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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ONR TR 12	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Amplification of Electrical Signals with Molecule-Based TRansistors: Power Amplificaiton up to a Kilohertz Frequency and Factors Limiting Higher Frequency Operation		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Elizabeth Paul Lofton, James W. Thackeray, Mark S. Wrighton		8. CONTRACT OR GRANT NUMBER(s) N00014-84-K-0291
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Massachusetts Institute of Technology Cambridge MA. 02139		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Work Unit #202-261
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, VA 22217		12. REPORT DATE 9/2?/86 NUMBER OF PAGES 15
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

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18. SUPPLEMENTARY NOTES

Prepared for publication in the Journal of Physical Chemistry

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

molecualr electronics, microelectrochemistry, microelectrodes, surface modification, molecule-based transistors, polyaniline, poly-3-methylthiophene

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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Abstract

Polyaniline- and poly(3-methylthiophene)-based transitors are demonstrated to amplify electrical signals at frequencies exceeding 100 Hz. The amplification of sinusoidal signals to the gate is established by showing the ratio of the average power in the drain circuit to that in the gate circuit exceeds unity. For the devices measured the amplification factor falls to unity between 100 and 1000 Hz. Measurements have been carried out at 298K for the microelectrochemical transistors immersed in aqueous or non-aqueous electrolyte solutions. The transistors consist of a pair of Au (or Pt) microelectrodes ($\sim$50 μm long x $\sim$2 μm wide x $\sim$0.1 μm high) connected by the redox polymer. The two microelectrodes serve as "source" and "drain" and the polymer serves as the "channel" of the device. The potential difference between source and drain is the drain potential, V_D, and current, I_D, flows between source and drain for gate potentials, V_G, where the polymer is conducting. The gate current, I_G, is associated with the charge needed to oxidize and reduce the polymer to change its conductivity. The amplification factor, A, is determined at a given frequency by measuring I_D (at fixed V_D) and I_G vs. time for sinusoidal variation in V_G between a potential where the device is off and a potential where the device is on. I_D and I_G are measured as a function of frequency to determine the frequency dependence of the average power in the drain and gate circuits. The maximum frequency for A > 1 is limited by (1) the conductivity changes of the polymer as a function of the state of charge (2) the volume of redox polymer used to make the device, and (3) the charge transport properties of the polymer. The results suggest that power amplification at frequencies that significantly exceed 10^3 Hz is possible for microelectrochemical devices.

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AMPLIFICATION OF ELECTRICAL SIGNALS WITH MOLECULE-BASED TRANSISTORS: POWER AMPLIFICATION UP TO A KILOHERTZ FREQUENCY AND FACTORS LIMITING HIGHER FREQUENCY OPERATION

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Abstract

Polyaniline- and poly(3-methylthiophene)-based transitors are demonstrated to amplify electrical signals at frequencies exceeding 100 Hz. The amplification of sinusoidal signals to the gate is established by showing the ratio of the average power in the drain circuit to that in the gate circuit exceeds unity. For the devices measured the amplification factor falls to unity between 100 and 1000 Hz. Measurements have been carried out at 298K for the microelectrochemical transistors immersed in aqueous or non-aqueous electrolyte solutions. The transistors consist of a pair of Au (or Pt) microelectrodes (~50 μm long x ~2 μm wide x ~0.1 μm high) connected by the redox polymer. The two microelectrodes serve as "source" and "drain" and the polymer serves as the "channel" of the device. The potential difference between source and drain is the drain potential, V_D, and current, I_D, flows between source and drain for gate potentials, V_G, where the polymer is conducting. The gate current, I_G, is associated with the charge needed to oxidize and reduce the polymer to change its conductivity. The amplification factor, $\underline{A}$, is determined at a given frequency by measuring I_D (at fixed V_D) and I_G vs. time for sinusoidal variation in V_G between a potential where the device is off and a potential where the device is on. I_D and I_G are measured as a function of frequency to determine the frequency dependence of the average power in the drain and gate circuits. The maximum frequency for A > 1 is limited by (1) the conductivity changes of the polymer as a function of the state of charge (2) the volume of redox polymer used to make the device, and (3) the charge transport properties of the polymer. The results suggest that power amplification at frequencies that significantly exceed 10^3 Hz is possible for microelectrochemical devices.

Introduction

We wish to report results which show that it is possible to amplify power with microelectrochemical devices termed molecule-based transitors.[1-3] There has recently appeared a review of such new kinds of electronic devices based on macromolecular materials.[4] The microelectrochemical devices for which power amplification is demonstrated here are based on the dramatic changes in conductivity associated with reversible electrochemical oxidation of polyaniline[2] or poly(3-methylthiophene).[3] These polymers can be formed via electrochemical oxidation of the monomers aniline[5] or 3-methylthiophene,[6] respectively. The polyaniline- and poly(3-methylthiophene)-based transistors are fabricated[2,3] by electrochemically forming the polymer on a pair of closely spaced (~1.2 μm) Au microelectrodes (50 μm long x 2μm wide x 0.1 μ high) such that the polymer connects the two microelectrodes, as illustrated in Scheme I. The new finding reported here is that it is possible to amplify

Device "Off"   Device "On"
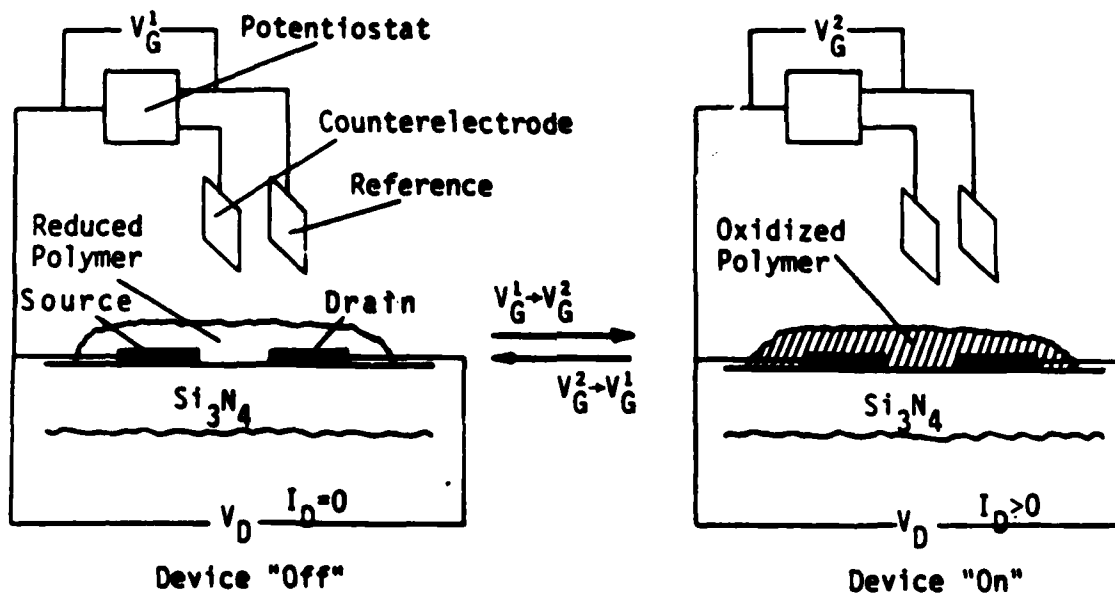
Scheme I. Redox polymer-based transistor where movement of the gate potential, V_G, from V_G^1 to V_G^2 turns the device on, $I_D > 0$, and movement of V_G from V_G^2 to V_G^1 turns the device off, $I_D = 0$, at a fixed drain potential, V_D. The gate current, I_G, is associated with the charge needed to oxidize and reduce the polymer connecting the source and drain.[2,3]

electrical power with the devices in the sense that the average power required to turn the device on and off, the average power in the gate circuit, P_{gate}, is less than the average power available in the drain circuit, P_{drain}. The ability to amplify power depends on the frequency of the gate signal. The devices have demonstrated ability to amplify power for frequencies below 1 kHz, but there is the prospect of making significantly faster microelectrochemical transistors using microfabrication techniques to reduce the volume of redox polymer needed to connect source and drain and to make the distance between source and drain smaller than the ~1 μm used so far.[1-3]

Power Amplification and Frequency Dependence

Demonstration that it is possible to amplify power with the device represented in Scheme I involves making measurements of the gate current, I_G, vs. gate potential, V_G, and of drain current, I_D, vs. time at fixed drain potential, V_D, for a sinusoidal variation of V_G from V_G^1, where the device is off ($I_D = 0$), to V_G^2 where the device is on ($I_D > 0$) and back to V_G^1. Figure 1 illustrates the kind of data required to assess power gain for a poly(3-methylthiophene)-based transistor at a frequency, f, of 1 Hz. The amplification factor, A, is taken to be the ratio of P_{drain} to P_{gate}, equation (1). Whenever the value of A exceeds one, power gain is realized. The value

$$\text{Power Amplification Factor} \equiv \underline{A} = P_{drain}/P_{gate} \qquad (1)$$

of A depends on f, because the value of P_{gate} increases as f increases. In the best case P_{gate} increases linearly with f, because I_G increases linearly with the voltage sweep rate for electrodes modified with redox active polymers.[7] In such a case A is proportional to f^{-1}. Often, however, surface-confined redox polymers do not give a linear relationship between I_G and f particularly

at high f, because charge transport through polymers is relatively slow.[8]

Generally, slow charge transport can be attributed to a combination of slow

electron exchange between sub-units of the polymer and ion movement into, or

out of, the polymer to balance charge. Charge transport through a redox

polymer is sometimes found to be a diffusion process, and the value of I_G is

then proportional to the square root of the voltage sweep rate. The

consequence of low values of the diffusion coefficient for charge transport,

D_{ct}, is that at some value of f, the redox polymer-based device will not be

turned "on" to the maximum value of I_D for a given value of V_G. The point is

that the "best case" f dependence of $\underline{A}$ is an f^{-1} dependence, and low D_{ct} values

can complicate matters further because the device may not switch at the

frequency of the gate signal. Not surprisingly, the maximum value of f where $\underline{A}$

> 1 will, in general, depend on the nature of the polymer and parameters that

affect its charge transport properties. For so-called conducting polymers like

polyaniline or poly(3-methylthiophene) the factors affecting switching speed

have not been fully elaborated, but since the process is electrochemical the

factors affecting conventional redox polymers[8] will likely also influence the

properties of conducting polymers.

Interestingly, for a given polymer under set conditions a redox

polymer-based transistor will have a maximum f where $\underline{A}$ > 1 that depends on the

geometry of the device. This follows from the following considerations.

First, the maximum value of P_{drain} is directly proportional to the maximum

value of I_D; I_D increases for smaller source-drain separations. Thus, larger

values of $\underline{A}$ would be possible by using submicron microfabrication techniques

to place the source and drain closer together than in devices fabricated so

far.[1-3] Second, the maximum value of P_{gate} (for the best case) is directly proportional to the amount of redox polymer that is used to connect source and drain. Again, by using different microfabrication techniques it should be possible to change the geometry of the device in a way that allows the use of qualitatively less polymer than in the microelectrochemical transistors described to this time.[1-3]

Results and Discussion

Figure 1 illustrates the characterization of a poly(3-methylthiophene)-based transistor for 1 Hz operation. The transistor has a source-drain separation (gate length) of 1.2 μm and a gate width of ~100 μm. Thus, the area covered by the polymer is less than 5×10^{-6} cm^2 and involves ~10^{-8} C to switch from off ($I_D = 0$) to substantially on ($I_D > 1mA$). Polymer thicknesses corresponding to the charge passed in switching have been reported perviously[2,3] and are of the order of a few microns. As shown, I_D(peak) is 5mA, and this maximum value occurs at the maximum value of V_G, +0.95V vs SCE. The I_D(peak) at 1 Hz is essentially the same as obtained for V_G fixed at +0.95V vs SCE. The I_G(peak) at f = 1 Hz is 0.31 μA, much smaller than I_D (peak). Thus, at f = 1 Hz, $\underline{A} \sim 3 \times 10^3$. Figure 2 illustrates the f dependence of P_{drain}, showing that higher f does give a decline in P_{drain}. Further, I_D(peak) lags the V_G(peak) by about a half cycle at 100 Hz. As f is increased I_G(peak) increases, but not linearly, resulting in an increase in P_{gate} as f is increased. $\underline{A}$ falls to 1.0 between 100 and 1000 Hz. The data in Figure 2 show that the poly(3-methylthiophene)-based device only turns on to the maximum extent at the lowest f. Nonetheless, power gain can be realized for f < 10^3 Hz for several independently prepared devices.

Data shown in Figure 3 and 4 indicate that polyaniline-based transistors can operate at significantly higher f than the poly(3-methylthiophene)-based device characterized by data in Figure 1 and 2. The polyaniline-based device is about the same size as the poly(3-methylthiophene)-based device and involves about the same amount of charge to turn it on and off. The significant finding concerning the polyaniline-based device is that complete turn on can be achieved at >300 Hz; I_D(peak) is 130 μA, independent of f, Figure 3. Figure 4 shows the relationship between $\underline{A}$ and f, indicating that $\underline{A}$ falls from ~10^3 at 1 Hz to ~1 at 1 kHz frequency. Figure 4 also shows data relating I_G (peak) and f: I_G(peak) increases strongly with f, but not quite linearly. The somewhat

lower value of $\underline{A}$ at 1 Hz for the polyaniline- vs. the poly(3-methylthiophene)-based device stems mainly from the difference in the maximum conductivity of the polyaniline vs. poly(3-methylthiophene) that results in a smaller I_D(peak) for the polyaniline system.

The relatively slow switching of the poly(3-methylthiophene)-based device is essentially independent of the medium from $CH_3CN/0.1$ $\underline{M}$ [$\underline{n}$-Bu$_4$N]ClO$_4$. Increasing the electrolyte concentration to 0.5 $\underline{M}$, for example, does not increase the switching speed. Likewise, using aqueous/0.5 $\underline{M}$ NaHSO$_4$ (used for the polyaniline-based device) or aqueous/1.0 $\underline{M}$ HClO$_4$ leads to no significant increase of I_D(peak). Poly(3-methylthiophene) has been noted previously[9] to be less sensitive to the charge compensating anion than other conducting polymers such as polypyrrole.[10] It has already been established that the steady state electrical properties of poly(3-methylthiophene)-based transistors are largely independent of the medium.[3,11,12] The medium effects on the turn on/turn off rate need to be examined in greater detail,[11] but the results so far suggest that the polyaniline-based device is simply superior when operated under the same conditions, at least with respect to the ability to rapidly switch the polymers between the insulating and conducting states.
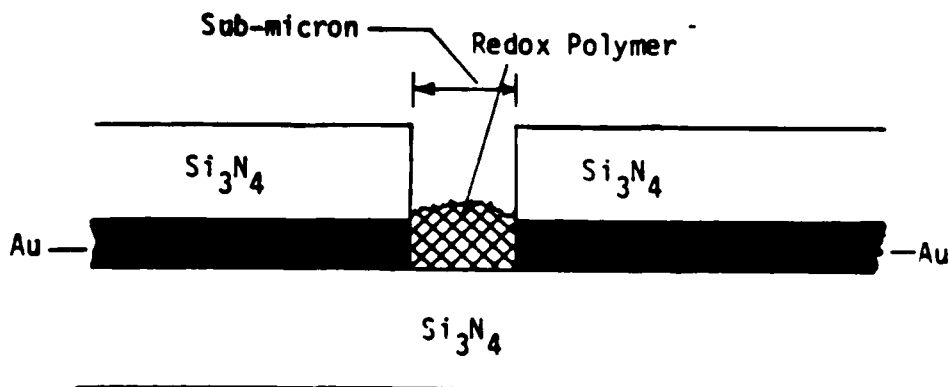
Scheme II. Proposed microelectrochemical device structure to minimize amount of redox polymer needed to connect source and drain.

Complete turn on/turn off of the polyaniline-based device at 1 kHz, Figure 3, is very intriguing, because this means that a device involving the use of less polymer can show $\underline{A} > 1$ at frequencies exceeding 1 kHz. Scheme II indicates one device geometry that would involve the use of a smaller amount of polymer than for the devices characterized here, Scheme I. The energy required to turn on the poly(3-methylthiophene)- or polyaniline-based transistor is about 10^{-8} J; this will also be decreased by the use of a smaller amount of redox polymer. Just how fast a microelectrochemical transistor can be switched is limited by how fast the electrode potential can be moved.[13] Microelectrodes (~ 1 μm crucial dimension) can be potentiostated in less than 10^{-5} s, because the double layer charging current is small.[14] Such considerations suggest that power gain is possible at significantly greater than the ~ 1 kHz demonstrated here. Work is in progress to prepare devices having the structure in Scheme II in order to move to higher frequencies with polymer-based transistors. In competition against solid state transistors,[15] microelectrochemical transistors are expected to be intrinsically slower, because ion movement is required for switching whereas electrons, not ions, move in solid state semiconductor devices. Thus, practical applications of microelectrochemical transistors are limited to lower frequency operation. It would appear that microelectrochemical transistors with chemically sensitive electrical characteristics will provide an opportunity for practical developments.[16] The operational frequencies established here surpass the needs for many chemical sensor applications.

References

1. (a) White, H.S.; Kittlesen, G.P.; Wrighton, M.S. J. Am. Chem. Soc., 1984, 106, 5375; (b) Kittlesen, G.P.; White, H.S.; Wrighton, M.S. J. Am. Chem. Soc., 1984, 106, 7389.

2. Paul, E.W.; Ricco, A.J.; Wrighton, M.S. J. Phys. Chem., 1985, 89, 1441.

3. Thackeray, J.W.; White, H.S.; Wrighton, M.S. J. Phys Chem., 1985, 89, 5133.

4. Chidsey, C.E.D.; Murray, R.W. Science, 1986, 231, 25.

5. Diaz, A.F.; Logan, J.A. J. Electroanal. Chem., 1980, 111, 111.

6. Tourillon, G.; Garnier, F. J. Phys. Chem., 1983, 87, 2289; J. Electroanal. Chem, 1983, 148, 299.

7. Murray, R.W. in "Electroanalytical Chemistry," vol. 13, A.J. Bard, ed., Dekker, New York, 1984, p. 191, and Annu. Rev. Mater. Sci., 1984, 14, 145.

8. (a) Oyama, N.; Anson, F.C. J. Electrochem. Soc., 1980, 127, 640; (b) Daum, P.; Lenhard, J.R.; Rolinson, D.; Murray, R.W. J. Am. Chem. Soc., 1980, 102, 4649; (c) Andrieux, C.P.; Dumas-Bouchiat, J.M.; Saveant, J.M. J. Electroanal. Chem., 1982, 131, 1; (d) Lewis, T.J.; White, H.S.; Wrighton, M.S. J. Am. Chem. Soc., 1984, 106, 6947.

9. Tourillon, G.; Garnier, F. J. Electroanal. Chem., 1984, 161, 51 and 407.

10. (a) Diaz, A. F. Chem. Script., 1981, 17, 145; (b) Wa;t,am. R.J.; Bargon, J. Diaz, A.F., 1983, 87, 1459.

11. Preliminary results show only modest (factor of ~2) variation in I_D(peak) for poly(3-methylthiophene) for devices operated in pH = 0 $HClO_4$, H_2SO_4, HBF_4, or HNO_3: Thackeray, J.W. Ph.D Thesis, M.I.T., 1985.

12. Thackeray, J.W.; Wrighton, M.S. J. Phys. Chem., submitted.

13. Bard, A.J.; Faulkner, L.R. "Electrochemical Methods", Wiley, New York, 1980, pp. 569-571.

14. (a)Howell, J.O.; Wightman, R.M. Anal. Chem., 1984, 56, 524; (b) Wightman, R.M. Anal. Chem., 1981, 53, 1125A.

15. Sze, S.M. "Physics of Semiconductor Devices", 2nd ed., Wiley, New York, 1981.

16. Wrighton, M.S.; Thackeray, J.W.; Natan, M.J.; Smith, D.K.; Lane, G.A.; Belanger, D. Phil. Trans. Roy. Soc. Ser. B, 1987, in press.

Figure Captions.

Figure 1. Plot of drain current, I_D, (V_D = 0.2 V) gate current, I_G, and gate potential, V_G, vs. time at a frequency of 1 Hz for a poly(3-methylthiophene)-based transistor operated at 298K in a non-aqueous solvent/electrolyte solution. The change in V_G is from V_G = 0.0V vs. SCE (device off, I_D = 0) to 0.95 vs SCE (device on, I_D = 5 mA). The value of $\underline{A} \approx 3 \times 10^3$. Note I_D is maximum at V_G = +0.95 V vs. SCE and the maximum value of I_D is >95% of the value of I_D when V_G is fixed at +0.95 V vs. SCE.

Figure 2. Frequency dependence of I_D for the device characterized by data in Figure 1. Note that the time axis is different for each frequency: the V_G peak to peak separation is 1s, 0.1s, and 0.01s at 1, 10, and 100 Hz, respectively, as reference points. Note that the maximum value of I_D declines as the frequency is increased and the maximum turn on lags the maximum V_G as frequency is increased. The maximum value of I_G increases from the 0.31 μA at 1Hz (Figure 1), but not linearly, as the frequency is increased. The integral of I_G vs. time for one half a cycle decreases with increasing frequency consistent with incomplete turn on reflected in lower I_D values at 10 and 100 Hz. The value of $\underline{A}$ declines from ~3 x 10^3 at 1 Hz, to ~250 at 10 Hz, and to ~10 at 100 Hz.

Figure 3. Data as in Figure 1 for a polyaniline-based transistor operated at 298K in aqueous electrolyte at 1, 10, 30, 100, and 300 Hz. Note that at all frequencies shown the maximum value of I_D is the same, 130 μA, indicating that the device turns on to the same extent at all frequencies. The change in V_G is

0.4 V from -0.1V vs. SCE (device off $I_D = 0$) to +0.3V vs. SCE (device on, $I_D =$ 130 μA).

Figure 4. Plots of the $\log_{10}$ (I_G(peak)) and $\log_{10}$ of amplification, $\underline{A}$, vs. $\log_{10}$ (frequency) for the polyaniline-based transistor characterized by the data in Figure 3.

Phase Relationship of Gate Potential, V_G, Gate Current, I_G, and Drain Current, I_D, at IHz of a Poly-3-methylthiophene Transistor, $0.1\ \underline{M}[(n-Bu)_4NClO_4]/CH_3CN$, $V_D = 0.200\ V$.

0.5 sec

$V_G = 0.95V$

$I_D = 5mA$

$I_G = 0.31\mu A$

TIME →
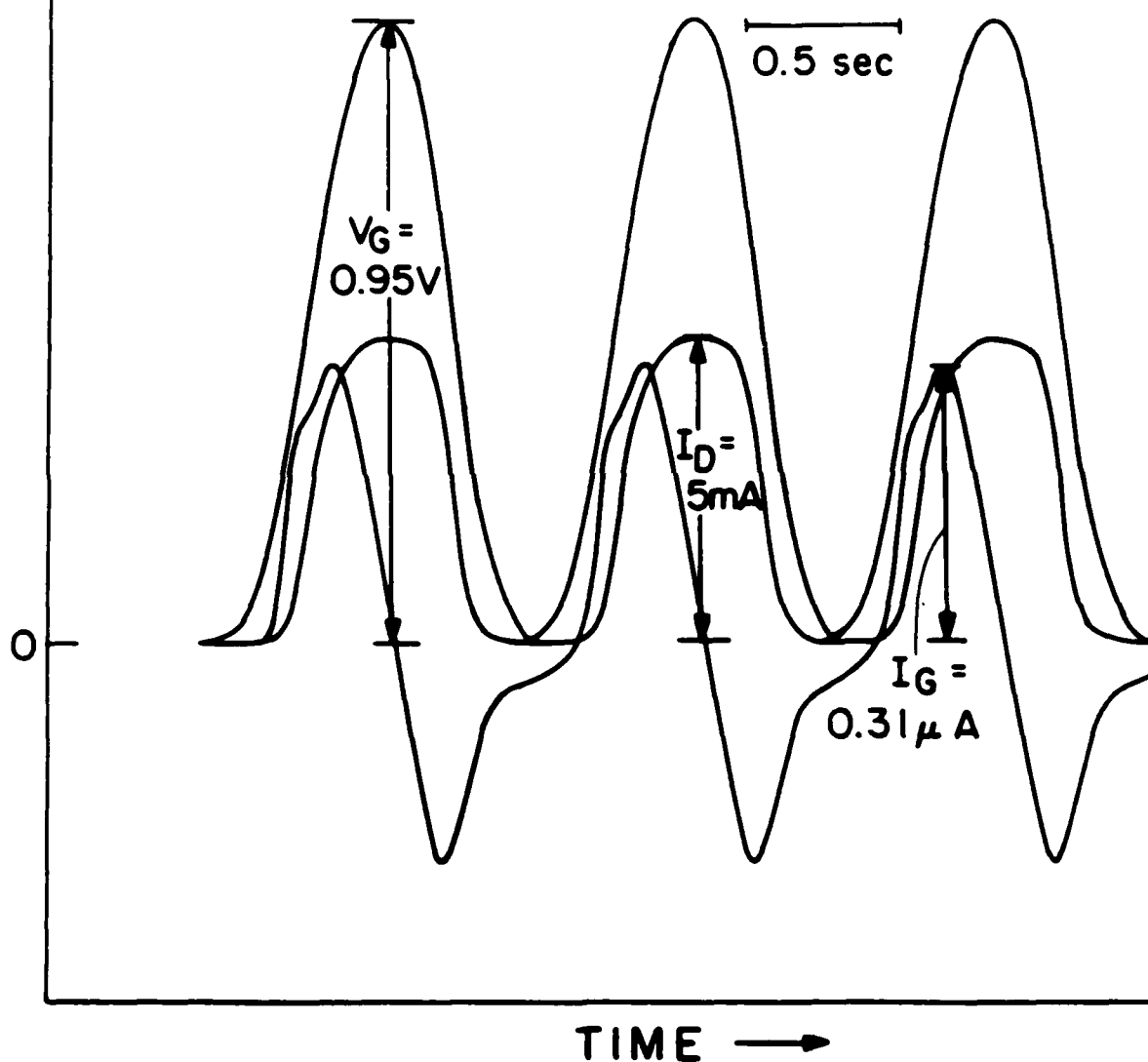
Frequency Response of Drain Current, I_D, at a Poly-3-methylthiophene transistor, $0.1 \underline{M}[(\underline{n}-Bu)_4 NClO_4]/CH_3CN$, $V_D = 0.200V$.

V_G

$I_D = 1mA$

$0.95V$

$1Hz$

$10Hz$

I_D

0

$100Hz$

TIME ⟶
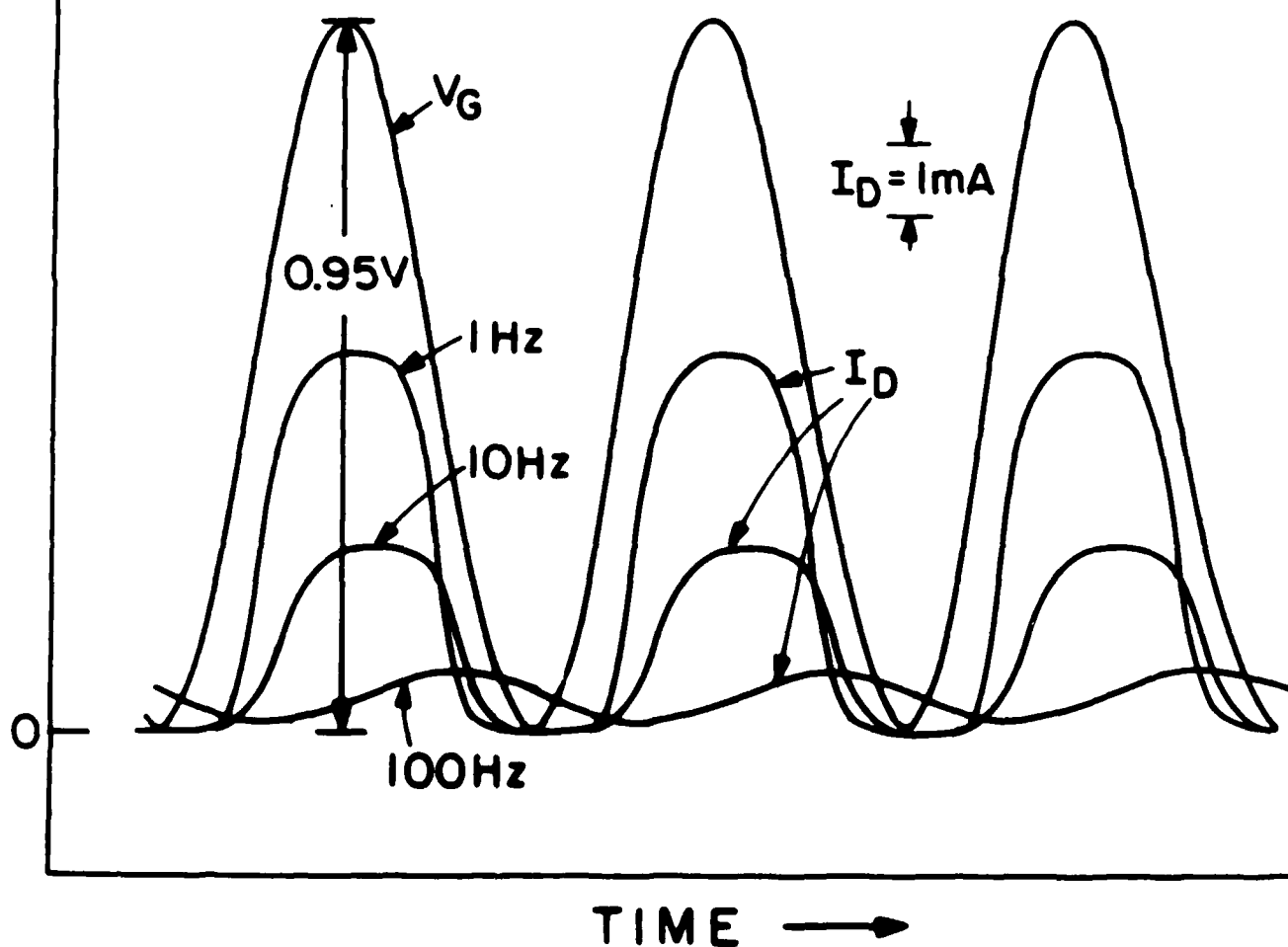
Phase Relationship of Gate Potential, V_G, Gate Current, I_G, and Drain Current, I_D, at Different Frequencies for a Polyaniline Transistor, 0.5 M NaHSO$_4$, V_D = 0.1 V.

Log(I_G) and Log(Amplification)
vs.
Log (Frequency)
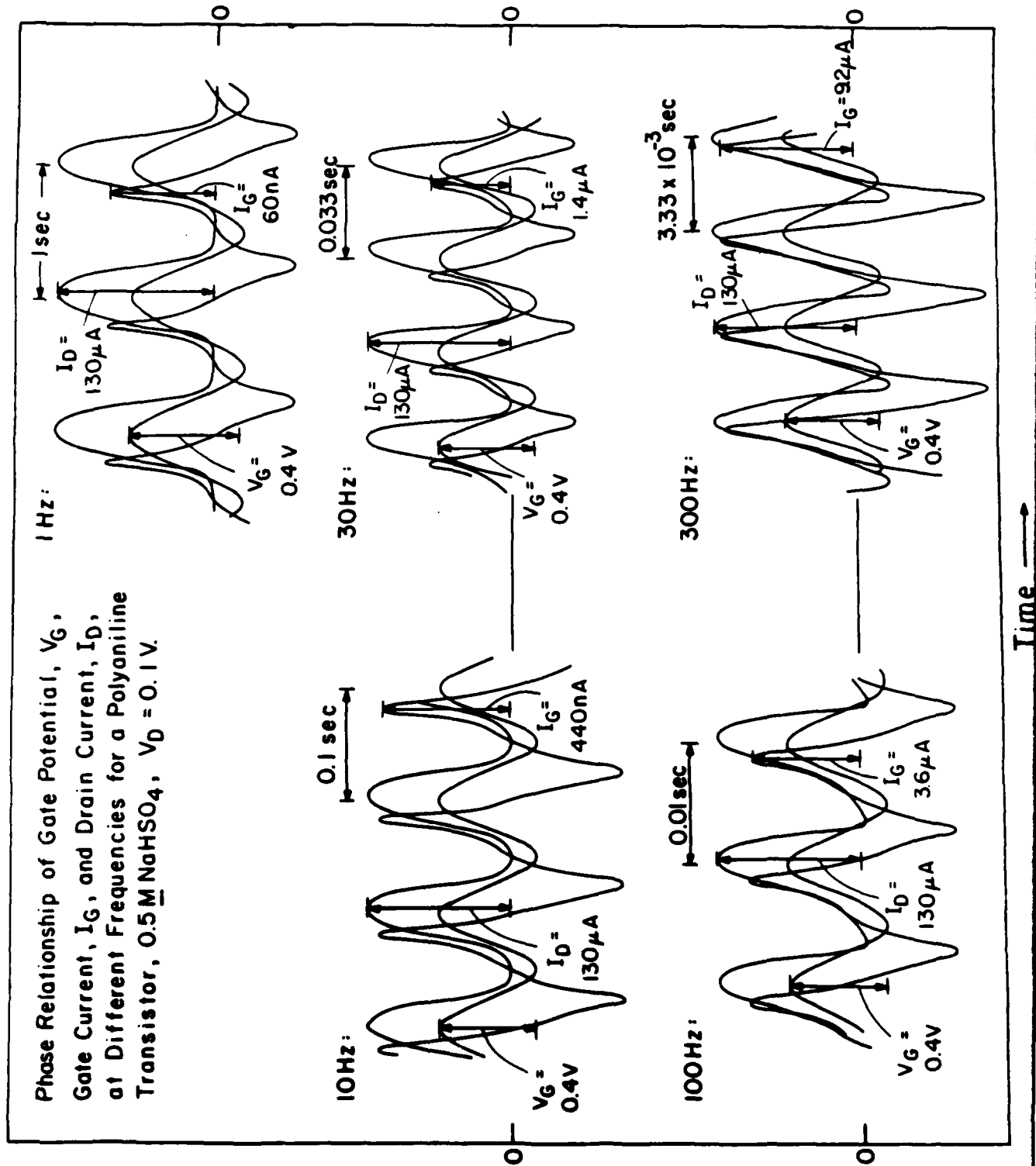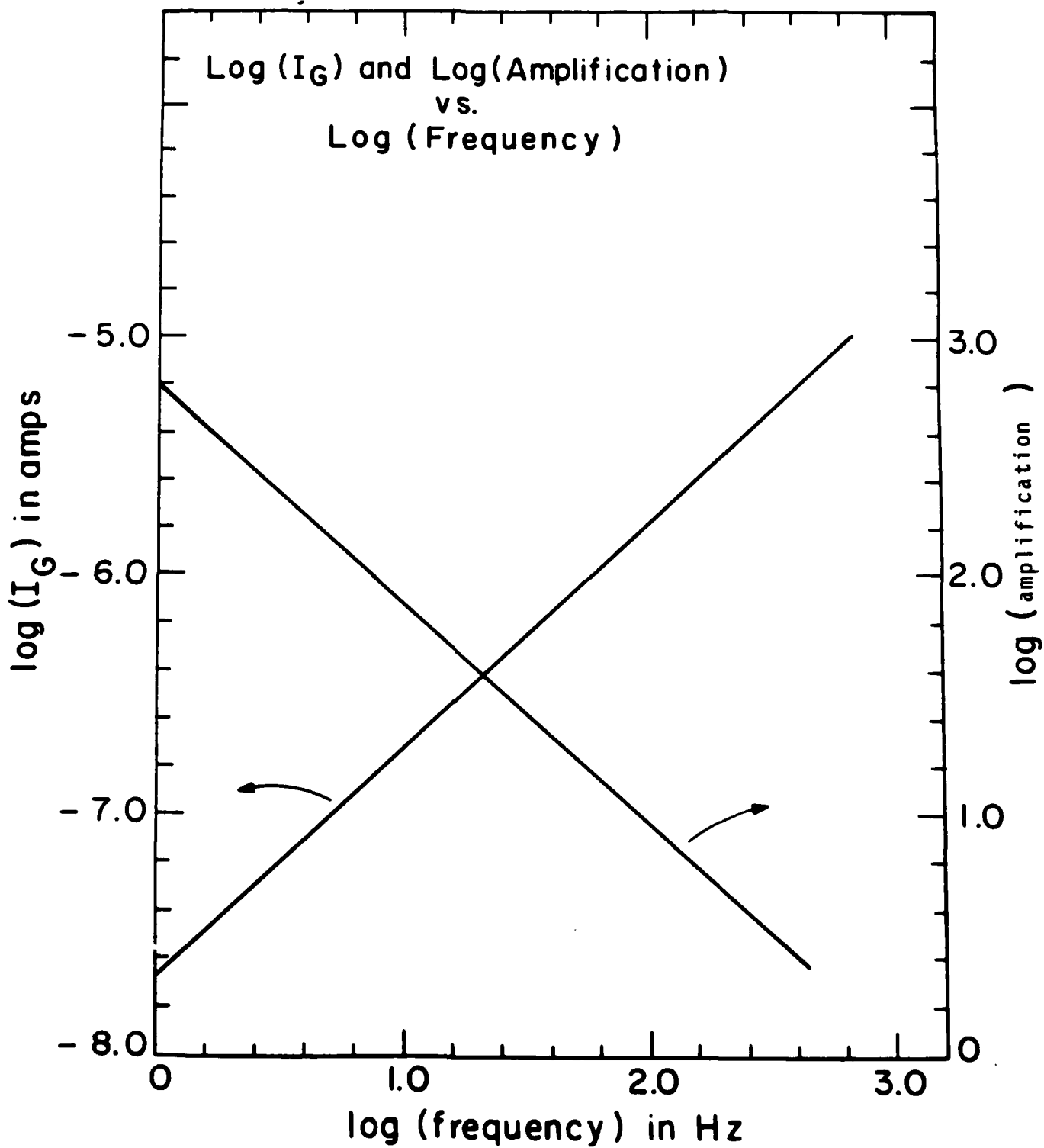
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