CONDUCTIVITY CHANGES DUE TO CHEMISORPTION ON ZINC-DOPED POLYCRYSTALLINE STANNIC OXIDE

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CHAPTER I

INTRODUCTION

During the past two decades there has been an increasing amount of interest in relating gas-solid interactions at a semiconductor surface to the electronic properties of the bulk material. The electrical and optical properties of several different forms of stannic oxide have been investigated by various groups using many techniques and evidence has been presented[1], that zinc-doped polycrystalline stannic oxide is an n-type semiconductor. Thus, the chemisorption of oxygen on sintered bodies of this material may serve as an example of a gas-semiconductor reaction which can be readily studied with the purpose of identifying important reaction mechanisms and parameters. Ultimately it should be possible to generalize results to apply to a wide group of similar compounds.

A recent literature survey on the electrical properties of this metal oxide has been done by Peterson[2]. The research group here at Oklahoma State University has found that electrical conductivity[3,4,5], photoconductivity[1,6] and luminescence[7] are influenced to some degree by the atmosphere around the sample. Based on a previously-suggested model which will be briefly discussed in Chapter II, the work reported here, then, has been designed specifically to study the effect of oxygen chemisorption on the electronic state of zinc-doped polycrystalline stannic oxide specimens. The technique used is to examine the time-variation of specimen conductivity following rapid uptake of air at fixed temperature.

The importance of being able to establish standardized initial conditions so that the results of a number of experiments could be systematically compared was evident from the beginning of the work. Consequently, a great deal of study was directed to this point and the details of the procedural cycle have been carefully noted. The experimental methods will be discussed in Chapter III along with a discussion of the apparatus. The results will be given in Chapter IV and discussed in Chapter V.

CHAPTER II

THEORETICAL BACKGROUND

Chemisorption can be described as a chemical reaction which takes place between molecules and the surfaces of solids. When oxygen is chemisorbed on a semiconductor, the reaction which occurs is thought to depend upon an electron transfer mechanism involving the formation of oxygen ions on the surface. The electrons forming these ions come from the conduction band, in the case of an n-type semiconductor, resulting in a negatively charged surface layer which hinders further charge transfer. A decrease in electrical conductivity should be expected because of the reduced free electron density. Thus, an observed change in electrical conductivity in the presence of a gas is considered by Stone as a proof of chemisorption[8].

Chemisorption Studies on Semiconductors

The kinetics of the chemisorption of gases on solids in general have been exhaustively discussed in a review article by Low[9]. Of all the metal oxides studied, zinc oxide has probably received the most attention. Morrison[10] studied n-type specimens of this material and presented evidence for the existence of two types of chemisorbed oxygen species, O^- and $O^=$. The investigations by Kokes[11] suggest that the O^- ion predominates at room temperature and the $O^=$ ion predominates above 200°C with significant fractions of each coexisting in the intermediate temperature range. In discussing the possibilities for adsorbed oxygen species on stannic oxide Matthews[1] proposed a third possibility, suggesting that the preferred species would be O_2^-.

The experimental study reported here emphasizes the electrical conductivity changes observed in stannic oxide specimens following a rapid increase in oxygen partial pressure of the ambient, and a model which is consistent with the results is given below.

The equally interesting question of what happens during the heat treatment process to which the samples were subjected for standardization purposes must be left to another study. For the present, it appears that heat treatments at higher temperatures, at lower pressures, and for increased lengths of time, all tend to leave the oxide specimens with a "cleaner" surface, i.e., holding less chemisorbed oxygen. Peshev and Vol'kenshtein[12] have discussed the possibility of two types of chemisorbed species--one which can be reversibly removed from a surface by pumping and a second which is irreversibly held on a surface during an entire experiment. On the other hand, investigations by Taylor and Liang[13] on the hydrogen-zinc oxide system revealed that when the solid covered with adsorbate was rapidly raised in temperature, a desorption followed by increased adsorption occurred. They suggested two adsorption sites of different activation energies. In the following theoretical development, an initial chemisorption density is assumed fixed--hence the term "fixing" process--by the particular history of heat and pressure treatment and this assumption will be shown to be consistent with experimental results. Thus the details of the desorption process are unimportant to the arguments made.

Chemisorption-Conductivity Relationship

To explain the relationship between the conductivity and chemisorption, the simple band model of an n-type semiconductor is assumed along with semiconductor statistics[14] giving the density of conduction electrons as,

$$n = \beta N_c \frac{N_d - N_a}{N_a} \exp\left[-\frac{E_d}{kT}\right] \qquad (1)$$

where N_c is the usual density-of-states function, N_a is the net bulk density of acceptor states, N_d is the bulk density of principal donor states with activation energy E_d below the conduction band, β is a weighting factor of the order of unity, and that $n << N_a < N_d$. This expression is appropriate for a well-compensated, wide band gap semiconductor/insulator such as stannic oxide.

The conductivity is related to the number of carriers by

$$\sigma = ne\mu \qquad (2)$$

where σ is the conductivity, e the electronic charge and μ the mobility. The conductivity is also related to a directly measurable quantity, the electric current, by

$$\sigma = \frac{iL}{VA} \qquad (3)$$

where i is the current, V is the applied voltage, L is the sample length and A its cross-sectional area. Combining (2) and (3) gives

$$i = \frac{e\mu VA}{L} n . \qquad (4)$$

In order to take into account the presence of both bulk acceptors and surface acceptors (chemisorbed oxygen ions), Matthews[1] proposed an effective acceptor density,

$$N_a^* = N_a + xq_o \tag{5}$$

where x is the surface-to-bulk ratio of the specimen and q_o is the equilibrium surface density of the initially chemisorbed species. If the chemisorption density is a function of time, then the total density of acceptors as a function of time becomes

$$N_a(t) = N_a + xq_o + xq(t) \tag{6}$$

or

$$N_a(t) = N_a^* + xq(t) \ . \tag{7}$$

Takings Equations (1) and (7) and substituting them into Equation (4), the current as a function of time becomes,

$$i(t) = c \left[\frac{N_d - N_a^* - xq(t)}{N_a^* + xq(t)}\right] \tag{8}$$

where

$$c = \frac{e\mu VA}{L} \beta N_c \exp\left[-\frac{E_d}{kT}\right] .$$

It can therefore be seen that a change in current may be related to the chemisorption rate.

Remembering that at t = 0 there are no additional chemisorbed species being added, Equation (8) reduces to

$$i(o) \equiv i_o = c\,\frac{N_d - N_a^*}{N_a^*} \qquad (9)$$

where the initial current depends on the temperature included in c and also on the surface density of chemisorbed species. Two extreme cases are of interest: first, a high acceptor density with $N_a^* \approx N_d$, and secondly, $N_a^* << N_d$. The large value of N_a^* would represent a large initial density of chemisorbed species and the small value implies essentially a clean surface or one with few chemisorbed species as an initial condition.

Equation (8) can be simplified with each of these two assumptions. The first case also takes $N_a^* >> xq(t)$ as well as $N_d \simeq N_a^*$, leaving

$$i(t) = i_o - \frac{xc}{N_a^*}\,q(t) \qquad (10)$$

using i_o as in Equation (9). If for the second case one assumes the donor density at $t = 0$ to be very large, then with $N_d >> N_a^* + xq(t)$ one has

$$i(t) = c\left[\frac{N_d}{N_a^* + xq(t)}\right] \qquad (11)$$

or inverting,

$$\frac{1}{i(t)} = \frac{N_a^* + aq(t)}{cN_d}\,. \qquad (12)$$

The question which now arises is what is the time dependence of the chemisorption density, $q(t)$? As pointed out by Low[9] an Elovich-type relationship between q and t fits a wide variety of experimental data obtained by many investigators who have studied chemisorption kinetics. The Elovich relationship is most readily expressed in the form

$$q(t) = B \ln \left[\frac{t + t'}{t'}\right] \tag{13}$$

where t is time, t' is a constant and B a constant of proportionality.

Assuming that the Elovich dependence characterizes the adsorption process in the present case of interest, one obtains an expression for the current as a function of time as proposed by Matthews[1] to be

$$i(t) = c \left[\frac{N_d - N_a^* - xB \ln \left(\frac{t + t'}{t'}\right)}{N_a^* + xB \ln \left(\frac{t + t'}{t'}\right)}\right] \tag{14}$$

with the simplified Equations (10) and (12) becoming respectively

$$i(t) = i_o - \frac{xcB}{N_a^*} \ln \left[\frac{t + t'}{t'}\right] \tag{15}$$

and

$$\frac{1}{i(t)} = \frac{N_a^* + xB \ln \left[\frac{t + t'}{t'}\right]}{cN_d} . \tag{16}$$

As will be subsequently seen, Equation (15) fits the experimental observations of the present study rather well. Matthews and Kohnke[3] have discussed the applicability of Equation (16) to photocurrent decay studies where illumination with intrinsic light left an initially "cleaner" surface.

One last caution: since the above treatment requires at least quasi-equilibrium to be valid, the magnitude and rapidity of changes must be small enough for such a restriction to be reasonable. Furthermore, for c to be a constant, the same donor level (energy E_d) must control the conductivity during the change studied.

CHAPTER III

APPARATUS AND EXPERIMENTAL METHODS

Apparatus

The apparatus consisted of three main parts: the electrical measurements and heater system, the vacuum chamber and sample holder, and the gas handling system. The electrical measurement and heater system is shown in Figure 1. The current measurement system utilized a floating 90 volt dry cell which provided voltage across the sample. The sample current was monitored on a Keithley 610B Electrometer. The 3 volt output from the electrometer was used along with a voltage divider circuit which reduced the 3 volt output to a 100 millivolt input to the Sargent strip chart recorder. Shielded coaxial cable, RG-58/u was used to make the connections between the sample, floating voltage, and the electrometer.

The heater system, as seen in Figure 1, was composed of two heaters: one supplied heat for the sample, and the other was mounted on the outer wall to reduce the heat loss to the surroundings. The main heater was a 35 ohm heater mounted in a copper block of radius 2 inches and thickness 1¼ inches. It was positioned just below, but not touching, the sample. The heater on the outside wall was a 30 ohm heater which helped to maintain temperature fluctuations to less than $1^{\circ}C$ during ambient gas change.

The temperature was monitored by utilizing three copper-constantan

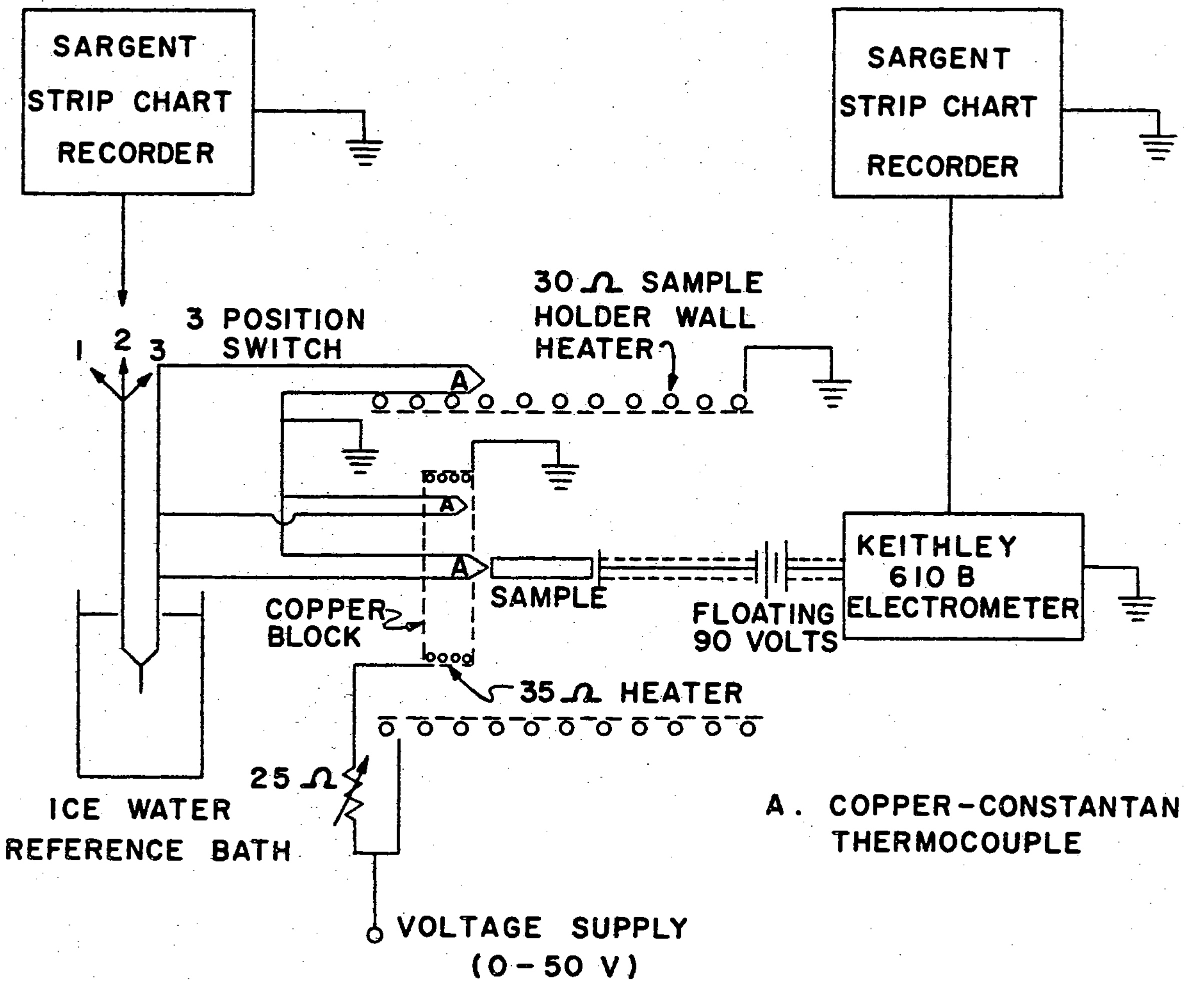

Figure 1. Electrical Measurement-Heater System

thermocouples. The three thermocouples were independent of each other and the desired one could be selected through the use of a three-position switch. Number 1 was placed against the bottom of the sample to obtain the sample temperature. Number 2 was on the copper block which contained the 35 ohm heater. Number 3 was on the outer wall of the vacuum chamber to assist in choosing the proper setting for minimum heat loss from within vacuum chamber. The output from any one of these thermocouples could be monitored on the Sargent strip chart recorder.

The vacuum chamber and sample holder placement is depicted in Figure 2. The copper block which contains the heater was suspended from the lid by two stainless steel rods. The sample holder, heater, and electrical connections could be removed with the lid for easy access. The vacuum chamber itself was constructed of stainless steel with a 6 inch diameter. An "O" ring was utilized to assure proper sealing when lid was in place. The heater leads were fed through the lid using glass-to-metal vacuum feed-throughs. The thermocouple leads and the "hot" lead to the sample were fed through quartz capillaries which were epoxy vacuum-sealed. A detailed picture of the sample holder itself can be seen in Figure 3. The sample is placed between two platinum contacts, with the upper one being pressed downward by a spring. The lower platinum contact was placed on a teflon insert for insulation. The thermocouple which was previously described as being on the bottom of the sample was placed on the bottom platinum contact and one side was used as ground for the current measuring system.

The gas handling system is shown in block diagram in Figure 4. This system allowed evacuation of the vacuum chamber to about 10 microns pressure and allowed dry ambient gases to be let into the sample chamber.

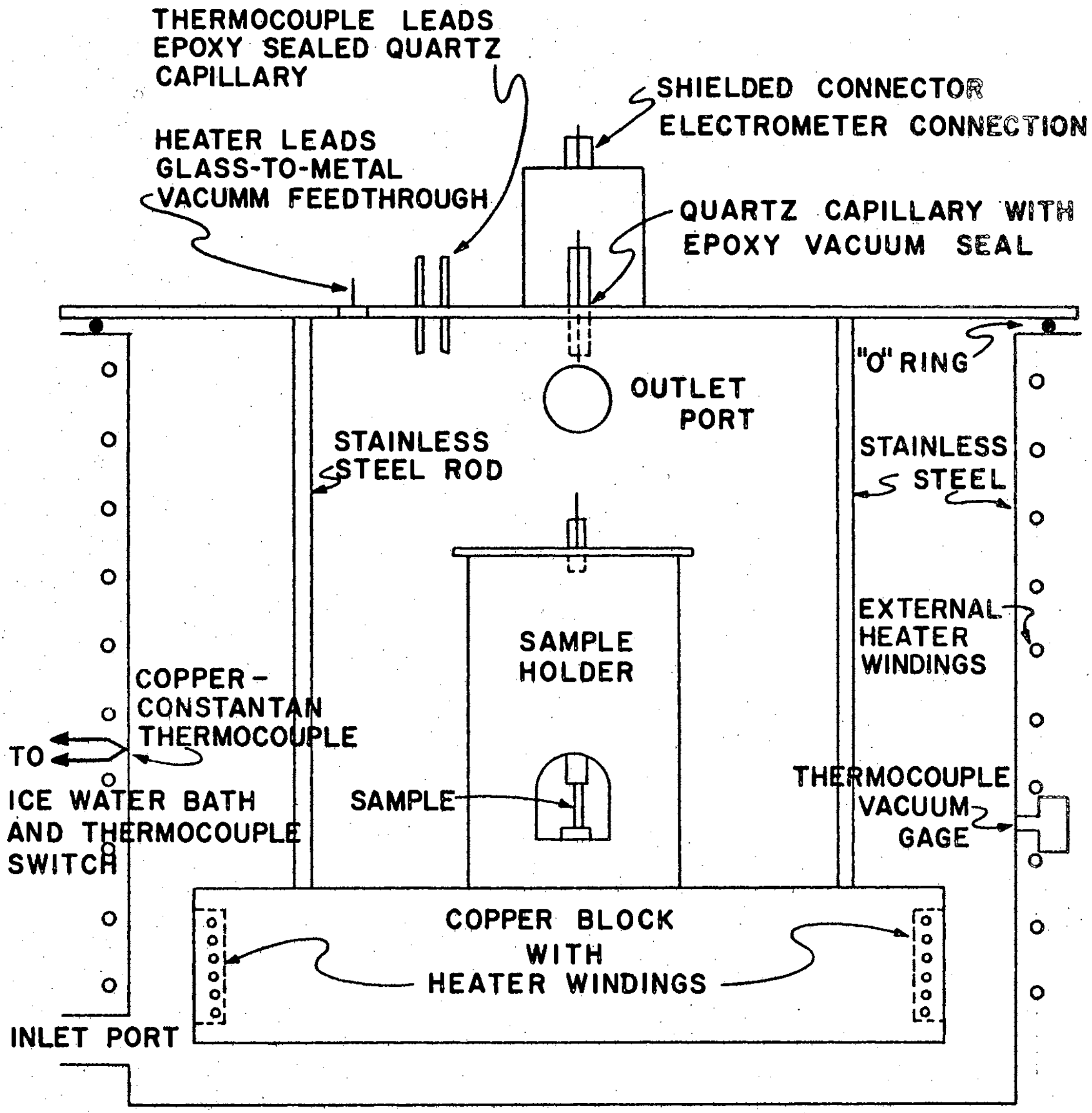

Figure 2. Vacuum Chamber and Sample Holder

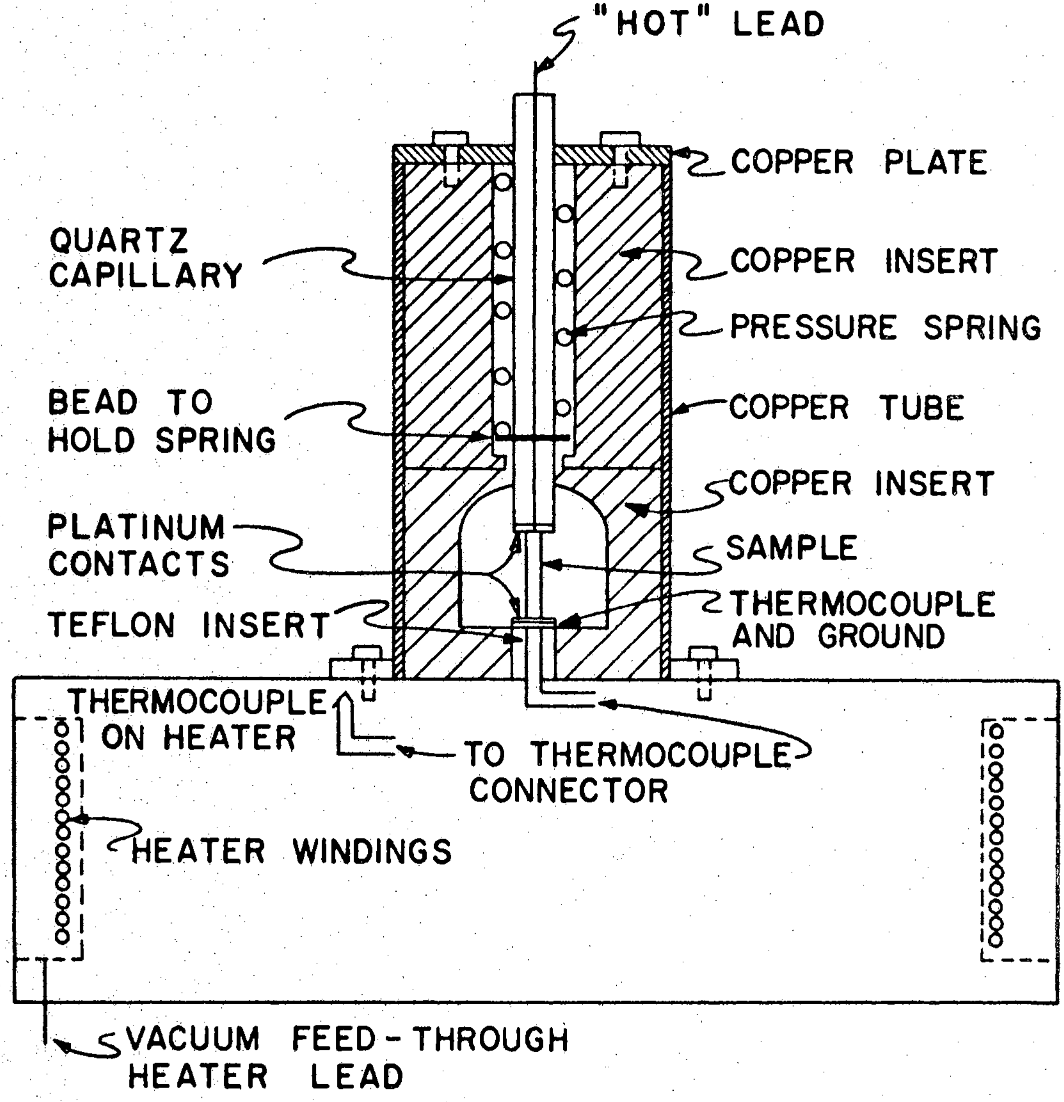

Figure 3. Enlarged View of the Sample Holder

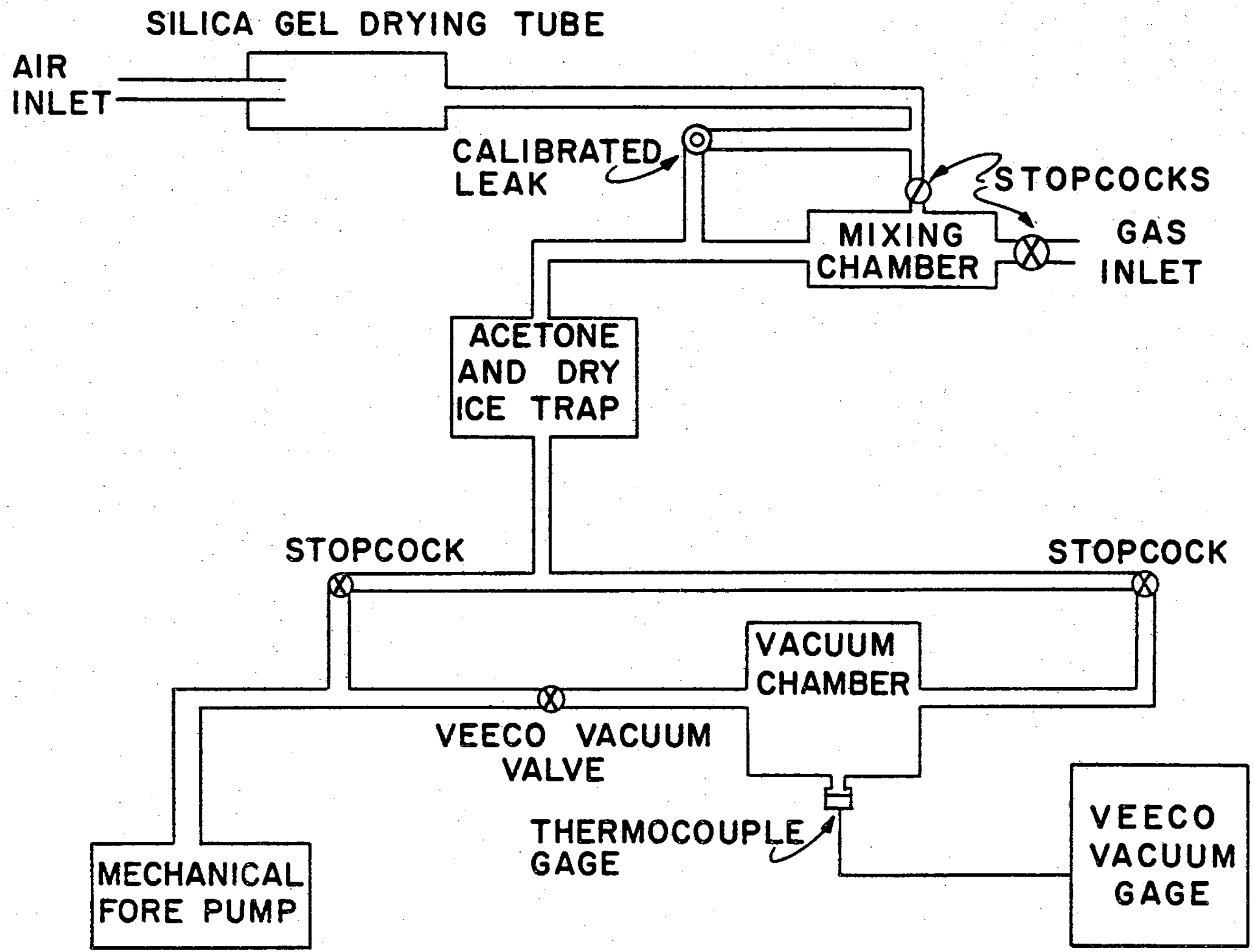

Figure 4. Gas Handling System

Entering air was routed through a silica gel drying tube and an acetone and dry ice trap, insuring that only dry air reached the sample. Other incoming gas could be introduced into the system through special inlet and were dried in the same acetone and dry ice trap. The Veeco vacuum value and two stopcocks allowed the vacuum chamber to be isolated from the remaining system. The external system could thus be flushed without disturbing any ambient gas which was in the vacuum chamber. The gas pressure in the vacuum chamber could at any time be monitored by the thermocouple gage and the Veeco Vacuum Gage meter. The pressure range monitored was from approximately 1 atmosphere to 10 microns.

Experimental Methods

The data taken in this study consisted of sample currents as a function of time resulting from a change in ambient. Since the specimen was shielded from light during the measurements, these are referred to as "dark" currents. They were monitored on both the electrometer and strip chart recorder.

The sample was prepared for a data run by subjecting it to what is termed a "fixing" procedure to bring it to a standard, reproducible, initial condition so that the results of a number of experiments could be compared in a systematic fashion. This fixing procedure consisted of holding the sample at a predetermined constant temperature and constant pressure for a given period of time. The current was periodically checked during this process. When a predetermined fixing time had been reached or when a particular value of the current was obtained, nitrogen was let into the system to a pressure of one atmosphere.

After the nitrogen was introduced into the system, the heater was adjusted--if necessary--to bring the system to a desired temperature for ambient change. The system was stabilized at this temperature and when ready to make the ambient change the nitrogen pressure was reduced to 10^3 microns by proper manipulation of the Veeco valve. This lowering was necessary in order to allow an influx of dry air. The dry air was then let in to a final pressure of one atmosphere by rapidly opening the stopcock. The chemisorption takes place when the dry air enters, hence the dark current and the temperature were monitored on the Sargent strip-chart recorders as functional of time with t = 0 being the time of dry air influx.

The current was monitored on the Sargent recorder by use of the electrometer output as previously described. The chart speeds used were five inches per minute for the first 150 seconds, one inch per minute for the time range of 150 - 1000 seconds and 1/5 inch per minute during the remainder of the decay.

A representative complete cycle of the experimental method is shown in Figure 5. The cycle as shown begins with the inlet of nitrogen which is the conclusion of the fixing procedure. The current changes after the nitrogen input arise from temperature changes due to having a better thermal conducting path of gas between the heater and specimen and between the specimen and chamber walls. As noted, then, several hours are required for the sample to reach a reasonable equilibrium state before the initiation of an experimental run. Just before the "dry air in" point the chamber pressure is reduced to 10^3 microns. On the particular cycle shown, the experimental data points for analysis were obtained between hours 6 and 9. Upon completion of the data run the vacuum valve was opened and the new fixing process for the next data run

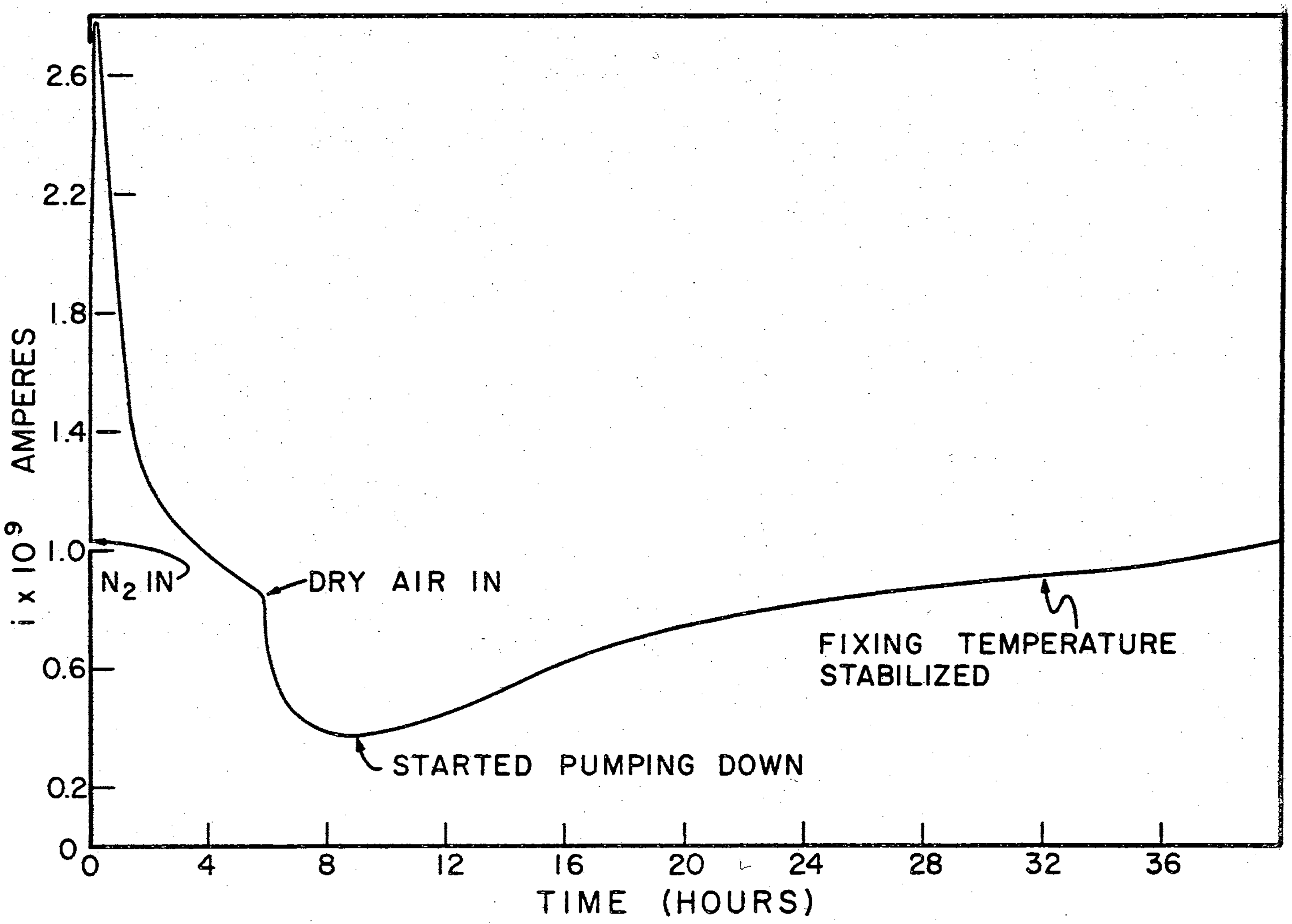

Figure 5. Complete Cycle of the Experimental Methods

was begun. At the stabilization point (hour 32), a constant temperature and pressure were once more attained, even though the sample current was still rising. "Fixing times" indicated on subsequent data graphs were measured from this time until the next "N_2 in" time.

CHAPTER IV

RESULTS

This chapter presents the results of the experimentation as described in the previous chapter. It should be noted that the measurements were taken on a single sample so that a better comparison between various data plots could be made. However, experience gained while studying a number of phenomena on specimens of this kind indicates little variation in properties between different samples so the results reported should be quite characteristic. The sample used is cataloged as S-22 in the laboratory sample book, having been pressed and fired by H. E. Matthews as described in his M.S. thesis[15]. The pressed ceramic pellet was prepared using reagent-grade stannic oxide powder with 0.7% zinc oxide as the dopant; after being pressed to 10,000 psi and fired at 1460°C for 4 hours, a rectangular slab was cut and cleaned using the method described by Rozeboom[16]. The dimensions of the sample were 4.915 mm x 1.743 mm x 1.181 mm with a density of approximately 6.4 gm/cm^3. The voltage used in the experiment was 65 volts.

The figures presented in this chapter each contain statements as to the conditions under which the current changes were recorded. The plotted data represented here are reasonably representative of all data taken for a particular set of experimental conditions. The results given are a direct consequence of the experimental procedures as outlined in Chapter III.

As mentioned in the experimental procedure section, nitrogen was added to the system to better stabilize its temperature so that a constant sample temperature could be maintained during the influx of dry air for the chemisorption effect. Figure 6 illustrates the variations of the sample current and the sample temperature with time due to the introduction of the nitrogen gas at 121°C and 10 microns of initial pressure. As can be seen in the figure, the current and temperature of the sample both reach a maximum at the same time and likewise both return to the initial conditions at the same time. Thus the only nitrogen atmosphere effect on the sample current during the time duration of the experiment can be attributed to the variations in sample temperature its presence causes. The sample temperature originally increases due to the influx of gas which allows better heat transfer from the heater to the sample and subsequently decreases as the sample slowly comes to temperature equilibrium with the outer walls of the sample chamber.

Figure 7, on the other hand, verifies that when an atmosphere containing oxygen is introduced there is definitely an additional effect changing sample current due to its presence. The current at any time is seen to be lower than that in Figure 6 even with the same initial conditions. The sample current reaches a maximum before the sample temperature does and has become greatly decreased by the time the temperature returns to its initial value. This result is consistent with the assumption that the oxygen in the dry air is chemisorbed on the sample surface and thus affects the sample current. Nitrogen and oxygen are the chief components of the dry air and since the nitrogen appears to not affect the current values at these temperatures, it could be safely used for sample temperature stabilization in the experimental procedures.

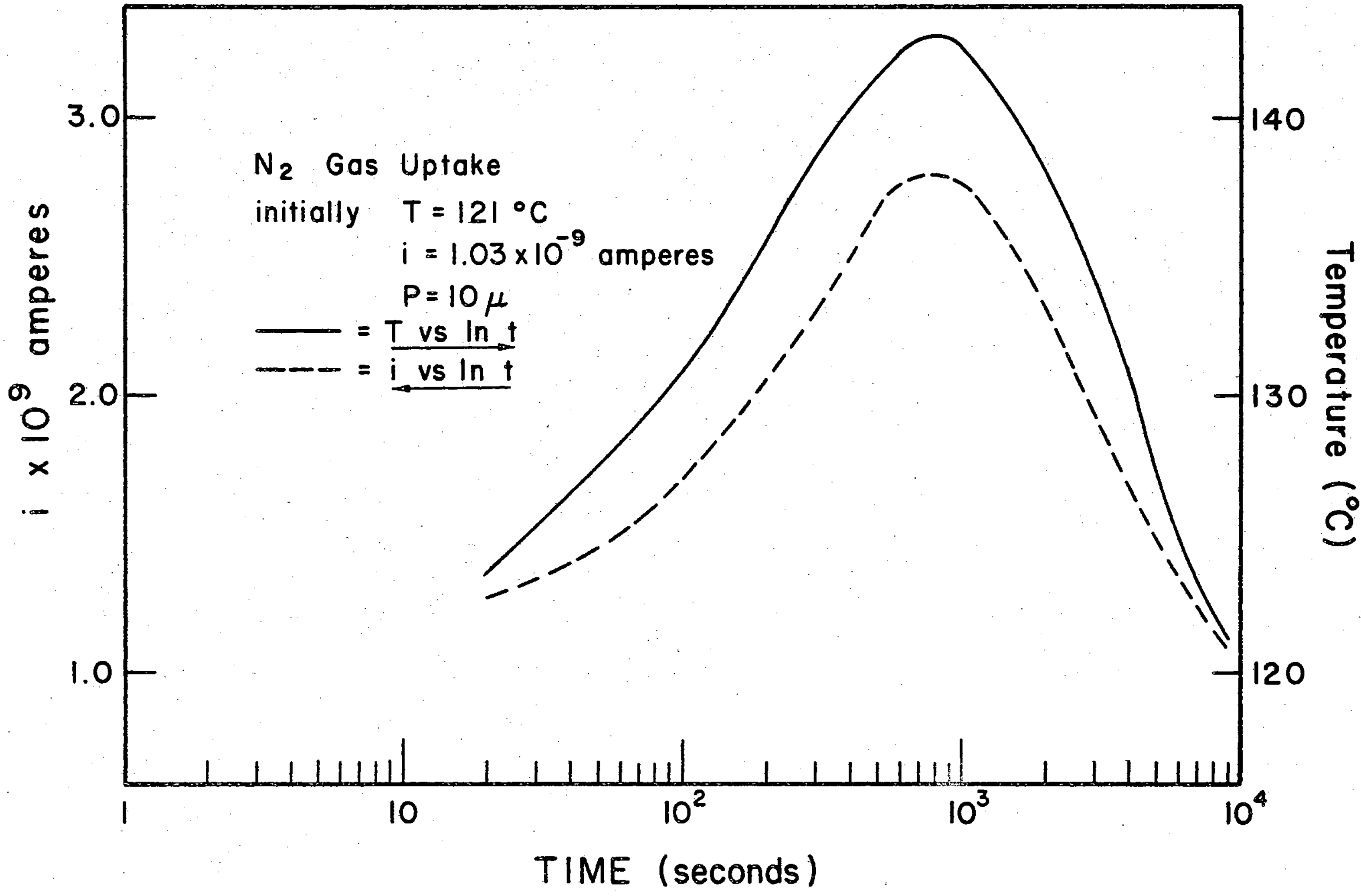

Figure 6. Dark Current and Temperature Versus Time With the Uptake of Nitrogen Gas at 121°C and 10 Microns.

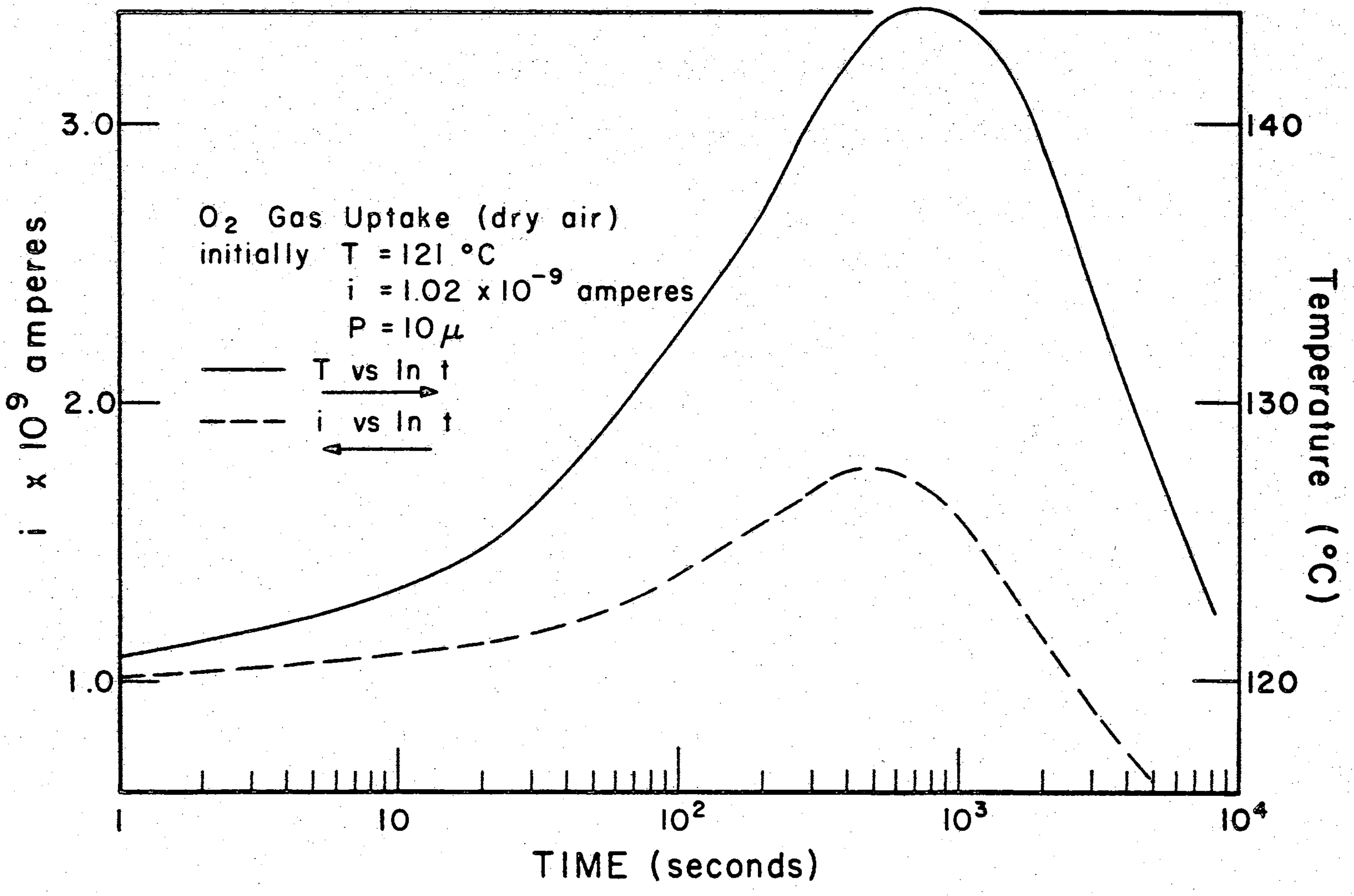

Figure 7. Dark Current and Temperature Versus Time With the Uptake of Oxygen Gas (Dry Air) at 121°C and 10 Microns.

The plots in Figure 8 represent how the rate of gas uptake can affect the conductivity and thus also the chemisorption rate. In an experiment on zinc oxide as reported by Cimino and co-workers[17], more gas was adsorbed over a period of time when introduced at slowly rising pressure. Figure 8 therefore illustrates the difference between a "rapid" uptake of dry air and a "slow" uptake of dry air on the stannic oxide specimen. The "rapid" uptake was accomplished by opening the stopcock as rapidly as possible for almost immediate gas influx, whereas "slow" uptake was accomplished by opening the stopcock a small amount and allowing approximately 10 seconds for the complete influx of dry air. A "rapid" uptake was then used in all following results for standardization of the experiments.

To illustrate the fact that past history of the sample plays an important role as to whether one has reproducible data or not, Figure 9 has been included in this study. The three plots of dark current decay were obtained for the same experiment as repeated on three consecutive days. Although the three plots represent the same recording temperature (121°C), and the same fixing procedure (123°C, 10 microns for 12 hours), it can plainly be seen that the runs are not independent of each other.

Since the initial sample current kept increasing with consecutive experiments, it was thought that with longer fixing times the current might reach a steady value which could serve as a reference level for reproducible conditions. This was studied with the results shown in Figure 10 where the temperature of the sample (118°C) and pressure (10 microns) was kept constant for 80 days. As can be seen, the current never quite leveled out even during this extended time period. It was found that after the extremely long period of heat treatment just de-

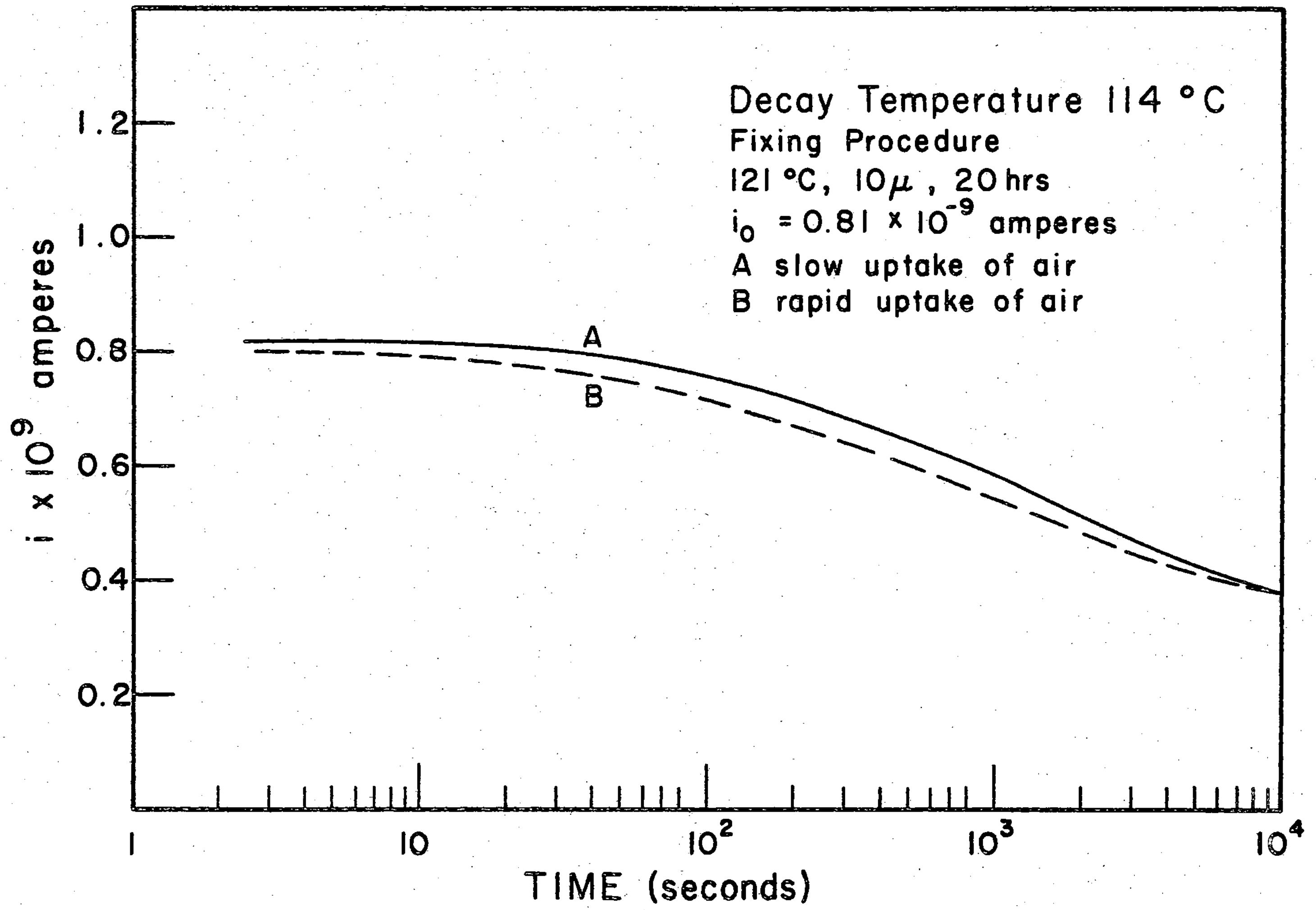

Figure 8. Dark Current Decay With Slow and Rapid Uptake of Dry Air

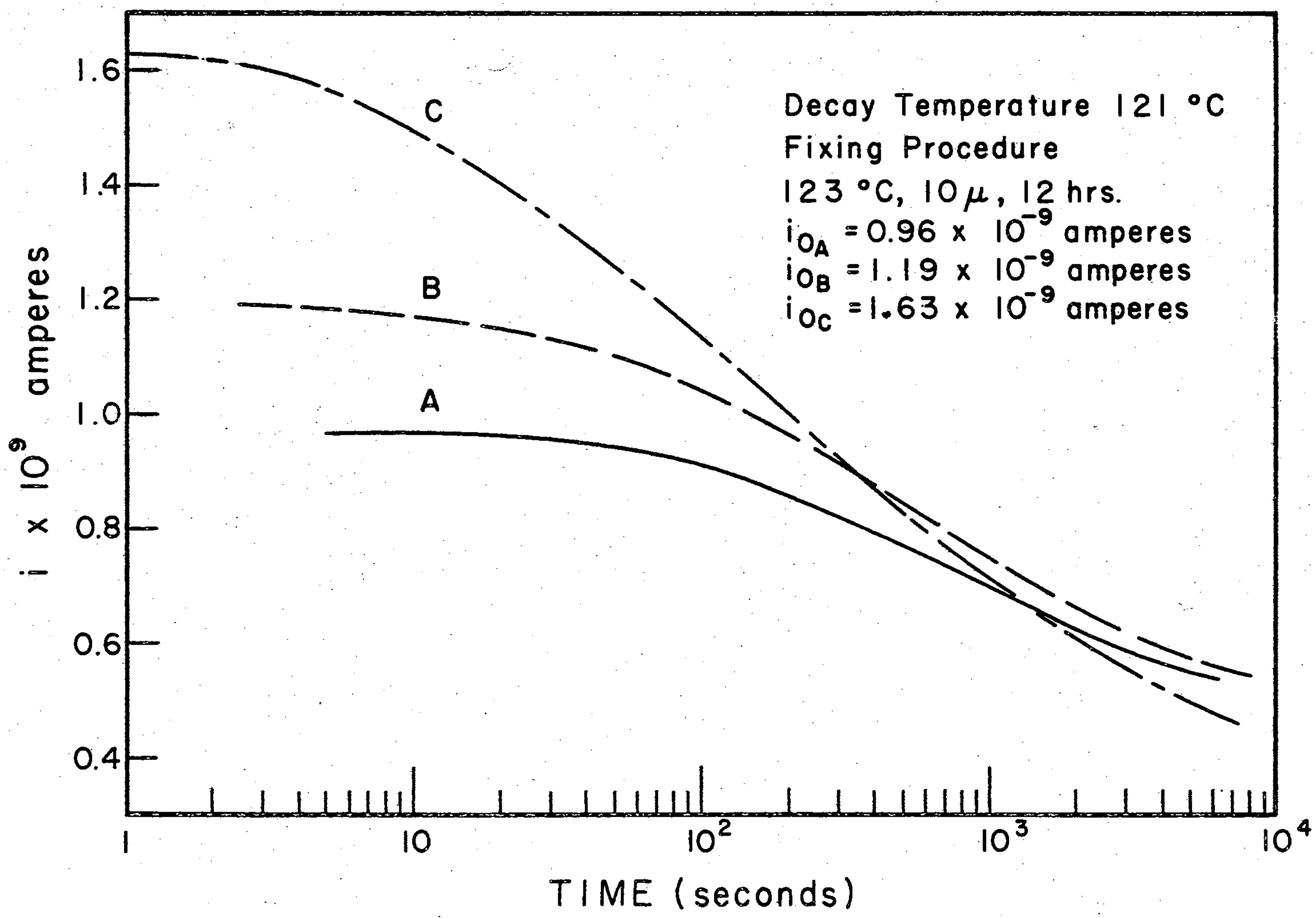

Figure 9. Dark Current Decays for Identical "Fixing" With Past History Neglected

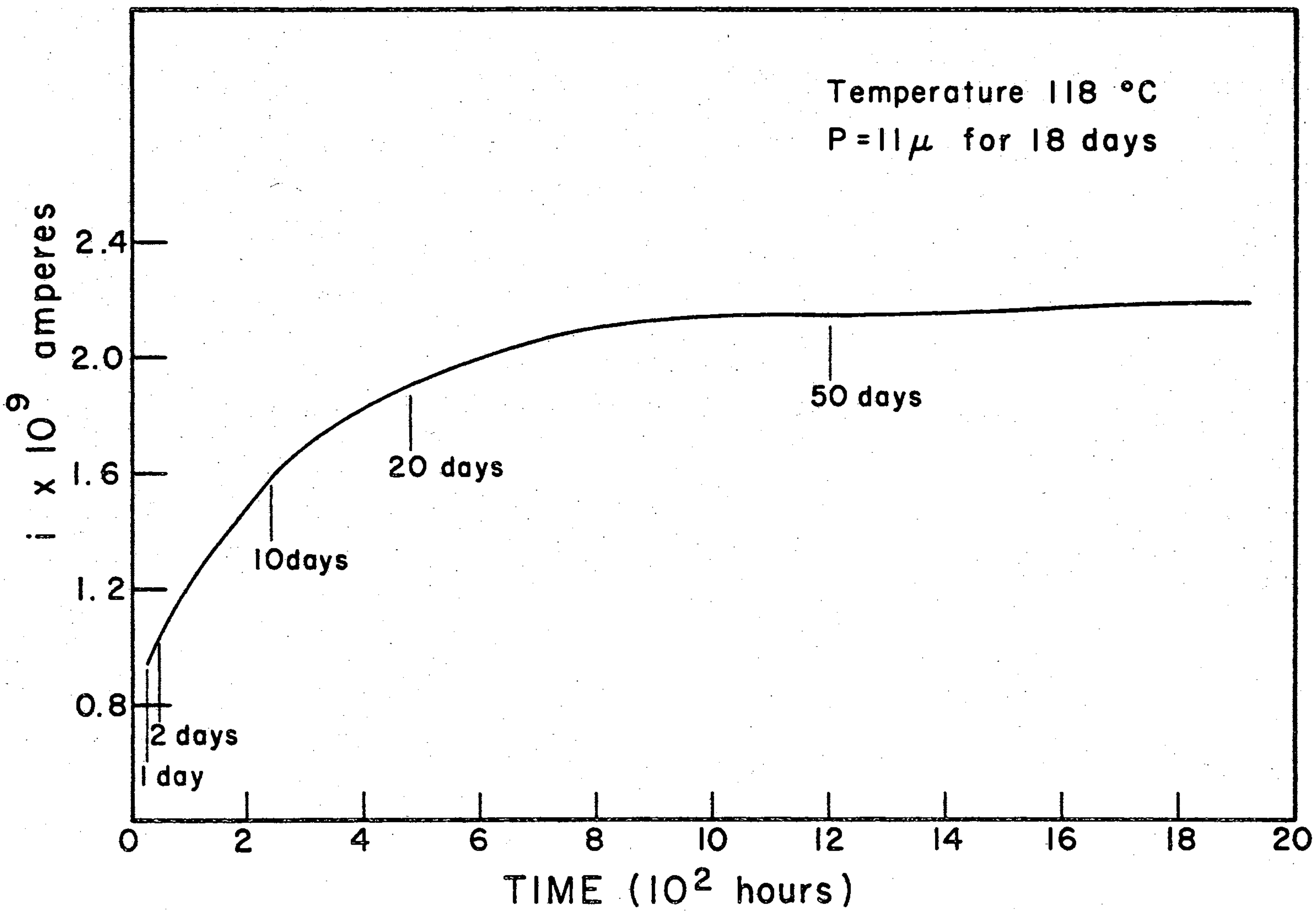

Figure 10. Current Change as Function of "Fixing" Time

scribed, one could obtain favorable reproducible initial conditions for the experiments with fixing times of the order of those used for the Figure 9 data. Even then there were slight indications that some past history might play a part in the experiment and a characteristic scattering of results for identical experiments can be seen in Figure 11. Some other possibilities for this observed scatter of initial currents are discussed later.

The plots in Figure 12 represent dark current decays recorded at different temperatures of the sample with each experimental run following the same fixing procedure of 121°C, 10 microns for 23 hours. As stated previously, the sample current is a function of temperature and here it can be seen that for the various decay temperatures there is indeed a change in the initial current for each experiment. The rate of decay can also be seen to be different for each decay temperature.

The data plotted in Figure 13 illustrate the effect that the fixing time has on the conductivity change or dark current decay with identical initial currents. The initial decay appears to be more rapid for the longer fixing time experiment, although the difference is small.

Figure 14 gives the dark current decay for the case where the sample is fixed for a long period of time. In fact, this is the data run taken immediately following the 80-day heat treatment described in Figure 10. Thus, the whole period can be considered the fixing time for this particular experiment. A plot of dark current decay with nearly identical fixing temperature and pressure, but having different fixing time and recording temperature is given in Figure 15. The fixing pro-

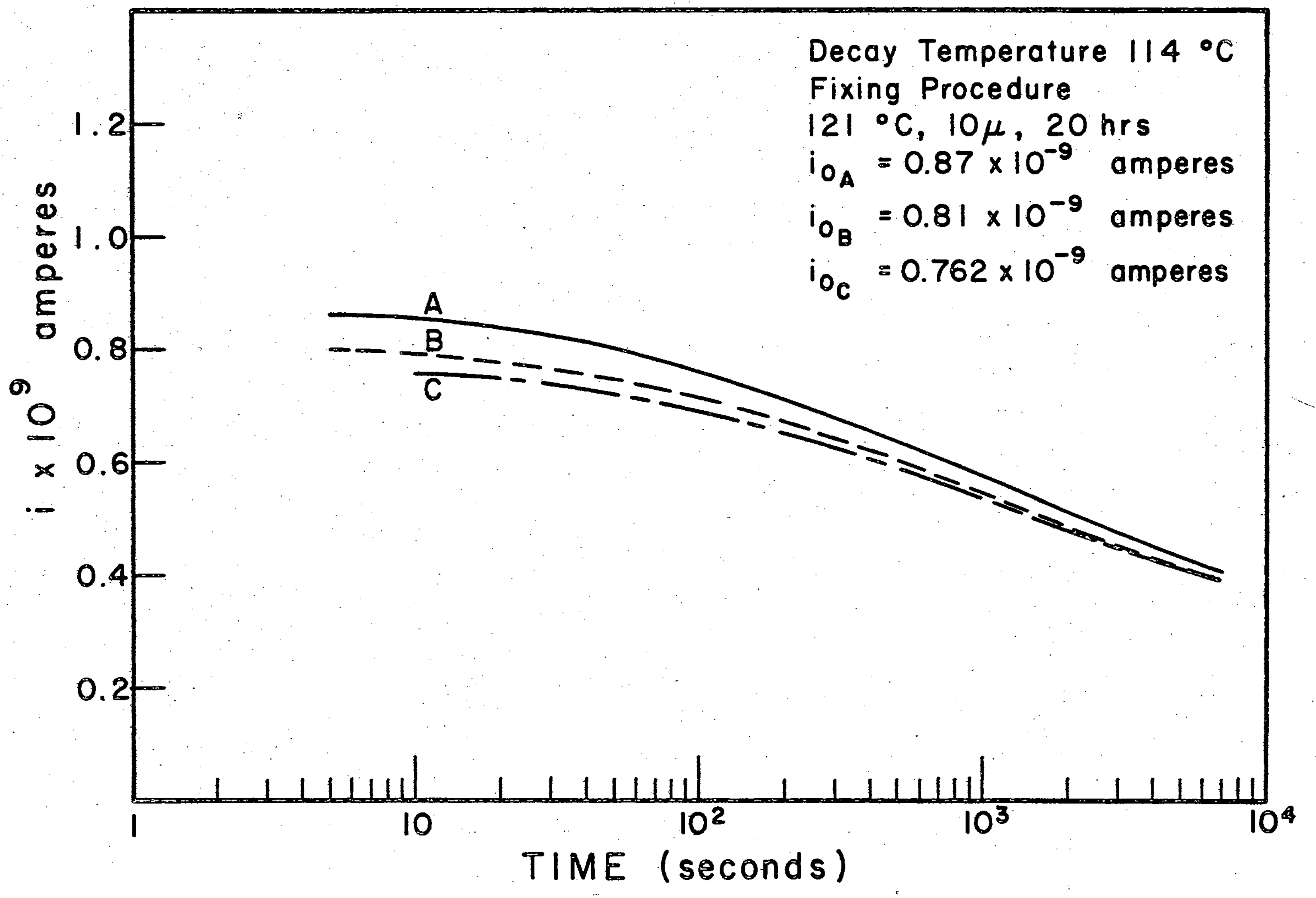

Figure 11. Dark Current Decay Spreading (114°C)

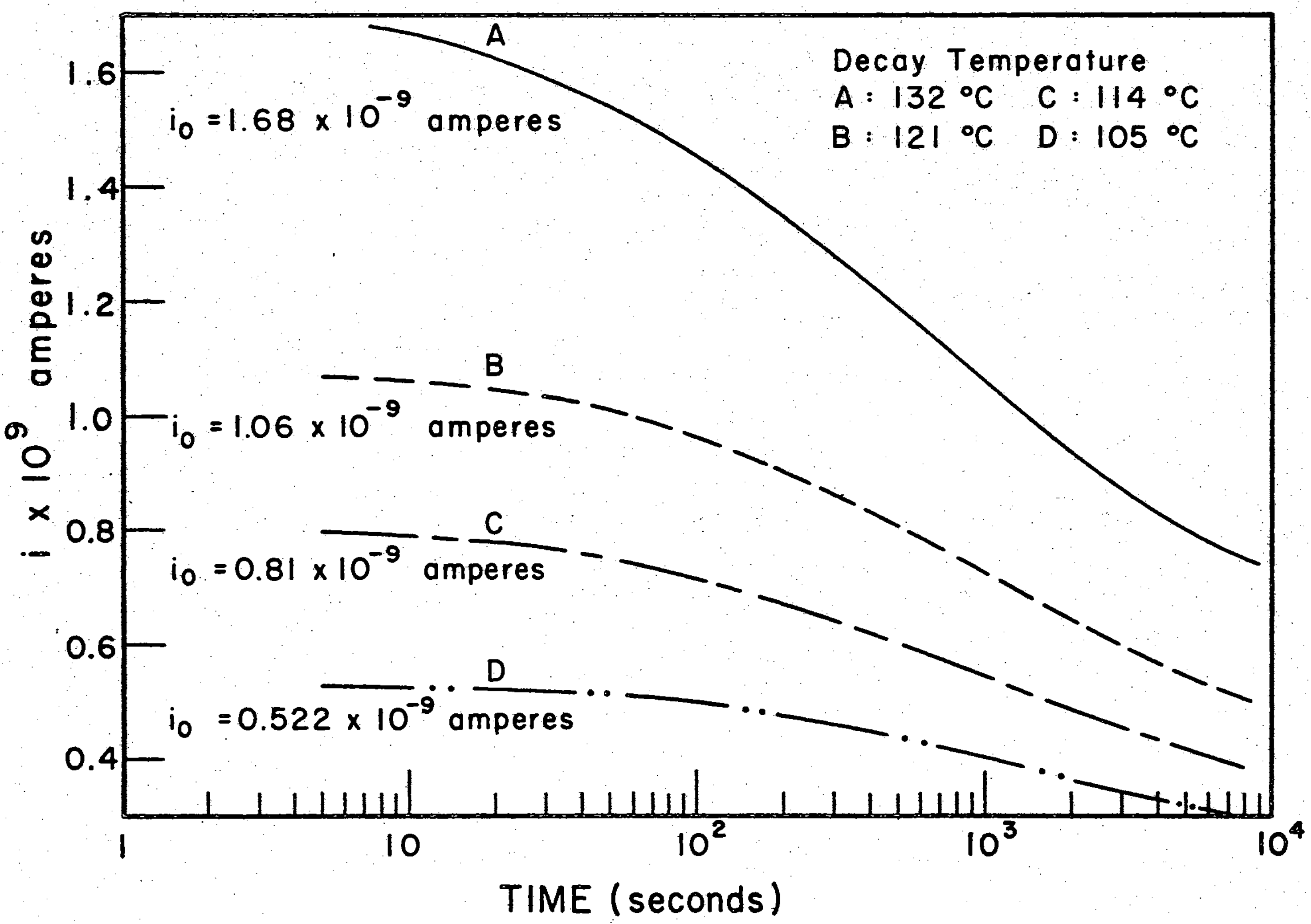

Figure 12. Dark Current Decays at Various Recording Temperatures. Fixing Procedure 121°C, 10 μ, 23 Hrs.

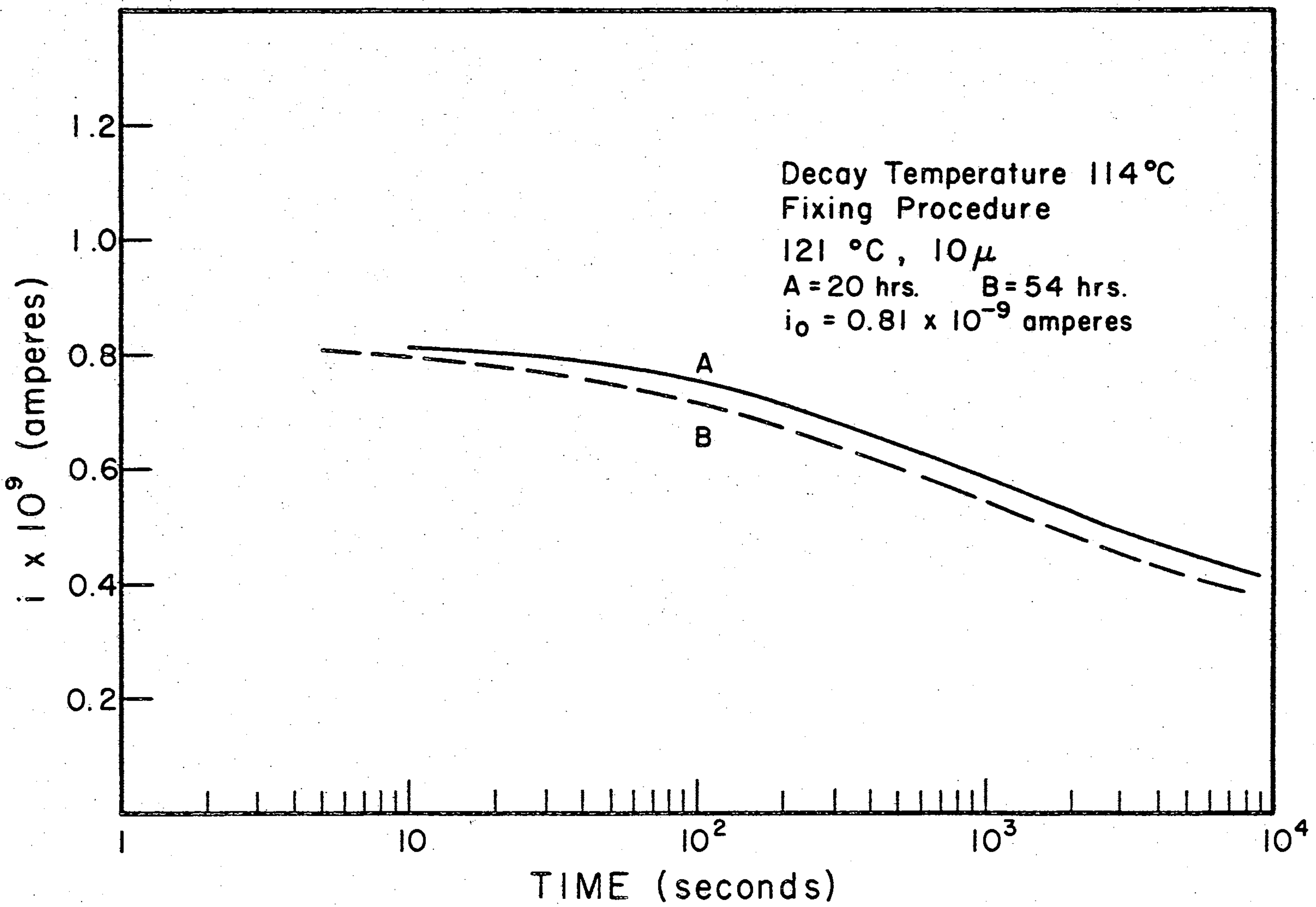

Figure 13. Dark Current Decays With Fixing Time Varied

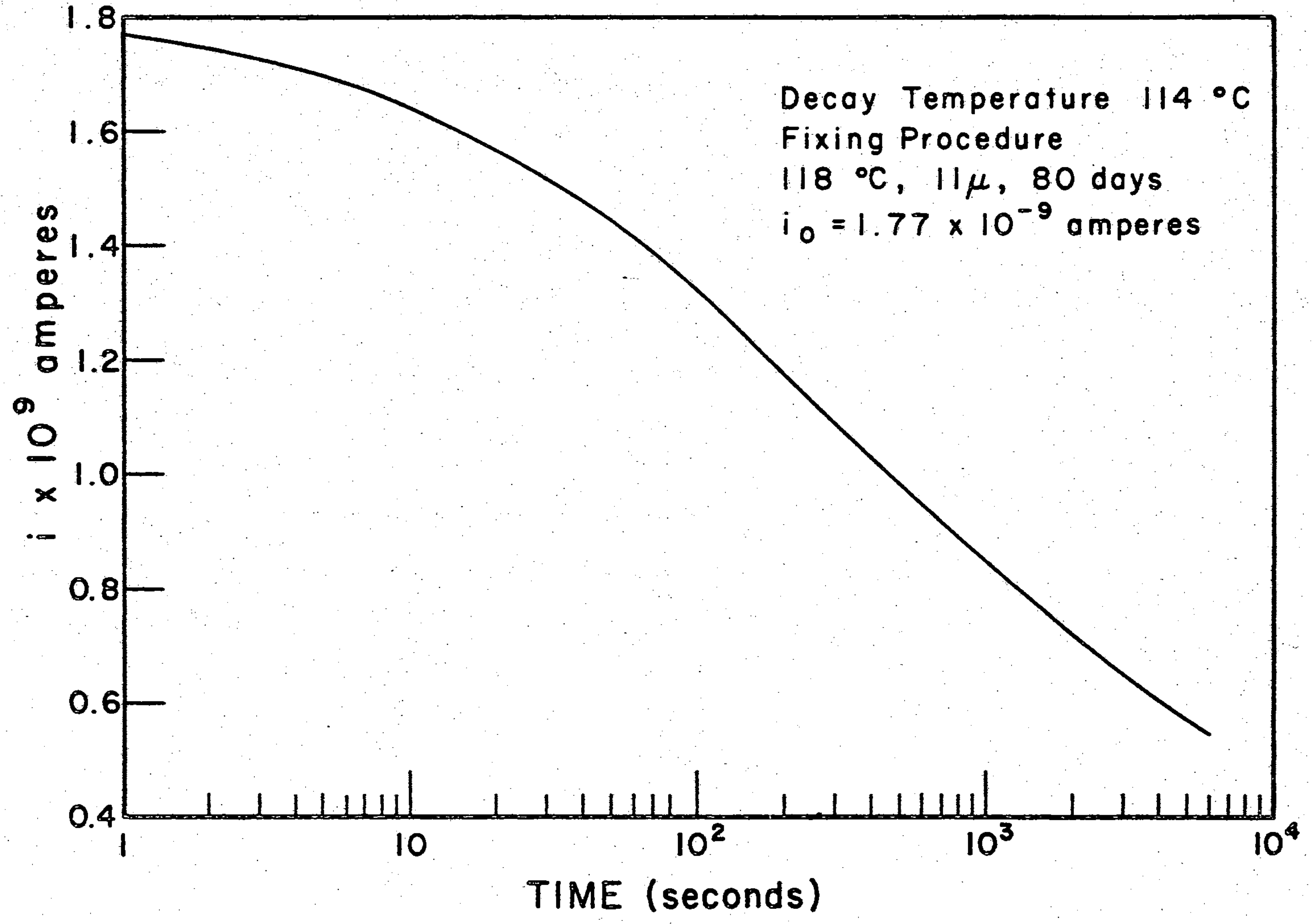

Figure 14. Dark Current Decay (114°C and Fixed for 80 Days at 118°C)

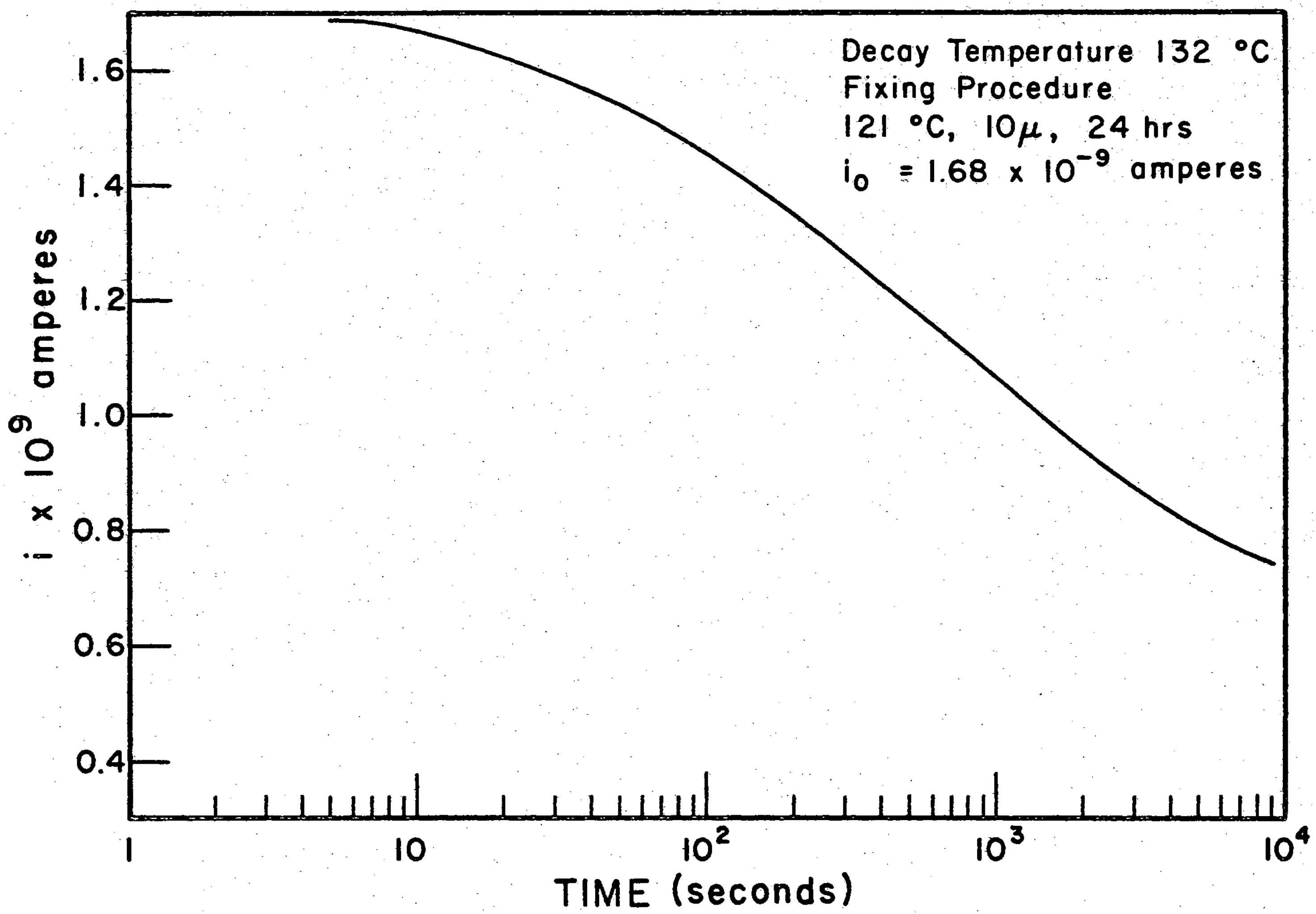

Figure 15. Dark Current Decay (132°C and Fixed for 24 Hrs at 121°C)

cedure was 121°C and 10 microns for 24 hours in this experiment. Figures 14 and 15 show that a particular initial sample current can be obtained either by fixing for a longer period of time or by raising the sample temperature at which the experiment is done.

The plots in Figures 16 and 17 illustrate dark current decays of the sample at nearly identical recording temperatures, with the fixing time being the only variable in the fixing procedure. Both recording and fixing occurred at higher temperatures than those used for the previous results mentioned so that values of initial current and representative decay curve shapes could be observed for these conditions. As can be seen, the dark current initial decay is markedly more rapid following a 155°C fix and the initial sample current is also much higher.

The temperature range of 106°C - 155°C was utilized in this study so as to limit consideration to surface effects. This should be well below the range where bulk effects such as oxygen vacancy creation and impurity ion diffusion can be significant.

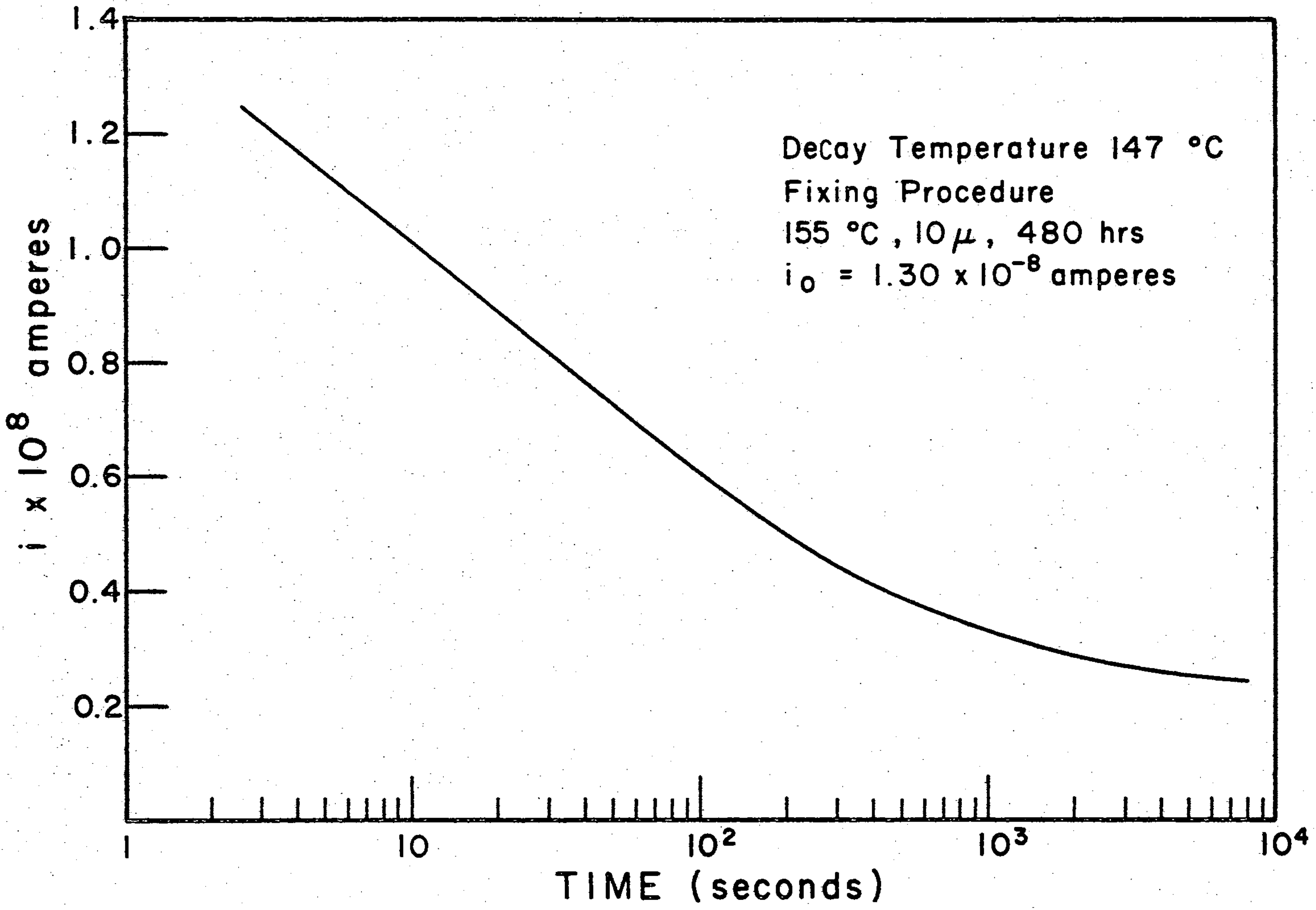

Figure 16. Dark Current Decay (147°C and Fixed for 480 Hrs at 155°C)

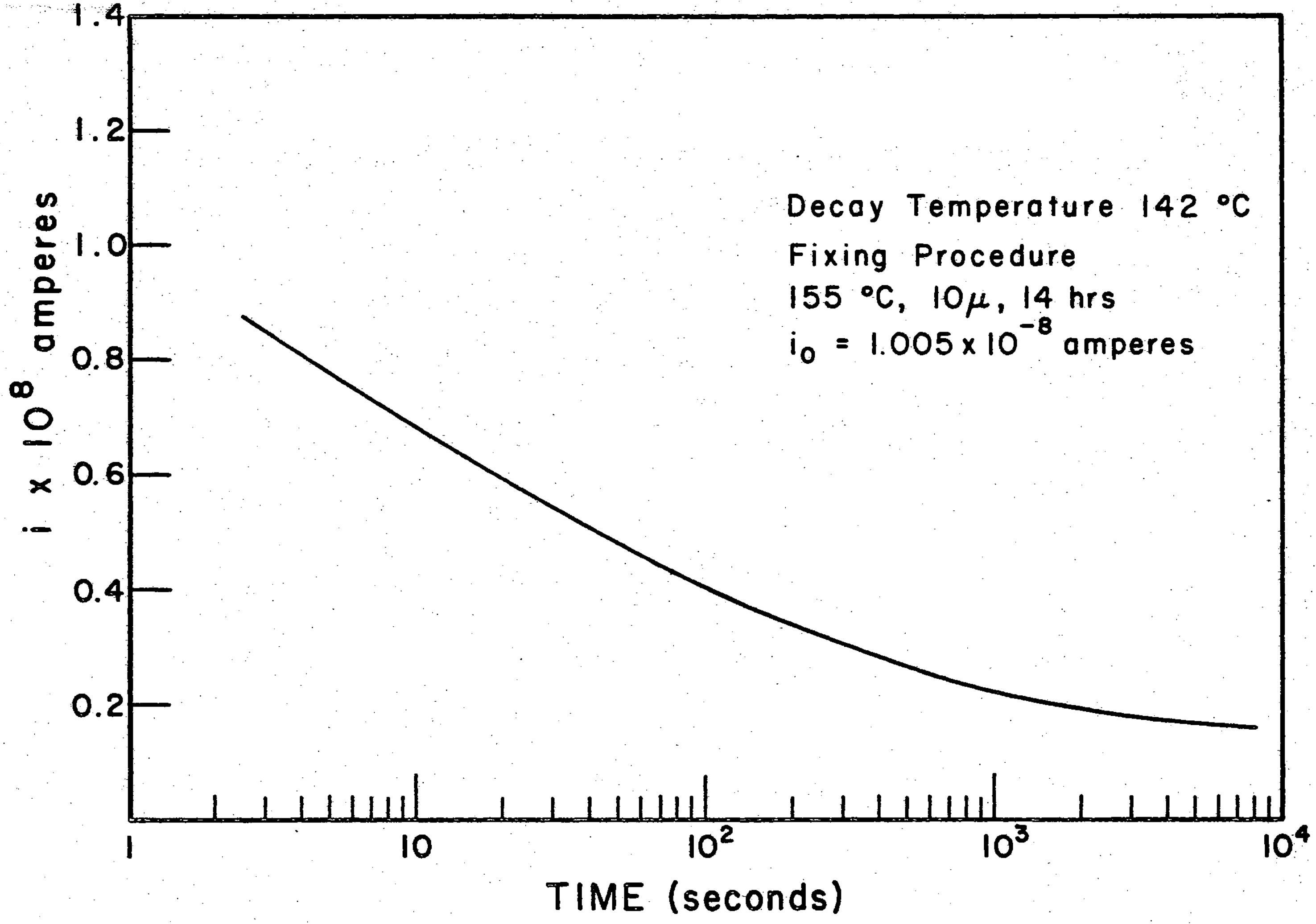

Figure 17. Dark Current Decay (142°C and Fixed for 14 Days at 155°C)

CHAPTER V

DISCUSSION AND SUMMARY

Before beginning the discussion of the results as given in the previous chapter, a brief review of the purpose of this study will be given. The study was undertaken with the goal of correlating various sets of data in an attempt to better understand how chemisorption affects the electrical conductivity of zinc-doped polycrystalline stannic oxide. Holding different combinations of experimental parameters constant has made it possible to make a better qualitative and quantitative analysis of the process than was previously possible. Additional insight has been gained concerning the physical origin of, and interrelation between, these same experimental parameters. Interpretations will be based on a mathematical model proposed by Matthews[1] and derived in Chapter II. It predicts that sample currents should decay with time according to the relationship

$$i(t) = c\left[\frac{N_d - N_a^* - xB \ln\left(\frac{t + t'}{t'}\right)}{N_a^* + xB \ln\left(\frac{t + t'}{t'}\right)}\right] \qquad (14)$$

following the imposition of a rapid increase in oxygen gas pressure.

It should be noted that some brief discussion has already been given in the descriptions of the figures in the previous chapter for the readers' better understanding of what the results represented. The first concern of this work was to enable one to obtain reproducible results from a number of experiments. Nitrogen gas was appropriately used for the sample temperature stabilization during ambient change as it was found not to affect the sample current during the interval of experimentation. The oxygen in the dry air is indeed the chemisorbate at the temperatures used as verified in Figure 7. The problem of controlling the influx of the ambient gas was shown in Figure 8 where a "slow" uptake of dry air resulted in a lower current after 9000 seconds than if there had been a "rapid" uptake of dry air. This is consistent with the observation that a slow increase in ambient pressure appears to allow a greater total amount of oxygen to be chemisorbed (vide Cimino, et. al. 17 for zinc oxide) since more chemisorbed gas is taken to a result in a decrease in conduction electrons and hence, a reduced current.

The problem associated with ignoring past history of the sample was clearly illustrated in Figure 9 where the three plots were taken on consecutive days. The fixing of the sample is essentially a desorption-type process with the current increases due to the resulting increase in conduction electron density. Since the initial current and the dark current decay of each succeeding experiment was affected, the fixing procedure appeared to be cumulative with the sample not fully taking on as many chemisorbed species during an experiment as were taken away during the following desorption process.

An attempt to overcome this increasing initial current for successive experiments was made by fixing the sample for a very long time and trying to obtain a maximum value for the current to serve as a reference level for independent experiments. The current, however, did not reach a maximum as seen in Figure 10, but did reach a level where the rate of increase was very small. Upon fixing for this long period of time it was found that the initial conditions for a number of subsequent experiments could be reproduced for comparison purposes. The reproducibility of the data was hampered to some degree by the methods employed in allowing an influx of dry air for the experiments. Typical spreading of the dark current decays for identical initial conditions is shown in Figure 11. This spreading is believed to have been caused either by a small amount of oxygen being present ss an impurity in the nitrogen resulting in a slight current decay, or due to the fact that it was necessary each time for the system to be pumped down to 1,000 microns of pressure in order to have an influx of ambient. The necessary opening of the vacuum valve was done manually with some variation occurring each time and it was possible for the temperature to vary by almost ½ °C prior to the start of the experiment.

The data taken best fitted the equation which was derived in Chapter II based on the assumption that the chemisorption density on the surface at t = 0 is quite large. Thus Equation (15),

$$i(t) = i_o - \frac{xcB}{N_a^*} \ln \left[\frac{t + t'}{t'}\right] \tag{15}$$

gives an appropriate description of the dark current decay curves. That this is true can be readily checked by observing i versus ln (t + t') as shown in Figure 18 where i versus ln t and i versus ln (t + t') are both plotted.

The effect of the recording temperature on the dark current decay for identical fixing procedure as seen in Figure 12 clearly verifies that the initial current does have a strong temperature dependence. Another way of describing the temperature behavior of the various decay

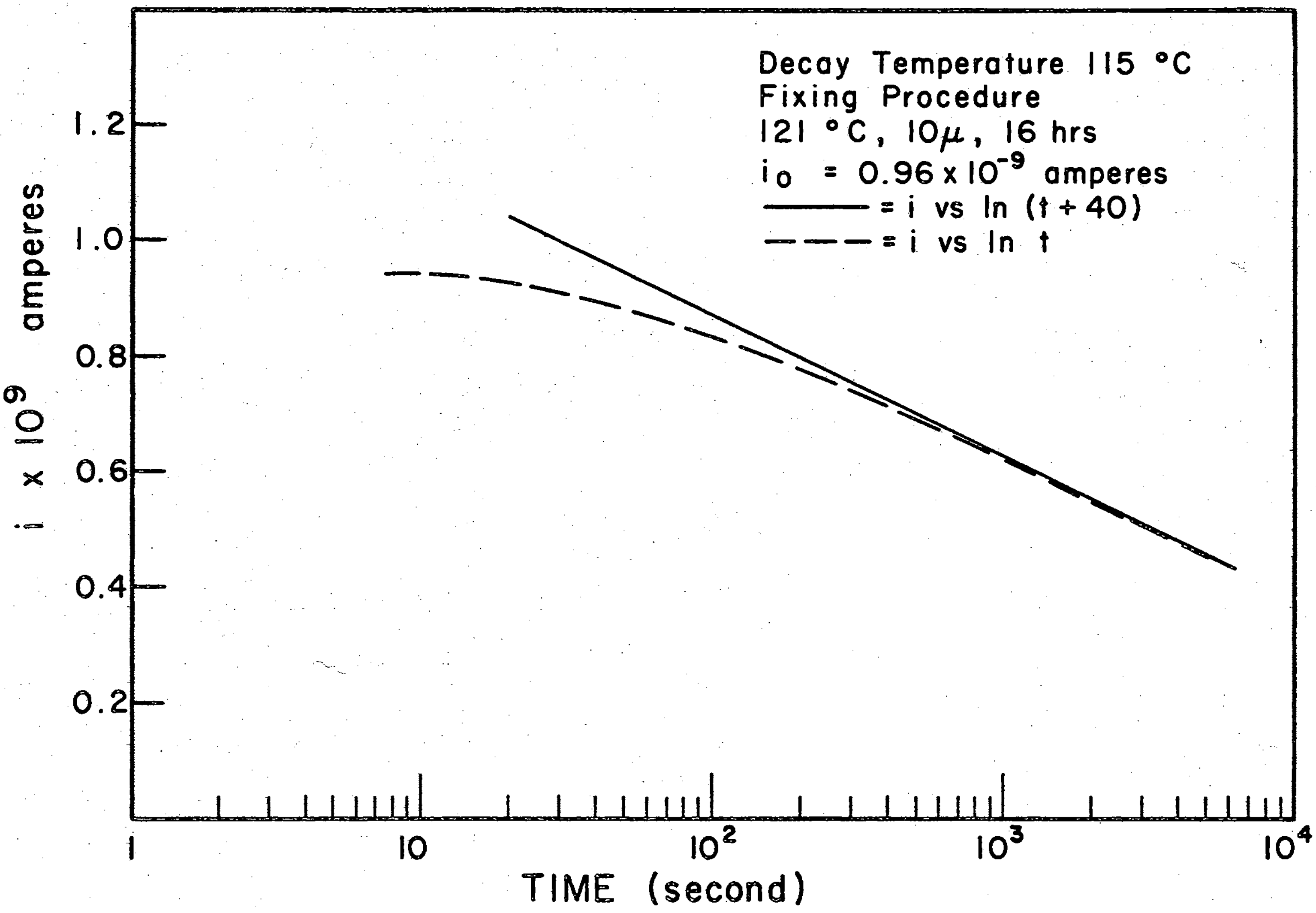

Figure 18. Dark Current Decay and Current Versus ln(t + t')

runs is to note each t' parameter as obtained graphically by fitting the observed i(t) to a ln (t + t') dependence. The t' value, the initial current, and the recording temperature for each plot in Figure 12 are given in Table I.

TABLE I

INFORMATION FROM THE PLOTS IN FIGURE 12

Recording Temperature (^{o}C)	Initial Current, i_o (x 10^{-9} amperes)	t' seconds
106	0.522	98
114	0.810	56
121	1.06	48
132	1.68	30

From the information in Table I certain comparisons can be made. First, although the temperature range is limited, the initial current i_o varies as exp [$-\varepsilon/kT$] as would be expected for a semiconductor. The activation energy ε calculated is 0.59 ev, in good agreement with one of the activation energies previously observed[3] in similar samples of this material. Secondly, over the same temperature range, it is observed that the graphically obtained t' varies directly with i/i_o, or empirically, $t' = A'/i_o$ with A' a constant for the constant fixing procedure. Since A' has units of ampere-seconds or coulombs, it is reasonable to believe that it is related to the surface charge on the sample which is in itself dependent upon the fixing procedure.

The effect due to varying the fixing time for two experiments with identical fixing temperatures, pressure, recording temperature, and initial current is seen in Figure 13 to be small. The t' is about 5 seconds less for the plot representing the longer fixing time. This perhaps could either be attributed to variations in opening the valve for the rapid influx of dry air as explained previously, or to the fact that the sample had been stabilized in a nitrogen atmosphere at the recording temperature for a longer time with the possibility of additional decay due to impurities in the nitrogen gas. The most straightforward explanation, however, is that the density of the chemisorbed species on the surface can be reduced by increased time of fixing, thus changing the constant A' in the empirical relationship, $t' = A'/i_o$ in the direction to be expected.

The initial current and the rate of dark current decay can be increased in two ways as seen in Figures 14 and 15. The sample can be fixed for a longer period of time or the decay temperature for the experiment can be increased, when for both experiments the fixing temperature and pressure are kept relatively the same. The "rate of dark current decay" here is taken to mean the amount of current change over a period of time. Thus the rate of change is greater for Figure 14 since the decrease was 1.30×10^{-9} amperes in 6000 seconds whereas Figure 15 shows a 0.90×10^{-9} ampere change in the same period of time.

Figures 16 and 17 show that as the fixing temperature and recording temperature are increased, the initial sample current greatly increases and also the decay rate increases. Again, the initial current is higher for a longer fixing time as just described. These two plots show in detail the fact that the dark current decay curves do tend to level off after a certain period of time. For the high fixing temperature and recording temperature this leveling off occurs much sooner than at lower fixing and recording temperatures. Such as those seen in Figure 12. This appears to be another characteristic of electrical conductivity changes due to chemisorption, as observed by Glemza and Kokes[18] when they made simultaneous measurements of the electrical conductivity and adsorption kinetics on zinc oxide and found a similar effect. They explained their leveling off of the current decay to a constant value to occur when the concentrations of the chemisorbed species reach stationary values. Qualitatively, this could result when the concentrations have become large enough to "pinch-off" further electron transfer across the surface charge layer barrier as discussed by Morrison[10].

Attempts to fit the experimental data to Equation 16 of Chapter II have proved less successful than analyses based on Equation 15. As pointed out previously, this is consistent with an assumption that the surface of the sample in its initial condition for the decay experiment has a rather large density of chemisorbed oxygen already present. Ultimately one would hope that analyses based on the full equation

$$i(t) = c \left[\frac{N_d - N_a^* - xB \ln\left(\frac{t + t'}{t'}\right)}{N_a^* + xB \ln\left(\frac{t + t'}{t'}\right)}\right] \qquad (14)$$

could be made, removing the need to rely on a simplified equation which may hold over only a limited portion of the experiment. Curve shapes have been obtained by Rozeboom[16] for different assumed compensation ratios (N_a^*/N_d) and values of other reduced parameters. However, further experimental confirmation of new relationships like that between t' and inverse initial current with the constant of proportionality A' dependent on the fixing procedure is needed before a complete quantitative analysis of the chemisorption process can be made from electrical measurements of this type.

Summary

Characteristic of this investigation was the ability to obtain standardized sets of initial conditions so that the results of a number of experiments could be compared in systematic fashion. This standardizing had been achieved by heating the sample for a very long period of time at 118°C and 11 microns pressure with most subsequent experiments being performed within the range of this temperature and pressure. The desired initial conditions for any experiment were obtained by carefully controlling and monitoring the fixing procedure.

The initial current, i_o, of a run was found to be strongly dependent on the fixing procedure prior to the start of the experiment. There were three ways in which the initial current for an experimental run at a fixed temperature could be varied. The first way was to vary the fixing <u>time</u> which revealed that with increased fixing time there was an increase in the initial current. The second way was to vary the fixing temperature. An increase in fixing temperature produced an increase in the initial current, i_o. The third way was to vary the <u>pressure</u> at which fixing occurs with an increase in initial current resulting from a decrease in fixing pressure. The fixing procedure thus appears to be a "cleaning" process whereby chemisorbed species on the specimen surface tend to be removed with an increase of fixing temperature and time, and a decrease in fixing pressure.

Another method by which the initial current, i_o, could be varied was to maintain a constant fixing procedure while obtaining data runs at several different sample temperatures. For an increase in recording temperature there was an increase in initial current accompanied by a decrease in parameter t' as seen in Figure 12 and Table I. With the data taken in the recording temperature range of 106°C to 132°C there was observed to be an empirical relationship between the initial current, i_o, and the decay parameter, t', given by $t' = A'/i_o$ where A' was found to be a constant for this particular fixing procedure. Dimensional analysis suggests that the constant A' is related in some fashion to the surface charge on the sample at the start of an experiment run.

The above would imply that the value of A' in the empirical relationship of $t' = A'/i_o$ should be influenced by the fixing procedure. Two particular experiments which indicated this are those plotted in Figure 14 and Figure 15. The initial currents for the experiments are quite similar and were obtained by different means. The value in Figure 14 was achieved by having a long fixing time whereas the value in Figure 15 resulted from using a higher recording temperature after a much shorter fixing time. The value of t' obtained graphically for the longer fixing time found to be approximately half the value of t' obtained for the short fixing time and increased recording temperature. Thus the value of A' for the shorter fix is approximately twice that from the data following the longer fix. The interesting point here is that the fixing procedure for Figure 15 was essentially the same as that for the data of Figure 12 and the A' values calculated from the $t'\ i_o$ products in each case were the same within experimental error. The A' for Figure 14 data is only half as large, a fact which is consistent with an assumption that A' is intimately related to the initial surface charge--and, therefore, to the initial chemisorbed oxygen density--since the longer fixing procedure should desorb more gas leaving the surface coverage less. Much work needs to be done yet, however, before the value of A' can be confidently accepted as a true criterion of the initial condition of the surface.

In conclusion, the conductivity changes observed when a zinc-doped polycrystalline stannic oxide specimen is subjected to a rapid increase of oxygen on the specimen surface through a tested mathematical model based upon the behavior of stannic oxide as a highly compensated semiconductor.

Special care has been taken in this study to find ways of providing a standard set of initial conditions so that the results of decay experiments can be correlated in a systematic fashion. Furthermore, a new parameter $A' = t' i_o$ has been proposed as a useful indicator of the initial coverage of the surface by the chemisorbed species.

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VITA

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