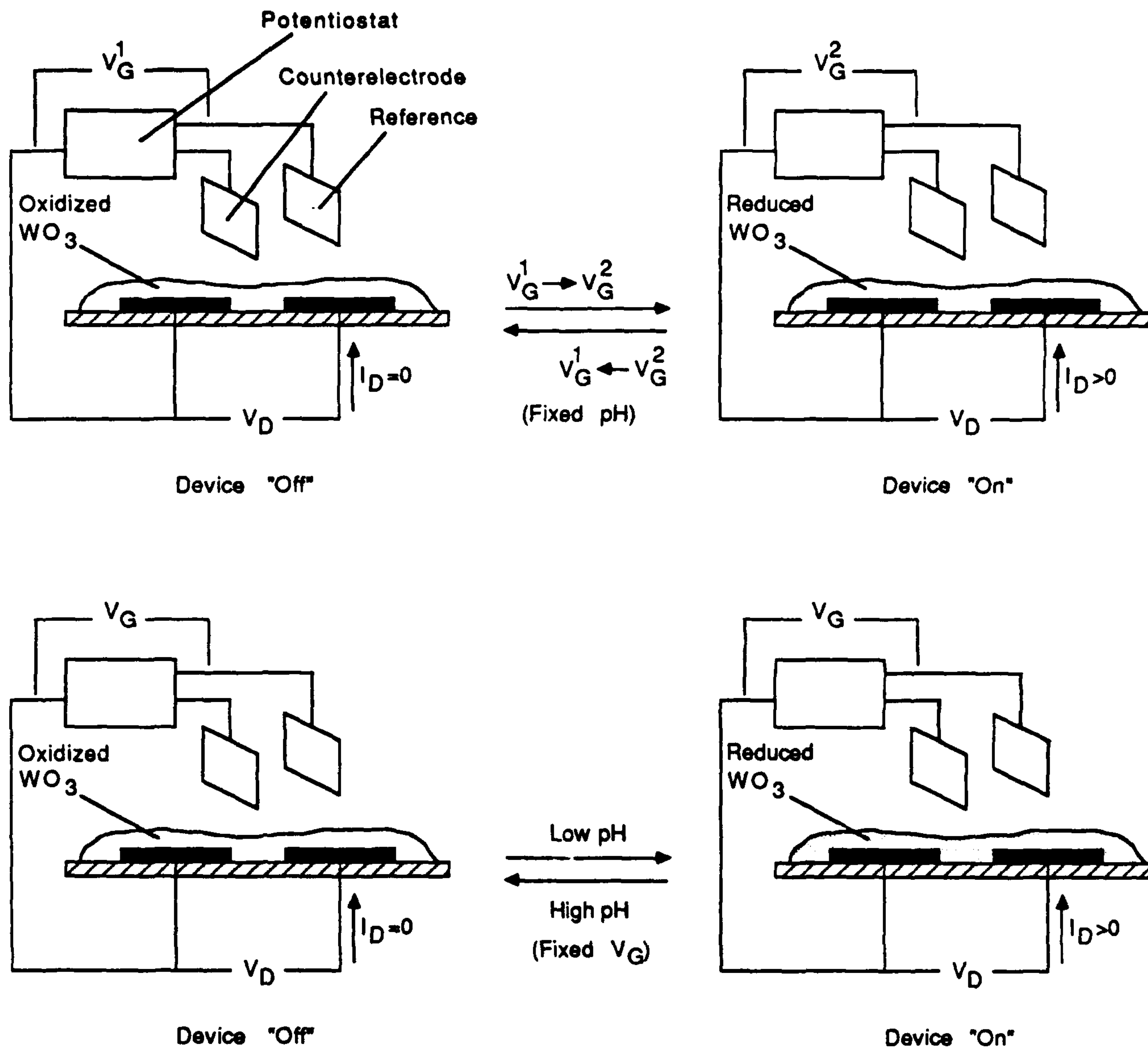
We wish to report a new microfabrication process for the selective modification of microelectrode arrays with a polycrystalline WO_3 film. Microelectrode arrays consisting of eight closely-spaced (~1.2 μm apart) Pt microelectrodes (~50 μm long, 2 μm wide, and 0.3 μm thick) have been fabricated and used in our laboratory for the study of redox active polymers[1,2] and inorganic materials.[2-5] A pair of microelectrodes connected by a redox active material can be used as a chemically sensitive transistor, because the conductivity of the redox active material depends on its state of charge.[6] For example, the WO_3-based device illustrated in Scheme I[3] is a pH-sensitive transistor by virtue of a pH dependence of the potential at which reduction occurs[3] to give conducting H_nWO_3,[7-10] equation (1). The WO_3-based transistor shows variations in I_D-V_G

$$WO_3 + nH^+ + ne^- \rightleftharpoons H_nWO_3 \qquad (1)$$

characteristics depending on pH and, therefore, can be used to detect pH changes at fixed V_G.[3]

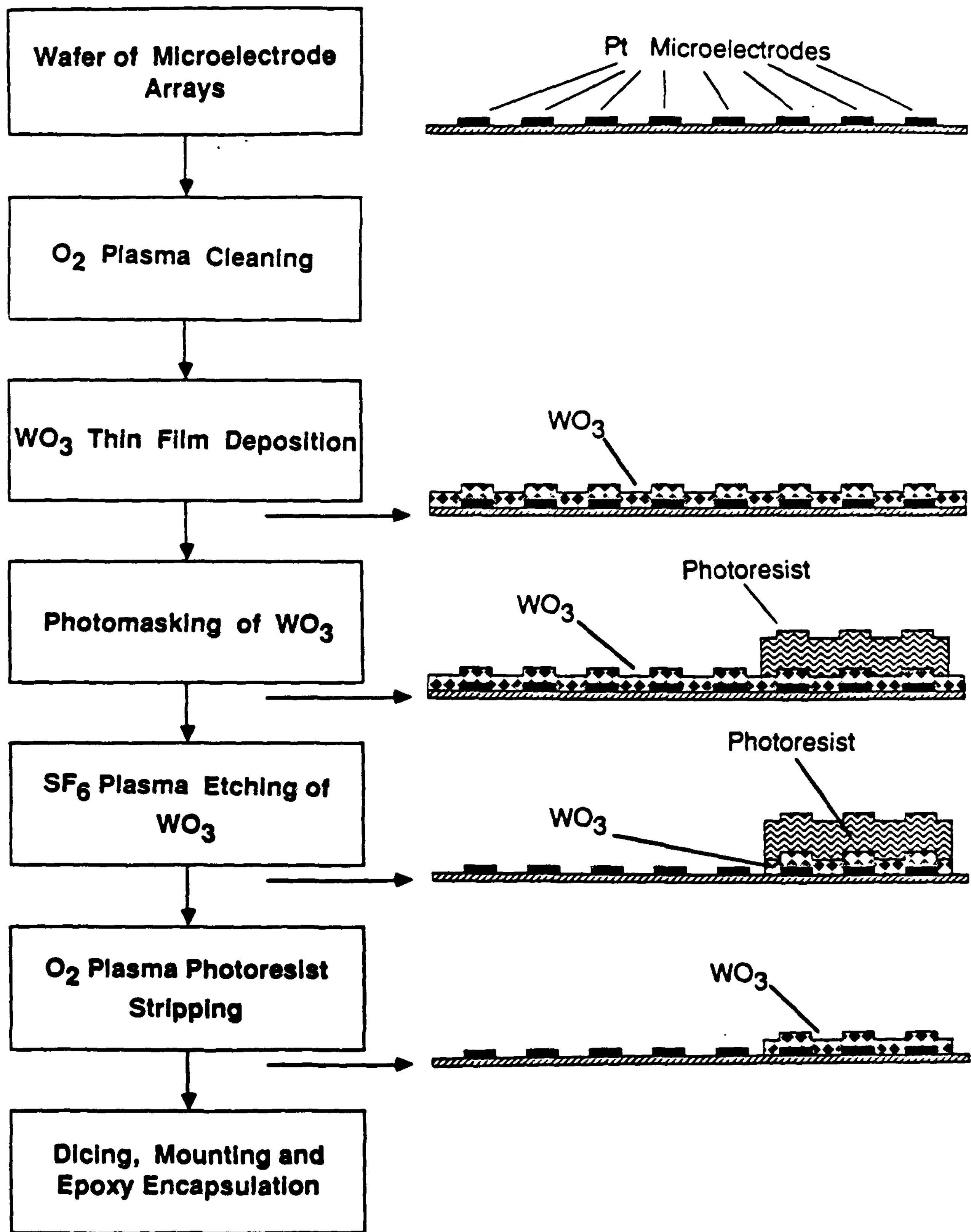
Microfabrication technology[11,12] is a possible route to preparation of large numbers of WO_3-based devices showing the same electrical characteristics. In this article we report a process for high resolution (~1 μm) patterning of WO_3 that yields selective modification of a microelectrode array. The results show that reproducible microelectrochemical response can be obtained and that



Scheme I. A WO_3-based transistor that turns on ($I_D>0$) when V_G is moved from $V_G{}^1$ where WO_3 is oxidized and insulating to $V_G{}^2$ where WO_3 is reduced and conducting. The WO_3-based device can also be turned on and off by varying the pH at fixed V_G.

non-modified microelectrodes can be left available for further functionalization. In addition to applications for microelectrochemical sensors the process may be applicable to high resolution electrochromic devices based on WO_3.[7] The patent literature contains various techniques for patterning WO_3 including deposition through masks[13] and etching by dissolution of WO_3 in alkaline solutions.[14] Such techniques, though, seem to be limited to linewidths of several millimeters. Other techniques involve polymer coordinated tungsten compounds ashed to the oxide by pyrolysis. This procedure is claimed to achieve ~5 µm resolution, but the quality of the WO_3 is not mentioned.[15] Our method of WO_3 patterning involves using photoresist to protect WO_3 and etching of unwanted WO_3. The etching process via an SF_6 plasma was deemed attractive, because likely W/O/F compounds, namely WF_6 and WOF_4, which might be formed by reaction of WO_3 with F· atoms generated in the SF_6 plasma, are volatile.[16] Importantly, the SF_6 plasma does not as rapidly etch organics[11,12] so that areas of WO_3 protected by photoresist will survive the etching process.

Scheme II summarizes the process that has been developed for selective modification of a Pt microelectrode array with WO_3. The process for preparation of the Pt microelectrode array has been reported previously,[1-6] and such arrays consist of eight, individually addressable Pt microelectrodes each ~50 µm long x ~2 µm wide x ~0.3 µm thick and separated from each other by ~1.2 µm. Before



Scheme II. Process for selective modification of a Microelectrode Array with WO_3.

WO_3-deposition Si wafers carrying Pt microelectrode arrays were cleaned in an O_2 plasma using a Harrick Plasma Cleaner. Using a process previously described,[3] the entire wafer was coated with a ~0.3 µm conformal coating of WO_3.

The WO_3-coated samples were dried at 200 °C for 30 min (dehydration bake). Positive photoresist KTI 1370SF was syringed onto the wafers which were then spun at 3000 rpm for 30 seconds. After a 25 min soft bake at 90 °C the wafers were exposed through a mask with ~8 mW/cm^2 intensity at 320 nm for 45 seconds using a Karl Suss High Resolution Aligner. The mask used was designed to allow exposure of all photoresist except that covering the desired pattern of WO_3, Scheme II. The photoresist was developed for 60 seconds in a 1:1 mixture of KTI 312 positive photoresist developer and deionized H_2O, followed by extensive rinse with deionized H_2O and air-blow drying. The photoresist protecting desired WO_3 was hard-baked at 135 °C for 25 min. The unprotected WO_3 was completely etched away in an SF_6 plasma at 200 W forward power for approximately 4 min. Finally the protective photoresist layer on top of WO_3 was removed in an O_2 plasma at 300 W forward power for 6 min. The O_2 plasma does not attack WO_3.

Figure 1 shows the photomask layout for patterning WO_3 in the fabrication of one microelectrode array. Surface profiling indicates that a ~0.3 µm thick layer of material conformally coats three electrodes of the microelectrode array, and SEM pictures demonstrate that material,

presumably WO_3, has been deposited where we originally intended to confine it. Proof for the composition of this material is deduced from the Auger electron spectroscopy and the electrochemical response of the WO_3 in aqueous solution. Additionally, Auger shows that WO_3 is completely removed by the SF_6 plasma from areas not protected by photoresist.

Microfabricated WO_3-based devices have been characterized by cyclic voltammetry in various buffered aqueous solutions, Figure 2. The position and the shape of the reduction wave of WO_3, as expected from equation (1), depend on the availability of the intercalating species,[3] i.e. H^+. The onset of reduction shifts to more negative potentials as the proton concentration decreases.

The fact that all the microelectrodes that appear connected with WO_3 in the SEM picture give identical response, when driven individually or when driven together, confirms that these microelectrodes are connected with WO_3 in the electrical sense.[1-6] Microelectrodes 1 through 5, which are supposed to be clean of WO_3 show no electrochemical response characteristic of WO_3, consistent with the absence of WO_3 from Auger electron spectroscopy. The cyclic voltammetry results are the same as previously reported from non-patterned WO_3 deposited in the manner used here.[3]

Taking the voltage between WO_3 and the reference electrode (SCE) as the gate voltage, V_G, the WO_3 itself can, in analogy to a Si MOSFET, be thought of as the channel.[6]

Applying a small drain voltage, V_D = 25 mV, between two adjacent microelectrodes connected with WO_3, Scheme I, we observe, Figure 3, an increasing drain current, I_D, as WO_3 is progressively driven to a more negative potential. Figure 3 also shows the effect of $[H^+]$ on the threshold voltage of I_D in various aqueous solutions. The WO_3-based devices described here are pH sensitive in the sense that a change in the pH alters the drain current at a given V_G, as previously reported.[3] Finally, the electrochemical and electronic response of the WO_3-based devices confirm that the photolithographically processed WO_3 retains the essential properties of the material.

In summary, we have demonstrated a photolithographic/ dry etching process for patterning WO_3 in a dimensional regime routinely employed in VLSI technology. Using this process we are able to confine WO_3 over a defined fraction of electrodes of a microelectrode array to produce a pH-sensitive microelectrochemical transistor. Significantly, the new process allows the rapid preparation of a large number of microelectrochemical devices having the same electrical characteristics. Moreover, the process leaves a fraction of microelectrodes of the array available to achieve a low level of integration of microelectrochemical devices by further functionalization of the array.

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References

[1]H. S. White, G. P. Kittlesen, and M. S. Wrighton, J. Am. Chem. Soc. **106**, 5375 (1984).

[2]E. W. Paul, A. J. Ricco, and M. S. Wrighton, J.Phys. Chem. **89**, 1441 (1985).

[3]M. J. Natan, T. E. Mallouk, and M. S. Wrighton, J. Phys. Chem. **91**, 648 (1987).

[4]M. J. Natan, D. Bélanger, M. K. Carpenter, and M. S. Wrighton, J. Phys. Chem. **91**, 1834 (1987).

[5]D. F. Lyons, M. O. Schloh, J. J. Hickman, and M. S. Wrighton, J. Phys. Chem., submitted.

[6]M. S. Wrighton, Comments on Inorg. Chem. **4**, 269 (1985).

[7]W. C. Dautremeont-Smith, Displays **3**, 3 (1982).

[8]B. Reichman, A. J. Bard, and D. J. Laser, J. Electrochem. Soc. **127**, 647 (1980).

[9]W. C. Dautremont-Smith, M. Green, and K. S. Kong, Electrochim. Acta **22**, 751 (1977).

[10]R. S. Crandall, B. W. Faughnan, Phys. Rev. Lett. **39**, 232 (1977).

[11]S. M. Sze, ed., *VLSI Technolgy*, McGraw-Hill, 1983, p.324.

[12]S. K. Ghandi, *VLSI Fabrication Principles*, John Wiley & Sons, 1983.

[13]P. M. Heyman, R. L. Quin, and I. Goroy, U.S. Patent No. 3 981 560 (1976).

[14]K. Y. Tenri, Y. I. Nishinomiya, H. H. Tenri, and H. U. Wakayama, U.S. Patent No. 4 123 841 (1978).

[15]Chem. Abstacts **101**, 181267q (1984).

[16]F. A. Cotton, and G. Wilkinson, Advanced Inorganic Chemistry, 4th Edition, John Wiley & Sons, p. 861 and p. 866.

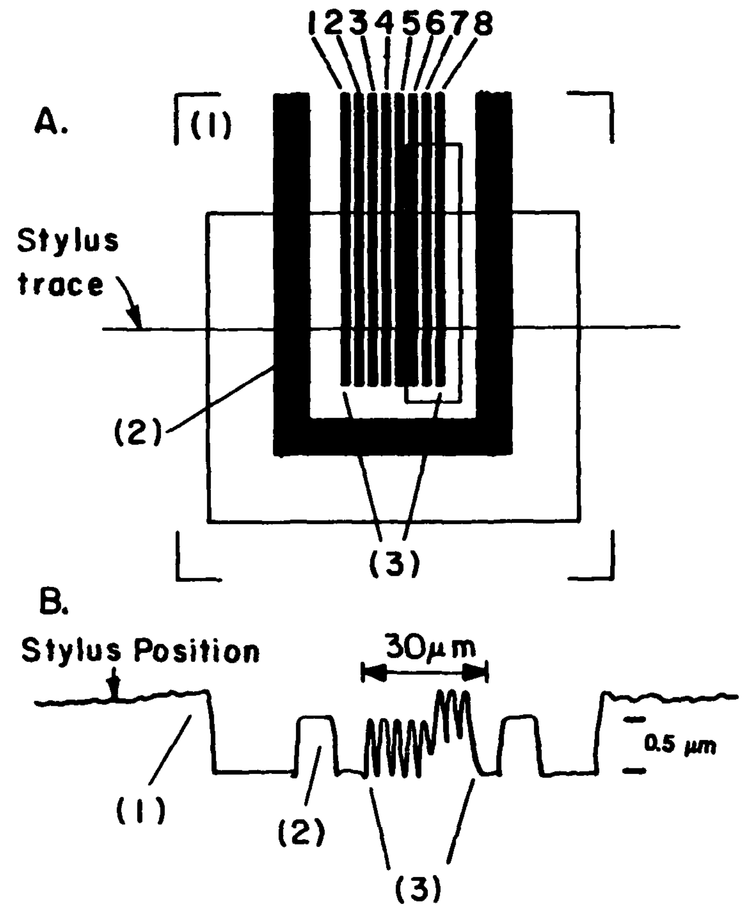
Figure Captions

Figure 1. Comparison of the photomask used for the WO_3 confinement and the actual devices, as characterized by surface profilometry and SEM. **(A)** Photomask layout for the patterning of WO_3 over three electrodes of an eight microelectrode array; **(B)** Surface profile; the stylus begins on the Si_3N_4 encapsulation layer (1), moves to the Pt protective barrier (2), and to the individual microelectrodes (3) three of which are coated conformally with ~0.3 μm of WO_3; **(C)** SEM of one chip produced by the process shown in Scheme II.

Figure 2. Cyclic voltammograms of patterned WO_3 on electrodes #6, 7, and 8 (cf. Figure 1) in aqueous 1.0 M $HClO_4$ as a function of sweep rate. The fact that #6, 7, or 8 give the same response and the same response as #6-8 driven together shows that all of the WO_3 is accessible by addressing any one of the three WO_3-coated and connected electrodes. Microelectrodes #1-5 show no detectable WO_3 at 500 mV/s.

Figure 3. I_D-V_G characteristics of a WO_3-based transistor (cf. Figure 1 and Scheme I) in several aqueous electrolytes showing that the threshold value of V_G shifts with pH;

pH $\approx$ 0 (0.5 M H_2SO_4 and 1.0 M $HClO_4$) and pH $\approx$ 7 (phosphate buffer and 0.1 M $NaClO_4$).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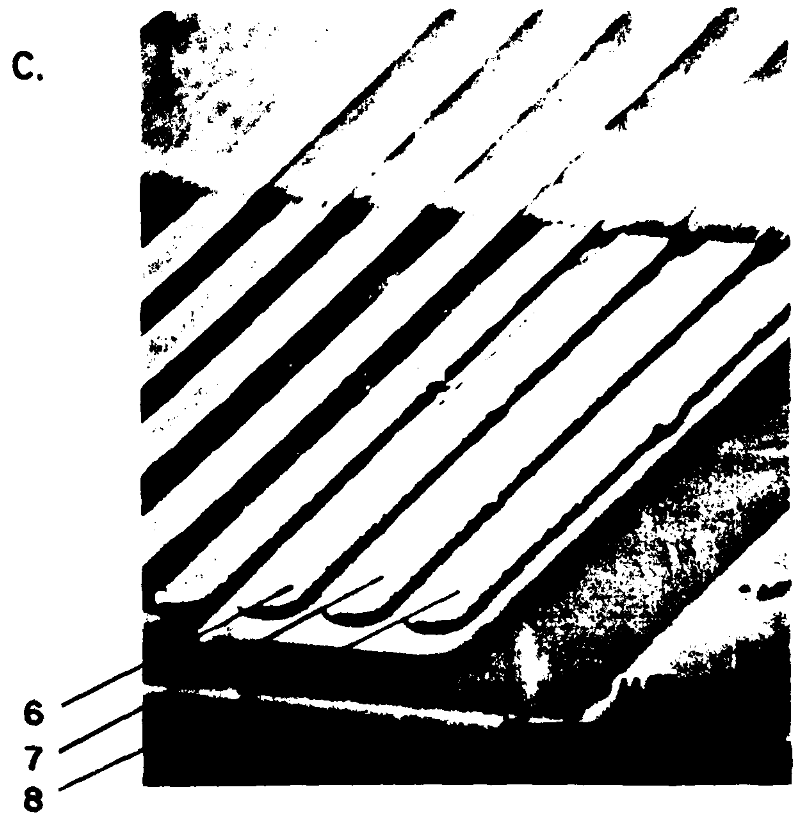
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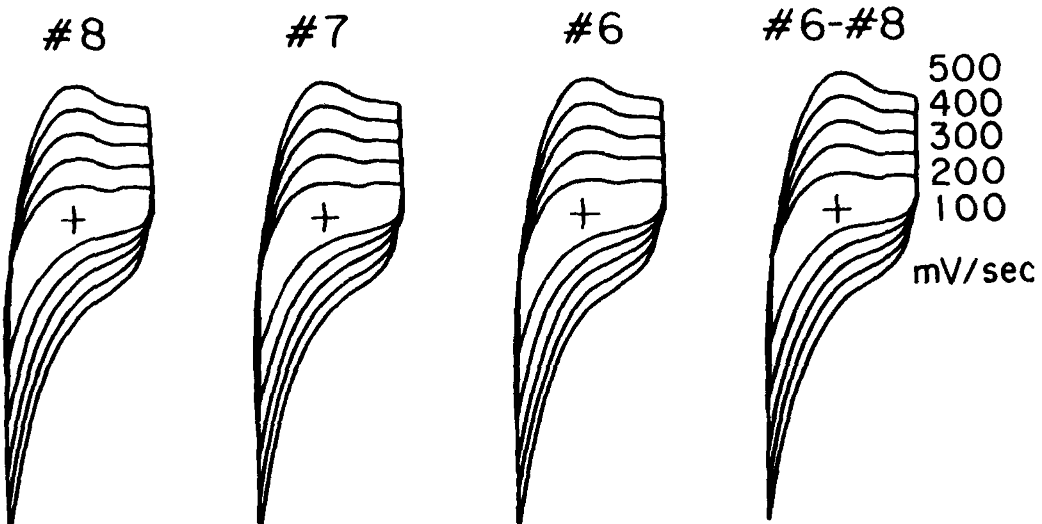
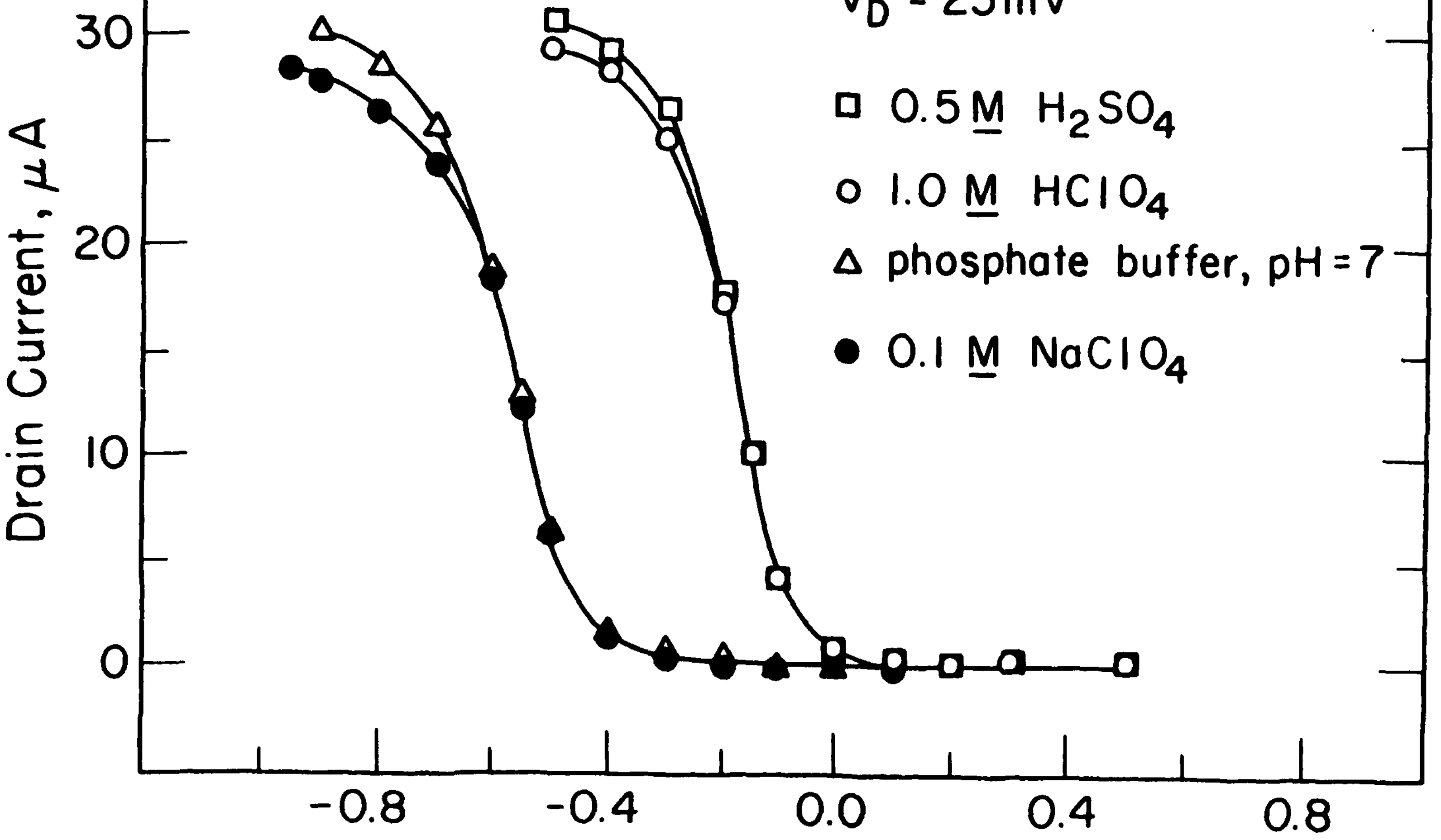
Cyclic Voltammetry of a Three Electrode Confined, WO_3 - Based Device in H_2O, 1.0 M $HClO_4$





I_D vs. V_G at Fixed V_D for a Three Electrode Confined, WO_3-Based Transistor in Aqueous Solutions
$V_D = 25 mV$
0.5 M H_2SO_4
1.0 M $HClO_4$
phosphate buffer, pH = 7
0.1 M $NaClO_4$
Drain Current, μA
30
20
10
0
-0.8
-0.4
0.0
0.4
0.8
Gate Voltage (V_G), V vs. SCE

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