

THE INFLUENCE OF A D. C. ELECTRIC FIELD ON CHEMISORPTION  
OF OXYGEN ON ZINC OXIDE

by

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## ABSTRACT

An experimental system and procedures are developed to determine the effect of electrostatic fields on the chemisorption of oxygen on zinc oxide thin films. A theoretical model is constructed, and the theoretical performance curves are compared with experimental data. The experimental results are qualitatively similar to the theoretical predictions.

The adsorption-desorption process of oxygen on zinc oxide can be controlled by the application of transverse electrostatic fields. Results show  $1.67 \times 10^{-12}$  grams of oxygen adsorbed per square centimeter of oxide surface per volt per centimeter.

## CHAPTER 1

### INTRODUCTION

All reactions between gas and solids begin with adsorption, the entrance of the gas into the solid. It is customary to distinguish between adsorption which implies a solution or concentration of the gas in the solid and absorption which might be typified by the action of a sponge. In fact it is difficult to separate the phenomena, and the general term sorption is sometimes used for both processes.

The word adsorption will be used here to describe any reaction in which a gas is bound to a solid in some more or less permanent fashion. This bonding is the first step in any rusting, oxidation, catalysis, or gas drying process. The commercial aspects of these problems have generated a great deal of effort aimed at understanding adsorption processes. Unfortunately there is no general theory which explains adsorption. However some processes have begun to be understood, especially in the case of adsorption on semiconductors.

A major difficulty with adsorbents is their non-specific nature. For example, an adsorbent for water vapor will take up other condensable gases, and this limits the use of adsorption for gas separation.

Adsorbents are often used for the removal of carbon dioxide or carbon monoxide from confined environments, i.e. submarines. Other applications include separation of sulfur dioxide from smelter stack



gases or oxygen from hydrocarbons. Again the adsorbent must be discarded after use or recycled by heating.

In view of the foregoing discussion, it is clear that a need exists for an adsorbent which can be recycled in situ without heating. If the adsorbent were specific for a certain gas or class of gases, this would be an even greater advantage in terms of industrial and scientific applications. The term specific is defined, in this case, as being chemically reactive with only certain particular gases.

Adsorption on semiconductors has been studied for a number of years, and in 1961 a book by a Russian author, Volkenshtein, appeared. Volkenshtein suggested that a semiconductor could serve as an adsorbent which would be specific to a particular type of gas and could be cycled by application of electrical fields.

The electrostatic field method of controlling chemisorption is attractive as it offers low power requirements and unsophisticated circuitry and requires no direct contact between the adsorbent surface and field circuitry.

## CHAPTER 2

### CHEMISORPTION ON ZINC OXIDE

#### Zinc Oxide

Zinc oxide is an n-type semiconductor belonging to the II-VI family of chemical compounds. Zinc oxide exhibits the properties characteristic of the compounds in this family (Heiland, Mollwo, and Stockman, 1959, p. 195). At room temperature zinc oxide crystals have the hexagonal wurtzite lattice structure. In this lattice arrangement zinc ions and oxygen ions possess the same relative arrangement, but the oxygen ions are placed in the closest hexagonal packing. Half of the tetrahedral interstitial positions are occupied by the zinc ions.

In addition to the allowed energy levels for electrons in the conduction and valence bands, zinc oxide crystals also contain discrete energy levels within the forbidden region (Morrison, 1955, p. 261). These forbidden band energy levels are localized at impurity atoms and crystal imperfections. An energy plot of the zinc oxide band structure is shown in Fig. 1. (Figures appear at end of text, starting on page 28.)

It has been established that excess interstitial zinc atoms are primarily responsible for the forbidden region levels (Morrison, 1955, p. 261). These levels are located at approximately .04 eV below the conduction band edge and as a result, the ionization energy of the interstitial zinc atoms is quite low. At room temperature most of these atoms are ionized, and the n-type conductivity observed in zinc

oxide results from electrons that are thermally excited into the conduction band from these ionized interstitial zinc atoms.

Investigations have been performed on different forms of zinc oxide by various workers (Heiland et al., 1959; Barry and Stone, 1960; McDaniel, Mitchell, and Watson, 1967). These forms include single crystals, powder, sintered pellets, and evaporated thin layers. Zinc oxide powders and evaporated layers are commonly used in surface property investigations as they each possess a large effective surface area.

In this experiment, evaporated thin layers were used because of the ease of fabrication, handling, and their adaptability to electric field experimental configurations.

The thin evaporated layers of zinc oxide fabricated for this experiment were translucent. The observable colors of thin zinc oxide layers result primarily from optical interference (Heiland et al., 1959, p. 196). The surface of these layers is rough and nonreflective and has been found to possess statistically ordered crystallites. These surface crystallites are responsible for the large specific area typical of evaporated layers. The size of the crystallites is dependent on the thickness of the layer. A layer having a thickness of 1000 angstroms will have crystallites of the order of 300 angstroms (Heiland et al., 1959, p. 196).

### Chemisorption

#### Mechanism of Chemisorption

Chemisorption in a gas-semiconductor system is generally initiated when a gas molecule strikes the semiconductor surface and is

physically adsorbed. While physically adsorbed, the molecule migrates over the semiconductor surface until it contacts a preferred site which has sufficient activation energy to form a chemical bond with the gas molecule. The molecule is then said to be chemisorbed (Trapnell and Hayward, 1964, p. 2). Quite often, however, a molecule is desorbed before a preferred site is found. Hence, chemisorption can be understood as a chemical adsorption reaction occurring in two steps: physical adsorption and chemisorption.

The chief distinction between these two stages lies primarily in the strength and type of bond which holds the gas molecule to the semiconductor surface. The physical adsorption bond is essentially a Van der Waals force which is of sufficient strength to weakly bind the gas molecule to the surface and yet allow the molecule to move about the surface. The chemisorption bond involves an actual electron exchange between the preferred site and gas molecule, and requires a much higher heat of activation. The resulting chemisorption bond will be much stronger than the physical adsorption bond.

The chemisorption bond requires the direct contact of adsorbate with the substrate (Trapnell and Hayward, 1964, p. 4); therefore chemisorption can account for at most a monolayer of coverage. Physical adsorption does not depend on direct contact of the gas molecules with the substrate and therefore is not limited to monolayer of coverage.

#### Zinc Oxide Chemisorptive Properties

Zinc oxide may chemisorb oxygen in the form of  $O_2^-$ , or  $O^-$ , or  $O^=$ . This gas-semiconductor reaction is known as depletion

chemisorption. Excess interstitial zinc atoms serve as the donors of electrons for this process.

These donor electrons come from the conduction band and are supplied by the ionized interstitial zinc atoms (see Chapter 2, page 3, Zinc Oxide). Therefore it is felt that adsorption will be non-localized on the surface.

Barry and Stone (1960, p. 128) present a somewhat different picture of ZnO chemisorption. They suggest that adsorption of oxygen molecules is localized to zinc atoms in the crystal face. For dissociative chemisorption they mention that zinc atoms in the next lower layer may also act as adsorption sites, thus leading to multilayer adsorption.

Most investigators incline to the non-localized view discussed above. However, the work of Barry and Stone is of interest and their ideas warrant further investigation.

Zinc oxide shows a strong correlation between adsorption and its electrical and optical properties (Morrison, 1955, p. 260). For example, zinc oxide strongly adsorbs ultraviolet light which corresponds to its band gap of approximately 3.2 eV. The radiation produces electron-hole pairs within the zinc oxide crystal.

Chemisorption of oxygen has a direct influence on the surface conductivity of zinc oxide. Depletion of surface electrons occurs when oxygen molecules combine with electrons in the zinc oxide conduction band to form oxygen ions. The resulting negatively charged surface further reduces conductivity by repelling free electrons from this

high-mobility region (Hoenig and Lane, 1968). If the zinc oxide is illuminated to produce electrons and holes, the holes will migrate toward the negatively charged semiconductor surface and discharge the chemisorbed oxygen ions. The neutralized oxygen molecules then desorb into the gas phase.

### Rate of Chemisorption

If the mean free path of the gas is less than the field plate spacing (see Fig. 4), the rate of adsorption can be expressed in terms of the number of gas molecules, in the gas phase, which collide per second with a unit area of surface at an ambient pressure  $p$ . This adsorption rate, defined as molecules adsorbed per  $\text{cm}^2$  per second, can be written as (Trapnell and Hayward, 1964, p. 87):

$$u = sp/\sqrt{2\pi mkT}. \quad (1)$$

The sticking probability,  $s$ , is defined as the fraction of the gas molecule-surface collisions which result in chemisorption. For a single activated adsorption reaction,  $s$  can be expressed as

$$s = \sigma f(\theta) e^{-E/RT}. \quad (2)$$

The term  $f(\theta)$  is the probability that a molecule out of the gas phase will collide with a vacant chemisorption site and is a function of the degree of surface coverage. In this equation the temperature is denoted by  $T$ , while  $E$  is the activation energy required for chemisorption. Therefore  $u$  can be expressed as

$$u = \sigma p f(\theta) e^{-E/RT} / \sqrt{2\pi m k T}. \quad (3)$$

For a system operating in a partial vacuum, the number of physically adsorbed molecules will be neglected as a first approximation. It can be assumed that desorption will take place primarily from occupied sites. The velocity of desorption,  $u$ , is then

$$u' = K f'(\theta) e^{-E'/RT}. \quad (4)$$

The terms  $E'$  and  $K$  are the activation energy of desorption and the velocity constant respectively.  $f'(\theta)$  equals the proportion of sites available for desorption at coverage  $\theta$ .

The number of gas molecules which are chemisorbed per unit area, per unit time, is equal to the difference between the chemisorption and desorption rates. Therefore by combining expressions (3) and (4) the net rate of chemisorption can be expressed as

$$\begin{aligned} N_{fr} &= u - u' \\ &= [\sigma p f(\theta) e^{-E/RT} / \sqrt{2\pi m k T}] - K f'(\theta) e^{-E'/RT}. \end{aligned} \quad (5)$$

The chemisorption rate is therefore a function of pressure, temperature, degree of surface coverage, and the mass of the gas molecules.

If the mean free path of the gas is greater than the plate spacing, a gaseous boundary layer will begin to form which will limit the speed of reaction. An approximation for the mean free path length is

$$\ell_{\text{cm}} \sim 5/p, \quad (6)$$

where  $\ell$  is the path length in centimeters and  $p$  is the vacuum system pressure in microns (Kennard, 1938, Chapter 8).

As is discussed in Chapter 4, page 19, the plate spacing of the zinc oxide plate assembly is 0.15 cm. Therefore for test pressures below 30 microns, the chemisorption rate will be retarded by this gaseous boundary layer.

The chemisorption of  $O_2$  on ZnO proceeds until a potential barrier builds which limits further chemisorption. A widely accepted theory which is applicable to this "limiting action" is known as the boundary layer theory.

#### Boundary Layer Theory

Oxygen tends to be adsorbed on zinc oxide as negative ions (Trapnell and Hayward, 1964, p. 261). This partially full conduction band supplies the electrons for negative ion formation. As these conduction band electrons are rapidly depleted, additional electrons must be furnished, by levels deep in the crystal, for chemisorption to continue.

This removal of electrons causes a charge transfer between the semiconductor bulk and surface. The chemisorption-limiting potential barrier increases the activation energy for adsorption while decreasing the heat of adsorption.



For illustration, at zero coverage the activation energy of adsorption is equal to  $\eta$  (Barry and Stone, 1960, p. 138). As the potential,  $V$ , builds up, the activation energy becomes  $(\eta + V)$ . Furthermore, the heat of adsorption,  $(\alpha - \phi)e$ , becomes  $(\alpha - \phi - V)e$  as the potential barrier develops.

The term  $\phi$  is the work function of the oxide and can be expressed as the work necessary to remove an electron from the semiconductor bulk to a point just outside its surface.  $\alpha$  is defined as the electron affinity of the oxygen molecule. In other words,  $\alpha$  is a measure of the attraction of the oxygen molecule for an electron from the conduction band of the zinc oxide crystal.

The height of the potential barrier is a function of the number of electrons removed from the bulk. It will increase in magnitude as chemisorption continues until the potential energy of the electrons on either side of the depletion region (interface) is equal. At this point, further increases in chemisorption do not occur.

This type of chemisorption is described as "depletive" chemisorption because it results in a reduction of the majority charge carriers by the adsorbate. The potential barrier inhibits adsorption from proceeding to full monolayer coverage.

The boundary layer theory can be used to quantitatively describe the mechanisms of depletive chemisorption (Trapnell and Hayward, 1964; Stone, 1961).

If oxygen is chemisorbed on the surface of zinc as  $O^-$ , the energy of chemisorption for the first atom adsorbed will be

$$(\alpha - \phi)e + K. \quad (7)$$

K is the interaction energy of the oxygen ion with the oxide surface.  $(\alpha - \phi)e$  is described as the heat of adsorption for zero coverage of the semiconductor surface. As adsorption continues, a potential barrier V builds up. The Fermi Level decreases by the amount V, and the energy of chemisorption becomes

$$(\alpha - \phi - V)e + K. \quad (8)$$

When the potential barrier reaches the value  $V_f$ , the potential for chemisorption is zero:

$$(\alpha - \phi - V_f)e + K = 0. \quad (9)$$

At this stage, further chemisorption is precluded.

In order to find the number of adsorbed ions,  $N_f$ , in terms of the potential barrier,  $V_f$ , it is assumed that every donor site has yielded its electron and that the charge density,  $\rho$ , in the boundary region is a constant. Therefore,

$$\rho = en_o. \quad (10)$$

and applying Poisson's equation we get

$$d^2V/dx^2 = 4\pi\rho/k. \quad (11)$$

Integrating equation (11) between  $x = 0$  and  $x = \ell$  where  $\ell$  is the width of the boundary layer, we get

$$V_f = (2\pi\rho/k)l^2 = 2\pi en_o l^2/k. \quad (12)$$

The total charge in the boundary layer equals the magnitude of the charge in the chemisorbed layer. Therefore

$$V_f = 2\pi e N_f^2 / n_o k \quad (13)$$

and

$$N_f = (n_o k V_f / 2\pi e)^{1/2} \quad (14)$$

where  $N_f$  is expressed as molecules chemisorbed per  $\text{cm}^2$ .

## CHAPTER 3

### FIELD EFFECT

#### Field Effect Theory

It has been suggested that an electric field can influence chemisorption on a semiconductor by either attracting or repelling charge carriers near the surface (Volkenshtein, 1963, p. 126). The effect of this field-induced charge transfer is to change the position of the Fermi Level at the surface of the semiconductor. If the field is oriented to attract electrons toward the zinc oxide surface, the Fermi Level will approach the bottom of the conduction band and chemisorption of oxygen will be enhanced. A field which is oriented to repel electrons from the surface will force the Fermi Level downward toward the valence band. This field orientation would be expected to inhibit chemisorption of oxygen and cause desorption from the semiconductor surface.

In this connection, Volkenshtein (1963) suggests that the effect of an electric field on semiconductor thin films (evaporated layers) will be to increase the adsorption capacity of the surface facing the positive field plate while decreasing the capacity of the surface facing the negative field plate, but not to the same degree. Figure 2 shows the influence of an electric field whose direction is perpendicular to the plane of the oxide surface on the zinc oxide thin film band structure.

### Field Effect Calculations

The maximum shift of the Fermi Level due to the application of a DC electric field is the product of the Debye length and field existing at the semiconductor surface (Battelle, 1967). The Debye length is a measure of the distance over which departures from electrical neutrality, under all conditions, smooth themselves out (Adler, 1964, p. 151).

The Debye length for an extrinsic semiconductor is

$$L_D = \sqrt{(kT/q) (\epsilon/qn_o)}. \quad (15)$$

The field strength at the semiconductor surface, due to this external field, equals the magnitude of the field in the gap between the positive and negative plates divided by the relative dielectric constant of zinc oxide (Lindmayer and Wrigley, 1965, p. 324).

$$F = (V_g/d) (\epsilon/\epsilon_r). \quad (16)$$

Therefore  $V_s$ , the maximum shift of the Fermi Level, will be equal to the product of equations (15) and (16)

$$V_s = (V_g/d) [(kT/q) (\epsilon/qn_o \epsilon_r^2)]^{1/2} \quad (17)$$

The field at the semiconductor surface is now the sum of the original field across the semiconductor boundary layer and the external field imposed by the DC voltage source. Likewise, the new potential barrier

value will be equal to the sum of equations (13) and (17).

$$V_n = V_f + V_s. \quad (18)$$

The change in the number of adsorbed molecules per  $\text{cm}^2$  is

$$\Delta N_f = \sqrt{n_o k / 2\pi e} (\sqrt{V_n} - \sqrt{V_f}). \quad (19)$$

We have no accurate data on the exact specific surface of the semiconductor (zinc oxide) used in this experiment, but Heiland et al. (1959, p. 195) states that the specific surface of active zinc oxide may be in excess of  $80 \text{ m}^2/\text{g}$ . Specific surface is defined as surface area which is chemically reactive with the adsorbate and is much larger than the nominal or linearly measured surface. To obtain a numerical answer for the number of adsorbed molecules, this figure ( $80 \text{ m}^2/\text{g}$ ) will be used in the calculations.

The adsorption-effective surface area is approximately  $2.0 \times 10^4 \text{ cm}^2$  (see Chapter 4, page 18, Preparation of Zinc Oxide Plates).

The total change in the amount of adsorbed molecules in the system is

$$\Delta N_{ft} = 2.0 \times 10^4 \sqrt{\epsilon_o k / 2\pi e} (\sqrt{V_n} - \sqrt{V_f}). \quad (20)$$

To arrive at an actual number for  $N_{ft}$  as a function of  $V_s$ , the following values for zinc oxide parameters were used (Barry and Stone, 1960, p. 139):

$$n_o = 10^{19} \text{ Donors per cm}^3$$

$$V_f = 0.055 \text{ eV.}$$

Therefore,

$$\Delta N_{ft} = 6.5 \times 10^{16} (\sqrt{V_s + 0.055} - 0.235) \text{ molecules.} \quad (21)$$

The number of adsorbed molecules is therefore a function of the shift in the Fermi Level resulting from the applied electric field.

## CHAPTER 4

### DESIGN OF EXPERIMENTAL SYSTEM

#### Vacuum System

The vacuum system consisted of a stainless steel vacuum chamber, a Welch Duo-Seal rotary mechanical pump, a Consolidated Vacuum Corp. 300-watt oil diffusion pump, and two pressure gauges.

The vacuum chamber, into which the zinc oxide plate assembly was placed, had interior dimensions of 73 mm diameter by 254 mm length. The fittings and tubing leading into the chamber added substantially to its volume. The over-all volume of the system was approximately 2.05 liters. Figure 3 shows a diagram of the vacuum chamber and associated fittings.

The mechanical pump was used to back the diffusion pump and also had a direct connection to the vacuum system through a bellows sealed valve. For fast pump cycles, in which a high vacuum was not required, the mechanical pump was used alone to pump down the system.

An ultra high vacuum valve was used to regulate the quantity of test gas within the vacuum system. System pressure was monitored by a discharge vacuum gauge for pressures of 5 microns or less. A calibrated pirani vacuum gauge was used to monitor pressures in excess of 5 microns.



### Field Voltage Apparatus

A source of DC field voltage was provided by a Gyra Electronics Corporation reversible polarity DC power supply. This power supply has an infinitely adjustable output ranging from 0 to 3000 vdc. The field voltage was supplied to the zinc oxide plate assembly by a high voltage twin feed-through connector (Fig. 3).

### Preparation of Zinc Oxide Plates

The substrates for the evaporated zinc layers were 4 round stainless steel plates, 6.36 cm in diameter and 1 mm thick. The nominal surface area of these 4 plates was  $250 \text{ cm}^2$ . The plates were sand blasted and then cleaned with Alconox, acetone, and finally rinsed in distilled water before deposition of zinc.

Zinc was evaporated onto each side of the stainless steel plates at a pressure of  $5 \times 10^{-6}$  torr to a thickness of approximately 2000 Å. These zinc coated plates were oxidized in an atmosphere of pure oxygen at  $600^\circ \text{C}$  for 14 hours.

The total volume of zinc oxide in the system is the product of the nominal surface area times the oxide thickness. Taking  $2.0 \times 10^{-5}$  cm as the depth of the oxide and  $250 \text{ cm}^2$  as the surface area, the volume of zinc oxide was  $5.0 \times 10^{-3} \text{ cm}^3$ . The density of zinc oxide is approximately  $5.0 \text{ g/cm}^3$ . Therefore the mass of zinc oxide on the plates was of the order of  $2.50 \times 10^{-3} \text{ g}$ . Assuming that the specific surface of the zinc oxide is of the order of  $80 \text{ m}^2/\text{g}$  (see Chapter 2, page 4, Chemisorption), the total adsorption-effective surface area of oxide in the system was approximately  $2.0 \times 10^4 \text{ cm}^2$ .

### Zinc Oxide Plate Assembly

The zinc oxide coated plates were situated between 5 uncoated stainless steel plates. These uncoated plates were of the same dimensions as the zinc oxide plates. The 9 plates were mounted on a glass jig as shown in Fig. 4. The plates were separated by 1.5 mm glass spacers. The total geometrical area of the 4 zinc oxide coated plates was approximately  $250 \text{ cm}^2$ . Electrical contact was made to the plates by means of stainless steel tabs which had been spot welded to the plates. Nickel wire was used to connect the plates to the high voltage twin feed-through connector.

The experiment was set up so that a positive power supply voltage made the uncoated plates positive with respect to the zinc oxide substrate plates. The electric field between the uncoated and zinc coated plates resulting from this polarity voltage was designated as a positive field. This positive field should cause adsorption as noted by a decrease in system pressure. Likewise, a negative field produced by a voltage of opposite polarity should cause desorption as noted by an increase in system pressure. Figure 5 shows a schematic of the electric field-producing circuit.

The ideal gas law was used to relate pressure changes to the numbers of gas molecules adsorbed or desorbed. The gas law states that

$$PV_0 = nRT \quad (22)$$

where  $n$  = number of gram-moles.

The heat liberated during chemisorption is too small to appreciably alter the temperature of the gas in the over-all vacuum system; so the reaction is essentially isothermal. Since the volume of the system and the gas constant,  $R$ , are constant, changes in  $n$  are proportional to changes in  $P$ .

Therefore,

$$\Delta n = \Delta PV_o / RT. \quad (23)$$

Assuming that pressure changes are caused just by adsorption or desorption,  $n$  equals the number of moles adsorbed or desorbed from the zinc oxide plates. Therefore  $\Delta N_{ft}$ , the number of oxygen molecules adsorbed or desorbed, is equal to the product of  $n$  and Avogadro's number.

$$\begin{aligned} \Delta N_{ft} &= 6.02 \times 10^{23} \Delta n \\ &= 6.02 \times 10^{23} \Delta PV_o / RT. \end{aligned} \quad (24)$$

These results were used for calculations of  $\Delta N_{ft}$  from the experimental data.

## CHAPTER 5

### EXPERIMENT

#### Objectives of Experiment

The experimental procedures were designed to determine the amount of adsorption/desorption as a function of field voltage and base pressure. This was done by relating pressure changes due to field-induced adsorption/desorption to molecules of gas being adsorbed or desorbed by the zinc oxide plates.

Repeatability of the data was noted by repeating the experiment a minimum of three times for each data point. An assessment of zinc oxide adsorption/desorption life was made by noting any degradation of results from repeated adsorption/desorption cycles.

Finally, it was of interest to determine if the field-induced adsorption/desorption was specific to oxygen as opposed to nitrogen.

#### Pre-Run Preparations

Prior to taking data on adsorption/desorption, the vacuum system was twice flushed out with oxygen. The flush cycle consisted of first pumping down to  $10^{-6}$  torr and then backfilling with oxygen to a pressure of one atmosphere. The purpose of this was to reduce to a very low value the concentration of other residual gases in the system with respect to oxygen.

Then before each experimental run, the vacuum system was pumped down to  $10^{-6}$  torr, then filled with oxygen to a pressure of 50 microns. The system was allowed to sit at this pressure for 5 minutes to oxygenate the vacuum system to a stabilized reference value. It has been established that zinc oxide has a relatively fast response time in this pressure range (McDaniel et al., 1967, p. 18). This pressure was also low enough to allow quick pump down cycles to the desired test pressures.

#### Procedures for Taking Data

##### Chemisorption with Oxygen as Test Gas

The procedure for taking data was to set the system at the base pressure of interest and to allow the system to stabilize for 5 minutes. The pressure was monitored for two minutes on the pirani gauge with readings taken every 30 seconds. The field voltage was then applied, and any changes in pressure were noted. The pressure was then monitored for 2 additional minutes, with readings noted first 15 seconds after the field was applied, then every 30 seconds.

##### Chemisorption of Nitrogen

To show that the reaction was specific to oxygen, nitrogen was substituted for oxygen in the experiment. The system was first flushed out with nitrogen and prepared according to the pre-run preparations. Two experimental runs were then taken following the same procedures as described above for oxygen.

## CHAPTER 6

### RESULTS

As was predicted in Chapter 3, page 13, FIELD EFFECTS, adsorption and desorption on zinc oxide were controllable by transverse electric fields. Figure 5 shows the amounts of adsorption and desorption for positive and negative field voltages for various base (test) pressures. Base pressure, in this case, was taken as the pressure at which the system was stabilized before the transverse field was applied.

For positive fields, it is seen that the amounts of adsorption increase as the field voltage increases. However, for negative transverse fields, the desorption curves appear to asymptotically approach a limit as the negative field voltage increases. Actually, for higher base pressures, the curves reverse themselves at certain values of field voltages. The 20-micron base curve in Fig. 6 reverses at -250 volts; while the 40-micron base curve is seen to reverse at -100 volts. This seems to indicate that a field induced discharge resulting in a loss of field strength was occurring at a fairly constant value of pressure-voltage (i.e., approximately 500 micron volts).

A limit to desorption is predicted by the theoretical curve seen in Fig. 6. A negative field voltage of sufficient magnitude should be able to force the potential barrier to a value where complete desorption occurs. However, there was no such limit to the amount of adsorption as the positive field voltage increased.

Amounts of adsorption for a given positive field were less than corresponding amounts of desorption for a negative field of the same magnitude. This was also predicted in the theoretical curves.

It was noted that as base pressures increased, desorption increased but adsorption decreased. A reason for this result is seen in the mode of operation. With the electric field off, the system was filled to the base pressure with oxygen. But zinc oxide normally adsorbs oxygen, so that by the time that the field was applied, part of the adsorption capacity of the oxide was taken up. Therefore desorption effects should be greater than adsorption effects.

Figure 7 shows the pressure versus time relation occurring with application of an adsorption-enhancement field, for two different values of the applied fields.

The two runs taken with nitrogen in the system (after flushing the system with nitrogen) showed no adsorption taking place on zinc oxide as evidenced by decreases in system pressure. However the first desorption run showed a very slight increase in pressure occurring on application of the negative field. The slight desorption was undoubtedly due to a small amount of residual chemisorbed oxygen in the semiconductor being released by the field. This speculation was borne out by the results of the second consecutive run in nitrogen which showed no desorption at all taking place when the field was applied.

The results of the experiment were used to compute a "figure of merit" for zinc oxide. This figure of merit was computed in terms of grams of oxygen adsorbed per square centimeter of geometric surface

area per unit voltage gradient. Taking the amount of oxygen adsorbed at the base pressure of 5 microns and field voltage of +800 volts, the figure of merit is

$$L = 1.67 \times 10^{-12} \text{ (grams O}_2 \text{ cm/cm}^2 \text{ volt)}.$$

No detailed studies were undertaken on the long-term stability of the zinc oxide system. At this time we can only indicate that no degradation was noted in the response of the zinc oxide after 3 months of operation involving hundreds of adsorption and desorption cycles. For the pressures and temperature ranges encountered in this experiment, the zinc oxide reactions have been completely reversible.



## CHAPTER 7

### DISCUSSION AND CONCLUSIONS

#### Comparison of Theory and Experiment

The experimental results show, in general, qualitative agreement with the theoretical curves (Fig. 6). It is of interest to note that the field induced desorption does show the limiting behavior, at low base pressures, predicted by theory in Chapter 3, page 13, FIELD EFFECT.

Quantitative differences between theoretical and experimental results are due to the idealized theoretical model used for the calculations. Parameters of the model such as donor density, Debye length, dielectric constant, and specific area were "educated estimates" of the characteristics of the actual zinc oxide used in the experiments.

The important result of this experiment is that a practical means of influencing chemisorption on a semiconductor has been shown to be possible.

#### Future Efforts

Many other parameters in the realm of controllable chemisorption remain to be investigated. The actual adsorbent-effective life of zinc oxide has not yet been determined. Zinc oxide preparation techniques and binding procedures can greatly affect the reversible and irreversible adsorbent capacity of the oxide (Barry and Stone, 1960, p. 124).

It will be of interest to investigate the effects of oxide preparation on field-controlled chemisorption reactions.

The figure of merit shows that  $1.67 \times 10^{-12}$  grams of oxygen can be adsorbed per square centimeter of surface per volt per centimeter. An improvement in these results should follow upon use of an adsorbent having a greater specific surface area than zinc oxide thin films, i.e., zinc oxide powder.

It is apparent that many investigations remain to be carried out before our knowledge in this area is complete. That further investigations are warranted is clear, both from the promising results to date and from the many scientific and industrial applications that await the development of a controllable chemisorber.

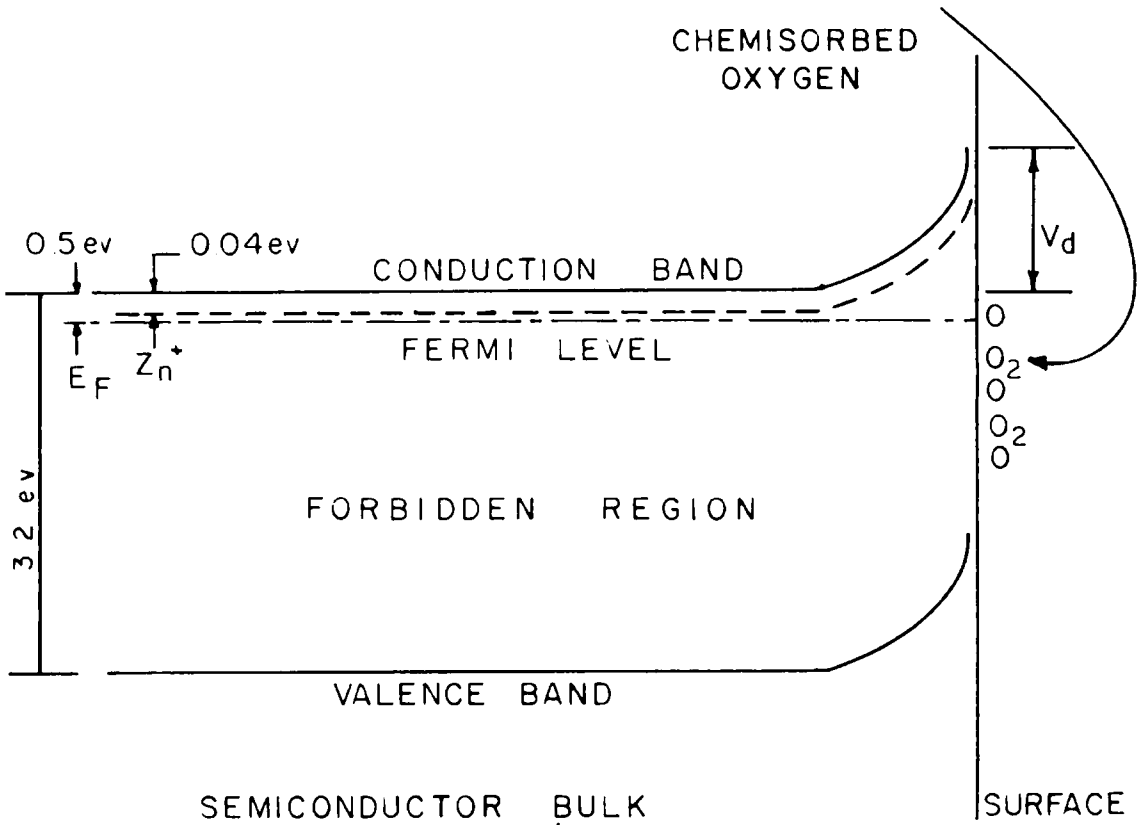


Fig. 1. Energy Plot of ZnO Band Structure

$L$  = THICKNESS OF THIN LAYER

SOLID LINE DENOTES BAND STRUCTURE - NO FIELD APPLIED

DOTTED LINE DENOTES EFFECT OF TRANSVERSE FIELD

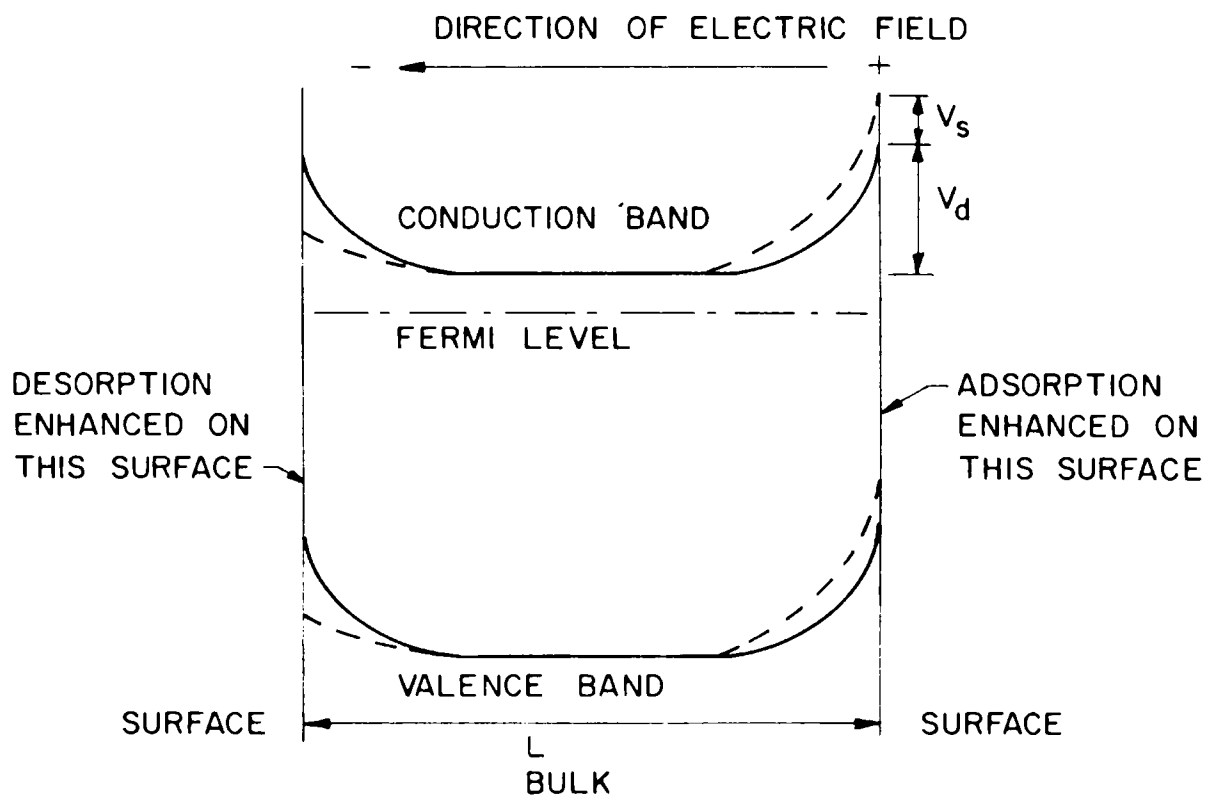


Fig. 2. Influences of Field on ZnO Thin Film Band Structure

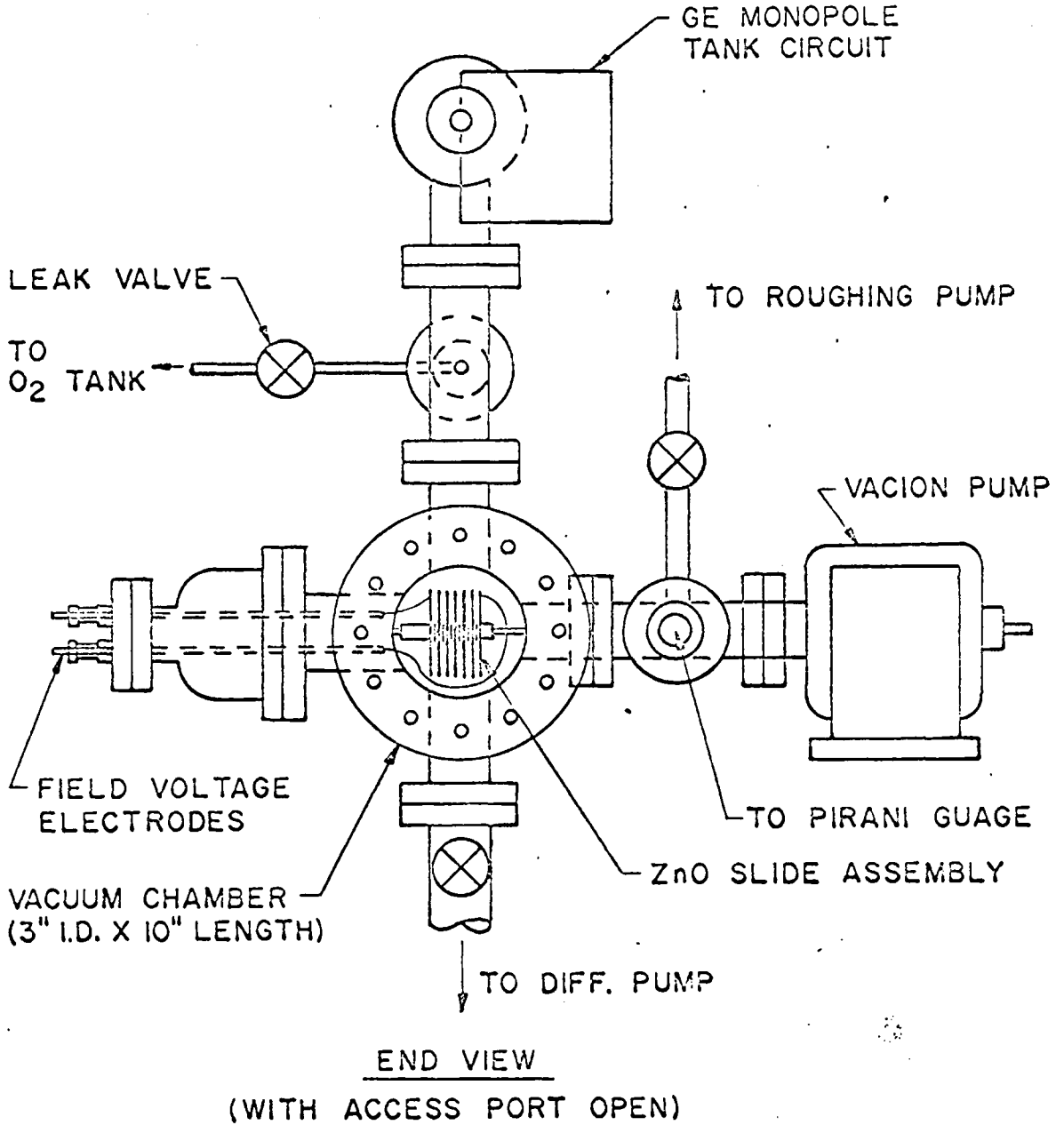
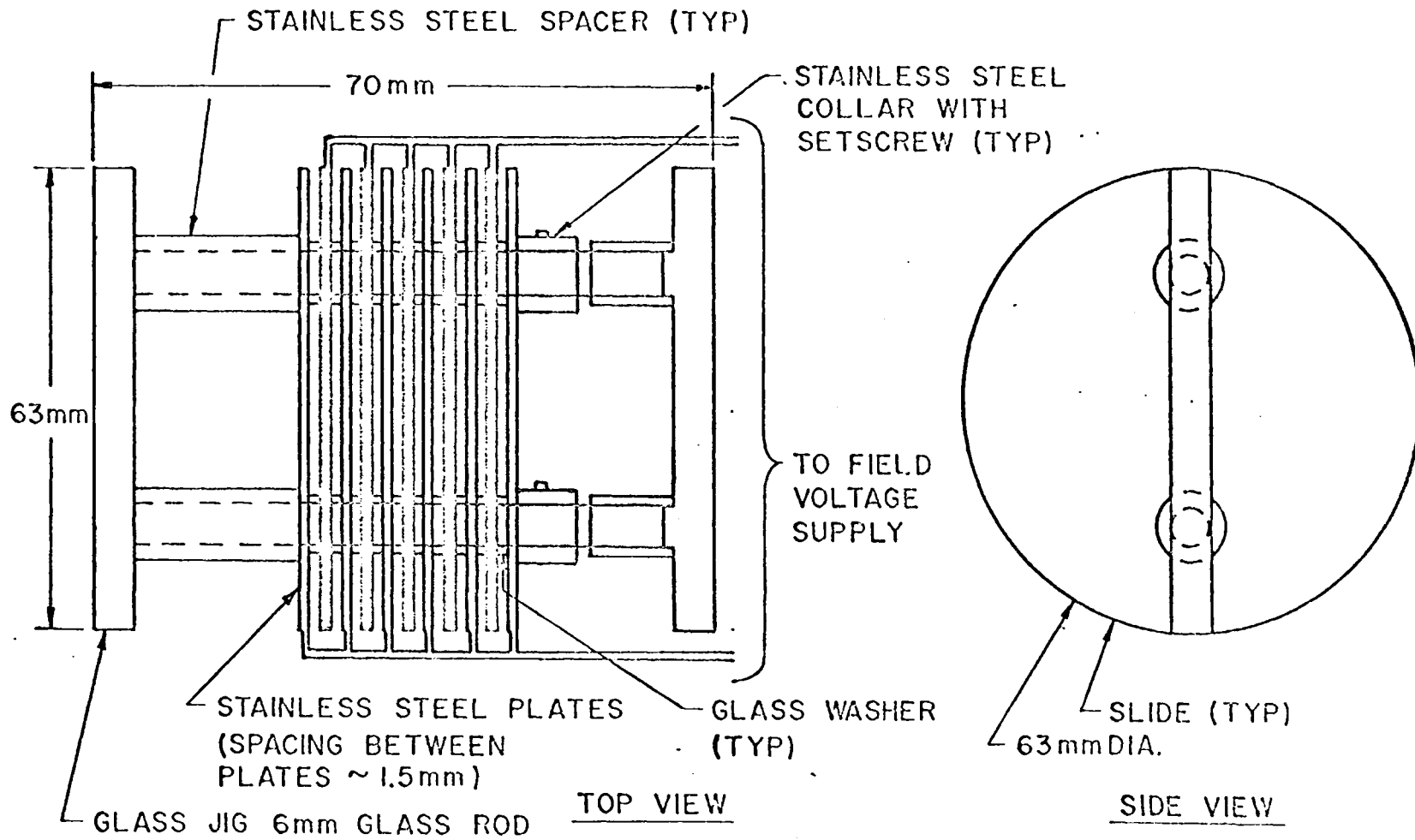


Fig. 3. Vacuum System for ZnO Studies



NOTE: DARK STAINLESS STEEL PLATES ARE COATED ON BOTH SIDES WITH ZnO

Fig. 4. ZnO Plate Assembly

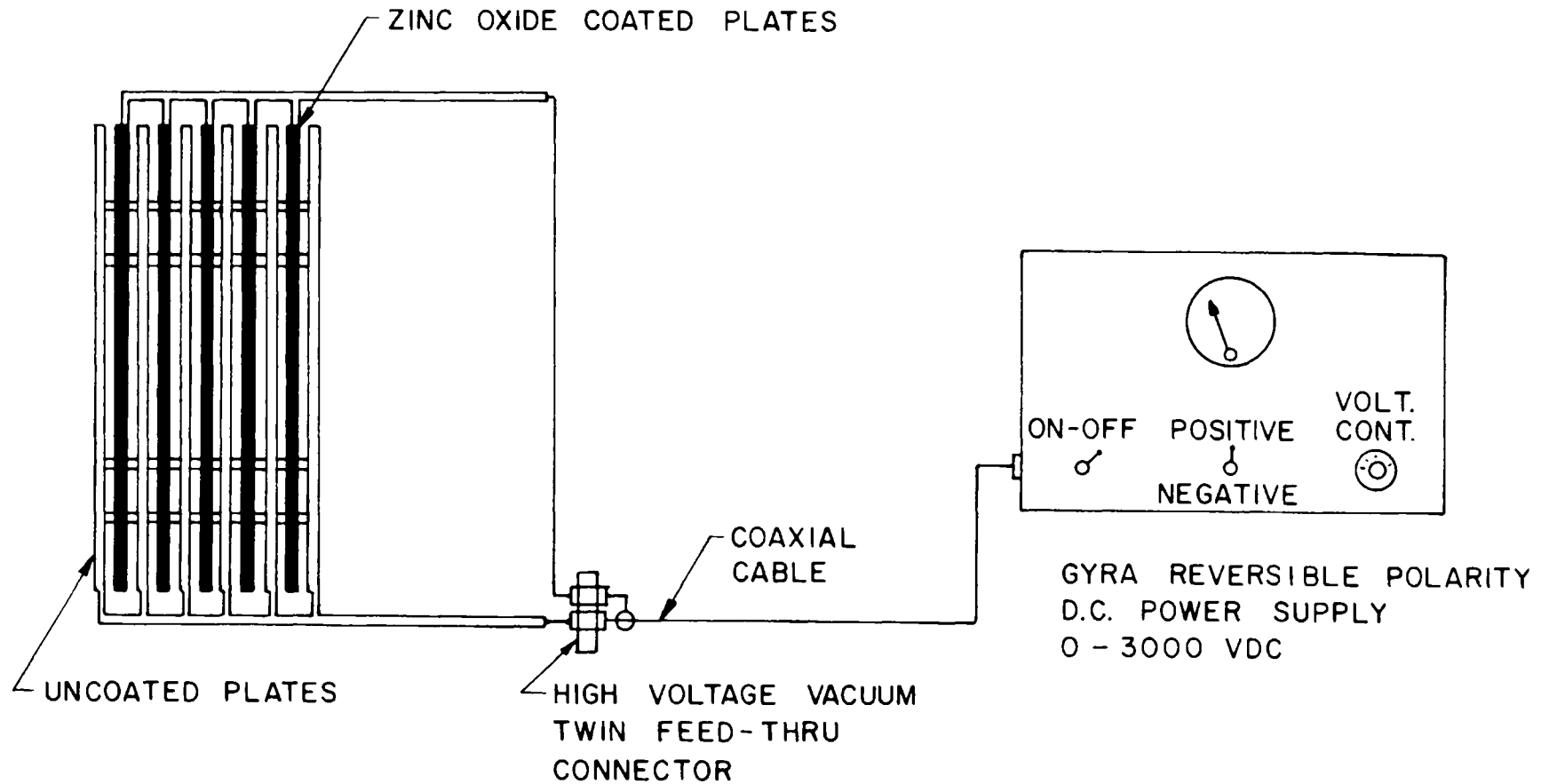


Fig. 5. Electric Schematic

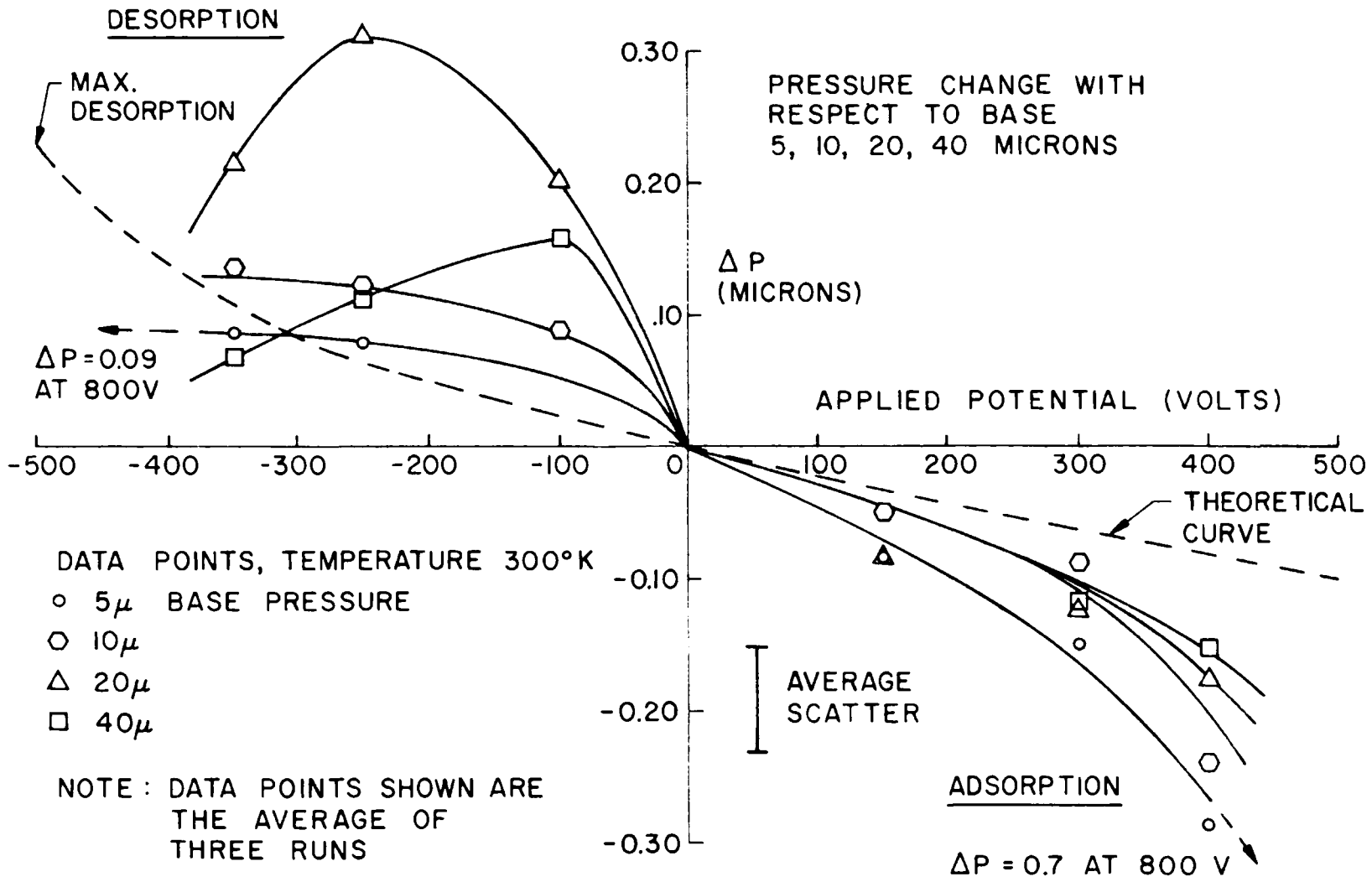


Fig. 6. Experimental Curve: Adsorption-desorption vs. Applied Potential



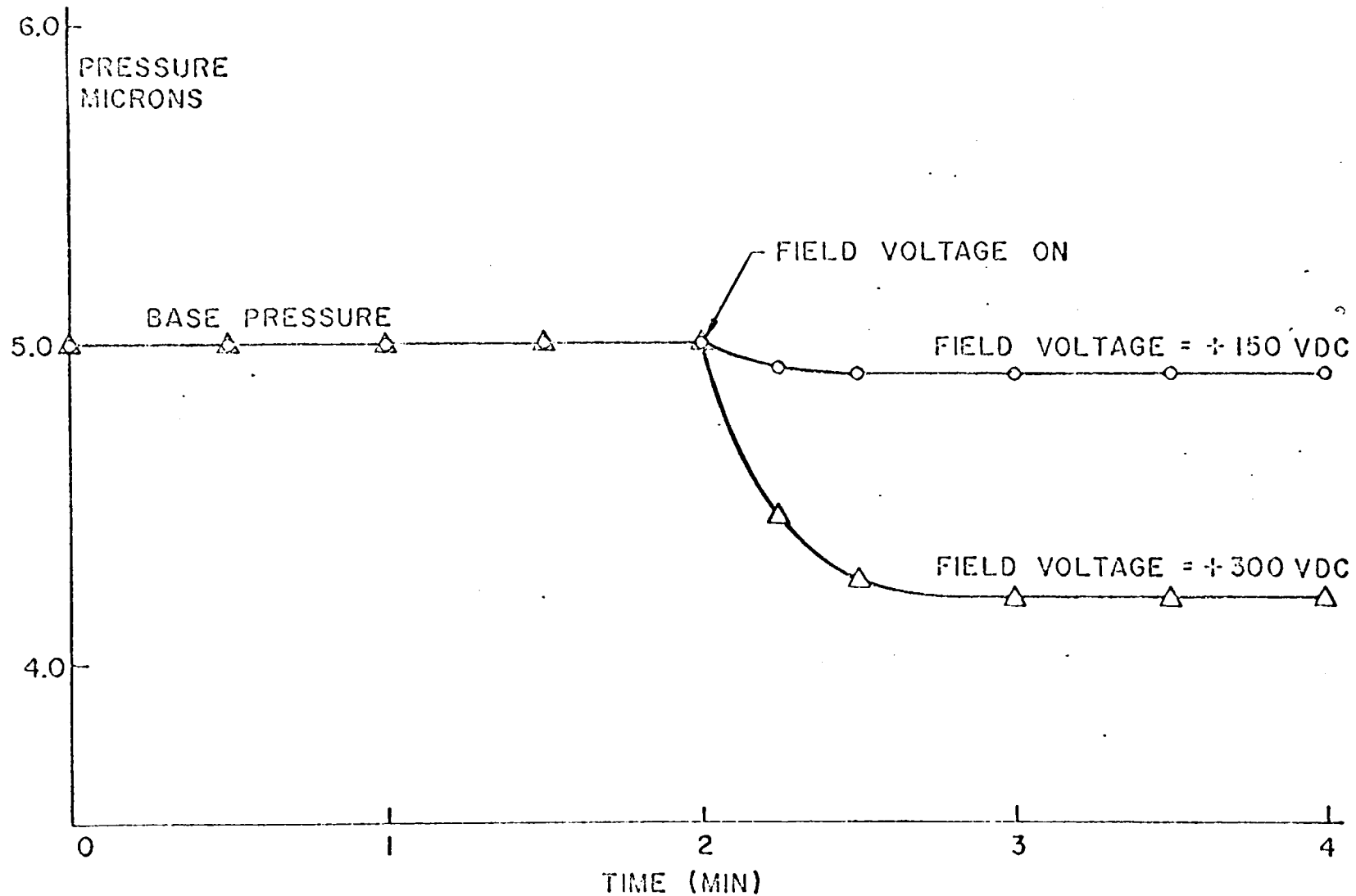


Fig. 7. Pressure vs. Time

## NOMENCLATURE

d	Gap width
e	Electron charge
E	Activation energy of chemisorption
E'	Activation energy of desorption
F	Field strength at semiconductor surface
k	Boltzmann constant
K	Interaction energy of $O^-$ ion with surface
$\ell$	Thickness of boundary layer
L	Figure of merit for zinc oxide
$L_D$	Debye length of extrinsic semiconductor
m	Mass of gas molecule
n	Number of gram-moles
$n_o$	Concentration of donor sites
$N_f$	Number of adsorbed ions per $cm^2$
$N_{fr}$	Net rate of chemisorption per $cm^2$
$N_{ft}$	Total number of adsorbed ions
p	Pressure
R	Universal gas constant
T	Temperature in $^{\circ}K$
V	Potential barrier
$V_g$	Gap voltage

$V_f$	Potential barrier for which energy of chemisorption is zero
$V_n$	Potential barrier with field applied
$V_s$	Shift in potential barrier due to field
$V_o$	Volume of vacuum system
$x$	Distance into boundary layer
$\alpha$	Electron affinity of the atom
$\epsilon$	Dielectric constant of zinc oxide
$\epsilon_r$	Relative dielectric constant
$\sigma$	Condensation coefficient
$\phi$	Work function of zinc oxide
$\rho$	Charge density in boundary layer
$\eta$	Activation energy of adsorption

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