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DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

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DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

I. INTRODUCTION, ABSTRACT, AND SUMMARY OF EARLIER REPORTS

This report will cover the work performed from 1 July 1968 through 31 December 1968 on Grant NsG-458 between the University of Arizona and the National Aeronautics and Space Administration.

This contract was set up to support the development of new types of detectors for analysis of planetary atmospheres. Initially, the interest was in detectors for use under partial vacuum conditions; recently the program has been extended to include detectors for use at one atmosphere.

Results to date have included detectors for O_2 and H_2 under partial vacuum conditions (Publications 1, 3, 4). Experiments on detectors for use at higher pressures began in 1966, and systems for CO, H_2, and O_2 were reported in 1967 and 1968 (Publications 8, 12). In 1968 studies began on an electrically controlled adsorbent. It was demonstrated that under proper conditions a thin film of semiconductor material could be electrically cycled to *adsorb* and *desorb* a *specific* gas. This work was extended to obtain quantitative data on the use of semiconductors as controllable adsorbents (Publication 12).

In 1968 a new technique for dry replication and measurement of the thickness of thin films was developed. A commercial material, Press-O-Film, was shown to be satisfactory when properly used. This technique is most useful for studies of semiconductor thin films where normal interference techniques are not practical because of the nonreflective nature of the film (Publication 13).

II. RESULTS DURING THE LAST SIX MONTHS

A. Chemisorption of Oxygen on ZnO and Its Control by Electric Fields

In our earlier reports we discussed the phenomenon of electroadsorption and gave a detailed report of our experimental demonstration of the phenomenon. At that time we indicated that the transition from a laboratory demonstration to a semicommercial process was the next objective.

The major problem was the obvious variations in our ZnO films, from batch to batch, and our lack of test procedure to control the ZnO fabrication process. This is exactly the difficulty that plagued the early days of the semiconductor industry.

For this reason we have spent the last six months building an automatic test system that will allow us to test batches of thin films, under controlled conditions, without wasting staff time in rather tedious work that can be done by a machine. This will be particularly advantageous when we begin doping the ZnO films with controlled amounts of impurities. We will want to compare films with controlled amounts of different elements, and many batches of ZnO films will have to be tested.

The details of the new apparatus are shown in Figure 1. Here we need only note that the slide or slides being tested are exposed to oxygen and then illuminated with ultraviolet light in the presence of an electric field gradient. The ultraviolet light is cycled on and off by an automatic controller* and the change in ZnO resistance is recorded as a function of time.

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*The electronic timer for this work was designed by Mr. Robert Helber and built by Mr. James Payne.

This change in resistance is due to holes which move from the ZnO bulk to the surface and discharge adsorbed oxygen ions. The motion of these holes can be controlled by the external electric field, and the combination of these optical and electric field techniques allows us to measure the amount of oxygen adsorbed and desorbed. A typical experimental record is shown in Figure 2. Here we have plotted the ZnO conduction current as a function of time as the ultraviolet source is switched: 10 seconds on, 10 seconds off.

When there is zero voltage on the screen, the holes only move to the surface by natural diffusion and the amount of oxygen desorbed is small, as evidenced by the small value of ΔI, the difference between the maximum and minimum current in each cycle.

If now a -2750 volt potential is placed on the screen, the average current decreases because electrons are being pushed away from the surface. At the same time holes are drawn to the surface where they discharge a large fraction of the adsorbed oxygen. The oxygen then readsorbs as soon as the ultraviolet light goes out, and the holes are lost by recombination processes. This increased adsorption-desorption phenomenon has an effect on the span ΔI. The span is greater with -2750 volts on the screen because partial desorption of oxygen has occurred during the "UV on" part of the cycle. This increase in span may then be used as a measure of the amount of oxygen desorbed during the cycle. This is the technique that we use to measure the amount of oxygen adsorbed and desorbed from the ZnO. This is much simpler than measuring the change in gas pressure unless a large number of ZnO coated plates are used.

When we have determined the optimum ZnO production technique, we will return to the experiments devoted to measurement of the exact quantity of oxygen adsorbed and desorbed in each cycle. Other experiments on electrocatalysis and separation of one gas from another will be practical when a reliable ZnO test procedure has been developed.

In this connection it is worth noting that the topic of electroadsorption has been taken up by several organizations, and S. A. Hoenig has been invited to speak on this topic at the Union Carbide Research Laboratories in Niagara Falls on 31 January 1969. An increase in the number of scientists working on this topic will make for more rapid advances and better exchange of information.

Returning for a moment to the present experiments, it is interesting to comment on the effect of a positive screen voltage, which is not shown in Figure 2. If the screen is raised to a +2750 volt potential, an increase in average current is observed because the field draws electrons toward the surface where they have a high mobility. The amount of adsorbed oxygen and hence ΔI is unchanged because the surface is already saturated with oxygen.

B. Carbon Monoxide and Palladium

Palladium emits a current of positive ions when heated. This ion current is strongly dependent upon the presence of hydrogen or carbon monoxide in the ambient gas. The effect is specific and may be used for detection of these gases. The actual phenomena involved are still not clear, and we have two investigations in this area under way at the moment. Mr. Ashcraft is studying the heat of reaction of CO on hot palladium, as a function of temperature, for a senior project. Mr. Pope is using the EAl

Quadrupole mass spectrometer* to study the ions emitted from hot palladium in the presence of various gases. He will use the results for his Master of Science in Electrical Engineering thesis.

At the moment we do not intend to give an explanation for the mechanism involved in this reaction because the experiments are not complete. However, the data are most interesting, and some definite trends have emerged.

Mr. Ashcraft's apparatus is shown schematically in Figure 3. The thermistor is a General Electric Man-Made Diamond Thermistor** which is used to detect the small change in temperature that occurs when CO comes in contact with hot Pd. The thermocouple is used to calibrate the thermistor in terms of resistance vs. temperature. This dual system is necessary because the thermistor characteristics are nonlinear and drift slightly with time.

For operation, the Pd wire is heated by a DC current, in a flow of pure nitrogen, until the system is stabilized. Then a minute (∿ 1%) amount of CO is added to the flow, and the temperature change is monitored by the thermistor and a recorder. The CO/Pd reaction is exothermic and a temperature rise is observed, but the heat release is very small and the measurement is not an easy one. Mr. Ashcraft has done a most careful and painstaking experiment to obtain these results.

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*The cooperation of Dr. C. Giffin and the Jet Propulsion Laboratory in allowing us to retain this instrument is gratefully acknowledged.

**Gift of General Electric via Mr. Lloyd Mattson of the GE Edmore, Michigan, Division.

In Figure 4 we show the temperature vs. time response of the system when cycled with a series of exposures at a fixed CO + N_2 mixture. Several features of Figure 4 are worthy of note. First, the fact that the temperature increase does not decay as long as the CO is flowing in the system suggests that the phenomenon is a surface reaction rather than mere adsorption which would generate a pulse of heat that would decay in one or two seconds. The second thing of interest in Figure 4 is the drop in filament temperature from cycle to cycle. This is a repeatable phenomena and may be due to the solubility of CO in Pd, which increases the metal's electrical resistance. Since the DC supply is of the constant voltage type, the current through the wire decreases as the resistance increases and the wire cools slightly. If the wire is heated for several hours in a pure N_2 atmosphere, the original condition is restored as the CO desorbs.

Mr. Ashcraft has also measured the effect of palladium temperature on the heat released in the reaction. This was not possible when we were observing only the positive ions emitted by the palladium. If, as we suspect, the change in ion emission is due to the increase in temperature, we should be able to correlate the two phenomena and begin to understand the processes involved.

Mr. Ashcraft's data indicates that the sensitivity of the CO/Pd system increases as the temperature drops from 800°C to 250°C. This suggests the possibility that the detector might be operated in a thermal detection mode at 250°C rather than an ion detection mode at 800°C. This would have the other advantage that the detector would be less likely to set off an explosion if it operated at 250°C rather than 800°C. This is an important consideration in a gas detector which may operate in an explosive environment.

Mr. Pope has examined the ion emission from hot palladium, with a mass spectrometer. There is no question that the ions emitted are those of the easily ionized impurities Na, K, and Ca in order of their abundance.

In other experiments we have noted that the ion current from hot palladium was sensitive to H_2, CO, and certain halogenated gases such as freon. It was suggested that the hot palladium induced dissociation which in turn yielded chlorine to react with the palladium. A possible reaction would be

$$C\,Cl_2\,F_2 \xrightarrow{Pd} C\,Cl\,F + Cl + F$$

Mr. Pope has set up the system so that the ions from the hot palladium can go directly to the quadrupole. The usual thermal electron source is also available so that the neutral gases can be ionized for analysis. The two systems can be operated independently for different experiments.

This apparatus has involved some very complex construction by Mr. Pope, and the complete system will allow us to perform some unique experiments. At the moment, Mr. Pope has just begun to introduce gases like H_2, O_2, CCl_2F_2 into the system, and the results are inconclusive at this time.

C. Other Experiments on Ion-Electron Emission from Hot Filaments

As part of Mr. Pope's experiments we have looked at the ion-electron emission from hot filaments and at techniques for preventing these ions from reaching a substrate. This work has direct application to the contamination of semiconductors during evaporation of metal interconnections. An interesting point is the discovery that if the metal being evaporated can alloy with the filament, a burst of electrons is emitted during the evaporation process. The results have appeared in *Solid State Technology* (Publication 14).

D. Other Experiments in the Field Emission and Space Systems Laboratory

We have started experiments on exo-electron emission. This work is supported by the Advanced Research Projects Agency. Mr. William Ott joined the group in November after his discharge from the Navy. He will work on this program for his Master of Science in Electrical Engineering thesis.

The program objective is the investigation of pre-fracture phenomena in brittle materials. The exo-electron emission is a surface phenomenon which is thought to be related to dislocation motion. Microphonon phenomena and their relation to brittle fracture will be investigated by the co-principal investigator, Dr. R. H. Chambers of the Physics Department.

Only preliminary results are available at present, but there are definite indications of pre-fracture exo-electron emission. The apparatus and the techniques are similar to those used on NsG-458, and cooperative use of equipment permits economical operation.

The Jet Propulsion Laboratory supported study of Field Ionization Techniques in Mass Spectrometry has ended. Mr. W. Farwell finished his course work in September, 1968, and is writing his Master of Science thesis on this work in absentia. The program demonstrated that field ionization can be used with a mass spectrometer, but the monopole-quadrupole configuration is not ideally suited for field ionization. The problem arises because high energy neutrals pass through the line-of-site analyzer and produce electrons at the first multiplier stage.

A more effective application of the quadrupole system is the replacement of the normal, thermal, electron source with a 100-point comb that is used to generate field emitted electrons which in turn bombard gas molecules and generate ions for analysis. This type of system has a number of advantages:

(1) Low power consumption - a typical thermal electron source will dissipate about 30 watts. A field electron source dissipates a microwatt to produce the same ion current at the spectrometer inlet.

(2) The electron energies are more peaked with field emission than with thermal emission. This in turn means that the ions will have a narrow range of energies and may be focused more exactly.

(3) Field electrons generate a more accurate ion spectra when a mixture of gases is present. This is particularly apparent when there is residual water in the gas mixture. Hot tungsten filaments pump water by forming tungsten oxides and hydrogen. If a gas mixture is analyzed in a mass spectrometer with a thermal electron source, the water peak is severely reduced in comparison with, say, the nitrogen-carbon monoxide peak. If a field electron source is used, this distortion of the spectra is greatly reduced.

With a platinum field electron source the M/e = 18 peak is comparable in size to the 28 peak in a VacIon pumped system.

(4) The spectra produced by the field emission electron source are comparable in resolution to the best spectra produced by the normal EA1 thermal source. The fact that a device has been developed, in one year, to the stage where it is as effective as the better commercial equipment suggests that a substantial further improvement is possible.

We feel that there are a number of applications of this electron source in commercial mass spectrometers and in special apparatus for planetary experiments. Discussion has been opened with a commercial manufacturer of spectrometers with the hope of investigating this application in more detail.

III. PLANS FOR THE NEXT SIX MONTHS

We plan to continue with the ZnO electroadsorption studies with emphasis on the control of adsorption by doping the ZnO.

The CO/Pd studies will continue with the hope of gaining understanding of the reaction mechanism.

We are cooperating with another University department that would like to use the Corona Water Vapor Detector* for field experiments. The other group will supply the manpower and we will provide technical assistance.

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*This detector was discussed in our proposal dated 15 April 1966. Work was stopped because of our feeling that other detectors were more applicable to the space program.

IV. PERSONNEL

A. Students Who Were Supported by NsG-458 and Their Present Activities

(1) Donald Collins, M. S., 1963. Received Ph.D. from California Institute of Technology in 1968.

(2) George Rozgonyi, Ph.D., 1963. Senior Staff Member, Bell Telephone Laboratories, Murray Hill, New Jersey. (Partial support under NsG-458)

(3) Donald Creighton, Ph.D., 1964. Professor, University of Missouri, Rolla. (Partial support under NsG-458)

(4) Melvin Eisenstadt, Ph.D., 1965. Associate Professor, University of California, Santa Barbara.

(5) Major C. W. Carlson, M. S., 1965. Active duty, U. S. Army.

(6) John Lane, M. S., 1968. Philco Ford Co., Tucson.

(7) Herman Sulsona, Ph.D., 1968. Professor and Chairman, Department of Mechanical Engineering, University of Puerto Rico, Mayaguez. (Partial support under NsG-458)

(8) William Farwell, will receive MSEE, June, 1969. Hughes Aircraft Co., Culver City.

B. Students and Staff Presently Employed in the Laboratory

(1) James Payne - Electronics Technician

(2) William Ott
(3) Richard Pope
(4) Robert Helber
Graduate students working toward MSEE degrees

(5) John Ashcraft - Undergraduate student, senior term paper project.

(6) James Hathaway - Undergraduate student

(7) Connie Kaufman - Part-time secretary

Mr. Henry Anderson was employed at the laboratory for two years on an undergraduate term project with the ammonia detector. He was taken ill in March, 1968, and died 10 December 1968. His untimely death has brought the ammonia detector project to a halt. We still feel that this is a a unique system for detection of ammonia; the project will begin again when an undergraduate student is available. Mr. Anderson was liked by everyone who knew him.

V. PUBLICATIONS GENERATED TO DATE BY RESEARCH ON CONTRACT NsG-458

(S. A. Hoenig and others)

1. Chemisorption Detector for Oxygen, *Rev. Sci. Instr.*, 35, 15 (1964) (with D. Collins).

2. Protection of Copper in High Temperature Air, *Rev. Sci. Instr.*, 35, 904 (1964).

3. Chemisorption Detector for Hydrogen, *Rev. Sci. Instr.*, 36, No. 1, 66 (1965) (with M. Eisenstadt).

4. Change in the Thermionic Emission Current of Palladium Due to Chemisorption of Atomic and Molecular Hydrogen, *J. Chem. Phys.*, 45, No. 1, 127-132, (July 1966) (with M. Eisenstadt).

5. Beam Source for Molecular and Atomic Hydrogen, *Rev. Sci. Instr.*, 36, No. 12, 1878-1879 (1965) (by M. Eisenstadt).

6. Use of Liquid Nitrogen Cooled Shield to Protect Proton Accelerator against Oil Vapor Contamination, *Rev. Sci. Instr.*, 37, 7, 977 (1966).

7. A Low Cost, High Temperature (1300°C) Vacuum Furnace, *J. Vacuum Science and Technology*, 3, 6, 351 (1966).

8. Detection of Hydrogen in Air by Means of Alkali Ion Current from Hot Palladium, *Rev. Sci. Instr.*, 38, 1, 92-94 (Jan. 1967) (with C. W. Carlson and J. Abramowitz).

9. Polarization Sensitivity of the RCA 6903 Photocathode Tube, *Applied Optics*, 5, No. 6, 1091-1092 (1966) (with A. Cutler).

10. Contamination of MOS Field Effect Transistors by Alkali Ions Emitted from Hot Tungsten or Molybdenum Filaments - Removal by Electric Fields, *Electronic Communicator*, p. 1617 (Nov./Dec. 1967).

11. The Electronic "Sponge" - Selective Gas Adsorber, *Industrial Research*, p. 9 (May 1968).

12. Chemisorption of Oxygen on ZnO - Effect of DC Electric Fields, *Surface Science*, 11, 163 (1968) (with J. Lane).

13. Replication versus Metallization for Interference Microscopy of Thin Films, *J. Vacuum Science and Technology*, 5, 6, 125 (June 1968) (with J. Lane).

14. Ion and Electron Currents from Hot Filaments - Effect of Alloying on Electron Emission, *Solid State Technology*, 11, 12, 53, (Dec. 1968) (with R. Pope)

15. Emission of High Energy Electrons during Alloy-Evaporation Processes on Hot Metal Filaments, submitted to *Applied Physics Letters*, (with R. Pope).

VI. LIST OF FIGURES

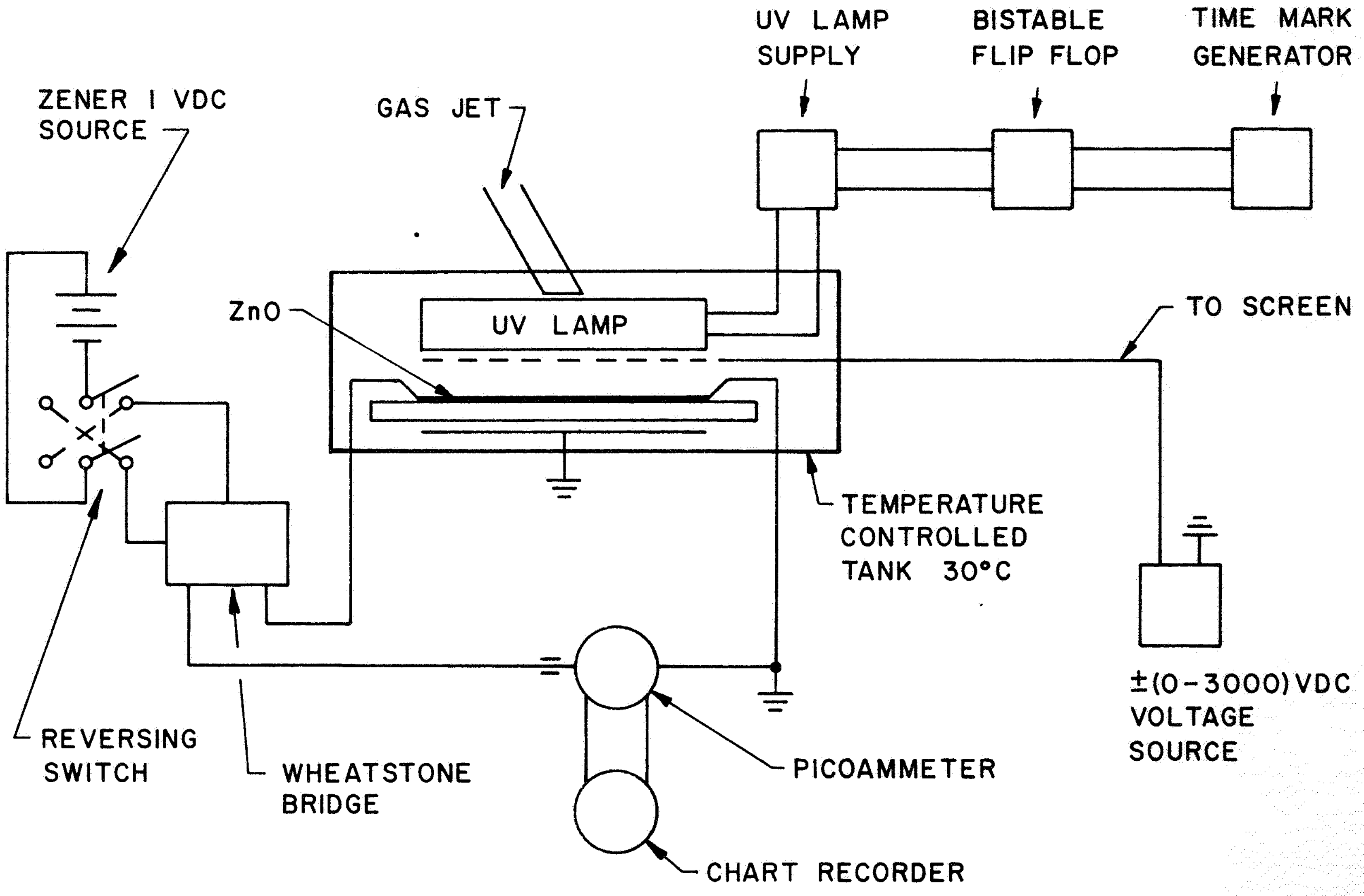

FIGURE 1

Experimental System for ZnO Electroadsorption Studies

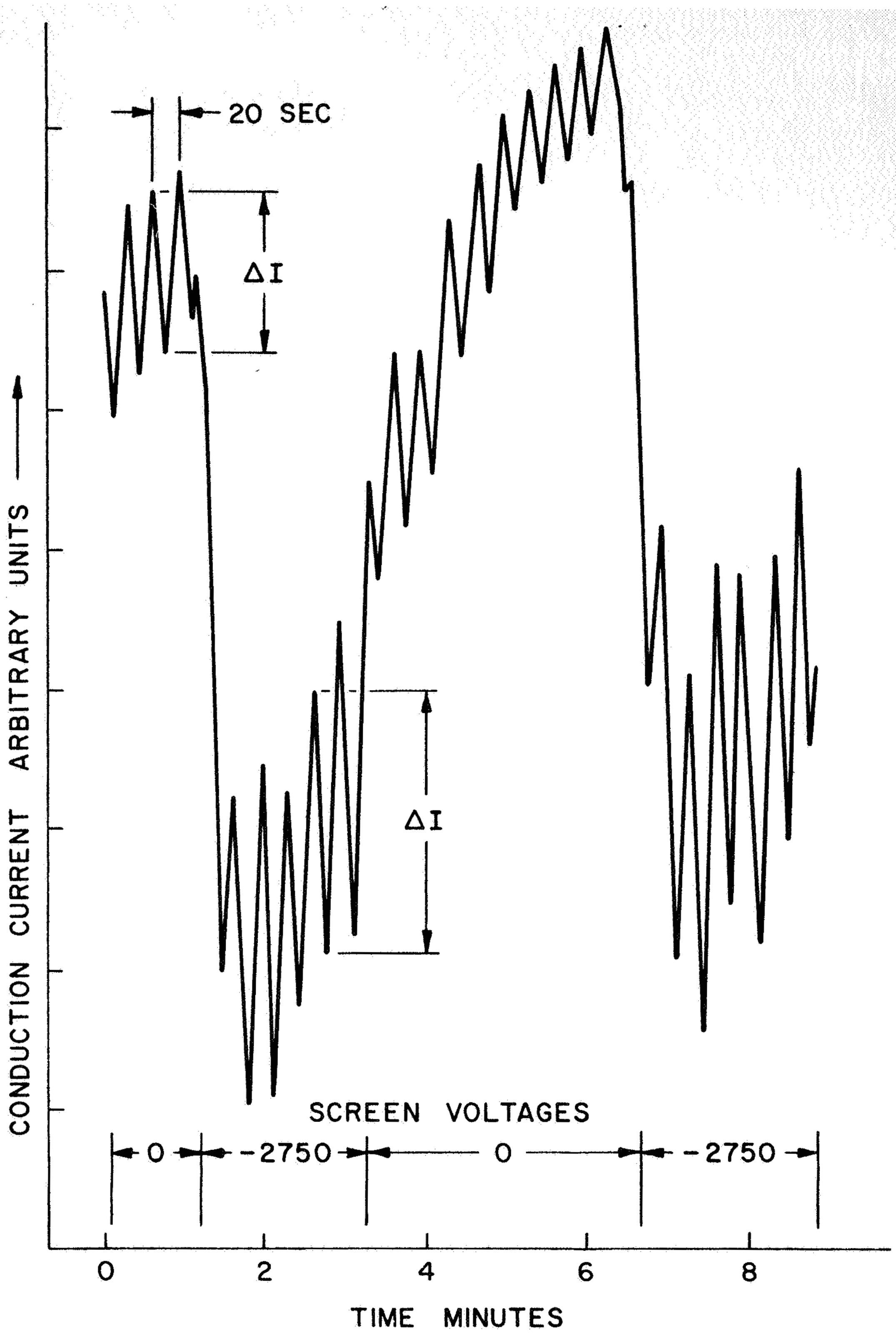

FIGURE 2

ZnO Conduction Current vs. Time and Screen Voltage

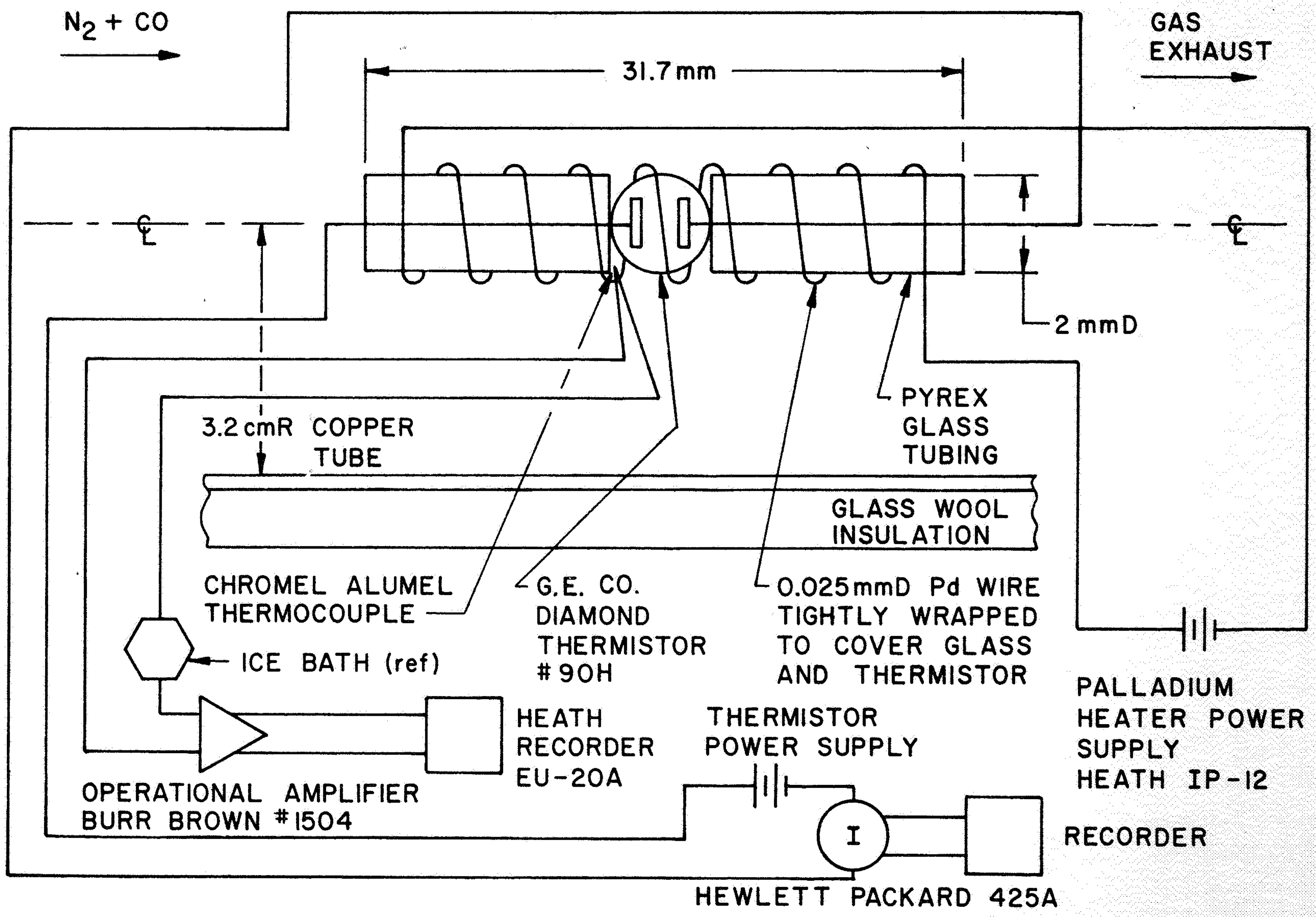

FIGURE 3

Apparatus for CO/Pd Reaction Studies

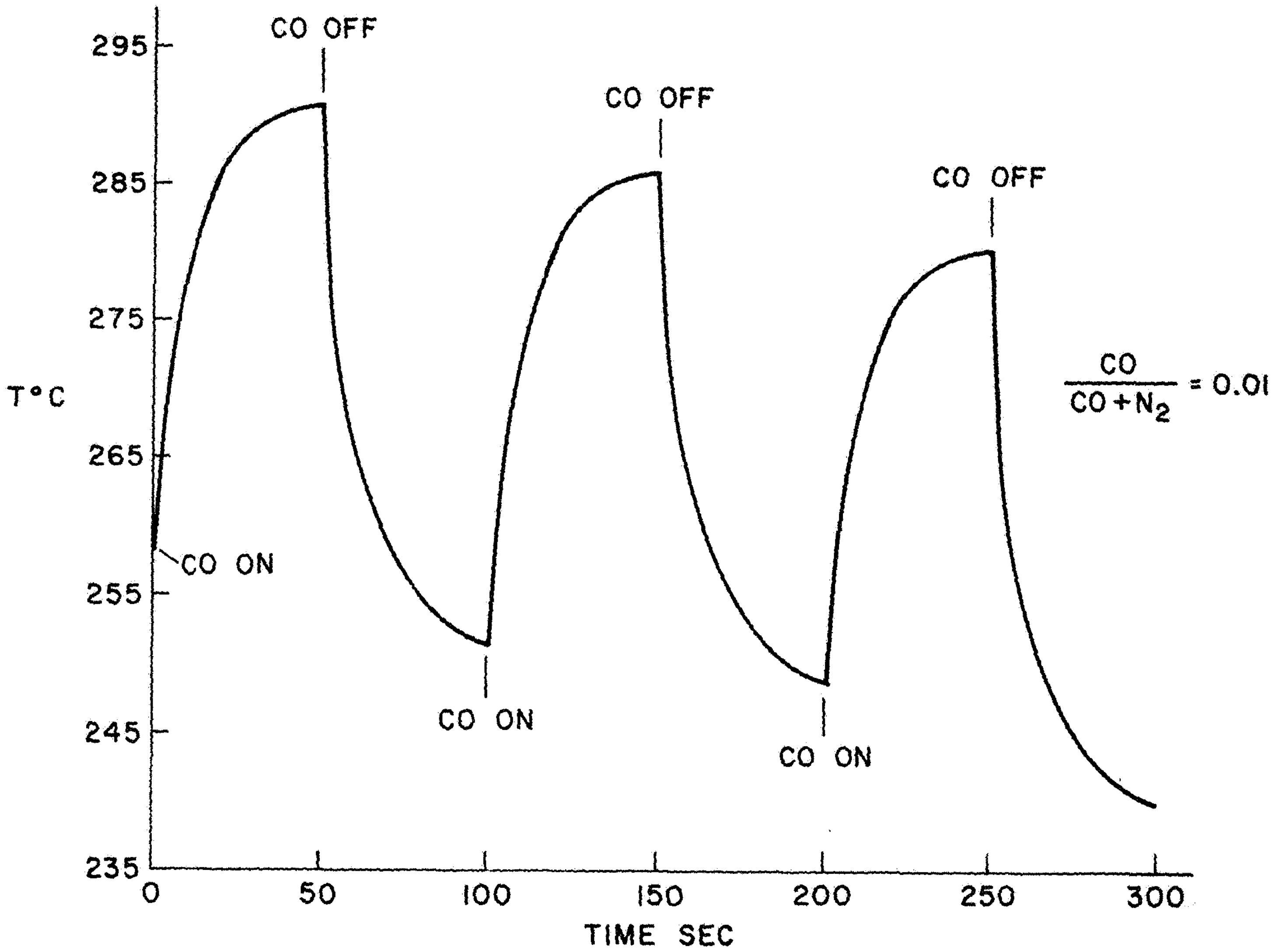

FIGURE 4

Temperature vs. Time for Several Cycles of CO Exposure